

A molecularly impermeable polymer from two-dimensional polyaramids

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

Version 0:

Reviewer comments:

Referee #1

(Remarks to the Author)

This manuscript reports the synthesis of a 2D amide-linked polymer (2DPA-1) and its ultrathin films, showcasing molecular impermeability. The authors prepared films with controlled thicknesses (down to 4 nm) using TFA-dissolved polymer solutions and demonstrated their nearly complete gas impermeability, a feature distinguishing them from other polymer-based films. Additionally, they developed a viable method for transferring ultrathin films using PS coatings, offering guidance for producing defect-free ultrathin films. The films demonstrated high performance in protecting 3D perovskites. However, the material's characterization and classification are unclear. Although described as a polymer, its ordered structure and interlayer simulations resemble COFs, raising questions about the reliability of structural claims and simulation results if the material is not a COF (COFs have long-range ordered structures with high crystallinity). Moreover, TFA's strong acidic nature could degrade polymer structures, requiring further investigation into their material's chemical stability, especially the ordered structure depicted in Fig. 1A. Overall, this manuscript could be considered for publication only if all the major issues below can be well addressed:

1. The authors emphasize the excellent chemical stability and processability of their material, 2DPA-1. However, there is insufficient evidence to support its claimed chemical stability. Additionally, the processability is primarily demonstrated through film preparation using TFA-dissolved solutions. This is a method previously reported for COF materials (e.g., *Angew. Chem. Int. Ed.* 2020, 59, 5165). Furthermore, various established methods, such as in situ growth, stacking of nanosheets, and interfacial polymerization, are available for directly processing COFs into membranes or films, all of which exhibit adequate processability (e.g., *Angew. Chem. Int. Ed.* 2024, e202421661; *Angew. Chem. Int. Ed.* 2022, 61, e202207559). Notably, most imine-linked COFs are also chemically stable. Thus, the comparison of 2DPA-1 to COFs regarding chemical stability and processability in the manuscript may not be entirely accurate.
2. The characterization used to confirm framework formation through monomer condensation is insufficient. It is recommended to include FTIR and ¹³C NMR analyses to clearly demonstrate polyamide linkages. Given the structure depicted in Fig. 1A, 2DPA-1 is expected to be highly porous. Therefore, gas sorption experiments are suggested to evaluate its microporosity and pore size distribution. Ar sorption could be considered if N₂ sorption at 77 K is unavailable due to N₂ impermeability.
3. The authors classify their material as polymers rather than COFs. Crystallinity, reflecting the degree of ordered structures, is a key distinction between polymers and COFs. The manuscript describes 2DPA-1 as having highly ordered frameworks and includes simulations of bilayers with various interlayer shifts. Such structural illustrations and simulations are typically applicable to COFs. Clarification is needed: Is 2DPA-1 a COF? If not, the structural illustration in Fig. 1A may be misleading, and the simulations/discussions about interlayer shifts would lack relevance. If it is a COF, please confirm this through PXRD patterns showing clear low-theta diffraction peaks. Based on the mentioned d-spacing (~1 nm), the diffraction peak should appear around 6-8°. However, the structural illustrations suggesting order are inconsistent with the PXRD discussion, where the authors conclude that 2DPA-1 lacks long-range order.
4. The main text refers broadly to the Supplementary Information (SI) when discussing results. To improve clarity, specific references (e.g., Supplementary Fig. 1) should be included to help readers efficiently locate corresponding figures in the SI.
5. Can the authors provide a photograph of the 2DPA-1 solution in TFA? Is the material fully dissolved or merely dispersed in TFA? Typically, TFA delaminates 2D COFs to produce nanosheets for film fabrication. What is the structural state of 2DPA-1 in TFA? The TEM image in Fig. 1B shows nanoplatelets with lateral sizes around 10 nm. What are their

- thicknesses? Preparing continuous 4-nm-thick films would be barely possible if the nanoplatelets are significantly thicker.
6. TFA, a strong organic acid, often compromises polymer and COF structures. Can the authors provide clear evidence to support the identical structure between their polymer and film? The use of aggressive TFA could also compromise practical applications. Are there any mild alternatives to replace TFA for film preparation. Weight loss of 5% in TGA is typical for polymers, which may not lead to the conclusion that the pores are not blocked by water. To confirm this, the film should be in situ treated under higher temperatures like 120 °C to completely remove water and other potential gases followed by gas permeance tests.
 7. During film preparation, PS was used as a supporting layer, then dissolved to transfer the film. It is challenging to completely remove PS using simple solvent washing, especially for PS beneath 2DPA-1 films. Please confirm whether PS was effectively removed. Residual PS chains could infiltrate 2DPA-1 pores, potentially blocking them and rendering the films impermeable.
 8. Scanning electron microscopy images of the 2DPA-1 films should be provided to show their morphologies.
 9. In Fig. 2B, the correlation between N₂ permeability and material crystallinity is shown. How was the degree of crystallinity of these materials quantified?
 10. The gas permeance tests were conducted in single-component systems. Would it be possible to extend these tests to binary-component systems, such as a mixture of N₂ and H₂? This approach could offer deeper insights into the separation mechanism, clarifying whether it is driven by chemical affinity or size-based exclusion.

Referee #2

(Remarks to the Author)

In this manuscript, Strano&Bunch, and co-workers demonstrate the impermeability of the polyaramide ultrathin films and demonstrate potential application in the protection of perovskites. The study is very interesting and goes beyond common approaches that demonstrate the impermeability of 2D films attaining the N₂ permeability below 3.1×10^{-9} Barrer. The authors carried out a significant amount of experiments to prove the impermeability phenomenon as well as DFT calculations to further understand the underlying mechanism. The presented study is definitely interesting and constitutes new methodologies, in particular use of light microscopy for analysis of a larger sample size, which wasn't possible using AFM and other methods. Moreover, the obtained results provide novel method combinations for future studies that involve studies of similar 2D materials and their applications. Most of the similar studies that were performed on graphene on other 2D materials use data solely obtained using AFM on nano to micron range area, which further limits the applicability of the findings. In that regard, this study is really interesting and also demonstrates the potential use of obtained results and developed methodologies, making this study particularly interesting for Nature readers. However, there are certain points that need to be addressed before proceeding further:

1. Figure 1B shows the TEM image of the 2DPA-1 films, I am curious about the dark spots, what do they constitute? Are these impurities?
2. Authors claim the absence of long-range order crystallinity of 2DPA-1 films unlike COFs based on the XRD pattern provided in Figure S1. However, the long-range order crystallinity peak in COFs usually appears below 2 θ of 10 degrees in the XRD pattern. Given this authors should provide the XRD scan range below 10 degrees and usually the range of 2-60 if possible for comparison with COFs and to claim the absence of crystalline peaks.
3. Similar studies have been demonstrated before, in particular by Scott Bunch and colleagues, however, the experimental setup was never shown. It would be very useful for replications if authors show the experimental setup schematics for pressurization setup as well as gas permeation.
4. Figure 2B shows the benchmark of the 2DPA-1 permeability. However, it's not very clear what is the permeability of the 2DPA-1 films and how the comparison is made. How the crystallinity of the films is measured?
5. The absence of solvents and water in the polyaramide pores could indeed affect impermeability, specifically for some of the gases. Therefore, the authors used the TGA (Figure S22) to support this claim. Although TGA offers a plausible way for the presence of solvents and other volatiles in the polymeric network, it is not a proper way to assess if the solvents are trapped within the pores. The proper way would be to degass samples under a vacuum at temperatures below 150 C and measure the weight of the sample afterward. Indeed this is a standard protocol for measuring the porosity of microporous materials as solvent trapped in the pores can affect the measurement results.
6. Extended Figure 8 shows the position of the N₂ molecule concerning the pore-to-pore offset from the side view, it would also be very useful if the structures presented in Figure 8A were shown from the top view.
7. It is impressive to see that the authors measured the permeability after more than 1000 days (>3 years). I was curious how the measurements at 1000 and more days were conducted, based on the gap is it possible to estimate that samples were re-checked after a prolonged time? Was the sample kept in the measurement setup for more than 1000 days under pressure? Some clarification would really help.
8. It is noteworthy to see that NMR spectroscopy was used to assess the degree of polymerization; as the degree of the polymerization increases (r), the authors observed a downfield shift shown in Figure S17. The spectra need to be calibrated, commonly based on the deuterated solvent peak, are the spectra shown in Figure S17 calibrated? Can you also show the whole range for better assessment?
9. Encapsulation with 2DPA-1 films enhanced the stability of perovskites by 3-fold. How does the 2DPA-1 encapsulation affect the performance of the perovskites, does it reduce the efficiency, can authors comment on this?
10. The impermeability of O₂, CO₂, He, and H₂ wasn't impressive due to absence of persistent bulges. The authors mention that this could be correlated with the poor rim seal. One of the methods to improve the rim seal could be Pt deposition using a Focused-ion beam (FIB) used in earlier studies for graphene (Science, 2014, 344, 289-292). It could improve the rim seal for obtaining measurements with other gases.

Referee #3

(Remarks to the Author)

Summary:

This manuscript describes the preparation and evaluation of an aramid-based 2D polymer with exceptional impermeability to gas. These polymers are able to maintain a sealed chamber of gas pressure for extended periods of time. The low permeability of these polymers is combined with the fact that they can be solution processed like conventional polymers and unlike other highly impermeable materials such as graphene.

Comments:

The properties of this aramid polymer are extremely interesting. The characterization of this material is extremely important. It is surprising that the material does not display any long range order. What is the largest area or size of film that can be spin cast?

Why are the pores occluded? Most of the COF literature has found that AA, AA', or some other variant of eclipsed stacking geometry is observed due to the fact that the most energetically favorable stacking arrangement is driven by maximizing the amount of non-covalent interactions between the layers. If the materials produced here do produce large 2D platelets, why aren't the pores accessible?

The structural characterization of the 2DPA is somewhat ambiguous. The powder X-ray diffraction patterns indicate that the bulk material is amorphous. The BET analysis shows that the material has no accessible surface area. Solution phase proton NMR analysis is included here, but the authors use an unconventional method to claim that the dissolved structures match a perfect hexagonal model. The spectrum shown in Figure S15 shows many overlapping signals in the aromatic region, which are compared to end groups that are not likely to have formed with high levels of conversion. A "perfect" hexagonal structure would result in a highly symmetrical structure, producing a spectrum with only a few peaks. The aromatic region of this spectrum (δ 9-10 ppm) shows two, broad peaks. However, each aromatic ring in the proposed structure has three chemically equivalent protons, which should produce only one signal indicating that there is a mismatch between the proposed structure and the experimental NMR spectrum. The integration of the peaks represents the total number of protons in the aromatic region vs the proposed endgroups, but these ratios are not matched to the theoretical structure shown. It would be challenging to make conclusions from these data anyway since the total number of endgroups are not known. Endgroup analysis is typically used in polymer chemistry when the functional group at the end of the polymer is created through the initiation step of the polymerization. In this case the total number of endgroups is determined by the mechanism and can be used to quantitatively measure the degree of polymerization. This is not the case here. The concept of "skewness" is not well defined, and it is not clear to this referee how it can be used to conclude that the material is of 2D nature, rather than a 3D network for example.

Conclusions:

The results from this work are compelling, and the properties observed are unique (and remarkable) for processable polymeric materials. However, it isn't clear why these materials have such good properties. They have no long-range order (by X-ray diffraction methods) making it difficult to characterize the structure and the bulk structure is ambiguous by NMR analysis. It is also not clear how a relatively simple step-growth polymerization would result in a 2D material with few macroscopic defects, rather than a mixture of 2D and 3D network polymers.

Version 1:

Reviewer comments:

Referee #1

(Remarks to the Author)

The authors have conducted extensive additional experiments that satisfactorily address my previous concerns. I now have only one minor comment regarding the introduction of the term "nonporous COFs" in the revised manuscript. COFs, by definition, are porous, crystalline polymers, as first reported in Science 2005, 310, 1166-1170. The use of the term "nonporous COFs" appears conceptually inconsistent with this foundational definition and may need reconsideration or further clarification. In membrane or film form, COFs could exhibit impermeability or very limited permeability to ultrafine gas molecules. However, such behavior typically results from unique stacking configurations, such as random stacking, that obstruct accessible channels and create highly tortuous transport pathways. Nevertheless, the COF frameworks still possess inherent porosity.

Referee #2

(Remarks to the Author)

Authors have done sufficient work to satisfy the majority of questions. Still, there is no compelling information regarding the crystallinity of 2DPA-1 films. I suggest showing a diffraction pattern from high-resolution TEM for crystallinity. This would provide more compelling evidence.

The authors measured the BET analysis and obtained a surface area of $74 \pm 10 \text{ m}^2 \text{ g}^{-1}$ and claimed a pore volume of $0.41 \pm 0.07 \text{ cm}^3 \text{ g}^{-1}$. This number is extremely high for a non-porous material and suggests high porosity. I suggest checking

it again and calculating once more to make sure that this pore volume is correct.

Referee #3

(Remarks to the Author)

The authors have provided a very thorough response to all of the referee's comments.

This referee appreciates that this is a new approach to the synthesis so the characterization needs to be somewhat unconventional (the authors previously published work on this topic notwithstanding). I think the authors have satisfactorily answered my original concerns, and I will note that the recent JACS paper describing the proton NMR characterization technique used to characterize the 2D polyamides was enormously convincing. With all of these revisions, this manuscript should be acceptable for publication.

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Reviewer #1:

Reviewer: *This manuscript reports the synthesis of a 2D amide-linked polymer (2DPA-1) and its ultrathin films, showcasing molecular impermeability. The authors prepared films with controlled thicknesses (down to 4 nm) using TFA-dissolved polymer solutions and demonstrated their nearly complete gas impermeability, a feature distinguishing them from other polymer-based films. Additionally, they developed a viable method for transferring ultrathin films using PS coatings, offering guidance for producing defect-free ultrathin films. The films demonstrated high performance in protecting 3D perovskites. However, the material's characterization and classification are unclear. Although described as a polymer, its ordered structure and interlayer simulations resemble COFs, raising questions about the reliability of structural claims and simulation results if the material is not a COF (COFs have long-range ordered structures with high crystallinity). Moreover, TFA's strong acidic nature could degrade polymer structures, requiring further investigation into their material's chemical stability, especially the ordered structure depicted in Fig. 1A. Overall, this manuscript could be considered for publication only if all the major issues below can be well addressed.*

Our Response: We thank the reviewer for their thorough review of our work and for recognizing its potential importance to the scientific community. Before addressing the specific comments of the reviewer, we would like to indicate that we have made the following key revisions to our manuscript. The key revisions include:

- Demonstrated chemical stability and processability of 2DPA-1 in TFA and non-TFA solvents
 - ¹H NMR in TFA and milder solvents (**Figs. R1-2, R19, and Supplementary Fig. 1**) showing no evidence of chemical degradation
 - [REDACTED]
- Refined structural characterization to connect bulk 2DPA-1 to molecularly ordered films
 - Experimental FTIR and Raman spectra assigned and compared to DFT simulated molecular models confirming chemical structure (**Figs. R4, R14-15, Supplementary Fig. 2, and Supplementary Table 1**)
 - [REDACTED] REDACTED [REDACTED]
 - Polarized PL of molecularly ordered thin films confirming nanoplatelet in-plane alignment and ordering explaining impermeability (**Fig. R6 and Supplementary Fig. 4**)
- Showed lack of accessible microporous structure with various gas probes
 - Adsorption isotherms of CH₄, CO₂, He, and H₂ on 2DPA-1 measured by the U.S. National Institute for Standards and Technology confirming no microporosity (**Supplementary Fig. 10**)
 - [REDACTED] REDACTED [REDACTED]
- Verified inhibition of molecular transport via staggered unit cells rather than solvent clogging
 - TGA-MS of gas evolution from 2DPA-1 confirming the absence of microporous-trapped solvents or water (**Supplementary Fig. 12**)
 - *In situ* AFM of bulges at elevated temperatures showing persistent impermeability at high temperatures (**Supplementary Fig. 13**)

Reviewer #1:

- DFT simulations of energetically favored offset stacking explaining the structural aspects of impermeability (off-set platelet stacking) (**Supplementary Fig. 14**)
- Enhanced clarity on the film morphology and experimental apparatuses used in this study
 - SEM and AFM compared with explanatory schematics, confirming film morphology leading to impermeability (**Supplementary Figs. 5 and 7**)

Changes made to the manuscript (excerpts highlighted in light grey) that are marked in **blue** and ~~red-strikethrough~~ text represent additions and subtractions, respectively. The same format is followed for figures, with the exception of review-only figures (labeled as **Fig. R#**). Relevant references are included at the end of each response as numbered brackets [#].

Reviewer #1:

Reviewer: *The authors emphasize the excellent chemical stability and processability of their material, 2DPA-1. However, there is insufficient evidence to support its claimed chemical stability.*

Our Response: We appreciate the opportunity to clarify and expand upon our claims for the chemical stability of 2DPA-1. The chemical stability of 2DPA-1 is imparted by the irreversible nature of the amide bonds that have a high dissociation energy; however, transamidation is a potential side reaction common to many polyaramids [1, 2]. We recently investigated the potential for 2DPA-1 transamidation in trifluoroacetic acid (TFA) via ^1H NMR over the course of 24 h [3] (**Figs. R1-2**). No evident changes in chemical structure are observed over the first 9 h in TFA. Marginal changes in the chemical structure occur after sitting in TFA for 24 h, suggesting some transamidation can occur if the sample remains in highly acidic conditions for an extended period, but this is beyond the exposure that 2DPA-1 would experience prior to film processing (typically < 1 h).

We also assessed ^1H NMR of 2DPA-1 exposed to water for 539 days (1.5 years), a more relevant environmental matrix for longitudinal chemical stability (**Supplementary Fig. 1**). The 2DPA-1 to water mass ratio was approximately 1:1. Our data depict a negligible change in the ratio of main disk to end-group protons (the r -value) from $r = 5.15$ to $r = 5.45$ after long-term storage in potentially hydrolyzing water, confirming long-term chemical stability. The only observable difference is a change in signal to noise of the ^1H -NMR spectrum between the two dispersions, leading to a 6% change in r -value, within the measurement noise. We conclude that there is no notable effect of water on any other aspect of the sample, including its molecular structure. These data support the chemical stability of this material in protic polar solvents and the lack of hygroscopic degradation observed by the sustained gas barrier properties over 1000 days in ambient humidity conditions.

REDACTED

SI amendment

“Chemical Stability and Processability of 2DPA-1

The chemical stability of 2DPA-1 is imparted by the irreversible nature of its amide bonds having a high dissociation energy. Transamidation, a potential side reaction common to many polyaramids [1, 2], is not observed for 2DPA-1 when exposed to TFA for 9 h [3]. Marginal changes in the chemical structure occur after sitting in TFA for 24 h, suggesting some transamidation can occur if the sample remains in highly acidic conditions for an extended period, but this is beyond the exposure that 2DPA-1 would experience prior to film processing.

One-dimensional (1D) polyaramids are notoriously hygroscopic [4]. Using ^1H NMR, we find no notable effect of water on the chemical or molecular structure of 2DPA-1 after 539 d (1.5 y) of exposure (Supplementary Fig. 1). The data depict a slight increase in the r -value from 5.15 to 5.45 after long-term exposure. The aromatic region and end group region also showed sharp peaks before water storage. Both observations indicate the presence of small particles prior to water storage, which may have disappeared due to particle aggregation or sedimentation. These data support the chemical stability of this material in protic polar solvents and the lack of hygroscopic degradation observed by the sustained gas barrier properties over 1000 d in ambient humidity conditions (Fig. S14).”

Reviewer #1:

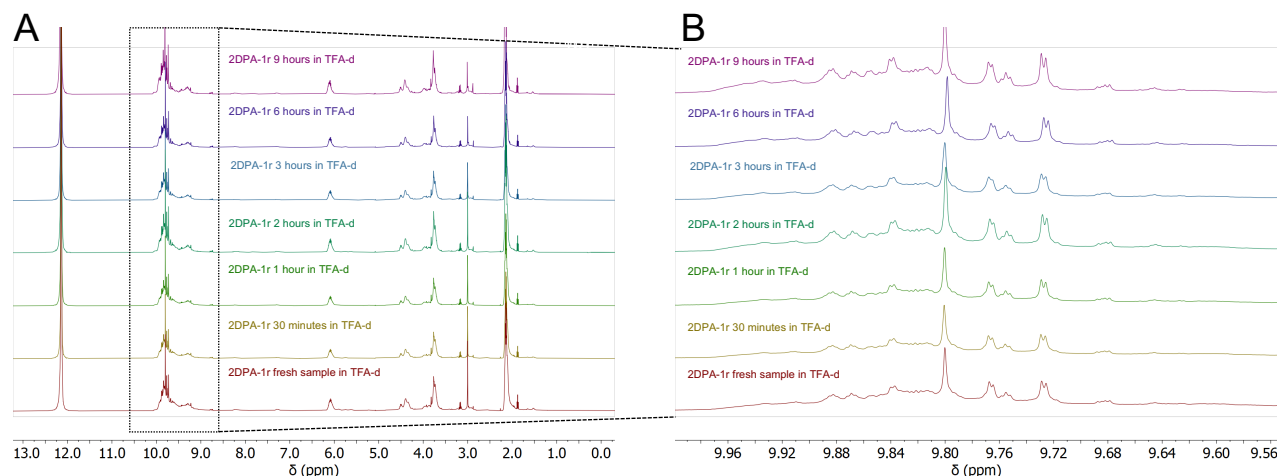


Fig. R1. (a) Repetitive ^1H NMR measurements of the same 2DPA-1r ($r = 7.56$) in TFA-d sample after left on the bench for certain amount of time. (b) Enlarged aromatic region of 2DPA-1r ^1H NMR spectra that were measured after being left on the bench for certain amount of time.

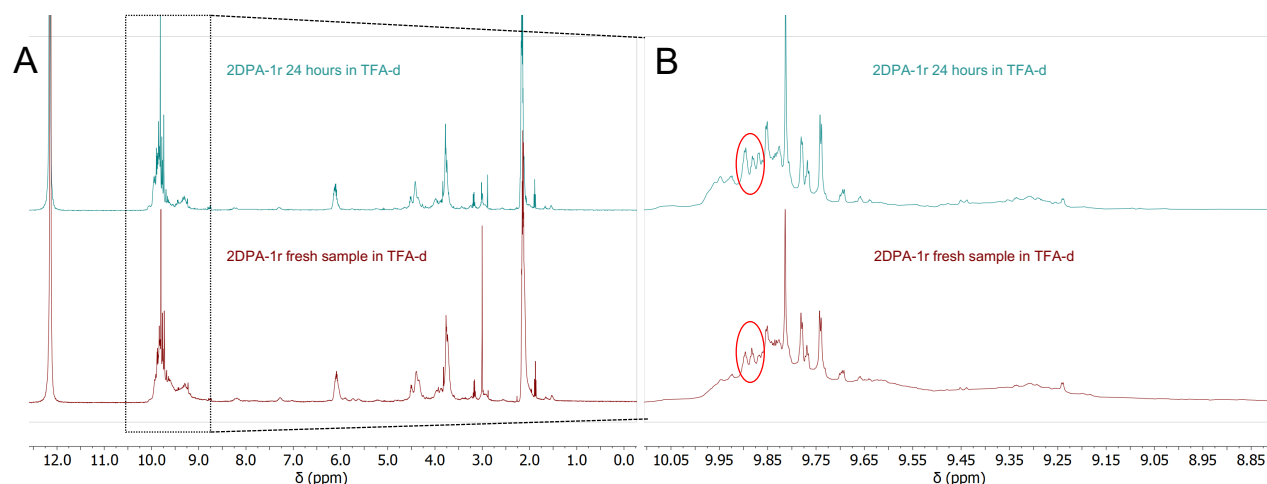
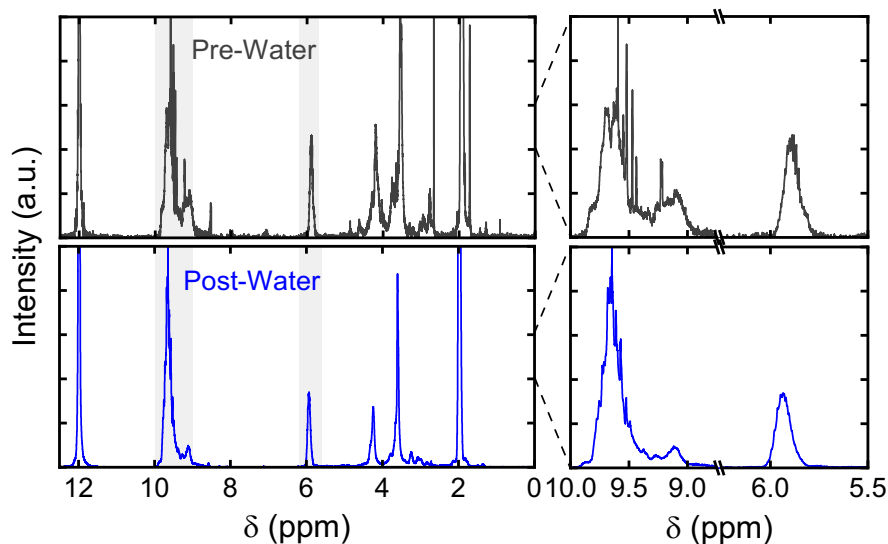


Fig. R2. (a) Repetitive ^1H NMR measurements of the same 2DPA-1r ($r = 7.56$) in TFA-d sample freshly prepared and left on the bench for 24 hours. (b) Enlarged aromatic region of 2DPA-1r ^1H NMR spectra that were freshly prepared and left on the bench for 24 hours.

Reviewer #1:



Supplementary Fig. 1.

¹H NMR of 2DPA-1 platelets before (dark grey) and after (blue) storing in deionized water for 539 d. Panels on the right highlight the spectral regions (shaded light grey) of the chemical shift for the aromatic cores and end groups centered around roughly 9.5 ppm and 5.8 ppm, respectively. Our data depict a marginal increase in the *r*-value from 5.15 to 5.45 after long-term exposure.

- [1] G. Li & M. Szostak, *Nat. Commun.* 9, 4165 (2018)
- [2] P. Acosta-Guzman *et al.*, *Molecules*, 23, 2382 (2018)
- [3] Z. Wei *et al.*, *J. Am. Chem. Soc.* 147, 5921–5932 (2025)
- [4] M. Akay *et al.*, *Comp. Sci. Technol.* 5, 565-571 (1997)

Reviewer: Additionally, the processability is primarily demonstrated through film preparation using TFA-dissolved solutions. This is a method previously reported for COF materials (e.g., *Angew. Chem. Int. Ed.* 2020, 59, 5165). Furthermore, various established methods, such as in situ growth, stacking of nanosheets, and interfacial polymerization, are available for directly processing COFs into membranes or films, all of which exhibit adequate processability (e.g., *Angew. Chem. Int. Ed.* 2024, e202421661; *Angew. Chem. Int. Ed.* 2022, 61, e202207559). Notably, most imine-linked COFs are also chemically stable. Thus, the comparison of 2DPA-1 to COFs regarding chemical stability and processability in the manuscript may not be entirely accurate.

Our Response: We thank the reviewer for their input on the comparison between stability/processability of covalent organic frameworks (COFs) against 2D polyaramids. Our discussion was intended to highlight the limitations of COFs synthesized via conventional solvothermal methods. As indicated by the reviewer, there have been various developments over the years to improve both the stability and processability of COFs. We have incorporated these references in the Main Text to more appropriately reflect these developments (see below).

The more important comparison is that 2D polyaramids represent the first-ever 2D polymer barriers. COFs films, while widely explored as gas separation membranes, tend to have a large porous structure that has rendered them unsuitable as barriers. Some covalent triazine frameworks have been theorized to have gas barrier properties comparable to that demonstrated in this work [1], but this level of performance has yet to be realized experimentally due to defects formed

Reviewer #1:

during synthesis/processing [2]. We have adjusted the Main Text accordingly to account for this discussion and improve the clarity by which we are comparing COFs with 2D polyaramids.

Main Text amendment

“When dispersed in trifluoroacetic acid (TFA) or dimethylsulfoxide (DMSO), 2DPA-1 forms nanoplatelets $O \sim 10$ nm in diameter (Fig. 1A-B). Unit cells formed by repeating inert amide linkages with triazine cores afford 2DPA-1 a high degree of both chemical stability and processability (Supplementary Figs. 1-2)—a consolidation of properties not commonly found in covalent organic framework (COF) analogues synthesized via conventional solvothermal methods [3]. Several strategies exist to process COFs for thin film applications [4-6], but experimental realization of nonporous COFs [1] remains wanting due to the formation of defects [2].”

[1] Y. Wang *et al.*, *ACS Appl. Mater. Interf.* 8, 8694–8701 (2016)

[2] P. Katekomol *et al.*, *Chem. Mater.* 25, 1542–1548 (2013)

[3] X. Li *et al.*, *Nat. Nanotechnol.* 10, 785–790 (2015)

[4] D.W. Burke *et al.*, *Angew. Chem.* 132, 5203–5209 (2020)

[5] X. Shi *et al.*, *Angew Chem. Int. Ed.* 64, e202421661 (2024)

[6] X. Shi *et al.*, *Angew Chem. Int. Ed.* 61, e202207559 (2022)

Reviewer: *The characterization used to confirm framework formation through monomer condensation is insufficient. It is recommended to include FTIR and ^{13}C NMR analyses to clearly demonstrate polyamide linkages.*

Our Response: In response to the reviewer’s concern regarding the overall molecular structure of 2DPA-1, we reproduced and expanded an analysis of the vibrational spectra of both as-produced 2DPA-1 powder and the spun nanofilms. Specifically, we’ve collected attenuated total reflectance Fourier-transform infrared (ATR-FTIR) and Raman spectra for both bulk 2DPA-1 and the spin-coated thin film structure and compared them against simulated vibrational spectra of a 2DPA-1 monolayer in vacuum (Supplementary Fig. 2). The resulting spectra confirm the presence of polyamide linkages with triazine cores representative of 2DPA-1. Notably, we find good agreement between the thin film and bulk samples, supporting their synonymous chemical structure. Detailed analysis below.

We performed a normal mode analysis on the vibrational density of states (VDOS) for peak assignment of the simulated structure (Supplementary Table 1 and Movie S2). Characterization of 2DPA-1 via ^{13}C NMR was reported in our recently published work [1] and is included below for the reviewer’s convenience (Fig. R3). In brief, we conducted model ^{13}C NMR measurements on two 2DPA-1 (one with $r = 3.23$ the other one with $r = 7.56$) at a concentration of 15 mg mL^{-1} in deuterated trifluoroacetic acid, TFA-d, (d1=10s with 2048 scans). As shown in Fig. R3, both spectra exhibit three distinct peaks within the range of 171–167 ppm, corresponding to carbons on triazine cores, carbons on amide linkages, and carbon on the ester bonds.

Raman spectra (Supplementary Fig. 2A) were measured for 2DPA-1 using a 785-nm excitation laser to minimize interference from photoluminescence. We find generally good agreement between the bulk spectrum, which was prepared by drop-casting 5 mg mL^{-1} 2DPA-1 in trifluoroacetic acid (TFA) and then air dried, and the simulated Raman spectrum. A control of drop-casted TFA without 2DPA-1 is included for comparison (Fig. R4). Amide I and II bands are assigned between roughly $1450\text{--}1650 \text{ cm}^{-1}$ to primarily C–C aromatic stretching and C=O stretching of the amide groups [2, 3]. Amide III bands are assigned between roughly $1220\text{--}1280 \text{ cm}^{-1}$ as C–N stretching and N–H in-plane bending [2, 3]. Residual TFA is identified in both the

Reviewer #1:

bulk and 35-nm film samples at approximately 260 cm^{-1} and 2150 cm^{-1} due to processing techniques [4]. The thin-film samples were measured by transferring a 35-nm spin-coated 2DPA-1 film onto a gold-sputtered, surface-enhanced Raman scattering (SERS) substrate. While several of the amide bands are detected in the thin film, the signal is relatively weak over background photoluminescence due to the limited sample cross-section. However, a strong Raman band appears at 710 cm^{-1} for the 35-nm film, which we attribute to symmetric stretching of the triazine cores [5-7]. The total symmetric stretching vibration of triazine cores is typically observed between $680\text{--}690\text{ cm}^{-1}$ but has been observed to shift to higher wavenumbers due to interaction with SERS substrates, along with significant signal enhancements due to preferential ordering at the SERS surface [6, 7].

ATR-FTIR spectra (**Supplementary Fig. 2B**) were measured using a Bruker ATR-FTIR Spectrometer with a reflection diamond ATR module. We again find good agreement between the bulk and simulated FTIR spectra. The bulk material in this case was simply 2DPA-1 powder. No TFA was used for obtaining the bulk sample. Amide I and II bands are assigned to C=O and N-H bending as well as C=O stretching of the amide groups between roughly $1500\text{--}1750\text{ cm}^{-1}$ (**Supplementary Table 1**). Amide III bands are assigned to strong C-N stretching between roughly $1110\text{--}1350\text{ cm}^{-1}$ (**Supplementary Table 1**). Strong N-H stretching around 3500 cm^{-1} in the simulated spectrum is found to be markedly broadened in the experimental data, a common occurrence due to inter- and intramolecular hydrogen bonding interactions that can weaken or shift the stretching frequency. To obtain signal from the 35-nm 2DPA-1 films used in this study, we transferred three films sequentially onto copper film substrates (thickness $\sim 100\text{ nm}$) to maximize both sample cross-section and reflectance. The ATR-FTIR spectrum mirrors that of the bulk sample with the addition of signal from TFA (1830 cm^{-1} , 2100 cm^{-1} , and 2300 cm^{-1}) [4]. The most notable difference, however, is the relative suppression of the C-N stretching around 1250 cm^{-1} from the bulk sample to the thin film. The mechanistic reasoning for this change requires further investigation beyond this work, but our initial belief is that this is due to the sensitivity of ATR-FTIR to molecular ordering through longitudinal vibrational modes [8].

We have adjusted the text of Methods and SI accordingly to account for this new data and discussion (see below).

