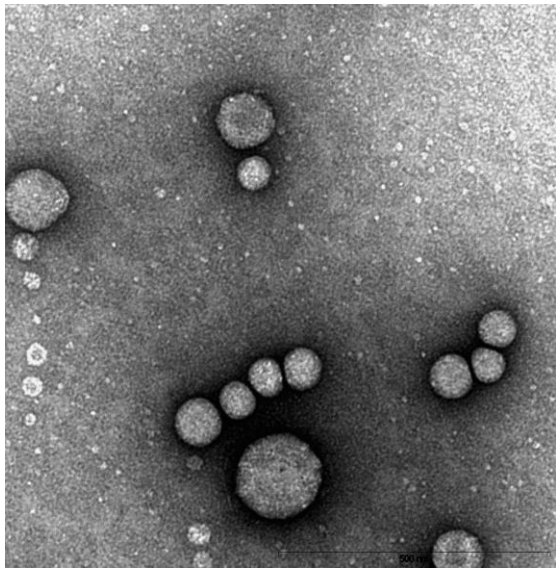
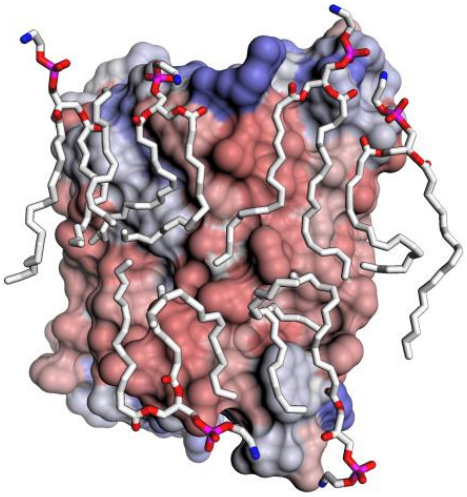
RESEARCH BACKGROUND





1998-2006
(MS + INDUSTRY)

Pilot, lab and full scale studies of membranes and other water treatment technologies
Desalination major focus

2006-2010
(PHD)

Biomimetic membranes!
Earliest studies and Proposal to use aquaporins in membanes

2010-2012
(Postdoc+)

Aquaporin structure, 2D crystallization

BIOLOGICAL, BIOMIMETIC, AND BIOINSPIRED MEMBRANES

Manish Kumar

Department of Chemical Engineering

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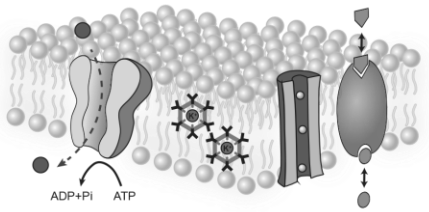
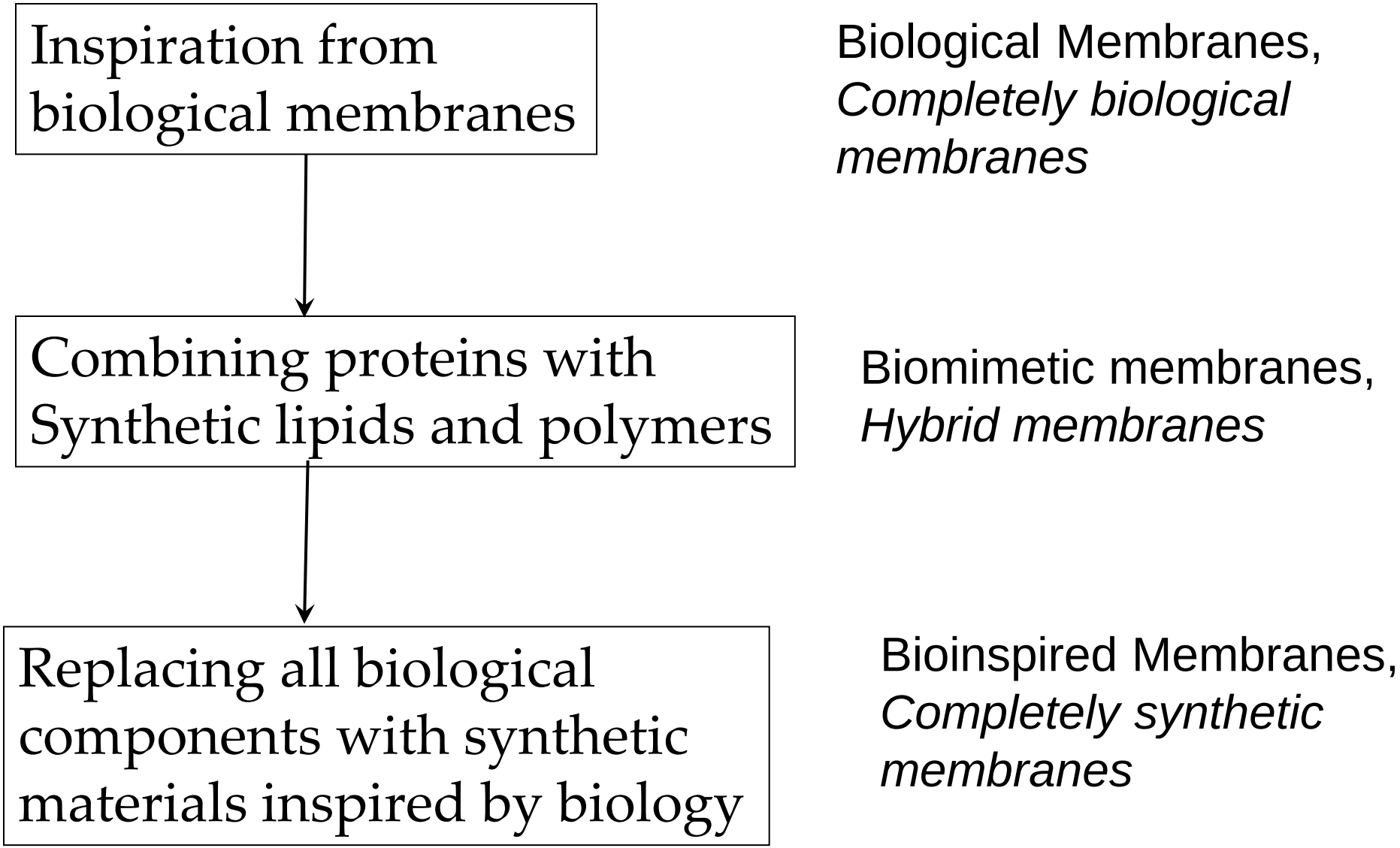
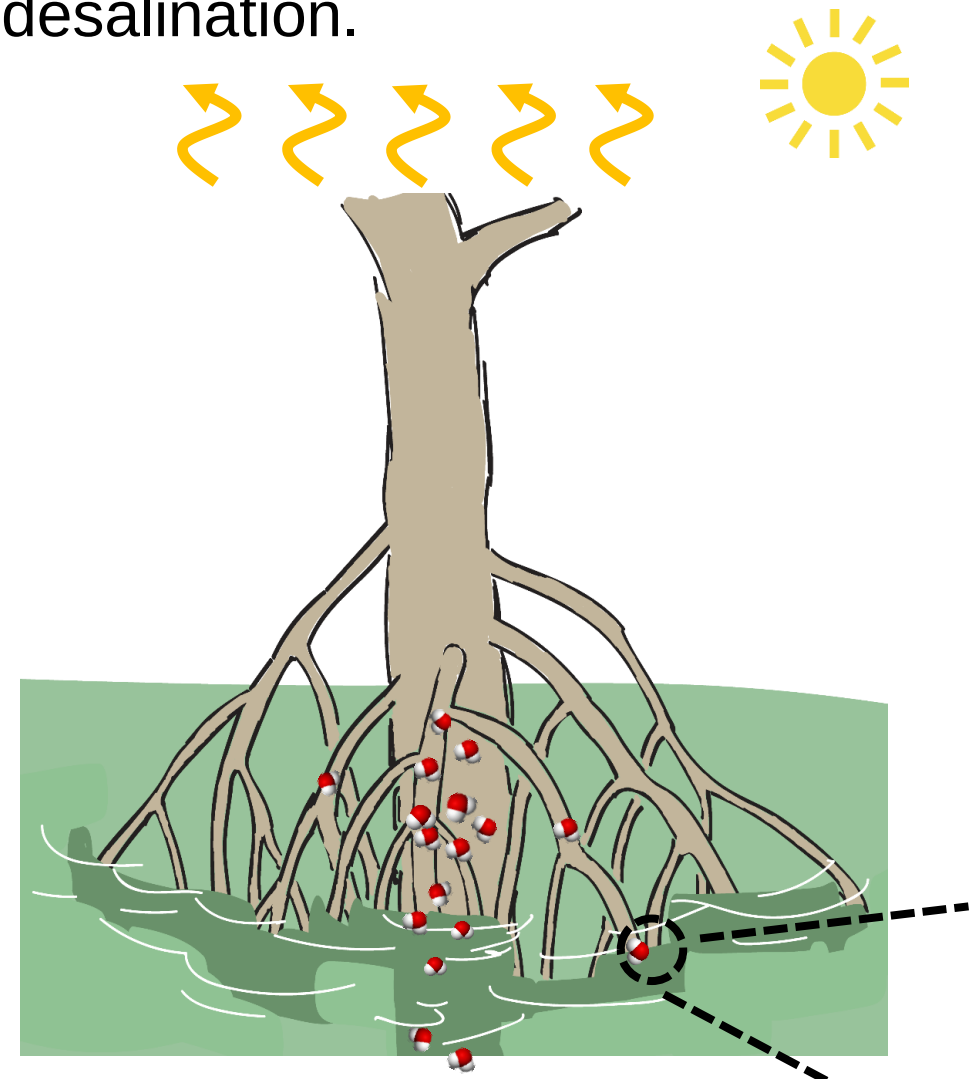
PennState



