

Accurate stacking engineering of MOF nanosheets as membranes for precise H₂ sieving

Corresponding Author: Professor Haihui Wang

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors reported a changing stacking mode for the nanosheet-stacked Cu-BDC based MOF membrane based on DFT studies. This is an important topic and I agree with the authors that a precise regulation of stacking order between AA and AB configurations between nanosheets is challenging, and approaches that can achieve this are highly welcome. It is an interesting approach also because it modulates the pore size in the stacked MOF film. However, I have concerns that (a) authors do not validate the theoretical finding and (b) even if they manage to do, this approach has limitations which was not probed.

Stacking arrangement is the key highlight of this manuscript. However, it is only based on the DFT data. It is not clear whether the thin film membrane have the stacking arrangement as proposed. The scattering from the film is poor and the structure was not confirmed. This is also a major concern because DFT simulation for stacking is in vacuum environment. However, it is well known (e.g., from literature in GO and other emerging materials such as COFs), that the stacking arrangement is highly sensitive to the environment which includes pressure, guests (gases), solvent (humidity), etc.

While the work done here is interesting to understand diffusion-based selectivity under ideal circumstances (0 bar transmembrane pressure difference, no humidity), it is certainly not an indication of how good is the membrane that is developed for separation application. For this, they need to validate membrane separation in pressurized conditions (at least 1 bar transmembrane pressure difference). If not, I would recommend to remove figure 4c, where comparison with state-of-the-art membranes have been made.

Figure 4c: This figure is not complete. Several notable materials such as zeolite, silica, and carbon molecular sieves have not been included. As mentioned above, only comparison from pressurized test should be carried out.

I have also other concerns that need to be addressed before it is considered

In lines 163-164, the authors state, "where excessive linkers act as moderators covering the surface of the nanosheets, thereby impeding out-of-plane growth of MOF nanosheets with precisely controlled thickness." To me this sounds counter-intuitive.

In lines 185-186, are the Al signals in XPS from the 3d or 2p levels? The descriptions are inconsistent between the figure and the caption.

The best membrane in this work is the Cu(BDC)-NO₂ membrane, with an aperture size of approximately 0.372 nm according to the authors. However, this aperture is not selective for H₂/CO₂ gas pairs, as it is too large for both molecules (0.289 and 0.33 nm for H₂ and CO₂, respectively).

The SAED data in Fig. 3 is unclear. High-definition figures with detailed calculations for hkl in the electron diffraction image should be provided (latter in SI). Does this agree with the proposed structure?

The resolution of this supplementary figure 1 needs to be improved.

Reviewer #2

(Remarks to the Author)

In this manuscript, the authors propose a new strategy to adjust the stacking modes of MOF nanosheets with different sliding degrees via linker polarity regulation. Both theoretical calculations and experimental results demonstrate that a high linker polarity promotes neighboring nanosheets to a maximum AB stacking due to steric hindrance effects, leading to a controlled effective pore aperture of the membrane and consequently to improved molecular sieving. This theoretical finding was

confirmed by synthesis of a series of CuBDC-based nanosheets with different linkers.

It is indeed an attractive work. MOF nanosheets can show the desired in-plane pores – but this advantage could not be exploited so far due to random stacking. And this is the big novelty of the manuscript: The polarity of the MOF nanosheets controls AA and AB stacking modes.

Another novelty is that the introduction of distinct functional groups can regulate the in-plane nanosheet apertures. This theoretical finding was confirmed by synthesis of a series of CuBDC-based nanosheets with different linkers.

The paper is well organized with solid data. I highly support publication of this paper in Nature Communication. It brings fresh wind into the field of 2D membranes. However, the authors need to make efforts to improve some of the discussions before acceptance. Here are some suggestions and comments:

(1) Give in a scheme the difference of gas transport through AA and AB stacked MOF nanosheets.

(2) Linker polarity controls AA or AB stacking. If stacked, stability of stacking is an issue. Can the stacked nanosheets be fixed through covalent bondings?

(3) The paper is clearly written. But the reviewer cannot understand the sentence “Through computational analysis, the theoretical apertures of a series of monolayer nanosheets are 0.700, 0.580, 0.695, 0.545, 0.737 and 0.651 nm (Supplementary Fig. 1) identified along the $(\bar{2} 01)$ plane...”. Apertures ... along ... $(\bar{2} 01)$ plane. We have crystallographic directions and crystallographic planes. “...BDC-based linkers to form a porous 2D network that stacks along the $(\bar{2} 01)$ crystal axis...” Does this mean that the pores are not perpendicular to the stack or perpendicular to the plane of the nanosheet?

(4) It took the reviewer some time to understand the meaning of “sliding amount” and “sliding path” in Fig. 1. The first impression was that SLIDING describes some movement like “sliding roof of a car”. Is DISTORTION a better description? I am not sure; a native speaker should decide it.

(5) The interplay of calculations and experiments are one of the strengths of the manuscript. However, it would be helpful for the readers to say at every position whether it is a theoretical or experimental finding.

Reviewer #3

(Remarks to the Author)

Wang's group has carefully designed 2D-MOFs in terms of their stacking mode for the efficient separation of H₂ from CO₂ and CH₄ mixtures. The method is clear and the idea is brilliant, as we saw at the recent MOF-2024 conference in Singapore.

Before publishing this manuscript, I have a few questions:

1) How do the polarity of linkers and the stacking mode of 2D MOFs affect the heat of adsorption of gas for H₂/CO₂ and H₂/CH₄ mixtures?

2) Have you observed the effect of pore blockage inside the membrane due to the strong interaction of the gas molecules with the framework? Are there any findings from calculation studies? Could you please comment on this?

Reviewer #4

(Remarks to the Author)

In this manuscript, the authors adjusted the stacking modes in MOF nanosheet membranes by linker polarity regulation. They found a high linker polarity promotes neighboring nanosheets to a maximum AB stacking due to steric hindrance effects. It has been proved to control the effective pore aperture of the MOF nanosheet membranes and even enhance the molecular sieving performance. It is a meaningful work, which has draw attention to this unrevealed issue in 2D nanosheet membrane fields for the first time. The strategy for precise regulation of stacking modes is also innovative and smart. Overall, I think this paper is well-written and the presented concept is clear and interesting which would coincide with the scope and novelty standards of Nature Communications. Hence, this paper can be accepted for publication after carefully addressing the following comments with minor revision.

1. Engineering the pore size/shape of the stacking MOF-nanosheet with different functional groups is very interesting, this reviewer is wondering, if any experimental or computational work has ever discussed such point? If not, this could be emphasized in the work, e.g. in Abstract or Introduction.

2. In Fig 1a, the authors discussed the sliding degree from 0 to 100%, and I am not quite sure how the authors determined the sliding values.

3. The author has discussed seven different types of MOF nanosheets in Figure 2 to investigate the effect of linker type on the stacking property. However, they only choose three of them to investigate the separation performance. Why? The author should present the reason.

4. Is PBE exchange-correlation functional including DFT-D3 dispersion correction with Becke-Johnson (BJ) damping scheme widely used for MOFs?

5. The authors showed a lot of distance/size data in Fig. 2, how were they calculated or defined? Please give more details.

6. The authors claimed that “The thickness of the nanosheets is notably influenced by the Cu/linker ratio, where excessive linkers act as moderator covering on the surface of the nanosheets, thereby impeding out-of-plane growth of MOF nanosheets with precisely controlled thickness.” Please provide the evidence of the change in morphology of the nanosheets at different Cu/linker ratios.

7. The authors prepared the MOF nanosheets using DMF as solvent, whether DMF was removed in the following process? Otherwise, it will also affect the membrane structure and the gas separation performance.

Reviewer #5

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have addressed most of my comments. It is unfortunate that the membrane's performance deteriorates completely at a slight overpressure (1.1 bar), which makes it challenging to apply these membranes in practical applications. This point is often overlooked in the literature. It should be highlighted in the main text, and Figure R2 should be added in SI. Author should also list potential reason as to why membrane performance fails at slight pressurization.

Reviewer #2

(Remarks to the Author)

I carefully studied the 4 reviews and the 4 answers of the authors. In principle, all reviewer support publication after revision.

Speaking for my review (number 2), I am completely satisfied.

There is, however, one remark. On line 55, the authors themselves cite "Prof Wang's group" which is unusual since other groups are cited without the title prof, such as Yang et al., Zhao et al. It would be more common to say "Wang's group" or "Wang and coworker" or so.

Reviewer #3

(Remarks to the Author)

The authors answered and revised all queries raised by reviewers.

The paper is great!

It was a very enjoyable reading for me.

I would like to say huge congratulations to all authors.

Reviewer #4

(Remarks to the Author)

The author have addressed all the concerns, and I suggest to accept this manuscript in the journal of Nature Communications.

Reviewer #5

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Version 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have addressed my comments. Very pleased to see the inclusion of text on the pressurization issue, which will help the discussion of this important topic in the field, helping to advance the field.

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Response to the Reviewers' Comments

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

Reviewer #1: The authors reported a changing stacking mode for the nanosheet-stacked Cu-BDC based MOF membrane based on DFT studies. This is an important topic and I agree with the authors that a precise regulation of stacking order between AA and AB configurations between nanosheets is challenging, and approaches that can achieve this are highly welcome. It is an interesting approach also because it modulates the pore size in the stacked MOF film.

Response: Thank you for your encouragement and valuable suggestions. We have revised our manuscript prudently according to your comments point-by-point. We hope these added experiments and explanations can help the readers understand our work more easily.

1. However, I have concerns that (a) authors do not validate the theoretical finding and (b) even if they manage to do, this approach has limitations which was not probed. Stacking arrangement is the key highlight of this manuscript. However, it is only based on the DFT data. It is not clear whether the thin film membrane have the stacking arrangement as proposed. The scattering from the film is poor and the structure was not confirmed. This is also a major concern because DFT simulation for stacking is in vacuum environment. However, it is well known (e.g., from literature in GO and other emerging materials such as COFs), that the stacking arrangement is highly sensitive to the environment which includes pressure, guests (gases), solvent (humidity), etc.

Response: Thank you very much for your valuable comments. We agree with you that the stacking modes of some nanosheets (such as GO and COFs) sometimes can be altered by introducing different solvents, applying pressure or incorporating CO₂ molecules. But the case in this work is totally different, where more details are discussed as below.

1. Experimental evidence of stacking arrangement

In previous manuscript, we admit that the X-ray signals are weak due to the ultrathin thickness of around 600 nm. To confirm the stacking structure experimentally, we attempted to deposit thicker nanosheet films, with thicknesses of approximately 3 μm , to enhance the intensity of the X-ray signals from the films, employing much slower scanning speed ($2^\circ/\text{min}$). As expected, more details on the nanosheets arrangement structure appeared. As shown in Fig. R1, new peaks at 8.2° can be observed in the XRD patterns of the CuBDC-(OH)₂ and CuBDC-(Br)₂ nanosheet films, corresponding to the (110) reflection of the AA stacking mode, which cannot be found in the XRD patterns of the simulated AB stacking mode. The scattering signals well matched with AA stacking demonstrate that the CuBDC-(OH)₂ and CuBDC-(Br)₂ nanosheet films adopt AA stacking mode. For the CuBDC-NO₂ nanosheet film, the newly appeared diffraction peaks at 8.2° and 18.0° , corresponding to the (110) and ($\bar{1}30$) reflections, respectively, match well with the XRD patterns of the simulated AB_{0.17} stacking mode. Such experimental results are also in agreement with their corresponding simulated structures, where the nanosheets stack in the lowest formation energy.