SI amendment

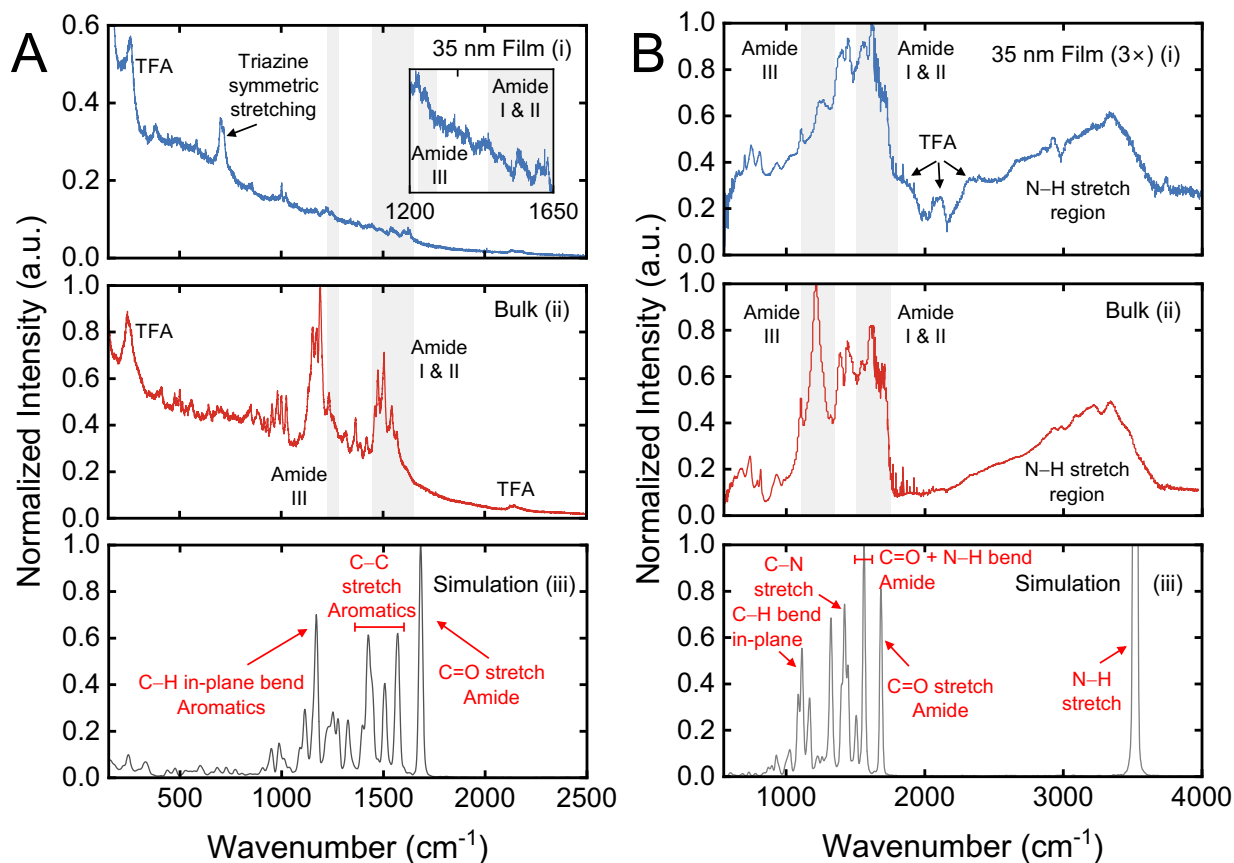
“Raman, ATR-FTIR, and Photoluminescence (PL) Spectroscopy of 2DPA-1

Raman spectra (Supplementary Fig. 2A) were measured for 2DPA-1 using a 785-nm excitation laser to minimize interference from photoluminescence (PL). We find generally good agreement between the bulk spectrum and the simulated Raman spectrum. Amide I and II bands are assigned between roughly $1450\text{--}1650\text{ cm}^{-1}$ to C-C aromatic stretching and C=O stretching of the amide groups [2, 3]. Amide III bands are assigned between roughly $1220\text{--}1280\text{ cm}^{-1}$ as C-N stretching and N-H in-plane bending [2, 3]. Residual TFA is identified in both the bulk and 35-nm film samples at approximately 260 cm^{-1} and 2150 cm^{-1} [4] due to processing techniques. While several of the amide bands are detected in the thin film, the signal is relatively weak over background photoluminescence due to the limited sample cross-section. However, a strong Raman band appears at 710 cm^{-1} for the 35-nm film, which we attribute to symmetric stretching of the triazine cores [5-7]. The total symmetric stretching vibration of triazine cores is typically observed between $680\text{--}690\text{ cm}^{-1}$ but has been observed to shift to higher wavenumbers due to interaction with SERS substrates, along with significant signal enhancements due to preferential ordering at the SERS surface [6, 7].

ATR-FTIR spectra (Supplementary Fig. 2B) were measured using a Bruker ATR-FTIR Spectrometer with a reflection diamond ATR module. We again find good agreement between the bulk and simulated FTIR spectra. Amide I and II bands are assigned to C-C aromatic stretching and C=O stretching of the amide groups between roughly $1500\text{--}1750\text{ cm}^{-1}$ (Supplementary Table 1). Amide III bands are assigned to strong C-N stretching between

Reviewer #1:

roughly 1110–1350 cm^{-1} (Supplementary Table 1). Strong N–H stretching observed around 3500 cm^{-1} in the simulated spectrum is found to be markedly broadened in the experimental data, a common occurrence due to inter- and intramolecular hydrogen bonding interactions that can weaken or shift the stretching frequency. The ATR-FTIR spectrum of the triple-stacked 35-nm film (~ 100 nm total thickness) mirrors that of the bulk sample with the addition of signal from TFA (1830 cm^{-1} , 2100 cm^{-1} , and 2300 cm^{-1}) [4]. The most notable difference, however, is the relative suppression of the C–N stretching around 1250 cm^{-1} from the bulk sample to the thin film. The mechanistic reasoning for this change requires further investigation beyond this work, but our initial hypothesis is that this is due to the sensitivity of ATR-FTIR to molecular ordering through longitudinal vibrational modes [8].”



Supplementary Fig. 2.

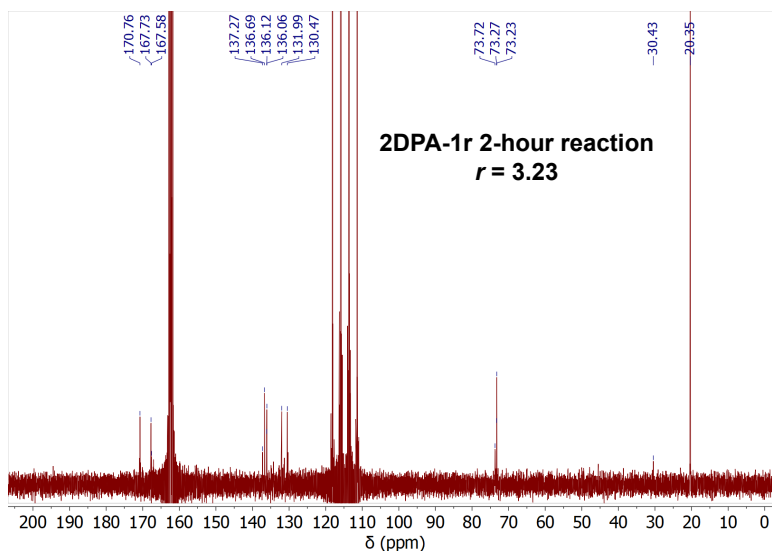
Raman (A) and ATR-FTIR (B) spectra of 2DPA-1 measured for (i) 35-nm film, (ii) bulk sample, and compared against (iii) simulations with peak assignments, noted in red. The light gray shaded regions highlight the Amide I, II, and III bands. For Raman, samples were measured using 532-nm excitation light source on gold SERS substrates, and the bulk sample was prepared by drop-casting 5 mg ml^{-1} 2DPA-1 dissolved in trifluoroacetic acid, TFA. The inset in Panel A(i) highlights the Raman signal between 1200–1650 cm^{-1} . ATR-FTIR samples were collected with a copper film backing. Signal of thin film samples were achieved with ATR-FTIR by sequentially stacking three 35-nm films for a total thickness of ~ 100 nm, while the bulk sample was 2DPA-1 powder.

Supplementary Table 1.

Various bands in IR and Raman spectrum and the corresponding normal modes determined from vibrational density of states (VDOS).

Reviewer #1:

Frequency (cm ⁻¹)		Normal Mode Frequencies (cm ⁻¹)	Description
IR	VDOS		
1113.64	1109.57	1105, 1106, 1109, 1110, 1114, 1115	Stretching between C (triazine) and N (amide)
1168.61	1162.51	1154, 1155, 1156, 1157, 1162, 1168, 1169	C–H in-plane bending
1323.34	1327.42	1314, 1317, 1320, 1323, 1327, 1329, 1340	Some mode in triazine + N–H bending in amide
1421.07	1423.10	1408, 1411, 1413, 1415, 1417	N–H stretching + C–N stretching (triazine).
1506.58	1504.54	1506, 1511	C=O bending + C–N stretching (amide); N–H bending + C–N stretching (triazine)
1561.55	1565.62	1544, 1545, 1546, 1556, 1561, 1563	N–H bending (amide) + connected C–N stretching (triazine); e _{1u} band (benzene)
1683.7	1681.66	1672	C=O stretching in the amide linkage
3516.02	3520.09	3500, 3502, 3511	N–H stretching/bending in the amide linkage
Raman	VDOS		
1252.09	1229.69	1213, 1220, 1221, 1222, 1246	C–H bending (benzene) + N–H bending (amide)
1276.52	1276.52	1261, 1269, 1274, 1275, 1282, 1284, 1286	



Reviewer #1:

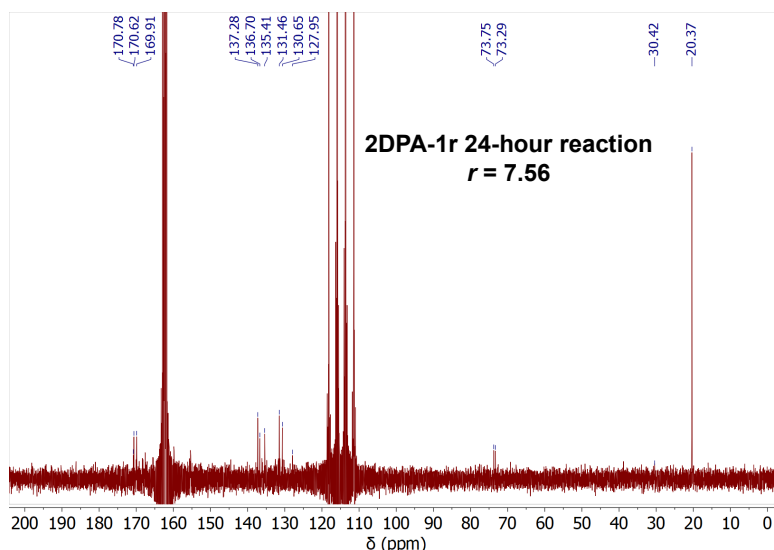


Fig. R3. ^{13}C NMR spectra of 2DPA-1r 2-hour reaction (top) and 24-hour reaction (bottom), taken from ref. [1].

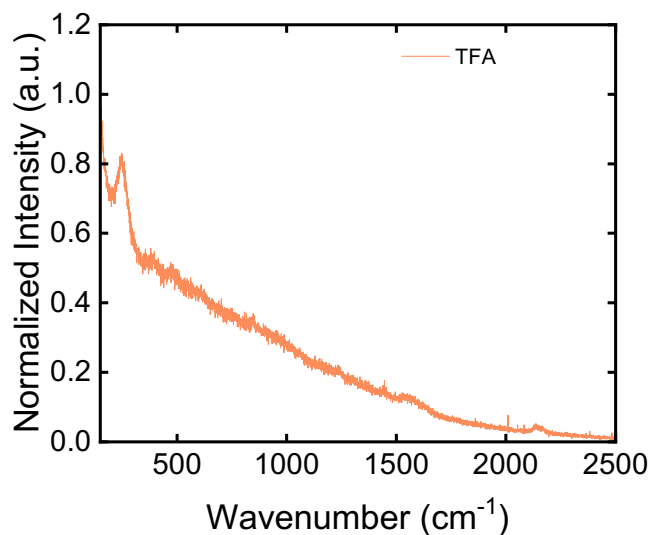


Fig. R4. Raman spectra for TFA drop-cast onto SERS substrate without 2DPA-1 as a control.

- [1] Z. Wei *et al.*, *J. Am. Chem. Soc.* 147, 5921–5932 (2025)
- [2] P.K. Kim *et al.*, *Polymer*, 27, 34-46 (1986)
- [3] G. Washer *et al.*, *J. Mater. Civ. Eng.* 29, 226-234 (2009)
- [4] N. Fuson *et al.*, *J. Chem. Phys.* 20, 1627-1634 (1952)
- [5] J. Goubeau *et al.*, *J. Phys. Chem.* 58, 1078-1081 (1954)
- [6] E. Koglin *et al.*, *J. Phys. Chem.* 100, 5078-5089 (1996)
- [7] N.E. Mircescu *et al.*, *Vib. Spectrosc.* 62, 165-171 (2012)
- [8] G. Laroche *et al.*, *Appl. Surf. Sci.* 273, 632-637 (2013)
- [9] T. Dorfmueller *et al.*, *Dynamic Light Scattering*, John Wiley and Sons (1977)
- [10] D.W. Noid *et al.*, *J. Chem. Phys.* 67, 404-408 (1977)
- [11] T.D. Kuhne *et al.*, *J. Chem. Phys.* 152, 194103 (2020)
- [12] B.J. Gellatly *et al.*, *J. Mol. Biol.* 161, 305-322 (1982)
- [13] M. Brehm *et al.*, *J. Chem. Phys.* 152, 164105 (2020)
- [14] M. Thomas *et al.*, *Phys. Chem. Chem. Phys.* 17, 3207-3213 (2015)

Reviewer #1:

- [15] M. Thomas *et al.*, *Phys. Chem. Chem. Phys.* 15, 6608-6622 (2013)
- [16] S. Roy *et al.*, *J. Chem. Phys.* 125, 5971-5982 (2021)
- [17] M. Brehm and B. Kirchner, *J. Chem. Inf. Model.* 51, 2007-2023 (2011)
- [18] M. Thomas *et al.*, *J. Chem. Phys.* 141, 024510 (2014)
- [19] G. Mathias and M.D. Baer, *J. Chem. Theory Comput.* 7, 2028-2039 (2011)
- [20] G. Schaftenaar *et al.*, *J. Comput. Aided Mol. Des.* 14, 123-124 (2000)

Reviewer: *Given the structure depicted in Fig. 1A, 2DPA-1 is expected to be highly porous. Therefore, gas sorption experiments are suggested to evaluate its microporosity and pore size distribution. Ar sorption could be considered if N₂ sorption at 77 K is unavailable due to N₂ impermeability.*

Our Response: We thank the reviewer for their suggestion. In response, we collaborated with the U.S. National Institute of Standards and Technology (NIST), who maintain a suite of precision instrumentation for gas adsorption. We include extensive data from their measurements and have now included them as authors. These data indicate, as we expected, no microporosity in 2DPA-1 when measuring adsorption isotherms with N₂, He, H₂, CH₄, and CO₂—consistent with the molecular impermeability observed and reported in our manuscript. Note that NIST did not have access to Ar for testing, but we are certain that the extensive panel of gases we did test will prove adequate to address the reviewer’s concerns with this point. Detailed analysis of the procedure is provided below.

To further explore the limits of pore accessibility in 2DPA-1, we first measured N₂ isotherms (**Supplementary Fig. 10A-B**) at 77 K up to 100 kPa (1 P/P₀) on a low-pressure manometric instrument (Autosorb 6100, Anton Paar, Ashland, VA). The N₂ adsorption isotherm of powder 2DPA-1 follows a Type II isotherm with a type H3 hysteresis loop, which can be attributed to non-rigid aggregates of plate-like particles or a pore network consisting of macropores that are not completely filled with condensate [1]. The BET specific surface area from the average of two aliquots is $(74 \pm 10) \text{ m}^2 \text{ g}^{-1}$. The pore size distribution of bulk (powder) 2DPA-1 consists of mostly mesopores, with an average mode pore width of approximately $(11.1 \pm 2.6) \text{ nm}$, and some macroporosity. Bulk 2DPA-1 has a total pore volume of $(0.41 \pm 0.07) \text{ cm}^3 \text{ g}^{-1}$. Given the mode pore width is similar in size to the ~10–15 nm diameter 2DPA-1 nanoplatelets (**Fig. 1b** of Main Text), this pseudo porosity is likely from interparticle space from non-rigid aggregation of the 2DPA-1 nanoplatelets.

Unary He, H₂, CH₄, and CO₂ adsorption isotherms (**Supplementary Fig. 10C**) on 2DPA-1 at 298 K up to 1 MPa were measured on a high-pressure manometric instrument (BELSORP-VC, Microtrac Bel). At 150 kPa, negligible He and H₂ adsorption were observed ($<7 \mu\text{mol g}^{-1}$), with only marginal adsorption of CO₂ ($380 \mu\text{mol g}^{-1}$) and CH₄ ($60 \mu\text{mol g}^{-1}$). Therefore, despite the inability of 2DPA-1 films to form persistent bulges with these smaller gases and the ~1-nm diameter pore of the unit cell, the adsorption isotherms corroborate the notion that 2DPA-1 is a nonporous material. The inability of these gases to access the pore is in line with high diffusive barriers observed for triazine frameworks with comparable pore sizes [2] and can likely be explained by a staggered pore-to-pore configuration of stacked 2DPA-1 platelets in the lamellar film, which can lead to exacerbated energy barriers for permeation (**Supplementary Figs. 17-20**). Findings from the additional adsorption isotherm analysis have been incorporated into the Main Text, Methods, and SI as shown below.

Reviewer #1:

Main Text amendment

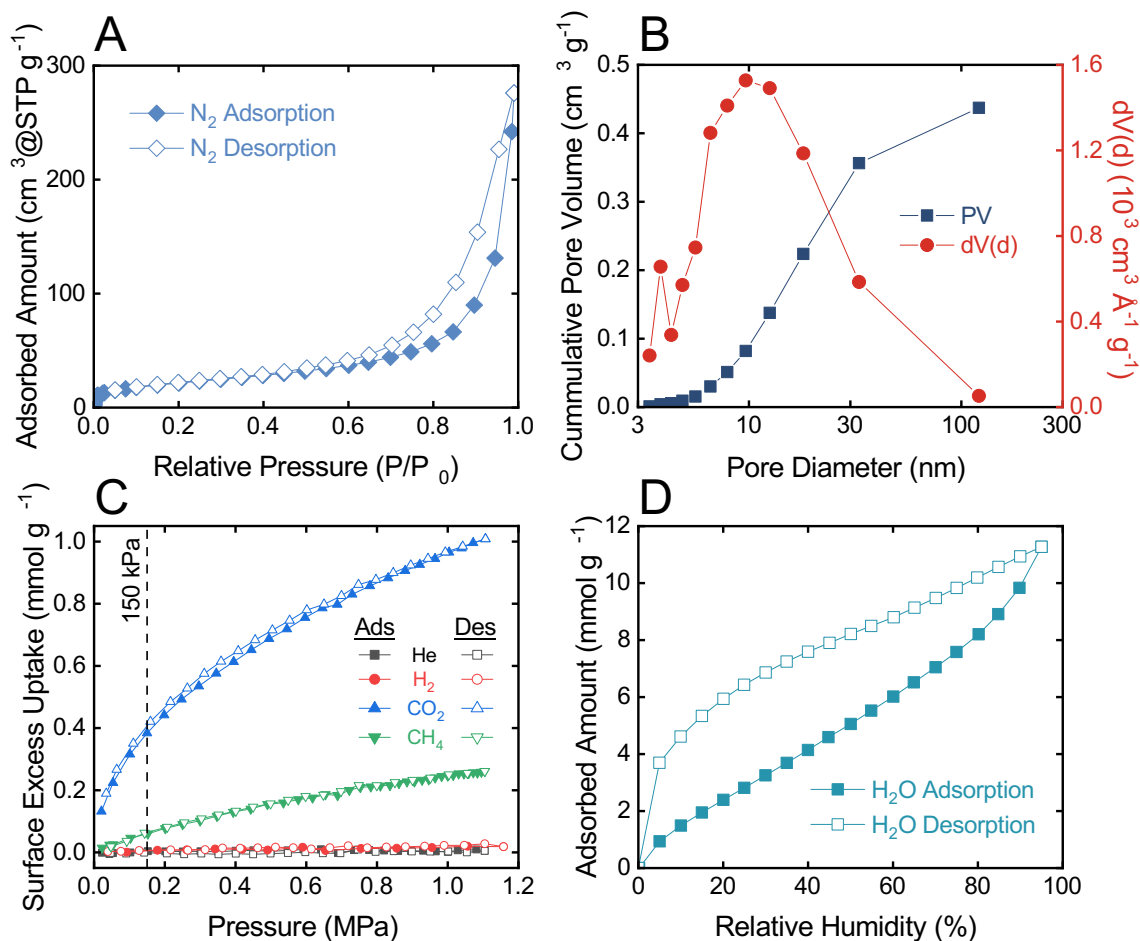
“The ability of 2DPA-1 films to trap gas within the microwells is not exclusive to N₂. We observed similar multi-day persistence for bulges filled with sulfur hexafluoride (SF₆), argon (Ar), and methane (CH₄, Fig. 3A-D), suggesting that 2DPA-1 is likewise impermeable to gases larger or similar in size to N₂. We note that the formation of persistent bulges was not observed for smaller gases such as oxygen (O₂), carbon dioxide (CO₂), helium (He), or hydrogen (H₂). We measured unary adsorption isotherms for CH₄, CO₂, He, and H₂ on 2DPA-1 platelets at 298 K up to 1 MPa (SI). At 150 kPa, negligible He and H₂ adsorption were observed ($<7 \mu\text{mol g}^{-1}$), with only marginal adsorption of CO₂ ($380 \mu\text{mol g}^{-1}$) and CH₄ ($60 \mu\text{mol g}^{-1}$). Despite the inability of 2DPA-1 films to form persistent bulges with some of these smaller gases, the adsorption isotherms corroborate the notion that 2DPA-1 is a nonporous material.”

SI amendment

“Gas Adsorption and Thermal Degradation Analyses

The N₂ adsorption isotherm of for 2DPA-1 platelets follows Type II isotherm behavior (Supplementary Fig. 10A). It also possesses a type H3 hysteresis loop, which can be attributed to non-rigid aggregates of plate-like particles or pore network consisting of macropores that are not completely filled with condensate [1]. The BET specific surface area from the average of two aliquots is $(74 \pm 10) \text{ m}^2 \text{ g}^{-1}$. The pore size distribution of powder 2DPA-1 consists of mostly mesopores, with an average mode pore width of approximately $(11.1 \pm 2.6) \text{ nm}$, and some macro-porosity (Supplementary Fig. 10B). Bulk 2DPA-1 platelets have a total pore volume of $(0.41 \pm 0.07) \text{ cm}^3 \text{ g}^{-1}$. Given the mode pore width is similar in size to the 2DPA-1 nanoplatelets (approximately 10 nm to 15 nm, Fig. 1b of Main Text), this pseudo porosity is likely from interparticle space due to non-rigid aggregation of the 2DPA-1 platelets. The adsorption of water on 2DPA-1 at low relative humidity (RH) implies an intrinsic hydrophilicity of the material (Supplementary Fig. 10D).

...”



Reviewer #1:

Supplementary Fig. 10.

Adsorption isotherms for 2DPA-1 using various probe molecules. (A-B) Representative N₂ adsorption isotherm at 77 K (B) and the corresponding pore size distribution determined from BJH method (B). (C) Unary He, H₂, and CO₂ adsorption isotherms at 298 K. (D) H₂O vapor adsorption isotherm at 298 K with N₂ as carrier gas.

[1] M. Thommes *et al.*, *Pure Appl. Chem.* 87, 1051-1069 (2015)

[2] Y. Wang *et al.*, *ACS Appl. Mater. Interf.* 8, 8697-8701 (2016)

Reviewer: *The authors classify their material as polymers rather than COFs. Crystallinity, reflecting the degree of ordered structures, is a key distinction between polymers and COFs. The manuscript describes 2DPA-1 as having highly ordered frameworks and includes simulations of bilayers with various interlayer shifts. Such structural illustrations and simulations are typically applicable to COFs. Clarification is needed: Is 2DPA-1 a COF? If not, the structural illustration in Fig. 1A may be misleading, and the simulations/discussions about interlayer shifts would lack relevance. If it is a COF, please confirm this through PXRD patterns showing clear low-theta diffraction peaks. Based on the mentioned d-spacing (~1 nm), the diffraction peak should appear around 6-8°. However, the structural illustrations suggesting order are inconsistent with the PXRD discussion, where the authors conclude that 2DPA-1 lacks long-range order.*

Our Response: We appreciate the reviewer's perspectives on polymers versus COFs, but we must respectfully challenge the notion of crystallinity being the distinguishing factor between a conventional 1D polymer (e.g., a linear or branched polymer) and a 2D polymer (e.g., a COF). Below we provide evidence to show that 2DPA-1 is indeed a molecularly ordered 2D polymer albeit not crystalline. It is decidedly not a COF and lacks the long-range order that would be assigned as crystallinity. This evidence is provided by a combination of powder X-ray diffraction (PXRD) and wide-angle X-ray scattering (WAXS) measured for as-synthesized and chemically modified 2DPA-1 structures, simulated PXRD from theoretical model structures, and anisotropic polarized photoluminescence (PL) of the thin film.

A 2D polymer is defined as a material that is topologically planar, covalently linked, and molecularly thin [1]—all properties that we previously demonstrated for 2DPA-1 [2]. The long-debated requirement for 2D polymers to be crystalline materials stems from the ease with which the structure of crystalline 2D polymers can be characterized and compared against model structures. However, this view has been steadily losing favor as a stringent requirement due to the increasing presence of topologically 2D macromolecular sheets with irregular crosslinks [3]. Diffraction peaks captured by PXRD reflects the long-range order of the system and depends strongly on structural characteristics, such as crystallite domain size and the layer-to-layer offset, or “stacking disorder,” of the 2D macromolecular sheets [4]. Consequently, the degree of crystallinity measured for 2D polymers like COFs often depends on synthesis conditions that affect their alignment [5, 6], such as solvent-induced reordering.

Our illustration in Fig. 1A of the Main Text depicts the theoretical structure of a single monolayer of 2DPA-1. The reviewer is correct that we would anticipate sharp diffraction peaks representative of crystallinity in PXRD if the multi-layer platelets of 2DPA-1 formed eclipsed (AA stacked) structures. However, as depicted in Fig. 1C of the Main Text, we posit a lamellar structure with in-plane ordering but no precisely defined stacking order, and shuffled unit cell

Supplementary Fig. 3A REDACTED the importance of stacking order on the crystallinity measured in 2DPA-1 samples via PXRD REDACTED

Reviewer #1:

. Simulated XRD data were calculated from the CIF structure file using Powder Pattern Function in CCDC Mercury software.

When compared against model 2DPA-1 structures, we find that measured PXRD of 2DPA-1 does not reflect the diffraction patterns that would be expected for AA or AB stacking modes (**Supplementary Fig. 3A(i-ii)**). Instead, the broad PXRD of 2DPA-1 is consistent with the dispersive scattering that would occur from random offsets between layers (**Supplementary Fig. 3A(iii)**).

REDACTED

It is important to note that the absence of crystallinity does not mean that the system is a disordered, amorphous material. Numerous non-crystalline and para-crystalline materials possess orientational ordering that is not captured by conventional X-ray techniques, including ordered polyaramid and cellulose fibers [7, 8]. Beyond XRD or direct imaging by electron microscopy, non-crystalline ordering can be detected using polarization-sensitive approaches [9]. We demonstrate in-plane orientational ordering of a 35-nm 2DPA-1 film using polarized photoluminescence, PL (**Supplementary Fig. 4**). We find that when excited at 532 nm with a polarized laser, the PL emission of the 35-nm 2DPA-1 film depends on its orientation with respect to the beam path. Specifically, the thin film emission transitions from roughly 1400 cm^{-1} (575 nm) when excited orthogonal to the beam path to 2270 cm^{-1} (605 nm) when excited parallel to the beam path. This twofold symmetry is consistent with anisotropic platelets oriented parallel to the substrate with a transition dipole along the long axis of the platelet [2]. We note that the emission window reported is beyond that of SiO_2 to eliminate signal interference (**Fig. R6**). Interestingly, for each spectrum we find a sharp Raman signature between approximately 2410 cm^{-1} and 2435 cm^{-1} that is uncommon for most materials. This signature was not generated by the simulation of a 2DPA-1 monolayer. Notably, the location of this Raman band is in good agreement with second-order features from overtones of fundamental modes observed in highly ordered pyrolytic graphite (HOPG) that do not appear in monolayer graphene [10-12]. We hypothesize that this Raman band may be an additional signature of molecular ordering from stacked doublet formation, but this will be the subject of a subsequent study.

We have adjusted the text in the caption of Fig. 1A, the Main Text, and the SI to improve clarity and incorporate some of the findings discussed here. Panels B-E of **Supplementary Fig. 3** are discussed in a later response.

“Fig. 1 | 2DPA-1 Nanoplatelets as Free-Standing Thin Films for Bulge Formation. (A) Theoretical structure of 2DPA-1 monolayer nanoplatelets.”

Main Text amendment

Reviewer #1:

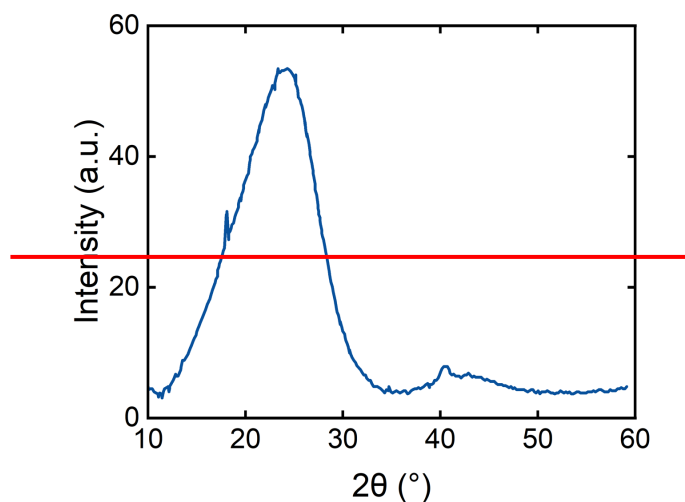
“Powder X-ray diffraction (PXRD) suggests 2DPA-1 lacks long-range order (SI); however, a combination of polarized photoluminescence (Supplementary Fig. 4) and scanning transmission electron microscopy (STEM) of spin-coated 2DPA-1 thin films reveals anisotropy in the form of layered, orientational ordering (Fig. 1C-E).”

SI amendment

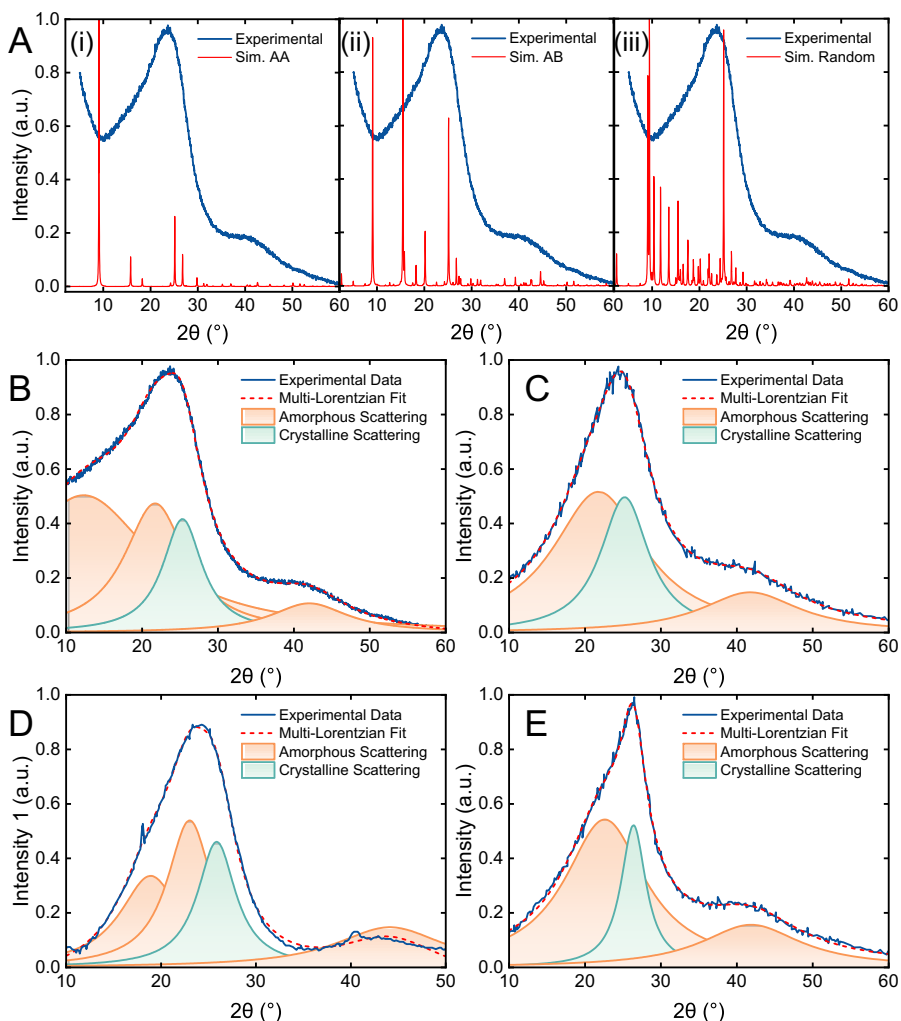
“Raman, ATR-FTIR, and Photoluminescence (PL) Spectroscopy of 2DPA-1

...

Numerous non-crystalline and para-crystalline materials possess orientational ordering that is not captured by conventional X-ray techniques, including ordered polyaramid and cellulose fibers [7, 8]. Beyond XRD or direct imaging by electron microscopy, non-crystalline ordering can be detected using polarization-sensitive approaches [9]. We demonstrate orientational ordering of a 35-nm 2DPA-1 film using polarized PL (**Supplementary Fig. 4**). We find that when excited at 532 nm with a polarized laser, the PL emission of the 35-nm 2DPA-1 film depends on its orientation with respect to the beam path. Specifically, the thin film emission transitions from roughly 1400 cm^{-1} (575 nm) when excited orthogonal to the beam path to 2270 cm^{-1} (605 nm) when excited parallel to the beam path. This twofold symmetry is consistent with anisotropic platelets oriented parallel to the substrate with a transition dipole along the long axis of the platelet [2]. We note that the emission window reported is beyond that of SiO_2 to eliminate signal interference. Interestingly, for each spectrum we find a sharp Raman signature between approximately 2410 cm^{-1} and 2435 cm^{-1} that is uncommon for most materials. This signature was not generated by the simulation of a 2DPA-1 monolayer. Notably, the location of this Raman band is in good agreement with second-order features from overtones of fundamental modes observed in highly ordered pyrolytic graphite (HOPG) that do not appear in monolayer graphene [10-12]. The origin of this Raman band requires further exploration.”



