nature portfolio

Peer Review File

Green and large-scale production of covalent organic framework nanofiltration membranes

Corresponding Author: Professor Juergen Caro

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

Version 0:

Decision Letter:

** Please ensure you delete the link to your author homepage in this e-mail if you wish to forward it to your coauthors **

Dear Professor Caro,

Thank you for submitting your manuscript, "Covalent organic framework nanofiltration membranes: Green and scale-up preparation", 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 interest, some important points are raised. We are interested in the possibility of publishing your study in Communications Materials, but would like to consider your response to these concerns in the form of a revised manuscript before we make a decision on publication.

One particular point, which is recommended by two reviewers, is related to the integration of the comparison of presented COF-based materials with related porous or conventional membrane materials. We believe that such a comparison would be a beneficial addition to the current manuscript.

We therefore invite you to revise and resubmit your manuscript, taking into account the points raised.

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.

When submitting your revised manuscript, please include the following:

-A response letter with a point-by-point reply to each of the referee comments and a description of changes made. Please include the complete referee report in the response letter. Please note that the response letter must be separate to the cover letter to the editors.

-A marked-up version of the manuscript with all changes to the text in a different colored font. Please do not include tracked changes or comments. Please select the file type ‘Revised Manuscript - Marked Up’ when uploading the manuscript file to our online system.

-A clean version of the manuscript. Please select the file type ‘Article File’.

-An updated Editorial Policy checklist, uploaded as a ‘Related Manuscript File’ type. This checklist is to ensure your paper complies with all relevant editorial policies. If needed, please revise your manuscript in response to these points. Please note that this form is a dynamic ‘smart pdf’ and must therefore be downloaded and completed in Adobe Reader. Clicking this link will download a zip file containing the pdf.

In the event that your manuscript is accepted we will provide detailed guidance on our journal policies and formatting. You may however wish to ensure that the manuscript complies with our house style at this stage. See our style and formatting guide (https://www.nature.com/documents/commsj-phys-style-formatting-guide-accept.pdf) and checklist (https://www.nature.com/documents/commsj-phys-style-formatting-checklist-article.pdf) for reference.

Data availability statements and data citations policy: All Communications Materials manuscripts must include a section titled "Data Availability" at the end of the Methods section or main text (if no Methods). More information on this policy, and a list of examples, is available at http://www.nature.com/authors/policies/data/data-availability-statements-data-citations.pdf.

In particular, the Data availability statement should include:
- Accession codes for deposited data
- Other unique identifiers (such as DOIs and hyperlinks for any other datasets)
- At a minimum, a statement confirming that all relevant data are available from the authors
- If applicable, a statement regarding data available with restrictions
- If a dataset has a Digital Object Identifier (DOI) as its unique identifier, we strongly encourage including this in the Reference list and citing the dataset in the Data Availability Statement.

DATA SOURCES: We strongly encourage authors to deposit all new data associated with the paper in a persistent repository where they can be freely and enduringly accessed. We recommend submitting the data to discipline-specific, community-recognized repositories, where possible and a list of recommended repositories is provided at http://www.nature.com/sdata/policies/repositories.

If a community resource is unavailable, data can be submitted to generalist repositories such as figshare or Dryad Digital Repository. Please provide a unique identifier for the data (for example a DOI or a permanent URL) in the data availability statement, if possible. If the repository does not provide identifiers, we encourage authors to supply the search terms that will return the data. For data that have been obtained from publically available sources, please provide a URL and the specific data product name in the data availability statement. Data with a DOI should be further cited in the methods reference section.

Please refer to our data policies at http://www.nature.com/authors/policies/availability.html.

Please use the following link to submit your documents:

Link Redacted

** This url links to your confidential home page and associated information about manuscripts you may have submitted or be reviewing for us. If you wish to forward this email to co-authors, please delete the link to your homepage first **

We hope to receive your revised paper within three months; please let us know if you aren't able to submit it within this time so that we can discuss how best to proceed. If we don't hear from you, and the revision process takes significantly longer, we will close your file. In this event, we will still 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.

Please do not hesitate to contact me if you have any questions or would like to discuss these revisions further. We look forward to seeing the revised manuscript and thank you for the opportunity to review your work.

Best regards,

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

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

Reviewer report on "Covalent organic framework nanofiltration membranes: Green and scale-up preparation" by R. Wang et al., submitted for publication in Communications Materials.

Nanofiltration membranes are key to the solution of some of the most severe problems that our environment is presently confronted with. In this context, covalent organic frameworks are distinguished due to a series of unique properties, including their regularity, stability and extendibility. It is true, however, that attainment of these properties is only possible under adequate production condition, which, in addition, are subject to strict requirements concerning their environmental compatibility.
The paper nicely introduces into the great relevance and the challenges of this topic. I have read it with great interest and may confirm that my response to the questions 1 to 5 in your invitation letter to this review are affirmative. It were, in particular, the figures which I have found most informative. An impressive list of references nicely documents the actuality of the topic considered in this paper. In addition, the authors might like to refer, in their list of references, to as well the IUPAC technical reports (i.e. the corresponding publications in Pure and Applied Chemistry) with reference to terms like permeability, permeance and/or diffusion.

Publication is warmly recommended.

Reviewer #2 (Remarks to the Author):

In this work, Wang et al. report a comprehensive review manuscript for COFs film for nanofiltration membranes. This manuscript covers the background of the COFs film, fabrication techniques, and potential scalable approaches with outlooks of COFs membranes. I believe that this manuscript can serve as a guide for designing COFs membranes for molecular separation. I recommend this manuscript be published in Communication Materials with some minor revisions as below:
Below are the specific comments:
1. It would be nice to see the authors write a small section to briefly compare the advantages and disadvantages of COFs compared to other materials for nanofiltration membranes. This will help the readers to understand more about the current needs of the field.

2. The authors stated that “Recent studies have shown that COFMs exhibit solvent-responsive behaviors, enabling them to create narrower pore sizes in certain solvents and effectively separate pharmaceutical ingredients. Moreover, 3D COFMs, which have narrower pore sizes than 2D COFMs, also demonstrate strong separation capabilities for active drugs” in the manuscript.

However, the sentences do not explain the reasons for 3D COFMs having narrower pore sizes than 2D COFMs. I recommend the authors elaborate on this part in more detail.

3. In Addition to the last comment, it would help readers understand how to tune the pore sizes of the COFs to adjust the molecular cut-off and separation performance. I recommend the authors write a small paragraph about state-of-the-art strategies.

