
Supplementary information

**A molecularly impermeable polymer from
two-dimensional polyaramids**

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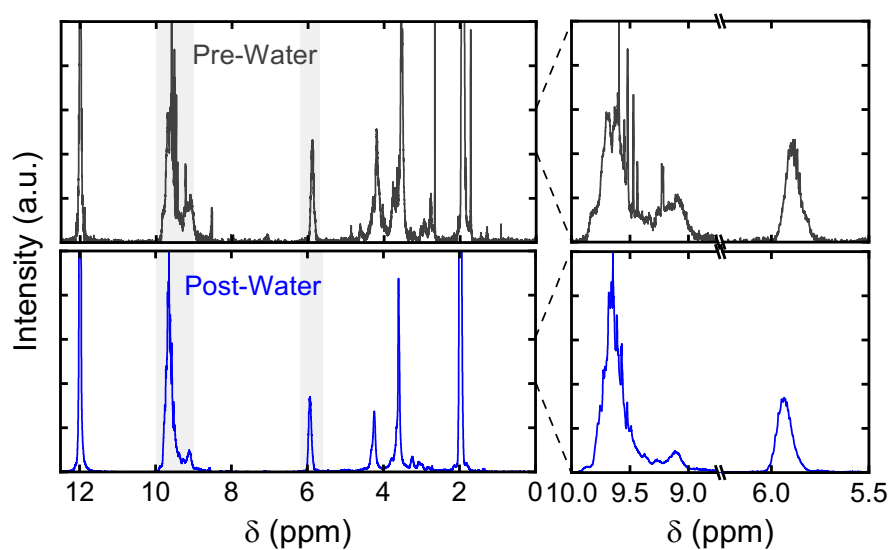
Supplementary Information for
A Molecularly Impermeable Polymer from Two-Dimensional Polyaramids

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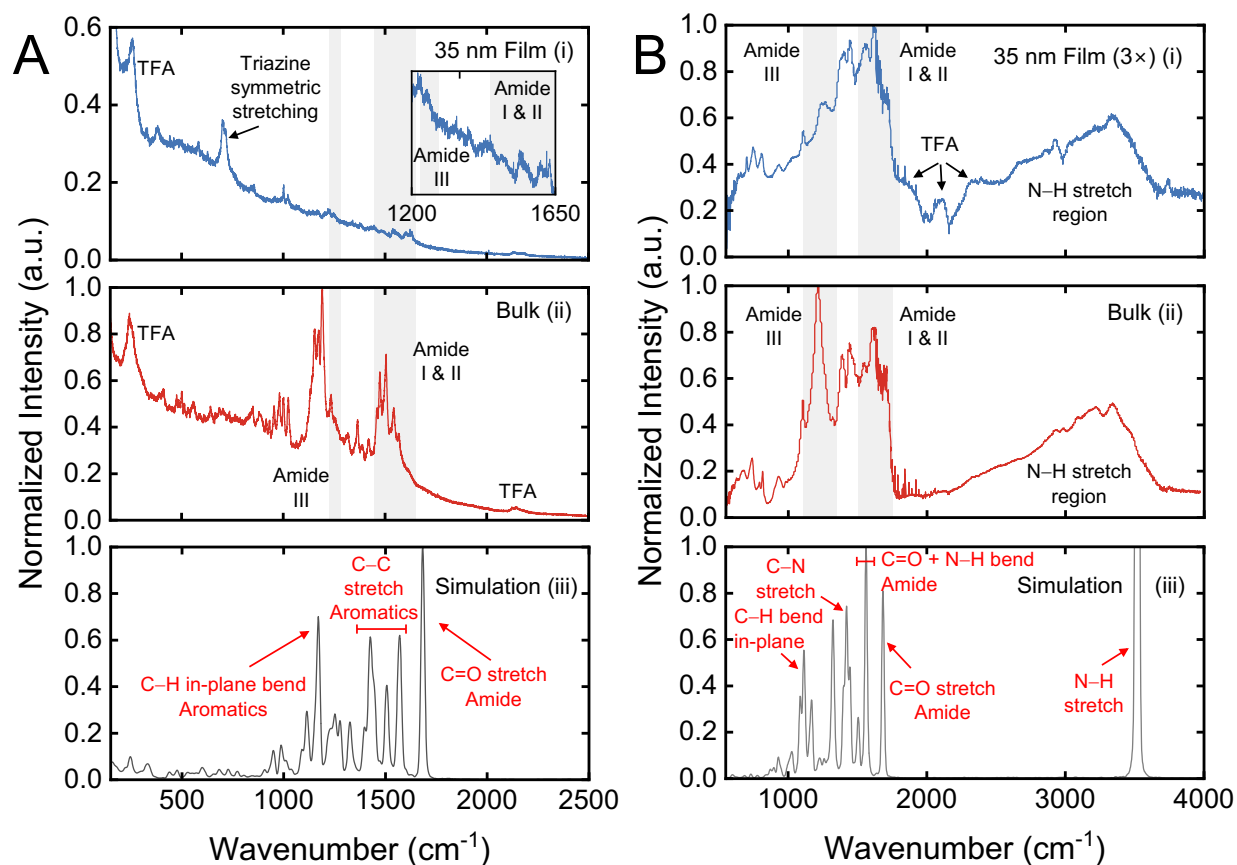
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Supplementary Figs. 1 – 29
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Supplementary References



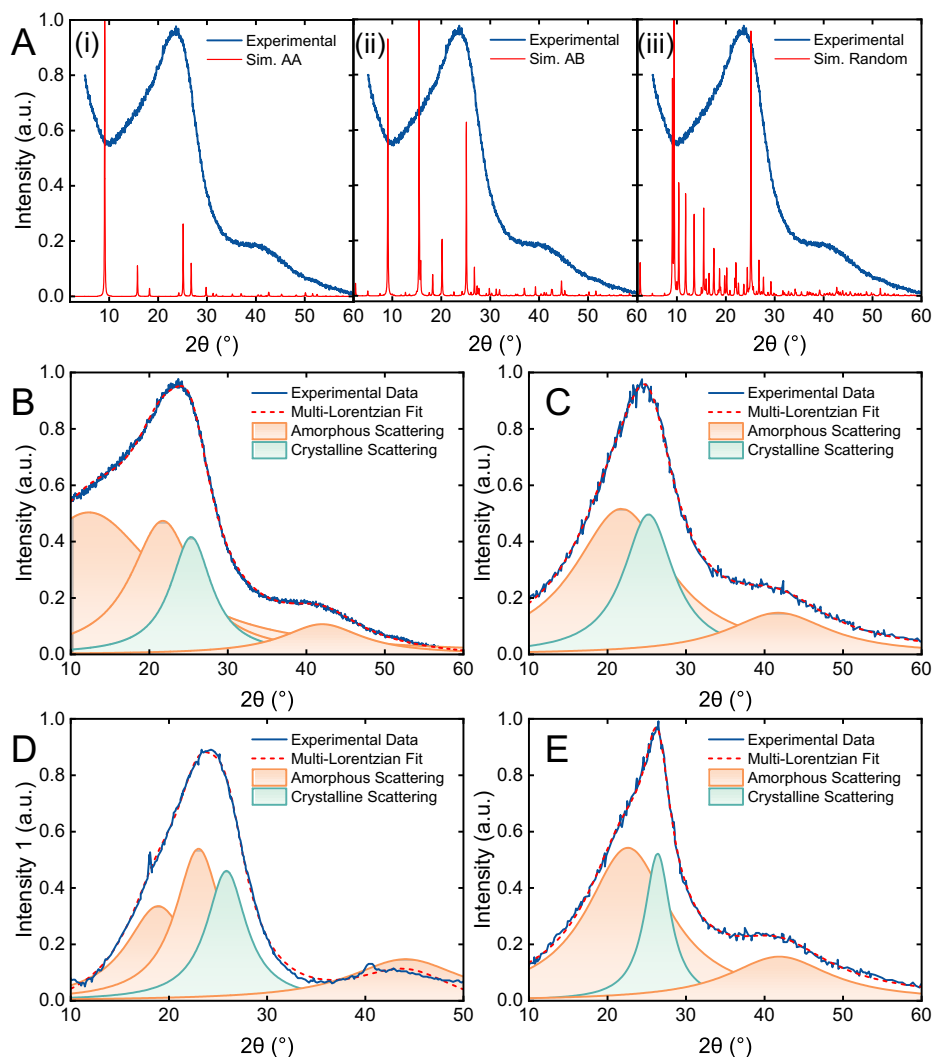
Supplementary Fig. 1.

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.



