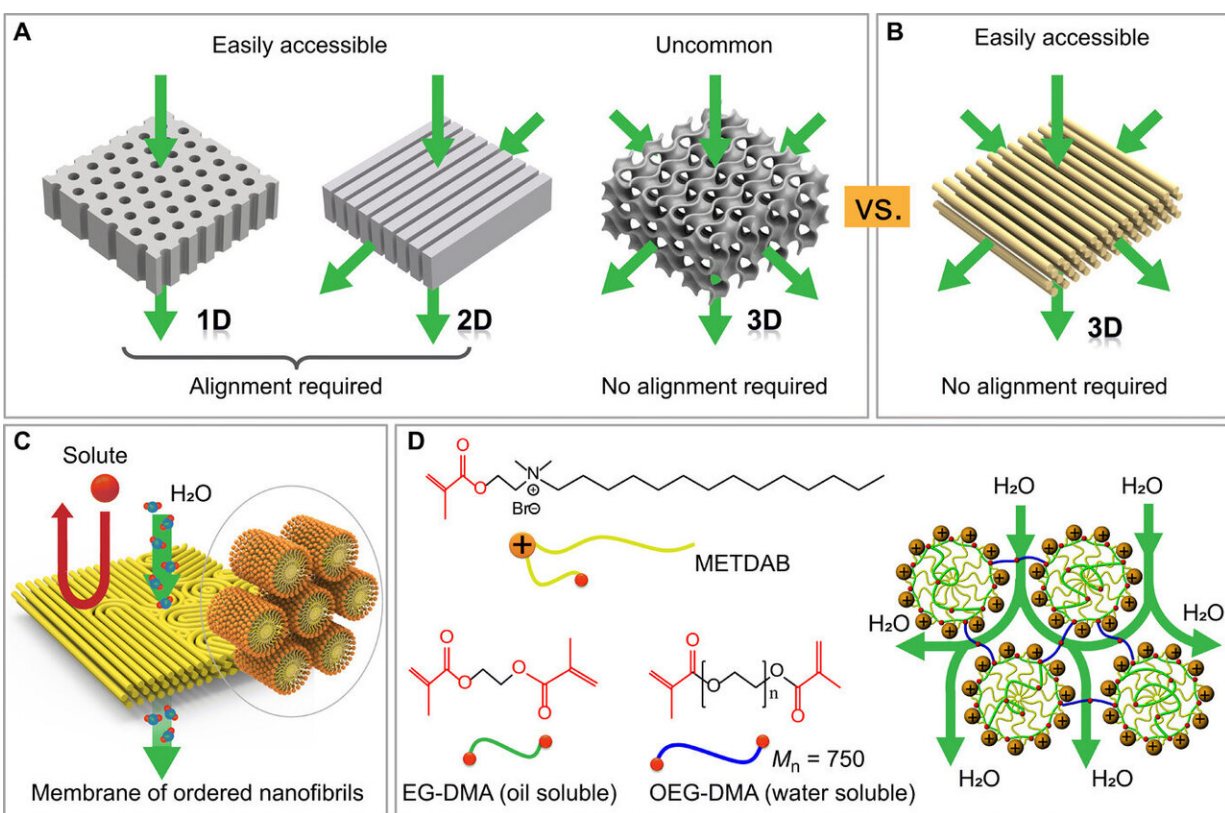


Self-assembled membrane with water-continuous transport pathways for precise nanofiltration

August 21 2019, by Thamarasee Jeewandara



Schematic illustration of self-assembled structures used to fabricate nanoporous polymer membranes. (A) The two readily obtained morphologies, i.e., lamellae and cylinders, require alignment of the structures to optimize transport. (A) Schematic illustration showing self-assembled morphologies used as templates for fabricating nanoporous polymer membranes. Two easily obtained morphologies, i.e., lamellae and cylinders, while used for forming nanopores, require alignment of the self-assembled domains. 3D interconnected gyroids are