4. There are n/a typo in the Reference 29, 76, 80, and 97.

5. Some of the references in the main text are not correctly formatted.

Reviewer #3 (Remarks to the Author):

The authors summarize the recent development of COF nanofiltration membranes in their fabrications and properties, and the challenges of this field. The manuscript is well organized and written, and I suggest it is published before they answer the following questions.
1. In Figure 2 and Table 1, the authors seem conflate the concepts of “solution casting” with “mixed matrix”, which they need to clarify this confusion.
2. In the section of process efficiency, the definition of preparation efficiency is unclear, and it is better to consider to combine the membrane size with synthesize time here.
3. The crystal structures including the structural design, dimension, compositions, pore sizes and environment and crystallinity of COFMs are less discussed in the manuscript.
4. The comparisons of COF membranes with other membranes such as MOFs, polymers, PIMs and zeolites, etc including structures and properties are necessary.
5. The separation mechanism and transition process of molecules though COFMs are other important issues which needs to be discussed in the summary.

** Visit Nature Research's author and referees' website at www.nature.com/authors for information about policies, services and author benefits**

Communications Materials is committed to improving transparency in authorship. As part of our efforts in this direction, we are now requesting that all authors identified as ‘corresponding author’ create and link their Open Researcher and Contributor Identifier (ORCID) with their account on the Manuscript Tracking System prior to acceptance. ORCID helps the scientific community achieve unambiguous attribution of all scholarly contributions. You can create and link your ORCID from the home page of the Manuscript Tracking System by clicking on ‘Modify my Springer Nature account’ and following the instructions in the link below. Please also inform all co-authors that they can add their ORCIDs to their accounts and that they must do so prior to acceptance.
https://www.springernature.com/gp/researchers/orcid/orcid-for-nature-research

For more information please visit http://www.springernature.com/orcid

If you experience problems in linking your ORCID, please contact the Platform Support Helpdesk.

Version 1:

Decision Letter:

** Please ensure you delete the link to your author homepage in this e-mail if you wish to forward it to your coauthors **

Dear Professor Caro,

Your manuscript titled "Covalent organic framework nanofiltration membranes: Green and scale-up preparation" has now been seen again by our referees, whose comments appear below. In light of their advice I am delighted to say that we are happy, in principle, to publish a suitably revised version in Communications Materials.

We therefore invite you to edit your manuscript to comply with our journal policies and formatting style in order to maximise the accessibility and therefore the impact of your work.

EDITORIAL REQUESTS
* Your manuscript should comply with our policies and format requirements, detailed in our style and formatting guide (https://www.nature.com/documents/commsj-phys-style-formatting-guide-accept.pdf).

* Please edit your manuscript according to the editorial requests in the attached table, and outline revisions made in the right hand column. If you have any questions or concerns about any of our requests, please do not hesitate to contact me. It is important that each request be addressed in order to avoid delays in accepting your manuscript. Please upload the completed table with your manuscript files as a Related Manuscript file.

* The editorial requests table also includes a full list of the files that must be provided upon resubmission. Please upload your files according to this table.

* An updated editorial policy checklist that verifies compliance with all required editorial policies must be completed and uploaded with the revised manuscript. All points on the policy checklist must be addressed; if needed, please revise your manuscript in response to these points. Please note that this form is a dynamic ‘smart pdf’ and must therefore be downloaded and completed in Adobe Reader. Clicking this link will download a zip file containing the pdf.

Editorial policy checklist: https://www.nature.com/documents/nr-editorial-policy-checklist.zip

OPEN ACCESS
Communications Materials is a fully open access journal. Articles are made freely accessible on publication. For further information about article processing charges, open access funding, and advice and support from Nature Research, please visit https://www.nature.com/commsmat/open-access

At acceptance, you will be provided with instructions for completing the open access licence agreement on behalf of all authors. This grants us the necessary permissions to publish your paper. Additionally, you will be asked to declare that all required third party permissions have been obtained, and to provide billing information in order to pay the article-processing charge (APC).

Please use the following link to submit your revised files:

Link Redacted

** This url links to your confidential home page and associated information about manuscripts you may have submitted or be reviewing for us. If you wish to forward this email to co-authors, please delete the link to your homepage first **

We hope to hear from you within two weeks; please let us know if the process may take longer.

Best regards,

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

REVIEWERS' COMMENTS:

Reviewer #2 (Remarks to the Author):

Wang et al. have addressed all the comments I raised. I support the publication.

Reviewer #3 (Remarks to the Author):

I was happy with the revised manuscript, so I suggest it to be accepted.

** Visit Nature Research's author and referees' website at www.nature.com/authors for information about policies, services and author benefits**

Open Access This Peer Review File is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.
In cases where reviewers are anonymous, credit should be given to 'Anonymous Referee' and the source.
The images or other third party material in this Peer Review File are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.
To view a copy of this license, visit https://creativecommons.org/licenses/by/4.0/

Many thanks to the reviewers for their valuable comments and suggestions. The followings are the point-by-point answers to the concerns:

Response to Reviewer 1

Comments to the Author

Reviewer report on "Covalent organic framework nanofiltration membranes: Green and scale-up preparation" by R. Wang et al., submitted for publication in Communications Materials.

Nanofiltration membranes are key to the solution of some of the most severe problems that our environment is presently confronted with. In this context, covalent organic frameworks are distinguished due to a series of unique properties, including their regularity, stability and extendibility. It is true, however, that attainment of these properties is only possible under adequate production condition, which, in addition, are subject to strict requirements concerning their environmental compatibility.

The paper nicely introduces into the great relevance and the challenges of this topic. I have read it with great interest and may confirm that my response to the questions 1 to 5 in your invitation letter to this review are affirmative. It were, in particular, the figures which I have found most informative. An impressive list of references nicely documents the actuality of the topic considered in this paper. In addition, the authors might like to refer, in their list of references, to as well the IUPAC technical reports (i.e. the corresponding publications in Pure and Applied Chemistry) with reference to terms like permeability, permeance and/or diffusion.

Publication is warmly recommended.

Response: Thank you very much for your positive evaluation of our manuscript. We fully agree with your comments. In the manuscript, we acknowledge and highlight the fact that these properties including regularity, stability, and extendibility of COFs can only be achieved under appropriate production conditions, which are subject to strict requirements regarding environmental compatibility. In addition, we appreciate the suggestion to include IUPAC technical reports on some terms of membrane separation. We have cited the literature titled "**Terminology for membranes and membrane processes (IUPAC Recommendations 1996)**" published in Pure and Applied Chemistry.

Response to Reviewer 2

Comments to the Author

In this work, Wang et al. report a comprehensive review manuscript for COFs film for nanofiltration membranes. This manuscript covers the background of the COFs film, fabrication techniques, and potential scalable approaches with outlooks of COFs membranes. I believe that this manuscript can serve as a guide for designing COFs membranes for molecular separation. I recommend this manuscript be published in Communication Materials with some minor revisions as below:

Response: Thank you very much for your positive evaluation of our manuscript. We carefully revised the manuscript according to your advice and addressed your concerns point by point.