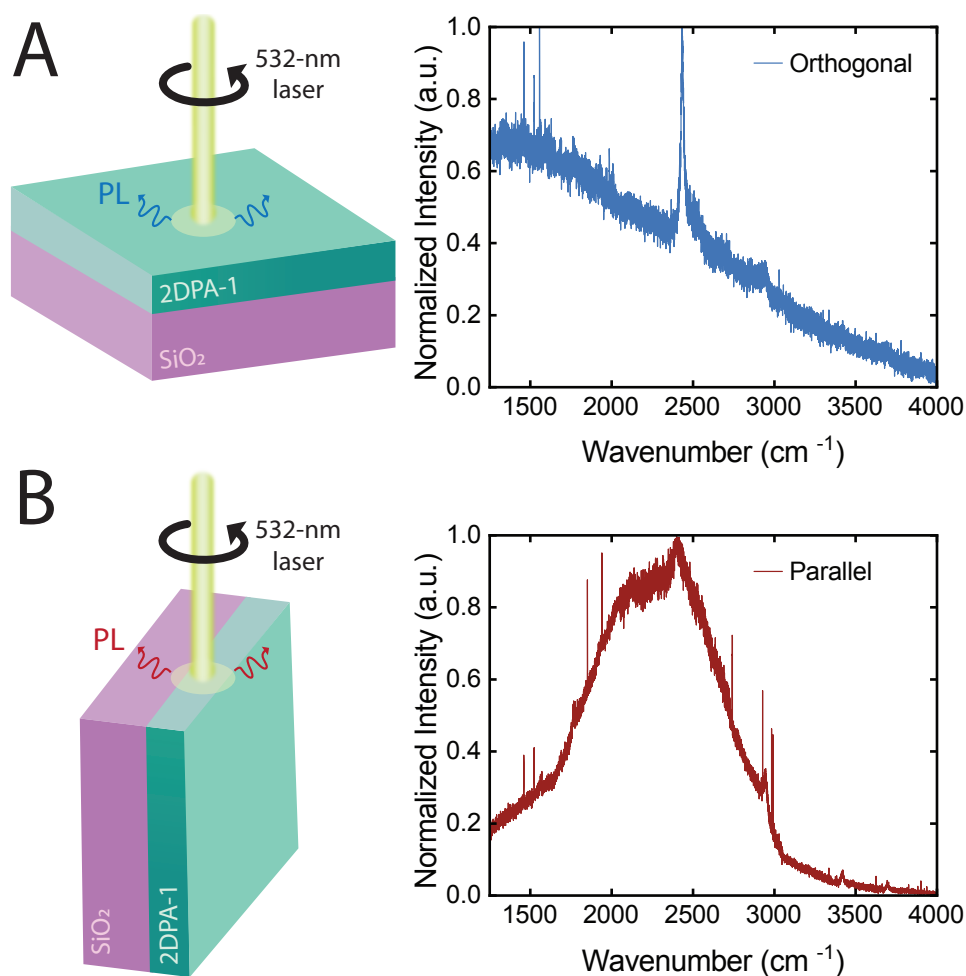
Supplementary Fig. 2.

Raman and ATR-FTIR spectroscopy of 2DPA-1. Raman (A) and ATR-FTIR (B) spectra of 2DPA-1 were 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 $\sim 100 \text{ nm}$, while the bulk sample was 2DPA-1 powder.



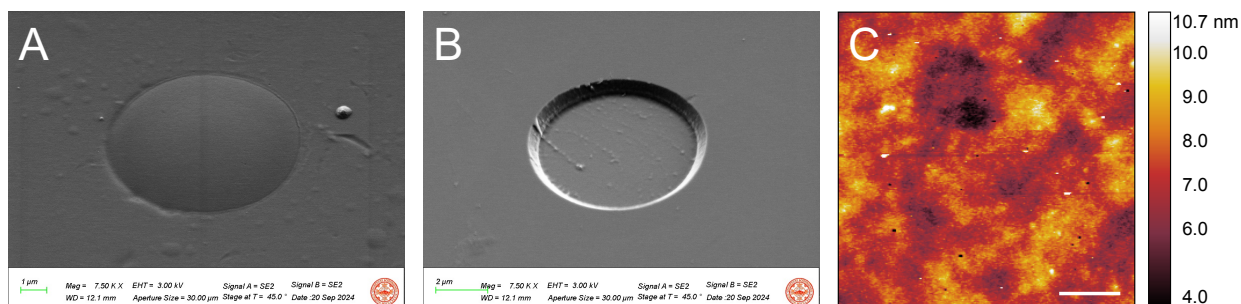
Supplementary Fig. 3.

Powder X-ray diffraction, PXRD, of 2DPA-1. 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 %.



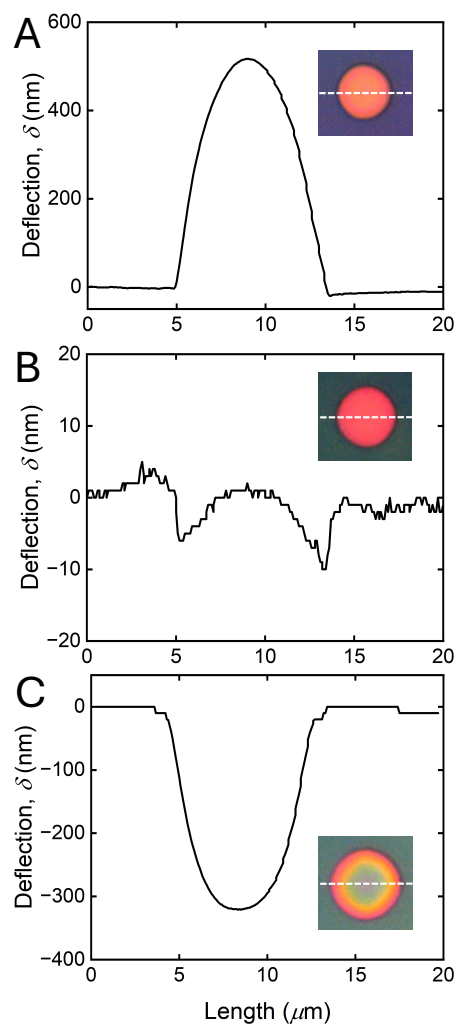
Supplementary Fig. 4.

Photoluminescence, PL, measurements of 35-nm 2DPA-1 film. Film was measured 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.



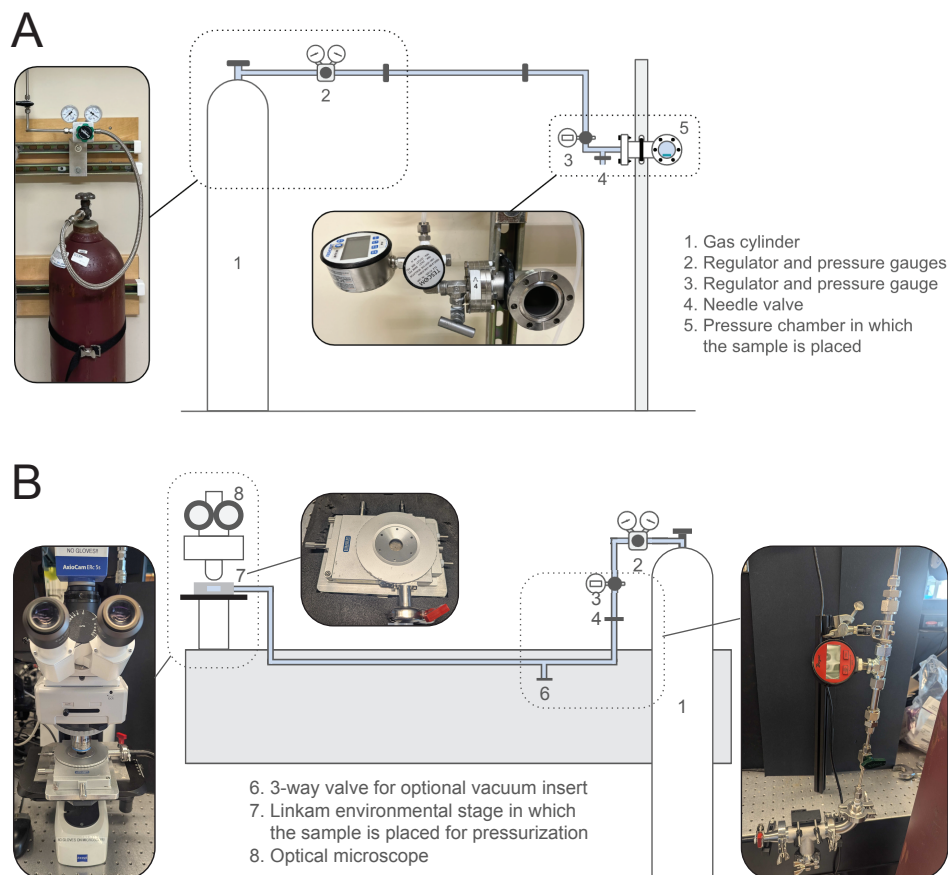
Supplementary Fig. 5.

Scanning emission microscopy, SEM, images of a 35-nm 2DPA-1 film. (A) Suspended and (B) collapsed film over a 10- μm -diameter well etched 1 μm into a SiO_2/Si substrate. (C) AFM image of 2DPA-1 nanofilm surface topology. Scale bar represents 2 μm . Root mean square, RMS, roughness was determined over a 5 $\mu\text{m} \times 5 \mu\text{m}$ area.



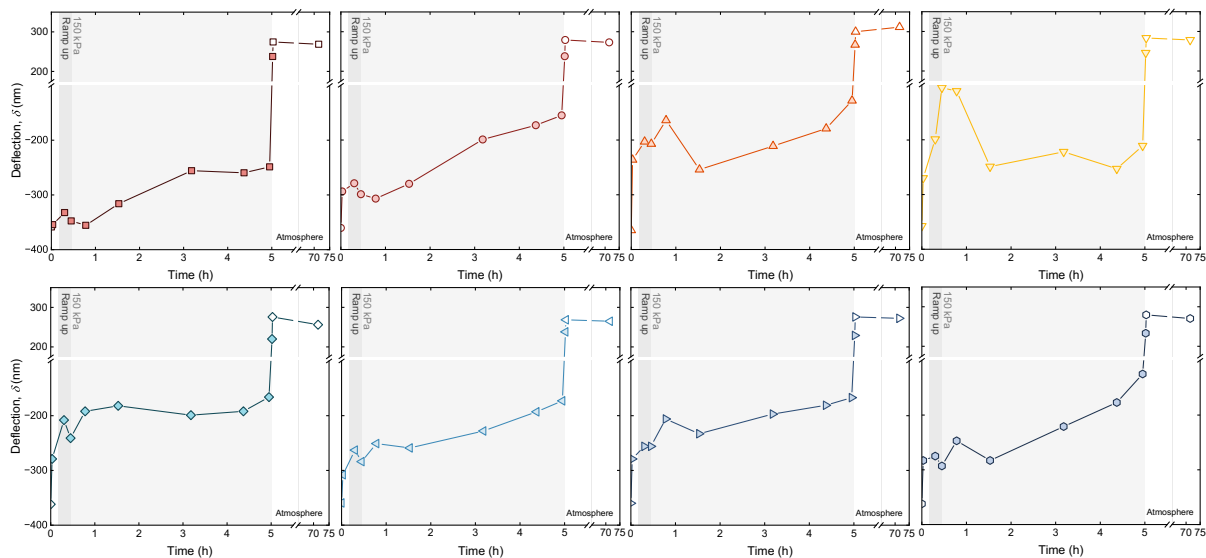
Supplementary Fig. 6.