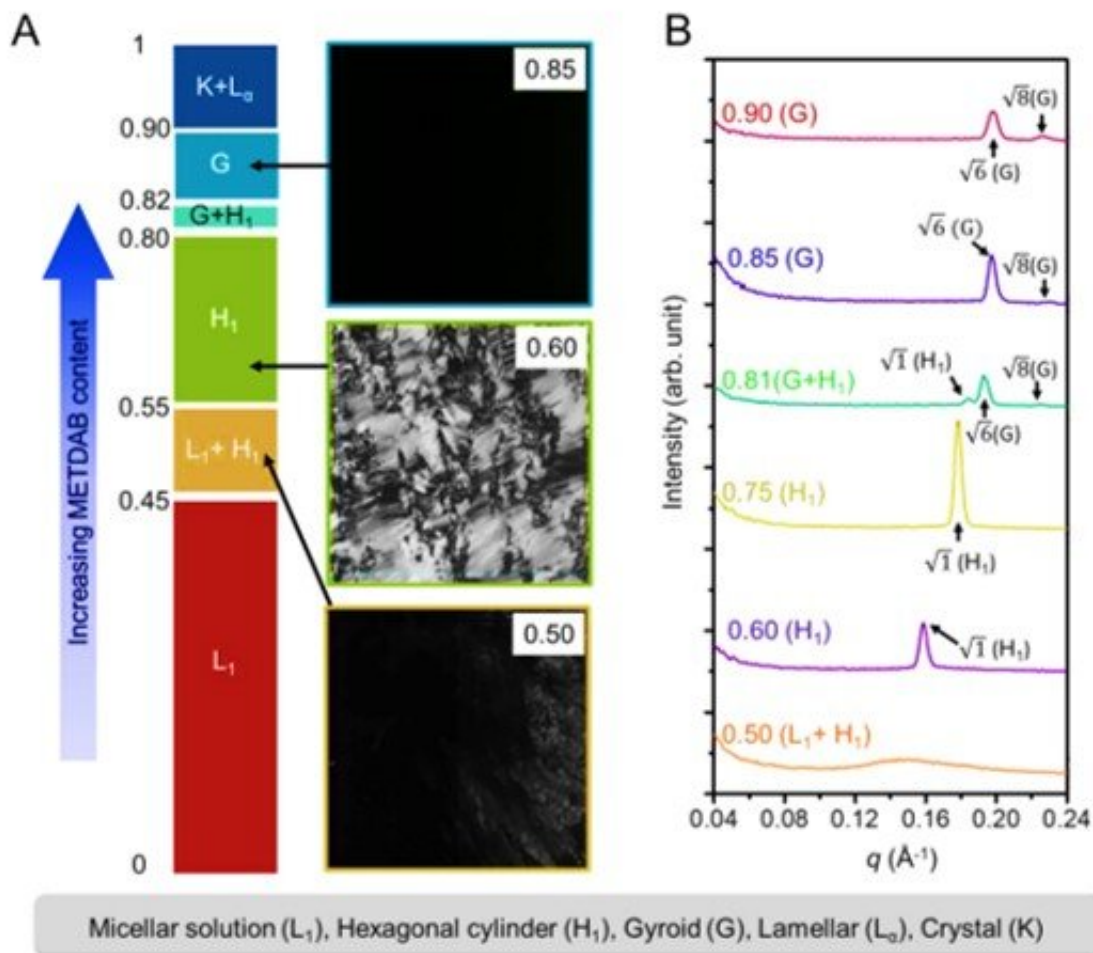
not universally observed in BCP and LC systems and, where they occur, usually exhibit narrow windows of stability. (B) Proposed morphology for fabricating membranes that can be easily templated from mesophases of hexagonally packed cylinders and requires no alignment to enhance flux. (C) Schematic illustration for preparation of size exclusion nanofiltration membranes from cross-linking of a direct hexagonal cylinder lyotropic mesophase (H₁). The cross-linked sample contains hexagonally packed molecular fibrils in the continuous water phase, which allows water to permeate through the gap between nanofibers but rejects larger-size solutes because of size exclusion. (D) Molecular structures of the polymerizable surfactant METDAB, the water-soluble cross-linker OEG-DMA, and the oily cross-linker EG-DMA for the formulation of the desired H₁ mesophase. EG-DMA (in green) copolymerizes with the surfactant in the hydrophobic core, and water-soluble OEG-DMA (in blue) bridges each cylinder into a network, the morphology of which provides a continuous aqueous transport path, as schematically illustrated. Mn, number-average molecular weight. Credit: Science Advances, doi: 10.1126/sciadv.aav9308

Self-assembled materials are attractive for next-generation materials, but their potential to assemble at the nanoscale and form nanostructures (cylinders, lamellae etc.) remains challenging. In a recent report, Xundu Feng and colleagues at the interdisciplinary departments of chemical and environmental engineering, biomolecular engineering, chemistry and the center for advanced low-dimension materials in the U.S., France, Japan and China, proposed and demonstrated a new approach to prevent the existing challenges. In the study, they explored size-selective transport in the water-continuous medium of a nanostructured polymer template formed using a self-assembled [lyotropic](#) H₁ (hexagonal cylindrical shaped) mesophase (a state of matter between liquid and solid). They optimized the [mesophase](#) composition to facilitate high-fidelity retention of the H₁ structure on photoinduced crosslinking.

