

Functional Nanoporous Membranes

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Research team: Hupp is an inorganic chemist with expertise in the design and synthesis of mesoporous molecular materials. He also has expertise in the characterization of porous thin-film materials properties. Nguyen is an organic chemist with extensive experience in synthetic chemistry, polymer chemistry, and catalytic chemistry. Snurr is a chemical engineer with expertise in hierarchical modeling, especially molecular binding and transport modeling in zeolitic materials.

Objectives: We proposed to exploit new developments at Northwestern in nanoscale supramolecular coordination chemistry and molecular materials chemistry to develop uniform, high porosity, high transport rate, membranes featuring size, shape, and chemical affinity tunable pores and displaying excellent chemical separation properties.¹ Our initial activities have focused on: a) materials design and fabrication, especially thin-film materials fabrication, b) materials characterization, c) proof-of-concept evaluation of size-selective molecular transport behavior, d) proof-of-concept evaluation of novel nanoscale channel tailoring methodologies, e) experimental and computational modeling of molecule/materials affinities and chemical interactions, f) design and construction of molecular building blocks for superior second-generation thin films and nanoporous membranes, and g) testing preliminary hypotheses regarding catalyst immobilization and stabilization.

Background: Separations processes have become essential and ubiquitous components of a number of key manufacturing technologies, including those used to produce pharmaceuticals (chiral separations), semiconductors (solvent purification), pesticides, commodity chemicals (liquid nitrogen, liquid oxygen, petrochemical feedstocks), and many specialty chemicals. Traditional separation methods such as distillation rely upon phase changes and, therefore, usually are energy intensive. Furthermore, the thermal demands that typically accompany these methods can render them inapplicable to delicate products or to products incapable of achieving significant volatility. Chromatographic methods, on the other hand, lack these complications, but typically are limited by slow products throughput – an unacceptable feature in most manufacturing-scale applications. Depending on the eluent used, chromatographic methods also can present significant solvent waste disposal problems when applied to manufacturing scale processes.

Membrane-based separations represent a potentially extremely attractive alternative approach in chemical manufacturing. Membrane methods rely upon size selective, shape selective and or charge selective passage of desired compounds from one phase to another. The driving force for transport is typically a chemical concentration gradient, but assistance from electrical gradients, temperature gradients, or pressure is possible. Key issues are selectivity, systematic tunability, materials stability, and transport efficiency. Also of considerable current interest is coupling separation events to chemical processing events such as catalysis. For molecule-sized separation targets, these issues are inherently nano-scale design and engineering problems. They are clearly amenable to attack, therefore, via nanoscale materials invention, development and utilization.

Accomplishments: The proposed research builds on an efficient and structurally versatile organometallic synthetic approach recently developed at Northwestern for microporous materials fabrication. The Hupp and Nguyen laboratories have developed a wide variety of micro- and mesoporous molecular materials based on metallocyclophanes as building blocks (rhenium(I)carbonyl corners with a variety of rigid imine, pyridines, or azine ligands as edges).² The available macrocycles, either in the form of “molecular

¹ "Supramolecular Chemistry-Functional Structures on Mesoscale", S. T. Nguyen, D. L. Gin, J. T. Hupp, and X. Zhang, *Proc. Nat. Acad. Sci.*, **2000**, submitted

² a) "Self Assembly of Luminescent Molecular Squares Featuring Octahedral Rhenium Corners", R. V. Slone, J. T. Hupp, C. L. Stern, and T. E. Albrecht-Schmitt, *Inorg. Chem.* **1996**, *35*, 4096-4097. b) "Synthesis, Characterization

squares” or “molecular rectangles”, can be obtained in quantitative yield via a coordination-chemistry-based self-assembly process and range in size (minimum cavity diameter) from less than 5 Å to greater than 30 Å (Figure 1). The size of the macrocycles is dependent on the length of the bridging ligands and can be adjusted over an enormous range.