Comment 1: *It would be nice to see the authors write a small section to briefly compare the advantages and disadvantages of COFs compared to other materials for nanofiltration membranes. This will help the readers to understand more about the current needs of the field.*

Response: We appreciate your suggestion to include a comparison of COFs with other materials for nanofiltration membranes. We agree that this addition will provide valuable context for readers and have added a new section (**Section 2.3 Advantages and disadvantages**) to discuss the advantages and disadvantages of COFs in comparison to other materials. The relevant discussions are as follows:

2.3 Advantages and disadvantages

To objectively evaluate covalent organic framework membranes (COFMs), a comprehensive comparison was conducted between COFs and other common membrane materials - metal-organic frameworks (MOFs), hydrogen-bonded organic frameworks (HOFs), polymers of intrinsic microporosity (PIMs), zeolites, traditional polymers, and layered 2D materials - focusing on pore structure, crystallinity, stability, diversity, designability, processing, key advantages, and limitations (**Table 1**). COFs feature highly ordered and tunable pores (typically 1~3 nm), enabling precise molecular sieving for selective separation of small molecules or ions. Their chemical versatility allows functional group modifications to enhance properties like hydrophilicity, antifouling, or target-specific interactions. COFMs also demonstrate superior stability in harsh environments (e.g., organic solvents, acids/bases) compared to conventional polymers, making them suitable for diverse separation applications. However, challenges remain in green and scale-up preparation of defect-free COFMs. Additionally, pore alignment and intergrowth issues in thin-film configurations can compromise permeability and selectivity. While COFMs theoretically allow pore-size engineering, achieving sub-nanometer precision (<1 nm) for gas

separation and ion sieving is difficult, limiting their competitiveness with other advanced membranes. Overall, COFMs show promise for high-precision separations but require breakthroughs in green and scalable fabrication, as well as sub-nanopore control, to bridge the gap between lab research and industrial adoption.

Table 1 The comparative advantages and disadvantages of COF nanofiltration membranes relative to other materials.

Material	Pore	Crystallinity	Stability	Diversity and designability	Processing	Key Advantages	Main Limitations
COFs	Micropore/ mesopore	Modest to high crystallinity	Generally good chemical stability	Excellent	Insoluble	Pore size tunability, tailored functionality	Complex synthesis
MOFs	Micropore/ mesopore	Very high crystallinity	Poor to good stability	Excellent	Insoluble	High surface area, diversity	Limited stability, interfacial defects with polymers
HOFs	Micropore/ mesopore	Modest to high crystallinity	Poor	Good	Soluble in special solvent	Mild synthesis	Poor stability
PIMs	Micropore	Amorphous	Moderate	Good	Soluble	Intrinsic porosity, solution processing	Aging issues, limited pore size control
Zeolite	Micropore	Very high crystallinity	Thermal stability but acid/base sensitive	Good	Insoluble	Thermal/chemical robustness, low cost	Limited pore tunability, synthesis complexity
Polymer	Micropore/ mesopore	Amorphous	Good	Good	Soluble	Low cost, scalable fabrication	Trade-off between permeability and selectivity, aging
Layered 2D materials	Micropore	Modest to high crystallinity	Good mechanical stability but swelling	Good	Complex exfoliation process	Ultrathin, tunable interlayer channels	Difficulty in controlling stacking defects

Comment 2: *The authors stated that "Recent studies have shown that COFMs exhibit solvent-responsive behaviors, enabling them to create narrower pore sizes in certain solvents and effectively separate pharmaceutical ingredients. Moreover, 3D COFMs, which have narrower pore sizes than 2D COFMs, also demonstrate strong separation capabilities for active drugs" in the manuscript.*

However, the sentences do not explain the reasons for 3D COFMs having narrower pore sizes than 2D COFMs. I recommend the authors elaborate on this part in more detail.

Response: Thank you very much for your careful comment. We agree with the reviewer's point that the reasons why 3D COFMs have narrower pore sizes than 2D COFMs were not sufficiently explained in the original manuscript. To address this, we have revised the relevant formulation as follows in the revised version:

Additionally, 3D COFMs, with their narrower pore sizes resulting from complex topology and

structural interpenetration, exhibit robust capabilities in separating active drugs.

Comment 3: *In Addition to the last comment, it would help readers understand how to tune the pore sizes of the COFs to adjust the molecular cut-off and separation performance. I recommend the authors write a small paragraph about state-of-the-art strategies.*

Response: Thank you for highlighting the importance of clarifying pore size modulation strategies in COFs. As suggested, we have added a dedicated paragraph in **Section 2.1** ("**Pore engineering of COF nanofiltration membranes**") to discuss state-of-the-art approaches for tuning COF pore sizes and a dedicated paragraph in **Section 2.2** ("**Separation mechanism of COF nanofiltration membranes**") to showcase their impact on molecular separation. The relevant discussions are as follows:

2.1 Pore engineering of COF nanofiltration membranes

As discussed above, pore size is usually critical in membrane-based separation. For COFMs, it can be adjusted through monomer and topology design, stacking mode regulation, and pore wall modification. Monomers, as fundamental building units, vary in molecular size and topology, directly influencing the apertures and geometry of the synthesized COF materials (**Figure 2a**). Moreover, the choice of monomer can also dictate the chemical functionality and stability of the resulting COF materials, which are essential for specific separation applications[49]. For instance, monomers with rigid, planar structures tend to form more robust and ordered frameworks with well-defined pore sizes, while flexible monomers may lead to more dynamic or amorphous structures[50,51]. The topology design, which refers to the spatial arrangement of monomers within the framework, further refines the pore architecture[52]. Common topologies such as 2D hexagonal or 3D cubic frameworks offer distinct advantages in terms of pore accessibility and mechanical strength. Stacking mode regulation, particularly in 2D COFs, allows for the tuning of interlayer distances *via* spatial resistances[53] or restacking technology[54–56], which can significantly impact the overall porosity and pore size (**Figure 2b**). This approach is commonly used in COFMs to create angstrom-scale pores for ion sieving and gas separation, overcoming pore size limitations of COFs and expanding their application in membrane separation. However, ensuring uniform pore size remains challenging through this strategy, particularly with restacking technology. Finally, pore wall modification through post-synthetic functionalization or pre-modified monomer introduces additional chemical moieties that not only can reduce pore size of COFMs but also can enhance selectivity towards specific molecules through improve the host-guest interactions with the target species[57] (**Figure 2c**). This strategic incorporation of functional groups can also influence the overall stability and hydrophilic/hydrophobicity

of the COFMs, making them more adaptable to various applications. For instance, hydrophilic moieties can facilitate the entry of water molecules into the COFMs pores. Furthermore, the introduction of charged or polar functionalities can facilitate specific interactions, such as hydrogen bonding or electrostatic attraction, which are crucial for the selective separation of target molecules or ions. By tailoring the chemical environment within the pores, the properties of COFMs can be fine-tuned to achieve optimal separation performances. This approach underscores the versatility of COFMs and their potential to address complex challenges in material science and engineering. Together, these strategies provide a comprehensive toolkit for tailoring COFMs to meet the precise requirements of various membrane-based separation processes.