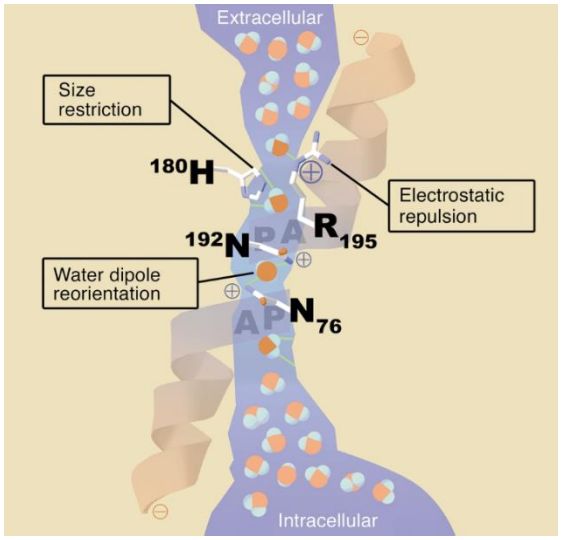


This has also been our innovation roadmap

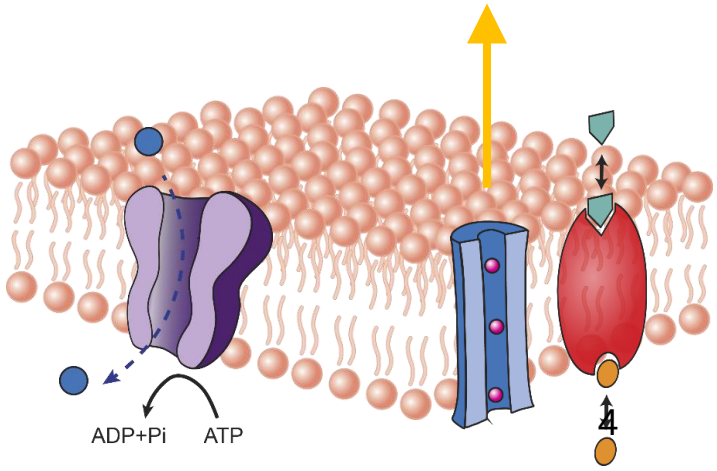
Nature presents excellent examples for energy efficient desalination.