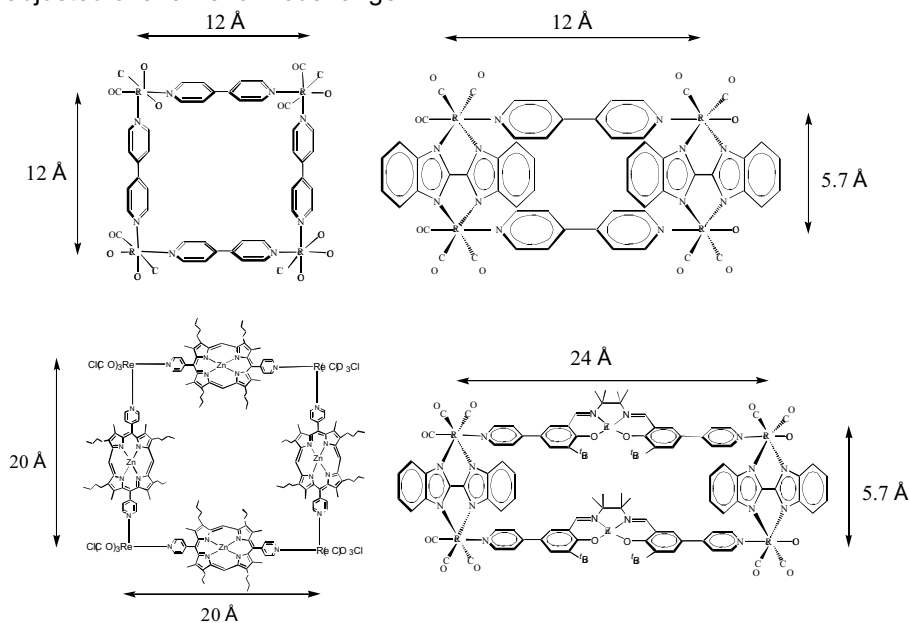


Figure 1. Representative examples of molecular squares and rectangles (MSaR) containing different ligand frameworks.

comprised of small and intermediate-sized molecular squares, condensed-phase transport is *20 to 50 times faster* than observed for related amorphous metallopolymers featuring similar size cutoffs. Furthermore, well-defined “membrane permeation” type behavior has been observed experimentally, i.e. transport rates vary inversely with film thickness.

To obtain materials featuring greater selectivity, the molecular cavity can be tailored with sterically or chemically demanding molecules and size cutoffs are correspondingly altered (Figure 2b).^{4b,c} Ligation of the receptor to the porphyrin square platform occurs within minutes (from microgravimetric and spectroscopic measurements)^{4b} and provides us with a very large class of compounds for selective transport of molecular and ionic species. Cavity size and shape manipulation, as well as chemical affinity manipulation, has been accomplished in this modular fashion. More than 100 channel or cavity variants have been prepared, including six chiral variants and one catalytic variant.

These molecular-square and rectangle- (MSaR) based assemblies can be configured as thin-film materials. Related single-crystal X-ray studies (Figure 2a) show that the squares typically form semi-infinite one-dimensional channel structures. We find that the films, when supported on conductive surfaces, can be used as “electrochemical molecular sieves”. Depending on the composition of the square, the size cut-off for film-transport of candidate permeant molecules varies from ca. 5 Å up to ca. 20 Å. In all cases, the measured cut-off predictably correlates with the cavity width of the isolated square.^{3,4a} We have also found that for thin films

and Preliminary Host-Guest Binding Studies of Porphyrinic Molecular Squares Featuring *fac*-Tricarbonyl Rhenium(I) Chloro Corners”, R. V. Slone and J. T. Hupp, *Inorg. Chem.*, **1997**, 36, 5422-5423. c) “Luminescent Transition-Metal-Containing Cyclophanes (“Molecular Squares”): Covalent Self Assembly, Host-Guest Studies and Preliminary Nanoporous Materials Applications”, R. V. Slone, K. D. Benkstein, S. Bélanger, J. T. Hupp, I. A. Guzei, and A. L. Rheingold, *Coord. Chem. Rev.*, **1998**, 171, 221-243. d) “Synthesis and Characterization of Molecular Rectangles Based Upon Rhenium-Thiolate Dimers”, K. D. Benkstein, J. T. Hupp, and C. L. Stern, *Inorg. Chem.*, **1998**, 37, 5404-5405. e) “Molecular Rectangles Based Upon Rhenium(I) Coordination Chemistry”, K. D. Benkstein, J. T. Hupp, and C. L. Stern, *J. Am. Chem. Soc.*, **1998**, 120, 12982-12983.

³ “Microporous Inorganic Molecular Materials” M. E. Williams, J. T. Hupp In *The Encyclopedia of Electrochemistry*, Vol. 10, A. J. Bard; M. Stratmann, Eds.; Wiley-VCH Publishers: Germany, 2000, submitted.

⁴ a) “Thin-Film Molecular Materials Based on Tetrametallic “Squares”: Nanoscale Porosity and Size Selective Guest Transport Characteristics”, S. Bélanger, J. T. Hupp, C. L. Stern, R. V. Slone, D. F. Watson, and T. M. Carrell, *J. Am. Chem. Soc.*, **1999**, 121, 557-563. b) “Rapid Derivatization of Mesoporous Thin-Film Materials Based on Re(I) Zinc-Porphyrin “Molecular Squares”: Selective Modification of Mesopore Size and Shape by Binding of Aromatic Nitrogen Donor Ligands”, S. Bélanger, M. H. Keefe, J. Welch, and J. T. Hupp, *Coord. Chem. Rev.*, **1999**, 192, 29-45. c) “Porphyrin-Based Thin-Film Molecular Materials Featuring Highly Adjustable Nanoscale Porosity and Permeability Characteristics”, S. Bélanger and J. T. Hupp, *Angew. Chem., Int. Ed. Engl.*, **1999**, 38, 2222-2224.