Deflection profiles of suspended films and their corresponding optical images. Data collected after transfer to silicon oxide substrate and subsequent etching of polystyrene support layer. (A) Bulged up film, (B) flat film, and (C), dimpled downward film. The dimpled downward film was only formed after including a 50 °C annealing step prior to etching the polystyrene support layer.



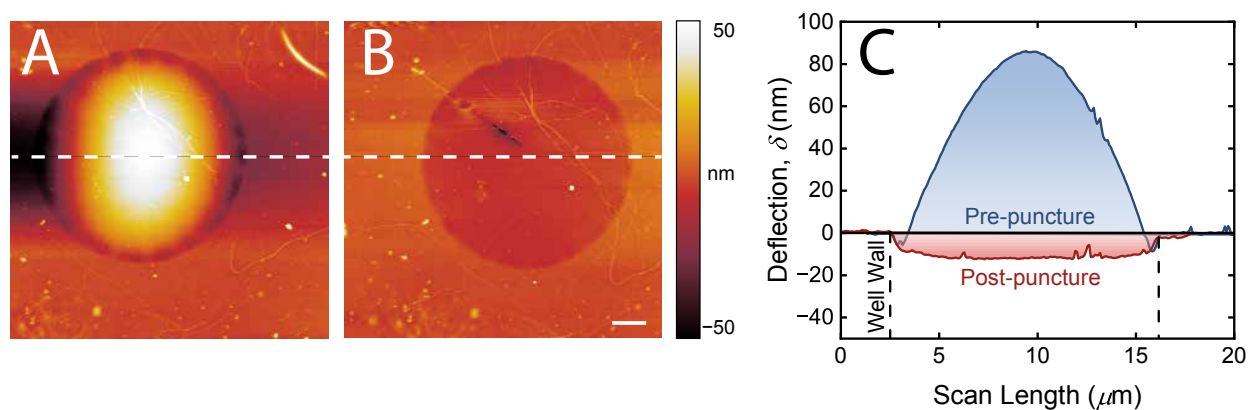
Supplementary Fig. 7.

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 H_2 , is ideal for optically monitoring bulge pressurization dynamics and can be retrofitted with a vacuum insert. Inset images depict photographs of pressurization apparatus in highlighted regions (dashed line).



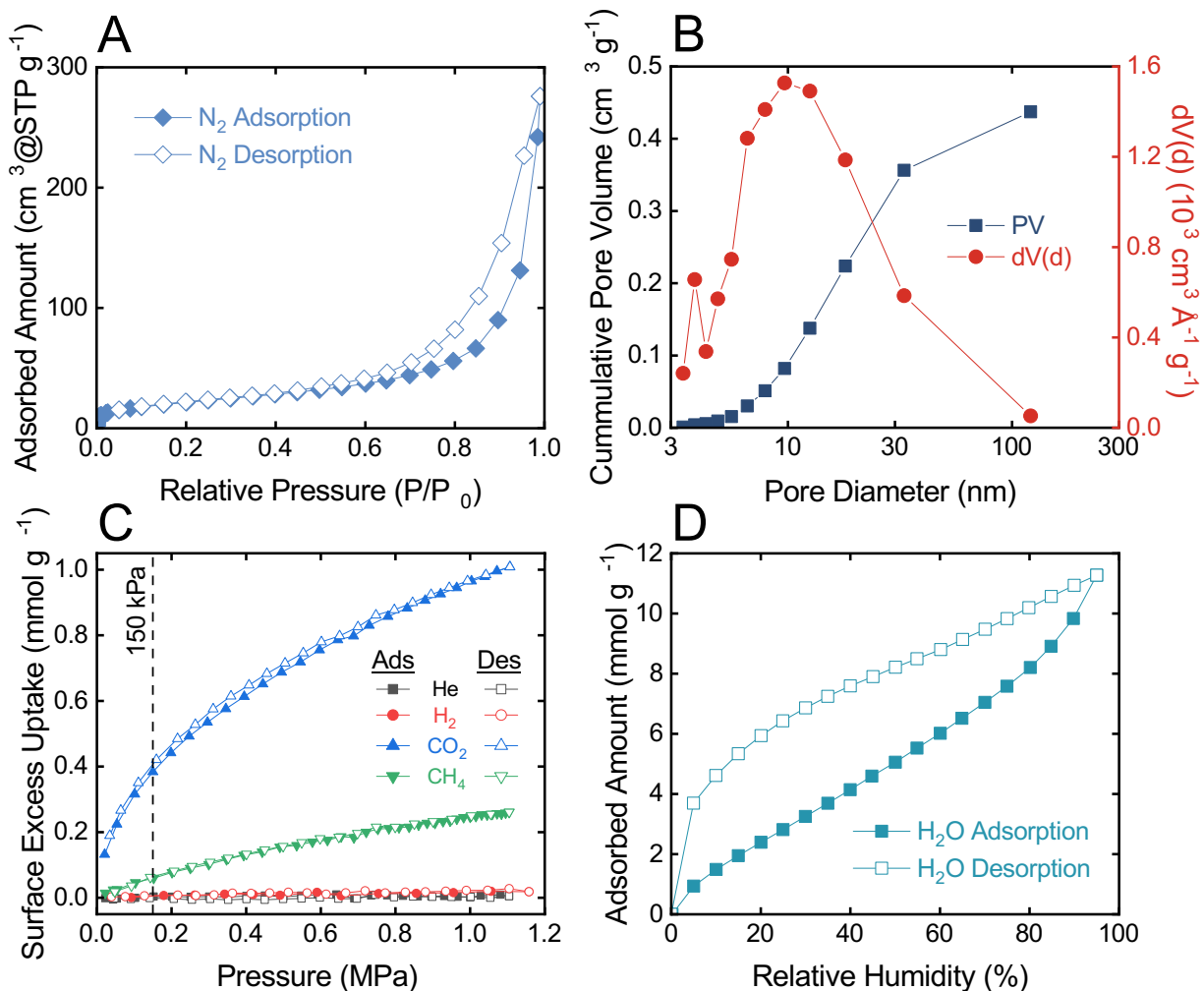
Supplementary Fig. 8.

Deflection of eight bulges determined before, during, and after pressurization with 150 kPa N_2 . Deflection of bulges measured via AFM before and after pressurization are represented by symbols without fill color. Deflection of bulges estimated using RGB optical analysis while confined within the glass-sealed environmental chamber are represented by symbols with fill color.



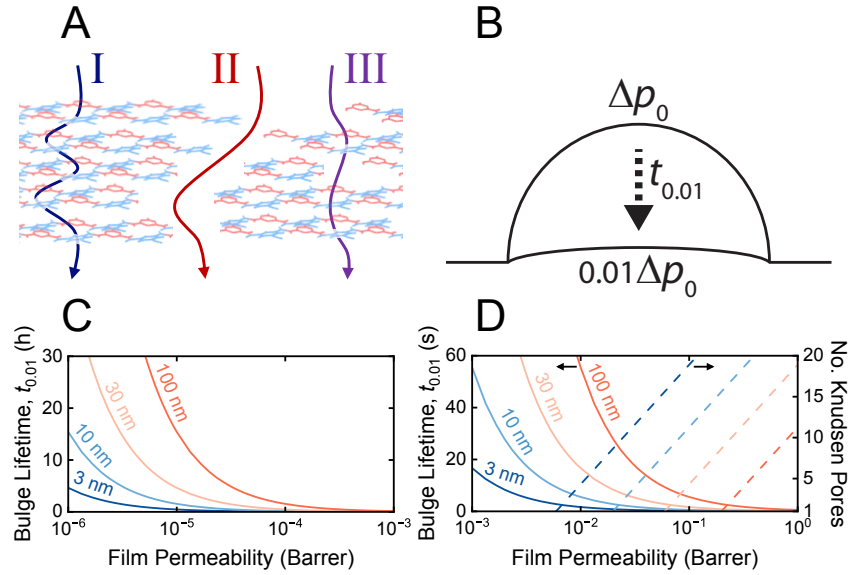
Supplementary Fig. 9.

Puncturing inflated bulge. Atomic force microscopy, AFM, image of bulge (A) before and (B) after being punctured by the AFM tip. The scale bar (solid white line) represents 2 μm . (C) Cross-sectional deflection profiles corresponding to slices from panels A and B, marked by the dashed white lines. Dashed black lines are approximations for the walls of the microwell.