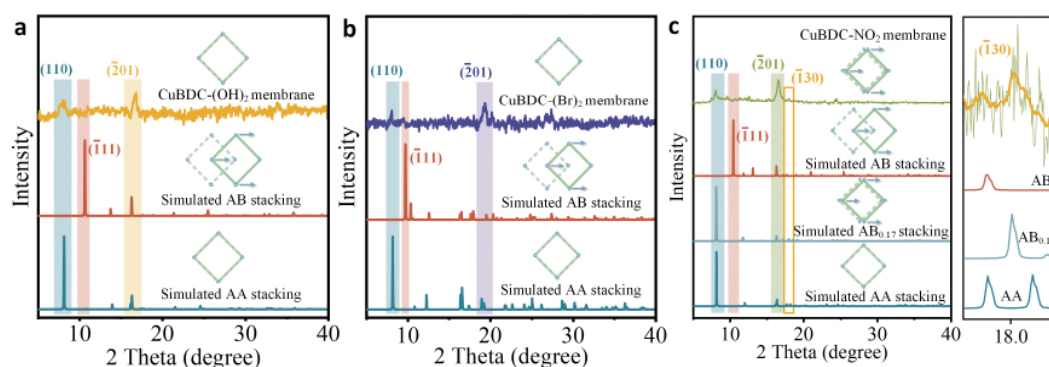


Fig. R1 XRD patterns of the a) CuBDC-(OH)₂, b) CuBDC-(Br)₂ and c) CuBDC-NO₂ nanosheets stacks. The enlarged area on the right of Fig. R1c corresponds to the yellow rectangular wireframe area depicted on the left.

2. Reliability analysis of DFT simulations

The stacking structures of the nanosheets at normal temperature and pressure are almost the same as predicted from DFT simulations in vacuum environment, as evidenced by the consistency between the experimental XRD results and the simulated ones of the stacking modes. It is demonstrated that there is no obvious difference in the stacking arrangement of nanosheets in vacuum and actual environments, at least for the CuBDC-(OH)₂, CuBDC-(Br)₂ and CuBDC-NO₂ nanosheets. Therefore, it is reasonable

and credible to predict the nanosheets stacking structure by DFT simulations.

According to your comments, we have added Fig. R1 as Figs. 3o-q in the revised manuscript (page 5), the corresponding explanations have also been added in the revised manuscript (page 6), highlighted in yellow.

2. While the work done here is interesting to understand diffusion-based selectivity under ideal circumstances (0 bar transmembrane pressure difference, no humidity), it is certainly not an indication of how good is the membrane that is developed for separation application. For this, they need to validate membrane separation in pressurized conditions (at least 1 bar transmembrane pressure difference). Figure 4c: This figure is not complete. Several notable materials such as zeolite, silica, and carbon molecular sieves have not been included. As mentioned above, only comparison from pressurized test should be carried out. If not, I would recommend to remove figure 4c, where comparison with state-of-the-art membranes have been made.

Response: Thank you for your comments. Gas separation performance of the membrane was evaluated through the classical Wicke-Kallenbach method (*Nature* 606, 706-712 (2022)). A gas mixture with a flow rate ratio of 1:1 (total flow rate of 50 mL min⁻¹) was applied to the feed side of the membrane, and the permeate gas was removed from the permeate side by the sweep gas (flow rate of 25 mL min⁻¹). Pressures at both the feed side and permeate side were maintained at 1 bar. The driving force for gas permeation is the partial pressure difference of each component across the membrane, which results from the different gas concentrations between the feed side and the permeate side. Herein, the partial pressure difference of each gas is 0.5 bar (as the driving force), although there is no total pressure difference across the membrane.

Moreover, we attempted to perform the gas separation tests under pressurized conditions, but unfortunately, the results were unfavorable. As shown in Fig. R2, upon increasing the pressure to 1.1 bar, the H₂/CH₄ selectivity of the CuBDC-(Br)₂ nanosheet membrane declines to only 9.8. Fortunately, the membrane separation performance can be recovered after pressure relief. We have to admit that it is still challenging for 2D nanosheet membranes to separate gas molecules under elevated pressure. That is why most experiments were carried out at atmospheric pressure. Although the membrane separation performance under ideal circumstances cannot reflect the efficacy for further applications, it is meaningful for understanding the stacking mode of MOF nanosheets.

According to your comments, we have removed Fig. 4c, Supplementary Fig. 22,

and Supplementary Table 12 from the previous manuscript and supporting information. More explanations have also been added in the revised manuscript (page 11), highlighted in yellow.

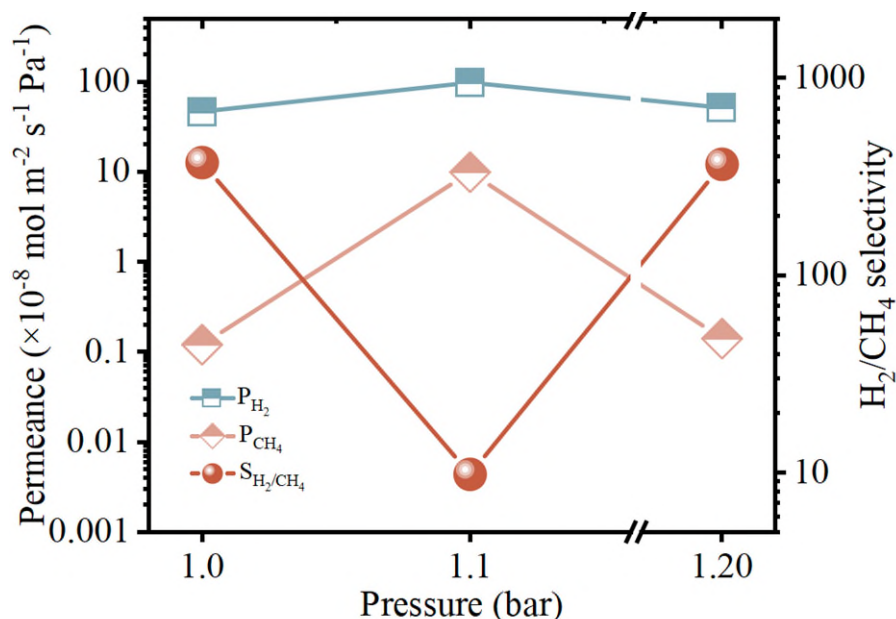


Fig. R2 Gas separation performance of the CuBDC-(Br)₂ nanosheet membrane for H₂/CH₄ binary mixtures under various pressure conditions.

3. In lines 163-164, the authors state, "where excessive linkers act as moderators covering the surface of the nanosheets, thereby impeding out-of-plane growth of MOF nanosheets with precisely controlled thickness." To me this sounds counter-intuitive.

Response: Thank you very much for your comments. In order to study the nanosheet growth mechanism, we prepared a series of MOF nanosheets at varying metal/linker ratios, where their corresponding morphological structure can be observed in Figs. R3-R5. It is obvious that different metal/linker ratios significantly influence the growth behavior of MOF nanosheets. At higher metal/linker ratios, MOF crystals tend to grow in multiple layers. Conversely, at lower metal/linker ratios, the growth of MOF nanosheets along the vertical direction is inhibited, leading to the formation of ultrathin nanosheets. Additionally, the diffusion of metal ions and linkers slows down as the temperature decreases, thereby limiting nanosheet growth in a vertical direction. The metal/linker ratio serves as a major factor in governing the morphology of nanosheets, exhibiting a consistent trend of variation, even under varying temperature conditions. More importantly, such nanosheet growth mechanism is consistent for three kinds of different materials (CuBDC-(Br)₂, CuBDC-(OH)₂ and CuBDC-NO₂). Similar

phenomena have also been reported in the relevant literatures. For example, *Chem. Eng. J.* 227,145 (2013) and *Sci. Rep.* 8, 9597 (2018) discussed the effect of excess linker on the growth of MOF crystals, which was in accordance with our findings.

According to your comments, we have added Figs. R3-R5 as Supplementary Figs. 14-16 in the revised supporting information (pages 18-20), the corresponding discussions and reaction details have also been added in the revised manuscript (pages 5 and 10), highlighted in yellow.

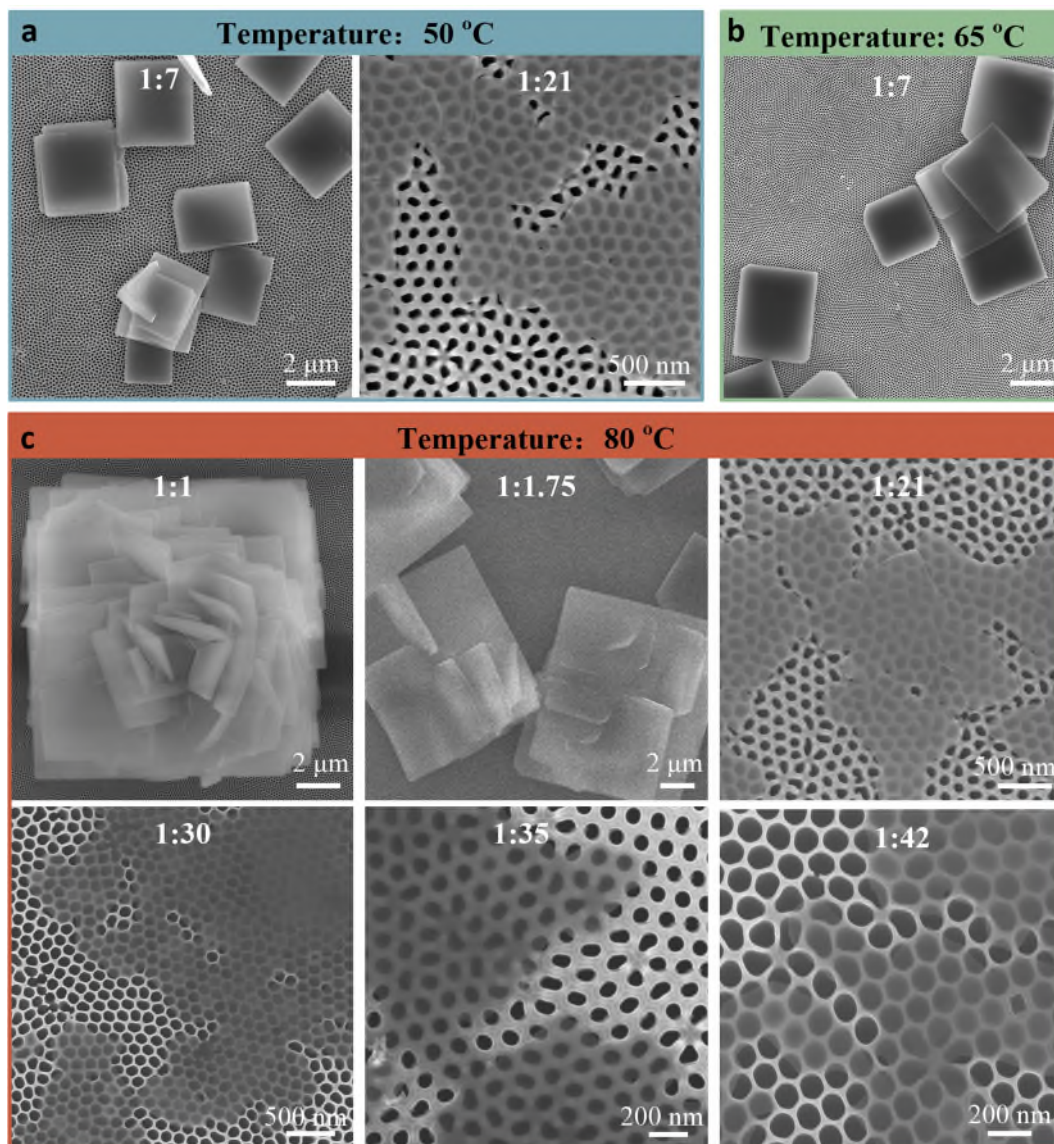


Fig. R3 The SEM images of the CuBDC-(Br)₂ nanosheets prepared under different reaction conditions. Values of Cu/linker ratio and reaction temperature are given, with all reactions carried out for 30 min.

