

Large-Area Supramolecular Crystalline Thin Films of Polyoxometalates with Controlled 1-nm Pores Enabling Ultra-Selective Molecular Transport

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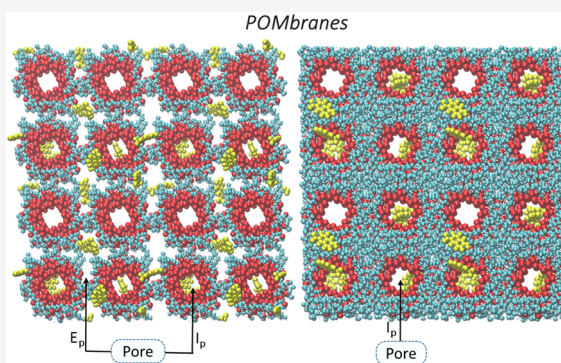
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ABSTRACT: Achieving angstrom-level control over porosity is a long-standing challenge in translating molecular design into selective membranes. We present the supramolecular assembly of crown-type $[P_8W_{48}O_{184}]^{40-}$ polyoxometalate (POM) by alkylammonium functionalization using $[C_nH_{2n+1}]_4N^+$, where $n = 4$ (Q_4P_8), 7 (Q_7P_8), and 10 ($Q_{10}P_8$), into continuous POM thin films (*POMbranes*) featuring periodically aligned ~ 1 nm intrinsic pores (I_p) of P_8 (visualized with electron microscopy). Alkyl chain length modulations direct supramolecular packing and tune the extrinsic porosity (E_p) in *POMbranes* across large lateral dimensions (~ 50 cm²) while preserving I_p . Q_7P_8 and $Q_{10}P_8$ *POMbranes* with restricted E_p enforce precise sieving via I_p , whereas Q_4P_8 permits dual-path transport through I_p and E_p , as confirmed by cross-flow separations and molecular dynamics simulations. Q_7P_8 and $Q_{10}P_8$ *POMbranes* deliver single-digit pore selectivity (isoporosity) and $\sim 10\times$ higher separation efficiency for narrow molecular weight differences (100–200 Da) than state-of-the-art benchmark membranes, establishing a scalable strategy to embed crystalline nanopores for selective separation.



INTRODUCTION

Precise molecular separations are central to technologies spanning water purification,^{1,2} isotope enrichment,³ and carbon capture.⁴ In each of these domains, the ability to distinguish molecules differing by subnanometer dimensions⁵ or by as little as 100–200 Da⁶ in mass determines process selectivity,^{7,8} efficiency,⁹ scalability, and environmental sustainability.^{7–10} Biological membranes serve as precise molecular gates, balancing permeability and selectivity with rigid nanopores: (i) Aquaporins (~ 0.3 nm) permit only single water molecules;¹¹ (ii) bacterial porin OmpF (~ 1.1 – 1.8 nm) enables diffusion of small hydrophilic molecules while excluding solutes >500 Da via size and electrostatic effects;¹² (iii) the nuclear pore complex (NPC) (~ 3 – 10 nm), a sophisticated eukaryotic transport system, allows metabolites and ions while blocking uncontrolled macromolecules.¹³ Biological nanopores reveal that size and chemistry govern selectivity; mimicking this precision in synthetic membranes is essential for scalable, energy-efficient separations. Despite decades of innovation, the performance of synthetic membranes is constrained by the permeability-selectivity trade-off,^{8–10} a consequence of the difficulty in *pore programming* for both rapid transport and sharp molecular discrimination.^{7,8,14,15}

Conventional polymer membranes rely on inefficient chain packing, forming interconnected voids that generate transport pathways with broad, dynamic pore distributions.^{16–22} While polymers are valued for their mechanical robustness, processability, and scalability across reverse osmosis, forward osmosis, ultrafiltration, and nanofiltration, they progressively lose selectivity due to chain relaxation, physical aging, and fouling.¹ Overcoming these trade-offs requires materials with angstrom-scale precision in pore size, shape, and defined bonding principles preserved across macroscopic dimensions.^{10,12,14} Predefined pores with subnanometer apertures and defined geometry, such as metal organic frameworks (MOFs),^{23,24} covalent organic frameworks (COFs),^{25–27} hydrogen-bonded organic frameworks (HOFs),^{28,29} porous organic cages (POCs),³⁰ porous aromatic frameworks (PAFs),^{31,32} other self-assembled materials,³³ single-layer graphene films,³⁴ and subnanometer-thin porous zeolite

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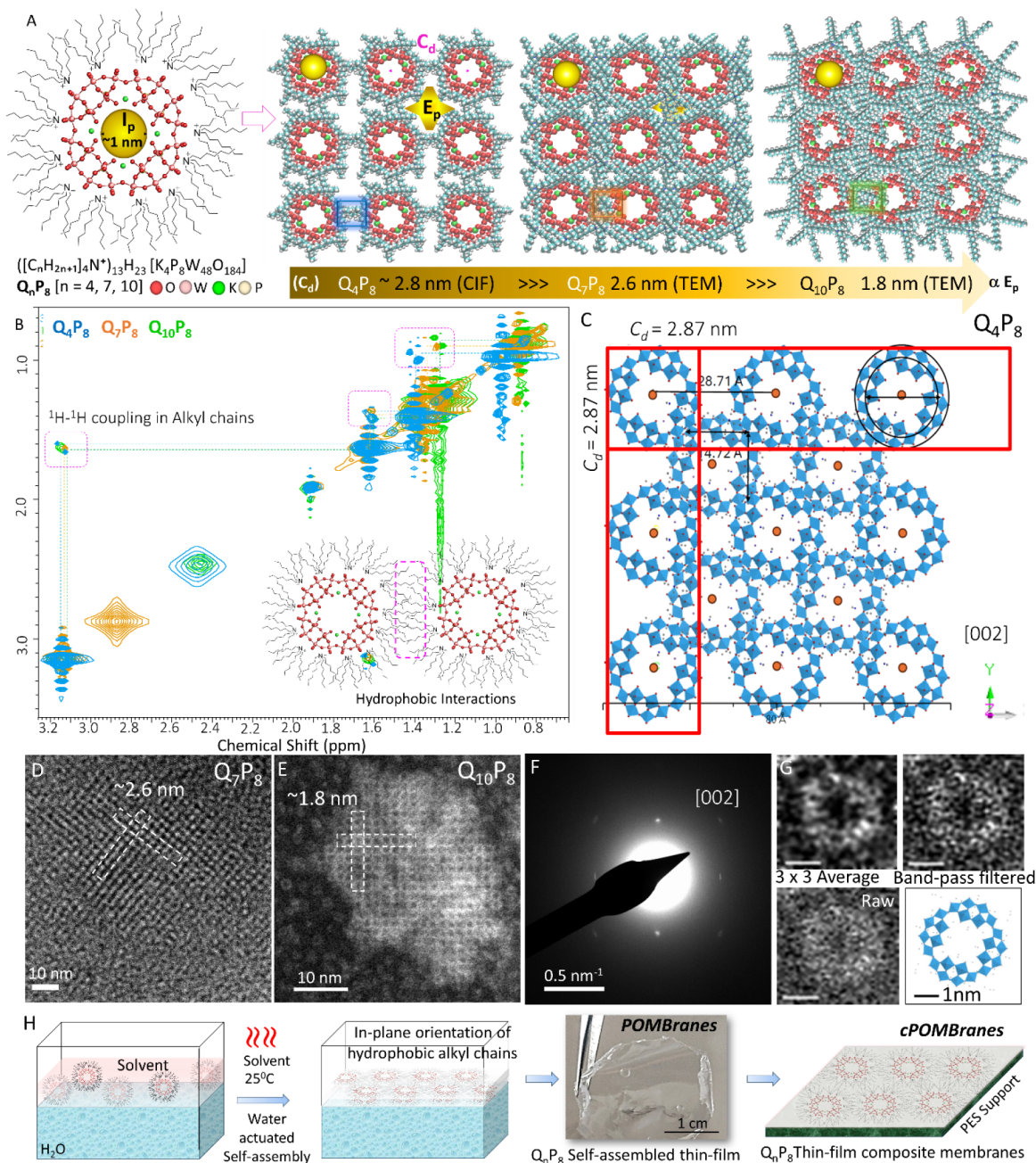