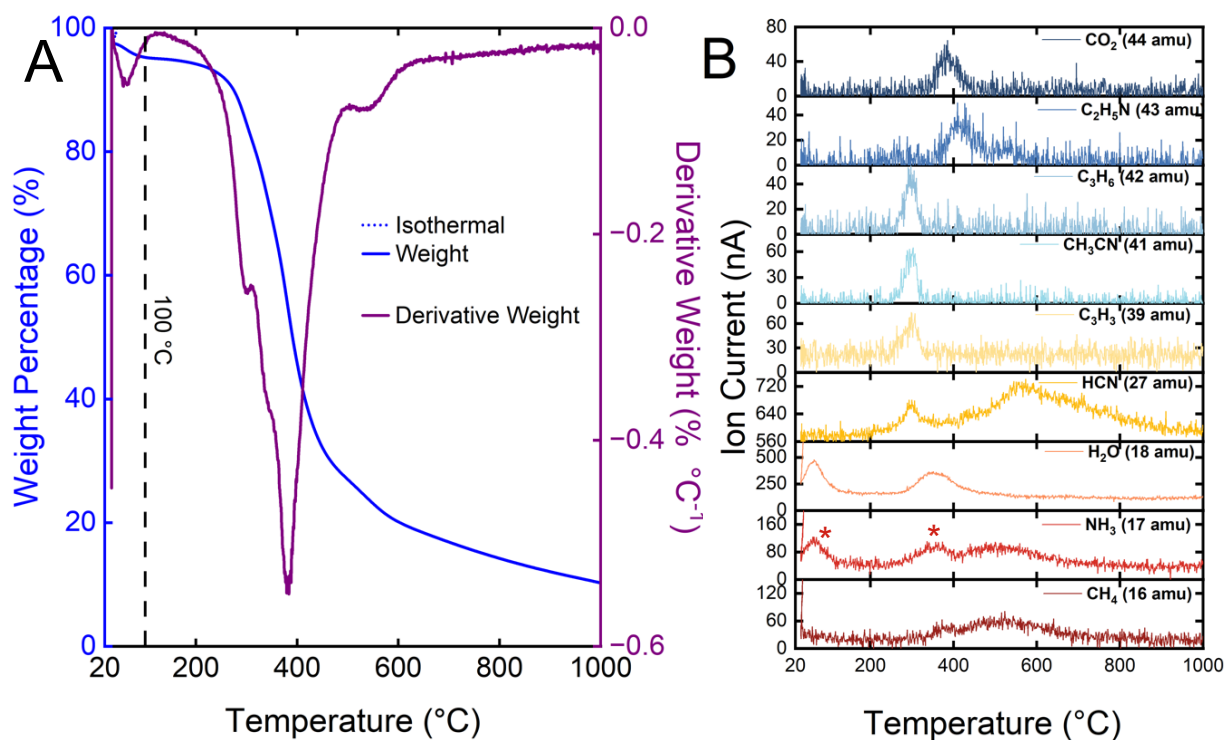
Supplementary Fig. 10.

Gas adsorption measurements for bulk 2DPA-1 using various probe molecules. (A-B) Representative (A) N_2 adsorption isotherm at 77 K and the (B) corresponding pore size distribution determined from BJH method. (C) Unary He, H_2 , CH_4 , and CO_2 adsorption isotherms at 298 K. (D) H_2O vapor adsorption isotherm at 298 K with N_2 as carrier gas.



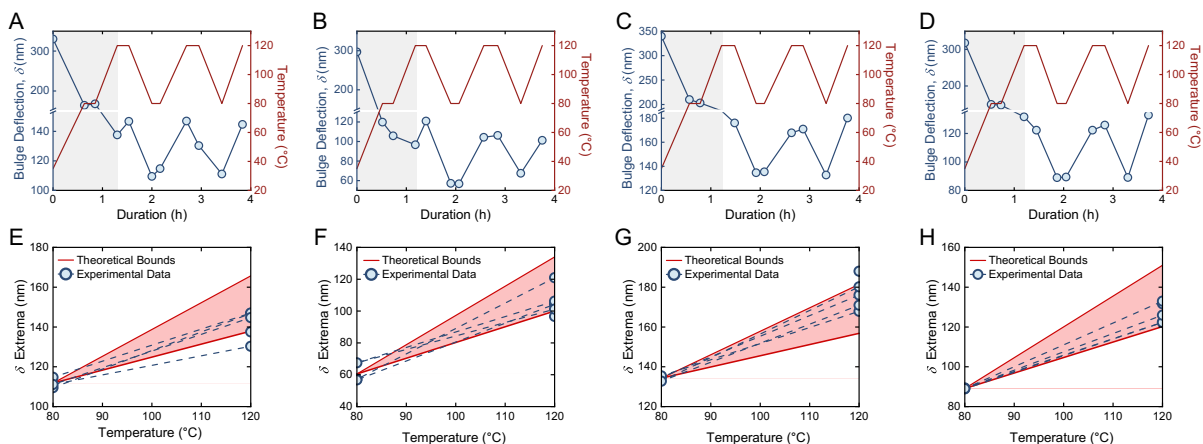
Supplementary Fig. 11.

Bulge deflation mechanisms. (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.



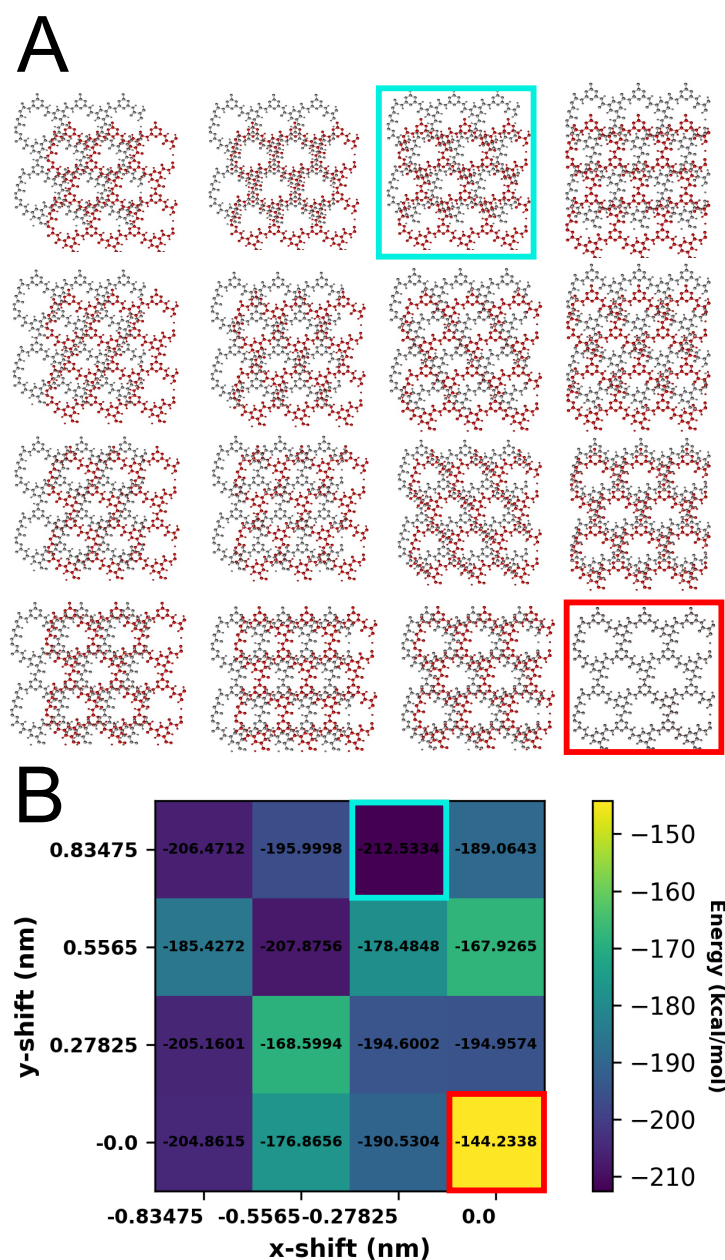
Supplementary Fig. 12.

Thermogravimetric analysis and mass spectrometry, TGA-MS, 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.



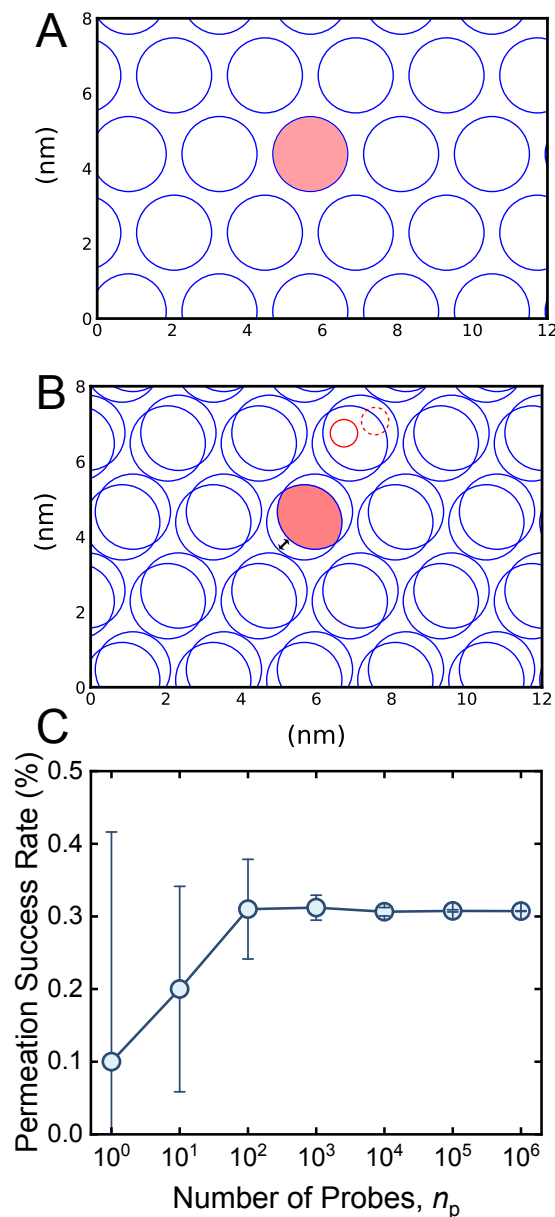
Supplementary Fig. 13.

Temperature dependence of bulge deflection. (A-D) In-situ bulge deflections (left y-axis) measured at elevated temperatures (right y-axis) over time while heating to $90\text{ }^{\circ}\text{C}$ to evaporate surface-bound water or residual TFA. The initial temperature ramp is highlighted by the light grey shaded region. The step rate was $0.05\text{ }^{\circ}\text{C s}^{-1}$. After ramp-up, temperatures were oscillated between $80\text{ }^{\circ}\text{C}$ and $120\text{ }^{\circ}\text{C}$. (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.