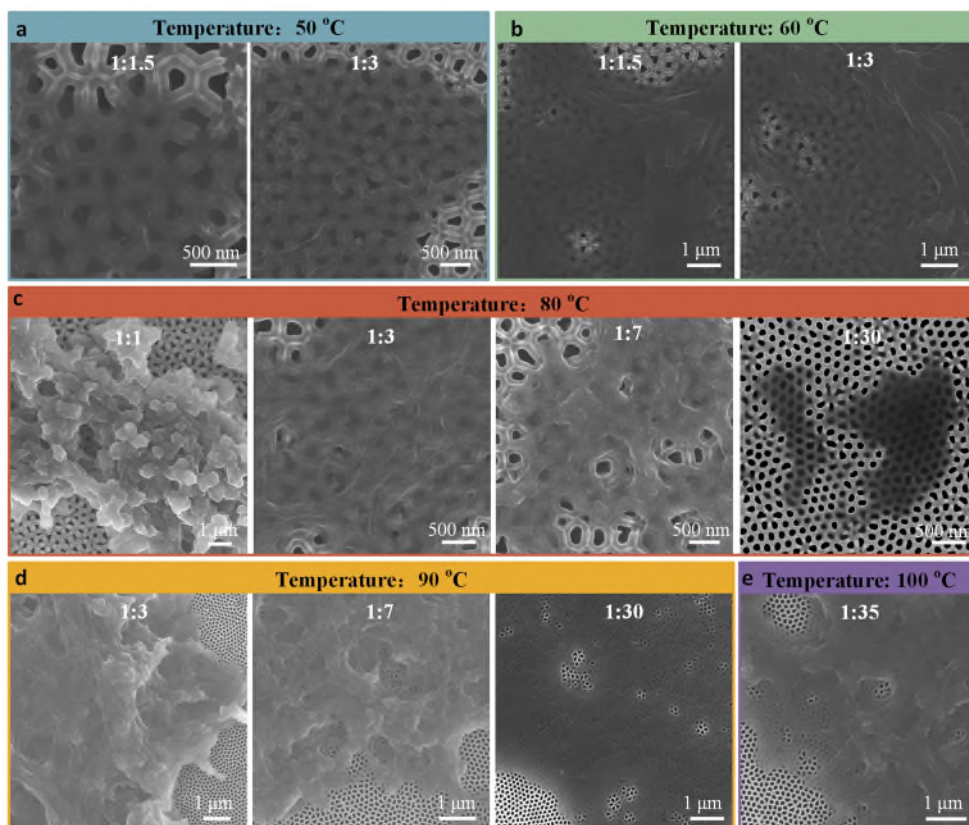


Fig. R4 The SEM images of the CuBDC-(OH)₂ nanosheets prepared under different reaction conditions. Values of Cu/linker ratio and reaction temperature are given, with all reactions carried out for 30 min.

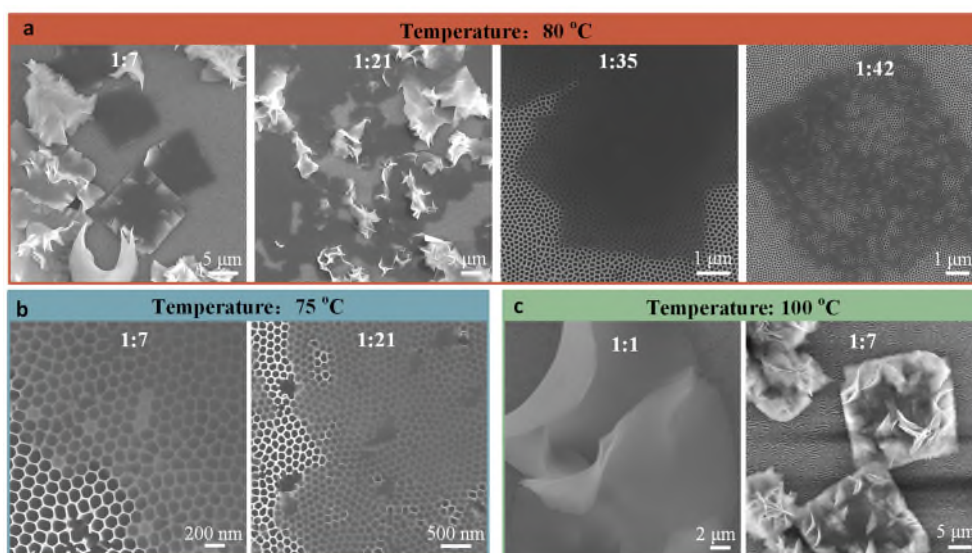


Fig. R5 The SEM images of the CuBDC-NO₂ nanosheets prepared under different reaction conditions. Values of Cu/linker ratio and reaction temperature are given, with all reactions carried out for 30 min.

4. In lines 185-186, are the Al signals in XPS from the 3d or 2p levels? The descriptions are inconsistent between the figure and the caption.

Response: Thank you for your kind reminding. We have carefully examined the relevant parts of the manuscript and confirmed that the Al signals in XPS are from the 2p levels. According to your comments, we have corrected the corresponding description of “Al 3d” to “Al 2p” in the revised manuscript (page 5), highlighted in yellow.

5. The best membrane in this work is the Cu(BDC)-NO₂ membrane, with an aperture size of approximately 0.372 nm according to the authors. However, this aperture is not selective for H₂/CO₂ gas pairs, as it is too large for both molecules (0.289 and 0.33 nm for H₂ and CO₂, respectively).

Response: Thank you for your comments. In order to clarify the reason behind, more experiments and simulations are added.

Firstly, we investigated the adsorption properties of the CuBDC-NO₂ nanosheets on different gas molecules. Fig. R6a shows that the CuBDC-NO₂ nanosheets present much higher adsorption capacity for CO₂ compared to the other two gases. In addition, as shown in Fig. R6b, the heat of adsorption for CO₂ on CuBDC-NO₂ nanosheets is -27.0 kJ/mol, whose absolute value is higher than that for H₂ (-14.2 kJ/mol), N₂ (-16.1 kJ/mol) and CH₄ (-20.7 kJ/mol). It is attributed to the electron-withdrawing property of the -NO₂ group in the CuBDC-NO₂ structure, which facilitates interaction between the -NO₂ group and CO₂ molecules (*Chem. Sci.* 11, 5339-5346 (2020); *J. Chem. Phys.* 132, 044705 (2010)), leading to a stronger affinity for CO₂. Moreover, the -NO₂ group acts as a binding site for CO₂ molecules through dipole-quadrupole interaction (*J. Am. Chem. Soc.* 131, 3875-3877 (2009)). Consequently, the CO₂ molecules adsorbed on CuBDC-NO₂ nanosheets further provide increased resistance for their diffusion, thus resulting in markedly lower CO₂ permeance and higher H₂/CO₂ selectivity.

Moreover, the probability distribution of the center of mass (COM) of gas molecules was studied through Monte Carlo (MC) simulations to ascertain the distribution of H₂, CO₂, N₂ and CH₄ molecules within the framework under ambient conditions. As shown in Fig. R7, the relatively high peak density values observed indicate a significant adsorption affinity of CO₂ for the framework, leading to a reduced diffusion rate of CO₂ molecules through the membrane, effectively decreasing CO₂ permeance. In contrast, the extremely low density values detected for H₂ molecules in

the probability distribution of COM imply tiny adsorption of H₂ within the framework, which promotes fast H₂ diffusion through the membrane and leads to high H₂/CO₂ selectivity.

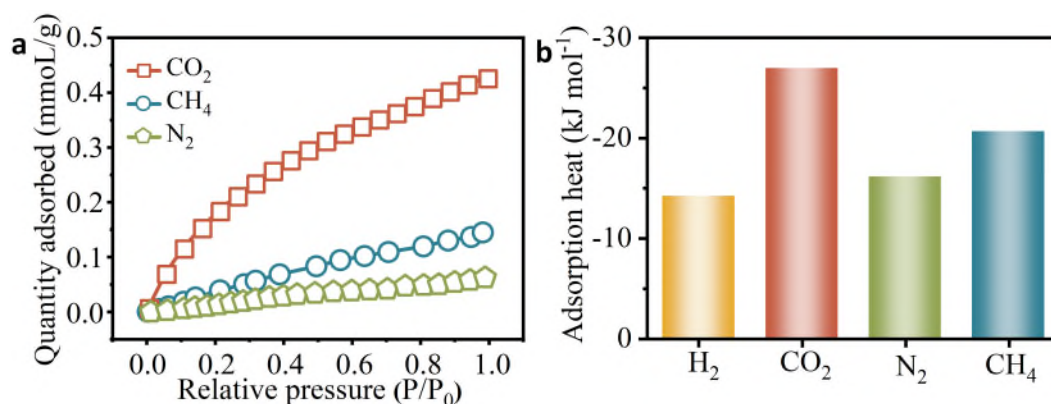


Fig. R6 a) Gas adsorption isotherms of the CuBDC-NO₂ nanosheets measured experimentally at 25 °C. b) Heat of adsorption of various gases calculated through Monte Carlo (MC) simulations.