Reviewer #1:

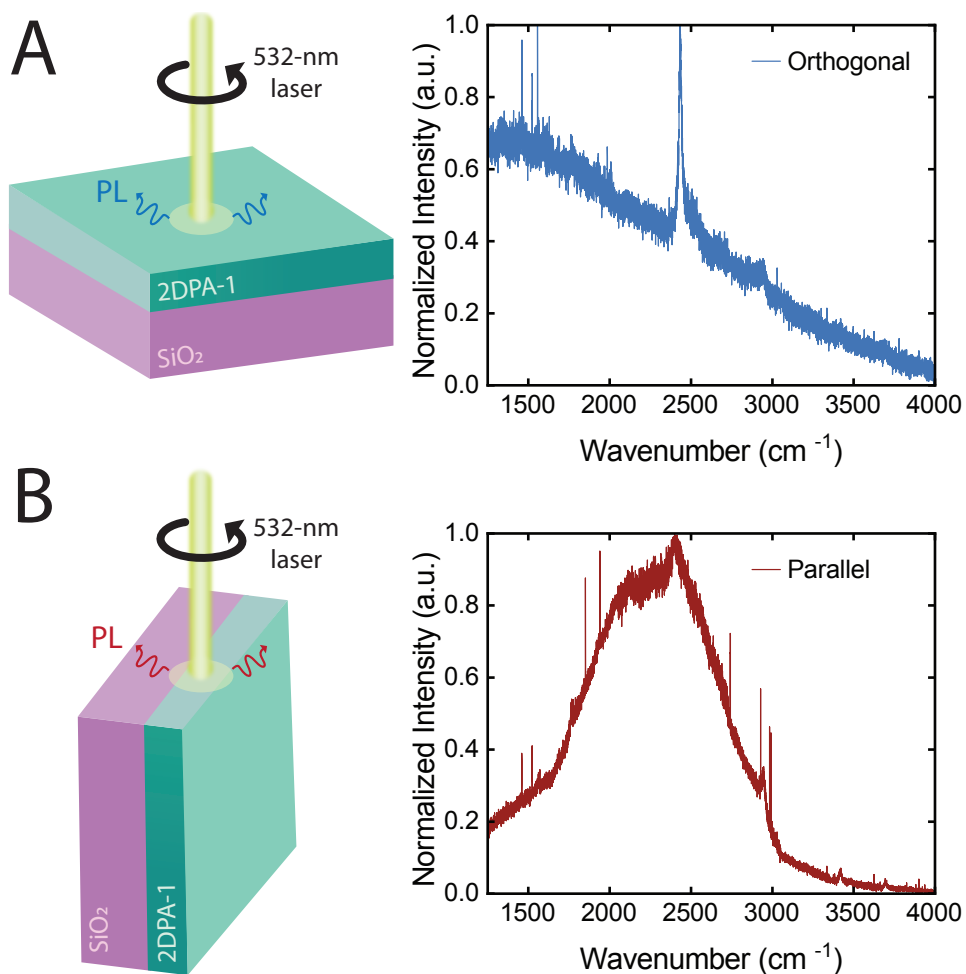


Supplementary Fig. 3. REDACTED

Powder X-ray diffraction (PXRD) of 2DPA-1. REDACTED Experimental data compared against diffraction peaks simulated for 2DPA-1 stacked in (A) eclipsed, i.e., AA, (B) offset, i.e., AB, and (C) random layer-to-layer configurations. (B-E) Measured PXRD of 2DPA-1 fit by Lorentzian curves. The red dashed curve represents the cumulative fit of all Lorentzian curves to the overall data. Using the peak position centered between 25° to 26° (2θ) as the pseudo-crystalline signal, the degree of crystallinity is estimated as (A) 13.6 %, (B) 27.7 %, (C) 23.6 %, and (D) 18.0 %.

REDACTED

REDACTED



Supplementary Fig. 4.

Photoluminescence, PL, measurements of 35-nm 2DPA-1 film on a SiO₂ substrate placed (A) orthogonal and (B) parallel to the beam path of a polarized 532-nm excitation laser source. Illustrations of measurement configuration are on the left, with the resulting data plotted on the right. The emission window reported is just beyond that of SiO₂ to eliminate signal interference.

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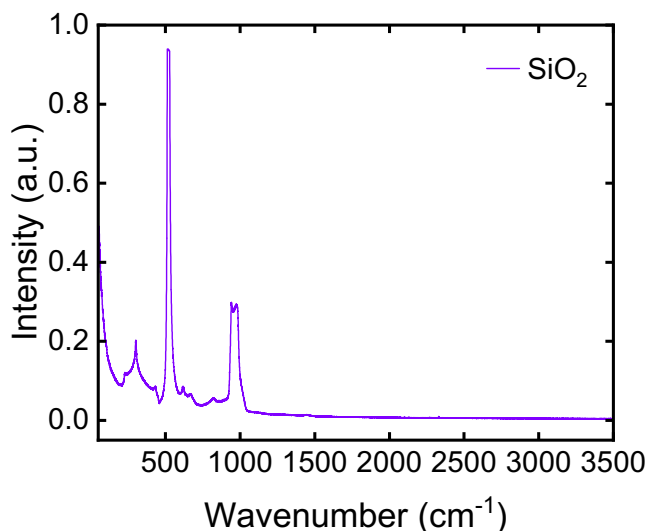


Fig. R6. Emission of SiO₂ substrate when excited at 532 nm.

- [1] A.M. Evans *et al.*, *Chem. Rev.* 122, 442-564 (2022)
- [2] Y. Zeng *et al.*, *Nature*, 602, 91-95 (2022)
- [3] A.B. Marco *et al.*, *Angew. Chem.* 129, 7050-7055 (2017)
- [4] S. Van Gele *et al.*, *JACS Au*, 5, 388-398 (2025)
- [5] X. Wang *et al.*, *Nat. Chem.* 10, 1180-1189 (2018)
- [6] P. Kharel *et al.*, *J. Am. Chem. Soc.* 147, 11821-11828 (2025)
- [7] S. Marina *et al.*, *Mater. Horiz.* 9, 1196 (2022)
- [8] J.L. Bregado *et al.*, *Fluid Phase Equilibria*, 491, 56-76 (2019)
- [9] B.A. Collins *et al.*, *Nat. Mater.* 11, 536-543 (2012)
- [10] Y. Wang *et al.*, *Chem. Mater.* 2, 557-563 (1990)
- [11] R.J. Nemanich and S.A. Solin, *Phys. Rev. B*, 20, 392-401 (1979)
- [12] R. Al-Jishi and G. Dresselhaus, *Phys. Rev. B*, 26, 4514-4522 (1982)

Reviewer: The main text refers broadly to the Supplementary Information (SI) when discussing results. To improve clarity, specific references (e.g., Supplementary Fig. 1) should be included to help readers efficiently locate corresponding figures in the SI.

Our Response: We thank the reviewer for their recommendation and have made the adjustments throughout the Main Text, Methods, and SI accordingly to improve clarity for future readership.

Reviewer: Can the authors provide a photograph of the 2DPA-1 solution in TFA? Is the material fully dissolved or merely dispersed in TFA? Typically, TFA delaminates 2D COFs to produce nanosheets for film fabrication. What is the structural state of 2DPA-1 in TFA? The TEM image in Fig. 1B shows nanoplatelets with lateral sizes around 10 nm. What are their thicknesses? Preparing continuous 4-nm-thick films would be barely possible if the nanoplatelets are significantly thicker.

Our Response: We agree with the reviewer's overarching sentiment here—preparing films as thin as 4 nm requires solution-phase platelets that are, themselves, molecularly thin. To address the first part of the reviewer's question, we have provided photographs of 2DPA-1 dissolved in TFA at a concentration of 5 mg mL⁻¹ in contrast to solvents that it disperses in rather than

Reviewer #1:

dissolves, including acetone, hexane, and chloroform (**Fig. R7**). The difference in solubility is evidenced by the translucency of 2DPA-1 in TFA compared to the cloudiness of the non-soluble solvents, consistent with classical colloidal behavior. We used quantitative ^1H -NMR to determine the solubilized concentration of 2DPA-1 within other non-TFA solvents (**Table R1**, calculation details below).

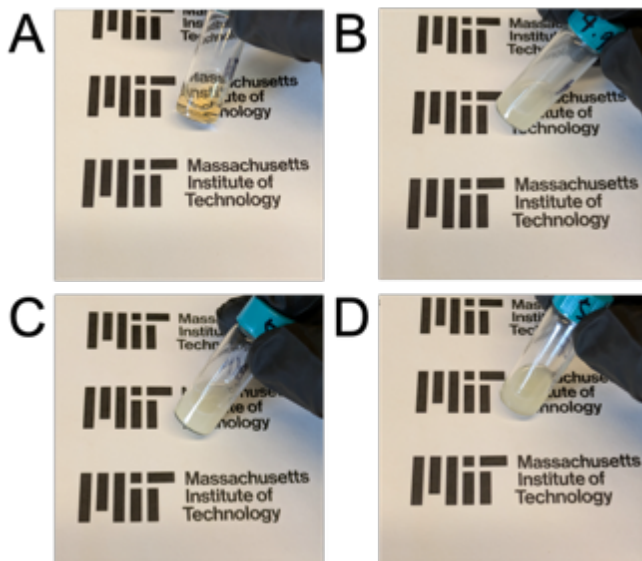
We then developed computational tools for quantitative analysis of over 3000 platelets from TEM images, measuring disk diameter, circularity, and electron beam extinction to estimate thickness (**Figs. R8-9**)—all of which can be found in our recently submitted manuscript on *ChemRxiv* [1]. TEM image processing confirmed the presence of distinct quantized layers that suggest particle stacking below 8 layers ($< 3\text{ nm}$). In the solution phase, relevant to spin coating, we anticipate even less platelet-platelet stacking based on TFA's ability to disrupt hydrogen bonds, evidenced by photoacoustic measurements of 2DPA-1 in TFA previously reported in [2].

Solubility calculations followed the standard process of adding 2DPA-1 and calibrant molecules to each solvent, the latter of which was in known amounts. Then, after capturing ^1H -NMR spectra, we computed the concentration of 2DPA-1 relative to the calibrant using the following equation:

$$C_{2DPA-1} = \frac{I_{2DPA-1}}{I_{cal}} \frac{N_{cal}}{N_{2DPA-1}} C_{cal}$$

where C_x is the concentration, I_x is the integral peak area, and N_x is the number of nuclei of compound x . Additional developments for dissolving and spin-coating 2DPA-1 using more environmentally friendly solvents is discussed later in this response.

In the initial development of 2DPA-1, atomic force microscopy (AFM) was used to measure isolated monolayer platelets with molecular thickness of $\sim 3.7\text{ \AA}$ and diameters on the order of 10 nm via silylation of the hydrogen bonds [3]. Without silylation, the strong hydrogen bonding between 2DPA-1 platelets favors the formation of bi- and multi-layer stacks. In this study, the samples for TEM imaging of the nanoplatelets depicted in Fig. 1B of the Main Text were prepared by drop-casting a low concentration solution of 2DPA-1 onto a graphene-backed TEM grid. Here, dimethyl sulfoxide (DMSO) was used as the solvent for compatibility with the TEM grid.



Reviewer #1:

Fig. R7. Visualization of 2DPA-1 when dissolved in (A) TFA, compared against dispersed in non-soluble solvents: (B) acetone, (C) hexane, and (D) chloroform. All solutions are 5 mg mL⁻¹.

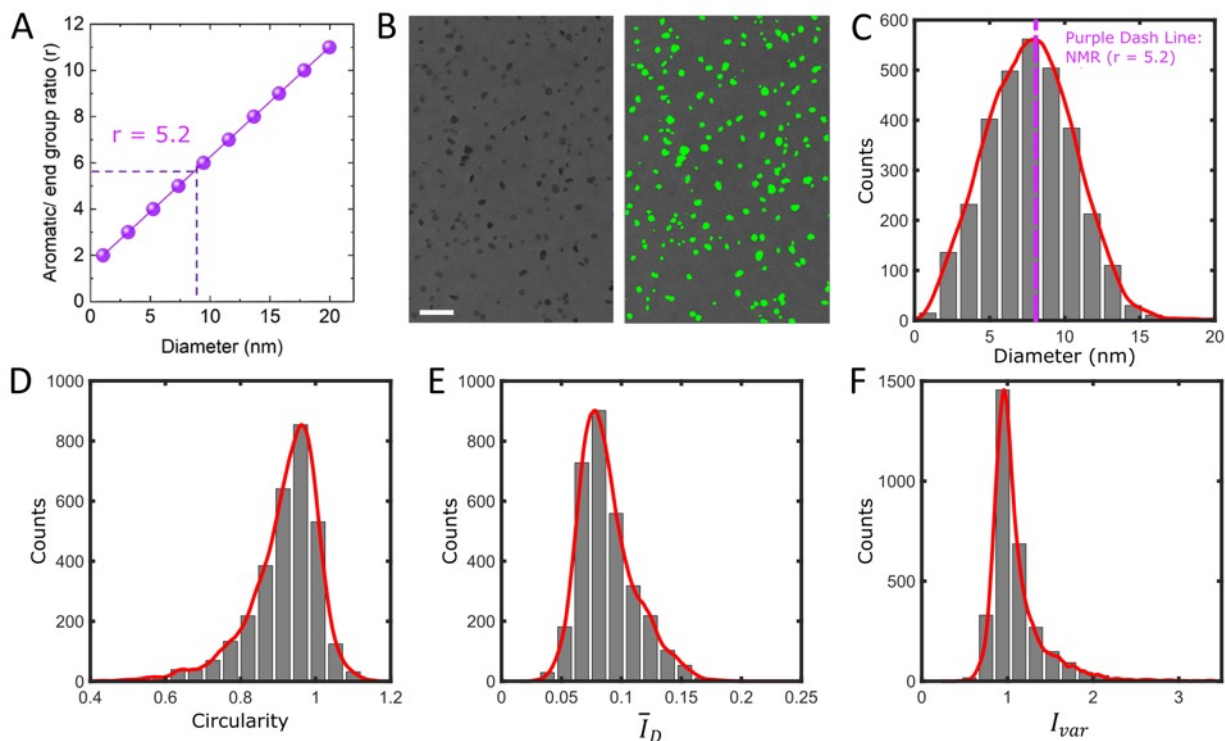


Fig. R8. NMR Size Characterization and TEM Image Processing of 2DPA-1 Platelets. (A) A plot of the theoretical relationship between the r -value calculated from NMR for 2DPA-1 used in this analysis and a perfect hexagonal platelet size from DFT calculations. (B) 2DPA-1 platelets suspended in DMSO were deposited on a single-layer graphene TEM grid where the single-layer graphene provides a reference background for flatness and extinction comparison. An example TEM image is shown on the left (i) with its image-segmented counterpart on the right (ii), where the 2DPA-1 platelets were adequately identified prior to calculating platelet statistics. After over 3,000 individual 2DPA-1 platelets were analyzed, distributions of key statistics were displayed: (C) 2DPA-1 platelet size distribution assuming circular discs, (D) platelet circularity, (E) normalized TEM image intensity - used as a proxy for thickness, and (F) normalized intensity variance - used as a proxy for smoothness.

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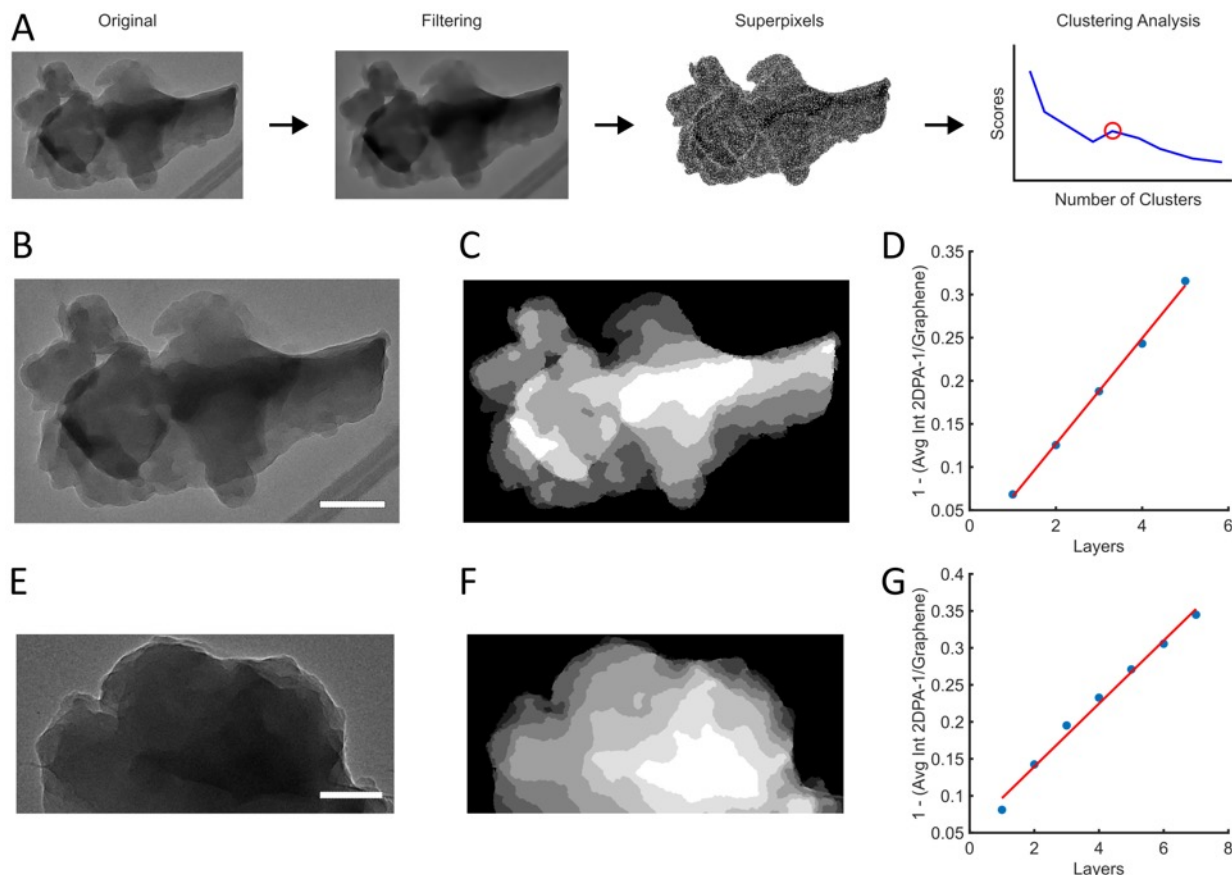


Fig. R9. Image-Based Layering Analysis of Solvent Retreated 2DPA-1. DMSO-treated 2DPA-1 platelets were imaged via TEM for algorithmic analysis. (A) Schematic representation of the image processing workflow, progressing from raw TEM data to cluster analysis for identifying material layers based on electron attenuation. (B, E) TEM images of platelets reveal overlapping, stepwise layers (scale bar: 100 nm). (C, F) Layer analysis results highlight identified layers consistent with visual inspection. (D, G) Normalized average pixel intensity for each layer is plotted against the layer number, showing a linear trend in intensity differences, suggesting stacked layers with similar electron attenuation and thickness.

Table R1. Solubilized concentration of 2DPA-1 in various solvents as determined by $^1\text{H-NMR}$

Solvent	2DPA-1 Solubility (g L ⁻¹)
Dimethyl Sulfoxide	278
Water	N.D.
Acetone	N.D.
Chloroform	N.D.
Methanol	N.D.
Ethanol	N.D.
Isopropanol	N.D.
Piperidine	N.D.
Acetic acid	N.D.

N.D. – not detected

Reviewer #1:

[1] X. Gong *et al.*, *ChemRxiv* (2025) DOI: 10.26434/chemrxiv-2025-0gjm

[2] Z. Wei *et al.*, *J. Am. Chem. Soc.* 147, 5921–5932 (2025)

[3] Y. Zeng *et al.*, *Nature*, 602, 91-95 (2022)

Reviewer: *TFA, a strong organic acid, often compromises polymer and COF structures. Can the authors provide clear evidence to support the identical structure between their polymer and film? The use of aggressive TFA could also compromise practical applications. Are there any mild alternatives to replace TFA for film preparation.*

Our Response: We kindly note that clear evidence exists to support the identical structure between 2DPA-1 in the bulk powder and spun nanofilm—even in the presence of TFA—was provided in our earlier responses; however, the reviewer brings up a valid point regarding the practical use of TFA as a solvent. Although TFA is a versatile solvent that has led to its widespread industrial usage as a solvent, catalyst, and reagent in various chemical processes, it is not considered to be a particularly sustainable option.

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[1] D.E. Bidstrup and C.J. Geankoplis, *J. Chem. Eng. Data*, 8, 170-173 (1963)

[2] J.H. Wang, *J. Phys. Chem.* 69, 4412-4412 (1965)

Reviewer: *Weight loss of 5% in TGA is typical for polymers, which may not lead to the conclusion that the pores are not blocked by water. To confirm this, the film should be in situ treated under*

Reviewer #1:

higher temperatures like 120 °C to completely remove water and other potential gases followed by gas permeance tests.

Our Response: We thank the reviewer for their insight and suggestion. It has prompted us to conduct an extensive study on the water interaction properties of our material. Below we demonstrate that, despite being a hydrophilic material, the molecularly impermeability of 2DPA-1 cannot be attributed to blockage by solvents (water or TFA) sorbed into the pores. This conclusion is supported by a combination of *in situ* AFM measurements up to 120 °C paired with TGA and mass spectrometry (TGA-MS) that show water completely evolved at 120 °C, yet bulges remain inflated.

First, we measured water vapor adsorption isotherms on the bulk material using an automated dynamic vapor sorption analyzer (VTI-SA+, TA Instruments) at ambient pressure and with nitrogen as the carrier gas. Our results confirm that 2DPA-1 is indeed hydrophilic, adsorbing water at low RH (**Supplementary Fig. 10D**, included in above in an earlier response to reviewer). This is to be expected given the high degree of hydrogen bonding of the material.

We agree with the reviewer's point that physi-sorbed water, which our analysis confirms is likely to be present, will be eliminated at 120 °C. If water-blocked pores are the root explanation for the molecular impermeability of 2DPA-1, we would expect complete collapse of the bulges at this elevated temperature. To more thoroughly investigate the potential impact of sorbed water on the gas impermeability of 2DPA-1, we used a temperature-controlled environmental AFM stage (Asylum Research, Cypher ES Environmental AFM) to capture real-time measurements of four additional bulge deflections with respect to temperature (**Supplementary Fig. 13**). We increased the temperature step wise to 120 °C and then oscillated between 120 °C and 80 °C. The step rate was 0.05 °C s⁻¹.

We find that all four bulge deflections decreased partially upon the initial heating ramp up to 120 °C but then appear to remain sealed thereafter, falsifying the hypothesis that the nanofilm is microporous but blocked by water or residual TFA. We attribute the decrease in height to a temporary and reversible opening of the rim seal, likely owing to influence of heating on the adhesion between the polymer film and SiO₂ substrate and their differing thermal expansion coefficients. We observe such rim opening upon abrupt pressure changes, as we show in Fig 2 of the manuscript, enabling controlled gas filling. When subsequently oscillating the temperature between 80°C and 120°C for 2.5 cycles, the bulge deflections similarly oscillated on the order of 10 nm consistent with the ideal gas law, as we calculate below. This confirms that the nanofilms, despite being only 35 nm thick, remain impermeable throughout the experiment.

Assuming no gas transport is occurring, we can predict the average change in the bulge deflection from 80 °C to a theoretical height at 120°C through the series of equations shown below, originating with the ideal gas law:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} ,$$

where 1 and 2 refer to states 1 and 2 of the bulge, and P , V , and T are the internal pressure, volume under the bulge, and temperature, respectively. By accounting for the geometry of the microwell system and using Hencky's solution to relate bulge deflection to a pressure difference [1], we can substitute in the following expressions

$$V_n = \pi r^2 L + \frac{\pi r^2 \delta_n}{2}$$

Reviewer #1:

and

$$P_n - P_{\text{ext}} = A\delta_n^3 + B\delta_n ,$$

where

$$A = \frac{16EdK(v)}{a^4} \text{ and } B = \frac{4S_0}{a^2} .$$

Here, r is the radius of the well, P_{ext} is the pressure external to the bulge (atmosphere). A is a constant equal to the ratio of E , the elastic modulus, d , the film thickness, $K(v)$, a constant dependent on Poisson's ratio, and a , the bulge diameter. B is a constant related to the self-tensioning, S_0 , of the bulge. Combining these expressions for P and V with the ideal gas law yields:

$$\frac{(A\delta_1^3 + B\delta_1 + P_{\text{atm}}) \left(2\pi rL + \frac{\pi r^2 \delta_1}{2} \right)}{T_1} = \frac{(A\delta_2^3 + B\delta_2 + P_{\text{atm}}) \left(2\pi rL + \frac{\pi r^2 \delta_2}{2} \right)}{T_2}$$

Thus, for a given T_1 , T_2 , and δ_1 , one can calculate δ_2 .

We set $T_1 = 80$, $T_2 = 120$, and δ_1 as the average experimental value at 80 °C within the oscillation regime. We note that a range of reported E for 2DPA-1 will influence the predictions [2]. We therefore include a feasible range of δ_2 that captures the potential variance in the modulus of the nanofilm. We find that 17 of the 20 (85%) experimentally determined deflections at 120 °C fall within the predicted range. Hence, our results do not indicate any discernable gas loss while oscillating between 80 and 120 °C and supports the notion that physi-sorbed water cannot be the mechanistic explanation for the film's measured impermeability.

The reviewer's suggestion also prompted us to expand upon our original thermogravimetric analysis (TGA) to inform the evolution of all gases from our material that may indicate trace solvents or water locked within the polymer nanoporous network. Specifically, we were interested to see if residual chemicals from synthesis, such as acetone, N-methyl pyrrolidone (NMP), pyridine, or water may be present. We carried out simultaneous TGA and mass spectrometry (TGA-MS) to analyze gas evolution at elevated temperatures during thermal degradation of 2DPA-1 ($r = 10.5$) in an inert N_2 atmosphere (**Supplementary Fig. 12**). The ramp rate was 10 °C min^{-1} up to 1000 °C. The off-gas was simultaneously analyzed a connected mass spectrometer. All details of this study are included as review only material. We have provided a brief discussion of the analysis below.

TGA-MS of 2DPA-1 shows no trace of acetone (58 atomic mass unit, amu), NMP (99 amu), or pyridine (79 amu) in low or high temperatures. This corroborates NMR results that show these chemicals are effectively removed during polymer purification [3]. As suspected from our original TGA, water vapor (18 amu) evolved from the 2DPA-1 sample between 65–90 °C, necessarily corresponding to surface-bound (i.e., physi-sorbed) water molecules as discussed earlier. This is reflected in the first peak of the DTG curve (**Supplementary Fig. 12A**). Water absorbed within highly confined pores requires substantially more energy to remove, often leading to desorption temperatures in excess of 100 °C [4-6]. Notably, we also detect water evolution from the 2DPA-1 sample between 300-450 °C. The release of water vapor observed at these elevated temperatures is beyond that expected from stronger confinement interactions and can instead be explained by the cleavage of the amide bonds during the thermal degradation of 2DPA-1. This is a well-studied mechanism in thermal degradation of similar polyaramids such as Kevlar and Nomex in which water is a common byproduct of thermal degradation [7, 8].

Reviewer #1:

In summary, we showed that, although 2DPA-1 is hydrophilic in nature and readily adsorbs water, it does not explain the molecular impermeability reported here. This analysis also rules out the potential role of residual TFA (boiling point 72.4 °C). We have included these results and discussion in the Methods, Main Text, and SI where applicable (see below).

Main Text amendment

“The impermeability of 2DPA-1 implies an absence of free volume required for molecular transport. The pore within the 2DPA-1 unit cell is estimated to be approximately 1 nm in diameter; hence, it is unlikely that a monolayer platelet would impose substantial resistance to most gas molecules. We ruled out the possibility that water or another relevant solvents could be occluding the pores via simultaneous thermogravimetric analysis with mass spectrometry (TGA-MS) and the observation of several bulges that remain inflated upon heating to 120 °C ~~a stable bulge even upon heating to 90 °C~~ (SI Supplementary Figs. 12-13).”

SI amendment

“Gas Adsorption and Thermal Degradation Analyses

...

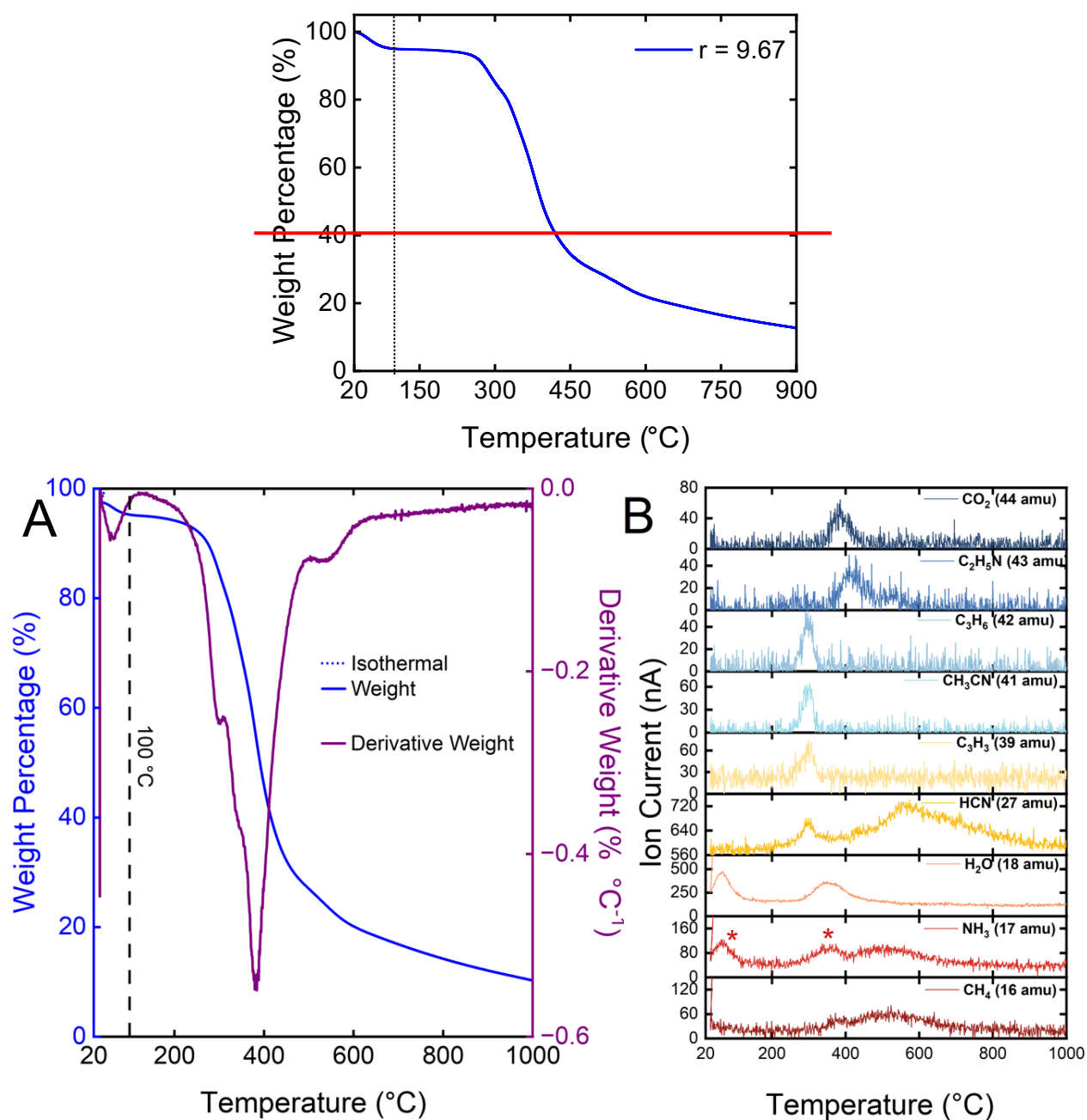
Simultaneous thermogravimetric analysis with mass spectrometry (TGA-MS) of 2DPA-1 shows no trace of acetone (58 atomic mass unit, amu), NMP (99 amu), or pyridine (79 amu) in low or high temperatures. This corroborates NMR results that show these chemicals are effectively removed during polymer purification [3]. Water vapor (18 amu) evolved from the 2DPA-1 sample between 65–90 °C likely corresponds to surface-bound (i.e., physisorbed) water molecules. This is reflected in the first peak of the derivative thermogravimetric curve (Supplementary Fig. 12A). Water absorbed within highly confined pores requires substantially more energy to remove, often leading to desorption temperatures in excess of 100 °C [4-6]. Notably, we also detect water evolution from the 2DPA-1 sample between 300-450 °C. The release of water vapor observed at these elevated temperatures is beyond that expected from stronger confinement interactions and can instead be explained by the cleavage of the amide bonds during the thermal degradation of 2DPA-1. This is a well-studied mechanism in thermal degradation of similar polyaramids such as Kevlar and Nomex in which water is a common byproduct of thermal degradation [7, 8].

As a hydrophilic material, water sorbed within the unit cell pores of 2DPA-1 thin films may influence molecular transport of other gases. We investigated the potential impact of sorbed water on the gas impermeability of 2DPA-1 via a temperature-controlled environmental AFM stage (Asylum Research, Cypher ES Environmental AFM) to capture real-time measurements of four bulge deflections with respect to temperature (Supplementary Fig. 13A-D). All four bulge deflections decreased upon the initial heating ramp up to 120 °C but did not result in complete deflation. We can thus conclude that pores blocked by water or residual TFA are not the root cause for the observed molecular impermeability of 2DPA-1, as the counter case would result in complete deflation upon vaporization up to 120 °C. We attribute the decrease in deflection to a temporary and reversible opening of the rim seal, likely owing to the influence of heating on thermal expansion of the 2DPA-1 thin film and adhesion between 2DPA-1 and the SiO₂ substrate. When subsequently oscillating the temperature between 80°C and 120°C for 2.5 cycles, the bulge deflections similarly oscillated on the order of 10 nm.

Assuming no gas transport is occurring, we can predict the average change in the bulge deflection from 80 °C to a theoretical height at 120°C through the series of equations shown below originating with the ideal gas law: $P_1 V_1 / T_1 = P_2 V_2 / T_2$. Here, the subscripts refer to states 1 and 2 of the bulge, and P , V , and T are the internal pressure, volume under the bulge, and temperature, respectively. By accounting for the geometry of the microwell system and using Hencky's solution to relate bulge deflection, δ , to a pressure difference [1] (eq. M3 of Methods), we can solve for δ_2 given T_1 , T_2 , and δ_1 .

We set $T_1 = 80$, $T_2 = 120$, and δ_1 as the average experimental value at 80 °C within the oscillation regime (Supplementary Fig. 13E-H), with theoretical upper and lower bounds defined by the range of elastic moduli reported for 2DPA-1 [2]. We find that 17 of the 20 (85%) experimentally determined deflections at 120 °C fall within the predicted range. Hence, our results do not indicate any discernable gas loss while oscillating between 80 and 120 °C and supports the notion that physisorbed water is not the mechanistic explanation for the film's measured impermeability.”