Figure 1. Constituents of Q_4P_8 , Q_7P_8 , and $Q_{10}P_8$ POMbranes. (A) Structural representation of Q_nP_8 featuring a crown-type supramolecular cluster of P_8 [$P_8W_{48}O_{184}$] $^{40-45}$, 3×3 network structures for Q_4P_8 (48), Q_7P_8 , and $Q_{10}P_8$ (energy-minimized structures using the conjugate gradient algorithm) showing intrinsic pores (I_p), extrinsic pores (E_p), and intercluster distances (C_d) along the [002] plane, derived from crystallography for Q_4P_8 and electron microscopy for Q_7P_8 and $Q_{10}P_8$. C_d and E_p decrease from Q_4P_8 to $Q_{10}P_8$ due to the close packing of larger alkyl chains. (B) Nuclear Overhauser Effect Spectroscopy (NOESY) NMR cross-peaks of Q_4P_8 , Q_7P_8 , and $Q_{10}P_8$ indicating 1H - 1H spatial correlations within the intermolecular alkyl chains (Inset: Intermolecular hydrophobic interactions in Q_nP_8). (C) The arrangement of P_8 in the Q_4P_8 structure exhibits exposed pores along the [002] crystallographic plane, with a consistent intercluster distance (C_d) of 2.87 nm along both axes (48). ADF-STEM image of crystallized 1 nm through-pore of P_8 clusters in (D) Q_7P_8 and (E) $Q_{10}P_8$. (F) Electron diffraction pattern indicating cubic in-plane packing. (G) Cluster analysis clearly reveals 1-nm-sized P_8 pores. (H) Water-induced hydrophobic association of intercluster alkyl chains, stabilized by the electrostatics of the larger anionic cluster in Q_nP_8 , drives supramolecular alignment to generate laterally ordered 1 nm pores within POMbranes on water and films transferred on polyether sulfone (PES) substrates (cPOMbranes).

membranes^{35,36} are ideal for accurate molecular separation.^{5,6,12} Yet, their adoption in membrane technology has been hindered by inadequate mechanical flexibility, limited solution processability, and difficulty in fabricating large-area defect-free films while preserving their structural order.³⁷

Biological nanopores¹¹⁻¹³ have inspired the search for synthetic analogues with precise pores, where the polyox-

ometalate (POM) family of discrete anionic metal-oxo clusters offers an ideal platform featuring intrinsic molecular cavities of 0.5–3 nm, resolved at crystallographic precision.³⁸⁻⁴⁴ Among these, the crown-type macrocyclic POM cluster [$P_8W_{48}O_{184}$] $^{40-}$ (P_8) containing ~ 1 nm pores,⁴⁵ is ideally suited for molecular recognition and size-selective sieving.^{46,47} Ease of functionalization, along with scalability, mechanical

stability, and structural consistency, provides a path to replicate nature's selectivity in synthetic membranes.

In this work, we have prepared P_8 featuring an intrinsic pore (I_p) of 1 nm, defined by its metal-oxo ring topology,⁴⁵ functionalized with alkyl chains ($Q_n = [C_nH_{2n+1}]_4N^+$, where $n = 4$ (Q_4), 7 (Q_7), and 10 (Q_{10})) to provide flexibility (elastic modulus), water stability, and ease of processing for large-area membranes. Supramolecular self-assembly of Q_nP_8 ($[C_nH_{2n+1}]_4N^+$)₁₃H₂₃[K₄P₈W₄₈O₁₈₄] ($n = 4, 7$, and 10), dominated by van der Waals forces and hydrophobic interactions of alkyl chains, promoted chain compaction in polar environments and stabilized the continuous, defect-free, self-standing crystalline thin films (*POMbranes*) with a periodic arrangement of I_p . Extrinsic porosity (E_p) is modulated by steric packing of extended alkyl chains without disrupting the periodicity of I_p in Q_4P_8 , Q_7P_8 , and $Q_{10}P_8$ *POMbranes*. Thin-film composite membranes (*cPOMbranes*) of Q_4P_8 , Q_7P_8 , and $Q_{10}P_8$ are fabricated onto polyether sulfone (PES), with a tunable thickness of the separating layer (~30–500 nm) over large lateral dimensions (~50 cm²), enabling continuous size-selective exclusion of solutes above 1 nm. Single-digit pore selectivity with precise 1 nm sieving is achieved in Q_7P_8 and $Q_{10}P_8$, whereas dual-path transport is observed in Q_4P_8 *cPOMbranes*. The exceptional separation efficiencies arising from the ordered-arrangement of P_8 pores within the *POMbranes* surpass the state-of-the-art membrane selectivity by 10-fold. This precisely demonstrates that chemical control at the molecular level can be directly translated into scalable high-resolution molecular separations.

■ RESULTS AND DISCUSSION

Designing *POMbranes* with Periodically Arranged 1-nm-Sized Pores of P_8

Designing single-digit pore membranes with a distinct molecular arrangement and permanent porosity to mimic biological nanopores^{11–13} remains challenging in advancing classical membrane technology for precise molecular separations.^{6,10,14,15} Key ingredients to design *POMbranes* (Figure 1) with single-digit pores are: (i) a permanently porous POM cluster (P_8) (thermally/chemically stable) with a 1 nm integrated pore (for precise molecular separation), functionalized with varied alkyl chains ($Q_n = [C_nH_{2n+1}]_4N^+$, where $n = 4$ (Q_4), 7 (Q_7), and 10 (Q_{10})) to incorporate (ii) flexibility (elasticity modulus), (iii) water stability, and (iv) ease of processability to fabricate large-area membranes of pristine Q_4P_8 , Q_7P_8 , and $Q_{10}P_8$.

Supramolecular interactions dominated by hydrophobic–hydrophobic interactions of alkyl chains (Figure 1) in Q_4P_8 , Q_7P_8 , and $Q_{10}P_8$ drive the in-plane ordered integration of ~1 nm intrinsic pores (I_p) generating a defined intercluster distance (C_d) and extrinsic pore (E_p) formation. Additionally, the variation in alkyl chain length tunes E_p by steric crowding and provides precise control over pore size distribution for selective molecular separation beyond ~1 nm via single-digit pores. The correlation between E_p versus I_p regulates pore distribution in the membrane, with inherently constant I_p (~1 nm), while varied E_p assists in tuning the solute selectivity. $E_p = I_p$ and $E_p < I_p$ result in single-digit selective isoporous membranes (↑solute selectivity), whereas $E_p > I_p$ (↓solute selectivity) (Figure 1).