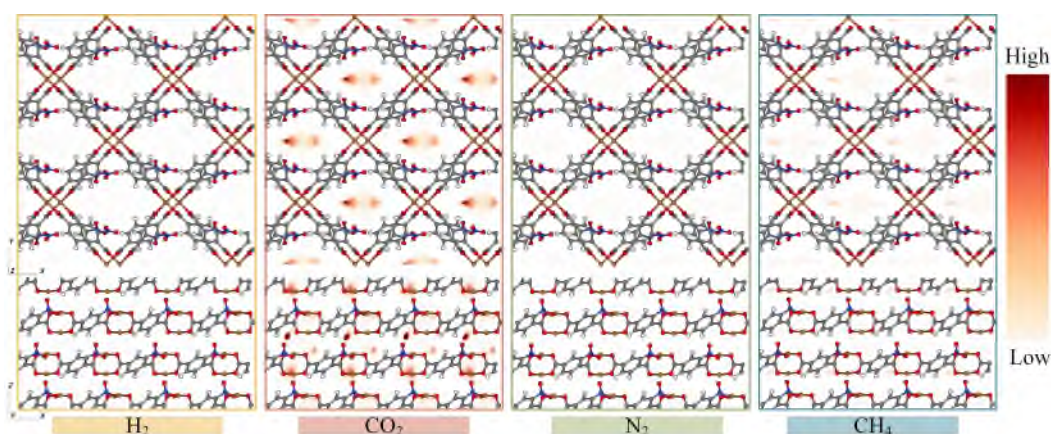


Fig. R7 2D density distributions of H₂, CO₂, N₂ and CH₄ molecules within the CuBDC-NO₂ framework under ambient conditions. Dark red and light yellow represent relatively high and low adsorption of different gas molecules by the framework, respectively. Cu, brown; O, red; N, blue; C, grey; H, white.

Both of the above experimental and simulated results suggest that adsorption indeed affects H₂/CO₂ separation of the CuBDC-NO₂ membrane. That is why it can still present good H₂/CO₂ separation performance, although the aperture is larger than both gas molecules.

According to your comments, we have added Figs. R6 and R7 as Supplementary Figs. 26 and 27 in the revised supporting information (pages 30-31), the corresponding explanations and simulation details have also been added in the revised manuscript

(pages 7-8) and supporting information (pages 3-4), highlighted in yellow.

6. The SAED data in Fig. 3 is unclear. High-definition figures with detailed calculations for hkl in the electron diffraction image should be provided (latter in SI). Does this agree with the proposed structure?

Response: Thank you very much for your valuable comments. We have carried out the TEM characterization of the nanosheets again, the TEM images and SAED figures with high definition are shown in Fig. R8 below. The diffraction rings from the SAED data corresponding to $(\bar{2}01)$ plane can be distinctly observed in the as-synthesized three kinds of nanosheets. The measured d -spacing values of the CuBDC-(OH)₂, CuBDC-(Br)₂ and CuBDC-NO₂ nanosheets are 0.54, 0.46 and 0.54 nm, respectively, agreeing with both the experimental XRD results and simulated results (Figs. 3o-q), which indicates these prepared MOF nanosheets present the proposed structure.

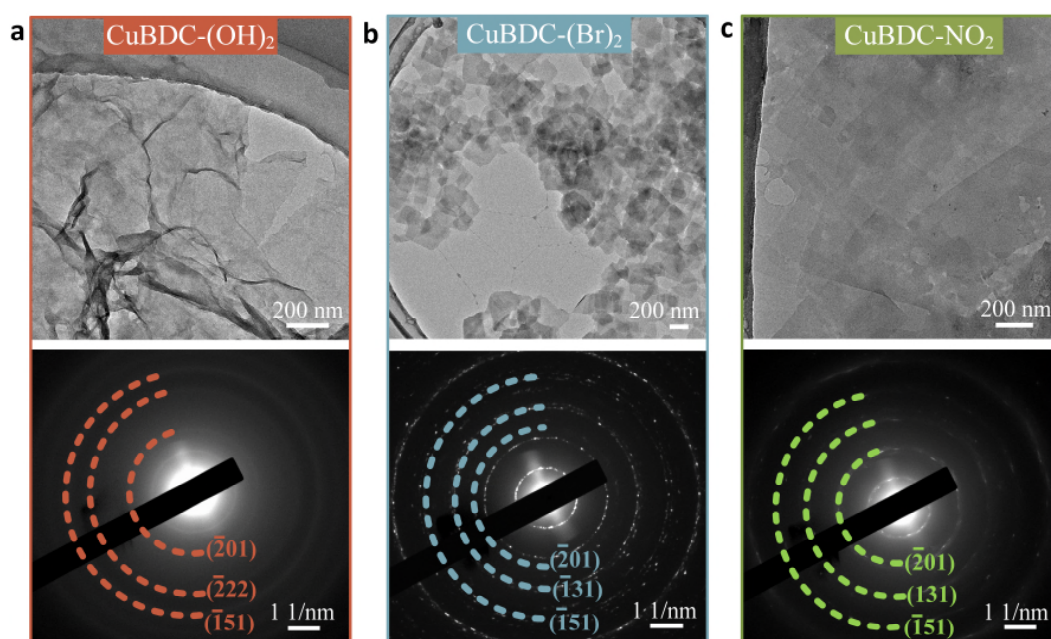


Fig. R8 TEM images and SAED patterns of the as-synthesized a) CuBDC-(OH)₂, b) CuBDC-(Br)₂ and c) CuBDC-NO₂ nanosheets.

Detailed calculations for hkl are given as follows (Zou X, Hovmöller S, Oleynikov P. Vol. 16. Oxford University Press, 2011):

A lattice point in the reciprocal lattice \mathbf{g}_{hkl} can be described as:

$$\mathbf{g}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \quad (1)$$

where hkl are called Miller indices. Each reciprocal lattice point hkl (reflection or diffraction spot) represents a set of parallel planes (called Bragg planes) in real space.

The orientation of the planes is determined by the Miller indices hkl , perpendicular to the reciprocal lattice vector \mathbf{g}_{hkl} . These planes cut the unit-cell axes an integer number of times per unit cell. Each Miller index tells us how many times a given set of planes cut a unit-cell axis. Each set of planes has its specific index.

The interplanar distance d_{hkl} , is inversely proportional to the length of the reciprocal lattice vector \mathbf{g}_{hkl}

$$d_{hkl} = 1/|\mathbf{g}_{hkl}| \quad (2)$$

Where

$$\mathbf{g}_{hkl}^2 = \frac{1}{d_{hkl}^2} = h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2klb^*c^* \cos\alpha^* + 2hla^*c^* \cos\beta^* + 2hka^*b^* \cos\gamma^* \quad (3)$$

According to your comments, we have replaced Fig. R8 as Figs. 3e-j in the revised manuscript (page 5), the corresponding explanations have also been added in the revised manuscript (page 5) and supporting information (page 4), highlighted in yellow.

7. The resolution of this supplementary figure 1 needs to be improved.

Response: Thank you for your comment. We have improved the image resolution from 100 dpi to 300 dpi. According to your comment, we have replaced Fig. R9 as Supplementary Fig. 1 in the revised supporting information (page 5), highlighted in yellow.

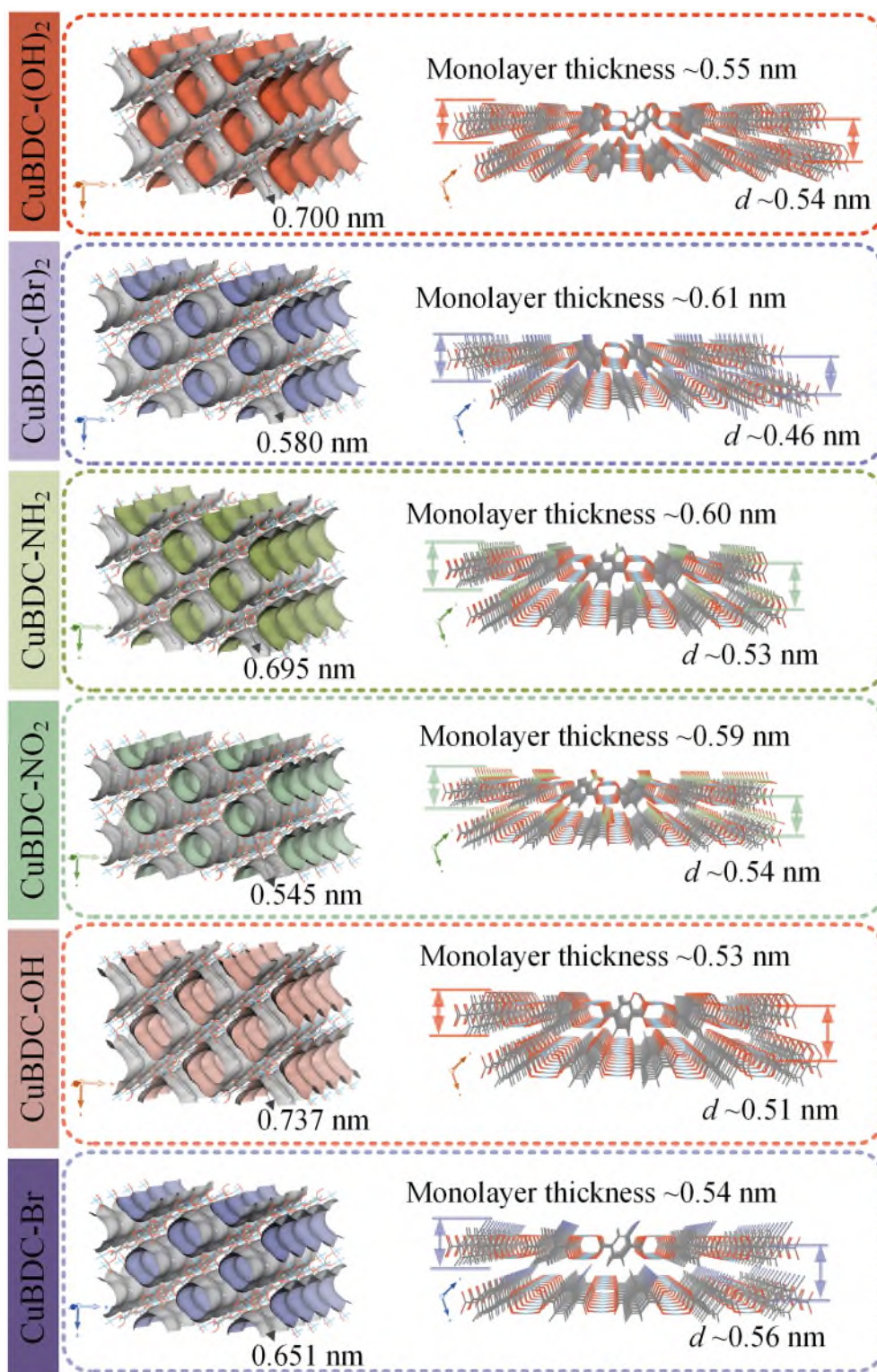


Fig. R9 Crystalline structures of bulk MOFs. The crystalline structures of bulk CuBDC-(OH)₂, CuBDC-(Br)₂, CuBDC-NH₂, CuBDC-NO₂, CuBDC-OH and CuBDC-Br optimized by DFT viewed along different directions, showing theoretical monolayer thickness, *d*-spacing and monolayer nanosheet aperture.

Response to Reviewer 2

Reviewer #2: In this manuscript, the authors propose a new strategy to adjust the stacking modes of MOF nanosheets with different sliding degrees via linker polarity regulation. Both theoretical calculations and experimental results demonstrate that a high linker polarity promotes neighboring nanosheets to a maximum AB stacking due to steric hindrance effects, leading to a controlled effective pore aperture of the membrane and consequently to improved molecular sieving. This theoretical finding was confirmed by synthesis of a series of CuBDC-based nanosheets with different linkers.