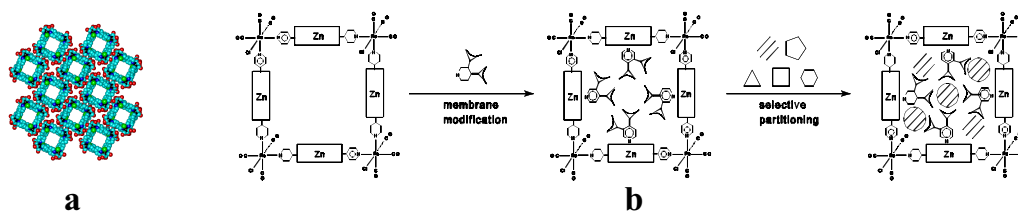


Figure 2. a) Space-filled representation of X-ray crystallographic structure (top view) of a segment square" material represented as a molecular sieve. b) The modification and tuning of these molecular squares.

Spatially-resolved condensed phase molecular transport through *single microcrystals* comprising thin films of microporous "molecular rectangles" has been demonstrated and quantified using a novel scanning electrochemical microscopy approach.³ *Shape*-selective molecular transport through supported films of molecular rectangles has also been demonstrated in the condensed phase.³ Films have also been assembled on porous supports and used to effect size-selective analyte transport between membrane separated reservoirs.⁵

The confined spaces defined by the interiors of molecular squares and rectangles suggest controlled environments for catalytic chemistry, where film-based arrays of catalytic sites could comprise unusual new catalytic membrane reactors. Using a supramolecular functional strategy like that shown in Figure 2b, we have succeeded in immobilizing functional catalysts in reactive solution environments; see Figure 3.

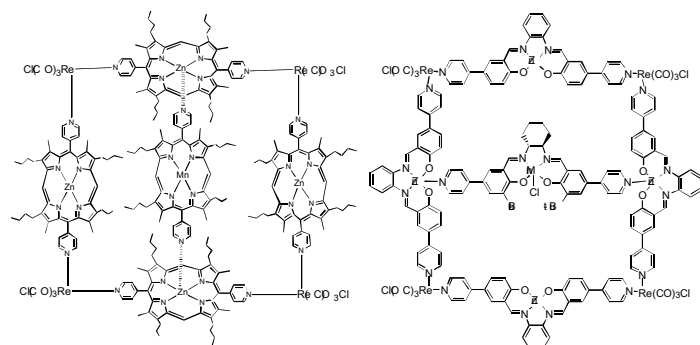


Figure 3. Square-encapsulated epoxidation catalysts.

The encapsulated catalysts show greatly enhanced chemical stability and very substantially lengthened functional lifetimes.⁶ Studies with even simpler model systems show that stabilization is engendered by sterically constraining catalyst active sites from destructively encountering similar sites.⁷ Returning to the fully encapsulated systems, the cavity imposes steric selectivity upon the otherwise indiscriminate catalytic reaction process (Figure 4).⁶ Post-synthetic modification of the cavity (Figure 2b) has permitted systematic modulation of the steric selectivity.

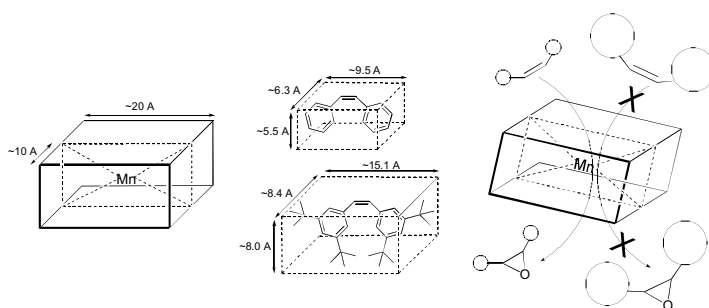


Figure 4. Size selective epoxidation of olefins by encapsulated catalysts.

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⁵ "Molecular Squares as Molecular Sieves: Size-Selective Transport Through Porous-Membrane-Supported Thin-Film Materials", K. F. Czaplewski, R. Q. Snurr, and J. T. Hupp, *Adv. Mater.*, **2001**, submitted

⁶ "Functional Inorganic Supramolecular Assemblies: Encapsulation-based Induction of Enzyme-like Stability and Selectivity for a Simple Epoxidation Catalyst" M. L. Merlau, M. d. P. Mejia, S. T. Nguyen, and J. T. Hupp, prepared for submission to *Science*.

⁷ "Enhanced Activity of Manganese (III) Porphyrin Epoxidation Catalysts Through Supramolecular Complexation", M. L. Merlau, W. J. Grande, S. T. Nguyen, and J. T. Hupp, *J. Mol. Catal. A, Chem.*, **2000**, *156*, 79-84.