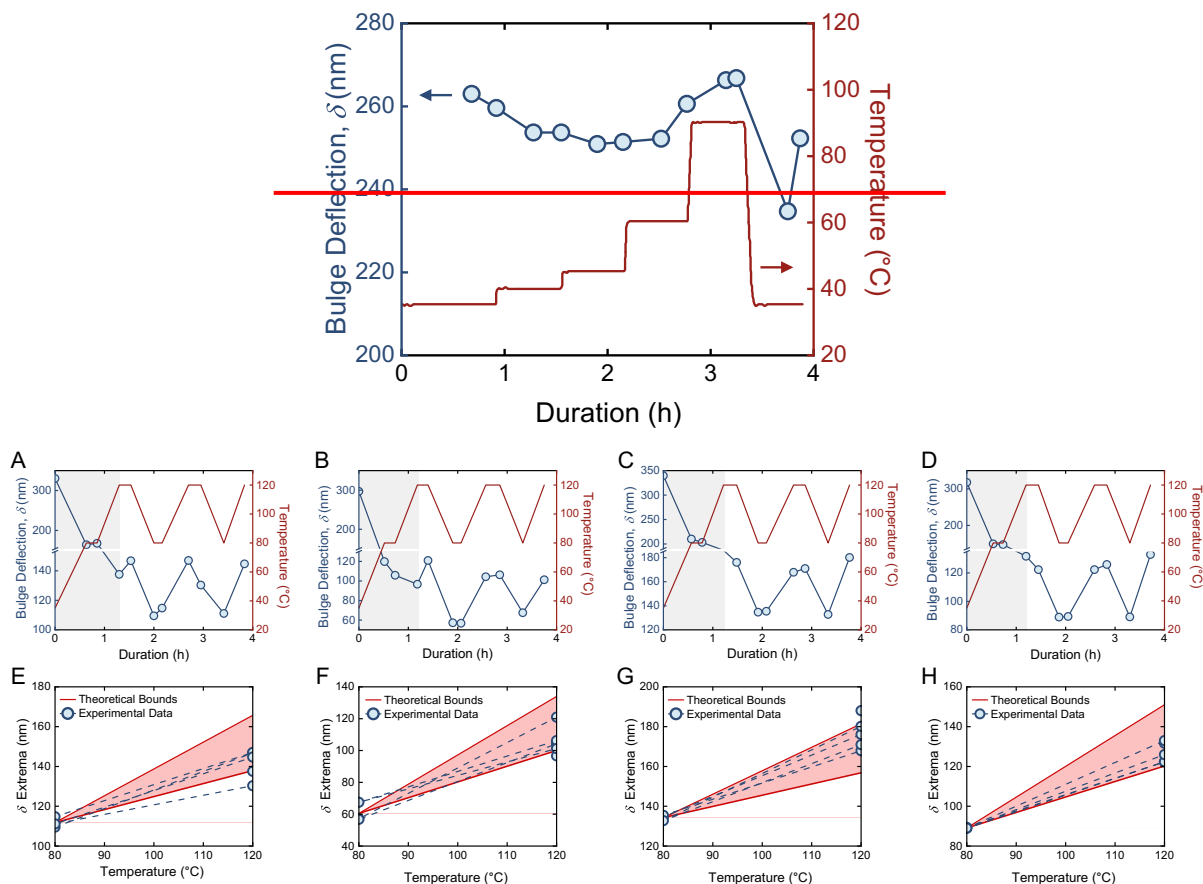
Reviewer #1:



Supplementary Fig. 12. Fig. S22.

Thermogravimetric analysis (TGA) of 2DPA-1 platelets, showing an onset temperature of 298.2 °C and weight loss of 5 % at 100 °C. TGA-MS results of 2DPA-1 with $r = 10.5$. (A) Weight loss (TG) and derivative weight loss (DTG) curves under nitrogen atmosphere. (B) Mass spectrum of the evolved gas captured during thermal degradation of 2DPA-1. *Denotes secondary ion for water.

Reviewer #1:



Supplementary Fig. 13. Fig. S23.

(A-D) *In-situ* bulge deflections (left y-axis) measured at elevated temperatures (right y-axis) over time while heating to 90 $^{\circ}\text{C}$ to evaporate surface-bound water or residual TFA. The initial temperature ramp is highlighted by the light grey shaded region. The step rate was 0.05 $^{\circ}\text{C s}^{-1}$. After ramp-up, temperatures were oscillated between 80 $^{\circ}\text{C}$ and 120 $^{\circ}\text{C}$. (E-H) Experimentally measured deflections compared to temperature-dependent theoretical upper and lower bounds that assume a fully impermeable bulge with trapped gas following the ideal gas law.

- [1] H. Hencky, *Z. Math. Phys.* 63, 311-317 (1915)
- [2] Y. Zeng *et al.*, *Nature*, 602, 91-95 (2022)
- [3] Z. Wei *et al.*, *J. Am. Chem. Soc.* 147, 5921-5932 (2025)
- [4] B. Malfait *et al.*, *J. Phys. Chem. C*, 126, 3520-3531 (2022)
- [5] P. Schweng *et al.*, *ChemSusChem*, 17, e202301906 (2024)
- [6] T. Honorio *et al.*, *Cem. Concr. Res.* 169, 107179 (2023)
- [7] J.R. Brown and A.J. Power, *Polymer Degradation and Stability*, 4 (1982)
- [8] G.M. Cai and W.D. Yu, *J. Therm. Anal. Calorim.* 104, 757-763 (2011)

Reviewer: During film preparation, PS was used as a supporting layer, then dissolved to transfer the film. It is challenging to completely remove PS using simple solvent washing, especially for PS beneath 2DPA-1 films. Please confirm whether PS was effectively removed. Residual PS chains could infiltrate 2DPA-1 pores, potentially blocking them and rendering the films impermeable.

Reviewer #1:

Our Response: We agree with the reviewer that complete removal of polystyrene via solvent washing is challenging. Our analysis below suggests that some residual polystyrene may exist, albeit in very low quantities that would not affect molecular transport across the film. If the pores were all molecularly accessible, as an alternative hypothesis, even a single remaining 1-nm pore would result in near immediate collapse of the bulges (**Supplementary Fig. 11**). Hence, all pores would have to be perfectly clogged via complete coverage of polystyrene. More-over, the polystyrene abundance would need to be such that each chain lodged into every available pore within the unit cells. Based on these findings, this scenario is very unlikely.

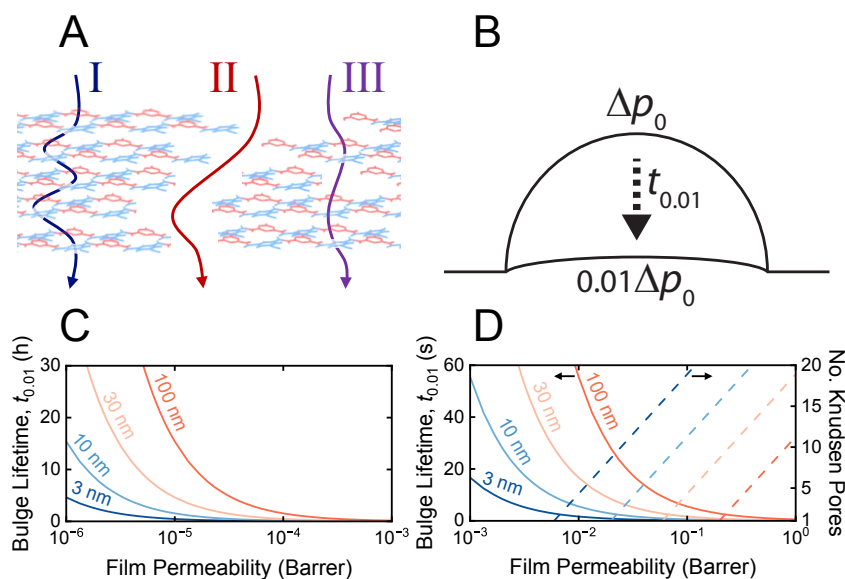
We note that the only method to guarantee complete removal of polystyrene is through thermal annealing at extreme temperatures, which would thermally decompose—if not entirely destroy—the 2DPA-1 film. We would also like to add a point of clarity that the solvent etching of polystyrene occurs with polystyrene in direct contact to chloroform rather than beneath the 2DPA-1 film. This is achieved by our method of wet transfer, wherein the 2DPA-1 surface is directly contacted to the SiO₂ substrate. This configuration ensures film stability via physical interactions between the 2DPA-1 and SiO₂, as etching in the inverse configuration (i.e., polystyrene in direct contact with SiO₂ and beneath 2DPA-1) leads to dispersion of 2DPA-1 platelets and a highly defective film.

We investigated the successful removal of polystyrene through ATR-FTIR and Raman analysis. **Fig. R14** shows the normalized IR spectra for a polystyrene film compared with bulk 2DPA-1 (no polystyrene exposure) and the 2DPA-1 nanofilm. Here, the bulk 2DPA-1 has no signal from polystyrene. There is no clear evidence for polystyrene above 1000 cm⁻¹. IR spectra for both 2DPA-1 samples mirror one another around 3000 cm⁻¹, representative of dispersed N-H stretching. The signature aromatic C-H and CH₂ stretching of polystyrene around 3000 cm⁻¹ [1] is not evident in the 2DPA-1 samples; however, this could be obscured by the peak broadening associated with hydrogen bonding in this region. Further, the strong aromatic ring modes of polystyrene between 1500–1600 cm⁻¹ overlap with those of 2DPA-1. An IR signature at 700 cm⁻¹ is observed in the 2DPA-1 film and not the bulk sample. This band is well-aligned with the aromatic ring bending of polystyrene [1] and may be representative of residual polystyrene; however, this band also overlaps strongly with that of TFA dimer absorptions between 686–712 cm⁻¹ [2]. Raman signatures confirmed the presence of residual TFA in the spin-coated nanofilms (**Supplementary Fig. 2** and **Fig. R4**), making it difficult to decipher the origin of the 700 cm⁻¹ IR band without additional characterization such as NMR. Unfortunately, NMR is not a feasible approach to characterize the 2DPA-1 thin film due to the lack of sufficient material for signal generation and lack of shared solvents between polystyrene and 2DPA-1. **Fig. R15** depicts four notable Raman bands found in polystyrene at 383 cm⁻¹, 620 cm⁻¹, 1001 cm⁻¹, and 1032 cm⁻¹. The strong bands observed in polystyrene at 1001 cm⁻¹ and 1032 cm⁻¹ are associated with symmetric in-plane aromatic stretching [3, 4], but they are not fully recovered in the 2DPA-1 thin film. Rather, the 2DPA-1 thin film depicts a higher order peak at 1022 cm⁻¹ that aligns well with the bulk 2DPA-1 sample. The asymmetric aromatic stretching band at 620 cm⁻¹ in polystyrene also does not appear in the 2DPA-1 thin film Raman spectra. Only the 383 cm⁻¹ Raman band for polystyrene (out-of-plane aromatic mode) may feasibly be present in the 2DPA-1 thin film; however, we note that it is a relatively weak and broad signal that overlaps closely with the 390 cm⁻¹ band.

To conclude, ATR-FTIR and Raman suggest residual polystyrene may persist, but its signal is quite weak relative to the 2DPA-1. We suspect any polystyrene remaining to be in the form of

Reviewer #1:

dispersed micro/nano-particles, occasionally observed via AFM imaging, rather than a uniform film. We therefore do not expect polystyrene to impact molecular transport measurements as we tend to select for clean bulges that have minimal debris (**Fig. 1H** of Main Text). The presence of a uniform film of polystyrene would also not be expected to influence molecular impermeability, as the permeability of N_2 across polystyrene is >0.5 Barrer [5]—nearly eight orders of magnitude higher than our measurements. While the reviewer is correct that polystyrene could theoretically penetrate the sub-nm pores of stacked 2DPA-1 films, the restriction of the segmental motion for the 1D chains within these strongly confined pores is expected to be entropically unfavorable [6].



Supplementary Fig. 11.

(A) Possible gas transport pathways through the 2DPA-1 layers. Mechanism I: activated translocation through 2DPA-1 pores; Mechanism II: effusion around 2DPA-1 platelets; Mechanism III: resistor-in-series model with activated translocation and effusion due to presence of non-ideal voids in lamellae. (B) Illustration of bulge deflation, quantified by its 99 % lifetime ($t_{0.01}$). This metric represents the amount of time required for the bulge to lose 99 % of its initial overpressure (Δp_0). (C-D) Bulge 99 % lifetime with respect to film permeability for various thicknesses. The baseline permeability of films possessing a discrete number of 1-nm Knudsen pores is shown in panel D with respect to film thickness.

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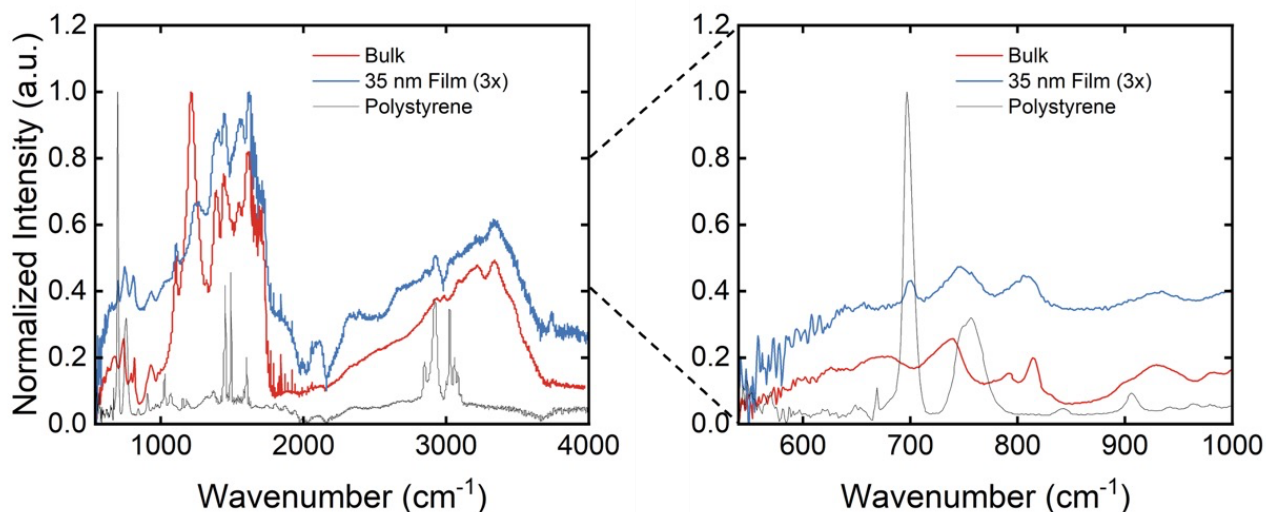


Fig. R14. ATR-FTIR spectra of bulk 2DPA-1 (red), 2DPA-1 nanofilm (blue), and polystyrene film (black). Complete spectra are shown on left. The right figure focuses on the spectra below 1000 cm^{-1} .

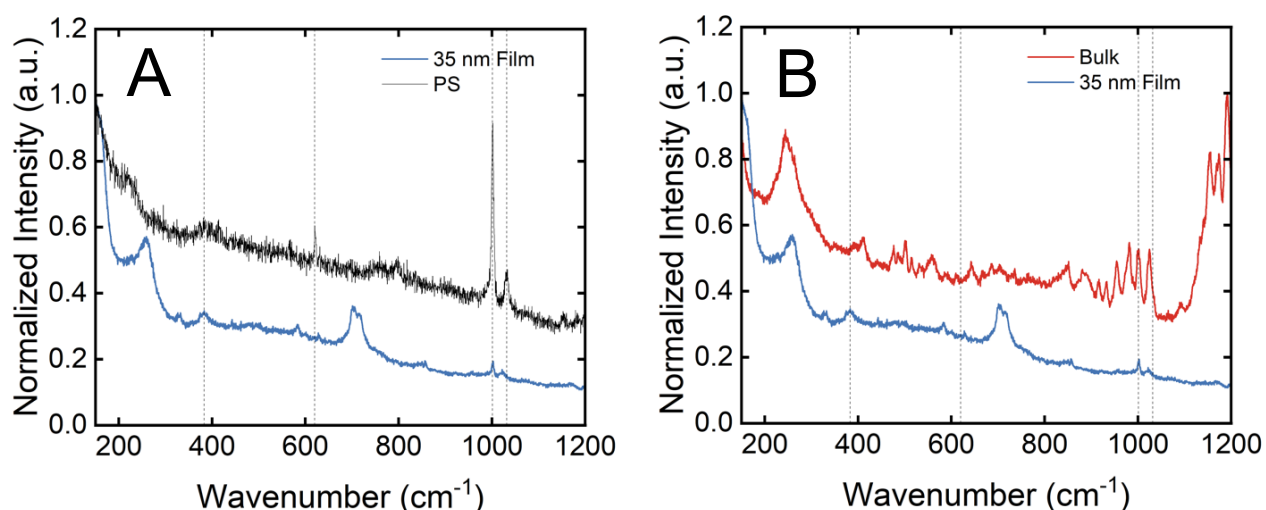


Fig. R15. Raman spectra comparing 35-nm 2DPA-1 film (blue) with (A) polystyrene film (black) and (B) bulk 2DPA-1 (red). The vertical dashed lines depict notable Raman peaks from polystyrene.

- [1] B. Smith, *Spectroscopy*, 36, 22-25 (2021)
- [2] R.L. Redington and K.C. Lin, *Spectrochimica Acta*, 27A, 2445-2460 (1971)
- [3] B. Jasse *et al.*, *J. Polym. Sci: Polym. Phys.* 16, 2157-2169 (1978)
- [4] J.R. Anema *et al.*, *J. Raman Spectrosc.* 41, 745-751 (2010)
- [5] A.W. Thornton *et al.*, *Polymer Gas Separation Membrane Database* (2012)
- [6] M.R. Smyda and S.C. Harvey, *J. Phys. Chem. B*, 116, 10928-10934 (2012)

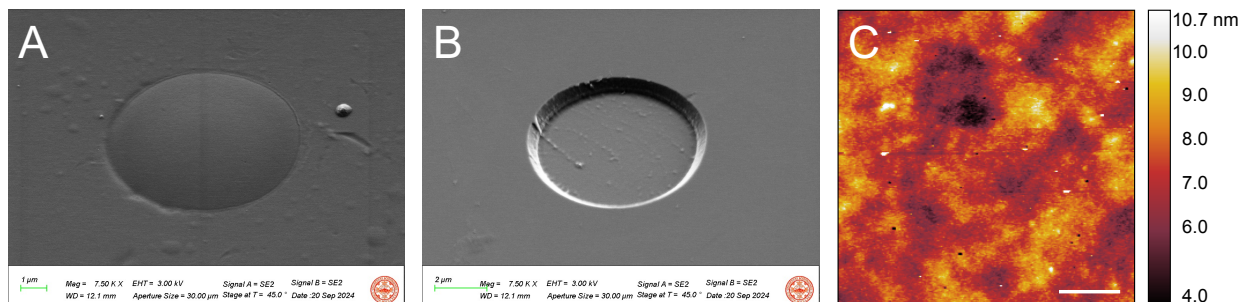
Reviewer: Scanning electron microscopy images of the 2DPA-1 films should be provided to show their morphologies.

Reviewer #1:

Our Response: We have included an SEM image of the microwell coated with 35-nm 2DPA-1 films in the suspended and collapsed state, along with AFM topography of the surface so that future readership can gain a more comprehensive understanding the of the film morphology.

Main Text amendment

“We measured the gas permeation properties of 2DPA-1 films (root mean square roughness < 1 nm) by suspending them over 1- μm deep microwells (Supplementary Fig. 5), etched into a silicon/silicon oxide (Si/SiO₂) wafer with a 285-nm oxide layer.”



Supplementary Fig. 5.

Scanning emission microscopy (SEM) images of a 35-nm 2DPA-1 film (A) suspended and (B) collapsed over a 10- μm -diameter well etched 1 μm into a SiO₂/Si substrate. (C) AFM image of 2DPA-1 nanofilm surface topography. Scale bar represents 2 μm . Root mean square, RMS, roughness was determined over a 5 μm $\times$ 5 μm area.

Reviewer: In Fig. 2B, the correlation between N₂ permeability and material crystallinity is shown. How was the degree of crystallinity of these materials quantified?

Our Response: We thank the reviewer for the question, as this was a point of confusion for Reviewers #2 as well. In our original draft, a degree of crystallinity (X_c) was never formally calculated for 2DPA-1 as a melting or crystallization temperature was not observed from differential scanning calorimetry (DSC, Fig. R16) within a safe operating window beneath the polymer’s onset degradation temperature ($\sim 300^\circ\text{C}$ see Supplementary Fig. 12A). Hence, the crystallinity of 2DPA-1 was depicted as a flat line from 0 to 100% in Fig. 2B of the Main Text to signify an unknown crystallinity while still comparing the permeability to relevant polymers.

We now leverage the powder X-ray diffraction (PXRD) to estimate the upper-bound of the crystallinity as $X_c = 20.7\% \pm 6.2\%$. Specifically, we estimated the X_c by taking a ratio of the pseudo-crystalline to amorphous signals from PXRD [1]. Here, we define the peak centered around $2\theta \approx 25^\circ$ as our pseudo-crystalline region due to its strong presence in all 2DPA-1 stacking configurations. Supplementary Fig. 3B-E depicts PXRD datasets that are well described by three- or four-peak Lorentzian fits. Averaging over four 2DPA-1 samples, we obtain $X_c = 20.7\% \pm 6.2\%$ that we assign as an upper-bound for 2DPA-1 crystallinity given the method’s likely overestimation of the crystalline peak area. This finding is in line with our initial discussion in the Main Text (and earlier in this response to reviewer) that 2DPA-1 lacks long-range order that would be detected as a high degree of crystallinity via PXRD. We have amended Fig. 2 and the Main Text to reflect this new data.

Main Text amendment

Reviewer #1:

“Crystallinity estimates of $20.7\% \pm 6.2\%$ from pPowder X-ray diffraction (PXRD) suggests 2DPA-1 lacks long-range order ([SI Supplementary Fig. 3](#))...”

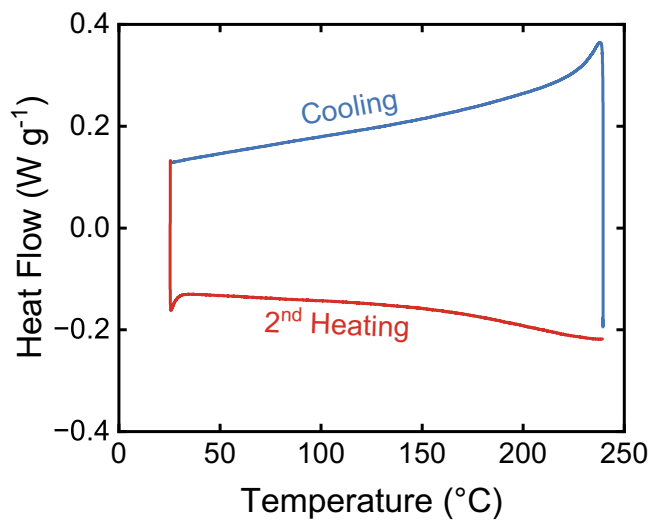
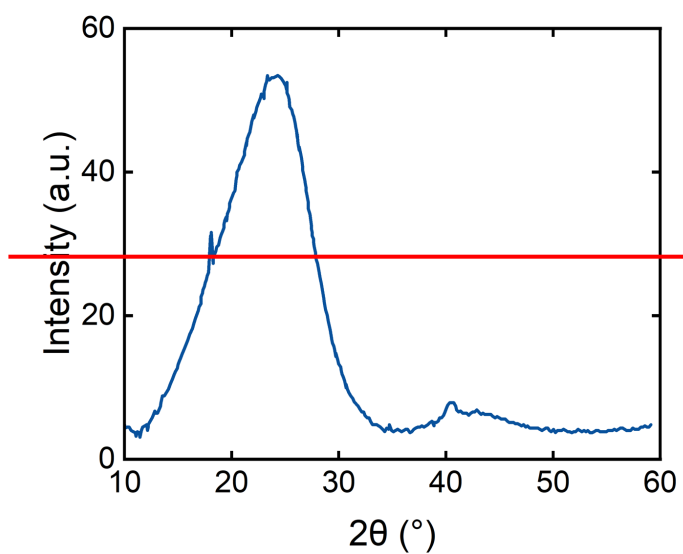
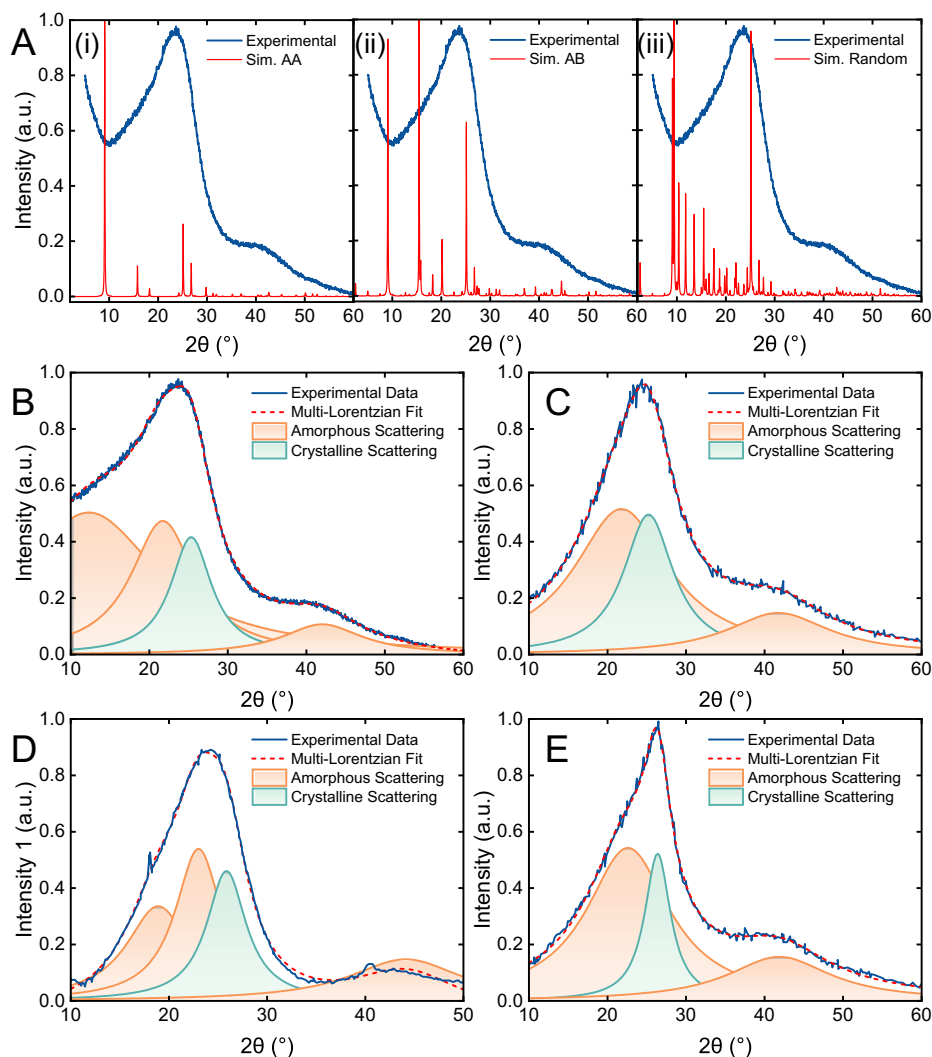


Fig. R16. Differential scanning calorimetry (DSC) of 2DPA-1 powder.



Reviewer #1:



Supplementary Fig. 3. Fig. S1.

Powder X-ray diffraction (PXRD) of 2DPA-1. ~~powder with $r = 9.67$~~ . Experimental data compared against diffraction peaks simulated for 2DPA-1 stacked in (A) eclipsed, i.e., AA, (B) offset, i.e., AB, and (C) random layer-to-layer configurations. (B-E) Measured PXRD of 2DPA-1 fit by Lorentzian curves. The red dashed curve represents the cumulative fit of all Lorentzian curves to the overall data. Using the peak position centered between 25° to 26° (2θ) as the pseudo-crystalline signal, the degree of crystallinity is estimated as (B) 13.6 %, (C) 27.7 %, (D) 23.6 %, and (E) 18.0 %.

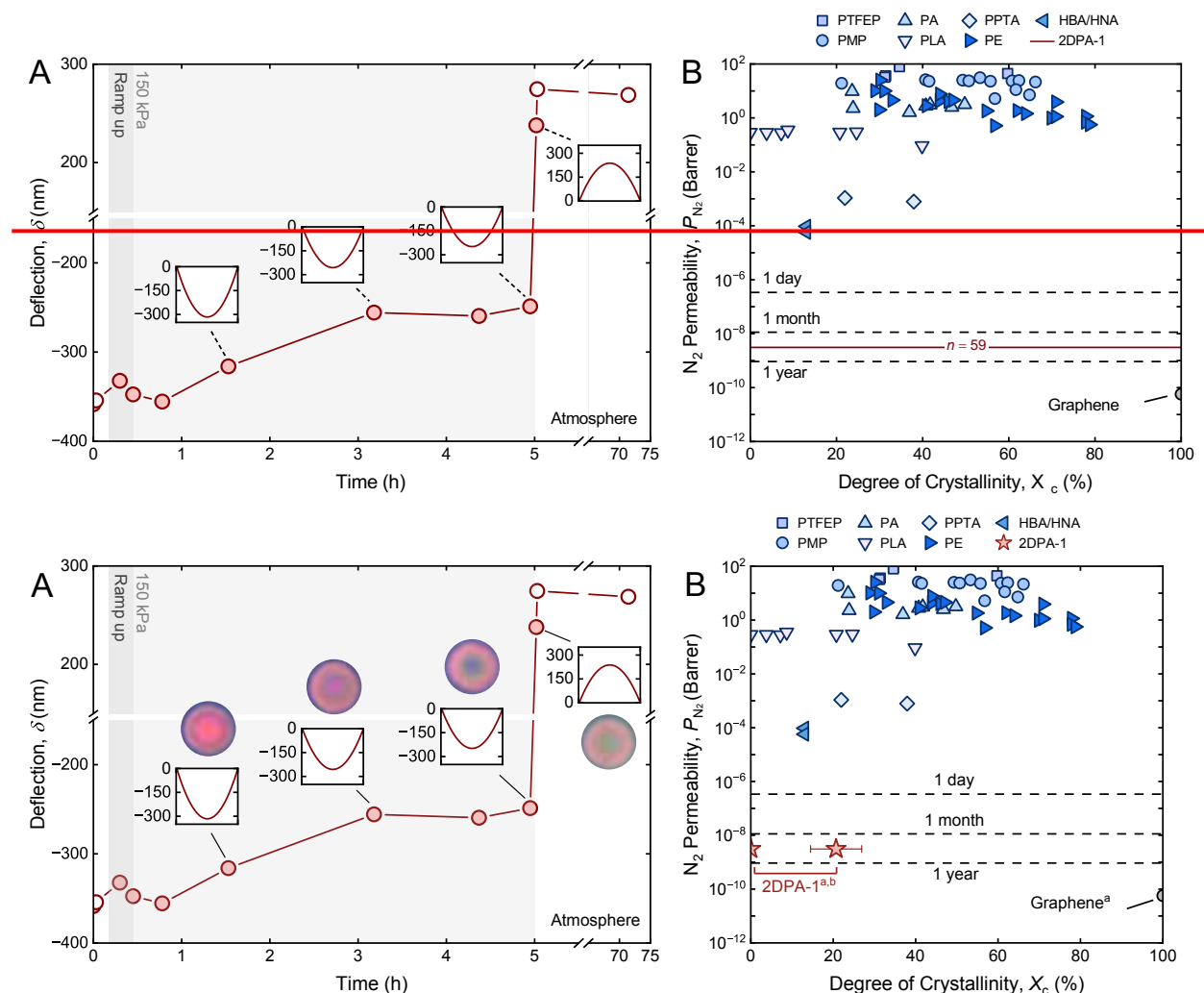


Fig. 2 | Observation of Dynamic Filling and N_2 Impermeability of 2DPA-1. (A) Deflection of 2DPA-1 dimples before, during, and after N_2 -pressurization in an environmental stage. White- and red-filled datapoints represent deflections determined directly via AFM measurement and indirectly via optical interference analysis, respectively. The dark grey shaded region indicates the pressure ramp-up period from 0 kPa to 150 kPa (gauge pressure), whereas the light grey shaded region indicates a 150 kPa gauge pressure of N_2 . Non-shaded (i.e., white) regions represent atmospheric pressure. The insets show cross-sectional profiles of bulge deflections at respective time steps taken from the optical analyses of the imaged bulges (pictured above insets). (B) N_2 permeability with respect to degree of crystallinity (X_c). The dashed black lines mark the maximum permeability allowed for a 35-nm bulge to remain inflated over various durations for the microwells used in this study. The red stars solid red line represents the threshold permeability for 2DPA-1 based on the observed persistence of 59 2DPA-1-covered microwells over 110 d after filling with 150 kPa N_2 . The N_2 permeability of liquid crystalline and glassy polymers, such as poly[bis(trifluoroethoxy phosphazene)] (PTFEP), polyacrylate (PA), poly(p-phenylene terephthalamide) (PPTA), poly(p-hydroxybenzoic acid-co-6-hydroxy-2-naphthioic acid) (HBA/HNA), poly(4-methyl-1-pentene) (PMP), poly(lactic acid) (PLA), and polyethylene (PE) are included from ref. 1 for comparison, along with the H_2 permeability of graphene. ^aPermeability values are at the method detection limit and may be considered effectively zero. ^bPXRD of four bulk samples was used to estimate the upper bound of X_c for 2DPA-1.

Reviewer #1:

[1] I. Uzun, *J. Polym. Res.*, 30, 394 (2023)

Reviewer: *The gas permeance tests were conducted in single-component systems. Would it be possible to extend these tests to binary-component systems, such as a mixture of N₂ and H₂? This approach could offer deeper insights into the separation mechanism, clarifying whether it is driven by chemical affinity or size-based exclusion.*

Our Response:

REDACTED

REDACTED

REDACTED

REDACTED

REDACTED

Reviewer #1:

REDACTED

REDACTED

REDACTED

REDACTED

Reviewer #1:

REDACTED

REDACTED

REDACTED

Reviewer #2:

Reviewer: *In this manuscript, Strano&Bunch, and co-workers demonstrate the impermeability of the polyaramide ultrathin films and demonstrate potential application in the protection of perovskites. The study is very interesting and goes beyond common approaches that demonstrate the impermeability of 2D films attaining the N₂ permeability below 3.1×10^{-9} Barrer. The authors carried out a significant amount of experiments to prove the impermeability phenomenon as well as DFT calculations to further understand the underlying mechanism. The presented study is definitely interesting and constitutes new methodologies, in particular use of light microscopy for analysis of a larger sample size, which wasn't possible using AFM and other methods. Moreover, the obtained results provide novel method combinations for future studies that involve studies of similar 2D materials and their applications. Most of the similar studies that were performed on graphene on other 2D materials use data solely obtained using AFM on nano to micron range area, which further limits the applicability of the findings. In that regard, this study is really interesting and also demonstrates the potential use of obtained results and developed methodologies, making this study particularly interesting for Nature readers. However, there are certain points that need to be addressed before proceeding further.*

Our Response: We thank the reviewer for carefully reviewing our work and for their recognition of the thought and effort that went in to conducting this study. The reviewer's insightful comments to help improve the impact of this work are also greatly appreciated. Before addressing the specific comments of the reviewer, we would like to indicate that we have made the following key revisions to our manuscript. The key revisions include:

- Demonstrated chemical stability and processability of 2DPA-1 in TFA and non-TFA solvents
 - ¹H NMR in TFA and milder solvents (**Figs. R1-2, R19, and Supplementary Fig. 1**) showing no evidence of chemical degradation
 - [REDACTED]
- Refined structural characterization to connect bulk 2DPA-1 to molecularly ordered films
 - Experimental FTIR and Raman spectra assigned and compared to DFT simulated molecular models confirming chemical structure (**Figs. R4, R14-15, Supplementary Fig. 2, and Supplementary Table 1**)
 - [REDACTED] REDACTED
 - Polarized PL of molecularly ordered thin films confirming nanoplatelet in-plane alignment and ordering explaining impermeability (**Fig. R6 and Supplementary Fig. 4**)
- Showed lack of accessible microporous structure with various gas probes
 - Adsorption isotherms of CH₄, CO₂, He, and H₂ on 2DPA-1 measured by the U.S. National Institute for Standards and Technology confirming no microporosity (**Supplementary Fig. 10**)
 - [REDACTED] REDACTED
- Verified inhibition of molecular transport via staggered unit cells rather than solvent clogging

Reviewer #2:

- TGA-MS of gas evolution from 2DPA-1 confirming the absence of microporous-trapped solvents or water (**Supplementary Fig. 12**)
- *In situ* AFM of bulges at elevated temperatures showing persistent impermeability at high temperatures (**Supplementary Fig. 13**)
- DFT simulations of energetically favored offset stacking explaining the structural aspects of impermeability (off-set platelet stacking) (**Supplementary Fig. 14**)
- Enhanced clarity on the film morphology and experimental apparatuses used in this study
 - SEM and AFM compared with explanatory schematics, confirming film morphology leading to impermeability (**Supplementary Figs. 5 and 7**)

Changes made to the manuscript (excerpts highlighted in light grey) that are marked in blue and ~~red-strikethrough~~ text represent additions and subtractions, respectively. The same format is followed for figures, with the exception of review-only figures (labeled as **Fig. R#**). Relevant references are included at the end of each response as numbered brackets [#].