Mangroves filter salty water driven by transpiration

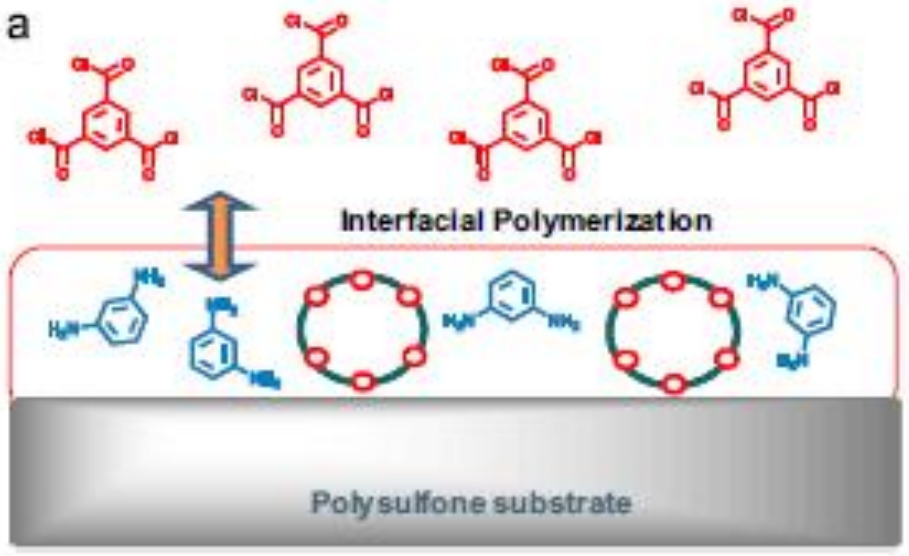


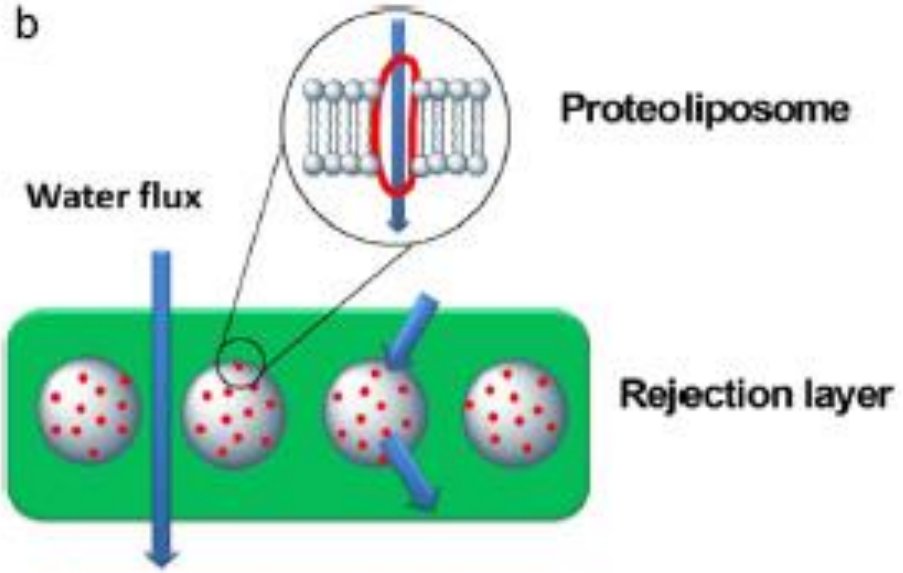
Biological water channel protein aquaporins



Aquaporin-based forward and reverse osmosis membranes have been created

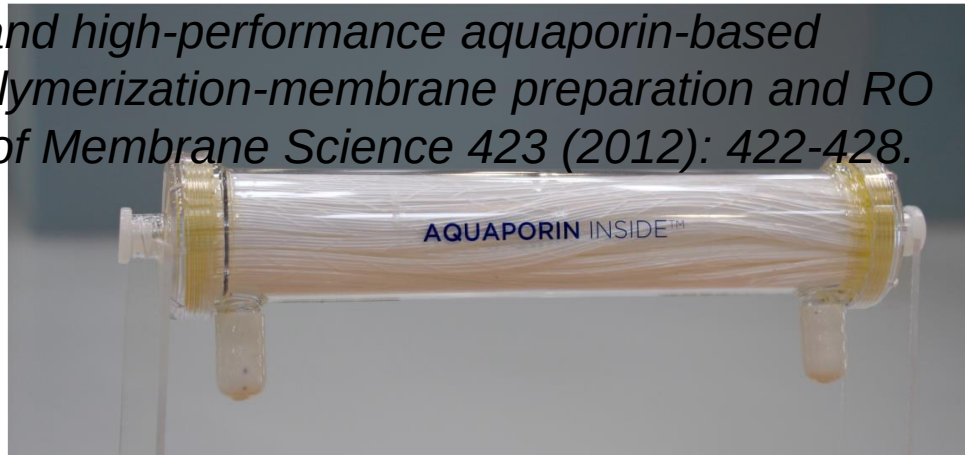
Aquaporin incorporated membranes are being developed as desalting membranes





Zhao, Yang, et al. "Synthesis of robust and high-performance aquaporin-based biomimetic membranes by interfacial polymerization-membrane preparation and RO performance characterization." Journal of Membrane Science 423 (2012): 422-428.