It is indeed an attractive work. MOF nanosheets can show the desired in-plane pores – but this advantage could not be exploited so far due to random stacking. And this is the big novelty of the manuscript: The polarity of the MOF nanosheets controls AA and AB stacking modes.

Another novelty is that the introduction of distinct functional groups can regulate the in-plane nanosheet apertures. This theoretical finding was confirmed by synthesis of a series of CuBDC-based nanosheets with different linkers.

The paper is well organized with solid data. I highly support publication of this paper in Nature Communication. It brings fresh wind into the field of 2D membranes. However, the authors need to make efforts to improve some of the discussions before acceptance. Here are some suggestions and comments.

Response: Thanks for your encouragement and kind comments. We have revised our manuscript prudently according to your suggestions point-by-point, and we hope these added experiments and explanations will help readers understand our work more easily.

1. Give in a scheme the difference of gas transport through AA and AB stacked MOF nanosheets.

Response: Thank you. The scheme of the differences in gas transport through AA and AB stacked MOF nanosheets is shown in Fig. R10. Considering the narrow free spacing (< 0.2 nm) between neighboring MOF nanosheets where gas molecules are not allowed to pass, gas molecules can only transport through the one-dimensional (1D) vertical channels constructed by in-plane pores of stacked MOF nanosheets in the membrane. For AA stacking, the neighboring nanosheets are highly overlapped, allowing gas molecules to pass through relatively larger 1D channels. The AB stacking structure with

the maximum staggered degree between neighboring nanosheets results in the formation of relatively smaller gas transport channels.

According to your comments, we have added Fig. R10 as Supplementary Fig. 12 in the revised supporting information (page 16). The corresponding explanations have also been added in the revised manuscript (page 4) and supporting information (page 16), highlighted in yellow.

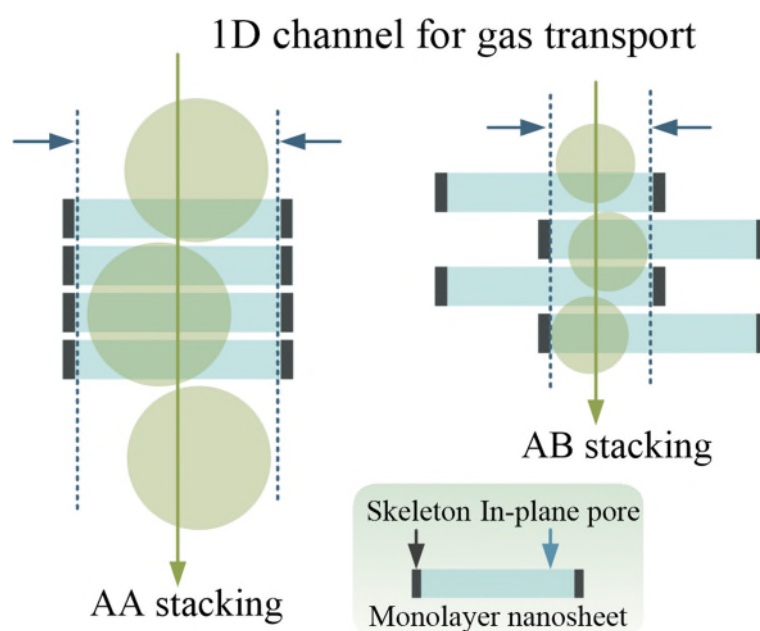


Fig. R10 Scheme of gas transport through AA and AB stacked MOF nanosheets.

2. *Linker polarity controls AA or AB stacking. If stacked, stability of stacking is an issue. Can the stacked nanosheets be fixed through covalent bondings?*

Response: Thank you very much for your valuable comments. The stability of stacked nanosheets is primarily influenced by intermolecular force rather than covalent bonds. The stability of nanosheet stacking is significantly enhanced by the presence of various polar groups. Incorporating polar functional groups into the nanosheets facilitates the formation of secondary bonds between the nanosheets, such as hydrogen bonding and halogen bonding, which contribute to the overall stability of the stacking. For example, hydrogen bonding introduced by functional groups such as -NH_2 and -OH , and halogen bonding introduced by groups such as -Br reinforce the stability of the stacked nanosheets.

According to your comments, we have added a corresponding discussion in the revised manuscript (page 5) and highlighted in yellow.

3. *The paper is clearly written. But the reviewer cannot understand the sentence “Through computational analysis, the theoretical apertures of a series of monolayer nanosheets are 0.700, 0.580, 0.695, 0.545, 0.737 and 0.651 nm (Supplementary Fig. 1) identified along the $(\bar{2}01)$ plane...”. Apertures ...along ... $(\bar{2}01)$ plane. We have crystallographic directions and crystallographic planes. “...BDC-based linkers to form a porous 2D network that stacks along the $(\bar{2}01)$ crystal axis...” Does this mean that the pores are not perpendicular to the stack or perpendicular to the plane of the nanosheet?*

Response: Thank you for your kind reminding. We are sorry for this inaccurate expression. We have rewritten these sentences for a clear description in the revised manuscript (page 2) and highlighted them as followed.

“These structures are similar to the previously reported CuBDC structure¹⁷, consisting of Cu coordinated with BDC-based linkers to form a porous 2D network that stacks along the normal direction of $(\bar{2}01)$ plane, maintained by van der Waals force, yielding a regular lattice structure. Through computational analysis, the theoretical apertures of a series of monolayer nanosheets are 0.700, 0.580, 0.695, 0.545, 0.737 and 0.651 nm (Supplementary Fig. 1) identified on the $(\bar{2}01)$ plane, which illustrates that the introduction of distinct functional groups can regulate the in-plane nanosheet apertures to different extents.”

4. *It took the reviewer some time to understand the meaning of “sliding amount” and “sliding path” in Fig. 1. The first impression was that SLIDING describes some movement like “sliding roof of a car”. Is DISTORTION a better description? I am not sure; a native speaker should decide it.*

Response: Thank you for your comments. Yes, you are right that the nanosheets stacking structure is similar to the concept of “sliding roof of a car” to some extent, which can adjust their relative position by moving one of them with various “sliding amounts” along the “sliding path”. The “sliding” emphasizes the relative movement between nanosheets, reflecting the dynamic behaviors that may occur during the stacking process. It can also be understood as “distortion” in the case of staggering from the point of the overall membrane compared with that in AA stacking mode. But from the point of each nanosheet, “sliding” could give more accurate details on various stacking structures, including “sliding amount”, “sliding path”, etc. Therefore, “sliding” seems better to describe this story.

5. *The interplay of calculations and experiments are one of the strengths of the manuscript. However, it would be helpful for the readers to say at every position whether it is a theoretical or experimental finding.*

Response: Thank you very much for your valuable comments. To enhance clarity and ensure that readers can easily distinguish between theoretical and experimental findings, we have emphasized it in each subheading of the revised manuscript (pages 2, 4 and 6) as followed and highlighted in yellow.

“Theoretical prediction driven MOF nanosheet stacking engineering”

“Experimental preparation of MOF nanosheets and corresponding membranes”

“Experimental investigation on separation performance”

Response to Reviewer 3

Reviewer #3: Wang's group has carefully designed 2D-MOFs in terms of their stacking mode for the efficient separation of H₂ from CO₂ and CH₄ mixtures. The method is clear and the idea is brilliant, as we saw at the recent MOF-2024 conference in Singapore. Before publishing this manuscript, I have a few questions.

Response: Thanks for your encouragement and kind comments. We have revised our manuscript prudently according to your suggestions point-by-point, and we hope these added experiments and explanations will help readers understand our work more easily.

1. How do the polarity of linkers and the stacking mode of 2D MOFs affect the heat of adsorption of gas for H₂/CO₂ and H₂/CH₄ mixtures?

Response: Thank you for your comments. According to your suggestion, we have calculated the adsorption heat for various gases in different stacking modes of 2D MOFs nanosheets with various linkers using the Widom test particle insertion method (*J. Chem. Phys.* 39, 2808-2812 (1963)) as shown in Figs. R11 and R12. The influence

of linker polarity and the stacking mode of 2D MOFs on the gas adsorption heat and membrane separation performance for H₂/CO₂ and H₂/CH₄ mixtures have been systematically explored as follows:

(i) Effect of linker polarity: As shown in Fig. R11 a, the introduction of diverse side chains induces variations in linker polarity, with dipole moments (μ , D) in the order of BDC-(OH)₂ < BDC-(Br)₂ < BDC-NO₂ < BDC-NH₂ < BDC-OH < BDC-Br. The adsorption heat (Q_{st} , kJ/mol) of CO₂ molecules is obviously influenced by the polarity of the linkers, compared with that of H₂ and CH₄. For most stacking modes, with the increased polarity of the linkers, the adsorption heat of CO₂ molecules with MOF nanosheets increases due to enhanced interaction (Figs. R11 and R12).

(ii) Effect of stacking mode: For the CuBDC-Br nanosheet with the highest polarity of a linker, the adsorption heat of CO₂ molecule with nanosheets increases sharply when the stacking modes change from AA to AB stacking (Figs. R11 and R12). It can be attributed that an increasing number of adsorption sites are exposed with increased staggering degree, leading to enhanced interaction between gas molecules and nanosheets. For the other five kinds of MOF nanosheets, there is no significant difference in the adsorption heat of gases (including CO₂, H₂ and CH₄) in various stacking modes, with a fluctuation ratio of approximately 20%.

As is known, higher adsorption heat of CO₂ indicates stronger interaction with the MOF nanosheets, leading to increased gas diffusion resistance, thus resulting in markedly lower CO₂ permeance and higher H₂/CO₂ selectivity. However, the adsorption heat for H₂ and CH₄ is much less than that of CO₂, indicating weaker adsorption with MOF nanosheets. As a result, the separation performance of H₂/CH₄ through the MOF nanosheet membranes is predominantly governed by size sieving, which is dependent on the effective aperture of membranes.

According to your comments, we have added Figs. R11 and R12 as Fig. 4c and Supplementary Fig. 25 in the revised manuscript (page 7) and supporting information (page 29), the corresponding explanations and simulation details have also been added in the revised manuscript (pages 7-8) and supporting information (pages 3-4), highlighted in yellow.