Reviewer #2:

Reviewer: *Figure 1B shows the TEM image of the 2DPA-1 films, I am curious about the dark spots, what do they constitute? Are these impurities?*

Our Response: We believe there may be a misunderstanding of Fig. 1B due to clarity issues of the caption and text in the Methods. Fig. 1B of the Main Text does depict a 2DPA-1 film but instead shows 2DPA-1 nanoplatelets—which we presume are the dark spots the reviewer is referring to. These nanoplatelets were dispersed onto a single-graphene-layer transmission electron microscopy (TEM) grid by drop-casting a dilute solution of 2DPA-1 in dimethyl sulfoxide (DMSO). The specimen was placed in a vacuum oven overnight, resulting in adsorbed nanoplatelets for imaging (Fig. 1B). Imaging of the 2DPA-1 nanofilm is shown in Fig. 1D of the Main Text, which highlights the lamellar ordering observed at the edge of the film. This film sample was prepared by spin-coating a solution of 10 mg mL⁻¹ 2DPA-1 in trifluoroacetic acid (TFA) directly onto a holey carbon TEM grid (CD-Flat, EMS). We have adjusted text in the Methods and Figure captions to clarify the sample and its contents.

The reviewer's interest in TEM characterization of the film is well-received. We developed computational tools for quantitative analysis of these nanoplatelet TEM images [1]. We analyzed over 3000 platelets from TEM imaging to generate distributions of platelet size, circularity, and thickness (**Figs. R8-9** – found in response to Reviewer #1). TEM analysis allowed us to estimate thickness of the platelets by assuming that electron beam attenuation increases approximately linearly with the number of layers in a platelet while minimizing the influence of interlayer effects, as per Beer's Law. Using segmentation assignments by an unsupervised algorithm for a large, recrystallized platelet (additional details in review-only material, **Fig. R9A**), raw TEM data were extracted for each layer group and sorted by mean intensity (**Fig. R9B-G**). Intensities were normalized to the graphene background to enable comparison across images. The linear increase in electron attenuation with additional layers is illustrated in **Fig. R9D and R9G**, where consistent fitted slopes across different platelets (**Fig. R9D**, slope = 0.061; **Fig. R9G**, slope = 0.056) indicate correct identification of single layers of 2DPA-1 within each image. While absolute thickness was not determined, the image processing approach confirmed the presence of distinct quantized layers that suggest particle stacking below 8 layers (< 3 nm).

Main Text amendment

“Fig. 1 | 2DPA-1 Nanoplatelets as Free-Standing Thin Films for Bulge Formation. (A) Theoretical structure of 2DPA-1 **monolayer platelet**. **(B)** TEM image of ~~TFA~~-dispersed 2DPA-1 nanoplatelets **adsorbed on the surface of a graphene-supported TEM grid**. Image taken at 110,000× magnification. Scale bar represents 50 nm. **(C)** Theoretical structure of a 2DPA-1 lamella with sparse voids formed due to imperfect packing between neighboring platelets. **(D-E)** Ordering of 2DPA-1 lamella **observed at the edge of a spin-coated nanofilm evidenced** by STEM **(D)** and corresponding intensity profile **(E)**. The scale bar represents 5 nm and the yellow dashed lines indicate the scan region. STEM taken at 4,000,000× magnification...”

[1] X. Gong *et al.*, *ChemRxiv* (2025) DOI: 10.26434/chemrxiv-2025-0gjm

Reviewer: *Authors claim the absence of long-range order crystallinity of 2DPA-1 films unlike COFs based on the XRD pattern provided in Figure S1. However, the long-range order crystallinity peak in COFs usually appears below 2theta of 10 degrees in the XRD pattern. Given this authors should provide the XRD scan range below 10 degrees and usually the range of 2-60 if possible for comparison with COFs and to claim the absence of crystalline peaks.*

Reviewer #2:

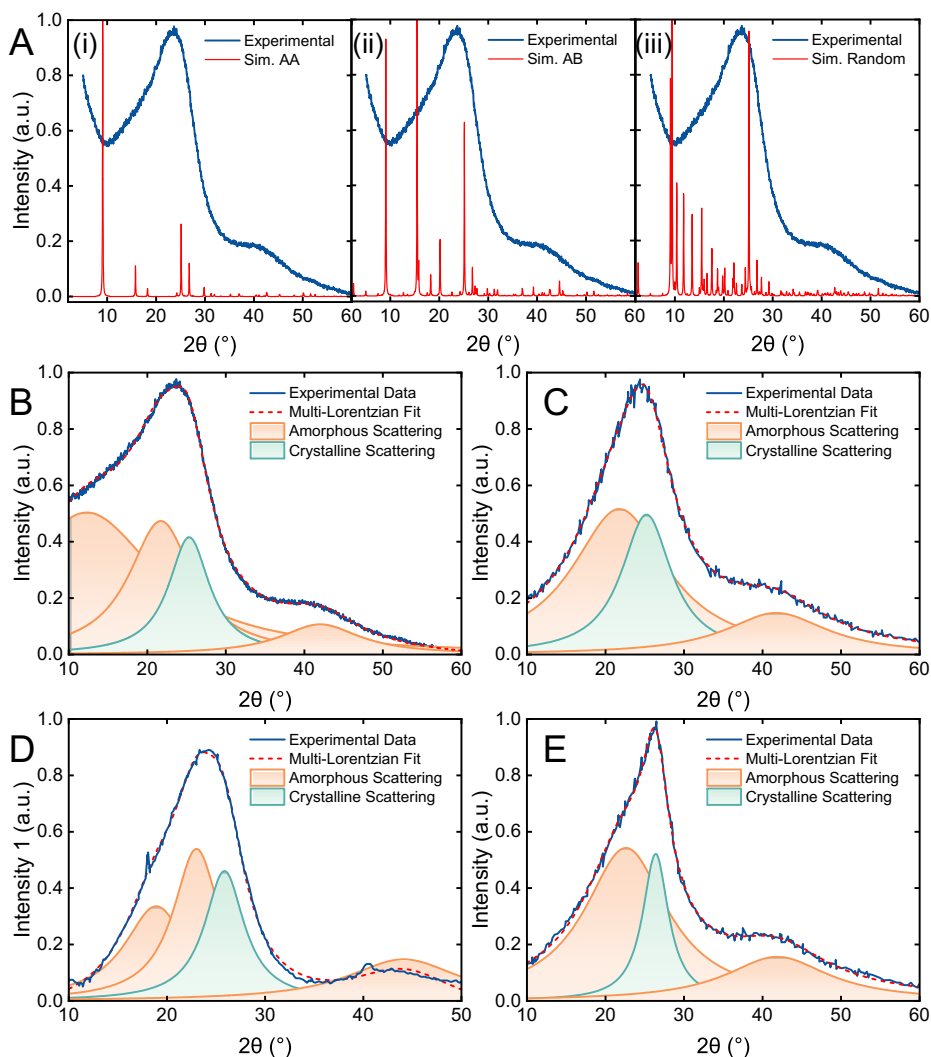
Our Response: We thank the reviewer for their suggestion and have extended our investigation of X-ray scattering to include PXRD from 5-60° (**Supplementary Fig. 3A**), REDACTED, REDACTED, and simulated predictions from the theoretical structure of multi-layer 2DPA-1 platelets. The reviewer is correct that a strong crystalline peak was predicted by simulations just below 10°; however, significant broadening of the X-ray scattering remains. We thus posit a lamellar structure with in-plane ordering but no precisely defined stacking order, as depicted in Fig. 1C of the Main Text, and supported by the discussion below.

Crystalline peaks captured by PXRD depend strongly on structural characteristics, such as crystallite domain size and the layer-to-layer offset, or “stacking disorder,” of the 2D macromolecular sheets [1]. When compared against model 2DPA-1 structures that were simulated from a CIF structure file using Powder Pattern Function in CCDC Mercury software, we find that the broad PXRD is more reflective of the dispersive scattering that would occur from random offsets between layers (**Supplementary Fig. 3A(iii)**), rather than eclipsed (AA stacked) or occluded (AB stacked) configurations that are common to COFs. We note that PXRD was only collected down to 5° because incident X-ray angles below that threshold would hit the zero-background holder rather than the sample itself.

REDACTED

REDACTED

Reviewer #2:



Supplementary Fig. 3. Fig. S1.

Powder X-ray diffraction (PXRD) of 2DPA-1. ~~powder with $r = 9.67$~~ . Experimental data compared against diffraction peaks simulated for 2DPA-1 stacked in (A) eclipsed, i.e., AA, (B) offset, i.e., AB, and (C) random layer-to-layer configurations. (B-E) Measured PXRD of 2DPA-1 fit by Lorentzian curves. The red dashed curve represents the cumulative fit of all Lorentzian curves to the overall data. Using the peak position centered between 25° to 26° (2 θ) as the pseudo-crystalline signal, the degree of crystallinity is estimated as (B) 13.6 %, (C) 27.7 %, (D) 23.6 %, and (E) 18.0 %.

- [1] S. Van Gele *et al.*, *JACS Au*, 5, 388-398 (2025)
- [2] X. Wang *et al.*, *Nat. Chem.* 10, 1180-1189 (2018)

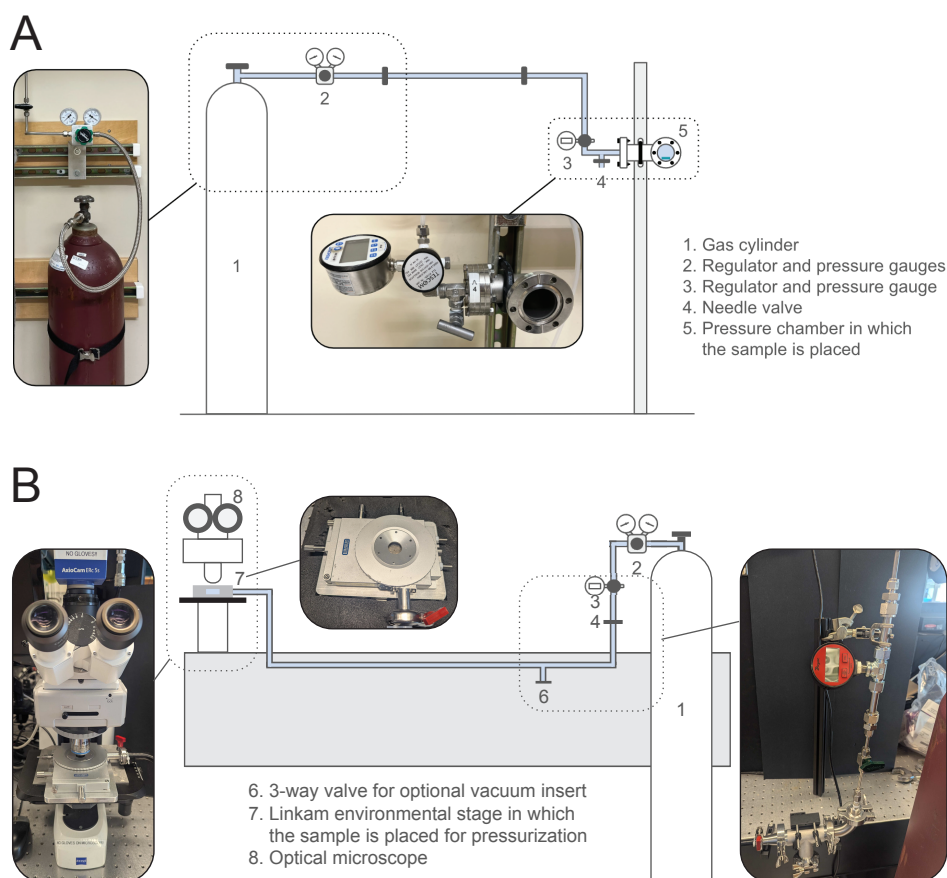
Reviewer: Similar studies have been demonstrated before, in particular by Scott Bunch and colleagues, however, the experimental setup was never shown. It would be very useful for replications if authors show the experimental setup schematics for pressurization setup as well as gas permeation.

Reviewer #2:

Our Response: We agree with the reviewer that graphical representation of the experimental setup would help reproducibility efforts. We have thus prepared a schematic representation, including photographs, of both experimental pressurization setups used to create and optically study the bulge platforms (**Supplementary Fig. 7**). We note that for gas permeation tests conducted in previous studies by Bunch *et al.*, the change in deflection of the bulges was measured on a separate atomic force microscope (AFM) after pressurizing the apparatus shown in **Supplementary Fig. 7A**. This study employed the same approach as well as introducing a new methodology to optically track real-time bulge pressurization *in situ* using the platform displayed in **Supplementary Fig. 7B**.

Main Text amendment

“By utilizing the optical interference described above—and beginning with negatively deflected dimples—we can observe dynamic gas filling using a pressurized microscopy stage (Fig. 2A, ~~and~~ movie S1, and **Supplementary Fig. 7**).”



Supplementary Fig. 7.

Schematic illustration of experimental platforms used to pressurize bulges. (A) Fully stainless steel, high-pressure chamber apparatus without optical window. This apparatus is ideal for pressurizing bulges up to extremely high pressure or with hazardous gases. (B) Pressurization apparatus using environmental Linkam stage (THMS350EV, Linkam Scientific) with optical window. This apparatus, although not viable for pressures above 200 kPa or hazardous gases such as H₂, is ideal for optically

Reviewer #2:

monitoring bulge pressurization dynamics and can be retrofitted with a vacuum insert. Inset images depict photographs of pressurization apparatus in highlighted regions (dashed line).

Reviewer: *Figure 2B shows the benchmark of the 2DPA-1 permeability. However, it's not very clear what is the permeability of the 2DPA-1 films and how the comparison is made. How the crystallinity of the films is measured?*

Our Response: We thank the reviewer for the question, as this was a point of confusion for another reviewer as well. In our original draft, a degree of crystallinity (X_c) was never formally calculated for 2DPA-1 as a melting or crystallization temperature was not observed from differential scanning calorimetry (DSC, **Fig. R16**) within a safe operating window beneath the polymer's onset degradation temperature ($\sim 300^\circ\text{C}$ see **Supplementary Fig. 12A**). Hence, the crystallinity of 2DPA-1 was depicted as a flat line from 0 to 100% in **Fig. 2B** of the Main Text to signify an unknown crystallinity while still comparing the permeability to relevant polymers. Below we estimate an upper bound for the crystallinity of 2DPA-1 as $X_c = 20.7\% \pm 6.2\%$ but demonstrate that, despite lacking crystallinity, it is still an ordered material. We provide evidence for this via anisotropic polarized photoluminescence (PL) of the thin film.

We now leverage the powder X-ray diffraction (PXRD) to estimate the upper-bound of the crystallinity as $X_c = 20.7\% \pm 6.2\%$. Specifically, we estimated the X_c by taking a ratio of the pseudo-crystalline to amorphous signals from PXRD [1]. Here, we define the peak centered around $2\theta \approx 25^\circ$ as our pseudo-crystalline region due to its strong presence in all 2DPA-1 stacking configurations. **Supplementary Fig. 3B-E** depicts PXRD datasets that are well described by three- or four-peak Lorentzian fits. Averaging over four 2DPA-1 samples, we obtain $X_c = 20.7\% \pm 6.2\%$ that we assign as an upper-bound for 2DPA-1 crystallinity given the method's likely overestimation of the crystalline peak area. This finding is in line with our initial discussion in the Main Text (and earlier in this response to reviewer) that 2DPA-1 lacks long-range order that would be detected as a high degree of crystallinity via PXRD.

It is important to note that the absence of crystallinity does not mean that the system is a disordered, amorphous material. Numerous non-crystalline and para-crystalline materials possess orientational ordering that is not captured by conventional X-ray techniques, including ordered polyaramid and cellulose fibers [2, 3]. Beyond XRD or direct imaging by electron microscopy, non-crystalline ordering can be detected using polarization-sensitive approaches [4]. We demonstrate orientational ordering of a 35-nm 2DPA-1 film using polarized photoluminescence, PL (**Supplementary Fig. 4**). We find that when excited at 532 nm with a polarized laser, the PL emission of the 35-nm 2DPA-1 film depends on its orientation with respect to the beam path. Specifically, the thin film emission transitions from roughly 1400 cm^{-1} (575 nm) when excited orthogonal to the beam path to 2270 cm^{-1} (605 nm) when excited parallel to the beam path. This twofold symmetry is consistent with anisotropic platelets oriented parallel to the substrate with a transition dipole along the long axis of the platelet [5]. We note that the emission window reported is beyond that of SiO_2 to eliminate signal interference (**Fig. R6**). Interestingly, for each spectrum we find a sharp Raman signature between approximately 2410 cm^{-1} and 2435 cm^{-1} that is uncommon for most materials. This signature was not generated by the simulation of a 2DPA-1 monolayer. Notably, the location of this Raman band is in good agreement with second-order features from overtones of fundamental modes observed in highly ordered pyrolytic graphite (HOPG) that do not appear in monolayer graphene [6-8]. We postulate that this Raman band may

Reviewer #2:

be an additional signature of molecular ordering from stacked doublet formation, but this requires further exploration beyond the scope of this study.

We have amended **Fig. 2**, the Main Text, and the SI to reflect some of the new findings discussed here.

Main Text amendment

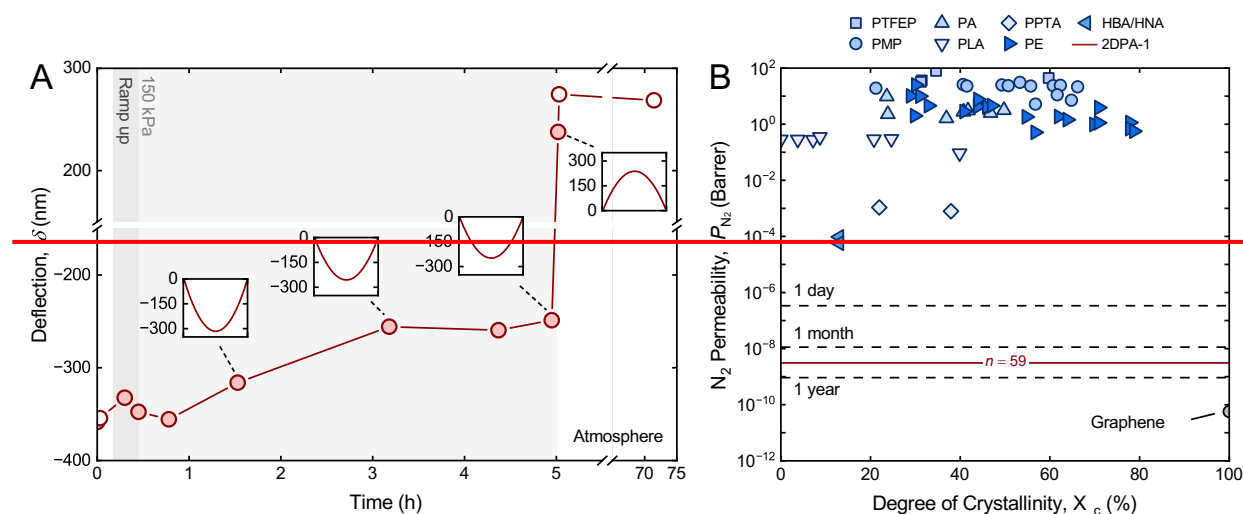
“Crystallinity estimates of $20.7 \% \pm 6.2 \%$ from pPowder X-ray diffraction (PXRD) suggests 2DPA-1 lacks long-range order ([SI Supplementary Fig. 3](#)); however, a combination of polarized photoluminescence ([Supplementary Fig. 4](#)) and scanning transmission electron microscopy (STEM) of spin-coated 2DPA-1 thin films reveals anisotropy in the form of layered, orientational ordering ([Fig. 1C-E](#)).”

SI amendment

“[Raman, ATR-FTIR, and Photoluminescence \(PL\) Spectroscopy of 2DPA-1](#)

...

Numerous non-crystalline and para-crystalline materials possess orientational ordering that is not captured by conventional X-ray techniques, including ordered polyaramid and cellulose fibers [7, 8]. Beyond XRD or direct imaging by electron microscopy, non-crystalline ordering can be detected using polarization-sensitive approaches [9]. We demonstrate orientational ordering of a 35-nm 2DPA-1 film using polarized PL ([Supplementary Fig. 4](#)). We find that when excited at 532 nm with a polarized laser, the PL emission of the 35-nm 2DPA-1 film depends on its orientation with respect to the beam path. Specifically, the thin film emission transitions from roughly 1400 cm^{-1} (575 nm) when excited orthogonal to the beam path to 2270 cm^{-1} (605 nm) when excited parallel to the beam path. This twofold symmetry is consistent with anisotropic platelets oriented parallel to the substrate with a transition dipole along the long axis of the platelet [2]. We note that the emission window reported is beyond that of SiO_2 to eliminate signal interference. Interestingly, for each spectrum we find a sharp Raman signature between approximately 2410 cm^{-1} and 2435 cm^{-1} that is uncommon for most materials. This signature was not generated by the simulation of a 2DPA-1 monolayer. Notably, the location of this Raman band is in good agreement with second-order features from overtones of fundamental modes observed in highly ordered pyrolytic graphite (HOPG) that do not appear in monolayer graphene [10-12]. The origin of this Raman band requires further exploration.”



Reviewer #2:

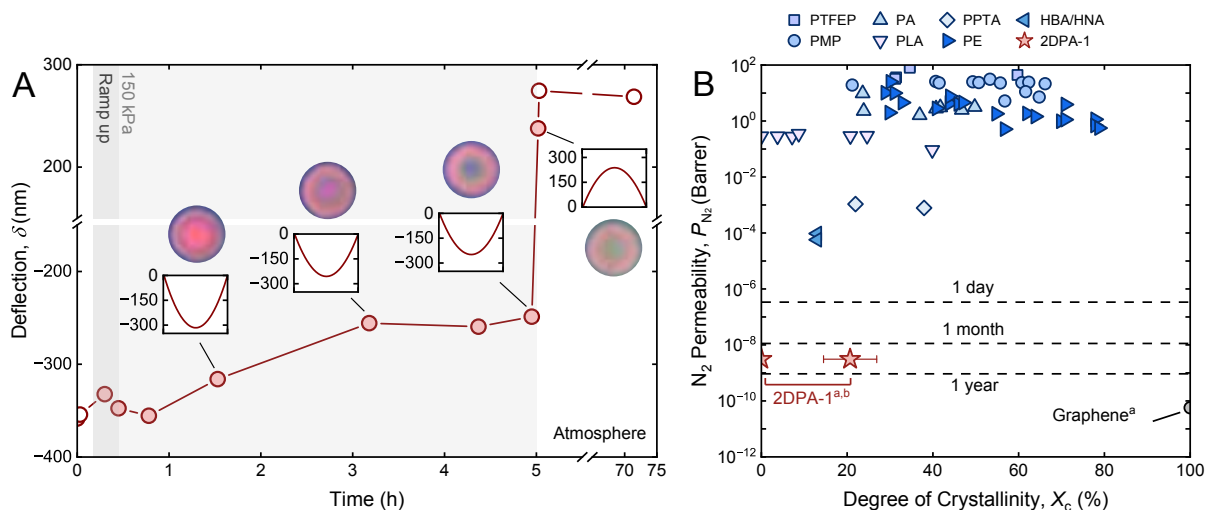
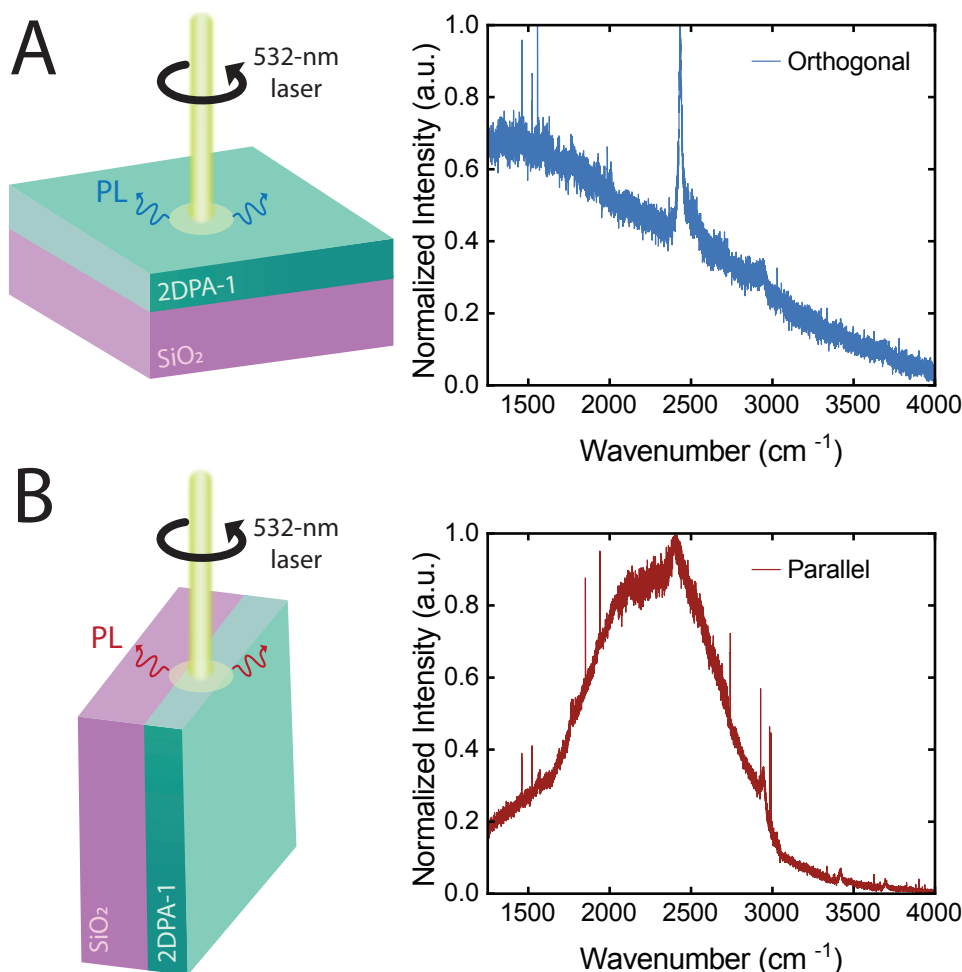


Fig. 2 | Observation of Dynamic Filling and N_2 Impermeability of 2DPA-1. (A) Deflection of 2DPA-1 dimples before, during, and after N_2 -pressurization in an environmental stage. White- and red-filled datapoints represent deflections determined directly via AFM measurement and indirectly via optical interference analysis, respectively. The dark grey shaded region indicates the pressure ramp-up period from 0 kPa to 150 kPa (gauge pressure), whereas the light grey shaded region indicates a 150 kPa gauge pressure of N_2 . Non-shaded (i.e., white) regions represent atmospheric pressure. The insets show cross-sectional profiles of bulge deflections at respective time steps taken from the optical analyses of the imaged bulges (pictured above insets). (B) N_2 permeability with respect to degree of crystallinity (X_c). The dashed black lines mark the maximum permeability allowed for a 35-nm bulge to remain inflated over various durations for the microwells used in this study. The red stars solid red line represents the threshold permeability for 2DPA-1 based on the observed persistence of 59 2DPA-1-covered microwells over 110 d after filling with 150 kPa N_2 . The N_2 permeability of liquid crystalline and glassy polymers, such as poly[bis(trifluoroethoxy phosphazene)] (PTFEP), polyacrylate (PA), poly(p-phenylene terephthalamide) (PPTA), poly(p-hydroxybenzoic acid-co-6-hydroxy-2-naphthioic acid) (HBA/HNA), poly(4-methyl-1-pentene) (PMP), poly(lactic acid) (PLA), and polyethylene (PE) are included from ref. 1 for comparison, along with the H_2 permeability of graphene. ^aPermeability values are at the method detection limit and may be considered effectively zero. ^bPXRD of four bulk samples was used to estimate the upper bound of X_c for 2DPA-1.

Reviewer #2:



Supplementary Fig. 4.

Photoluminescence, PL, measurements of 35-nm 2DPA-1 film on a SiO₂ substrate placed (A) orthogonal and (B) parallel to the beam path of a polarized 532-nm excitation laser source. Illustrations of measurement configuration are on the left, with the resulting data plotted on the right. The emission window reported is just beyond that of SiO₂ to eliminate signal interference.

- [1] I. Uzun, *J. Polym. Res.*, 30, 394 (2023)
- [2] S. Marina *et al.*, *Mater. Horiz.* 9, 1196 (2022)
- [3] J.L. Bregado *et al.*, *Fluid Phase Equilibria*, 491, 56-76 (2019)
- [4] B.A. Collins *et al.*, *Nat. Mater.* 11, 536-543 (2012)
- [5] Y. Zeng *et al.*, *Nature*, 602, 91-95 (2022)
- [6] Y. Wang *et al.*, *Chem. Mater.* 2, 557-563 (1990)
- [7] R.J. Nemanich and S.A. Solin, *Phys. Rev. B*, 20, 392-401 (1979)
- [8] R. Al-Jishi and G. Dresselhaus, *Phys. Rev. B*, 26, 4514-4522 (1982)

Reviewer: The absence of solvents and water in the polyaramide pores could indeed affect impermeability, specifically for some of the gases. Therefore, the authors used the TGA (Figure S22) to support this claim. Although TGA offers a plausible way for the presence of solvents and other volatiles in the polymeric network, it is not a proper way to assess if the solvents are trapped within the pores. The proper way would be to degass samples under a vacuum at temperatures below 150 C

Reviewer #2:

and measure the weight of the sample afterward. Indeed this is a standard protocol for measuring the porosity of microporous materials as solvent trapped in the pores can affect the measurement results.

Our Response: We thank the reviewer for their insight and suggestion. It has prompted us to conduct an extensive study on the water interaction properties of our material. Below we demonstrate that, despite being a hydrophilic material, the molecular impermeability of 2DPA-1 cannot be attributed to blockage by solvents (water or TFA) sorbed into the pores. This conclusion is supported by a combination of *in situ* AFM measurements up to 120 °C paired with TGA and mass spectrometry (TGA-MS) that show water completely evolved at 120 °C, yet bulges remain inflated.

First, we measured water vapor adsorption isotherms on the bulk material using an automated dynamic vapor sorption analyzer (VTI-SA+, TA Instruments) at ambient pressure and with nitrogen as the carrier gas. Our results confirm that 2DPA-1 is indeed hydrophilic, adsorbing water at low RH (**Supplementary Fig. 10D**). This is to be expected given the high degree of hydrogen bonding of the material. We note that data shown in **Supplementary Fig. 10A-C** will be discussed and highlighted in a later response.

We agree with the reviewer's point that physi-sorbed water, which our analysis confirms is likely to be present, will be eliminated at 120 °C. If water-blocked pores are the root explanation for the molecular impermeability of 2DPA-1, we would expect complete collapse of the bulges at this elevated temperature. To more thoroughly investigate the potential impact of sorbed water on the gas impermeability of 2DPA-1, we used a temperature-controlled environmental AFM stage (Asylum Research, Cypher ES Environmental AFM) to capture real-time measurements of four additional bulge deflections with respect to temperature (**Supplementary Fig. 13**). We increased the temperature step wise to 120 °C and then oscillated between 120 °C and 80 °C. The step rate was 0.05 °C s⁻¹.

We find that all four bulge deflections decreased partially upon the initial heating ramp up to 120 °C but then appear to remain sealed thereafter, falsifying the hypothesis that the nanofilm is microporous but blocked by water or residual TFA. We attribute the decrease in height to a temporary and reversible opening of the rim seal, likely owing to influence of heating on the adhesion between the polymer film and SiO₂ substrate and their differing thermal expansion coefficients. We observe such rim opening upon abrupt pressure changes, as we show in Fig 2 of the manuscript, enabling controlled gas filling. When subsequently oscillating the temperature between 80°C and 120°C for 2.5 cycles, the bulge deflections similarly oscillated on the order of 10 nm consistent with the ideal gas law, as we calculate below. This confirms that the nanofilms, despite being only 35 nm thick, remain impermeable throughout the experiment.

Assuming no gas transport is occurring, we can predict the average change in the bulge deflection from 80 °C to a theoretical height at 120°C through the series of equations shown below, originating with the ideal gas law:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} ,$$

where 1 and 2 refer to states 1 and 2 of the bulge, and P , V , and T are the internal pressure, volume under the bulge, and temperature, respectively. By accounting for the geometry of the microwell system and using Hencky's solution to relate bulge deflection to a pressure difference [1], we can substitute in the following expressions

Reviewer #2:

$$V_n = \pi r^2 L + \frac{\pi r^2 \delta_n}{2}$$

and

$$P_n - P_{\text{ext}} = A\delta_n^3 + B\delta_n ,$$

where

$$A = \frac{16EdK(v)}{a^4} \text{ and } B = \frac{4S_0}{a^2} .$$

Here, r is the radius of the well, P_{ext} is the pressure external to the bulge (atmosphere). A is a constant equal to the ratio of E , the elastic modulus, d , the film thickness, $K(v)$, a constant dependent on Poisson's ratio, and a , the bulge diameter. B is a constant related to the self-tensioning, S_0 , of the bulge. Combining these expressions for P and V with the ideal gas law yields:

$$\frac{(A\delta_1^3 + B\delta_1 + P_{\text{atm}}) \left(2\pi r L + \frac{\pi r^2 \delta_1}{2} \right)}{T_1} = \frac{(A\delta_2^3 + B\delta_2 + P_{\text{atm}}) \left(2\pi r L + \frac{\pi r^2 \delta_2}{2} \right)}{T_2}$$

Thus, for a given T_1 , T_2 , and δ_1 , one can calculate δ_2 .