Structural Characterization

The P_8 cluster $[P_8W_{48}O_{184}]^{40-}$ was synthesized following reported protocols⁴⁵ (Figures S1–S8). Functionalized variants (Q_4P_8 , Q_7P_8 , and $Q_{10}P_8$) were synthesized via counterion exchange in a biphasic solvent system, yielding polycrystalline Q_4P_8 and gel-type $Q_7P_8/Q_{10}P_8$, and were subsequently characterized to establish the structure (Figures S9–S52). ³¹P NMR of Q_4P_8 , Q_7P_8 , and $Q_{10}P_8$ showed a sharp singlet at ~5 ppm, indicating a symmetric environment of P and ascertaining the structural integrity of P_8 (Figures S11, S12, S21, S22, S30, S31). NOESY NMR showed through-space coupling of alkyl chain protons attached to neighboring P_8 clusters, confirming the spatial proximity via strong hydrophobic interactions in Q_4P_8 , Q_7P_8 , and $Q_{10}P_8$ (Figure 1B, Figures S9, S16, S25, S34). The intercluster distance C_d decreases with increasing alkyl chain length from Q_4 to Q_7 and Q_{10} , due to stronger alkyl–alkyl interactions and close packing of alkyl chains.

Structural analysis of Q_4P_8 from reported single-crystal data⁴⁸ revealed an intercluster distance of 2.87 nm among P_8 clusters along the [002] plane, with periodically arranged 1 nm pores exposed in both crystallographic directions (Figure 1, Figure S53). In contrast, asymmetric spacing of 3.34 and 2.87 nm in the [200]/[020] planes (Figure S53), respectively, indicates a phase variation in the packing of P_8 units, leading to more exposed extrinsic (interstitial) porosity. Transitioning from Q_4P_8 to Q_7P_8 and $Q_{10}P_8$, the primary structural modification is the increasing alkyl chain length that occupies the intercluster space (extrinsic pores) with insignificant alteration of overall lattice symmetry. Crystallization challenges in Q_7P_8 and $Q_{10}P_8$ always lead to insufficiently sized crystals that were not suitable for single-crystal analysis, but electron microscopy provided valuable insights into their packing behavior and single-crystalline nature.

Scalable Fabrication of Defect-Free *POMbranes*

The large-area defect-free and continuous free-standing thin films of Q_4P_8 , Q_7P_8 , and $Q_{10}P_8$ (*POMbranes*) were prepared using the air–liquid (solvent–water) interface via a bottom-up approach and characterized in detail (Figure 1, Figures S39–S55). HAADF-TEM images show periodically arranged 1 nm pores of P_8 within Q_7P_8 and $Q_{10}P_8$ *POMbranes*, exhibiting C_d of 2.6 (Figure 1D) and 1.8 nm (Figure 1E), respectively, in a cubic in-plane packing (Figure 1F). Clear visualization of single P_8 clusters with pores of ~1 nm in cluster analysis (Figure 1G) and Fourier diffraction analysis confirms the periodic arrangement in Q_7P_8 and $Q_{10}P_8$ (Figure S53), whereas the presence of large crystalline domains in Q_4P_8 (Figure S53) precluded detailed microscopic analysis. Indexing the powder XRD patterns of Q_4P_8 , Q_7P_8 , and $Q_{10}P_8$ films demonstrates overall crystallinity and periodicity in *POMbranes*, which is consistent with the structural features observed locally by electron microscopy (Figure S9). Figure 1H shows that water-induced hydrophobic association of intercluster alkyl chains, reinforced by the larger anionic cluster, drives supramolecular alignment to form laterally ordered 1 nm pores in Q_nP_8 *POMbranes* and the corresponding *cPOMbranes* on PES. Various control experiments measuring permeate flux, selectivity, and rejection rates were conducted to establish the relationship between E_p and I_p in various membranes (*vide infra* Figure 3).

The *cPOMbranes* (Q_4P_8 , Q_7P_8 , and $Q_{10}P_8$ thin films onto PES supports (Figure S56)) displayed mapping of tungsten W

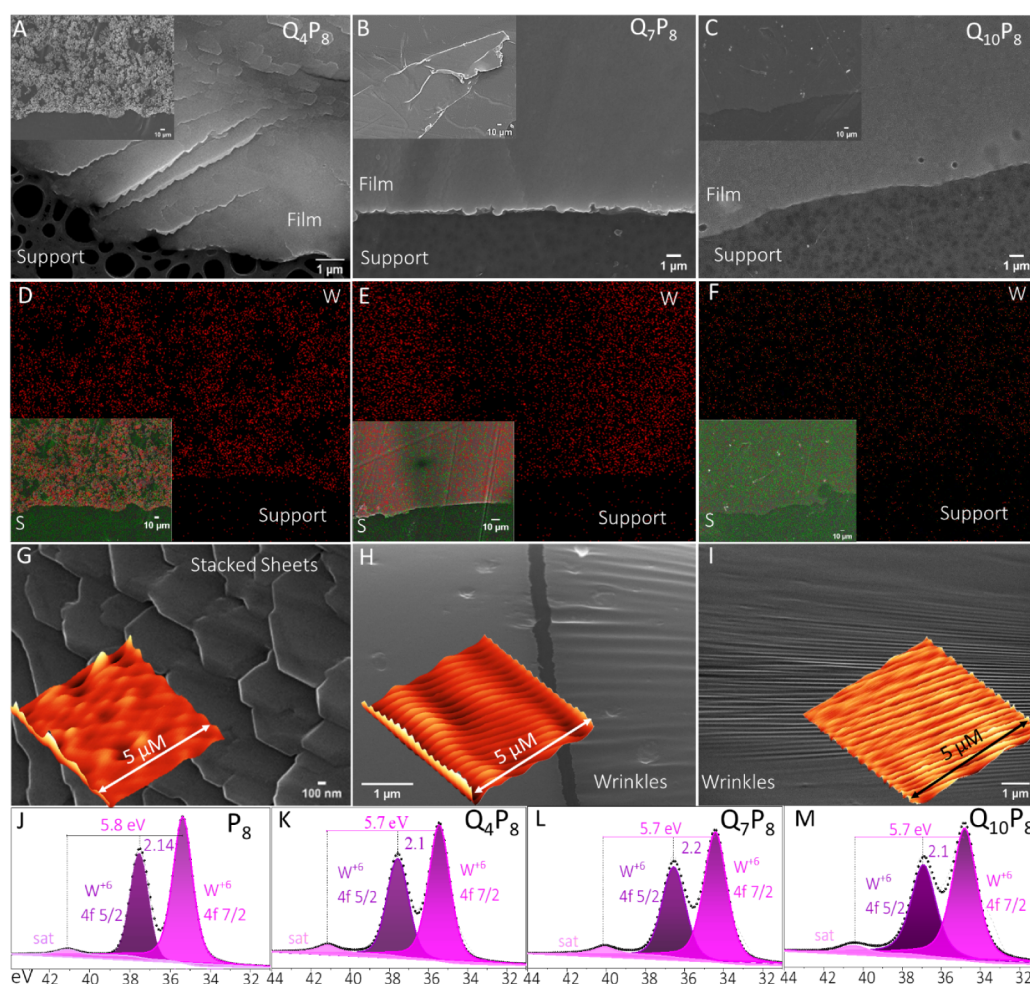


Figure 2. Morphological analysis of Q_4P_8 (column 1), Q_7P_8 (column 2), and $Q_{10}P_8$ (column 3) *POMbranes* and *cPOMbranes*: (A–C) Defect-free and continuous thin films. (D–F) Elemental mapping of W versus S of PES in *cPOMbranes* (scale $1\ \mu\text{m}$; inset: film on PES, scale $10\ \mu\text{m}$). (G) Q_4P_8 stacked sheets (scale $100\ \text{nm}$; inset: no wrinkling of *POMbranes* on PDMS support, AFM scale $5 \times 5\ \mu\text{m}$). (H, I) Wrinkling of Q_7P_8 and $Q_{10}P_8$ *POMbranes* (scale $1\ \mu\text{m}$; inset: on PDMS support, AFM scale $5 \times 5\ \mu\text{m}$). (J–M) High-resolution XPS spectra deconvoluted into W $4f_{5/2}$ and W $4f_{7/2}$ with respect to the corresponding binding energy in eV.