The resulting nanostructured polymer material was mechanically robust

with internally and externally crosslinked nanofibrils surrounded by a continuous aqueous medium. The research team fabricated a [membrane](#) with size selectivity at the 1 to 2 nm length scale and water permeabilities of $\sim 10 \text{ liters m}^{-2} \text{ hour}^{-1} \text{ bar}^{-1} \mu\text{m}$. The membranes displayed excellent anti-microbial properties for practical use. The results are now published on *Science Advances* and represent a breakthrough for the potential use of self-assembled membrane-based nanofiltration in practical applications of water purification.

Membrane separation for filtration is widely used in diverse technical applications, including seawater desalination, gas separation, food processing, fuel cells and the emerging fields of [sustainable power generation](#) and distillation. During nanofiltration, dissolved or suspended solutes ranging from 1 to 10 nm in size can be removed. New nanofiltration membranes are of particular interest for low-cost treatment of wastewaters to [remove organic contaminants](#) including pesticides and metabolites of pharmaceutical drugs. State-of-the-art membranes presently suffer from a trade-off [between permeability and selectivity](#) where increased permeability can result in decreased selectivity and vice-versa. Since the trade-off originated from the intrinsic structural limits of conventional membranes, materials scientists have incorporated self-assembled materials as an attractive solution to [realize highly selective separation](#) without compromising permeability.