We set $T_1 = 80$, $T_2 = 120$, and δ_1 as the average experimental value at 80 °C within the oscillation regime. We note that a range of reported E for 2DPA-1 will influence the predictions [2]. We therefore include a feasible range of δ_2 that captures the potential variance in the modulus of the nanofilm. We find that 17 of the 20 (85%) experimentally determined deflections at 120 °C fall within the predicted range. Hence, our results do not indicate any discernable gas loss while oscillating between 80 and 120 °C and supports the notion that physi-sorbed water cannot be the mechanistic explanation for the film's measured impermeability.

The reviewer's suggestion also prompted us to expand upon our original thermogravimetric analysis (TGA) to inform the evolution of all gases from our material that may indicate trace solvents or water locked within the polymer nanoporous network. Specifically, we were interested to see if residual chemicals from synthesis, such as acetone, N-methyl pyrrolidone (NMP), pyridine, or water may be present. We carried out simultaneous TGA and mass spectrometry (TGA-MS) to analyze gas evolution at elevated temperatures during thermal degradation of 2DPA-1 ($r = 10.5$) in an inert N_2 atmosphere (**Supplementary Fig. 12**). The ramp rate was 10 °C min^{-1} up to 1000 °C. The off-gas was simultaneously analyzed a connected mass spectrometer. All details of this study are included as review only material. We have provided a brief discussion of the analysis below.

TGA-MS of 2DPA-1 shows no trace of acetone (58 atomic mass unit, amu), NMP (99 amu), or pyridine (79 amu) in low or high temperatures. This corroborates NMR results that show these chemicals are effectively removed during polymer purification [3]. As suspected from our original TGA, water vapor (18 amu) evolved from the 2DPA-1 sample between 65–90 °C, likely corresponding to surface-bound (i.e., physi-sorbed) water molecules as discussed earlier. This is reflected in the first peak of the DTG curve (**Supplementary Fig. 12A**). Water absorbed within highly confined pores requires substantially more energy to remove, often leading to desorption temperatures in excess of 100 °C [4-6]. Notably, we also detect water evolution from the 2DPA-1 sample between 300-450 °C. The release of water vapor observed at these elevated temperatures is beyond that expected from stronger confinement interactions and can instead be explained by the cleavage of the amide bonds during the thermal degradation of 2DPA-1. This is a well-studied

Reviewer #2:

mechanism in thermal degradation of similar polyaramids such as Kevlar and Nomex in which water is a common byproduct of thermal degradation [7, 8].

In summary, we showed that, although 2DPA-1 is hydrophilic in nature and readily adsorbs water, it does not explain the molecular impermeability reported here. This analysis also rules out the potential role of residual TFA (boiling point 72.4 °C). We have included these results and discussion in the Methods, Main Text, and SI where applicable (see below).

Main Text amendment

“The impermeability of 2DPA-1 implies an absence of free volume required for molecular transport. The pore within the 2DPA-1 unit cell is estimated to be approximately 1 nm in diameter; hence, it is unlikely that a monolayer platelet would impose substantial resistance to most gas molecules. We ruled out the possibility that water or another relevant solvents could be occluding the pores via simultaneous thermogravimetric analysis with mass spectrometry (TGA-MS) and the observation of several bulges that remain inflated upon heating to 120 °C ~~a stable bulge even upon heating to 90 °C~~ (SI Supplementary Figs. 12-13).”

SI amendment

“Gas Adsorption and Thermal Degradation Analyses

...

Simultaneous thermogravimetric analysis with mass spectrometry (TGA-MS) of 2DPA-1 shows no trace of acetone (58 atomic mass unit, amu), NMP (99 amu), or pyridine (79 amu) in low or high temperatures. This corroborates NMR results that show these chemicals are effectively removed during polymer purification [3]. Water vapor (18 amu) evolved from the 2DPA-1 sample between 65–90 °C likely corresponds to surface-bound (i.e., physisorbed) water molecules. This is reflected in the first peak of the derivative thermogravimetric curve (Supplementary Fig. 12A). Water absorbed within highly confined pores requires substantially more energy to remove, often leading to desorption temperatures in excess of 100 °C [4-6]. Notably, we also detect water evolution from the 2DPA-1 sample between 300–450 °C. The release of water vapor observed at these elevated temperatures is beyond that expected from stronger confinement interactions and can instead be explained by the cleavage of the amide bonds during the thermal degradation of 2DPA-1. This is a well-studied mechanism in thermal degradation of similar polyaramids such as Kevlar and Nomex in which water is a common byproduct of thermal degradation [7, 8].

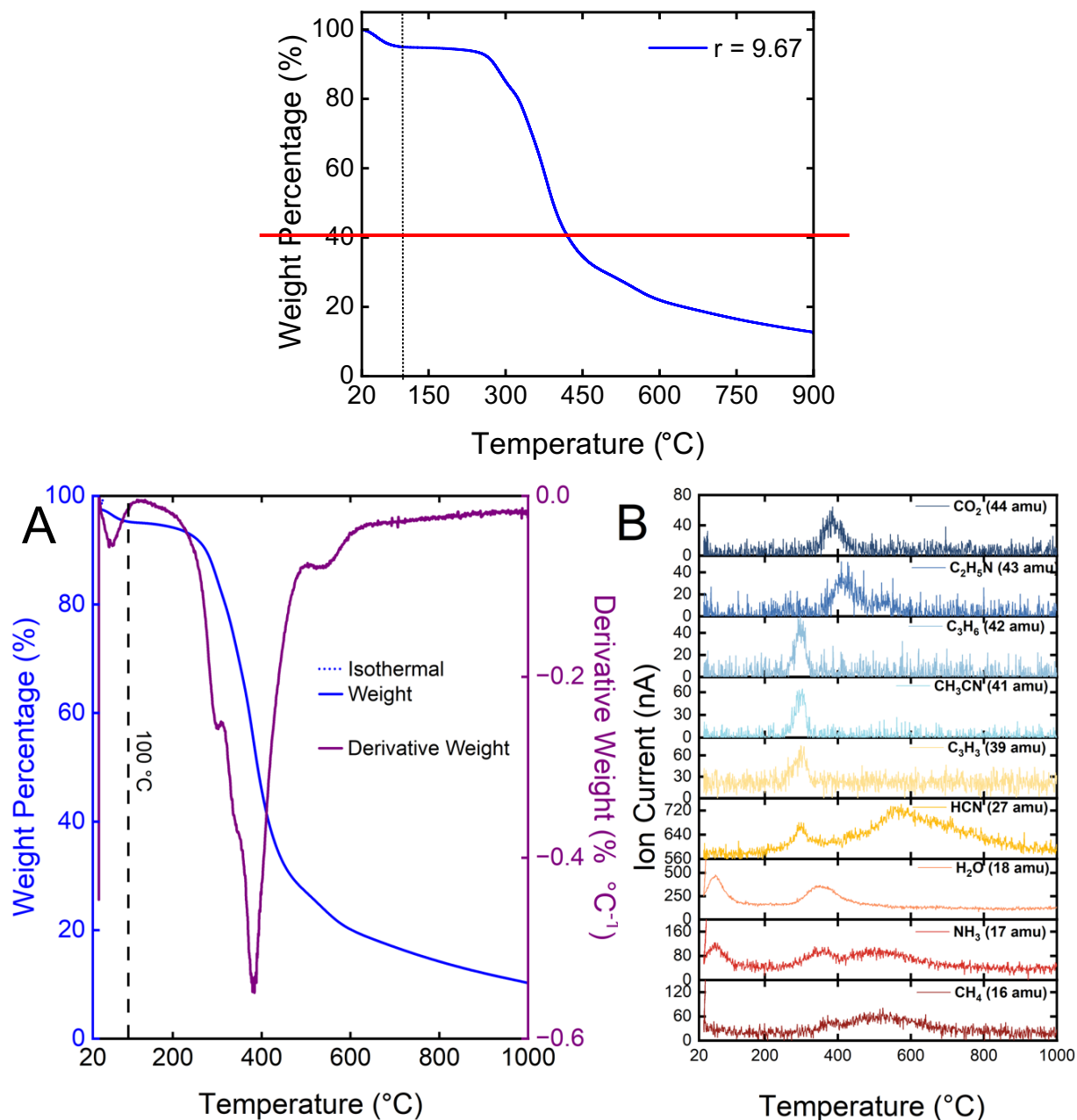
As a hydrophilic material, water sorbed within the unit cell pores of 2DPA-1 thin films may influence molecular transport of other gases. We investigated the potential impact of sorbed water on the gas impermeability of 2DPA-1 via a temperature-controlled environmental AFM stage (Asylum Research, Cypher ES Environmental AFM) to capture real-time measurements of four bulge deflections with respect to temperature (Supplementary Fig. 13A-D). All four bulge deflections decreased upon the initial heating ramp up to 120 °C but did not result in complete deflation. We can thus conclude that pores blocked by water or residual TFA are not the root cause for the observed molecular impermeability of 2DPA-1, as the counter case would result in complete deflation upon vaporization up to 120 °C. We attribute the decrease in deflection to a temporary and reversible opening of the rim seal, likely owing to the influence of heating on thermal expansion of the 2DPA-1 thin film and adhesion between 2DPA-1 and the SiO₂ substrate. When subsequently oscillating the temperature between 80°C and 120°C for 2.5 cycles, the bulge deflections similarly oscillated on the order of 10 nm.

Assuming no gas transport is occurring, we can predict the average change in the bulge deflection from 80 °C to a theoretical height at 120°C through the series of equations shown below originating with the ideal gas law: $P_1 V_1 / T_1 = P_2 V_2 / T_2$. Here, the subscripts refer to states 1 and 2 of the bulge, and P , V , and T are the internal pressure, volume under the bulge, and temperature, respectively. By accounting for the geometry of the microwell system and using Hencky's solution to relate bulge deflection, δ , to a pressure difference [1] (eq. M3 of Methods), we can solve for δ_2 given T_1 , T_2 , and δ_1 .

We set $T_1 = 80$, $T_2 = 120$, and δ_1 as the average experimental value at 80 °C within the oscillation regime (Supplementary Fig. 13E-H), with theoretical upper and lower bounds defined by the range of elastic moduli reported for 2DPA-1 [2]. We find that 17 of the 20 (85%) experimentally determined deflections at 120 °C fall within the predicted range. Hence, our results do not indicate any discernable gas loss while oscillating between 80 and 120 °C

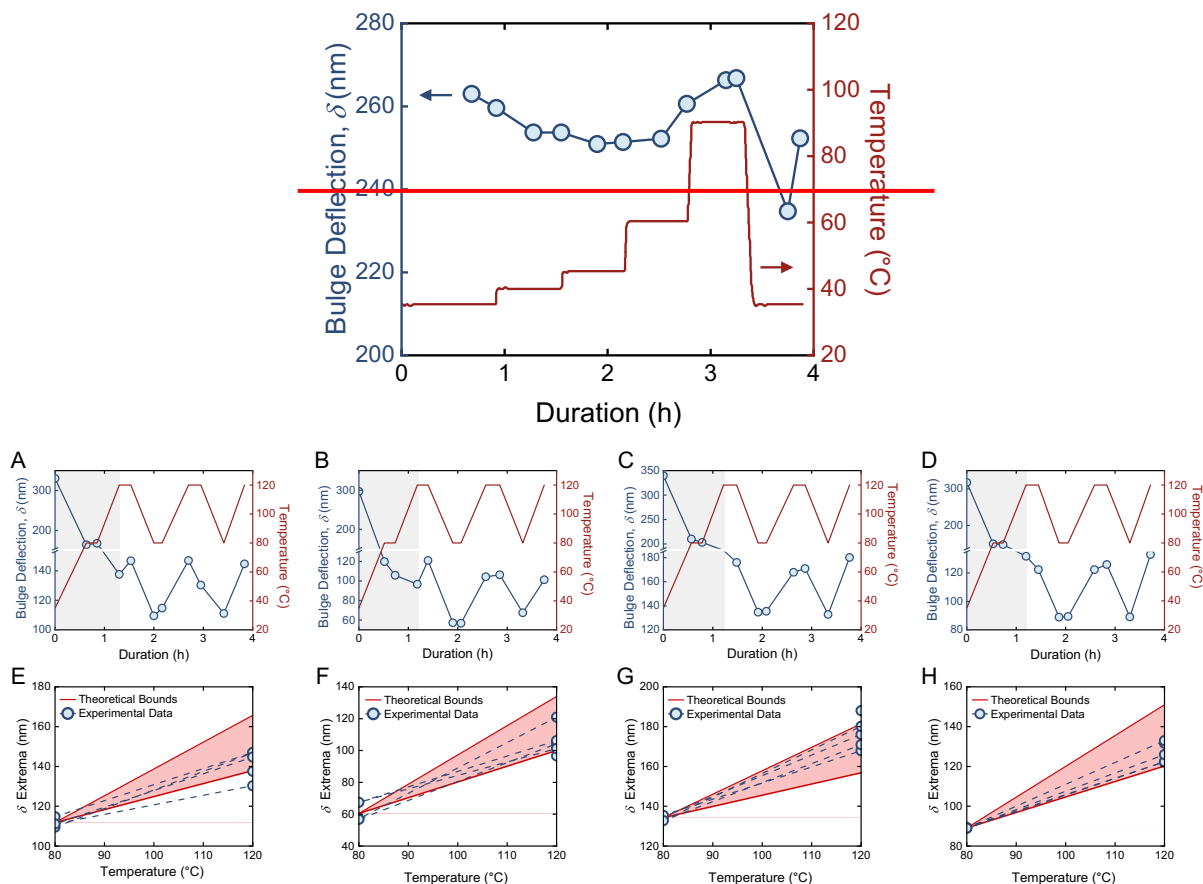
Reviewer #2:

and supports the notion that physi-sorbed water is not the mechanistic explanation for the film's measured impermeability."



Supplementary Fig. 12. Fig. S22. Thermogravimetric analysis (TGA) of 2DPA-1 platelets, showing an onset temperature of 298.2 °C and weight loss of 5 % at 100 °C. TGA-MS results of 2DPA-1 with $r = 10.5$. (A) Weight loss (TG) and derivative weight loss (DTG) curves under nitrogen atmosphere. (B) Mass spectrum of the evolved gas captured during thermal degradation of 2DPA-1.

Reviewer #2:



Supplementary Fig. 13. Fig. S23.

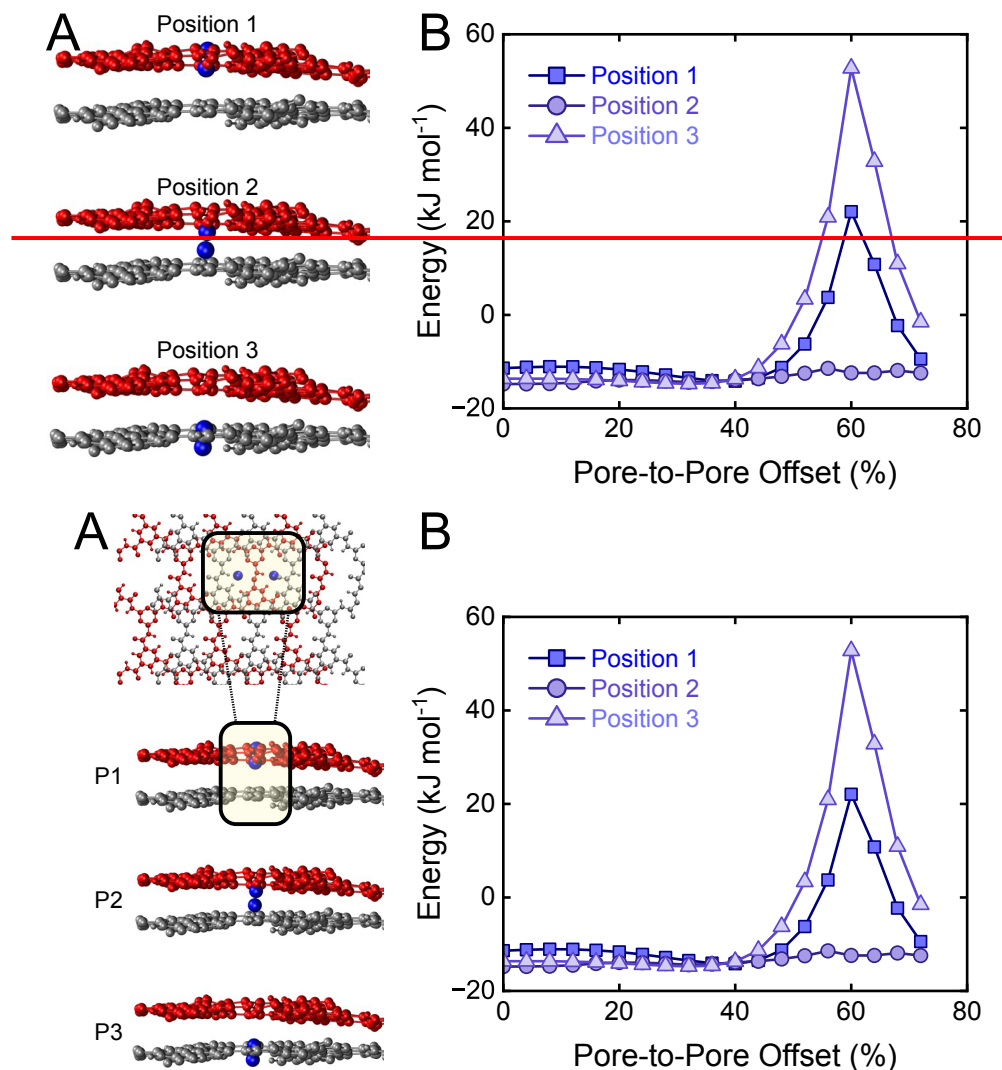
(A-D) *In-situ* bulge deflections (left y-axis) measured at elevated temperatures (right y-axis) over time while heating to 90 °C to evaporate surface-bound water or residual TFA. The initial temperature ramp is highlighted by the light grey shaded region. The step rate was 0.05 °C s⁻¹. After ramp-up, temperatures were oscillated between 80 °C and 120 °C. (E-H) Experimentally measured deflections compared to temperature-dependent theoretical upper and lower bounds that assume a fully impermeable bulge with trapped gas following the ideal gas law.

- [1] H. Hencky, *Z. Math. Phys.* 63, 311-317 (1915)
- [2] Y. Zeng *et al.*, *Nature*, 602, 91-95 (2022)
- [3] Z. Wei *et al.*, *J. Am. Chem. Soc.* 147, 5921–5932 (2025)
- [4] B. Malfait *et al.*, *J. Phys. Chem. C*, 126, 3520-3531 (2022)
- [5] P. Schweng *et al.*, *ChemSusChem*, 17, e202301906 (2024)
- [6] T. Honorio *et al.*, *Cem. Concr. Res.* 169, 107179 (2023)
- [7] J.R. Brown and A.J. Power, *Polymer Degradation and Stability*, 4 (1982)
- [8] G.M. Cai and W.D. Yu, *J. Therm. Anal. Calorim.* 104, 757-763 (2011)

Reviewer: Extended Figure 8 shows the position of the N₂ molecule concerning the pore-to-pore offset from the side view, it would also be very useful if the structures presented in Figure 8A were shown from the top view.

Reviewer #2:

Our Response: We have adjusted Extended Data Fig. 8 to improve the clarity for future readership (see below).



Extended Data Fig. 8.

N_2 -2DPA-1 interaction energies calculated by DFT. (A) Top-down schematic of offset 2DPA-1 bilayer [top image] along with cross-sectional images of the three fixed positions [P1-3, bottom images] within bilayer used to perform calculations. Yellow-shaded area highlights the corresponding location of gases in bilayer framework from top and cross-sectional views. (B) Energy profile with respect to the pore-to-pore offset in the bilayer.

Reviewer: It is impressive to see that the authors measured the permeability after more than 1000 days (>3 years). I was curious how the measurements at 1000 and more days were conducted, based on the gap is it possible to estimate that samples were re-checked after a prolonged time? Was the sample kept in the measurement setup for more than 1000 days under pressure? Some clarification would really help.

Reviewer #2:

Our Response: We appreciate the reviewer's interest in our 1000 day dataset. We believe longitudinal studies such as this one can shed invaluable insight on the long-term practical use life of a material that is not often found in published literature due to the intense time investments that are required. These 1000+ days longitudinal measurements were conducted by transferring 2DPA-1 nanofilms onto SiO₂ substrates with etched microwells. The bulges formed were not from direct pressurization of N₂, but rather, they were formed from trapped over-pressurized air during the film transfer process.

In this set of experiments, we stored these bulges in a pressure, temperature, and humidity monitored chamber. The samples were taken out periodically over the course of this experiment for AFM measurements of the deflection, using a Cypher S AFM (Asylum Research) in non-contact mode. The samples were measured frequently in the first year—the median and mean number of measurements were 14 and 16.3 for all 31 monitored bulges, respectively. In the latter two years of measurements, the median and mean were 4.1 and 4, respectively.

We expand upon our longitudinal analysis, attached as review-only material and titled, “Quantitative Assessment of Longitudinal Stability and Edge Sealing Through Advanced Bulge Test Characterization.” This review-only analysis more deeply investigates the behavior of our 1000-day+ sample and the impact of different factors on the rim seal of the bulges. Specifically, we discuss in more detail the physical relationship between the apparent fluctuations in the deflections of the 1000+ day sample with the random walk of gas molecules; we highlight the impact of temperature on the heights of bulges and the rim seal of the bulges; and we explore the different experimental factors that can lead to gas permeation in these samples

Reviewer: *It is noteworthy to see that NMR spectroscopy was used to assess the degree of polymerization; as the degree of the polymerization increases (r), the authors observed a downfield shift shown in Figure S17. The spectra need to be calibrated, commonly based on the deuterated solvent peak, are the spectra shown in Figure S17 calibrated? Can you also show the whole range for better assessment?*

Our Response: The spectra are calibrated by using the signal of trifluoroacetic acid (TFA) in deuterated TFA as the reference—located at ~12 ppm based on the measurements by Bruker Avance Neo spectrometer operating at 500.18 MHz. We include the whole range of the spectra for the reviewer's convenience (**Fig. R19**). During the review of this manuscript, we published a thorough investigation into the use of ¹H NMR trajectories for analyzing the growth and purification of 2D polyaramids [1]. Consequently, we are removing **Fig. S17** from the SI and will instead be directing future readership to this publication for a more comprehensive analysis on the solution-phase growth of 2DPA-1. Adjustments to the Methods and SI are shown below.

Reviewer #2:

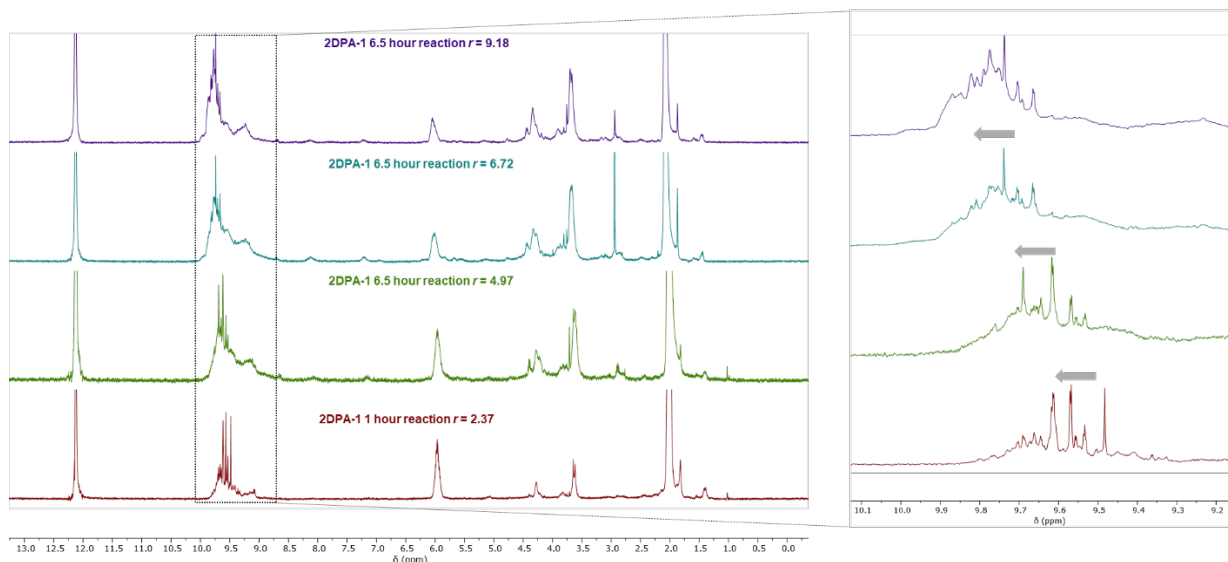


Fig. R19. Left: ^1H NMR spectra of 2DPA-1 with various r values in TFA-d. Right: enlarged aromatic proton peaks region of the spectra.

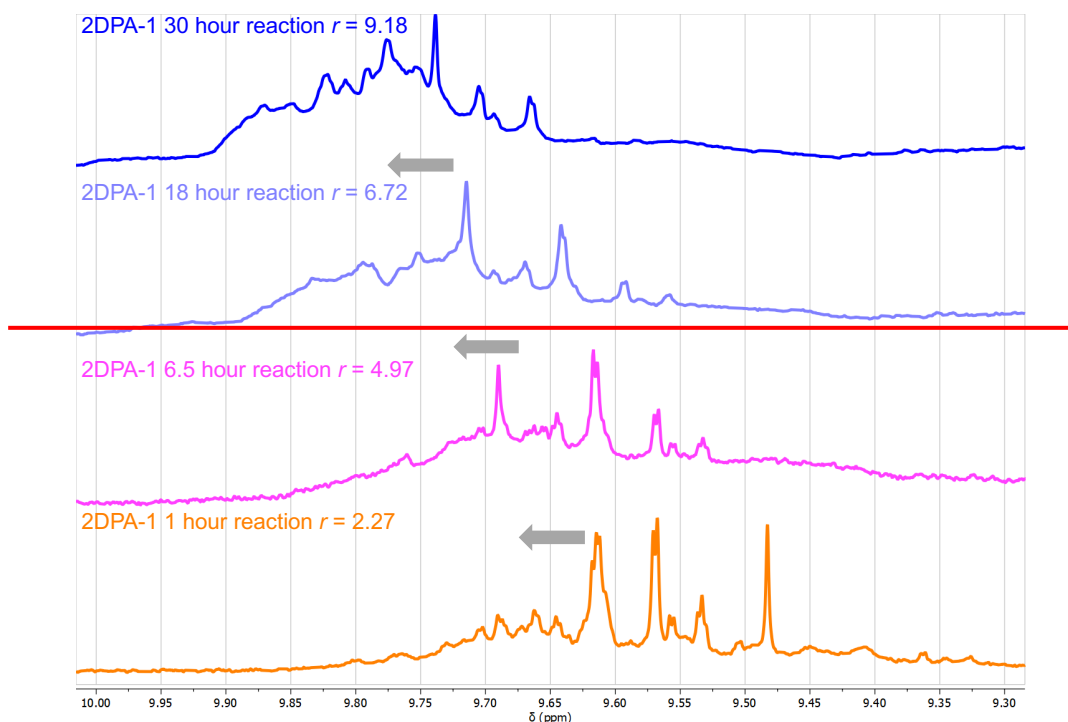


Fig. S17.

^1H NMR spectra of aromatic proton region for 2DPA-1 in deuterated TFA from aliquots extracted at different time points during synthesis showing the changes in relative weighting of downshifted and upshifted aromatic protons. Shifts are highlighted with gray arrows.

[1] Z. Wei *et al.*, *J. Am. Chem. Soc.* 147, 5921–5932 (2025)

Reviewer #2:

Reviewer: *Encapsulation with 2DPA-1 films enhanced the stability of perovskites by 3-fold. How does the 2DPA-1 encapsulation affect the performance of the perovskites, does it reduce the efficiency, can authors comment on this?*

Our Response: The reviewer poses a very interesting question that we do not have an answer for in this study. As the reviewer correctly alludes to, the long-term performance of perovskite cells depends on many factors beyond just the inhibition of O₂ and H₂O diffusion into the lattice structure [1]. We seek to answer these questions in future explorations. For the purpose of this study, the MAPbI₃ perovskite cells were used only as a platform to study the O₂ barrier properties of 2DPA-1 nanofilms due to our inability to form pressurized bulges with this gas. This platform also served as a testament to the scale-up potential for 2DPA-1 films, maintaining extraordinary gas barrier properties from the μm to cm scale.

[1] S. Zhang *et al.*, *Adv. Energy Mater.* 10, 2001610 (2020)

Reviewer: *The impermeability of O₂, CO₂, He, and H₂ wasn't impressive due to absence of persistent bulges. The authors mention that this could be correlated with the poor rim seal. One of the methods to improve the rim seal could be Pt deposition using a Focused-ion beam (FIB) used in earlier studies for graphene (Science, 2014, 344, 289-292). It could improve the rim seal for obtaining measurements with other gases.*

Our Response: The reviewer correctly notes that we were unable to form persistent bulges when pressurizing with O₂, CO₂, He, or H₂. Following discussion from the previous response, analysis of O₂ permeability through the O₂-sensitive MAPbI₃ perovskite platform (**Fig. 4D-F** of Main Text and **Extended Data Fig. 10**) revealed that 2DPA-1 is in fact an impressive O₂ barrier despite our inability to form a bulge with this gas—giving rise to our hypothesized rim seal mechanism. The reviewer notes a successful method for sealing the interface of graphene-SiN with Pt deposition, which we have included in the Main Text as a useful reference for future readership; however, we note that the timescale of bulge deflation for the above-mentioned gases (order of seconds) is unfortunately too fast to seal via a deposition technique post-pressurization.

We find no microporosity in 2DPA-1 when measuring adsorption isotherms with N₂, He, H₂, CH₄, and CO₂—consistent with the molecular impermeability observed and reported in our manuscript. Therefore, despite the inability of 2DPA-1 films to form persistent bulges with some of these smaller gases, the adsorption isotherms corroborate the notion that 2DPA-1 is a nonporous material. Detailed analysis of the procedure is provided below.

To further explore the limits of pore accessibility in 2DPA-1, we measured unary adsorption isotherms using various gas probes (**Supplementary Fig. 10**). We first measured N₂ isotherms (**Supplementary Fig. 10A-B**) at 77 K up to 100 kPa (1 P/P₀) on a low-pressure manometric instrument (Autosorb 6100, Anton Paar, Ashland, VA). The N₂ adsorption isotherm of powder 2DPA-1 follows a Type II isotherm with a type H3 hysteresis loop, which can be attributed to non-rigid aggregates of plate-like particles or a pore network consisting of macropores that are not completely filled with condensate [1]. The BET specific surface area from the average of two aliquots is $(74 \pm 10) \text{ m}^2 \text{ g}^{-1}$. The pore size distribution of bulk (powder) 2DPA-1 consists of mostly mesopores, with an average mode pore width of approximately $(11.1 \pm 2.6) \text{ nm}$, and some macroporosity. Bulk 2DPA-1 has a total pore volume of $(0.41 \pm 0.07) \text{ cm}^3 \text{ g}^{-1}$. Given the mode pore width is similar in size to the $\sim 10\text{--}15 \text{ nm}$ diameter 2DPA-1 nanoplatelets (**Fig 1b** of Main Text),

Reviewer #2:

this pseudo porosity is likely from interparticle space from non-rigid aggregation of the 2DPA-1 nanoplatelets.

Unary He, H₂, CH₄, and CO₂ adsorption isotherms (**Supplementary Fig. 10C**) on 2DPA-1 at 298 K up to 1 MPa were measured on a high-pressure manometric instrument (BELSORP-VC, Microtrac Bel). At 150 kPa, negligible He and H₂ adsorption were observed ($<7 \mu\text{mol g}^{-1}$), with only marginal adsorption of CO₂ ($380 \mu\text{mol g}^{-1}$) and CH₄ ($60 \mu\text{mol g}^{-1}$). Therefore, despite the inability of 2DPA-1 films to form persistent bulges with these smaller gases and the ~1-nm diameter pore of the unit cell, the adsorption isotherms corroborate the notion that 2DPA-1 is a nonporous material. The inability of these gases to access the pore is in line with high diffusive barriers observed for triazine frameworks with comparable pore sizes [2] and can likely be explained by a staggered pore-to-pore configuration of stacked 2DPA-1 platelets in the lamellar film, which can lead to exacerbated energy barriers for permeation (Figs. S8-S11 of SI).

Findings from the additional adsorption isotherm analysis have been incorporated into the Main Text, Methods, and SI as shown below.

Main Text amendment

“The ability of 2DPA-1 films to trap gas within the microwells is not exclusive to N₂. We observed similar multi-day persistence for bulges filled with sulfur hexafluoride (SF₆), argon (Ar), and methane (CH₄, Fig. 3A-D), suggesting that 2DPA-1 is likewise impermeable to gases larger or similar in size to N₂. We note that the formation of persistent bulges was not observed for smaller gases such as oxygen (O₂), carbon dioxide (CO₂), helium (He), or hydrogen (H₂). We measured unary adsorption isotherms for CH₄, CO₂, He, and H₂ on 2DPA-1 platelets at 298 K up to 1 MPa (SI). At 150 kPa, negligible He and H₂ adsorption were observed ($<7 \mu\text{mol g}^{-1}$), with only marginal adsorption of CO₂ ($380 \mu\text{mol g}^{-1}$) and CH₄ ($60 \mu\text{mol g}^{-1}$). Despite the inability of 2DPA-1 films to form persistent bulges with some of these smaller gases, the adsorption isotherms corroborate the notion that 2DPA-1 is a nonporous material.”