Table 1. Evaluation of *cPOMbranes* : Wettability, Surface Charge (at pH 6), and Mechanical Strength

Sr. No.	Material	Mechanical strength parameters			Contact angle		Zeta Potential (mV)
		Thickness (nm)	λ (nm)	Y_m (MPa)	Time: $t_{0\ s}$ ($^\circ$)	Time: $t_{25\ s}$ ($^\circ$)	
1.	Q_4P_8	490 ± 45	NA	NA	97.1 ± 0.3	68.26 ± 1.2	-30.19
2.	Q_7P_8	30 ± 4	303	22.8 ± 5	96.3 ± 1.1	92.12 ± 0.7	-36.03
3.	$Q_{10}P_8$	30 ± 3	359	38.1 ± 3	102.2 ± 0.6	98.25 ± 0.2	-25.22
4.	PES	NA	NA	NA	47.3 ± 0.7	40.35 ± 0.8	-28.70

(red) on the film surface (Figure 2A–C and Figure S57) and sulfur (S, green) of the PES support (Figure 2D–F and Figure S57), demarcating the clear boundary of the separating layer in *cPOMbranes*. The 2D hexagonal sheets of highly crystalline Q_4P_8 with $\sim 30 \pm 2\ \text{nm}$ sheet thickness (Figure 2A, G and Figure S52) were observed with an average roughness $R_q = 15.7 \pm 7\ \text{nm}$ (Figure S55) in thin films, indicating the integration of crystalline domains of P_8 clusters. Freestanding Q_7P_8 and $Q_{10}P_8$ *POMbranes* are devoid of any macroscopic defects, showing an even texture across the surface (Figure 2B–C, H–I) with an average roughness of $R_q = 6.9 \pm 2.4\ \text{nm}$ and $9.5 \pm 5\ \text{nm}$, respectively (Figure S55). The thickness of Q_4P_8 , Q_7P_8 , and $Q_{10}P_8$ thin films was measured as $490 \pm 45\ \text{nm}$, $30 \pm 4\ \text{nm}$, and $30 \pm 3\ \text{nm}$, respectively, calculated from the AFM

height profile over a $5\ \mu\text{m}$ area to validate film continuity and thickness (Figure S55).

The Q_7P_8 and $Q_{10}P_8$ *POMbranes* ($\sim 30\ \text{nm}$ thin) showed fine, continuous wrinkles (Figure 2H, I), representing their mechanical properties with Young's modulus $Y_M = 22.8 \pm 5\ \text{MPa}$ (Q_7P_8) and $38.1 \pm 3\ \text{MPa}$ ($Q_{10}P_8$), calculated using the wrinkling method (Table 1, Figure S54). Although Q_4P_8 *POMbrane* did not yield wrinkles and cracked upon releasing the applied stress, indicating its crystalline nature (Figure 2G (inset)), Q_7P_8 and $Q_{10}P_8$ films represent polymer-like flexibility and elasticity (Figure 2H, I (inset)).

Surface characteristics, such as hydrophilicity and surface charge were evaluated to determine separation conditions. Water contact angles indicate increasing hydrophobicity with

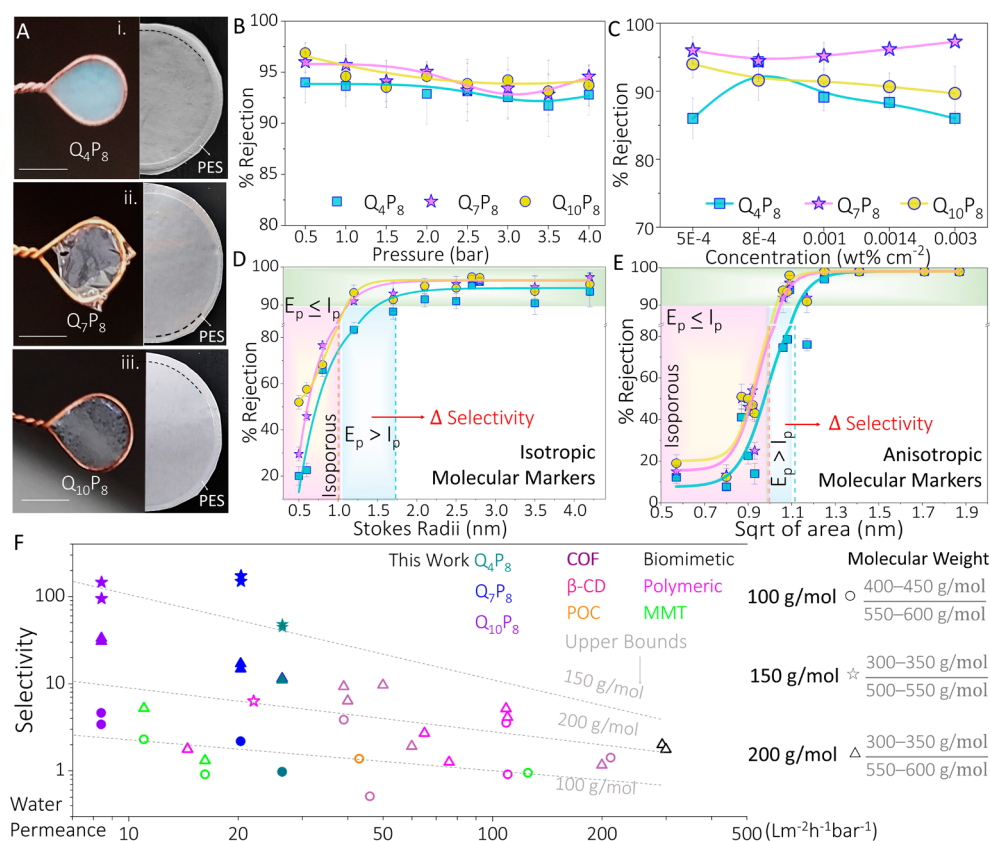


Figure 3. Separation performance of *cPOMbranes*. (A) Optical images of thin free-standing *Q₄P₈* (~490 nm), *Q₇P₈* (~30 nm), and *Q₁₀P₈* (~30 nm) *POMbranes* and their composite with PES *cPOMbranes* (1 cm scale, 2.5 cm membrane radius). Separation performance (% rejection) of various molecular markers, with respect to: (B) Applied pressure. (C) Concentration (AF, $\sqrt{\text{molecular area } 1.2 \text{ nm}^2} = 1.1 \text{ nm} > \text{Intrinsic pore size}$; indicating continuous *cPOMbranes* without pinholes/crack); (D) Isotropic molecular markers (PEG) with Stokes radius 0.5 to 4.2 nm (Table S3). (E) Anisotropic molecular markers (charged as well as neutral) of 0.5 to 1.9 nm (dimensions are the square root of molecular area, Table S4). (F) Trade-off between water permeance and separation selectivity between solutes of different molecular weights (MW) for *cPOMbranes* of various porous materials from literature and this work. The upper bound indicates the performance limit that can be utilized for different comparative purposes in versatile separations (Table S11). The separation performance of *Q₄P₈*, *Q₇P₈*, and *Q₁₀P₈* *cPOMbranes* was evaluated using a cross-flow filtration system (details in the SI).