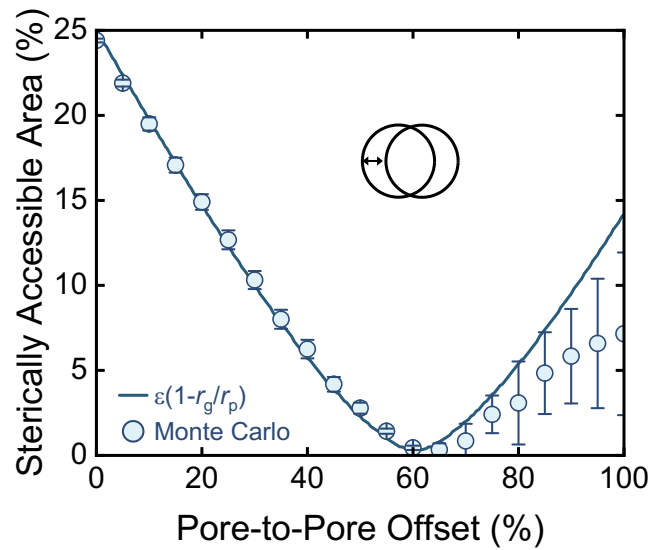
Supplementary Fig. 14.

Simulated energetics of 2DPA-1 bilayer stacking. 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, respectively.



Supplementary Fig. 15.

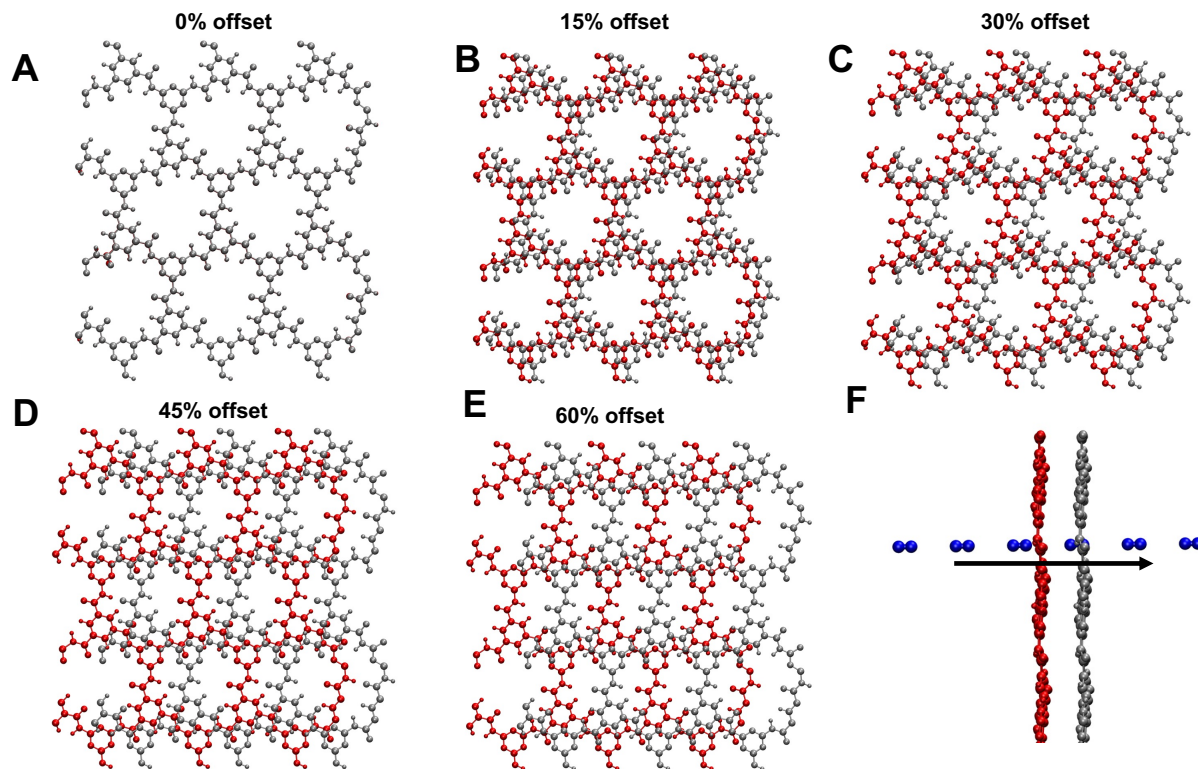
Monte Carlo simulations of stacked 2DPA-1 pores. (A-B) Geometric representation defect-free, 2DPA-1 frameworks. Blue circles represent the 1-nm-diameter pores and regions shaded red are examples of an “effective pore.” Panel A depicts a monolayer 2DPA-1 platelet. Panel B depicts a bilayer system, where the adjacent layers are offset 45° radially by $0.4r_p$. The red circles represent cases of a successful (solid line) and unsuccessful (dashed line) permeation event. (C) Sensitivity analysis for Monte Carlo simulations, comparing the permeation success rate to the number of probes, n_p , used to test the framework.



Supplementary Fig. 16.

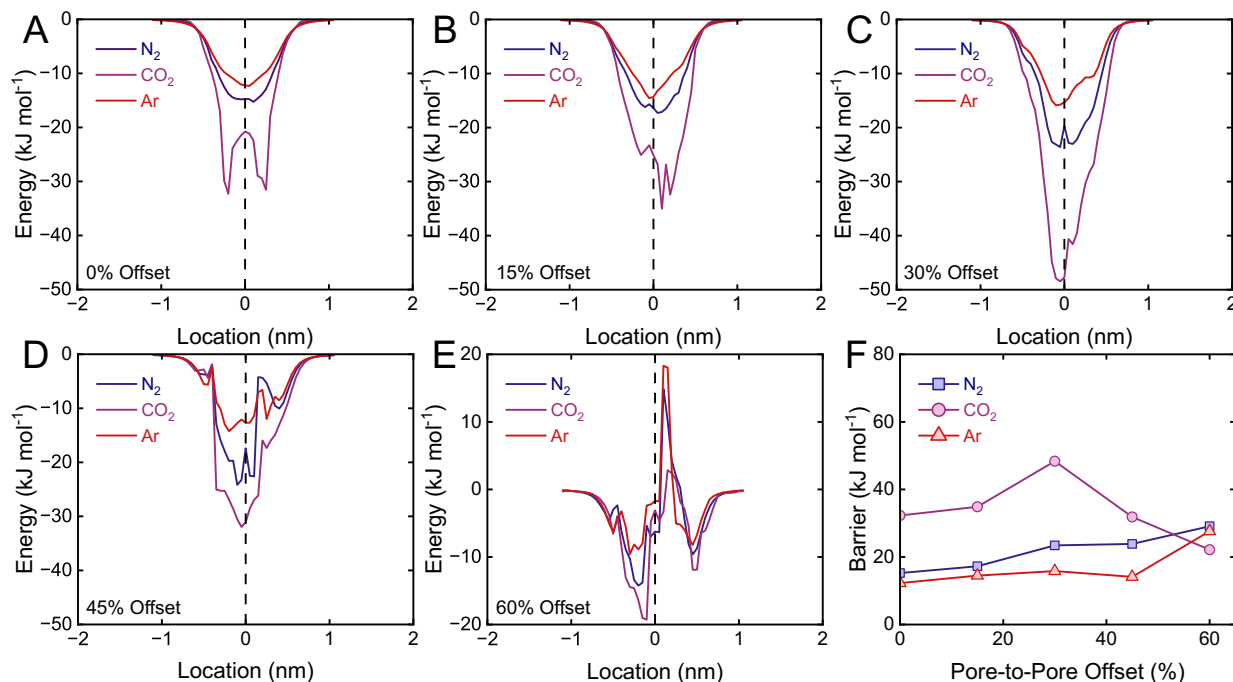
Sterically accessible area of 2DPA-1 bilayer pore with respect to pore-to-pore offset.

Sterically accessible area is defined as the percentage of area where successful permeation events can occur. Analytical solution from effusion scaling is shown as the solid blue line whereas as results from Monte Carlo simulations are represented as the blue circles.



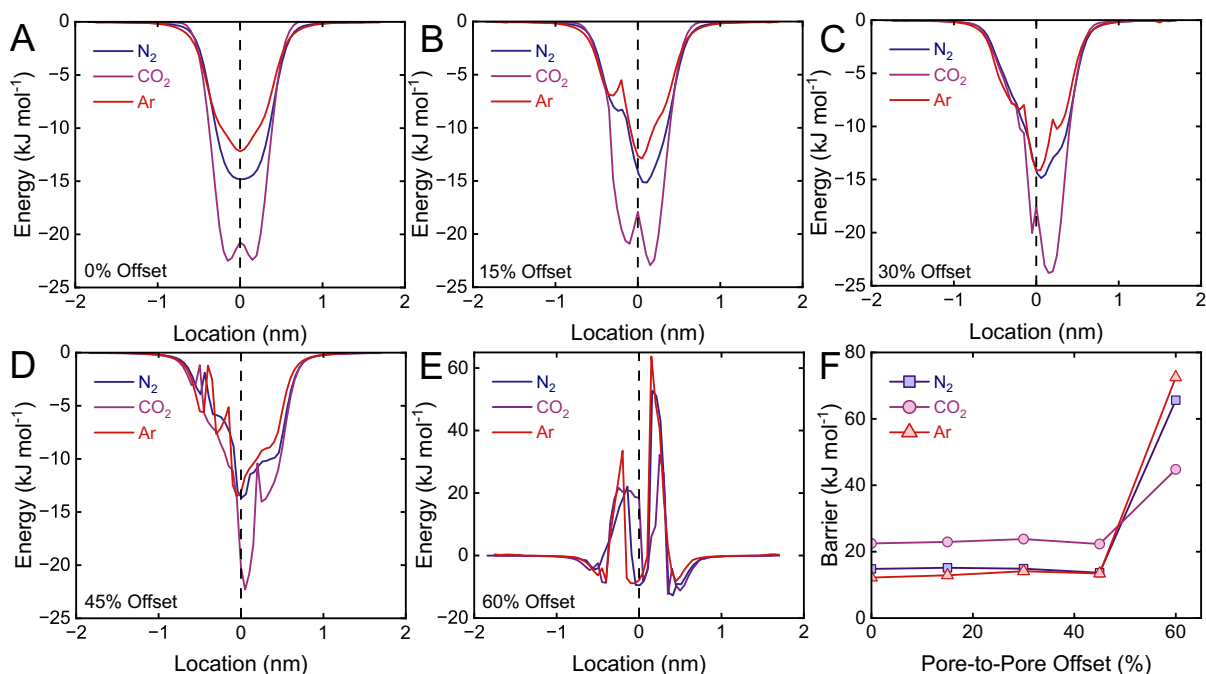
Supplementary Fig. 17.