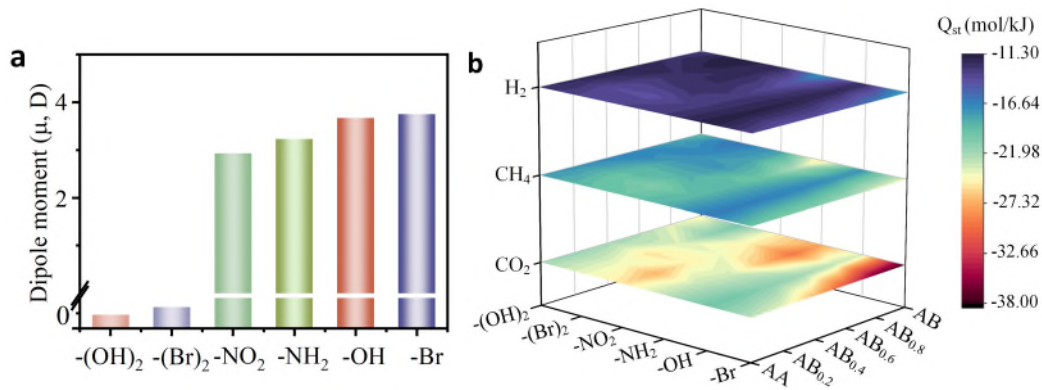


Fig. R11 a) Dipole moment of various linkers with different polarity. b) 3D adsorption heat map of H₂, CH₄ and CO₂ with CuBDC-(OH)₂, CuBDC-(Br)₂, CuBDC-NO₂, CuBDC-NH₂, CuBDC-OH and CuBDC-Br nanosheets in different stacking modes.

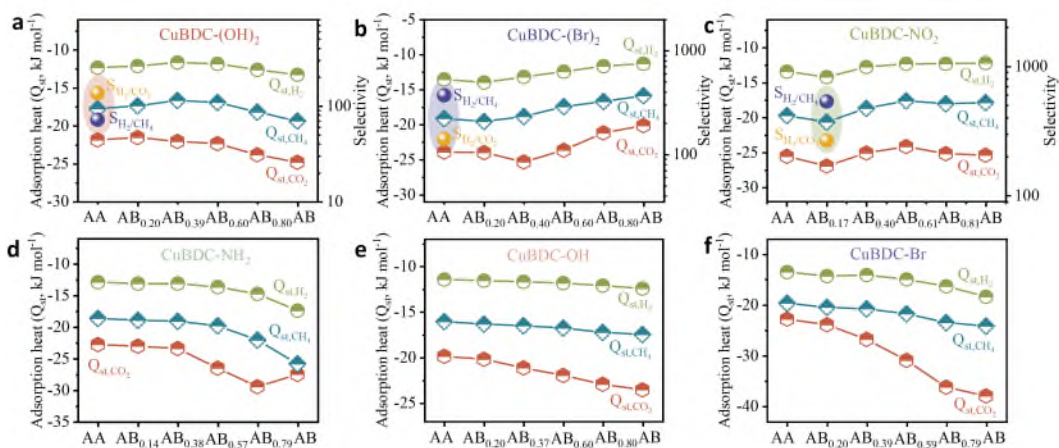


Fig. R12 Isosteric heat of adsorptions (Q_{st}) at infinite dilution of H₂, CH₄ and CO₂ with a) CuBDC-(OH)₂, b) CuBDC-(Br)₂, c) CuBDC-NO₂, d) CuBDC-NH₂, e) CuBDC-OH and f) CuBDC-Br nanosheets in different stacking modes.

2. Have you observed the effect of pore blockage inside the membrane due to the strong interaction of the gas molecules with the framework? Are there any findings from calculation studies? Could you please comment on this?

Response: Thank you very much for your valuable comments. We have thought about “pore blockage” from two aspects of the experiment and calculated it in detail, as follows.

(i) Experimental validation

Firstly, the experimental data of the gas permeance in the mixed-gas separation test and single-gas permeation test with the CuBDC-(Br)₂ nanosheet membranes are compared. The H₂ permeance in a mixture ($4.4 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$) is lower than its

single-gas permeance ($5.2 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$), indicating that CO_2 molecules are adsorbed due to interaction with the framework and somewhat hinder the diffusion of H_2 molecules in the mixture. However, this interaction does not result in pore blockage, as demonstrated by the membrane's long-term stability with an extended testing period of more than 300 hours (Fig. R13). The CuBDC-(Br)₂ nanosheet membrane displays excellent long-term stability, with only minor fluctuations in selectivity and permeance for H_2/CO_2 mixture separation (H_2/CO_2 selectivity of 129.3 ± 4.2 , H_2 permeance of $(4.5 \pm 0.06) \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$), demonstrating there is no pore blockage, otherwise the gas permeance would gradually decrease to even zero with time. These experimental results have confirmed that there is no pore blockage, although the interaction between gas molecules and framework exists.

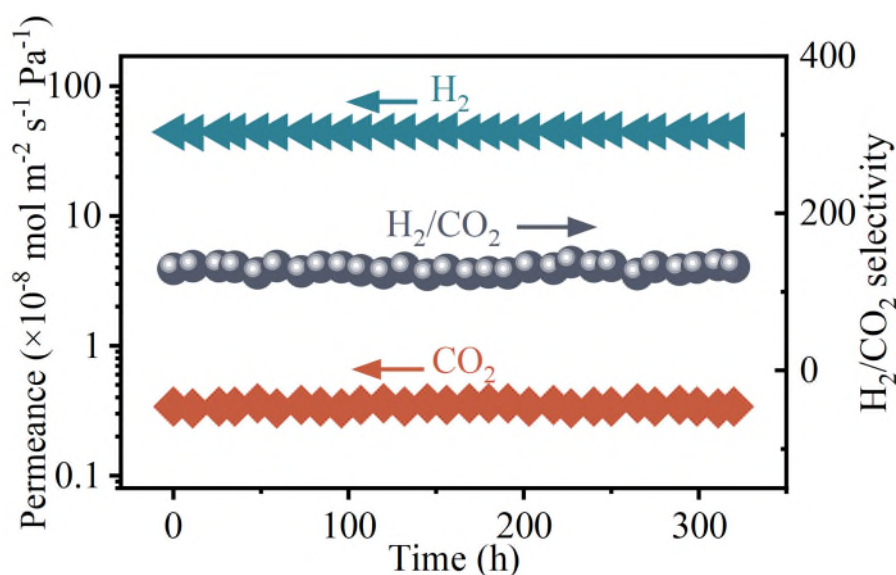


Fig. R13 Long-term stability of the H_2/CO_2 separation performance of the CuBDC-(Br)₂ nanosheet membrane.

(ii) Calculation study

As shown in Fig. R11, the adsorption heat of different gases is influenced by linker polarity and stacking modes, where CO_2 adsorption is significant with the MOF nanosheets compared with H_2 and CH_4 . It is the reason why the H_2 permeance tested in H_2/CO_2 mixture decreases to $\sim 85\%$ of that tested in a single H_2 permeation. It can be noted that all the gas adsorption heat with various MOF nanosheets is in the range of -11.3 kJ/mol and -38.0 kJ/mol , smaller than -40 kJ/mol , which is considered as physisorption (chemisorption: $-80 \sim -400 \text{ kJ/mol}$) driven by weak interactions (*Fuel* 315, 123120 (2022)), such as van der Waals forces, allowing for relatively easy desorption of gas molecules. Our calculation results have revealed that the gas molecules interact

with the framework, but the interaction is not strong enough to cause pore blockage.

According to your comments, we have added a corresponding description in the revised manuscript (page 8), highlighted in yellow.

Response to Reviewer 4

Reviewer #4: In this manuscript, the authors adjusted the stacking modes in MOF nanosheets membranes by linker polarity regulation. They found a high linker polarity promotes neighboring nanosheets to a maximum AB stacking due to steric hindrance effects. It has been proved to control the effective pore aperture of the MOF nanosheet membranes and even enhance the molecular sieving performance. It is a meaningful work, which has draw attention to this unrevealed issue in 2D nanosheet membrane fields for the first time. The strategy for precise regulation of stacking modes is also innovative and smart. Overall, I think this paper is well-written and the presented concept is clear and interesting which would coincide with the scope and novelty standards of Nature Communications. Hence, this paper can be accepted for publication after carefully addressing the following comments with minor revision.

Response: Thanks for your encouragement and kind comments. We have revised our manuscript prudently according to your suggestions point-by-point, and we hope these added experiments and explanations will help readers understand our work more easily.

1. Engineering the pore size/shape of the stacking MOF-nanosheet with different functional groups is very interesting, this reviewer is wondering, if any experimental or computational work has ever discussed such point? If not, this could be emphasized in the work, e.g. in Abstract or Introduction.

Response: Thank you very much for your valuable comments. Upon thoroughly reviewing all reported literatures, there are few experimental and computational works discussing this issue.

To the best of our knowledge, there is only one literature studied the MOF-nanosheets stacking mode, which was published by our group last year (*Angew. Chem.*

Int. Ed. 62, e202312995 (2023)). In our previous work, we have regulated the AA (highly overlapped) and AB (maximum staggered) binary stacking modes of the $[\text{Cu}_2\text{Br}(\text{IN})_2]_n$ nanosheets through drop casting by controlling the solvent droplet dynamic behavior, thus demonstrating the significant influence of the nanosheets stacking mode on the gas separation performance. However, achieving continuous regulation of stacking structures in MOF nanosheet membranes, especially the precise control of the stacking modes with different degrees, still remains extremely challenging, either experimentally or through theoretical calculations.

According to your comments, we have added more introductions in the revised manuscript (page 2) and highlighted in yellow.

2. In Fig 1a, the authors discussed the sliding degree from 0 to 100%, and I am not quite sure how the authors determined the sliding values.

Response: Thank you. As shown in Fig. R14, the sliding degree (x) in AB_x stacking of nanosheets is determined based on the relative position between the metal sites (denoted as M and M') from neighboring layers along the sliding direction, where the positions of M and M' coincide in case of AA stacking. It can be calculated as:

$$x = \frac{d_{M-M'}}{1/2d_{M-N}} \quad (4)$$

where $d_{M-M'}$ represents the distance between metal sites of M and M' along the sliding direction. d_{M-N} represents the distance between metal sites of M to N in one nanosheet.

For AA stacking, the sliding degree $x = 0$, the metal atoms from neighboring layers are perfectly coincided without any sliding ($d_{M-M'} = 0$), corresponding to completely overlapped stacking arrangement. For AB stacking, the sliding degree $x = 100\%$, the site of M' is directly coincided with the pore center of the neighboring nanosheet, which represents the maximum sliding degree. When the sliding degree $x \in (0, 100\%)$, a series of infinite stacking modes between AA and AB appear, such as $\text{AB}_{0.17}$, $\text{AB}_{0.21}\dots$

According to your comments, we have added Fig. R14 as Fig. 1b in the revised manuscript (page 3), and the corresponding explanation has also been added in the revised manuscript (page 2), highlighted in yellow.

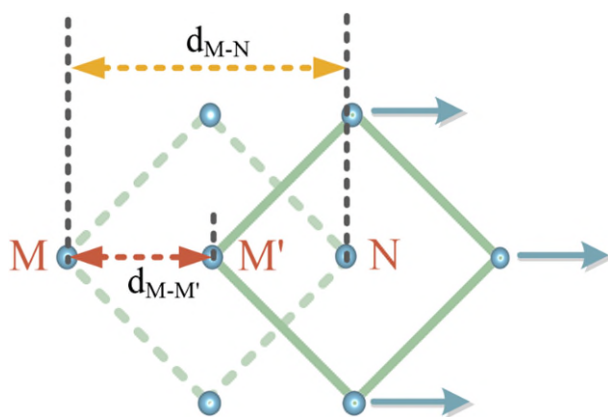


Fig. R14 Schematic diagram of neighboring nanosheets stacking.