longer alkyl chains: PES (~47.3°), *P₈* cluster (~61.2°), *Q₄P₈* (~97.1°), *Q₇P₈* (~96.3°), and *Q₁₀P₈* (~102.2°) (Figure S58 and Table 1). Contact angle over time showed minimal change for *Q₇P₈* (~5°) and *Q₁₀P₈* (~2°), but a significant decrease for *Q₄P₈* (~29°), indicating superior wettability (Table 1 and Figure S59).

Zeta potential measurements of *Q₄P₈*, *Q₇P₈*, and *Q₁₀P₈* *cPOMbranes* confirmed negatively charged surfaces (−15 to −35 mV, pH 2–10), indicating the assimilation of negatively charged and exposed *P₈* clusters (Table 1 and Figure S60). High-resolution XPS analysis of core-level binding energies for *P₈*, *Q₄P₈*, *Q₇P₈*, and *Q₁₀P₈* shows the integration of *P₈* clusters in *POMbranes*, exhibiting W 4f L-S splitting (~2.1 eV) in deconvoluted spectra, with peaks at W 4f_{7/2} (~35.3 eV) and W 4f_{5/2} (~37.4 eV). A satellite peak at ~41.0 eV, separated by 5.8 eV from W 4f_{7/2} in *P₈* were minor shifted to 5.7 eV in *Q₄P₈*, *Q₇P₈*, and *Q₁₀P₈*, confirming the +6 oxidation state of W (Figure 2J–M and Figure S45).

At different concentrations, all *cPOMbranes* were prepared to identify optimal conditions (Tables S1–S2). For *Q₇P₈* and *Q₁₀P₈* *cPOMbranes*, increasing concentration produced thicker films (Figure S47, Figure S61) and progressively lower permeance, with optimal performance at 0.0005 wt %·cm⁻² (~95% rejection of the 1.1 nm marker; PWP 19.8 ± 3 and 14.4

± 3 L·m⁻²·h⁻¹·bar⁻¹) (Table S5, Figure S61). In contrast, *Q₄P₈* showed increasing permeance with concentration (PWP ~ 22–27), attributed to larger *C_d* and enhanced *E_p* (Figure S61). However, selectivity declined above 0.0008 wt %·cm⁻² *Q₄P₈* forms crystalline, rigid 2D sheets that do not laterally coalesce at low concentrations, making ultrathin films discontinuous. Higher loading is therefore required to achieve defect-free continuity, resulting in thicker membranes compared to those of *Q₇P₈* and *Q₁₀P₈*. Hence, *cPOMbranes* were prepared with optimized loadings for *Q₄P₈* (0.0008 wt %·cm⁻²), *Q₇P₈*, and *Q₁₀P₈* (0.0005 wt %·cm⁻²) and then utilized for further separation experiments (Tables S3, S4) through continuous cross-flow filtration tests.

Precise Molecular Sieving with *cPOMbranes*

The *cPOMbranes* prepared at the optimized concentrations (Figure 3A) exhibiting film thicknesses of ~490 ± 45 nm (*Q₄P₈*), 30 ± 4 nm (*Q₇P₈*), and 30 ± 3 nm (*Q₁₀P₈*), showed increased water permeation with applied pressure from 0.5 to 4 bar while maintaining stable rejection of >1 nm solute markers, confirming mechanical and separation stability under elevated pressures (Figure 3B, Table S6). The consistent molecular sieving indicates that the pore size and structure are the primary determinants of solute rejection, as evident from molecular sieving experiments, where uniform 1 nm pores