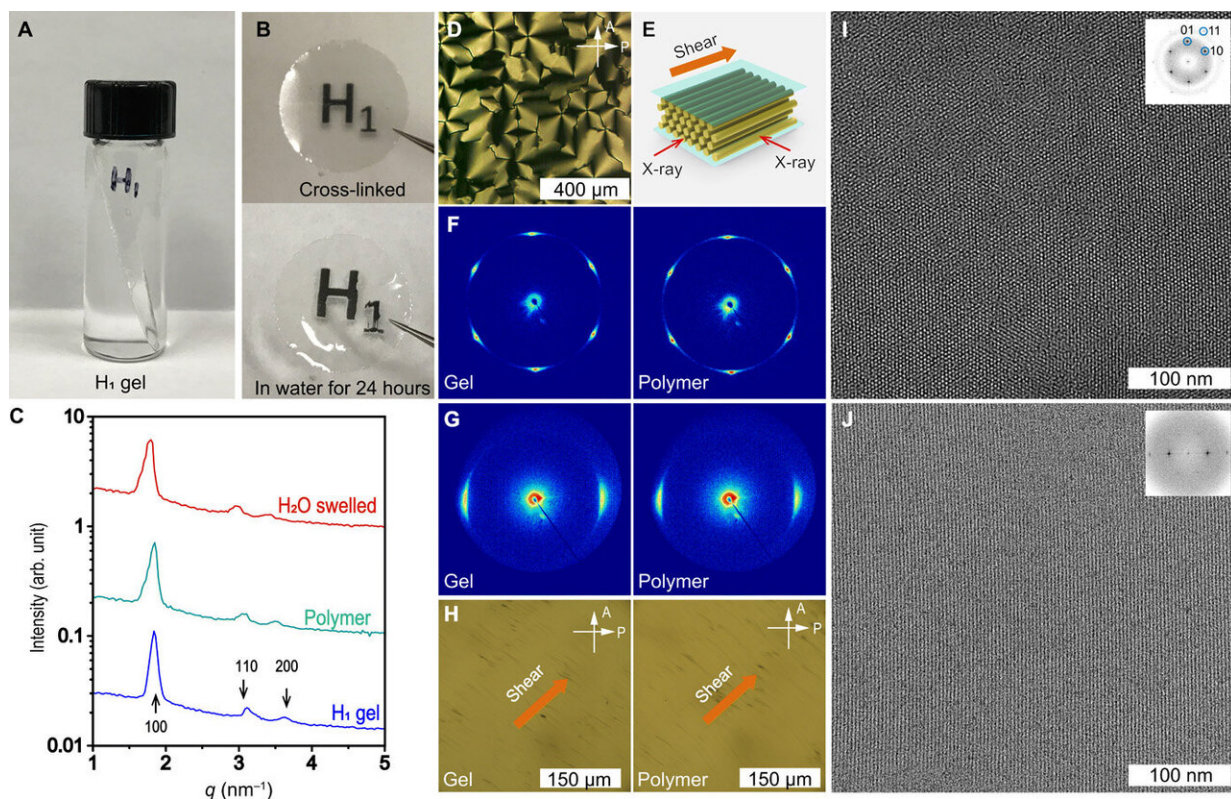


METDAB/water binary phase diagram as determined by POM (polarized optical microscopy) and x-ray scattering. The weight concentrations of METDAB are shown in the phase diagram. As the concentration of METDAB was increased, the surfactant/water mixtures followed a phase sequence of micellar solution (L_1), hexagonal cylinder (H_1), gyroid (G), lamellar (L_α), and crystal (K). Selective (A) POM images and (B) X-ray scattering data represent this sequence. Credit: Science Advances, doi: 10.1126/sciadv.aav9308

For example, block copolymers (BCPs) and small-molecule liquid crystals (LCs) can self-assemble into a series of mesophase forms with periodic nanoscale domains to contain thermodynamically defined sizes

and shapes. The well-ordered nanostructures found in BCPs and LCs in the form of [cylinders](#), [lamellae](#) and [gyroids](#) are attractive templates to fabricate [nanopore membranes](#). Self-assembling materials could provide useful templates to control the organization of discrete objects such as [water channel proteins](#) or [nanotubes](#), to function as nanofiltration pores. Although the nanopore membranes showed high selectivity and permeability for nanofiltration and ultrafiltration, scientists have encountered challenges during their practical development.

In the present work, Feng et al. developed a scalable approach to obtain highly permeable and selective nanofiltration membranes with attractive anti-biofouling properties for antimicrobial activities. The membrane contained hexagonally ordered molecular nanofibrils realized by crosslinking a direct cylindrical lyotropic LC. The membrane was mechanically robust and resilient against both dehydration and swelling by excess water. The self-assembled structure provided uniform and well-defined spacing between nanofibrils for high membrane selectivity and reduced membrane complexity, departing from [previously reported work](#). The new characteristics set the membranes apart from nanostructured membranes derived from lyotropic LCs reported to date, to offer a path toward practical nanofiltration.