3. The author has discussed seven different types of MOF nanosheets in Figure 2 to investigate the effect of linker type on the stacking property. However, they only choose three of them to investigate the separation performance. Why? The author should present the reason.

Response: Thank you for your comments. The selection of three kinds of CuBDC-(OH)₂, CuBDC-(Br)₂ and CuBDC-NO₂ nanosheets from the above toolbox of six types of MOFs to assemble into membranes experimentally for investigating separation performance was based on the efficacy of the stacked apertures in separating the target gas molecules. To be specific, CuBDC-(Br)₂ and CuBDC-NO₂ nanosheets exhibit relatively small stacking apertures (0.379 nm and 0.372 nm), which are suitable for gas sieving including H₂, CO₂ and CH₄ with a kinetic diameter of 0.29 nm, 0.33 nm and 0.38 nm. Moreover, for further comparison with a kind of MOF nanosheet membrane with relatively large pores, the CuBDC-(OH)₂ nanosheets with a stacking aperture of 0.641 nm are also chosen for experiments in order to elucidate the influence of pore size on gas separation efficiency. The selection of such three typical kinds of MOF nanosheet membranes enables us to understand the effect of stacking modes on gas separation, which is the major target of this work.

According to your comments, we have added corresponding explanations in the revised manuscript (pages 4-5) and highlighted in yellow.

4. Is PBE exchange-correlation functional including DFT-D3 dispersion correction with Becke-Johnson (BJ) damping scheme widely used for MOFs?

Response: Thank you very much for your valuable comments. Yes, the PBE exchange-correlation function combined with the DFT-D3 (BJ) dispersion correction is widely

used in the study of MOFs. For instance, the PBE-D3 (BJ) functional has been successfully employed in DFT calculations to investigate various MOFs, such as ZIF-8 (*Nat. Mater.* 20, 1015-1023 (2021)), UiO-66 (*J. Catal.* 331, 1-12 (2015)) and others (*J. Phys. Chem. C* 123, 9153-9167 (2019); *J. Phys. Chem. C* 119, 16920-16926 (2015); *RSC Adv.* 14, 22714-22762 (2024)). It has also been used in high-throughput screenings that considered a large number of MOFs (*Matter* 4, 1578-1597 (2021); *npj Comput. Mater.* 8, 112 (2022)), further demonstrating the robustness and accuracy of the PBE-D3 (BJ) functional.

According to your comments, we have added these relevant references to the supporting information (page 3) and highlighted them in yellow.

5. The authors showed a lot of distance/size data in Fig. 2, how were they calculated or defined? Please give more details.

Response: Thank you very much for your comments. Taking CuBDC-NO₂ for an illustrative instance, various distance/size data are given in detail, including the side-chain size of linker, aperture of monolayer MOF nanosheet, stacking aperture (ϕ_{stack}) and interlayer distance (d -spacing) of neighboring MOF nanosheets. As shown in Fig. R15a, the side-chain size in the linker is measured by calculating the distance from the carbon atom attached to a group on the linker to the furthest atom of the group (considering the van der Waals radii of the atoms involved). The aperture of a monolayer MOF nanosheet is defined as the in-plane pore size of the monolayer nanosheet, as shown in Fig. R15b. The ϕ_{stack} represents the aperture of neighboring MOF nanosheets stacked at the lowest formation energy (Fig. R15c). The ϕ_{stack} and the monolayer aperture were calculated using the Zeo++ software (*Micropor. Mesopor. Mater.* 149, 134-141 (2012)). The d -spacing value, which represents the interlayer distance of neighboring nanosheets, is determined by measuring the vertical distance between the centers of mass of the two layers (Fig. R15d).

According to your comments, the corresponding descriptions have been added to the revised supporting information (page 4), highlighted in yellow.

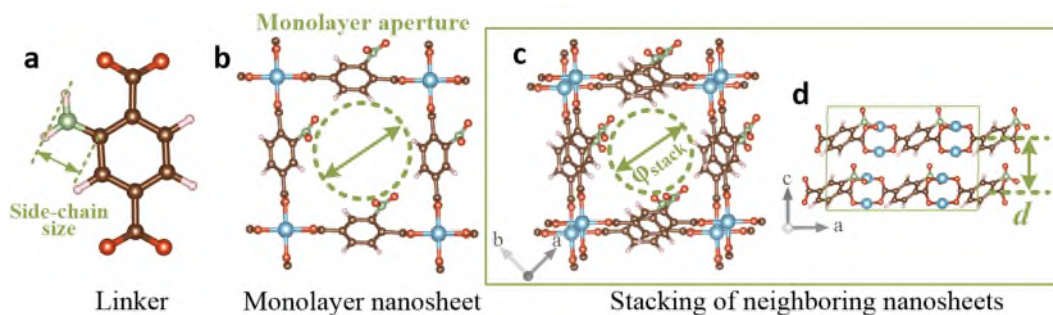


Fig. R15 Structures of the a) linker of CuBDC-NO₂, b) monolayer CuBDC-NO₂ nanosheet and c-d) stacked bilayer nanosheets along two directions.

6. The authors claimed that “The thickness of the nanosheets is notably influenced by the Cu/linker ratio, where excessive linkers act as moderator covering on the surface of the nanosheets, thereby impeding out-of-plane growth of MOF nanosheets with precisely controlled thickness.” Please provide the evidence of the change in morphology of the nanosheets at different Cu/linker ratios.

Response: Thank you very much for your comments. We prepared a series of MOF nanosheets at varying metal/linker ratios, where their corresponding morphological structure can be observed in Figs. R3-R5. It is obvious that different metal/linker ratios significantly influence the growth behavior of MOF nanosheets. At higher metal/linker ratios, MOF crystals tend to grow in multiple layers. Conversely, at lower metal/linker ratios, the growth of MOF nanosheets along the vertical direction is inhibited, leading to the formation of ultrathin nanosheets. Additionally, the diffusion of metal ions and linkers slows down as the temperature decreases, thereby limiting nanosheet growth in a vertical direction. The metal/linker ratio serves as a major factor in governing the morphology of nanosheets, exhibiting a consistent trend of variation, even under varying temperature conditions. More importantly, such nanosheet growth mechanism is consistent for three kinds of different materials (CuBDC-(Br)₂, CuBDC-(OH)₂ and CuBDC-NO₂).

According to your comments, we have added Figs. R3-R5 as Supplementary Figs. 14-16 in the revised supporting information (pages 18-20), the corresponding discussions and reaction details have also been added in the revised manuscript (pages 5 and 10), highlighted in yellow.

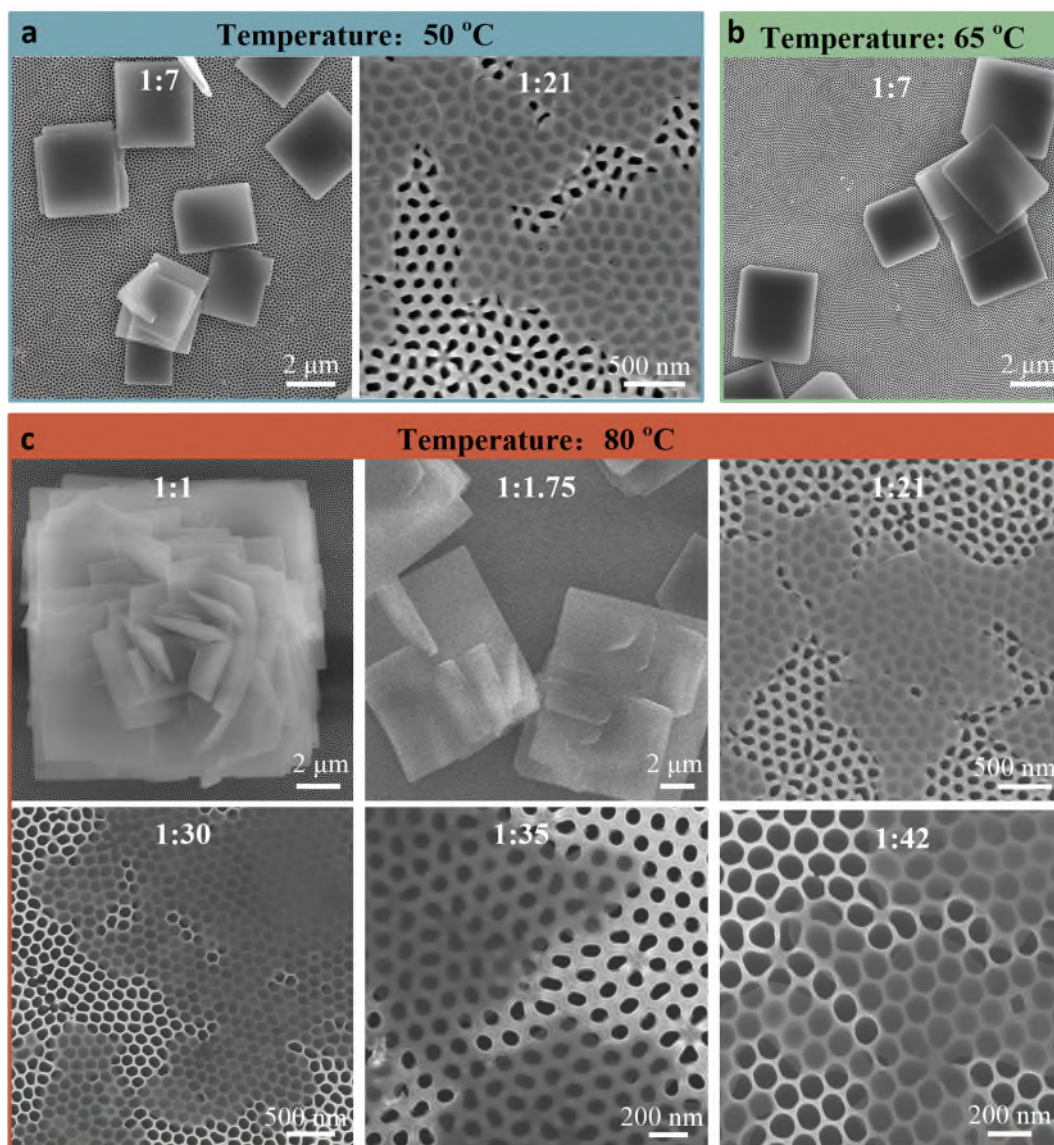


Fig. R3 The SEM images of the CuBDC-(Br)₂ nanosheets prepared under different reaction conditions. Values of Cu/linker ratio and reaction temperature are given, with all reactions carried out for 30 min.