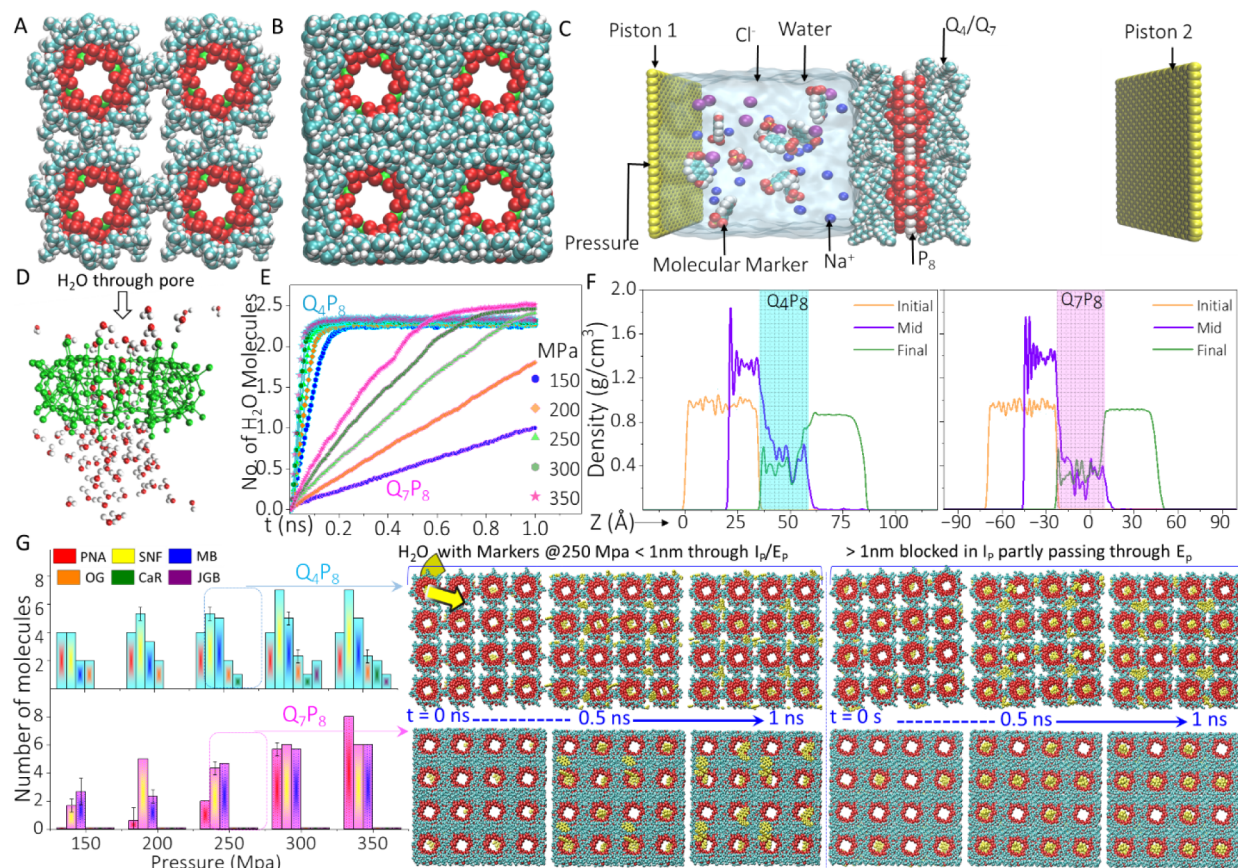


Figure 4. Molecular dynamics simulations of molecular marker transport through I_p and E_p of Q_4P_8 and Q_7P_8 . Minimized structures of (A) Q_4P_8 and (B) Q_7P_8 before molecular sieving simulations. Central porous regions depict the P_8 clusters (I_p) that are surrounded by alkyl chains of Q_4 or Q_7 (blue and white atoms). Q_4P_8 possesses both I_p as well as E_p , whereas Q_7P_8 possesses only I_p . (C) Atomistic snapshot of the molecular model for separation simulations depicting pressure-driven flow of water containing dye molecules of various sizes. (D) A snapshot showing permeation of water molecules through I_p (Figure S60). (E) Number of water molecules that permeate as a function of time and pressure for both Q_4P_8 and Q_7P_8 POMbranes. (F) Water density profile along z -axis at 150 MPa in Q_4P_8 and Q_7P_8 at three distinct periods of time: initially at the start of the simulation ("initial"), halfway through permeation ("mid") and at the end of the simulation at 20 ns ("final"). (G) Number of molecular markers (negative, positive, and neutral) <1 nm to >1 nm that permeate through Q_4P_8 ($I_p + E_p$) and Q_7P_8 (I_p) at different pressures. On the right are atomistic snapshots for Q_4P_8 and Q_7P_8 monolayers of POMbranes at 250 MPa depicting the passage of molecular markers <1 nm and blockage of >1 nm (partial blockage), respectively (Videos S1–S4).

consistently block molecular markers >1 nm (as evidenced with acid fuchsin (AF, 1.1 nm size) and orange G (OG, 1.0 nm) (Tables S3, S4) (Figures 3, 4). Q_4P_8 , Q_7P_8 , and $Q_{10}P_8$ cPOMbranes prepared at different concentrations with varying wt % (Figure 3C) demonstrated excellent separation of the 1.1-nm-sized molecular marker, which is larger than the intrinsic pore of P_8 (~ 1 nm), achieving $\sim 95\%$ rejection ($94.3 \pm 1.8\%$ with Q_4P_8 , $96.4 \pm 2.1\%$ with Q_7P_8 and $95.1 \pm 3.4\%$ with $Q_{10}P_8$) with corresponding permeance of ~ 27 , 20, and 19 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$, respectively. Extrinsic pores (>1 nm) in Q_4P_8 are conducive to relatively increased permeance with slightly compromised rejection; however, in Q_7P_8 and $Q_{10}P_8$, a dense network with an increased length of alkyl chains obstructs the extrinsic pores (>1 nm) and forces the solution of molecular markers to pass through the intrinsic pores.

The performance of the selective layer, referred to as Q_4P_8 , Q_7P_8 , and $Q_{10}P_8$ in cPOMbranes, is evaluated for separating various standard isotropic molecular markers (polyethylene glycol (PEG)) as well as anisotropic molecular markers (neutral and charged (+ve and -ve) molecules) (Tables S7–S10). This also allows us to define the utility of intrinsic (P_8 pore) versus extrinsic pores (due to the packing of alkyl chains

with defined intercluster distances). The separation performance of isotropic molecular markers (PEG) using $Q_7P_8/Q_{10}P_8$ (Figure 3D) effectively shows the utilization of intrinsic pores of P_8 (1 nm) by rejecting the permeation of PEG markers >1 nm Stokes radii (PEG 2000) with $>90\%$ rejection ($91.5 \pm 1.7\%$ with Q_7P_8 and $93.2 \pm 2.1\%$ with $Q_{10}P_8$). Whereas, Q_4P_8 allows the passage of PEG markers up to ~ 1.7 nm Stokes radii (PEG 4000), with $>90\%$ rejection ($90.7 \pm 1.9\%$) of larger PEG markers beyond PEG 6000 (2.1 nm), indicating the major contribution of extrinsic pores in separation (Figure 3D, Table S10, Figure S62). Achieving complete rejection (100%) is not possible with commercial PEG samples, as they are inherently polydisperse, including lower-molecular-weight oligomers.

The separation of anisotropic molecular markers in Figure 3E follows a similar trend as observed in Figure 3D for isotropic molecular markers, where $Q_7P_8/Q_{10}P_8$ shows $>90\%$ rejection ($92.4 \pm 1.6\%$ with Q_7P_8 and $91.2 \pm 2.7\%$ with $Q_{10}P_8$) of neutral markers with ~ 1.1 nm size. However, Q_4P_8 shows lesser rejection ($\sim 76.5 \pm 3.1\%$) pointing to the utility of extrinsic pores in addition to the intrinsic pores. Rejection of cationic (+ve) markers in Figure 3E shows accurate molecular sieving with $>95\%$ rejection for >1 nm and $<30\%$ for <1 nm

marker size. Further, the observed rejection of anionic (−ve) markers, yielding >90% for >1 nm and <50% for <1 nm marker size with $Q_4P_8/Q_7P_8/Q_{10}P_8$ confirms the efficacy and functionality of intrinsic pores. Flipping the *POMbranes* to evaluate orientation effects yielded similar cutoff profiles for isotropic PEG (Figures S63–S64). The long-term operational stability of *cPOMbranes* was evaluated for 48 h with pure water and for 24 h using anisotropic molecular markers (neutral, anionic, and cationic) (Figure S65). Water permeance and solute rejection did not change, indicating a stable pore structure and negligible compaction or fouling. Although the membranes are moderately hydrophobic (contact angles 96°–102°), their negative surface charge (−25 to −36 mV) is responsible for reducing the adhesion of charged foulants through electrostatic repulsion. The sustained exposure of *cPOMbranes* across a broad pH range (pH 4–10) resulted in retained initial permeance (Figure S65), highlighting their chemical robustness.

The $Q_4P_8/Q_7P_8/Q_{10}P_8$ *cPOMbranes* show true size-sieving separation using the well-defined pore apertures of P_8 clusters, contributing toward sieving through intrinsic pores aligned in an ordered pattern all over the membrane.

Molecular size selectivity of *POMbranes* is defined using conventional selectivity parameters (ratio of rejection coefficients for solutes A and B), widely applied in nanofiltration and molecular separation studies, enabling direct comparison of size discrimination across different membrane platforms. The transport performance of *cPOMbranes* is benchmarked within the well-established permeance-selectivity upper-bound framework, originally developed for polymer membranes^{1,8} and subsequently extended to ordered membranes like COF,⁴⁹ MOF,⁵⁰ POCs,³⁰ and macrocyclic polymers.⁶ In this representation, solvent permeance is plotted against molecular selectivity, and the upper-bound curves delineate the highest combinations of permeance and molecular selectivity reported across membrane classes. Isoporous *cPOMbranes* of ~1 nm I_p exhibit 10- to 20-fold higher selectivity for small molecular weight differences (150–200 Da) relative to state-of-the-art membranes (Figure 3F, Table S11), reflecting the uniformity and precision of the pore structure.