AQUAPORIN



There are challenges with scaling up AQP based membranes

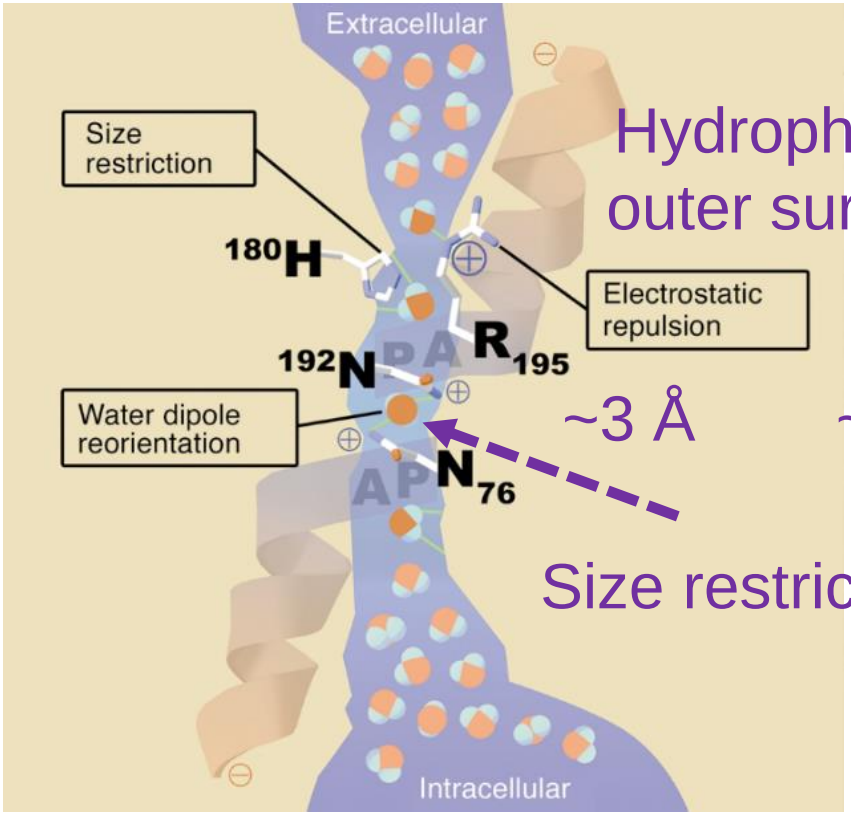
1. Stability

2. Unconventional processing required (aqueous self-assembly)

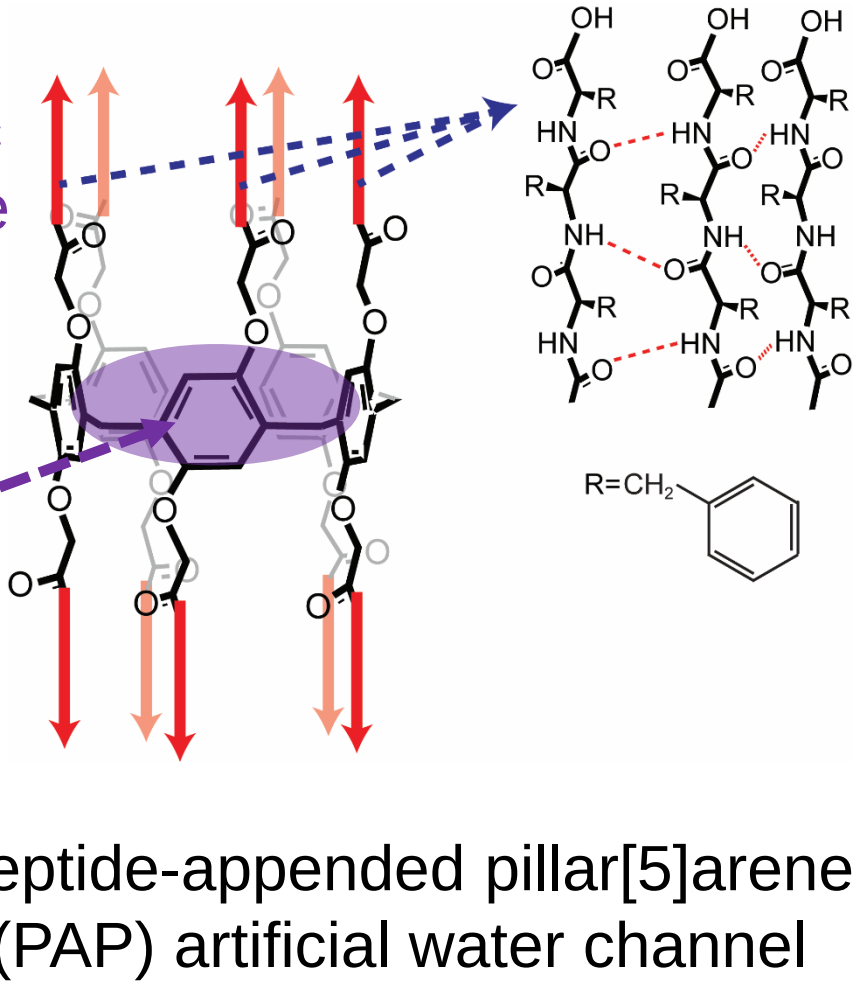
3. Mass production challenging

Grzelakowski, M., Cherenet, M.F., Shen, Y.X. and Kumar, M., 2015. A framework for accurate evaluation of the promise of aquaporin based biomimetic membranes. *Journal of Membrane Science, 479*, pp.223-231.

Can we design artificial water channels using organic chemistry?

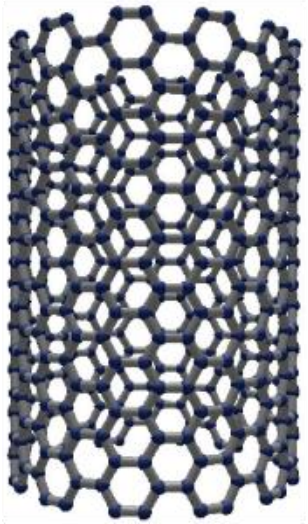
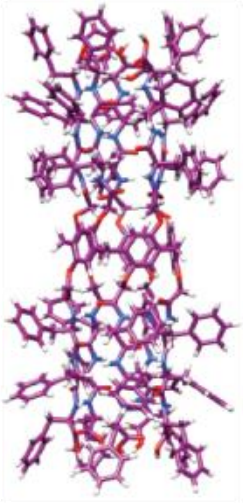