Simulation conditions for density functional theory, DFT, translocation calculations across 2DPA-1 bilayers. (A-E) Snapshots showing a 2DPA-1 bilayer at various interlayer offsets. (F) The gas translocation path for N₂ through the simulated 2DPA-1 bilayer.



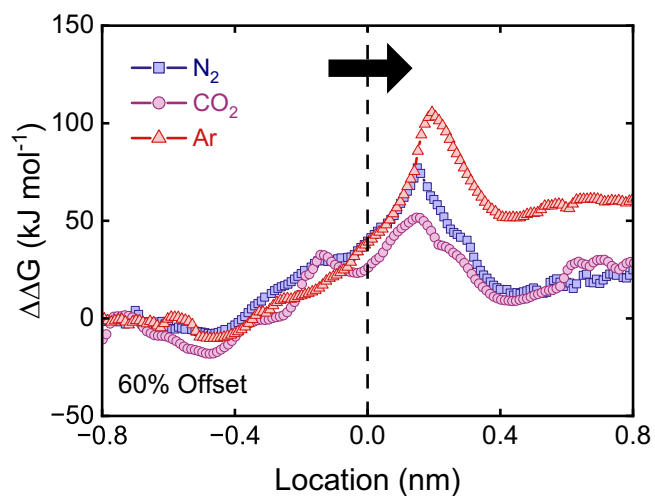
Supplementary Fig. 18.

Density functional theory, DFT, energy profiles with relaxed porous structure and relaxed gas molecules. (A-E) Energy profiles of N₂, CO₂, and Ar translocating through a 2DPA-1 bilayer with a pore-to-pore offset of 0 % (A), 15 % (B), 30 % (C), 45 % (D), and 60 % (E). The dashed line represents the center of the bilayer. (F) Computed energy barriers for N₂, CO₂, and Ar as a function of the bilayer pore-to-pore offset.



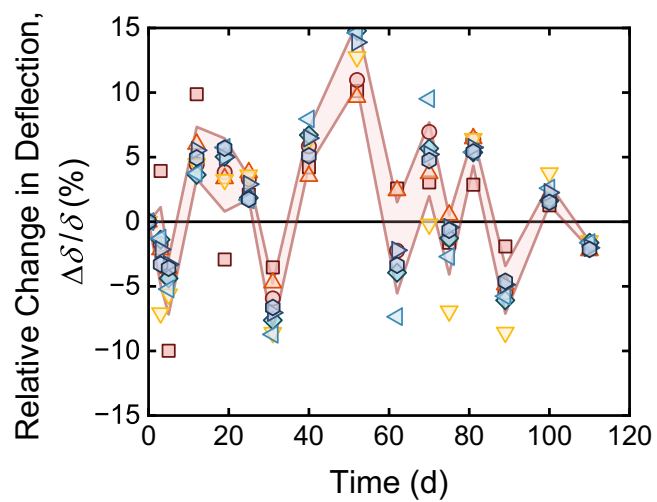
Supplementary Fig. 19.

Density functional theory, DFT, energy profiles with relaxed porous structure and fixed gas molecules. (A-E) Energy profiles of N_2 , CO_2 , and Ar translocating through a 2DPA-1 bilayer with a pore-to-pore offset of 0 % (A), 15 % (B), 30 % (C), 45 % (D), and 60 % (E). The dashed line represents the center of the bilayer. (F) Computed energy barriers for N_2 , CO_2 , and Ar as a function of the bilayer pore-to-pore offset.



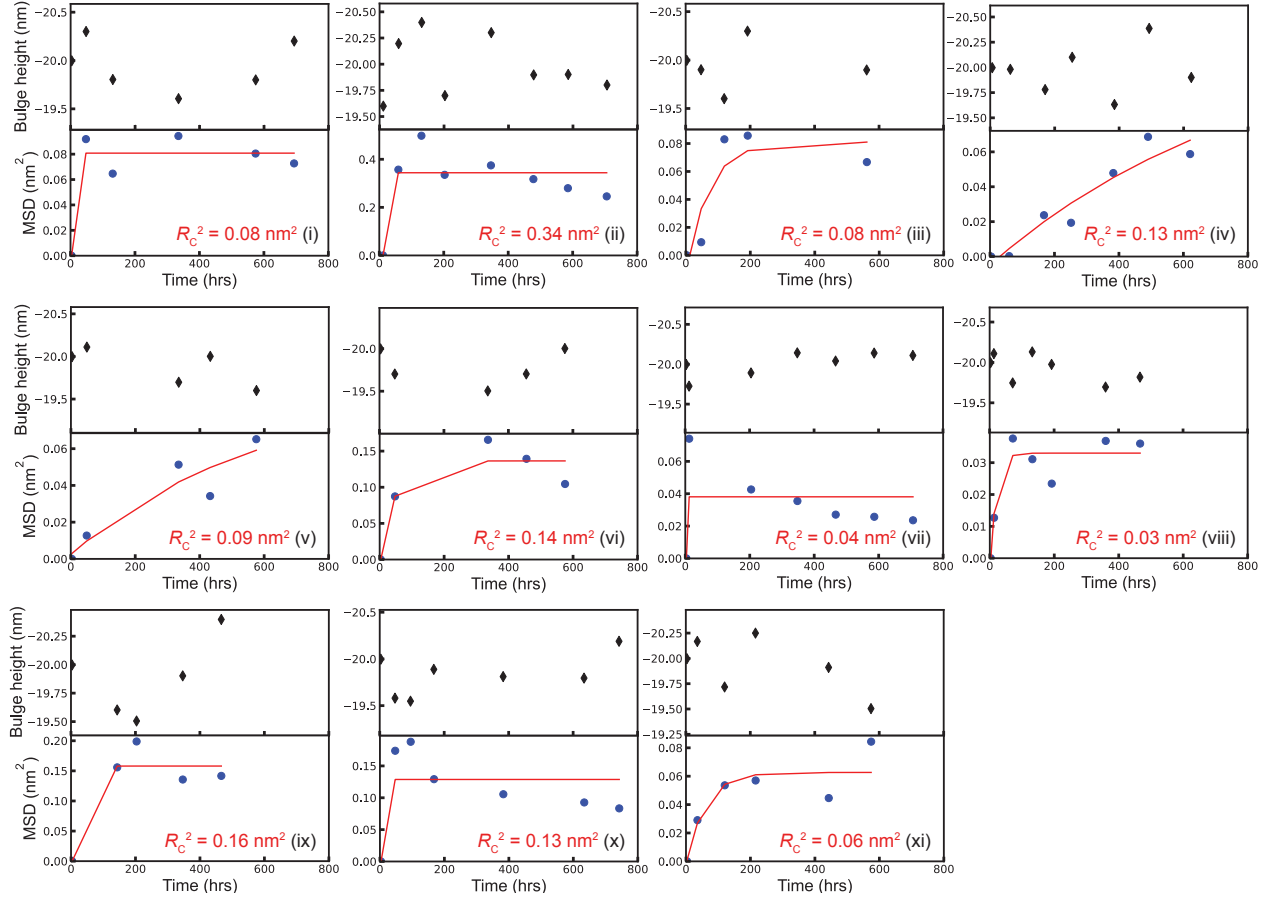
Supplementary Fig. 20.

Potential of mean force, PMF, profiles for gas translocation. Simulated for N₂, CO₂, and Ar translocating across a 2DPA-1 bilayer with a pore-to-pore offset of 60 %. The dashed line marks the center of the bilayer and the black arrow indicates the direction of the gas translocation.