The *cPOMbrane* data fall on or above the corresponding upper-bound envelope, demonstrating that *cPOMbranes* are among the highest-performing molecular separation membranes to date, underscoring their potential for demanding purification and process-intensification applications. To highlight the potential for industrial translation, Q_7P_8 *POMbranes* were fabricated directly on PES supports under varied processing conditions (Table S12), consistently retaining their high permeance and selectivity.

Molecular Simulation

Molecular dynamics simulations examined I_p/E_p pore utility, selectivity, and water permeation in Q_4P_8 and Q_7P_8 *POMbranes* composed of a monolayer where the pore-to-pore distance (C_d) is ~2.8 nm and ~2.42 nm, respectively (Figure 4A–C and Figure S66). Water– P_8 interactions, probed using radial distribution functions (RDFs), indicate that water mainly permeates via intrinsic/extrinsic pores rather than P_8 channels of bridging oxygen (Figure 4D and Figure S67).

Water permeation, quantified as the number of water molecules passing through the monolayer over time, shows a much steeper dependence for Q_4P_8 owing to the presence of both pore types (Figure 4E). Water density profiles as a

function of pressure (Figure 4F) show an initial density of ~1 g/cm³ in Q_4P_8 and Q_7P_8 models; upon pressure-driven flow, the density near the piston increases to ~2 g/cm³. The average density of water, ~0.4 g/cm³ resides inside the monolayer during 20 ns simulations due to hydrogen bonding with P_8 oxygens. The Q_4P_8 and Q_7P_8 simulation complements experimental rejection profiles for both small (<1 nm) and large (>1 nm) molecular markers (Figure 4G). All the markers in the case of Q_7P_8 pass through the I_p (Figure 4G and Videos S1, S2), whereas larger C_d in Q_4P_8 (~2.8 nm) facilitates the permeation of molecules through I_p as well as E_p (Figure 4G and Videos S3, S4). In Q_7P_8 , markers with molecular areas >1 nm (CaR, OG, and JGB) are completely rejected even at high pressures, whereas in Q_4P_8 , these markers exhibit permeation through the E_p at elevated pressures (Figure 4G). Free energy profiles calculated using umbrella sampling indicate that among smaller markers (<1 nm), PNA exhibits the lowest energy barrier (Figure S68), explaining its high permeation in both Q_4P_8 and Q_7P_8 monolayers, consistent with experimental findings. For larger markers (>1 nm), CaR has the highest energy barrier due to its size and electrostatic interactions with the P_8 pore, followed by JGB and OG (Figure S68). Simulations of the $Q_{10}P_8$ model were challenging due to its reduced C_d (~1.8 nm), resulting from steric hindrance from densely packed alkyl chains.

CONCLUSION

We demonstrate the scalable fabrication of isoporous crystalline *POMbranes* by integrating P_8 clusters with intrinsic ~1 nm pores into flexible, water-stable thin films spanning tens of square centimeters. By tuning alkyl chain length, we control extrinsic porosity and orient intrinsic pores of P_8 perpendicular to the direction of molecular transport, enabling precise molecular sieving via single-digit pores of Q_7P_8 and $Q_{10}P_8$ *POMbranes*. Molecular dynamics simulations and cross-flow experiments confirm sharp separation profiles (>90% rejection for solutes larger than 1 nm) and stable operation under pressure. These crystalline membranes surpass state-of-the-art systems by an order of magnitude in selectivity for molecules differing by only 100–200 Da, providing a generalizable strategy to embed crystalline nanopores into scalable films. Beyond the systems demonstrated here, this approach opens pathways to next-generation porous materials, such as three-dimensional POM architectures (POMZites), where higher pore density and connectivity can further advance molecular precision in pharmaceutical, chemical, and environmental separations.

METHODS

Synthesis of P_8 Cluster

Porous polyoxometallate cluster (P_8) was synthesized using a reported three-step sequential procedure.⁴⁵ First, $[P_2W_{18}O_{62}]^{6-}$ was synthesized by dissolving $Na_2WO_4 \cdot 2H_2O$ (300 g, 0.91 mol) and H_3PO_4 (250 mL, 4 M) in 350 mL DI water, adjusting the pH to 1.5–2.0 to induce oligo-condensation, yielding $\alpha-K_6P_2W_{18}O_{62} \cdot 14H_2O$ (240 g, 96%). For $[P_2W_{12}O_{48}]^{12-}$, the product (83 g, 0.017 mol) was dissolved in 300 mL water with tris buffer, followed by KCl and K_2CO_3 addition, raising the pH to 7.0–7.4 and yielding $K_{12}[H_2P_2W_{12}O_{48}]$ (62 g, 89%). Further, $[P_2W_{12}O_{48}]^{12-}$ (28 g) was added to a buffered acetic acid solution (pH 4.0–4.4) containing LiCl and LiOH. After 3–4 days at 25 °C, needle-like translucent crystals of P_8 formed, with the composition $K_{28}Li_3H_7[P_8W_{48}O_{184}] \cdot \sim 92H_2O$,

featuring a 1 nm porous cavity. Further details of structural characterizations are presented in [Supplementary Figures 1–8](#).

Synthesis of Q₄P₈

The porous P₈ (1.0 g) was functionalized with tetrabutylammonium bromide (Q₄Br) by ion exchange⁴⁸ to form Q₄P₈ using the reported procedure. P₈ was dissolved in pH 2.0 water and added to an aqueous Q₄Br solution (4 g). After stirring for 1 h at 25 °C, white precipitates formed, were washed, vacuum-filtered, and recrystallized in acetonitrile to yield rod-like transparent crystals of Q₄P₈ (C₁₆H₃₆N)₁₃H₂₃[K₄P₈W₄₈O₁₈₄]·2CH₃CN. Further details of structural characterizations are presented in [Supplementary Figures 9–20](#).

Synthesis of Q₇P₈ and Q₁₀P₈

The (Q₇P₈ and Q₁₀P₈) were synthesized by exchanging K⁺/Li⁺ ions from P₈ with tetraheptylammonium bromide (Q₇Br) and tetrakis-(decyl)ammonium bromide (Q₁₀Br), respectively. P₈ (0.74 g) was dissolved in 40 mL DI water (pH 2.0, adjusted with 0.5 M H₂SO₄) and added to 50 mL toluene containing Q₇Br (4.5 g) and Q₁₀Br (1.32 g), respectively. After 24 h of stirring at 25 °C, the organic layer (toluene) was separated and washed to obtain a clear solution. Later, toluene was removed under vacuum, and viscous products were isolated. Repeated hexane treatments removed unreacted Q₇Br, yielding pure Q₇P₈ (C₂₈H₆₀N)₁₃H₂₃[K₄P₈W₄₈O₁₈₄]·H₂O and Q₁₀P₈ (C₄₀H₈₄N)₁₃H₂₃[K₄P₈W₄₈O₁₈₄]·H₂O. Further details of structural characterization are presented in [Supplementary Figures 21–38](#).

Fabrication of Thin Films of Q₄P₈, Q₇P₈, and Q₁₀P₈ (POMbranes)

The large-area defect-free and continuous free-standing Q₄P₈, Q₇P₈, Q₁₀P₈ POMbranes were prepared using a liquid–liquid (nonsolvent–water) interface via a bottom-up approach. Q₄P₈ (4 mg) was dissolved in acetonitrile/toluene (2:4 mL) and poured over DI water (280 mL), forming thin films over a large area (72 cm²) within 8–10 h of evaporation at 25 °C and 50–60% humidity. Similarly, Q₇P₈/Q₁₀P₈ (4 mg each) in hexane (10 mL) formed thin films under identical conditions within 5 h with a tunable thickness ([Supplementary Section 3](#)). These thin films were easily transferred onto different substrates like glass, Si, Cu grid, etc., and used for various characterizations. Detailed structural and microscopic characterizations are presented in [Supplementary Figures 39–55](#).