Aquaporins



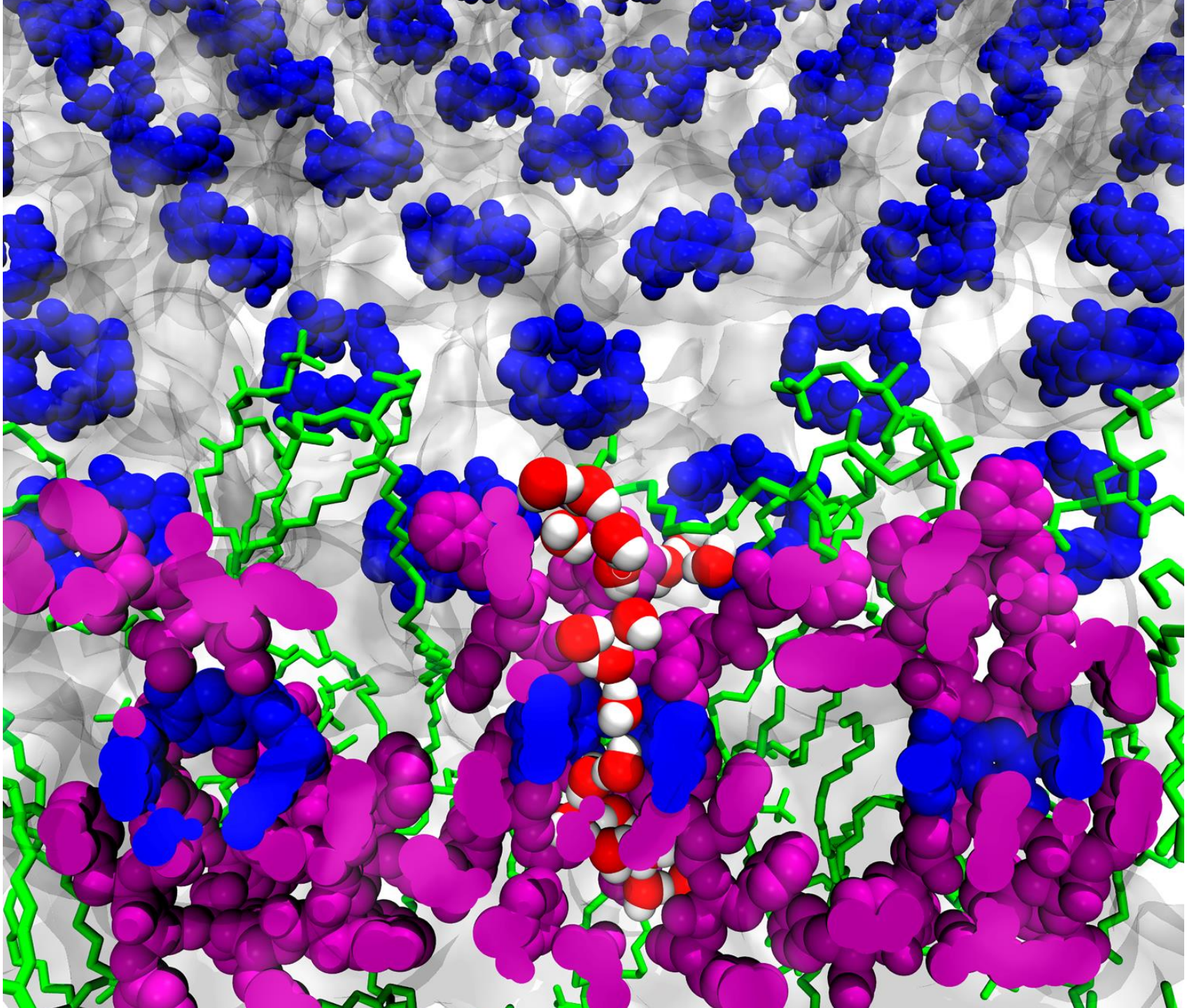
Peptide-appended pillar[5]arene (PAP) artificial water channel

1. Kozono, D. *et al*. *The Journal of Clinical Investigation* **109**, 1395-1399, (2002).
2. Shen, Y.-x. *et al. J. Membr. Sci.* **454**, 359-381, (2014).
3. Shen, Y.-x. *et al. Proc. Natl. Acad. Sci. U.S.A.* **112**, 9810-9815, (2015).

	Aquaporin 1	CNTs (12, 12)	Pillar[5]arene
			
Permeability per channel (H_2O/s)	4.0×10^9	9.0×10^8	3.5×10^8

The single channel permeability of PAP channels is within the range of that of AQPs and CNTs.

Shen, Y.-x. *et al.* Highly permeable artificial water channels that can self-assemble into two-dimensional arrays. *Proc. Natl. Acad. Sci. U.S.A.* **112**, 9810-9815, (2015).



Summary

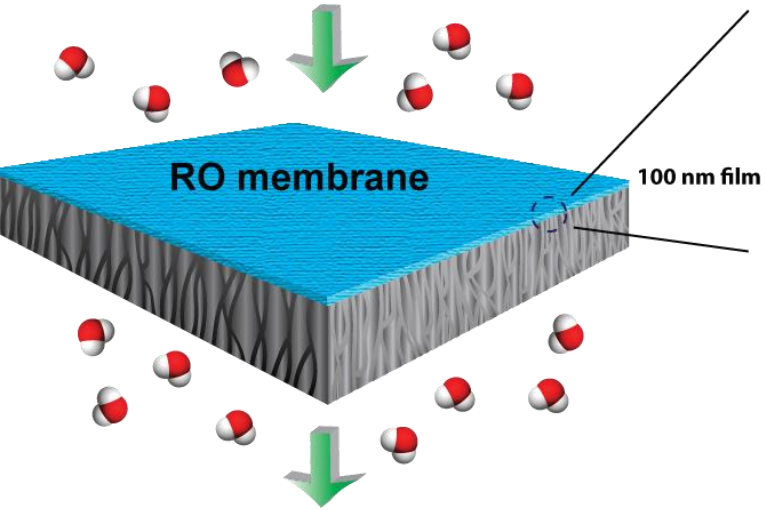
- Biological membranes are an excellent source of inspiration for engineered membranes
- Making combinations of biological and non-biological materials can lead to novel materials/insights
- Insights can be used to design practical and scalable high performance materials