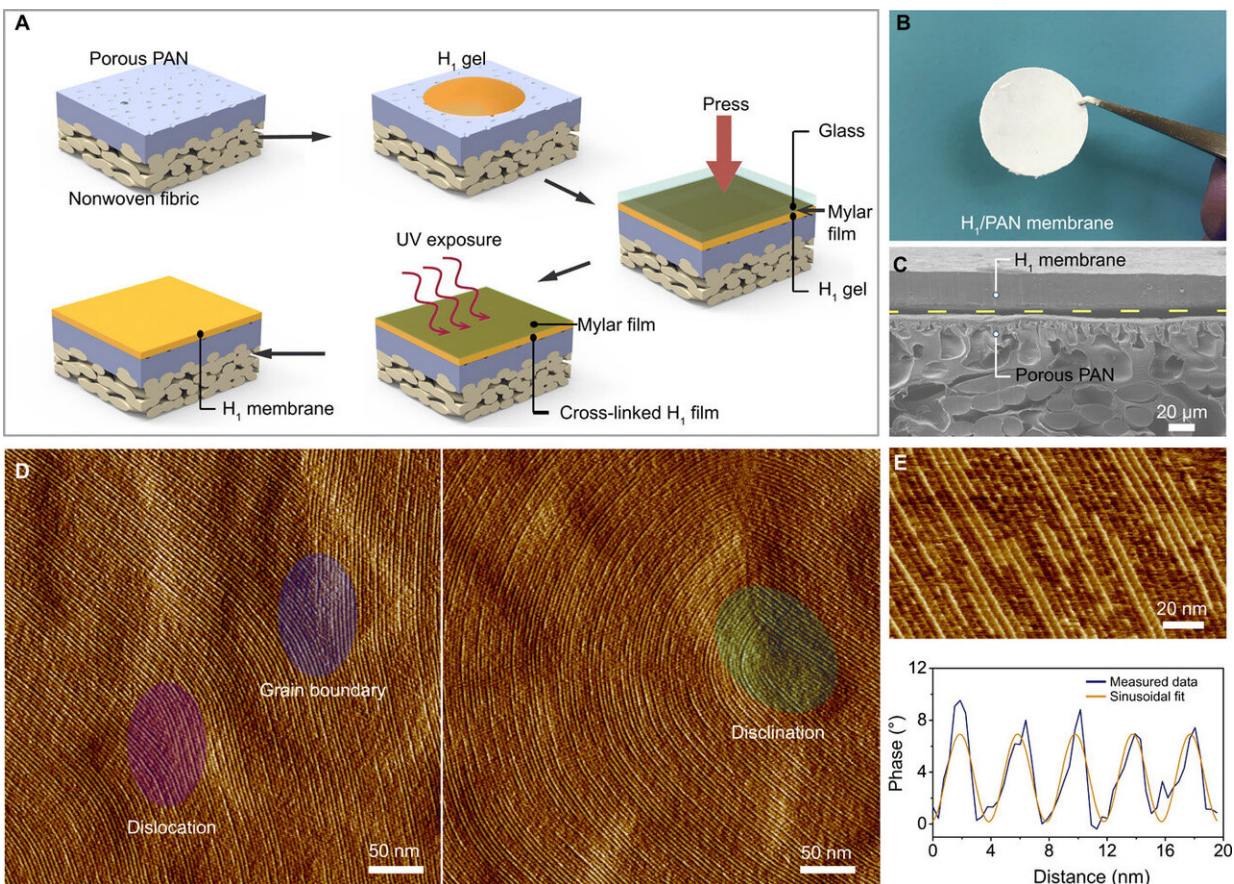


High-fidelity retention of the H1 mesophase morphology after UV-induced cross-linking with the aid of dual cross-linkers. (A) Photo of an H1 mesophase gel formed by 70 wt % METDAB, 22.8 wt % water, 5.4 wt % OEG-DMA, and 1.8 wt % EG-DMA. (B) Photos showing the corresponding cross-linked polymer film (40 μm thick) and the film integrity after immersion in water for 24 hours. (C) 1D integrated SAXS data display the structural consistency of the H1 morphology in the non-cross-linked gel, the cross-linked polymer, and the polymer after immersion in water for 24 hours. A small increase of the d_{100} spacing from 3.6 to 3.7 nm was found after 24 hours of water immersion, indicating that there was very little swelling of the sample. (D) POM image displaying the preservation of the typical LC texture found in cylindrical mesophases. (E) Schematic illustration of the shear alignment and the 2D SAXS measurements. 2D SAXS patterns before and after cross-linking, as obtained by incidence of the x-ray beam (F) parallel and (G) orthogonal to the shear direction. (H) POM images showing the essentially unchanged birefringent color of the oriented cylindrical micelles before and after cross-linking. The sample was positioned such that the original shear direction was at 45° with respect to each of the two crossed polarizers. TEM micrographs viewed along (I) and

orthogonal to (J) the shear direction showing aligned nanofibrils. Insets: Fast Fourier transform (FFT) images. Before microtoming, the polymer was immersed into a 0.1 wt % KI aqueous solution for 1 hour to replace Br[−] by I[−] to enhance the atomic number contrast for imaging. Photo credit: Xunda Feng, Yale University. Credit: Science Advances, doi: 10.1126/sciadv.aav9308