2.2 Separation mechanism of COF nanofiltration membranes

COFMs, as a class of porous separation membranes, utilize mechanisms such as physical size exclusion (**Figure 2d**) and chemical interactions—including electrostatic interaction (**Figure 2e**), bonding interactions (**Figure 2f**), solvation (**Figure 2g**), dielectric effects, and chemical adsorption—to achieve nanofiltration. Size exclusion, driven by the precise designability of COFMs' pore structures, plays a dominant role, blocking molecules larger than the pore size while allowing smaller ones to pass (**Figure 2d**). For instance, Lai and colleagues demonstrated that structural modifications can control the pore size of COFMs, directly impacting molecular separation performance[13,27]. Using the Langmuir-Blodgett method, they synthesized three ultrathin COFMs with varying carbon side chain lengths to adjust pore size. These membranes exhibited systematic changes in flux and molecular weight cut-off during OSN (**Figure 2h**).

Chemical interactions offer greater diversity than physical size screening. Electrostatic interaction becomes particularly significant in the scenarios of separating charged species, which significantly enhance selectivity towards target species due to the electrostatic repulsion (**Figure 2e**). For example, negatively charged COFMs prepared by EPD effectively reject negatively charged dye molecules despite their slightly smaller size than the COFMs' pores, while neutral molecules of the same molecular weight pass through[20] (**Figure 2i**). In addition, COFMs decorated with charged moieties in the pore wall also successfully achieve the ion sieving[29–32,35,58–61] and desalination[62–65] *via* the electrostatic interaction mechanism. Bonding interactions, such as hydrogen bonding, dipole interactions, π-π stacking, van der Waals forces, and stereoselective interactions, enhance selective recognition of specific species like metal ions or chiral molecules through tailored functional group modifications (**Figure 2f**). For instance, COFMs with sub-2-nanometer channels and abundant hydrogen bonding sites exhibit high permeability

for monovalent cations (K^+, Na^+, and Li^+) but low permeability for multivalent cations (Mg^{2+}) due to stronger hydrogen bonding interactions between the hydrated multivalent cations and the COF channel walls[37], resulting in high selectivity (**Figure 2j**). Solvation effect modulates transport kinetics by influencing the hydration states of both membrane channels and permeating species (**Figure 2g**). For instance, Sun and colleagues demonstrated the enhance ion selectivity by tuning the pore solvation abilities of COFMs, which were manipulated by adjusting the lengths of oligoether segments attached to the pore channels[33]. This study displayed that increasing the length of the oligoether chain facilitated ion transport, but the COFM with oligoether chains containing two ethylene oxide units exhibited the highest separation factor for Li^+/Mg^{2+}, achieving an exceptional selectivity of up to 1352. This was attributed to the most pronounced discrepancy in transmembrane energy barrier between Li^+ and Mg^{2+} in this specific COFMs (**Figure 2k**). This study provides insights into selective ion transport within confined nano-spaces and valuable design principles for developing highly selective COFMs. Notably, these mechanisms often operate synergistically-the ordered nanochannels may amplify chemical interactions through confined mass transfer process.