Fabrication of Thin Film Composite POMbranes (cPOMbranes)

Supported membranes of Q₄P₈, Q₇P₈, and Q₁₀P₈ were fabricated by transferring their interfacial POMbranes onto preprepared polyether sulfone (PES) and polyacrylonitrile (PAN) supports. The supports were fixed to a steel stand by using adhesive tape and placed in a glass bowl containing 250 mL of water. Q₄P₈, Q₇P₈, and Q₁₀P₈ POMbranes at the liquid–liquid interface were carefully transferred onto the supports, drained, and dried at room temperature (25 °C) for 24 h, then cured in water at 5 °C for 4–5 h. Detailed characterization of cPOMbranes is presented in [Supplementary Figures 56–60](#).

Separation Measurements

The separation performance of Q₄P₈, Q₇P₈, and Q₁₀P₈ cPOMbranes was evaluated using a cross-flow filtration system ([Supplementary Figures 61–65 Tables 1–12](#)). Approximately 1 L of feed solution was pumped from a tank through the membrane cell (effective membrane area: 14.5 cm²) using a diaphragm pump. Prior to testing, membranes were precompact with pure water at 1 bar for 4 hours. Membrane permeance (*P*) was calculated as

Where *V* is the permeate volume (L), *A* is the membrane area (m²), *t* is time (h), and Δ*p* is the transmembrane pressure (bar).

Permeance and separation efficiency were continuously monitored using isotropic (PEG, Stokes radii 0.47–4.17 nm ([Supplementary Table 3](#)) and anisotropic dye markers (effective sizes 0.7–1.8 nm ([Supplementary Table 3](#))). The feed dye concentration was 0.1 g/L. Rejection (*R*) was calculated as where *C_p* and *C_f* are solute concentrations in permeate and feed. At least four replicates were tested per membrane ([Table S3](#)).

Selectivity (*α*) is defined as the ratio of solute rejection factors of two species, A and B, under identical operating conditions—a convention commonly used for nanofiltration and organic solvent nanofiltration membranes^{1,6,8}

$$\text{Selectivity } (\alpha) = \frac{1 - R_A}{1 - R_B}$$

Where *R_A* and *R_B* are the rejection rates of solute A and solute B, respectively, which are calculated from the concentration of permeate (*C_p*) and feed (*C_f*) of solute A and solute B.

Upper-bound performance refers to permeability–selectivity trade-off limits historically established across high-performance polymeric, COF, and MOF membranes. In the conventional plot, solvent permeance is plotted on the *x*-axis, and selectivity (*α*) is plotted on the *y*-axis. Upper-bound curves reflect the maximum achievable combination of high permeance and high selectivity scenarios.^{1,6,8}

Large-area cPOMbranes are prepared with varied concentrations of Q₄P₈, Q₇P₈, and Q₁₀P₈ (0.0005 to 0.003 wt % cm^{−1}) to form freestanding thin films, which were carefully transferred onto PES supports and cut into appropriate proportions (no delamination observed) for placing them in the cross-flow cells of 45 mm diameter for selective separation experiments.

Molecular Sizes and Area Considerations

Polyethylene glycol (PEG) of different molecular weights, ranging from 400 to 20000 Da, was used as isotropic molecular markers (neutral) with respective Stokes radii in the range of 0.5–4.5 nm ([Supplementary Table 3](#)). Various anisotropic molecular markers with neutral, positive, and negative charges were utilized to study the separation performance. In order to unify and compare with the Stokes radii of isotropic markers, we have taken the square root of the geometry optimized molecular area in the range of 0.5–2 nm ([Supporting Information Table 4](#)).

Molecular Dynamics

Molecular dynamics simulations were carried out to investigate intrinsic *I_p* and extrinsic *E_p* pore utility of P₈ in Q₄P₈ and Q₇P₈, molecular selectivity, and water permeation through POMbranes. The simulation setup consists of two pistons, a POMbrane of four P₈ molecules surrounded by alkyl chains (Q₄/Q₇) and hydrogen atoms to neutralize charge, where the pore-to-pore distance (*C_d*) for the Q₄P₈ and Q₇P₈ model is ~2.8 and ~2.42 nm, respectively. Three systems with varying pore-to-pore distances were designed to study molecular marker rejection and compare with experiments (six molecular markers were selected: three with sizes below 1 nm and three above 1 nm, representing positive, negative, and neutral charges). Molecular markers and the alkyl chains are modeled using the General Amber Force Field (GAFF)⁵¹ by utilizing the Antechamber package⁵² with partial charges calculated using the AM1-BCC method.⁵³ The DFT calculations were performed with the ORCA^{54,55} package to calculate partial charges for P₈ using the PBE0 exchange-correlation functional⁵⁶ and def2-TZVP⁵⁷ basis set with D3 dispersion correction.⁵⁸ The water model used in the study is TIP3P.⁵⁹ Nonbonded interactions between atoms are modeled by Lennard-Jones potential along with the Lorentz–Berthelot rule for the cross interactions. The PPPM^{60,61} algorithm is used to compute the long-range electrostatic interactions. The cutoff for Lennard-Jones (LJ) and electrostatic interactions is set to 10 Å. Shake algorithm⁶² is used to freeze the O–H bonds in water molecules so as to avoid their deformation. The membrane is kept fixed throughout the whole simulation run. All the simulations are performed using the LAMMPS package.⁶³ Simulations were run in LAMMPS with a 1 fs time step at 300 K, using the Nose-Hoover thermostat with a damping constant of 100 ps. Pressure-driven permeation of water containing markers of various sizes used in experiments was carried out, with each simulation being repeated three times with independent starting configurations for collecting statistics. Force on pistons driving permeation was applied uniformly via the “fix aveforce” command: *F* = (*P* × *A*)/*n* where *F* is the force applied on the piston, *A* is the

surface area of the piston, and n is the total number of atoms in the piston.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.5c17644>.

Permeation of molecular marker (SNF ($< 1\text{nm}$)) through intrinsic pores of Q7P8 (MP4)

Retention of molecular marker (OG ($> 1\text{nm}$)) through intrinsic pores of Q7P8 (MP4)

Permeation of molecular marker (SNF ($< 1\text{nm}$)) through intrinsic and extrinsic pores of Q4P8 (MP4)

Permeation of molecular marker (OG ($> 1\text{nm}$)) through extrinsic pores of Q4P8 (MP4)

Experimental details include materials and methods; synthesis procedures; structural and morphological characterization, including PXRD, SEM, TEM, AFM, and profilometry data; spectroscopic characterization (NMR, FTIR, UV-vis, and XPS); thermal characterization (TGA); membrane fabrication protocols; membrane characterizations (zeta potential, contact angle); permeation and separation performance data; control experiments; stability and recyclability studies; molecular dynamics; and supplementary figures, tables, and videos supporting the main text (DOCX)

XYZ coordinates of energy minimized Q4P8 (TXT)

XYZ coordinates of energy minimized Q7P8 (TXT)

XYZ coordinates of energy minimized Q10P8 (TXT)

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Notes

The authors declare no competing financial interest.

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