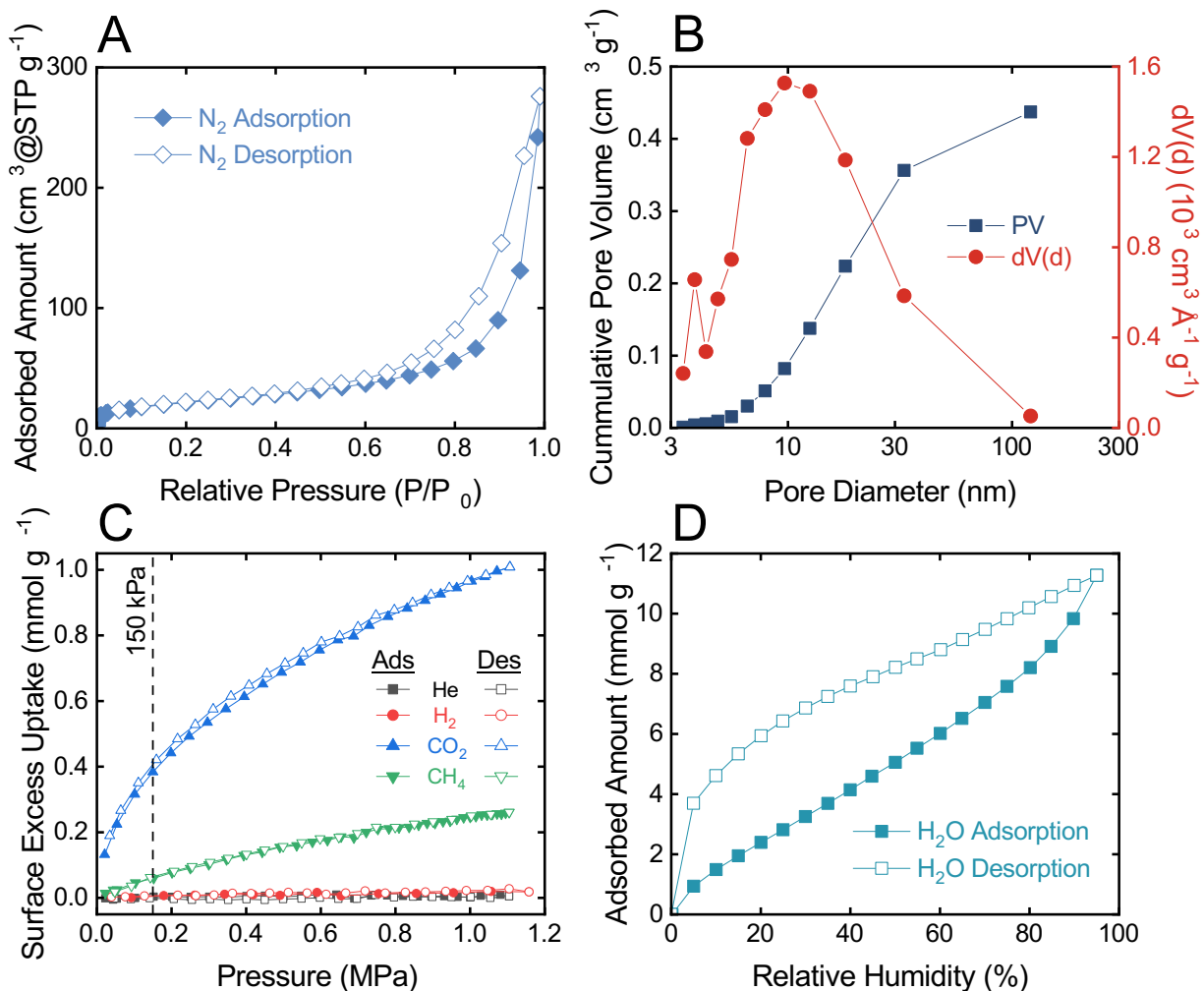
SI amendment

“Gas Adsorption and Thermal Degradation Analyses

The N₂ adsorption isotherm of for 2DPA-1 platelets follows Type II isotherm behavior (Supplementary Fig. 10A). It also possesses a type H3 hysteresis loop, which can be attributed to non-rigid aggregates of plate-like particles or pore network consisting of macropores that are not completely filled with condensate [1]. The BET specific surface area from the average of two aliquots is $(74 \pm 10) \text{ m}^2 \text{ g}^{-1}$. The pore size distribution of powder 2DPA-1 consists of mostly mesopores, with an average mode pore width of approximately $(11.1 \pm 2.6) \text{ nm}$, and some macro-porosity (Supplementary Fig. 10B). Bulk 2DPA-1 platelets have a total pore volume of $(0.41 \pm 0.07) \text{ cm}^3 \text{ g}^{-1}$. Given the mode pore width is similar in size to the 2DPA-1 nanoplatelets (approximately 10 nm to 15 nm, Fig. 1b of Main Text), this pseudo porosity is likely from interparticle space due to non-rigid aggregation of the 2DPA-1 platelets. The adsorption of water on 2DPA-1 at low relative humidity (RH) implies an intrinsic hydrophilicity of the material (Supplementary Fig. 10D).

...”

Reviewer #2:



Supplementary Fig. 10.

Adsorption isotherms for 2DPA-1 using various probe molecules. (A-B) Representative N_2 adsorption isotherm at 77 K (B) and the corresponding pore size distribution determined from BJH method (B). (C) Unary He, H_2 , and CO_2 adsorption isotherms at 298 K. (D) H_2O vapor adsorption isotherm at 298 K with N_2 as carrier gas.

- [1] M. Thommes *et al.*, *Pure Appl. Chem.* 87, 1051-1069 (2015)
 [2] Y. Wang *et al.*, *ACS Appl. Mater. Interf.* 8, 8697-8701 (2016)

Reviewer #3:

Reviewer: *This manuscript describes the preparation and evaluation of an aramid-based 2D polymer with exceptional impermeability to gas. These polymers are able to maintain a sealed chamber of gas pressure for extended periods of time. The low permeability of these polymers is combined with the fact that they can be solution processed like conventional polymers and unlike other highly impermeable materials such as graphene*

Our Response: We thank the reviewer for reviewing the quality our work and for providing insightful comments to help improve it. Before addressing the specific comments of the reviewer, we would like to indicate that we have made the following key revisions to our manuscript. The key revisions include:

- Demonstrated chemical stability and processability of 2DPA-1 in TFA and non-TFA solvents
 - ^1H NMR in TFA and milder solvents (**Figs. R1-2, R19, and Supplementary Fig. 1**) showing no evidence of chemical degradation
 - [REDACTED]
- Refined structural characterization to connect bulk 2DPA-1 to molecularly ordered films
 - Experimental FTIR and Raman spectra assigned and compared to DFT simulated molecular models confirming chemical structure (**Figs. R4, R14-15, Supplementary Fig. 2, and Supplementary Table 1**)
 - [REDACTED]
 - Polarized PL of molecularly ordered thin films confirming nanoplatelet in-plane alignment and ordering explaining impermeability (**Fig. R6 and Supplementary Fig. 4**)
- Showed lack of accessible microporous structure with various gas probes
 - Adsorption isotherms of CH_4 , CO_2 , He, and H_2 on 2DPA-1 measured by the U.S. National Institute for Standards and Technology confirming no microporosity (**Supplementary Fig. 10**)
 - [REDACTED]
- Verified inhibition of molecular transport via staggered unit cells rather than solvent clogging
 - TGA-MS of gas evolution from 2DPA-1 confirming the absence of microporous-trapped solvents or water (**Supplementary Fig. 12**)
 - *In situ* AFM of bulges at elevated temperatures showing persistent impermeability at high temperatures (**Supplementary Fig. 13**)
 - DFT simulations of energetically favored offset stacking explaining the structural aspects of impermeability (off-set platelet stacking) (**Supplementary Fig. 14**)
- Enhanced clarity on the film morphology and experimental apparatuses used in this study
 - SEM and AFM compared with explanatory schematics, confirming film morphology leading to impermeability (**Supplementary Figs. 5 and 7**)

Reviewer #3:

Changes made to the manuscript (excerpts highlighted in light grey) that are marked in **blue** and ~~red-strikethrough~~ text represent additions and subtractions, respectively. The same format is followed for figures, with the exception of review-only figures (labeled as **Fig. R#**). Relevant references are included at the end of each response as numbered brackets [#].

Reviewer #3:

Reviewer: *The properties of this aramid polymer are extremely interesting. The characterization of this material is extremely important. It is surprising that the material does not display any long range order. What is the largest area or size of film that can be spin cast?*

Our Response: We are pleased to receive positive feedback on the interest of this material, which we similarly find fascinating. Careful characterization is indeed important, particularly for molecular ordering. We address molecular ordering in response to some of the reviewer's latter questions. Here, we highlight that the size of spin-coated 2DPA-1 films is only limited to the size of the wafer used. We show a photograph of a 7-nm film spin-coated and subsequently transferred to a 6" wafer (**Fig. R20**) [1]. Scaling beyond wafer methods will likely require new approaches to coating, such as spray coating or drop-casting. These alternative deposition methods are subjects of future study to investigate whether the molecular ordering and barrier properties of the material remain regardless of deposition technique. Note that in this revision, we show that substituting the isopropyl end group with smaller methyl groups appears to allow for tighter packing and more crystalline structure begins to emerge, as shown by PXRD (see below).

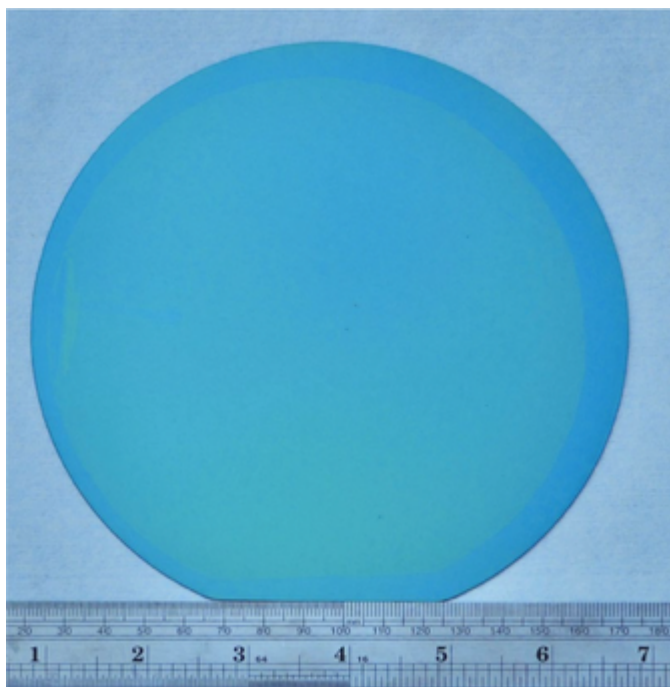


Fig. R20. Photograph of 7-nm 2DPA-1 thin film transferred onto 6-inch wafer, taken from ref [1].

[1] Y. Zeng *et al.*, *Nature*, 602, 91-95 (2022)

Reviewer: *Why are the pores occluded? Most of the COF literature has found that AA, AA', or some other variant of eclipsed stacking geometry is observed due to the fact that the most energetically favorable stacking arrangement is driven by maximizing the amount of non-covalent interactions between the layers. If the materials produced here do produce large 2D platelets, why aren't the pores accessible?*

Our Response: We thank the reviewer for bringing up this great question. Below we demonstrate through a combination of powder X-ray diffraction (PXRD) measurements of the as-synthesized

Reviewer #3:

and chemically modified material, paired with density functional theory (DFT) calculations, that partially occluded structures are the most energetically favorable. We thus posit a lamellar structure with in-plane ordering but no precisely defined stacking order, as depicted in **Fig. 1C** of the Main Text.

We first simulated the predicted PXRD for the theoretical structure of multi-layer 2DPA-1 platelets (**Fig. 1A** of Main Text) from the CIF structure file using Powder Pattern Function in CCDC Mercury software. 2DPA-1 platelets were first simulated in eclipsed (AA stacked) and occluded (AB stacked) configurations, common to COFs, to compare against our experimental measurements (**Supplementary Fig. 3A(i-ii)**). Crystalline peaks captured by PXRD depend strongly on structural characteristics, such as crystallite domain size and the layer-to-layer offset, or “stacking disorder,” of the 2D macromolecular sheets [1]. When compared against model 2DPA-1 structures, we find that the broad PXRD is more reflective of the dispersive scattering that would occur from random offsets between layers (**Supplementary Fig. 3A(iii)**).

REDACTED

To understand why 2DPA-1 platelets prefer partially occluded structures that are randomly dispersed, we performed DFT calculations on bilayer configurations with various interlayer offsets to determine the most stable configurations (minimum energy). The interlayer offsets were generated on a 4×4 grid in the X-Y plane with a maximum shift of 8.3475 Å along each axis. For each offset, the system was first relaxed by performing a geometric optimization in vacuum using DFT. The interlayer interaction energy, E_{int} , for the final optimized geometry was computed as

$$E_{\text{int}} = E_{\text{bl}} - E_{\text{ml-1}} - E_{\text{ml-2}} ,$$

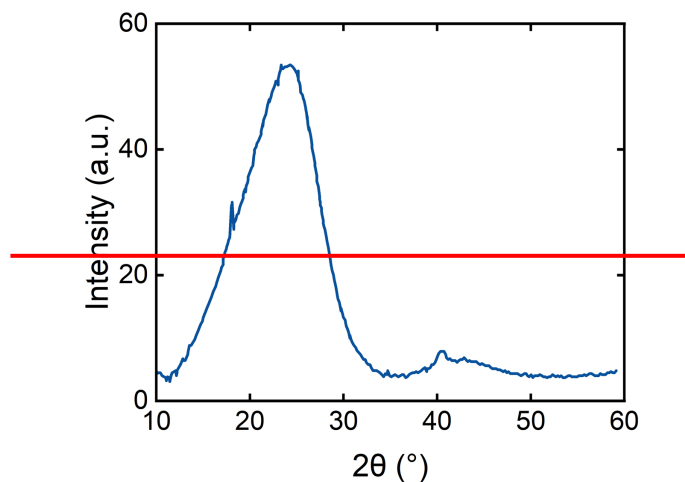
where E_{bl} is the energy of the bilayer and $E_{\text{ml-1}}$ and $E_{\text{ml-2}}$ are the energies of the two monolayers. Snapshots of the various bilayer configurations considered as well as the corresponding interlayer interaction energies are found in **Supplementary Fig. 14**. We find that staggered pores are the most energetically favorable stacking configurations, with eclipsed stacking (i.e., AA stacking) being the least favored. There are numerous stacking configurations with varied pore-to-pore offsets that possess similarly favorable energetics, likely explaining the proposed tendency to stack in the “random” staggered configurations that would explain the PXRD.

We have adjusted the Main Text, Methods, and SI accordingly to reflect the new insights discussed here.

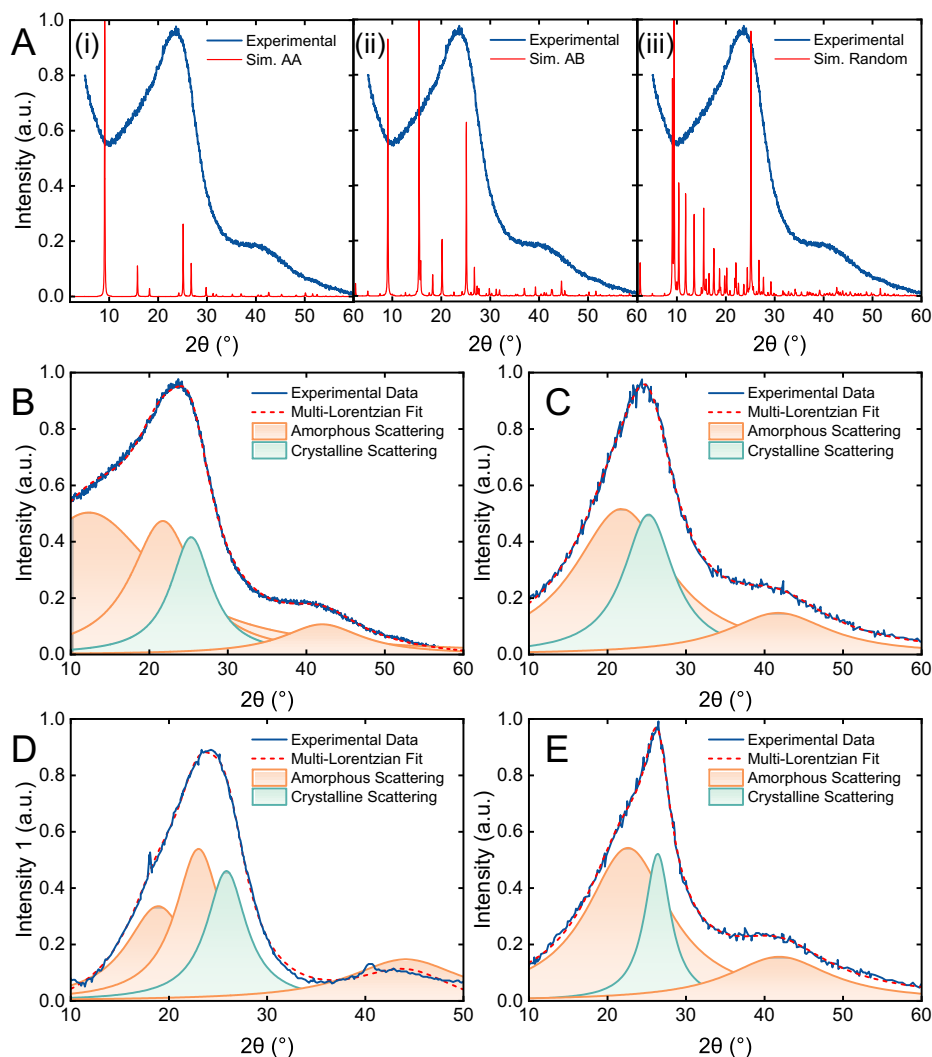
Main Text amendment

Reviewer #3:

“The impermeability of 2DPA-1 implies an absence of free volume required for molecular transport. The pore within the 2DPA-1 unit cell is estimated to be approximately 1 nm in diameter; hence, it is unlikely that a monolayer platelet would impose substantial resistance to most gas molecules. We ruled out the possibility that water or ~~an~~ other relevant solvents could be occluding the pores via simultaneous thermogravimetric analysis with mass spectrometry (TGA-MS) and the observation of several bulges that remain inflated upon heating to 120 °C ~~a stable bulge even upon heating to 90 °C~~ (SI Supplementary Figs. 12-13). We therefore suspect the impermeability necessitates a staggered configuration of stacked 2DPA-1 bilayers, similar to AB stacking in COFs, to reduce the effective pore size, enhance chemical interactions, and eliminate free volume. Density functional theory (DFT) calculations indicate that staggered pores are the most energetically favorable stacking configurations, with eclipsed stacking (i.e., AA stacking) being the least favored (Supplementary Fig. 14).”

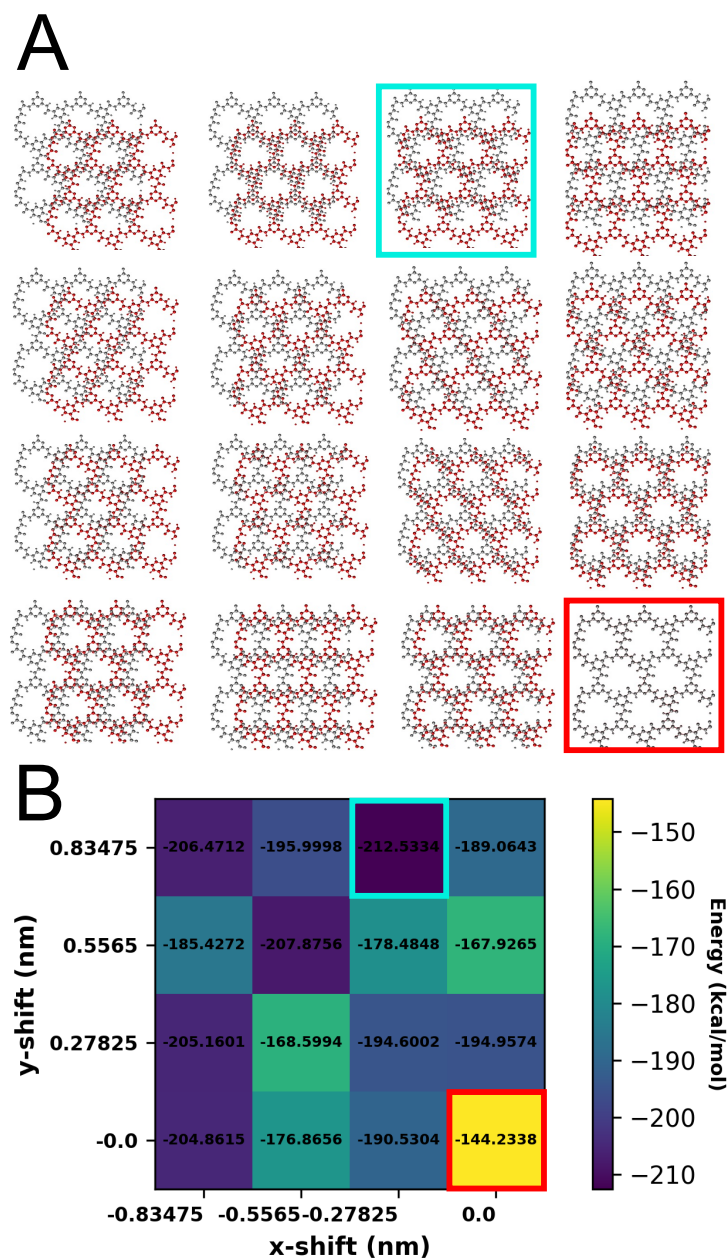


Reviewer #3:



Supplementary Fig. 3.

Powder X-ray diffraction (PXRD) of 2DPA-1. ~~powder with $r = 9.67$~~ . Experimental data compared against diffraction peaks simulated for 2DPA-1 stacked in (A) eclipsed, i.e., AA, (B) offset, i.e., AB, and (C) random layer-to-layer configurations. (B-E) Measured PXRD of 2DPA-1 fit by Lorentzian curves. The red dashed curve represents the cumulative fit of all Lorentzian curves to the overall data. Using the peak position centered between 25° to 26° (2θ) as the pseudo-crystalline signal, the degree of crystallinity is estimated as (B) 13.6 %, (C) 27.7 %, (D) 23.6 %, and (E) 18.0 %.



Supplementary Fig. 14.

Snapshots of various (A) interlayer offsets and the corresponding (B) interaction energies determined from density functional theory (DFT) calculations. Snapshots highlighted in cyan and red represent the lowest (i.e., most favorable) and highest (i.e., least favorable) energy configurations.

- [1] S. Van Gele *et al.*, *JACS Au*, 5, 388-398 (2025)
- [2] X. Wang *et al.*, *Nat. Chem.* 10, 1180-1189 (2018)

Reviewer: The structural characterization of the 2DPA is somewhat ambiguous: (1) The BET analysis shows that the material has no accessible surface area.

Reviewer #3:

Our Response: In response to the reviewer's feedback regarding the structural characterization of 2DPA-1 and following upon our analysis in the previous response on occluded pores, we measured unary adsorption isotherms using various gas probes to further explore the limits of pore accessibility in 2DPA-1 (**Supplementary Fig. 10**). We find no microporosity in 2DPA-1 when measuring adsorption isotherms with N₂, He, H₂, CH₄, and CO₂—consistent with the molecular impermeability observed and reported in our manuscript. Therefore, despite the inability of 2DPA-1 films to form persistent bulges with some of these smaller gases, the adsorption isotherms corroborate the notion that 2DPA-1 is a nonporous material. Detailed analysis of the procedure is provided below.

We first measured N₂ isotherms (**Supplementary Fig. 10A-B**) at 77 K up to 100 kPa (1 P/P₀) on a low-pressure manometric instrument (Autosorb 6100, Anton Paar, Ashland, VA). The N₂ adsorption isotherm of powder 2DPA-1 follows a Type II isotherm with a type H3 hysteresis loop, which can be attributed to non-rigid aggregates of plate-like particles or a pore network consisting of macropores that are not completely filled with condensate [1]. The BET specific surface area from the average of two aliquots is $(74 \pm 10) \text{ m}^2 \text{ g}^{-1}$. The pore size distribution of bulk (powder) 2DPA-1 consists of mostly mesopores, with an average mode pore width of approximately $(11.1 \pm 2.6) \text{ nm}$, and some macro-porosity. Bulk 2DPA-1 has a total pore volume of $(0.41 \pm 0.07) \text{ cm}^3 \text{ g}^{-1}$. Given the mode pore width is similar in size to the $\sim 10\text{--}15 \text{ nm}$ diameter 2DPA-1 nanoplatelets (**Fig 1B** of Main Text), this pseudo porosity is likely from interparticle space from non-rigid aggregation of the 2DPA-1 nanoplatelets.

Unary He, H₂, CH₄, and CO₂ adsorption isotherms (**Supplementary Fig. 10C**) on 2DPA-1 at 298 K up to 1 MPa were measured on a high-pressure manometric instrument (BELSORP-VC, Microtrac Bel). At 150 kPa, negligible He and H₂ adsorption were observed ($<7 \mu\text{mol g}^{-1}$), with only marginal adsorption of CO₂ ($380 \mu\text{mol g}^{-1}$) and CH₄ ($60 \mu\text{mol g}^{-1}$). Therefore, despite the inability of 2DPA-1 films to form persistent bulges with these smaller gases and the $\sim 1\text{-nm}$ diameter pore of the unit cell, the adsorption isotherms corroborate the notion that 2DPA-1 is a nonporous material. The inability of these gases to access the pore is in line with high diffusive barriers observed for triazine frameworks with comparable pore sizes [2] and can likely be explained by a staggered pore-to-pore configuration of stacked 2DPA-1 platelets in the lamellar film, which can lead to exacerbated energy barriers for permeation (**Supplementary Figs. 17-20**).

Findings from the additional adsorption isotherm analysis have been incorporated into the Main Text, Methods, and SI as shown below.

Main Text amendment

“The ability of 2DPA-1 films to trap gas within the microwells is not exclusive to N₂. We observed similar multi-day persistence for bulges filled with sulfur hexafluoride (SF₆), argon (Ar), and methane (CH₄, Fig. 3A-D), suggesting that 2DPA-1 is likewise impermeable to gases larger or similar in size to N₂. We note that the formation of persistent bulges was not observed for smaller gases such as oxygen (O₂), carbon dioxide (CO₂), helium (He), or hydrogen (H₂). We measured unary adsorption isotherms for CH₄, CO₂, He, and H₂ on 2DPA-1 platelets at 298 K up to 1 MPa (SI). At 150 kPa, negligible He and H₂ adsorption were observed ($<7 \mu\text{mol g}^{-1}$), with only marginal adsorption of CO₂ ($380 \mu\text{mol g}^{-1}$) and CH₄ ($60 \mu\text{mol g}^{-1}$). Despite the inability of 2DPA-1 films to form persistent bulges with some of these smaller gases, the adsorption isotherms corroborate the notion that 2DPA-1 is a nonporous material.”

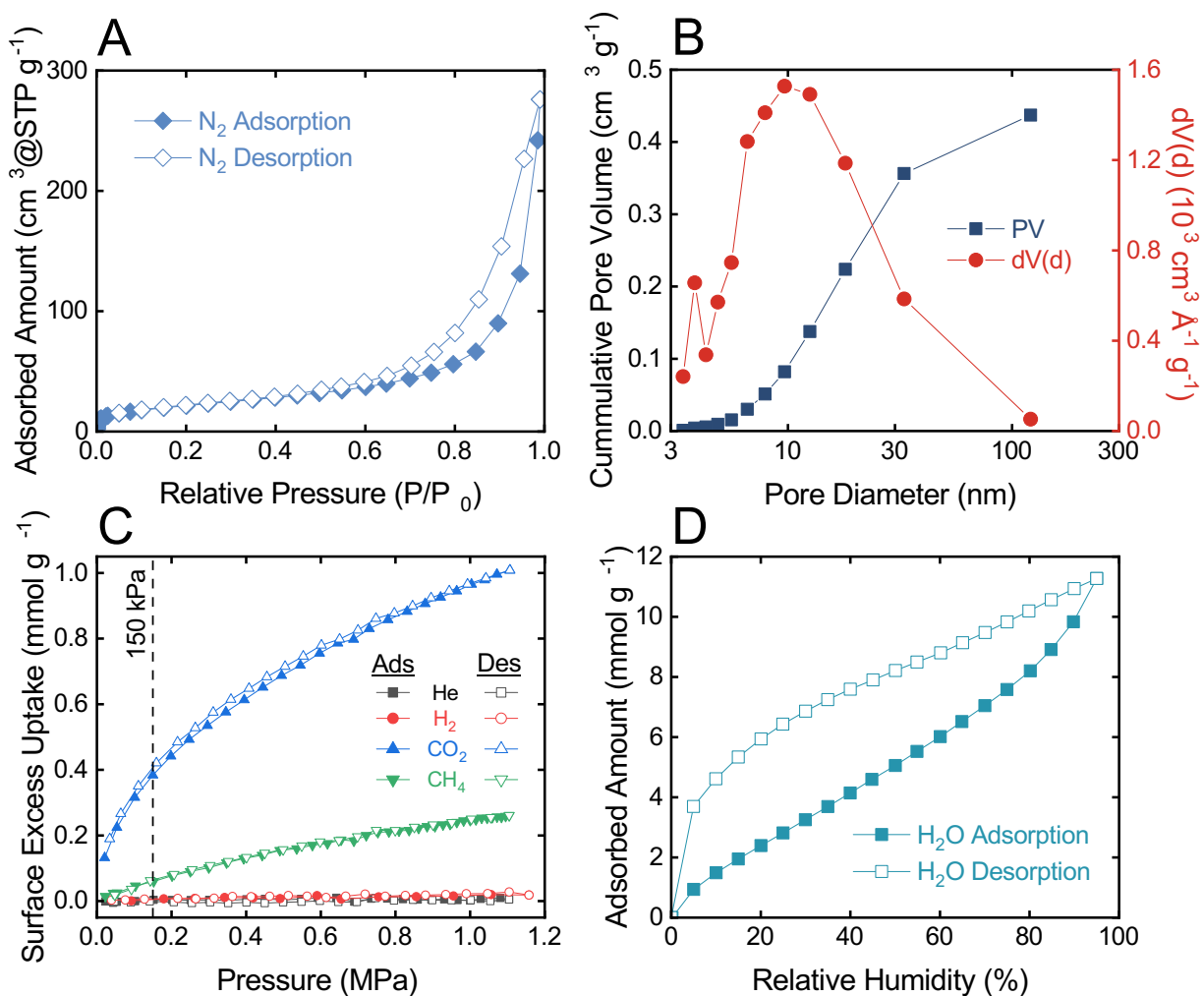
Reviewer #3:

SI amendment

“Gas Adsorption and Thermal Degradation Analyses

The N₂ adsorption isotherm of for 2DPA-1 platelets follows Type II isotherm behavior (Supplementary Fig. 10A). It also possesses a type H3 hysteresis loop, which can be attributed to non-rigid aggregates of plate-like particles or pore network consisting of macropores that are not completely filled with condensate [1]. The BET specific surface area from the average of two aliquots is $(74 \pm 10) \text{ m}^2 \text{ g}^{-1}$. The pore size distribution of powder 2DPA-1 consists of mostly mesopores, with an average mode pore width of approximately $(11.1 \pm 2.6) \text{ nm}$, and some macro-porosity (Supplementary Fig. 10B). Bulk 2DPA-1 platelets have a total pore volume of $(0.41 \pm 0.07) \text{ cm}^3 \text{ g}^{-1}$. Given the mode pore width is similar in size to the 2DPA-1 nanoplatelets (approximately 10 nm to 15 nm, Fig. 1b of Main Text), this pseudo porosity is likely from interparticle space due to non-rigid aggregation of the 2DPA-1 platelets. The adsorption of water on 2DPA-1 at low relative humidity (RH) implies an intrinsic hydrophilicity of the material (Supplementary Fig. 10D).

..”



Supplementary Fig. 10.

Adsorption isotherms for 2DPA-1 using various probe molecules. (A-B) Representative N₂ adsorption isotherm at 77 K (B) and the corresponding pore size distribution determined from BJH method (B). (C) Unary He, H₂, and CO₂ adsorption isotherms at 298 K. (D) H₂O vapor adsorption isotherm at 298 K with N₂ as carrier gas.

[1] M. Thommes *et al.*, *Pure Appl. Chem.* 87, 1051-1069 (2015)

Reviewer #3:

[2] Y. Wang *et al.*, *ACS Appl. Mater. Interf.* 8, 8697-8701 (2016)

Reviewer: *The structural characterization of the 2DPA is somewhat ambiguous: (2) The powder X-ray diffraction patterns indicate that the bulk material is amorphous.*

Our Response: Below we provide evidence to show that 2DPA-1 is indeed a molecularly ordered 2D polymer but lacks the long-range order that would be assigned as crystallinity. We estimate an upper bound on the degree of crystallinity, X_c , as $20.7 \% \pm 6.2 \%$. Evidence for molecular ordering is provided by a combination of PXRD [REDACTED] measured for as-synthesized and chemically modified 2DPA-1 structures, simulated PXRD from theoretical model structures, and anisotropic polarized photoluminescence (PL) of the 2DPA-1 thin film. Detailed discussion and analysis are given below.

Diffraction peaks captured by PXRD reflects the long-range order of the system and depends strongly on structural characteristics, such as crystallite domain size and the layer-to-layer offset, or “stacking disorder,” of the 2D macromolecular sheets [4]. Consequently, the degree of crystallinity measured for 2D polymers like COFs often depends on synthesis conditions that affect their alignment [5, 6], such as solvent-induced reordering. We demonstrate in **Supplementary Fig. 3A** [REDACTED] the importance of stacking order on the crystallinity measured in 2DPA-1 samples via PXRD [REDACTED]. Simulated XRD data were calculated from the CIF structure file using Powder Pattern Function in CCDC Mercury software. [REDACTED]

When compared against model 2DPA-1 structures, we find that measured PXRD of 2DPA-1 does not reflect the diffraction patterns that would be expected for AA or AB stacking modes (**Supplementary Fig. 3A(i-ii)**). Instead, the broad PXRD of 2DPA-1 is more reflective of the dispersive scattering that would occur from random offsets between layers (**Supplementary Fig. 3A(iii)**). [REDACTED]

To better quantify the long-range order, or lack thereof, of as-synthesized 2DPA-1 from measured PXRD, we estimated the X_c by taking a ratio of the pseudo-crystalline to amorphous signals from PXRD [7]. Here, we define the peak centered around $2\theta \approx 25^\circ$ as our pseudo-crystalline region due to its strong presence in all 2DPA-1 stacking configurations. **Supplementary Fig. 3B-E** depicts PXRD datasets that are well described by three- or four-peak Lorentzian fits. Averaging over four 2DPA-1 samples, we obtain $X_c = 20.7 \% \pm 6.2 \%$ that we assign as an upper-bound for 2DPA-1 crystallinity given the method’s likely overestimation of

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the crystalline peak area. These findings are in line with our initial discussion in the Main Text that as-synthesized 2DPA-1 lacks substantial long-range order that would be detected as a high degree of crystallinity via PXRD or other X-ray scattering methods.

It is important to note that the absence of crystallinity does not mean that the system is a disordered, amorphous material. Numerous non-crystalline and para-crystalline materials possess orientational ordering that is not captured by conventional X-ray techniques, including ordered polyaramid and cellulose fibers [8, 9]. Beyond XRD or direct imaging by electron microscopy, non-crystalline ordering can be detected using polarization-sensitive approaches [10]. We demonstrate orientational ordering of a 35-nm 2DPA-1 film using polarized photoluminescence, PL (**Supplementary Fig. 4**). We find that when excited at 532 nm with a polarized laser, the PL emission of the 35-nm 2DPA-1 film depends on its orientation with respect to the beam path. Specifically, the thin film emission transitions from roughly 1400 cm^{-1} (575 nm) when excited orthogonal to the beam path to 2270 cm^{-1} (605 nm) when excited parallel to the beam path. This twofold symmetry is consistent with anisotropic platelets oriented parallel to the substrate with a transition dipole along the long axis of the platelet [2]. We note that the emission window reported is beyond that of SiO_2 to eliminate signal interference (**Fig. R6**). Interestingly, for each spectrum we find a sharp Raman signature between approximately 2410 cm^{-1} and 2435 cm^{-1} that is uncommon for most materials. This signature was not generated by the simulation of a 2DPA-1 monolayer. Notably, the location of this Raman band is in good agreement with second-order features from overtones of fundamental modes observed in highly ordered pyrolytic graphite (HOPG) that do not appear in monolayer graphene [11-13]. We postulate that this Raman band may be an additional signature of molecular ordering from stacked doublet formation, but this requires further exploration beyond the scope of this study.