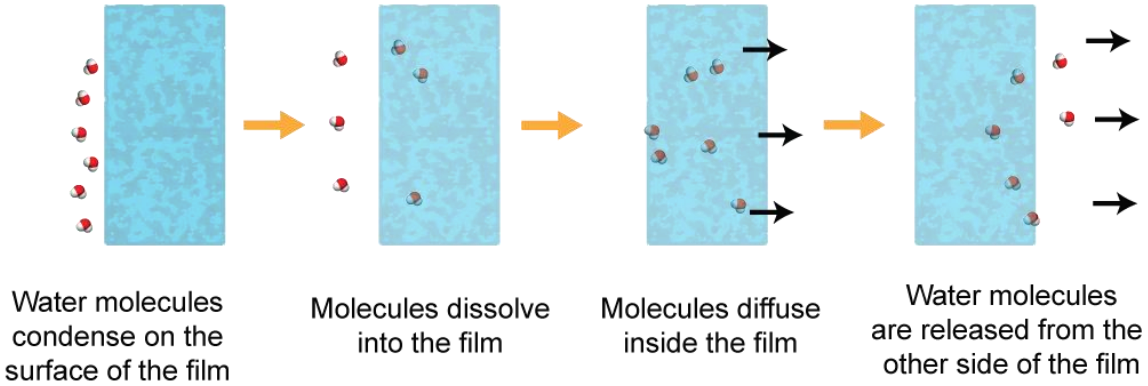
Acknowledgements

- Students and Postdocs
- Penn State
- FUNDING
  - NSF
  - DOE
  - USGS
  - US Army
  - Dow
  - PPG
  - Applied Biomimetic
  - W.L. Gore

QUESTIONS?

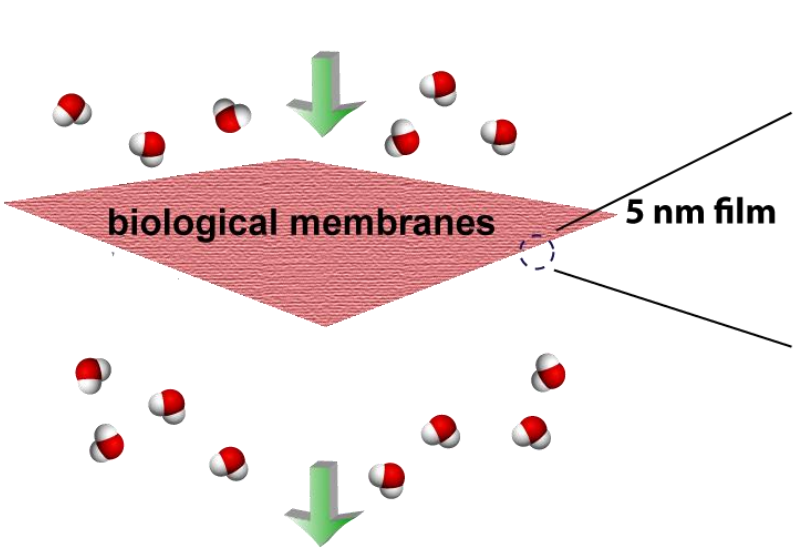
RO TRANSPORT MECHANISM

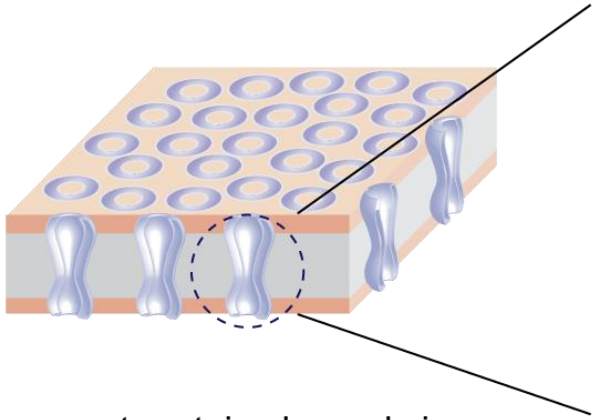




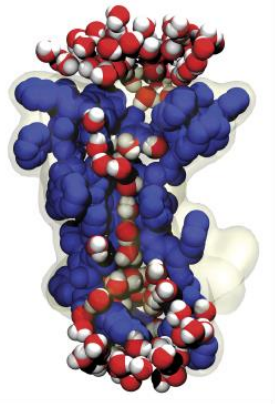
Solution-diffusion mechanism of reverse osmosis membrane
(Activation energy ~ 15 kcal/mole)

BIOMEMBRANE TRANSPORT MECHANISM



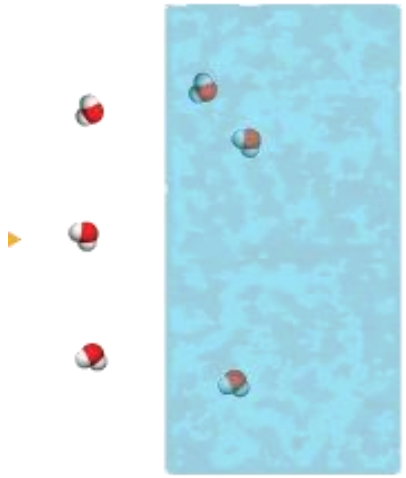


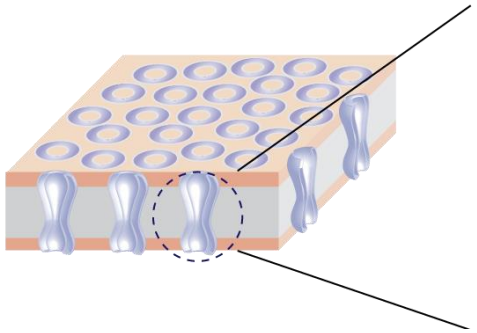
transport protein channels in
lipid bilayers
(Activation energy < 5 kcal/mole)

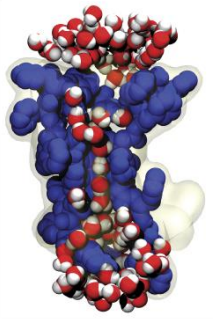


Single file water transport
in water channels

Materials utilizing channel based desalination include carbon nanotube membranes and graphene membranes (Mi).