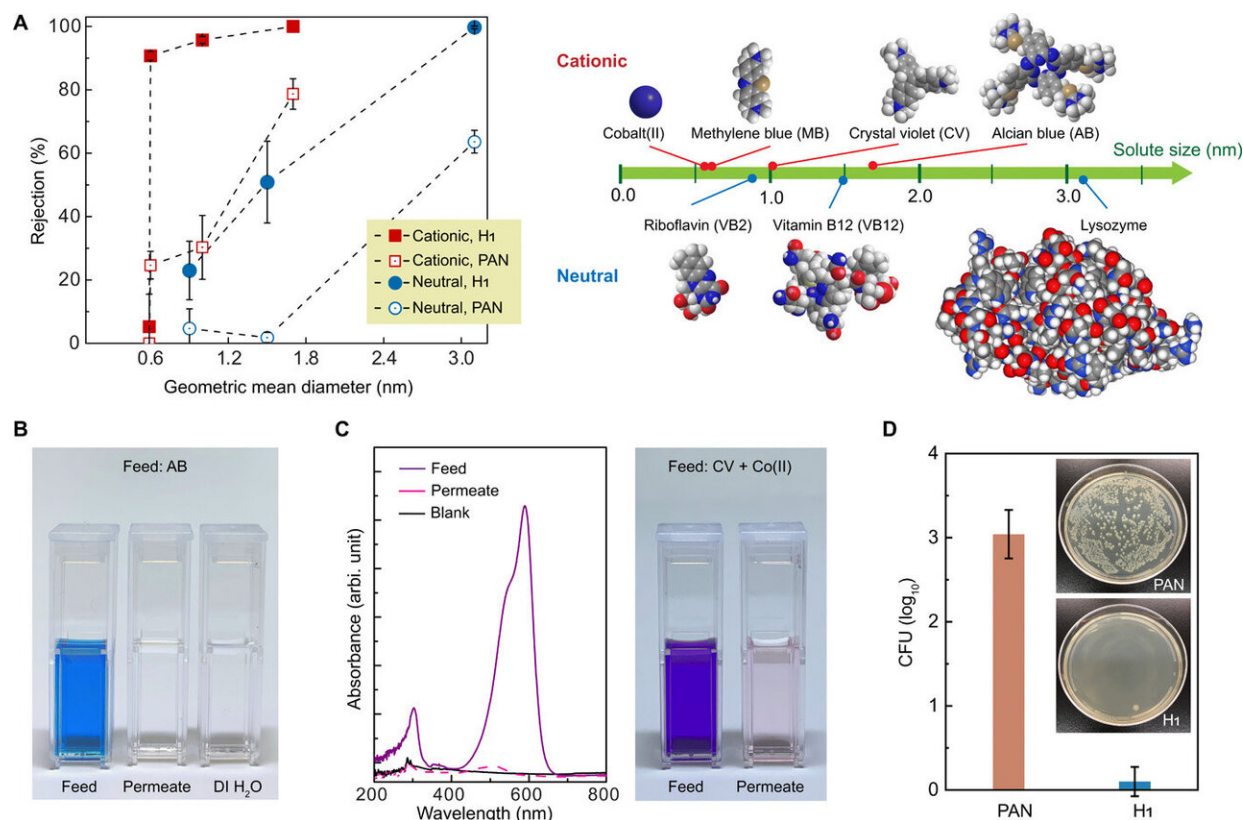
To form a polymerizable H₁ mesophase with water, the research team used a cationic surfactant, [2-\(methacryloyloxy\)ethyl tetradecyl dimethyl ammonium bromide](#) (METDAB) alongside additional crosslinkers of ethylene glycol dimethacrylate (EG-DMA) and oligo(ethylene glycol) dimethacrylate (OEG-DMA). The research team synthesized the surfactant monomer or surfmer in a single-step [Menshutkin reaction](#) and formed H₁ phases at room temperature using METDAB concentrations ranging from 55 to 80 weight percentage.

They performed detailed structural characterizations using high-resolution small-angle X-ray scattering (SAXS) with high-resolution microscopy to verify the retention of the H₁ mesophase after UV-initiated cross-linking. They optimized the composition to develop 70 weight percent METDAB with 22.8 weight percent water, 5.4 weight percent OEG-DMA and 1.8 weight percent EG-DMA with photoinitiator to form a stable, homogenous H₁ mesophase gel. The resulting gel sample showed excellent transparency to retain integrity after immersing in water for 24 hours for resistance against structural collapse due to water swelling. Feng et al. obtained a high-resolution TEM image of the sample to observe an ordered array of hexagonally packed nanofibrils displaying a six-fold symmetry.



Fabrication of H₁/PAN composite membranes and microscopic characterization of the membrane structures. (A) Schematic illustrating H₁ membrane fabrication on supporting PAN membranes. (B) Photograph of H₁/PAN composite membrane. (C) Cross-sectional SEM image showing the composite membrane. (D) AFM images showing the surface morphology of the H₁ membrane with closely packed nanofibrils. Topological defects including dislocations, disclinations, and grain boundaries are well preserved on the film surface, consistent with high-fidelity retention of the mesophase morphology on cross-linking. (E) Line profile analysis of the high-resolution image (scale bar, 20 nm) shows an interfibril distance of \sim 4 nm, in good agreement with SAXS and TEM measurements. Sinusoidal fit of the line profile provides a guide to the eye. Photo credit: Xunda Feng, Yale University. Credit: Science Advances, doi: 10.1126/sciadv.aav9308