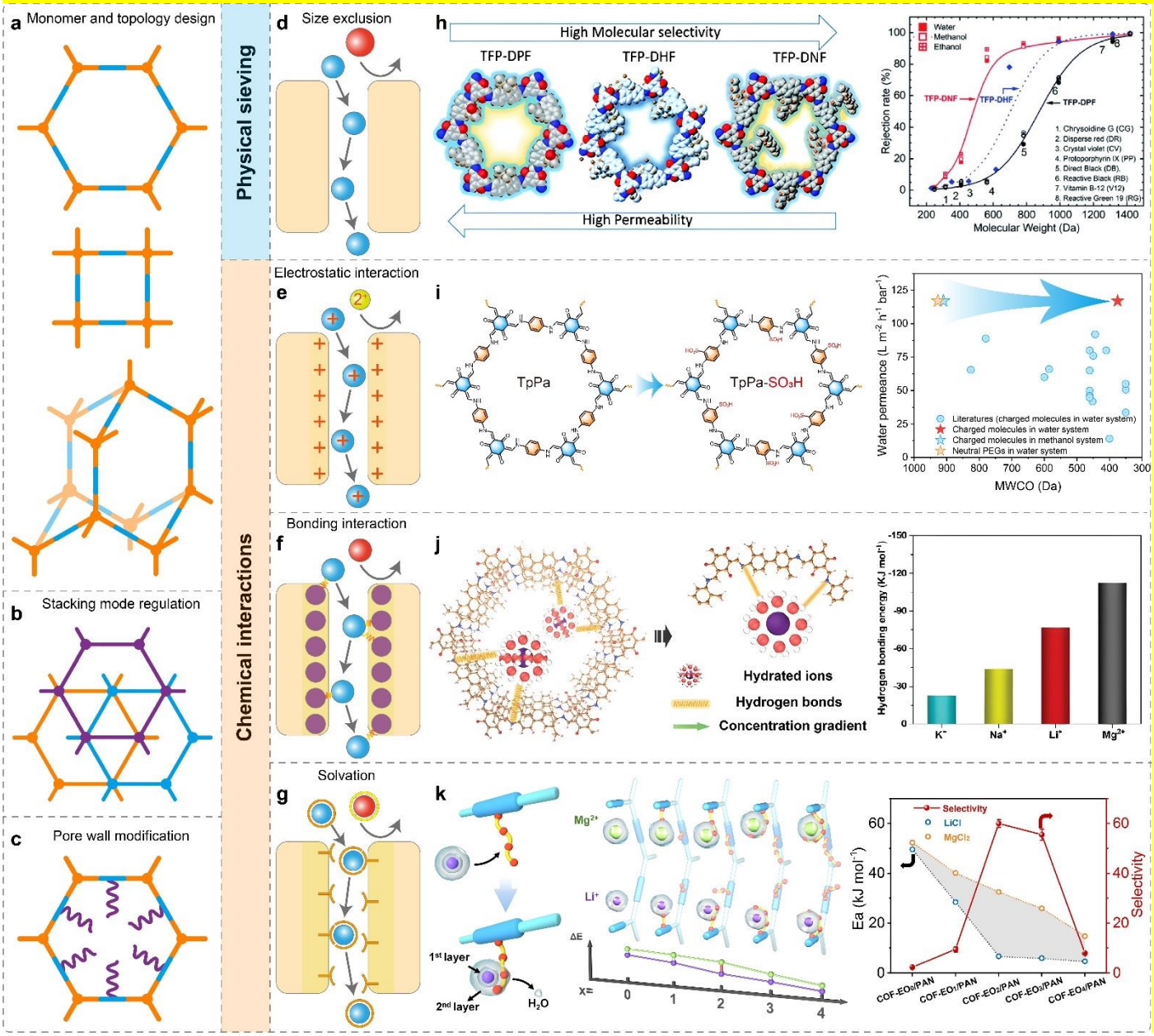

Figure 1 Main pore engineering strategies of **a**) Monomer and topology design, **b**) Stacking mode regulation, and **c**) Pore wall modification. Main separation mechanism of COF nanofiltration membranes including **d**) Size exclusion, **e**) Electrostatic interaction, **f**) Bonding interaction and **g**) Solvation as well as **h~k**) corresponding case studies. Figure **h** adapted with permission from ref.[27] (copyright Royal Society of Chemistry, 2020), Figure **i** adapted with permission from ref.[20] (copyright Wiley-VCH, 2022), Figure **j** adapted with permission from ref.[37] (copyright Wiley-VCH, 2021), Figure **k** adapted with permission from ref.[33] (copyright Proc. Natl. Acad. Sci. USA, 2024).

Comment 4: *There are n/a typo in the Reference 29, 76, 80, and 97.*

Response: Thank you for pointing out the typos in the references. We apologize for the inconvenience caused. Upon verification, we found that some of the references mentioned (29, 76, 80, and 97) were in the early view stage, which is why the volume/issue information was missing. In the revised manuscript, we have replaced

the missing information with the DOI numbers for these references to ensure accuracy and completeness. We have also double - checked all other references to avoid similar issues. We appreciate your attention to detail and hope that this revision meets your requirements.

Comment 5: *Some of the references in the main text are not correctly formatted.*

Response: Thank you for pointing out the issue regarding the incorrect formatting of some references in the main text. We have carefully reviewed all the references and have now corrected their formats according to the journal's requirements. We have double - checked to ensure that all the references are now accurately and consistently formatted, and that there are no other similar issues remaining.

Response to Reviewer 3

Comments to the Author

The authors summarize the recent development of COF nanofiltration membranes in their fabrications and properties, and the challenges of this field. The manuscript is well organized and written, and I suggest it is published before they answer the following questions.

Response: Thank you very much for your positive evaluation of our manuscript. We carefully revised the manuscript according to your advice and addressed your concerns point by point.

Comment 1: *In Figure 2 and Table 1, the authors seem conflate the concepts of "solution casting" with "mixed matrix", which they need to clarify this confusion.*

Response: Thank you very much for pointing out this issue. We have harmonized the relevant statements in the revised manuscript to avoid any confusion.

Comment 2: *In the section of process efficiency, the definition of preparation efficiency is unclear, and it is better to consider to combine the membrane size with synthesize time here.*

Response: Thank you for your insightful comment on the section of process efficiency. We acknowledge that the definition of preparation efficiency was not clear enough. We have revised the definition of preparation efficiency in the revised manuscript. Now, we have taken into account both the membrane size and the synthesis time. Specifically, we have defined the preparation efficiency as $\eta = \frac{A}{T_{total}}$. This new definition gives a more comprehensive and accurate evaluation of the process efficiency. The relevant discussions are as follows:

The production efficiency (η) is typically defined as the effective membrane area produced per unit time:

$$\eta = \frac{A}{T_{total}} \quad (1)$$

where A is membrane area produced, T_{total} is total production time (including fixed and variable times).

$$T_{total} = T_0 + T_v = T_0 + \frac{A}{v} \quad (2)$$

where T_0 is the fixed time including equipment preheating, cleaning, initialization, which is time independent of membrane area. T_v is the variable time including coating, drying, which is time dependent of membrane area. v is the production rate (m^2/h).

Substituting total time into the efficiency formula gives:

$$\eta = \frac{A}{T_0 + \frac{A}{v}} = \frac{v \times A}{T_0 \times v + A} \quad (3)$$

From equation (3), it can be found that for small A, the fixed time T_0 dominates the process, resulting in an efficiency of $\eta \approx \frac{A}{T_0}$, which indicates low efficiency. In contrast, when A is large, the variable time T_v becomes dominating, leading to an efficiency of $\eta \approx v$, which approaches the production rate v. This shift highlights the different factors influencing efficiency depending on the scale of A. Overall, membrane production efficiency η can be significantly improved by optimizing the production rate v and minimizing fixed time T_0, especially for large-scale production. Hence, the roll-to-roll continuous production is critical to improve the production efficiency of preparing COFMs. However, the reports of continuous production of COFMs are rare.

Fabrication methods with high production efficiency have the potential to push scale-up preparation of COFMs. In this review, we simplify equation (3) to $\eta = \frac{A}{T_v}$ due to the lack of information of fixed time T_0 in the lab research to evaluate the common fabrication methods of COFMs…

Comment 3: *The crystal structures including the structural design, dimension, compositions, pore sizes and environment and crystallinity of COFMs are less discussed in the manuscript.*

Response: Thank you for your valuable suggestions. We have added a dedicated paragraph in **Section 2.1** ("**Pore engineering of COF nanofiltration membranes**") to discuss the crystal structures and explores how structural design, dimension, pore sizes, and environment of COFMs influence separation performance through the lens of separation mechanisms (**Section 2.2 Separation mechanism of COF nanofiltration membranes**).

2.1 Pore engineering of COF nanofiltration membranes

As discussed above, pore size is usually critical in membrane-based separation. For COFMs, it can be adjusted through monomer and topology design, stacking mode regulation, and pore wall modification. Monomers, as fundamental building units, vary in molecular size and topology, directly influencing the apertures and geometry of the synthesized COF materials (**Figure 2a**). Moreover, the choice of monomer

