

MOLECULAR MEMBRANES

Researchers are developing synthetic approaches and theoretical models for novel microporous materials.

Principal Investigator: Randall Q. Snurr

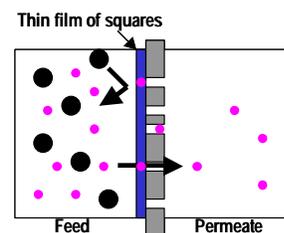
Collaborator: Joseph T. Hupp (Department of Chemistry)

Objective: A variety of discrete, metal-based coordination assemblies (molecular triangles, molecular squares (MS), molecular rectangles, etc.) featuring well-defined nanoscale cavities have been prepared over the past decade. A number of these supramolecular compounds have subsequently been used as building blocks for microporous molecular materials suitable for applications involving selective molecular transport, sensing, and chemical transformations. Another group of promising molecular membrane candidates includes zeolites, which are renowned for their adsorption and shape selectivity characteristics. The Snurr group is performing membrane experiments and developing a versatile molecular modeling platform to study properties of these microporous materials on the microscopic level.

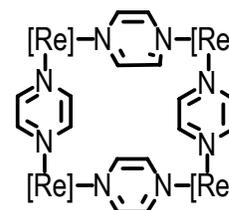
Approach: Thin molecular films are prepared by evaporatively casting suspensions of molecular squares (MS) in organic solvents on commercially available, polyester membranes. They are characterized by optical and luminescence microscopy, AFM and X-ray diffraction. The permeability of MS membranes is measured and then evaluated via a simple one-dimensional diffusion model $[J=(PD_f)\Delta C/l]$. Permeation can also be obtained from molecular dynamics (MD) calculations. Such simulations have been carried out to calculate permeation rates through zeolite membranes, and current work is also focused on the MS materials.

Results: The researchers have demonstrated size-selective transport through novel MS membranes by measuring permeabilities of various-sized molecules through 8 μm -thick films of pyrazine MS and 16 μm -thick films of zinc-dipyridyl porphyrin MS supported on polyester membranes. Tapping mode AFM and synchrotron source X-ray diffraction studies show that films made of pyrazine MS are crystalline, while those made of zinc-dipyridyl porphyrin are essentially featureless and amorphous. Transport studies reveal that a pyrazine MS film displays a strong preference for small phenol molecules vs larger iron phenanthroline complexes. The Snurr group has performed molecular simulations that suggest that phenol diffuses through intermolecular channels that weave between the molecules of pyrazine ($PD_f = 8 \pm 2 \times 10^{-8} \text{ cm}^2\text{s}^{-1}$). Transport studies based on thin films of much larger zinc-dipyridyl-porphyrin MS have established that both phenol ($PD_f = 5.6 \pm 0.6 \times 10^{-8} \text{ cm}^2\text{s}^{-1}$) and iron phenanthroline ($PD_f = 7 \pm 3 \times 10^{-9} \text{ cm}^2\text{s}^{-1}$) readily permeate, but that larger iron phenylsulfonate-phenanthroline is essentially completely blocked. Selective separation of small organic molecules has also been demonstrated. In a related study of molecular membranes based upon zeolites, the team led by Dr. Snurr has demonstrated that, surprisingly, the "cross term" diffusivities for mixtures play an important role at high loadings, as they reach the same order of magnitude as the main term diffusion coefficients. Using these diffusivities in engineering transport equations, it was possible to predict co-diffusion and counter-diffusion through membranes on macroscopic scales using only information from molecular simulation.

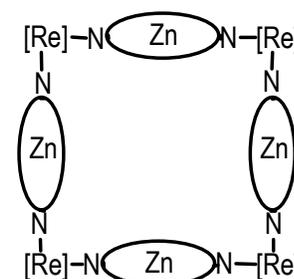
Publications: Czaplowski KF, Hupp JT, Snurr RQ *Adv. Mater.* **2001**, 13:1895; Sanborn MJ, Snurr RQ *AIChE J.* **2001**, 47:2032.



Schematic representation of size-selectivity in a membrane experiment.



Pyrazine molecular squares [Re] = $\text{Re}(\text{CO})_3\text{Cl}$.



Zinc-dipyridyl-porphyrin molecular squares; [Re] = $\text{Re}(\text{CO})_3\text{Cl}$; ovals = porphyrins.