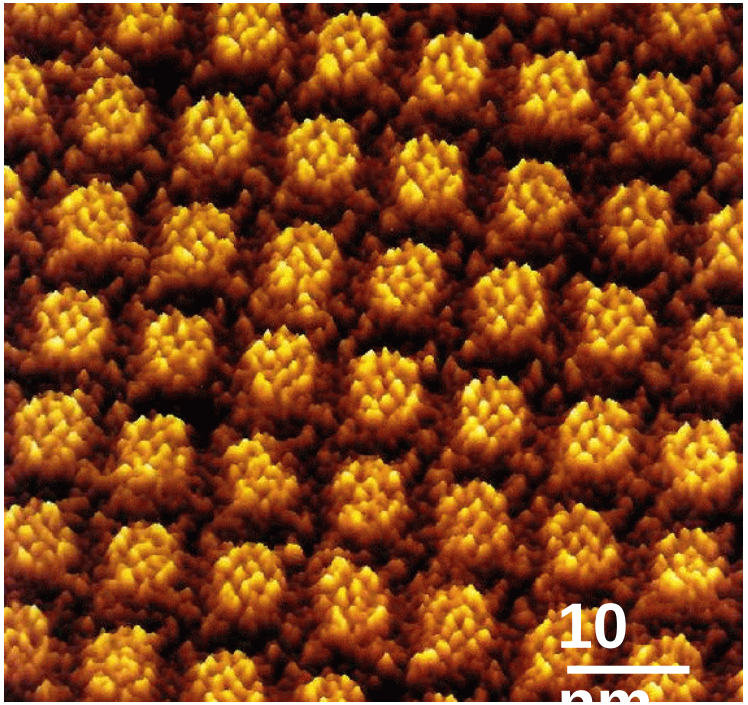
SOLUTION DIFFUSION DESALINATION

- \- 100 nm thickness
- \- 15 kcal/mol activation energy
- \- Imperfect rejection of uncharged solutes
- \+ Widely Available

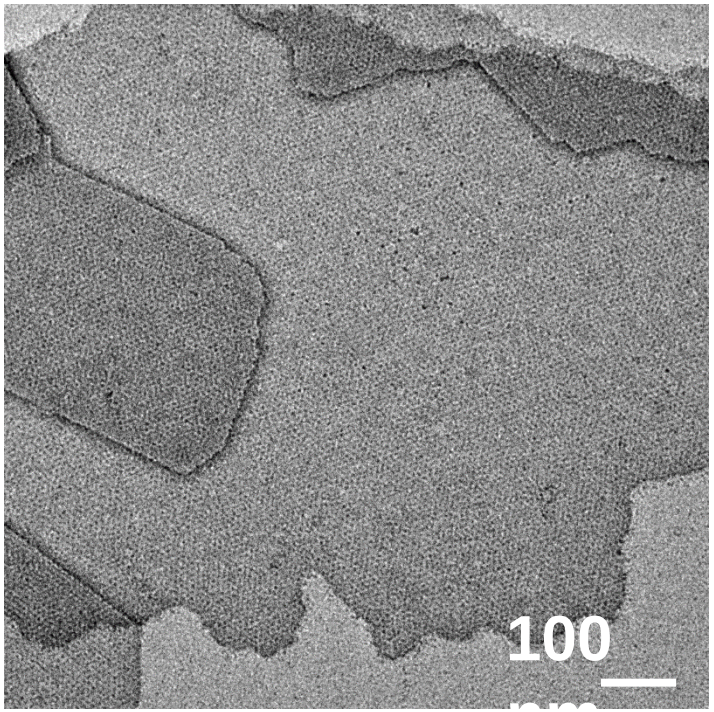
CHANNEL-BASED DESALINATION

+ 5-10 nm thickness
+ <5 kcal/mol activation energy
+ Potential for perfect rejection of solutes
- \- Just becoming available in nascent form

Membrane proteins can form 2D arrays in lipids and block copolymers



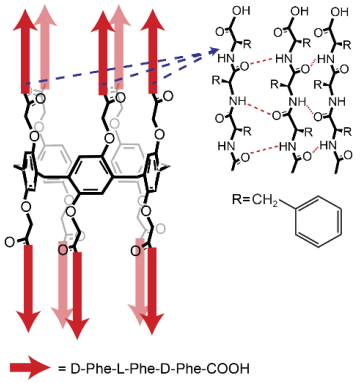
AqpZ-lipids 2D crystals

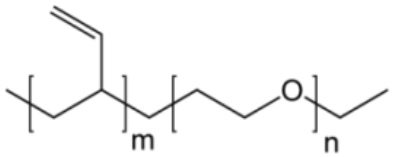


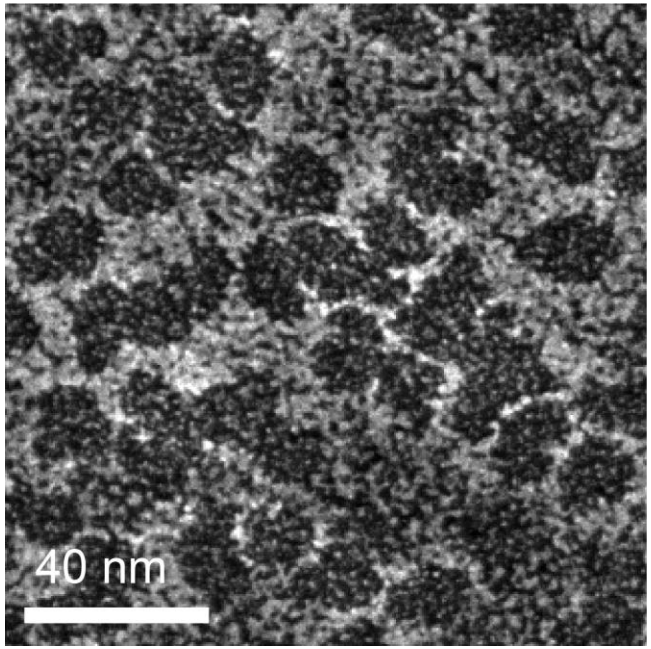
OmpF-PB-PEO 2D crystals

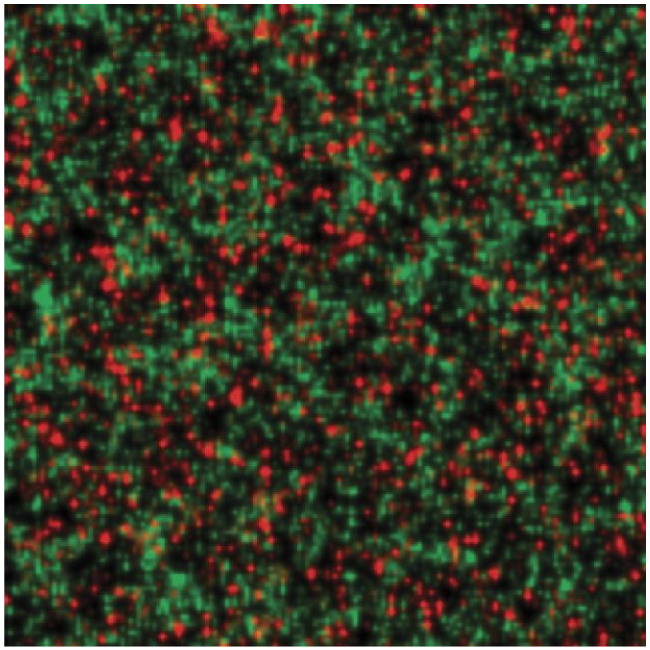
1. Scheuring, S. *et al*. *EMBO J.* **18**, 4981-4987, (1999).