can also dictate the chemical functionality and stability of the resulting COF materials, which are essential for specific separation applications[49]. For instance, monomers with rigid, planar structures tend to form more robust and ordered frameworks with well-defined pore sizes, while flexible monomers may lead to more dynamic or amorphous structures[50,51]. The topology design, which refers to the spatial arrangement of monomers within the framework, further refines the pore architecture[52]. Common topologies such as 2D hexagonal or 3D cubic frameworks offer distinct advantages in terms of pore accessibility and mechanical strength. Stacking mode regulation, particularly in 2D COFs, allows for the tuning of interlayer distances *via* spatial resistances[53] or restacking technology[54–56], which can significantly impact the overall porosity and pore size (**Figure 2b**). This approach is commonly used in COFMs to create angstrom-scale pores for ion sieving and gas separation, overcoming pore size limitations of COFs and expanding their application in membrane separation. However, ensuring uniform pore size remains challenging through this strategy, particularly with restacking technology. Finally, pore wall modification through post-synthetic functionalization or pre-modified monomer introduces additional chemical moieties that not only can reduce pore size of COFMs but also can enhance selectivity towards specific molecules through improve the host-guest interactions with the target species[57] (**Figure 2c**). This strategic incorporation of functional groups can also influence the overall stability and hydrophilic/hydrophobicity of the COFMs, making them more adaptable to various applications. For instance, hydrophilic moieties can facilitate the entry of water molecules into the COFMs pores. Furthermore, the introduction of charged or polar functionalities can facilitate specific interactions, such as hydrogen bonding or electrostatic attraction, which are crucial for the selective separation of target molecules or ions. By tailoring the chemical environment within the pores, the properties of COFMs can be fine-tuned to achieve optimal separation performances. This approach underscores the versatility of COFMs and their potential to address complex challenges in material science and engineering. Together, these strategies provide a comprehensive toolkit for tailoring COFMs to meet the precise requirements of various membrane-based separation processes.

2.2 Separation mechanism of COF nanofiltration membranes

COFMs, as a class of porous separation membranes, utilize mechanisms such as physical size exclusion (**Figure 2d**) and chemical interactions—including electrostatic interaction (**Figure 2e**), bonding interactions (**Figure 2f**), solvation (**Figure 2g**), dielectric effects, and chemical adsorption—to achieve nanofiltration. Size exclusion, driven by the precise designability of COFMs' pore structures, plays a dominant role, blocking molecules larger than the pore size while allowing smaller ones to pass (**Figure**

2d). For instance, Lai and colleagues demonstrated that structural modifications can control the pore size of COFMs, directly impacting molecular separation performance[13,27]. Using the Langmuir-Blodgett method, they synthesized three ultrathin COFMs with varying carbon side chain lengths to adjust pore size. These membranes exhibited systematic changes in flux and molecular weight cut-off during OSN (**Figure 2h**).

Chemical interactions offer greater diversity than physical size screening. Electrostatic interaction becomes particularly significant in the scenarios of separating charged species, which significantly enhance selectivity towards target species due to the electrostatic repulsion (**Figure 2e**). For example, negatively charged COFMs prepared by EPD effectively reject negatively charged dye molecules despite their slightly smaller size than the COFMs' pores, while neutral molecules of the same molecular weight pass through[20] (**Figure 2i**). In addition, COFMs decorated with charged moieties in the pore wall also successfully achieve the ion sieving[29–32,35,58–61] and desalination[62–65] *via* the electrostatic interaction mechanism. Bonding interactions, such as hydrogen bonding, dipole interactions, π-π stacking, van der Waals forces, and stereoselective interactions, enhance selective recognition of specific species like metal ions or chiral molecules through tailored functional group modifications (**Figure 2f**). For instance, COFMs with sub-2-nanometer channels and abundant hydrogen bonding sites exhibit high permeability for monovalent cations (K^+, Na^+, and Li^+) but low permeability for multivalent cations (Mg^{2+}) due to stronger hydrogen bonding interactions between the hydrated multivalent cations and the COF channel walls[37], resulting in high selectivity (**Figure 2j**). Solvation effect modulates transport kinetics by influencing the hydration states of both membrane channels and permeating species (**Figure 2g**). For instance, Sun and colleagues demonstrated the enhance ion selectivity by tuning the pore solvation abilities of COFMs, which were manipulated by adjusting the lengths of oligoether segments attached to the pore channels[33]. This study displayed that increasing the length of the oligoether chain facilitated ion transport, but the COFM with oligoether chains containing two ethylene oxide units exhibited the highest separation factor for Li^+/Mg^{2+}, achieving an exceptional selectivity of up to 1352. This was attributed to the most pronounced discrepancy in transmembrane energy barrier between Li^+ and Mg^{2+} in this specific COFMs (**Figure 2k**). This study provides insights into selective ion transport within confined nano-spaces and valuable design principles for developing highly selective COFMs. Notably, these mechanisms often operate synergistically-the ordered nanochannels may amplify chemical interactions through confined mass transfer process.