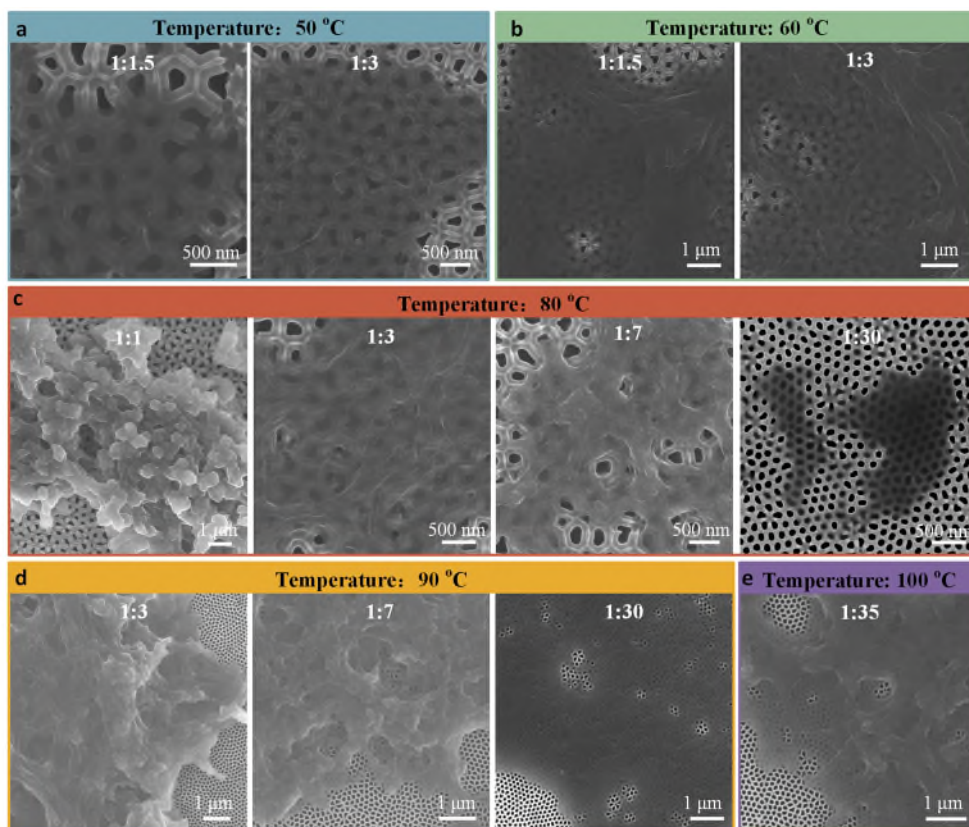


Fig. R4 The SEM images of the CuBDC-(OH)₂ nanosheets prepared under different reaction conditions. Values of Cu/linker ratio and reaction temperature are given, with all reactions carried out for 30 min.

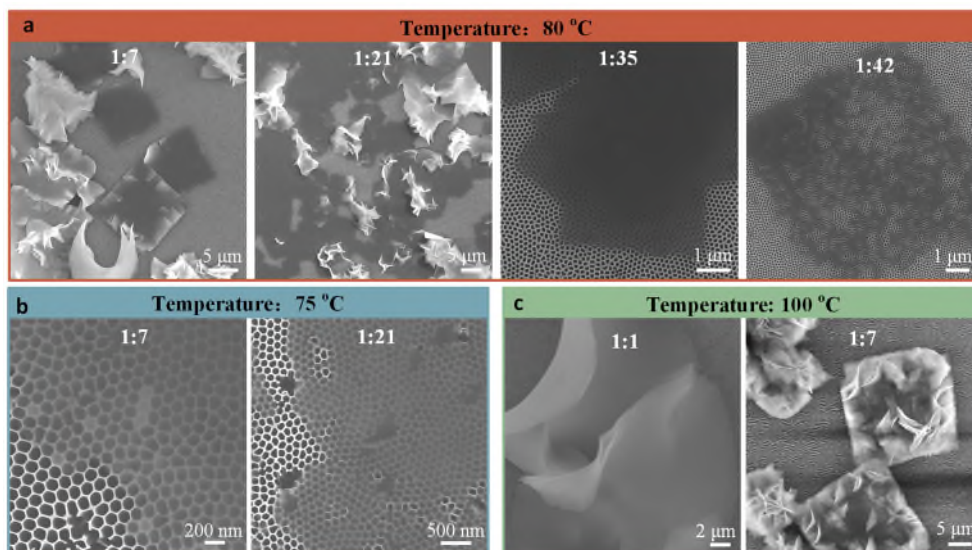


Fig. R5 The SEM images of the CuBDC-NO₂ nanosheets prepared under different reaction conditions. Values of Cu/linker ratio and reaction temperature are given, with all reactions carried out for 30 min.

7. The authors prepared the MOF nanosheets using DMF as solvent, whether DMF was removed in the following process? Otherwise, it will also affect the membrane structure and the gas separation performance.

Response: Thank you very much. We have completely removed the solvent during the subsequent treatment process to ensure that DMF does not affect the membrane structure or its gas separation performance. To eliminate residual DMF solvent, the synthesized MOF nanosheets were repeatedly washed with CH_2Cl_2 . We employed FTIR to analyze the $\text{CuBDC}(\text{OH})_2$, $\text{CuBDC}(\text{Br})_2$ and $\text{CuBDC}\text{-NO}_2$ nanosheets after thorough washing. As shown in Fig. R16, a distinct peak at 1664 cm^{-1} associated with the $\text{C}=\text{O}$ stretching vibration of DMF solvent (*Micropor. Mesopor. Mat.* 303, 110254 (2020)), can be observed in the nanosheets before washing, indicating the presence of DMF. After washing, the disappearance of such a peak confirms the complete removal of the solvent from the nanosheets.

According to your comments, we have added Fig. R16 as Supplementary Fig. 31 in the revised supporting information (page 35), and the corresponding discussions have also been added to the revised manuscript (page 10) and highlighted in yellow.

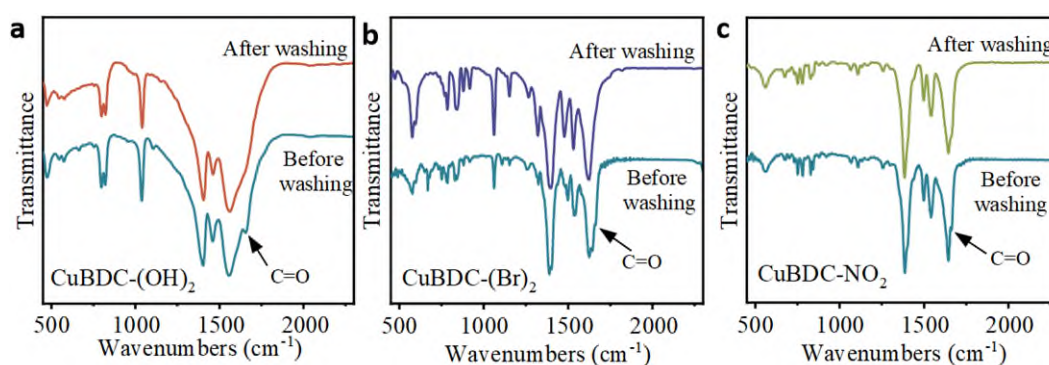


Fig. R16 FTIR spectra of the a) $\text{CuBDC}(\text{OH})_2$, b) $\text{CuBDC}(\text{Br})_2$ and c) $\text{CuBDC}\text{-NO}_2$ nanosheets before and after washing.

Response to Reviewer 5

Reviewer #5: I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Response: Thanks for your encouragement and kind comments. We have revised our manuscript prudently according to your suggestions point-by-point, and we hope these added experiments and explanations will help readers understand our work more easily.

-----The end-----

Response to the Reviewers' Comments

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

Reviewer #1: The authors have addressed most of my comments. It is unfortunate that the membrane's performance deteriorates completely at a slight overpressure (1.1 bar), which makes it challenging to apply these membranes in practical applications. This point is often overlooked in the literature. It should be highlighted in the main text, and Figure R2 should be added in SI. Author should also list potential reason as to why membrane performance fails at slight pressurization.

Response: Thank you for your valuable suggestions. The CuBDC-(Br)₂ nanosheet membrane was employed in pressurization experiment previously, where a notable deterioration in separation performance was observed when the feed pressure increased to 1.1 bar. It is attributed to the presence of non-selective transport pathways in the CuBDC-(Br)₂ nanosheet membrane, allows Knudsen and viscous flow dominating the membrane separation performance when the transmembrane pressure difference is greater than zero (*Nat. Commun.* 13, 5852 (2022), *Chem. Eng. J.* 442, 136336 (2022), *J. Mater. Chem. A* 3, 12205-12212 (2015) and *AIChE J.* 46, 779-789 (2000)).

We agree with you that the gas separation test under pressurized conditions is often overlooked in the literature. To the best of our knowledge, there is only a few studies having explored this issue (*Nat. Commun.* 13, 5852 (2022), *Nat. Commun.* 9, 155 (2018), *Adv. Funct. Mater.* 28, 1801511 (2018) and *J. Membr. Sci.* 638, 119669 (2021)). Unfortunately, all the above studies have observed the membrane separation performance deteriorated under increased feed pressure. For example, upon increasing the feed pressure to 1.4 bar (transmembrane pressure: 0.4 bar), the H₂/CO₂ selectivity of the g-C₃N₄ membrane decreased from 26 to 1, which was primarily attributed to the existence of non-selective transport pathways within the membrane (*Nat. Commun.* 13, 5852 (2022)).

For the practical applications of H₂/CO₂ separation where the operation pressure is larger than 10 bar, the membrane with good anti-pressure stability is urgently needed. The development of defect-free (or at least less defective) nanosheet membranes should be alternative, where novel membrane assembly strategy is required. Moreover, the type of monolayer nanosheet membranes without stacking defects also holds promise for addressing the pressure resistance challenges in the future (*Nat. Mater.* 22, 1387-1393 (2023), *Nat. Commun.* 9, 2632 (2018) and *J. Membr. Sci.* 618, 118745 (2021)).

According to your suggestions, we have added Figure R2 (deteriorated membrane's performance under pressurization) as Supplementary Fig. 31 in the revised supporting information (page 35), the corresponding explanations have also been added in the revised manuscript (page 8), highlighted in yellow.

Response to Reviewer 2

Reviewer #2: I carefully studied the 4 reviews and the 4 answers of the authors. In principle, all reviewer support publication after revision.

Speaking for my review (number 2), I am completely satisfied.

There is, however, one remark. On line 55, the authors themselves cite "Prof Wang's group" which is unusual since other groups are cited without the title prof, such as Yang et al., Zhao et al.

It would be more common to say "Wang's group" or "Wang and coworker" or so.

Response: Thanks for your encouragement and kind comments. According to your comments, we have revised the corresponding description of "Prof Wang's group" to "Wang's group" in the revised manuscript (page 2), highlighted in yellow.

Response to Reviewer 3

Reviewer #3: The authors answered and revised all queries raised by reviewers.

The paper is great:)

It was a very enjoyable reading for me.

I would like to say huge congratulations to all authors.

Response: Thanks for your encouragement. We are glad to hear that you enjoyed

reading our paper. Your support motivates us to continue our research in this field.

Response to Reviewer 4

Reviewer #4: The author have addressed all the concerns, and I suggest to accept this manuscript in the journal of Nature Communications.

Response: Thank you very much for your positive evaluation of our manuscript.

Response to Reviewer 5

Reviewer #5: I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Response: Thank you very much for your positive evaluation of our manuscript.

-----The end-----