PAP channels in PB12 BCPs



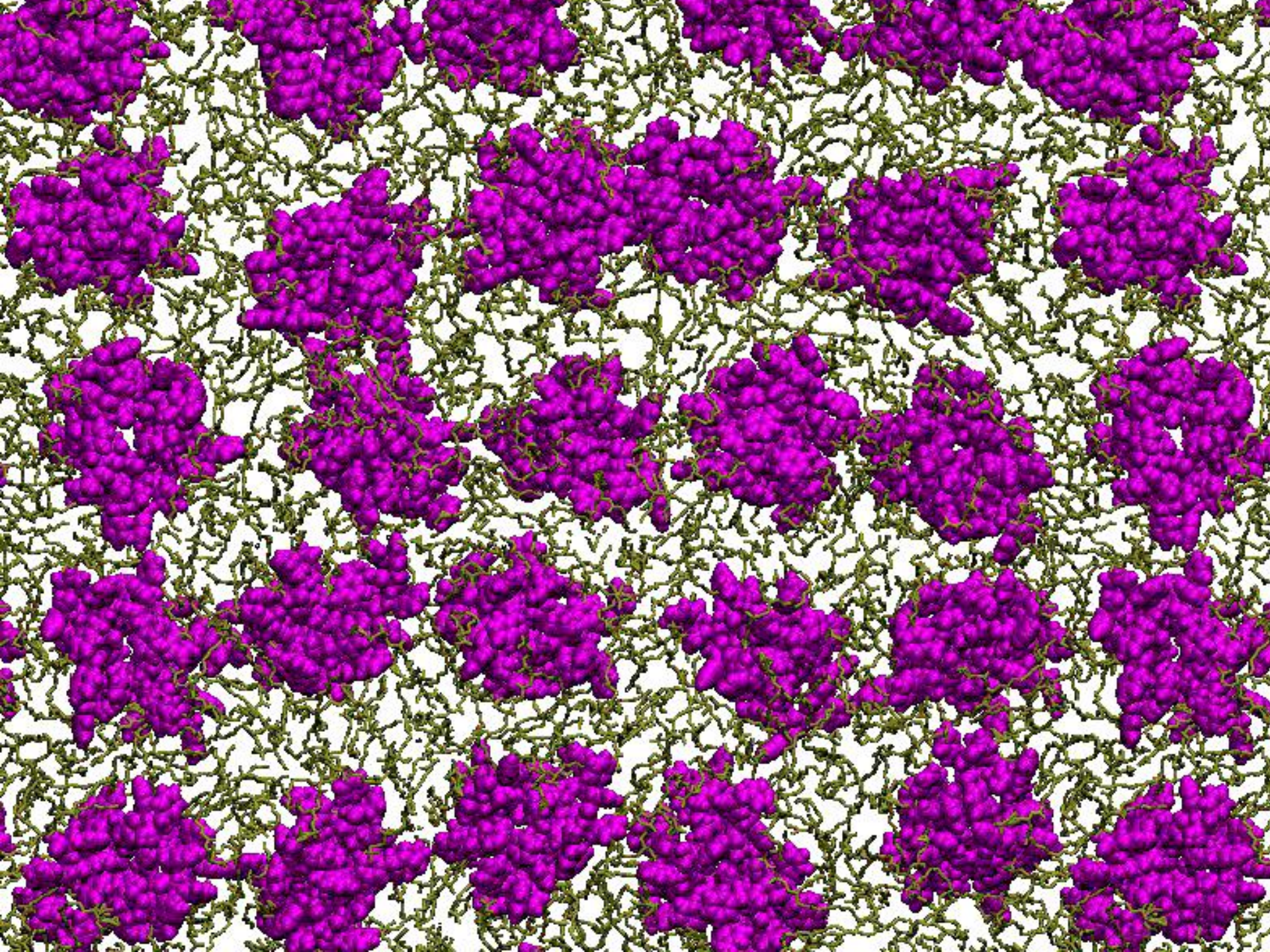






Green: uranium
Red: nitrogen

STEM image and EDS map



Aggregation of some proteins in membranes lead to formation of two dimensional sheets when protein content is high.[1,2]

Can we pack a lot of these channels in membranes to form sheets instead of vesicles?

[1] Hasler, Lorenz, et al. "2D crystallization of membrane proteins: rationales and examples." Journal of structural biology 121.2 (1998): 162-171.

[2]Kumar et al. "High-density reconstitution of functional water channels into vesicular and planar block copolymer membranes." *JACS* 134.45 (2012): 18631-18637.

2D arrays of PAP channels = very high pore density

- Current CNT membranes[1]:
  - $0.1\sim2.5\times10^3$ pores/μm^2
- Previous artificial channel based membranes in block copolymer templates[2:]
  - ~0.5-1 x 10^3 pores/ μm^2
- Pillar[5]arene channel 2D crystal pore density
  - ~2.6×10^5 pores/μm^2

[1]J. K. Holt *et al.*, Fast Mass Transport Through Sub-2-Nanometer Carbon Nanotubes. *Science* **312**, 1034-1037 (2006), Y. Baek *et al.*, High performance and antifouling vertically aligned carbon nanotube membrane for water purification. *J. Membr. Sci.* 460, 171-177 (2014).
[2]Xu, Ting, *et al.* "Subnanometer porous thin films by the co-assembly of nanotube subunits and block copolymers." *ACS nano* 5.2 (2011): 1376-1384.