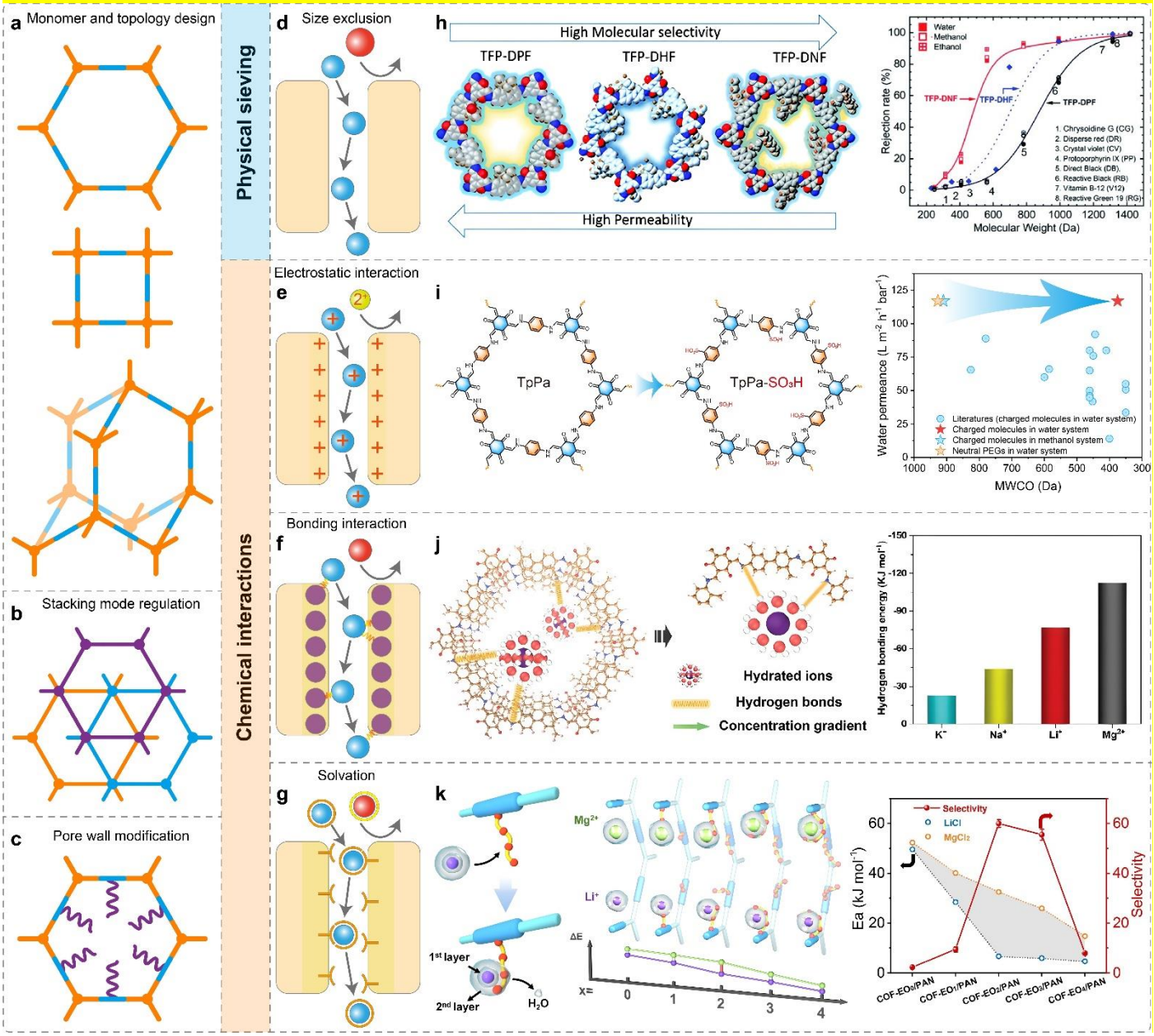

Figure 2 Main pore engineering strategies of **a**) Monomer and topology design, **b**) Stacking mode regulation, and **c**) Pore wall modification. Main separation mechanism of COF nanofiltration membranes including **d**) Size exclusion, **e**) Electrostatic interaction, **f**) Bonding interaction and **g**) Solvation as well as **h~k**) corresponding case studies. Figure **h** adapted with permission from ref.[27] (copyright Royal Society of Chemistry, 2020), Figure **i** adapted with permission from ref.[20] (copyright Wiley-VCH, 2022), Figure **j** adapted with permission from ref.[37] (copyright Wiley-VCH, 2021), Figure **k** adapted with permission from ref.[33] (copyright Proc. Natl. Acad. Sci. USA, 2024).

Comment 4: *The comparisons of COF membranes with other membranes such as MOFs, polymers, PIMs and zeolites, etc including structures and properties are necessary.*

Response: We appreciate your suggestion to include a comparison of COFs with other materials for nanofiltration membranes. We agree that this addition will provide valuable context for readers and have added

a new section (**Section 2.3 Advantages and disadvantages**) to discuss the advantages and disadvantages of COFs in comparison to other materials. The relevant discussions are as follows:

2.3 Advantages and disadvantages

To objectively evaluate covalent organic framework membranes (COFMs), a comprehensive comparison was conducted between COFs and other common membrane materials - metal-organic frameworks (MOFs), hydrogen-bonded organic frameworks (HOFs), polymers of intrinsic microporosity (PIMs), zeolites, traditional polymers, and layered 2D materials - focusing on pore structure, crystallinity, stability, diversity, designability, processing, key advantages, and limitations (**Table 1**). COFs feature highly ordered and tunable pores (typically 1~3 nm), enabling precise molecular sieving for selective separation of small molecules or ions. Their chemical versatility allows functional group modifications to enhance properties like hydrophilicity, antifouling, or target-specific interactions. COFMs also demonstrate superior stability in harsh environments (e.g., organic solvents, acids/bases) compared to conventional polymers, making them suitable for diverse separation applications. However, challenges remain in green and scale-up preparation of defect-free COFMs. Additionally, pore alignment and intergrowth issues in thin-film configurations can compromise permeability and selectivity. While COFMs theoretically allow pore-size engineering, achieving sub-nanometer precision (<1 nm) for gas separation and ion sieving is difficult, limiting their competitiveness with other advanced membranes. Overall, COFMs show promise for high-precision separations but require breakthroughs in green and scalable fabrication, as well as sub-nanopore control, to bridge the gap between lab research and industrial adoption.

Table 1 The comparative advantages and disadvantages of COF nanofiltration membranes relative to other materials.

Material	Pore	Crystallinity	Stability	Diversity and designability	Processing	Key Advantages	Main Limitations
COFs	Micropore/ mesopore	Modest to high crystallinity	Generally good chemical stability	Excellent	Insoluble	Pore size tunability, tailored functionality	Complex synthesis
MOFs	Micropore/ mesopore	Very high crystallinity	Poor to good stability	Excellent	Insoluble	High surface area, diversity	Limited stability, interfacial defects with polymers
HOFs	Micropore/ mesopore	Modest to high crystallinity	Poor	Good	Soluble in special solvent	Mild synthesis	Poor stability
PIMs	Micropore	Amorphous	Moderate	Good	Soluble	Intrinsic porosity, solution processing	Aging issues, limited pore size control

Zeolite	Micropore	Very high crystallinity	Thermal stability but acid/base sensitive	Good	Insoluble	Thermal/chemical robustness, low cost	Limited pore tunability, synthesis complexity
Polymer	Micropore/ mesopore	Amorphous	Good	Good	Soluble	Low cost, scalable fabrication	Trade-off between permeability and selectivity, aging
Layered 2D materials	Micropore	Modest to high crystallinity	Good mechanical stability but swelling	Good	Complex exfoliation process	Ultrathin, tunable interlayer channels	Difficulty in controlling stacking defects

Comment 5: *The separation mechanism and transition process of molecules though COFMs are other important issues which needs to be discussed in the summary.*

Response: Thank you for highlighting the importance of discussing separation mechanism of COFMs. We have added a dedicated paragraph in **Section 2.2** ("**Separation mechanism of COF nanofiltration membranes**") to showcase their impact on molecular separation. The relevant discussions are as follows:

2.2 Separation mechanism of COF nanofiltration membranes

COFMs, as a class of porous separation membranes, utilize mechanisms such as physical size exclusion (**Figure 2d**) and chemical interactions—including electrostatic interaction (**Figure 2e**), bonding interactions (**Figure 2f**), solvation (**Figure 2g**), dielectric effects, and chemical adsorption—to achieve nanofiltration. Size exclusion, driven by the precise designability of COFMs' pore structures, plays a dominant role, blocking molecules larger than the pore size while allowing smaller ones to pass (**Figure 2d**). For instance, Lai and colleagues demonstrated that structural modifications can control the pore size of COFMs, directly impacting molecular separation performance[13,27]. Using the Langmuir-Blodgett method, they synthesized three ultrathin COFMs with varying carbon side chain lengths to adjust pore size. These membranes exhibited systematic changes in flux and molecular weight cut-off during OSN (**Figure 2h**).