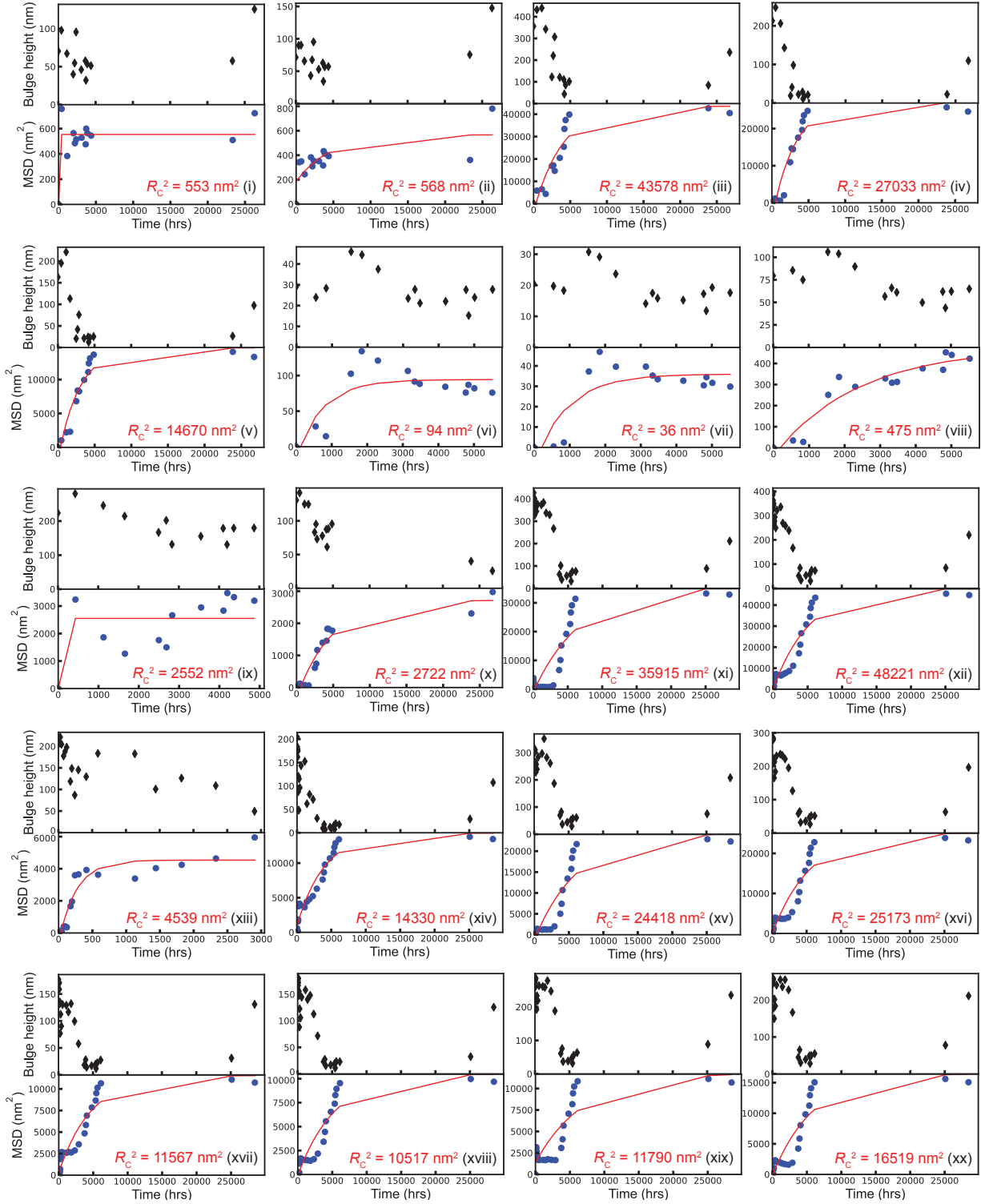
Supplementary Fig. 21.

Relative change in the deflection of bulges inflated with 150 kPa N₂ measured over 110 d.
The shaded region represents the average of the sampled values $\pm$ their standard deviation.



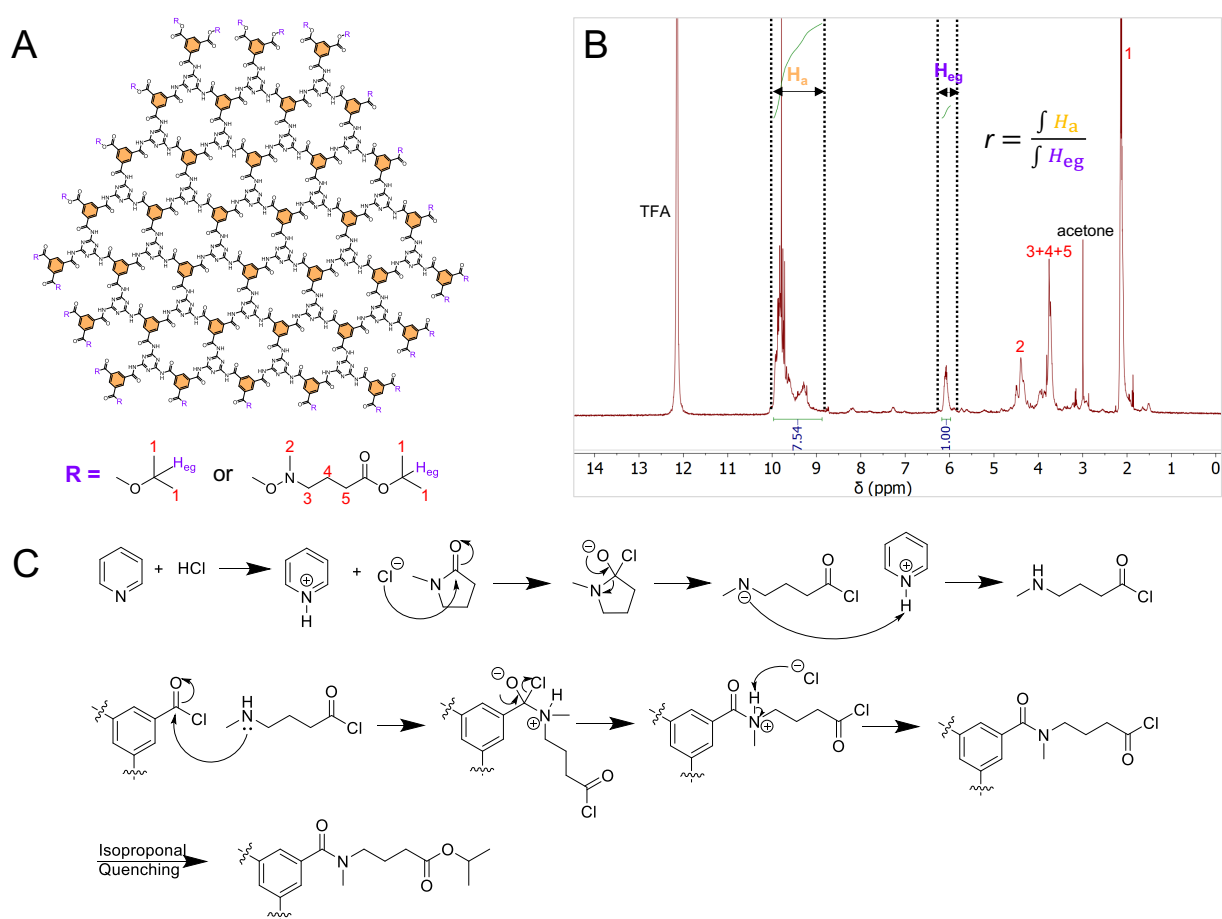
Supplementary Fig. 22.

Mean square displacement, MSD, analysis for longitudinal data of 11 graphene bulge deflections. Graphene deflection data taken from ref. 5, represented as black diamonds [top]. The MSD of these deflection data, represented as blue circles [bottom], are fit to the eq. M21 for confined diffusion (red line) by varying the squared confinement length, R_c^2 .



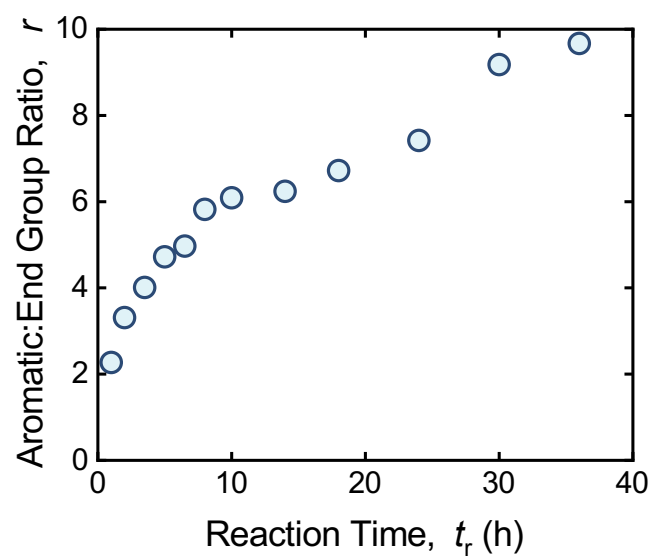
Supplementary Fig. 23.

Mean square displacement, MSD, analysis for longitudinal data of 20 air-trapped 2DPA-1 bulge deflections measured over 1000 d. 2DPA-1 deflection data represented as black diamonds [top]. The MSD of these deflection data, represented as blue circles [bottom], are fit to the eq. M21 for confined diffusion (red line) by varying the squared confinement length, R_c^2 .



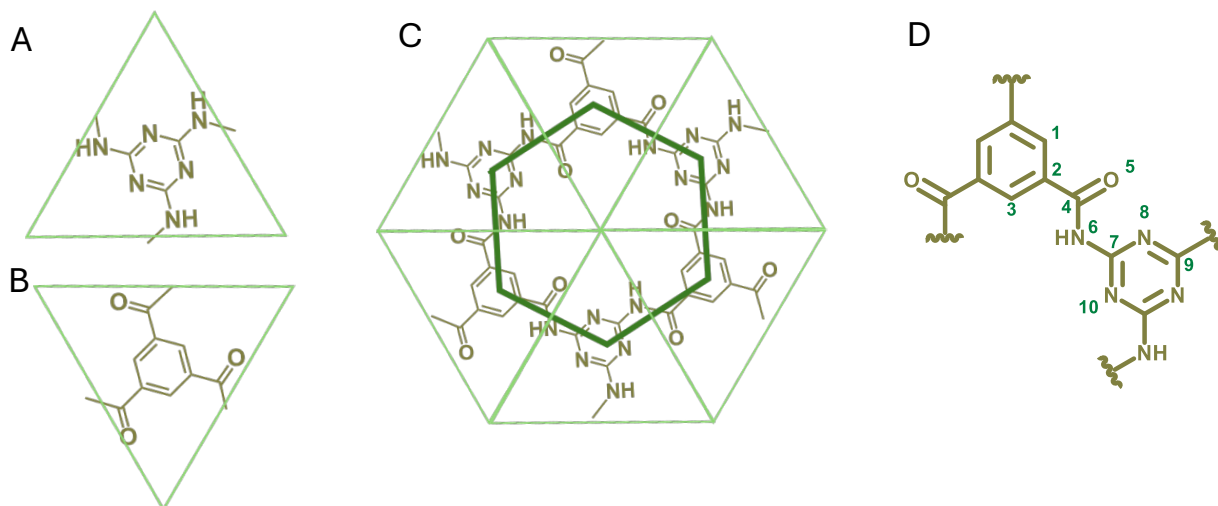
Supplementary Fig. 24.