We have amended Fig. 2, the Main Text, and the SI to reflect some of the new findings discussed here (see below).

Main Text amendment

“Crystallinity estimates of $20.7\% \pm 6.2\%$ from powder X-ray diffraction (PXRD) suggests 2DPA-1 lacks long-range order (**SI Supplementary Fig. 3**); however, a combination of polarized photoluminescence (**Supplementary Fig. 4**) and scanning transmission electron microscopy (STEM) of spin-coated 2DPA-1 thin films reveals anisotropy in the form of layered, orientational ordering (**Fig. 1C-E**).”

SI amendment

“Raman, ATR-FTIR, and Photoluminescence (PL) Spectroscopy of 2DPA-1

...

Numerous non-crystalline and para-crystalline materials possess orientational ordering that is not captured by conventional X-ray techniques, including ordered polyaramid and cellulose fibers [7, 8]. Beyond XRD or direct imaging by electron microscopy, non-crystalline ordering can be detected using polarization-sensitive approaches [9]. We demonstrate orientational ordering of a 35-nm 2DPA-1 film using polarized PL (**Supplementary Fig. 4**). We find that when excited at 532 nm with a polarized laser, the PL emission of the 35-nm 2DPA-1 film depends on its orientation with respect to the beam path. Specifically, the thin film emission transitions from roughly 1400 cm^{-1} (575 nm) when excited orthogonal to the beam path to 2270 cm^{-1} (605 nm) when excited parallel to the beam path. This twofold symmetry is consistent with anisotropic platelets oriented parallel to the substrate with a transition dipole along the long axis of the platelet [2]. We note that the emission window reported is beyond that of SiO_2 to eliminate signal interference. Interestingly, for each spectrum we find a sharp Raman signature between approximately 2410 cm^{-1} and 2435 cm^{-1} that is uncommon for most materials. This signature was not generated by

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the simulation of a 2DPA-1 monolayer. Notably, the location of this Raman band is in good agreement with second-order features from overtones of fundamental modes observed in highly ordered pyrolytic graphite (HOPG) that do not appear in monolayer graphene [10-12]. The origin of this Raman band requires further exploration.”

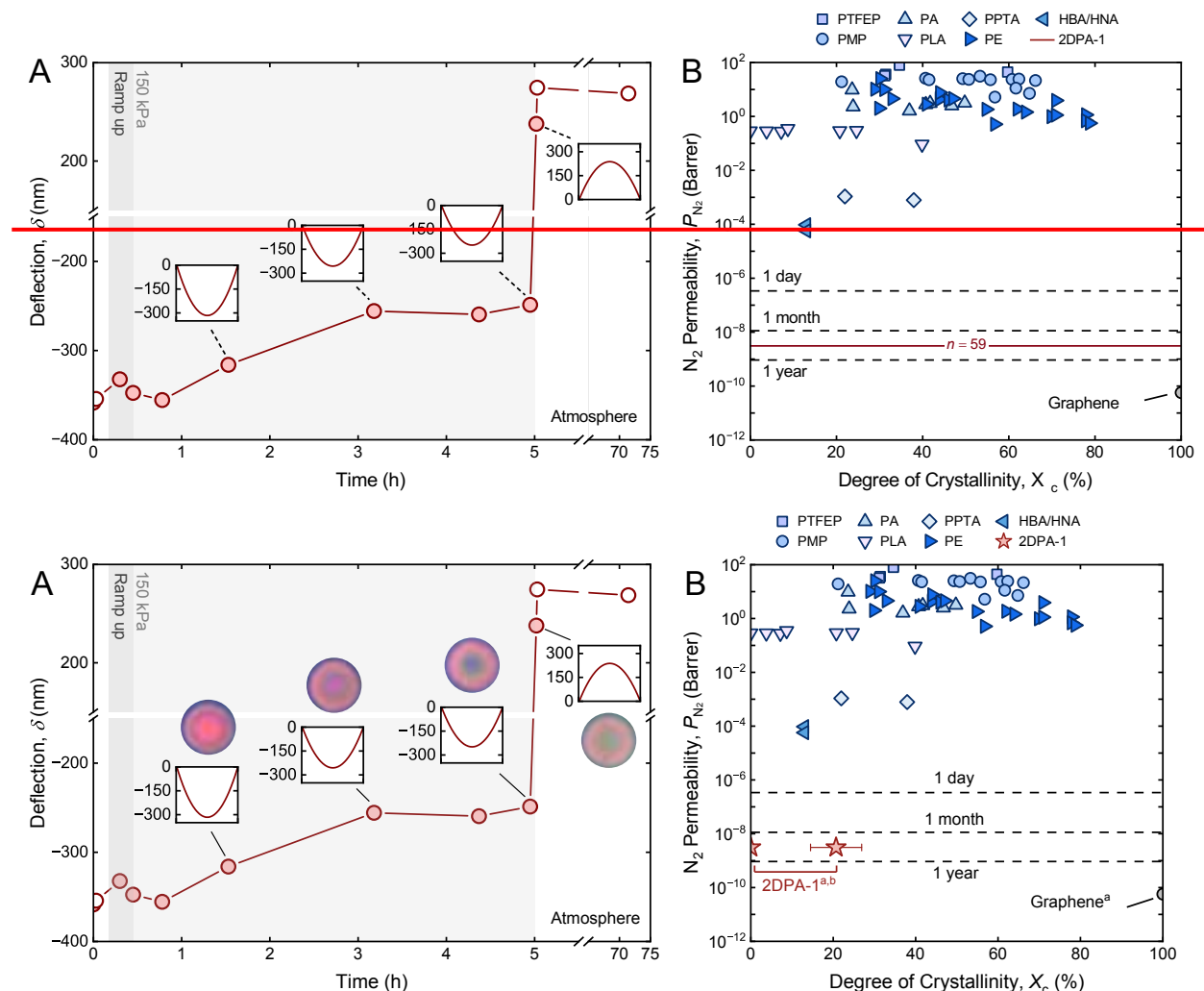
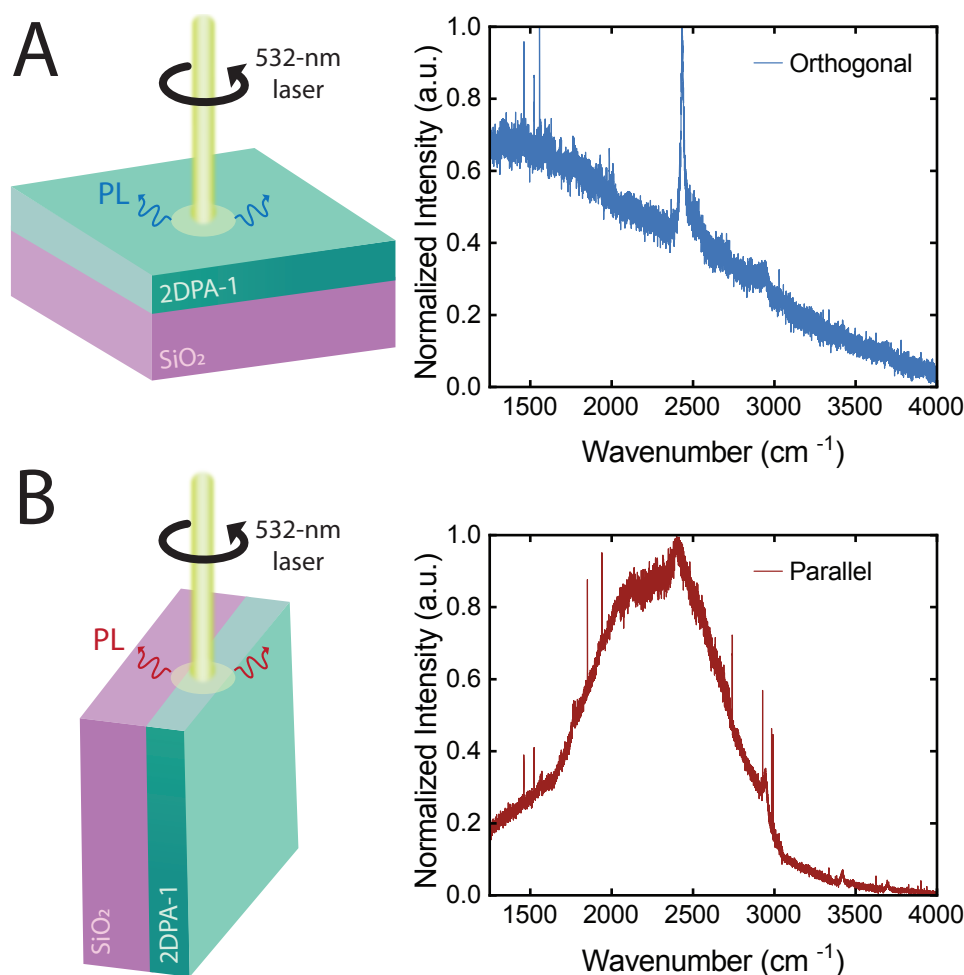


Fig. 2 | Observation of Dynamic Filling and N_2 Impermeability of 2DPA-1. (A) Deflection of 2DPA-1 dimples before, during, and after N_2 -pressurization in an environmental stage. White- and red-filled datapoints represent deflections determined directly via AFM measurement and indirectly via optical interference analysis, respectively. The dark grey shaded region indicates the pressure ramp-up period from 0 kPa to 150 kPa (gauge pressure), whereas the light grey shaded region indicates a 150 kPa gauge pressure of N_2 . Non-shaded (i.e., white) regions represent atmospheric pressure. The insets show cross-sectional profiles of bulge deflections at respective time steps taken from the optical analyses of the imaged bulges (pictured above insets). (B) N_2 permeability with respect to degree of crystallinity (X_c). The dashed black lines mark the maximum permeability allowed for a 35-nm bulge to remain inflated over various durations for the microwells used in this study. The red stars solid red line represents the threshold permeability for 2DPA-1 based on the observed persistence of 59 2DPA-1-covered microwells over 110 d after filling with 150 kPa N_2 . The N_2 permeability of liquid crystalline and glassy polymers, such as poly[bis(trifluoroethoxy phosphazene)] (PTFEP), polyacrylate (PA), poly(p-phenylene terephthalamide) (PPTA), poly(p-hydroxybenzoic acid-co-6-hydroxy-2-naphthioic acid) (HBA/HNA), poly(4-methyl-1-pentene)

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(PMP), poly(lactic acid) (PLA), and polyethylene (PE) are included from ref. 1 for comparison, along with the H₂ permeability of graphene. ^aPermeability values are at the method detection limit and may be considered effectively zero. ^bPXRD of four bulk samples was used to estimate the upper bound of X_c for 2DPA-1.



Supplementary Fig. 4.

Photoluminescence, PL, measurements of 35-nm 2DPA-1 film on a SiO₂ substrate placed (A) orthogonal and (B) parallel to the beam path of a polarized 532-nm excitation laser source. Illustrations of measurement configuration are on the left, with the resulting data plotted on the right. The emission window reported is just beyond that of SiO₂ to eliminate signal interference.

- [1] A.M. Evans *et al.*, *Chem. Rev.* 122, 442-564 (2022)
- [2] Y. Zeng *et al.*, *Nature*, 602, 91-95 (2022)
- [3] A.B. Marco *et al.*, *Angew. Chem.* 129, 7050-7055 (2017)
- [4] S. Van Gele *et al.*, *JACS Au*, 5, 388-398 (2025)
- [5] X. Wang *et al.*, *Nat. Chem.* 10, 1180-1189 (2018)
- [6] P. Kharel *et al.*, *J. Am. Chem. Soc.* 147, 11821-11828 (2025)
- [7] I. Uzun, *J. Polym. Res.*, 30, 394 (2023)
- [8] S. Marina *et al.*, *Mater. Horiz.* 9, 1196 (2022)
- [9] J.L. Bregado *et al.*, *Fluid Phase Equilibria*, 491, 56-76 (2019)
- [10] B.A. Collins *et al.*, *Nat. Mater.* 11, 536-543 (2012)
- [11] Y. Wang *et al.*, *Chem. Mater.* 2, 557-563 (1990)
- [12] R.J. Nemanich and S.A. Solin, *Phys. Rev. B*, 20, 392-401 (1979)

Reviewer #3:

[13] R. Al-Jishi and G. Dresselhaus, *Phys. Rev. B*, 26, 4514-4522 (1982)

Reviewer: *Solution phase proton NMR analysis is included here, but the authors use an unconventional method to claim that the dissolved structures match a perfect hexagonal model. The spectrum shown in Figure S15 shows many overlapping signals in the aromatic region, which are compared to end groups that are not likely to have formed with high levels of conversion. A “perfect” hexagonal structure would result in a highly symmetrical structure, producing a spectrum with only a few peaks. The aromatic region of this spectrum (δ 9-10 ppm) shows two, broad peaks. However, each aromatic ring in the proposed structure has three chemically equivalent protons, which should produce only one signal indicating that there is a mismatch between the proposed structure and the experimental NMR spectrum. The integration of the peaks represents the total number of protons in the aromatic region vs the proposed endgroups, but these ratios are not matched to the theoretical structure shown. It would be challenging to make conclusions from these data anyway since the total number of endgroups are not known. Endgroup analysis is typically used in polymer chemistry when the functional group at the end of the polymer is created through the initiation step of the polymerization. In this case the total number of endgroups is determined by the mechanism and can be used to quantitatively measure the degree of polymerization. This is not the case here.*

Our Response: The reviewer brings up a number of important questions related to the solution-phase characterization of 2DPA-1 platelets. We note that our recently published paper in *JACS* [1] focuses on the use of ^1H NMR trajectories for analyzing the growth and purification of 2D polyaramids. We believe this report should answer most, if not all, of the questions regarding the use of this technique for characterizing the 2D polyaramids in solution. For convenience, we have provided some discussion below that we believe should help clarify the questions presented by the reviewer.

First, we agree that, in polymer characterization, it is common to use the degree of polymerization calculated as the ratio of end groups compared to the number of main chain units. The r metric, used here, is akin to degree of polymerization but in a more generic form as, when used for 1D polymers, the calculation assumes a fixed number of end groups independent of the molecular weight. The r value is the ratio between the aromatic protons, of which there are three for our trimesoyl chloride monomer, and the ratio of the protons on the α -carbon of the end groups. As our platelets grow, in a perfect system, the number of aromatic protons will grow with the area of the platelet while the number of quenched end-groups grows with the circumference of the platelet, thus requiring the use of the perfect hexagon model. These end groups, which are initially acyl halides on the trimesoyl chloride monomer, are considered highly reactive species. Acyl halides are known to readily react with alcohols such as isopropanol, the main quenching agent used in this paper. Thus, we have confidence in the quantification of end groups and the use of r as a quantification akin to degree of polymerization.

In our recently published work [1], we tracked the change of r with respect to different reaction times, finding an overall increasing trend of r values with respect to increasing reaction time. To the reviewer's point, the non-linearity in the growth of r with respect to reaction time indicates that synthesized 2DPA-1 are not perfect hexagonal structures. Rather, some defects likely always exist in our materials.

Regarding the broadness of our peaks: the ^1H -NMR spectra of polymer solutions are known to have broadened peaks with a wide distribution of peaks. This can be seen, for example, in

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comparing the ^1H -NMR of styrene monomer with polystyrene. The broadened peaks are attributed to changes in T_2 relaxation times and the change in peak positions are attributed to variations in chemical environments. This is further complicated by polydispersity, as there would be a variety of different molecule sizes with similar NMR peaks. T_2 relaxation, or the spin-spin relaxation time, is inversely proportional to the width of an NMR peak. In a solution, the slower a molecule tumbles, the lower its T_2 relaxation and the broader its resultant peak. Thus, when comparing a monomer to a polymer, there is an expected increase in the peak width.

The chemical environment is also known to affect the peak positions in NMR, and the chemical environments of polymer solutions are more complex than monomer solutions, leading to a distribution of peaks in the polymer solution where there exists a single peak in the monomer solution. Small molecules, such as styrene, within a dilute enough sample, would not be interacting with any other styrene molecules or itself. Polymer molecules, however, even in a dilute sample, can interact with themselves. Thus, even if the molecular structure may suggest that only a fixed set of peaks should exist within a polymer, the intramolecular interactions cause shifts in the peak positions and lead to a more complex peak distribution.

It is also worth mentioning that the 2DPA-1 polymers we synthesized are always polydisperse samples rather than monodisperse. After purification, what we collect is a distribution of 2DPA-1 with various molecular weights. Aromatic protons on 2DPA-1 with different molecular weights will by necessity have different chemical environments. Therefore, the resulting aromatic proton peaks in ^1H NMR of 2DPA-1 are not one single peak; instead, those peaks are a combination of aromatic proton peaks with slightly different chemical environment, and this eventually leads to the peak broadening.

We have redirected some of the discussion in the Main Text to our recent publication for further details and have adjusted some of the text accordingly to reflect some of the discussion here.

Main Text amendment

At longer reaction times, r increases monotonically. While this growth ~~and~~ agrees well with theoretical values calculated for perfect hexagonal polycyclic structures, the lack of linearity implies platelet growth may incur some defect formation.

[1] Z. Wei *et al.*, *J. Am. Chem. Soc.* 147, 5921–5932 (2025)

Reviewer: *The concept of “skewness” is not well defined, and it is not clear to this referee how it can be used to conclude that the material is of 2D nature, rather than a 3D network for example.*

Our Response: Following our previous response, the concept of skewness (s) is more thoroughly fleshed out in our recent publication [1] that only became available after this manuscript was under review. We note that s is not a standalone metric for deciphering 2D vs 3D networks. Additional techniques, such as the anisotropic PL discussed above, are also needed.

To help clarify the concept and use of s , we define s as a metric for the skewness of the aromatic region. As discussed in our last response, the peak position and peak width are affected by the polymer's intramolecular interactions and tumbling rate. We note that, for oligomeric species of 2DPA-1, as the species grow, there is a quantifiable change in the distribution of the peak positions within the aromatic H region. We used the mathematical definition of skewness to quantify this shift in peak positions—referred to here as s .

Reviewer #3:

In addition, we realized that people have reported this type of aromatic peak shifting when synthesizing aramid dendrimers utilizing 1,3,5 benzamide core, similar to the 2D polyaramids explored in this work. As Bayliff et al [2], Luo et al [3], and Yuan et al [4] reported, downshifting or upshifting aromatic proton peaks in their ^1H NMR spectra helped differentiate the protons in the core versus the pendant in their aramid dendrimer materials. We also noticed the overall downshifting trend of aromatic proton peaks with respect to increasing reaction time. It is worth noting that this metric cannot necessarily be used to classify a material as 2D vs 3D. Rather, using the skewness of aromatic peak positions helps quantify the change in core vs pendant protons and hence provide us an additional metric to characterize the nature of the 2DPA-1 synthesis. Additional techniques, such as the anisotropic PL discussed above, are needed to characterize a 2D vs 3D structure.

- [1] Z. Wei et al., *J. Am. Chem. Soc.* 147, 5921–5932 (2025)
- [2] P.M. Bayliff et al., *Polym. Bull.* 29, 265-270 (1992)
- [3] X.-Z. Luo et al., *J. Am. Chem. Soc.* 135, 11684-11687 (2013)
- [4] L. Yuan et al., *J. Am. Chem. Soc.* 126, 11120-11121 (2004)

Reviewer: *The results from this work are compelling, and the properties observed are unique (and remarkable) for processable polymeric materials. However, it isn't clear why these materials have such good properties. They have no long-range order (by X-ray diffraction methods) making it difficult to characterize the structure and the bulk structure is ambiguous by NMR analysis. It is also not clear how a relatively simple step-growth polymerization would result in a 2D material with few macroscopic defects, rather than a mixture of 2D and 3D network polymers.*

Our Response: We thank the reviewer for their positive assessment of the work conducted in this study and their recognition of the remarkable nature of the measured polymer properties. We hope that our preceding data and discussion clarified that, although our material lacks long-range order which would be detected as crystallinity by conventional X-ray scattering techniques, it does still possess molecular order. The lamellar ordering of spin-coated 2DPA-1 nanofilms is evidenced by the TEM image analysis in the Main Text (**Fig. 1D-E**), the anisotropic PL discussed herein, and the PXRD/REDACTED investigation. Additionally, we recently submitted a manuscript for publication, now available on *ChemRxiv* [1], with a more detailed analysis of over 3000 platelets from TEM images, measuring disk diameter, circularity, electron beam extinction to estimate thickness, and quantized layering to support discussion on the molecular order of this material (**Figs. R8-9**).

Additionally, we hope our preceding discussion helped clarify our use of ^1H NMR trajectories to characterize the solution-phase properties of 2DPA-1 platelets. As mentioned previously, further details can be found in our recently published manuscript in *JACS* [2].

REDACTED

Lastly, we would like to respectfully note that the intent of this work was to reveal the extreme inhibition of molecular transport across 2DPA-1 nanofilms and the limits of these properties. Although supported in this work, complete validation of the polymer's 2D nature was demonstrated for the original synthesis of 2DPA-1 [3]. The mechanisms for achieving this 2D

Reviewer #3:

architecture over a more kinetically favored 3D network were explored in a follow-on study [4], which revealed that reactions featuring high bond planarity, templated auto-catalysis of the monomers, and balanced monomer activation rates can lead to near-perfect yield of 2D polymers via step-growth polymerization. Free volume elements are ubiquitous to the entangled chains of 3D network polymers, giving rise to molecular permeability in all polymers. Hence, a mixture of 2D and 3D polymer networks in 2DPA-1 is likely to result in measurable gas permeability across the nanofilm, which was not found in this study. Therefore, we feel confident in the findings of this study—which we postulate could only be enabled by the elimination of free volume by the tight packing of the 2D platelets that comprise 2DPA-1.

- [1] X. Gong *et al.*, *ChemRxiv* (2025) DOI: 10.26434/chemrxiv-2025-0gjmf
- [2] Z. Wei *et al.*, *J. Am. Chem. Soc.* 147, 5921–5932 (2025)
- [3] Y. Zeng *et al.*, *Nature*, 602, 91-95 (2022)
- [4] G. Zhang *et al.*, *J. Chem. Phys.* 154, 194901 (2021)

Reviewer #1:

Reviewer: *The authors have conducted extensive additional experiments that satisfactorily address my previous concerns. I now have only one minor comment regarding the introduction of the term "nonporous COFs" in the revised manuscript. COFs, by definition, are porous, crystalline polymers, as first reported in Science 2005, 310, 1166-1170. The use of the term "nonporous COFs" appears conceptually inconsistent with this foundational definition and may need reconsideration or further clarification. In membrane or film form, COFs could exhibit impermeability or very limited permeability to ultrafine gas molecules. However, such behavior typically results from unique stacking configurations, such as random stacking, that obstruct accessible channels and create highly tortuous transport pathways. Nevertheless, the COF frameworks still possess inherent porosity.*

Our Response: We thank the reviewer for their positive assessment of our original work and supplemental experiments. The reviewer raises a valid concern regarding the use of the word nonporous. We have reframed this to “impermeable COFs,” signifying overwhelmingly large energy barriers that prevent or severely hinder molecular transport across the porous structure.

Several strategies exist to process COFs for thin film applications¹⁴⁻¹⁶, but experimental realization of impermeable~~nonporous~~ COFs¹⁷ remains wanting due to the formation of defects¹⁸.

Reviewer #2:

Reviewer: *Authors have done sufficient work to satisfy the majority of questions. Still, there is no compelling information regarding the crystallinity of 2DPA-1 films. I suggest showing a diffraction pattern from high-resolution TEM for crystallinity. This would provide more compelling evidence. The authors measured the BET analysis and obtained a surface area of 74±10 m² g⁻¹ and claimed a pore volume of 0.41±0.07 cm³ g⁻¹. This number is extremely high for a non-porous material and suggests high porosity. I suggest checking it again and calculating once more to make sure that this pore volume is correct.*

Our Response: We appreciate the reviewer’s recognition of the quality of our supplemental work to support the findings of this study. We direct the reviewer to our recently accepted publication on transmission electron microscopy (TEM) analyses of 2DPA-1 [1], where we provided a selected area electron diffraction (SAED) pattern of the nanofilm. The SAED pattern is included here for convenience (**Fig. R1**) and provides additional structural organization insight. The diffraction spots and arcs suggest some degree of crystallinity, due to the ordered molecular packing observed.

We note that the interpretation of pore volume should be done with caution, as the evaluation of total pore volume determined from the N₂ sorption isotherm is not reliable with macropores present. Macropores are the result of interstitial spaces between imperfectly packed particulates and lead to additional adsorption that prevents isotherm plateau near $P/P_0 = 1$ and, consequently, also the use of the Gurvich rule to accurately measure pore volume [2]. As discussed in the Methods section (lines 73-592), the H3 hysteresis in the N₂ isotherms is attributed to non-rigid aggregates of plate-like particles or pore network consisting of macropores that are not completely filled with condensate [2].

When compared to typical porous covalent organic frameworks (order of $1000 \text{ m}^2 \text{ g}^{-1}$) [3], the measured BET surface area of 2DPA-1 is very low, and t -plot analyses (**Figs. R2-3**) corroborates that the entirety of the measured surface area by 2DPA-1 is due to external surface area from the imperfect packing of roughly 10-to-15-nm 2DPA-1 platelets (Fig. 1B in Main Text) rather than the surface area of the micropores inherent to the 2DPA-1 unit cell. In brief, the t -plot shows the adsorbed amount of gas plotted against the adsorption layer statistical thickness, t , using a reference t -curve (P/P_0 as a function of t from a nonporous material) [4]. The y-intercept and slope determine the micropore volume and external surface area, respectively. Our analysis of the adsorption isotherms with both the de Boer and Carbon Black models indicate zero or negligible contribution from micropores.

This also agrees well with other materials such as $\text{Mg}(\text{OH})_2$ [5] or natural clay [6], which typically produce measurable surface area due to external area from particulate packing. The external surface area measured for nanoparticle forms of these materials is commensurate with that observed for bulk 2DPA-1. We have provided an additional pore size distribution and pore volume determination via Quenched Solid density function theory (QSDFT) for comparison by the reviewer with our initial determination using the BHJ method (**Fig. R4**). QSDFT is based on the equilibrium branch, rather than the desorption branch, of the N_2 isotherm at 77 K using a kernel for carbon slit/cylindrical pores. QSDFT suggests a mode pore size of 13 nm and a pore volume of 0.30 cc g^{-1} , again contributed entirely from meso- and macropores rather than intrinsic micropores.

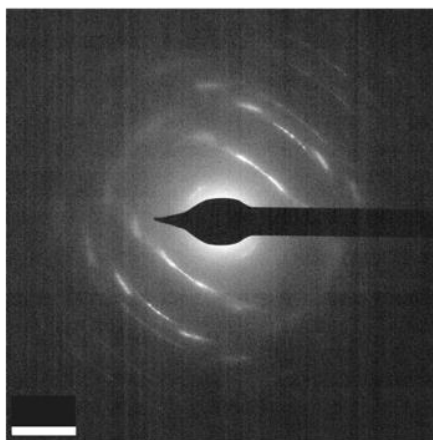


Fig. R1. Selected area electron diffraction (SAED) pattern, suggesting a well-to-partially ordered sheet-like structure (scale bar: 5 nm).

Method Parameters

Statistical Thickness Model deBoer

t-plot Method Results

Slope	5.099262 cm ³ STP/Åg
Intercept	-0.801857 cm ³ STP/Åg
Correlation coefficient, r	0.999872
Micropore Volume	0 cm ³ /g
Micropore Area	0.000 m ² /g
External Surface Area	78.534 m ² /g

Graph - t-plot Method

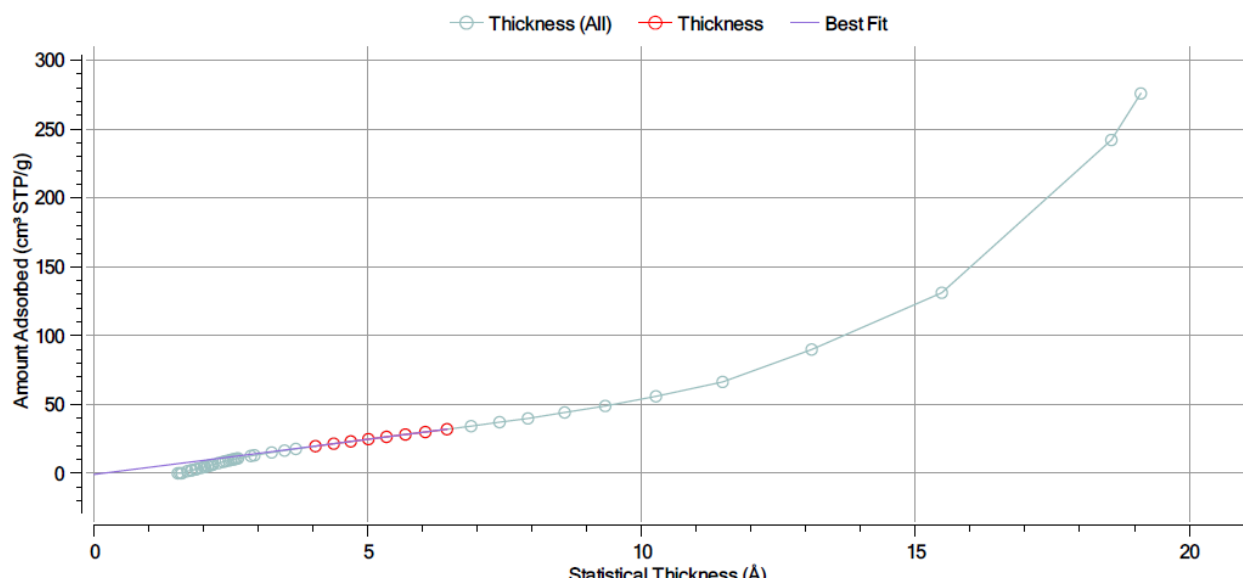


Fig. R2. t-plot analysis comparing external surface area to internal (i.e., micropore) surface area of 2DPA-1 using the deBoer model.

Method Parameters

Statistical Thickness Model Carbon Black

t-plot Method Results

Slope	4.970909 cm ³ STP/Åg
Intercept	0.001676 cm ³ STP/Åg
Correlation coefficient, r	0.999767
Micropore Volume	2.59878e-06 cm ³ /g
Micropore Area	1.452 m ² /g
STSA External Surface Area	77.082 m ² /g

Graph - t-plot Method

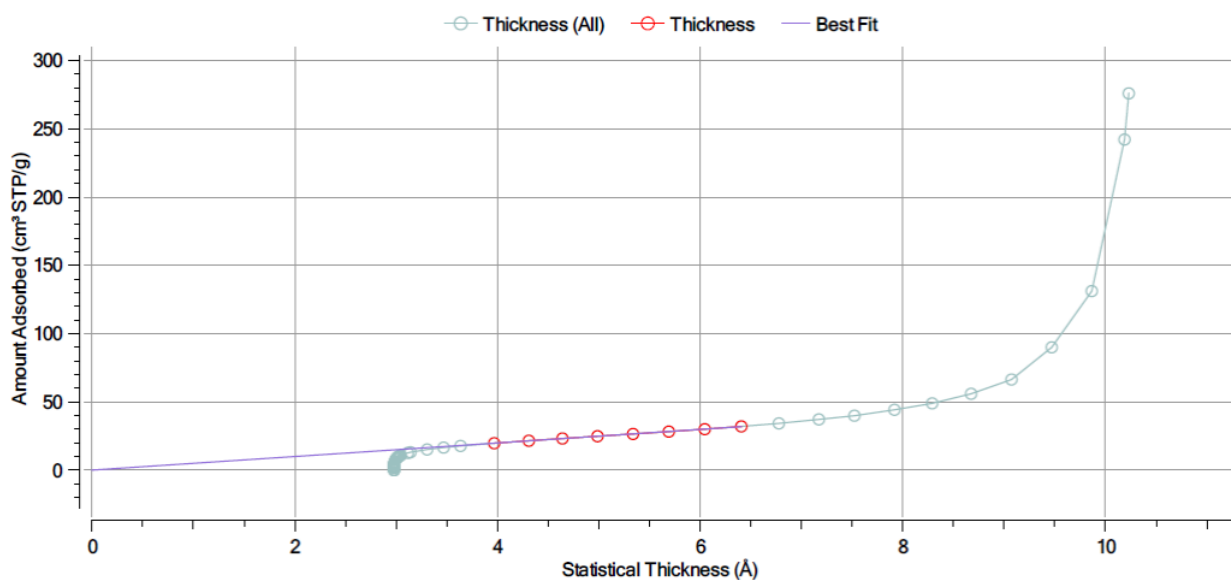


Fig. R3. *t*-plot analysis comparing external surface area to internal (i.e., micropore) surface area of 2DPA-1 using the Carbon Black model.

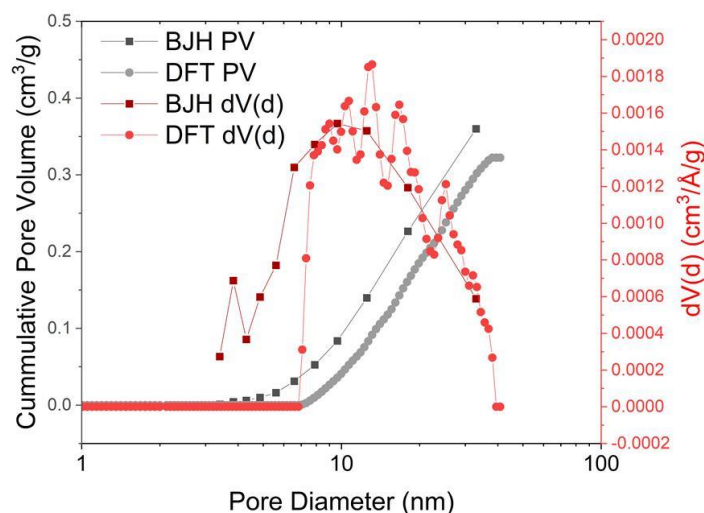


Fig. R4. Comparison of pore size distributions calculated by BJH and QSDFT methods.

- [1] X. Gong et al., *ACS Appl. Nano Mater.* 8, 16994-17003 (2025)
- [2] M. Thommes et al., *Pure Appl. Chem.* 87, 1051-1069 (2015)
- [3] X. Li et al., *Chem. Synth.* 4, 15 (2024)
- [4] J.H. de Boer et al., *J. Colloid Interf. Sci.* 21, 405-414 (1966)
- [5] J.C. Yu et al., *J. Phys. Chem. B*, 108, 64-70 (2004)
- [6] J. Rouquerol et al., *Adsorption by powders and porous solids: Principles, methodology, and Applications*, Chapter 11 (Academic Press, Oxford, UK) 2014

Reviewer #3:

Reviewer: *This referee appreciates that this is a new approach to the synthesis so the characterization needs to be somewhat unconventional (the authors previously published work on this topic notwithstanding). I think the authors have satisfactorily answered my original concerns, and I will note that the recent JACS paper describing the proton NMR characterization technique used to characterize the 2D polyamides was enormously convincing. With all of these revisions, this manuscript should be acceptable for publication.*

Our Response: We sincerely thank the reviewer for recognizing the importance and quality of our work and appreciate their favorable consideration.