Chemical interactions offer greater diversity than physical size screening. Electrostatic interaction becomes particularly significant in the scenarios of separating charged species, which significantly enhance selectivity towards target species due to the electrostatic repulsion (**Figure 2e**). For example, negatively charged COFMs prepared by EPD effectively reject negatively charged dye molecules despite their slightly smaller size than the COFMs' pores, while neutral molecules of the same molecular weight pass through[20] (**Figure 2i**). In addition, COFMs decorated with charged moieties in the pore wall also successfully achieve the ion sieving[29–32,35,58–61] and desalination[62–65] *via* the electrostatic interaction mechanism. Bonding interactions, such as hydrogen bonding, dipole interactions, π-π stacking, van der

Waals forces, and stereoselective interactions, enhance selective recognition of specific species like metal ions or chiral molecules through tailored functional group modifications (**Figure 2f**). For instance, COFMs with sub-2-nanometer channels and abundant hydrogen bonding sites exhibit high permeability for monovalent cations (K^+, Na^+, and Li^+) but low permeability for multivalent cations (Mg^{2+}) due to stronger hydrogen bonding interactions between the hydrated multivalent cations and the COF channel walls[37], resulting in high selectivity (**Figure 2j**). Solvation effect modulates transport kinetics by influencing the hydration states of both membrane channels and permeating species (**Figure 2g**). For instance, Sun and colleagues demonstrated the enhance ion selectivity by tuning the pore solvation abilities of COFMs, which were manipulated by adjusting the lengths of oligoether segments attached to the pore channels[33]. This study displayed that increasing the length of the oligoether chain facilitated ion transport, but the COFM with oligoether chains containing two ethylene oxide units exhibited the highest separation factor for Li^+/Mg^{2+}, achieving an exceptional selectivity of up to 1352. This was attributed to the most pronounced discrepancy in transmembrane energy barrier between Li^+ and Mg^{2+} in this specific COFMs (**Figure 2k**). This study provides insights into selective ion transport within confined nano-spaces and valuable design principles for developing highly selective COFMs. Notably, these mechanisms often operate synergistically-the ordered nanochannels may amplify chemical interactions through confined mass transfer process.

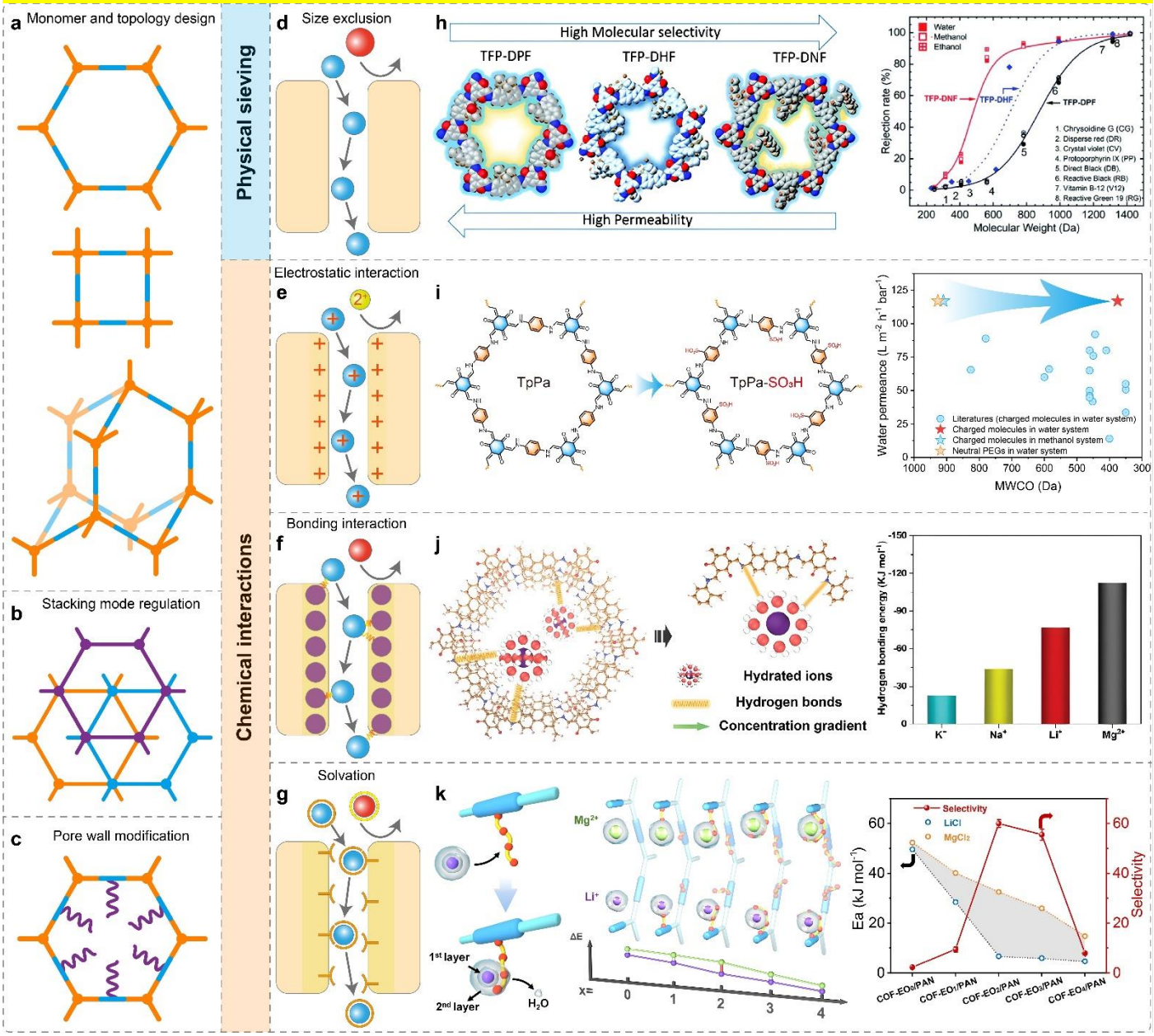

Figure 3 Main pore engineering strategies of **a**) Monomer and topology design, **b**) Stacking mode regulation, and **c**) Pore wall modification. Main separation mechanism of COF nanofiltration membranes including **d**) Size exclusion, **e**) Electrostatic interaction, **f**) Bonding interaction and **g**) Solvation as well as **h~k**) corresponding case studies. Figure **h** adapted with permission from ref.[27] (copyright Royal Society of Chemistry, 2020), Figure **i** adapted with permission from ref.[20] (copyright Wiley-VCH, 2022), Figure **j** adapted with permission from ref.[37] (copyright Wiley-VCH, 2021), Figure **k** adapted with permission from ref.[33] (copyright Proc. Natl. Acad. Sci. USA, 2024).

Thank you again for your constructive and valuable comments, which helped us to significantly improve the quality of our manuscript to make it clearer and more readable!

----------END----------