End-group analysis of 2DPA-1. (A) Chemical structure of 3×3 hexagonal 2DPA-1 platelet. (B) ^1H NMR spectrum of 2DPA-1 in deuterated TFA. (C) Side reaction mechanism that corresponds to the second type of end group in 2DPA-1 synthesis.



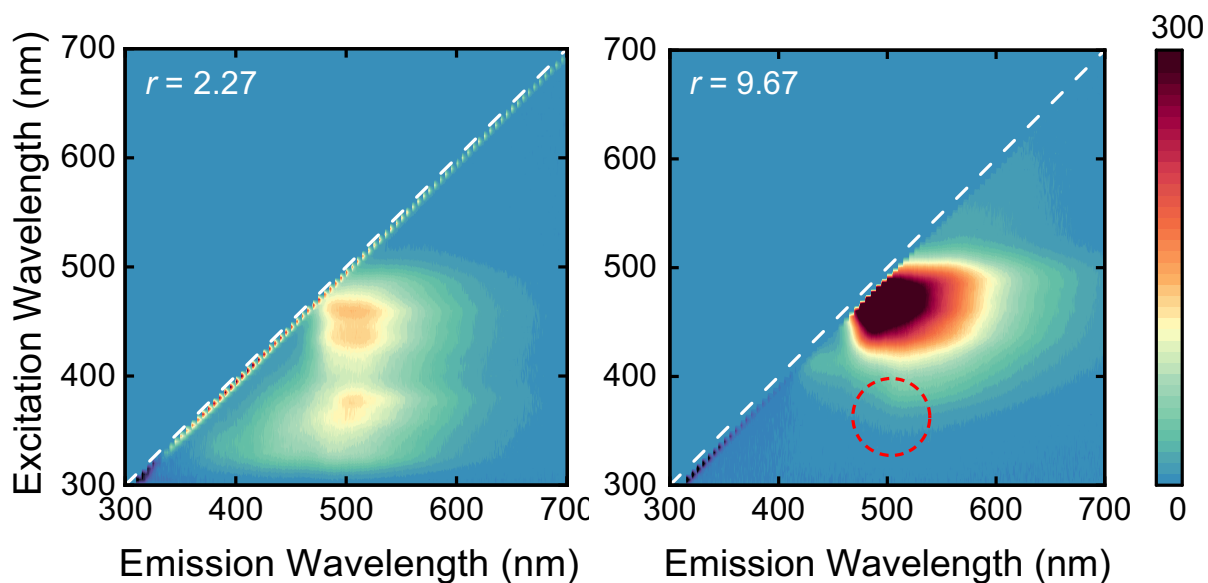
Supplementary Fig. 25.

Aromatic-to-end group ratio, r , with respect to solution-phase reaction time of 2DPA-1.



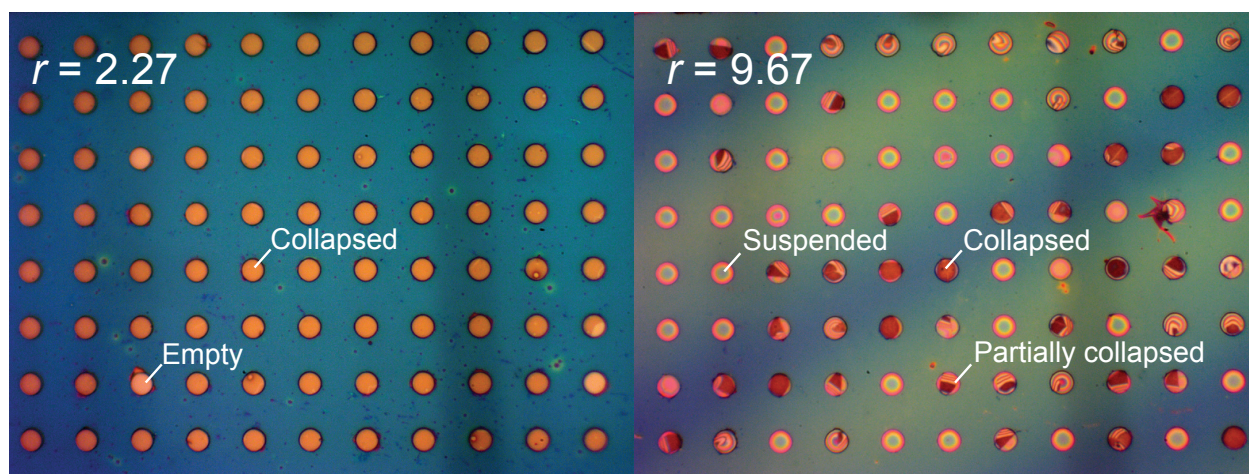
Supplementary Fig. 26.

Fragmentation of 2DPA-1 components. (A-B) Monomers within the infinite platelet, where the green triangle represents A_m . (C) A six-membered ring within an infinite platelet. The dark green hexagon denotes the calculated area of the six-membered ring unit cell. (D) A portion of the six-membered ring unit cell with different atoms labeled corresponding to Supplementary Table 2.



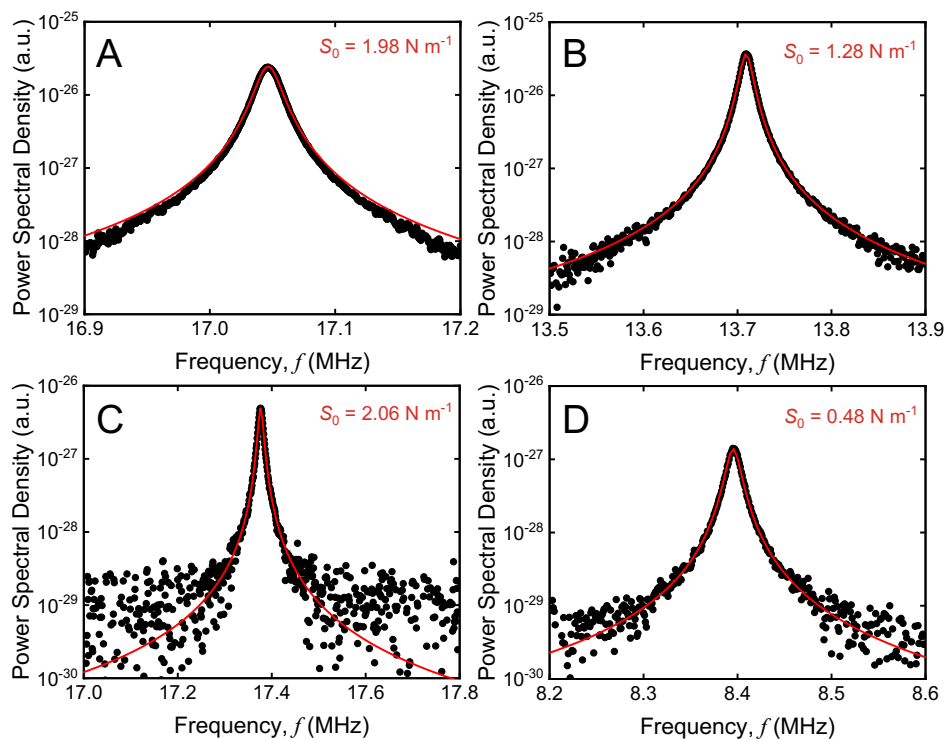
Supplementary Fig. 27.

Two-dimensional fluorescence emission versus excitation wavelength plots of 2DPA-1 in solution. 2DPA-1 platelets of $r = 2.27$ [left] and $r = 9.67$ [right] are compared. The red dashed line highlights the disappearance of a predominant excitation feature around 350 nm.



Supplementary Fig. 28.

Optical micrographs of 35-nm 2DPA-1 films transferred onto Si/SiO₂ substrate with microwells. Films made from 2DPA-1 platelets with $r = 2.27$ [left] and $r = 9.67$ [right] are compared. Yield of suspended films was calculated as the ratio of suspended films to the total number of coated microwells. Included in the total are empty wells due to rupturing of the film off the microwell, any films that collapsed (completely or partially) into the microwell, and fully suspended films.



Supplementary Fig. 29.

Power spectral density with respect to frequency of 35-nm 2DPA-1 resonators. Initial self-tensions of (A) 1.98 N m^{-1} , (B) 1.28 N m^{-1} , (C) 2.06 N m^{-1} , and (D) 0.48 N m^{-1} were extracted from a Lorentzian fit (red line).

Supplementary Table 1.

Vibrational density of states, VDOS, calculations. Various bands in IR and Raman spectrum and the corresponding normal modes determined from VDOS.

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	

Supplementary Table 2.**2DPA-1 bond length and angle estimates that were used for platelet density calculations.**

Bond Configuration	Length (Å)	Angle (Degrees)
C ₁ –C ₂	1.401 ^a	
C ₃ –C ₂	1.401 ^a	
C ₂ –C ₄	1.490 ^a	
C ₄ –N ₆	1.32 ^b	
N ₆ –C ₇	1.47 ^b	
C ₇ –N ₈	1.345 ^c	
C ₁ –C ₂ –C ₃		120 ^a
C ₃ –C ₂ –C ₄		123.7 ^a
C ₂ –C ₄ –O ₅		121 ^b
O ₅ –C ₄ –N ₆		125 ^b
C ₄ –N ₆ –C ₇		123 ^b
N ₆ –C ₇ –N ₈		117.4 ^c
N ₆ –C ₇ –N ₁₀		117.4 ^c
N ₈ –C ₇ –N ₁₀		125.3 ^c
C ₇ –N ₈ –C ₉		114.7 ^c

Values taken from refs. ^{3a}, ^{4b}, and ^{5c}.

Supplementary References

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