The water-continuous nature of the self-assembled, cross-linked H₁ mesophase and its mechanical resilience was attractive for membrane application, which Feng et al. tested as a proof-of-concept. For this, they produced a membrane by cross-linking a thin film of the H₁ mesophase with UV exposure, on a commercially sourced, polyacrylonitrile (PAN) ultrafiltration membrane. They then imaged the H₁/PAN composite membrane using a scanning electron microscope (SEM) and tested the surface morphology using atomic force microscopy (AFM). During the experiments, the composite membranes showed strong size selectivity toward charged organic dye molecules. Based on the transport data, Feng et al. showed that the membrane could effectively separate solutes on the basis of their size and charge.



Solute rejection and antibacterial properties of H₁ membranes. (A) Rejection data of H₁ membranes and PAN membranes for seven different solutes: Co(II)

(cobalt chloride), MB (methylene blue), CV (crystal violet), AB (Alcian blue), VB2 (riboflavin), VB12 (cobalamin), and lysozyme. Spacing filling models and estimated geometric mean diameters of the solutes are shown. Error bars represent 95% t test confidence limits derived from data variance across multiple measurements, typically two membranes and four permeate samples per membrane. (B) Photos of the feed solution of AB, the permeate from the H1 membrane, and deionized (DI) water as a reference, respectively. (C) UV-visible (UV-Vis) spectrum and photo showing competitive solute separation of CV and Co(II). (D) Quantification of bacterial growth in colony-forming units (CFU) in the samples and photographs (insets) showing control and H1-derived membrane samples after incubation with bacteria. Photo credit: Yizhou Zhang, University of Pennsylvania and Xinglin Lu, Yale University. Credit: Science Advances, doi: 10.1126/sciadv.aav9308.

The researchers propose additional investigations to highlight the boundary between porous and solution diffusion mechanisms in polymer membranes. For instance, the water permeability decreased up to 50 percent when they filtered charged solutes but remained unaltered in the presence of natural solutes. The permeabilities and function of the self-assembled nanomembranes developed in the study compared favorably with commercial nanofiltration membranes such as [Dow FILMTEC NF90-400](#). The research team observed water-facing quaternary ammonium groups on the nanofibrils to represent anti-biofouling behavior due to well-established anti-microbial properties of the functional groups. They studied the potential for anti-biofouling behavior of H₁ membranes using a standard colony-forming unit (CFU) enumeration assay.

During the experiments, they kept PAN membranes (control group) or H₁ membranes in contact with gram-negative bacteria (*Escherichia coli*) in suspension for 3 hours. When they sonicated the membranes mildly in saline solution, the bacteria detached from the surfaces for subsequent

culture on agar and overnight incubation. The results showed the number of viable *E. coli* cells on the H_1 membrane to be 3 orders of magnitude smaller than the control, proving anti-biofouling activity of the membranes. The results confirmed a strong antimicrobial response for H_1 , as anticipated due to the presence of quaternary ammonium groups.

In this way, Xundu Feng and colleagues reported a simple approach to engineer polymer nanofiltration membranes with a unique structure of ordered nanofibril arrays. In the approach, they used a cross-linkable, water-continuous lyotropic H_1 mesophase template to create the morphology of interest. They followed the engineering step with systematic, materials characterization techniques to confirm the formation of highly ordered nanostructures with high fidelity for mechanical robustness. The present work was the first to directly image the polymerized lyotropic H_1 mesophase.

The scientists synthesized the main constituent species of the system METDAB in a single step, using readily available and inexpensive reagents. Using the membrane, they demonstrated clear, size-based selectivity with molecular dyes as model solutes, alongside water permeabilities approximating $10 \text{ liters m}^{-2} \text{ hour}^{-1} \text{ bar}^{-1} \mu\text{m}$. The research team aims to optimize the procedures of fabrication to provide thinner selective layers by modifying the surface chemistry of the nanofibrils for water nanofiltration and treatment using antimicrobial membranes in practical applications.

More information: Xunda Feng et al. Precise nanofiltration in a fouling-resistant self-assembled membrane with water-continuous transport pathways, *Science Advances* (2019). [DOI: 10.1126/sciadv.aav9308](https://doi.org/10.1126/sciadv.aav9308)

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