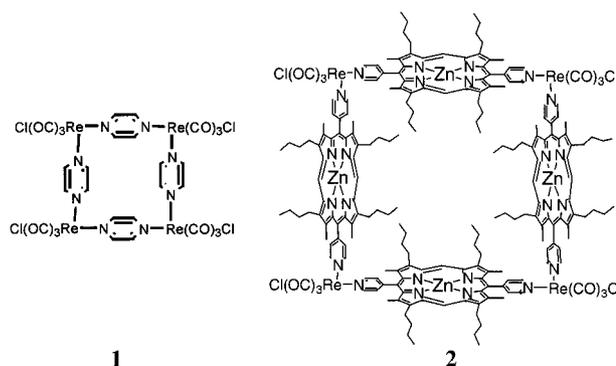


## Molecular Squares as Molecular Sieves: Size-Selective Transport Through Porous-Membrane-Supported Thin-Film Materials\*\*

By Kenneth F. Czaplewski, Joseph T. Hupp, and Randall Q. Snurr\*

There has been tremendous recent interest in the assembly or self-assembly of inorganic and organometallic “molecular squares”: cyclic structures typically featuring metal-ion corners and difunctional bridging ligands as edges.<sup>[1–15]</sup> Motivations include solution-phase catalysis, chemical sensing, and more general host/guest chemistry. Here we describe a solid-state application that may lead to further application in separations processes: size-selective molecular transport from a guest-containing solution to one initially free of guest species. Electrochemical molecular sieving (size-selective transport of redox-active species from solution to an underlying electrode rather than a receiving solution) has previously been demonstrated using thin films of molecular squares.<sup>[16–18]</sup> Molecular sieving or nanofiltration has also been demonstrated with mesoporous polycarbonate membranes that have had metallic gold deposited via electroless plating to yield roughly nanometer-sized channels,<sup>[19]</sup> in addition to more common zeolite and carbon molecular sieves. In this work, size-selective transport through novel “molecular square” membranes has been demonstrated by measuring the permeabilities of various sized molecules through thin films of pyrazine- and zinc-dipyridyl porphyrin molecular squares on polyester membrane supports.

For sieving or nanofiltration, thin-film assemblies of neutral molecular squares are appropriate, since any charge compensating ions in non-neutral assemblies might block the pores. From the literature,<sup>[20,21]</sup> neutral-square cavities range in size (minimum van der Waals diameter) from roughly 3 Å (pyrazine edges) to 18 Å (alkyl-functionalized dipyridyl porphyrins as edges). A pair of squares, **1** and **2**, that lie at the extremes of the cavity-size distribution have been examined in this work. Thin-films of squares were evaporatively cast on commercially available, polyester membranes (see Experimental



section) by using suspensions of **1** in 3:1 chloroform:acetonitrile or solutions of **2** in pure chloroform. In fabricating films of **1**, vacuum grease was used to mount the polyester membranes on glass slides, each featuring a 0.32 cm diameter hole. The membrane/slide combination was then exposed to water to fill the pores. Casting of the films at the organic-aqueous interface was accomplished after allowing the exposed membrane surface to dry and then adding the suspension of **1** dropwise to the center of the membranes. Films of **2** were cast by simply adding the solution dropwise to the center of the membranes lying dry on glass slides.

The active areas of the membranes were approximately 0.32 cm in diameter. Film thicknesses (**1** =  $8 \pm 1 \mu\text{m}$ , **2** =  $16 \pm 1 \mu\text{m}$ ) were determined by recording cross sectional brightness and luminescence images of coated membranes that had been microtomed after embedding in a polymer; see Figure 1. The cross sectional images additionally revealed that **2** effectively infiltrates the membrane pores yielding a total thickness

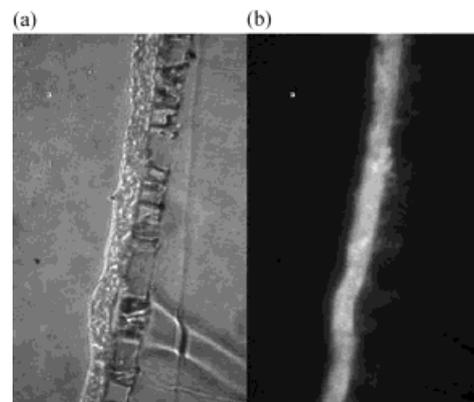


Fig. 1. a) Brightness and b) luminescence images of cross section of pyrazine-square coated membrane. The brightness image (a) shows the continuous thin film of **1** at the left center that was cast on the polyester membrane support, shown at the right center. The luminescence image (b) shows that the film of **1** does not penetrate the pores of the support membrane.

of 25  $\mu\text{m}$ , but that **1** is confined to the membrane surface. Tapping-mode atomic force microscopy studies in air showed that films of **1** are composed of closely packed particles typically measuring about 1  $\mu\text{m}$  in length and a few hundred nm in width. Films of **2**, on the other hand, are remarkably smooth (root mean square, rms, roughness <10 nm) and essentially featureless. Synchrotron source X-ray diffraction studies

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showed membrane-supported thin films of **1** to be, depending on exact preparative protocol, either crystalline (domain sizes of ca. 100 nm inferred from the Scherrer equation) or semi-crystalline. Related single crystal X-ray studies show that **1** forms one-dimensional channels.<sup>[20]</sup> Interestingly, films of high crystallinity proved considerably more leaky in molecular transport studies than did less crystalline films. Synchrotron interrogation of films of **2** revealed no crystallinity, implying a largely amorphous structure.

Simple U-tube transport studies (mechanically stirred reservoirs; Fig. 2) were undertaken with 5 mM aqueous solutions of phenol (**3**; diameter ( $d$ )  $\sim$  5.7 Å), Fe(1,10-phenanthro-

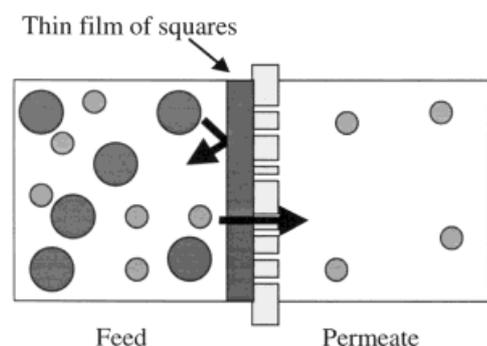
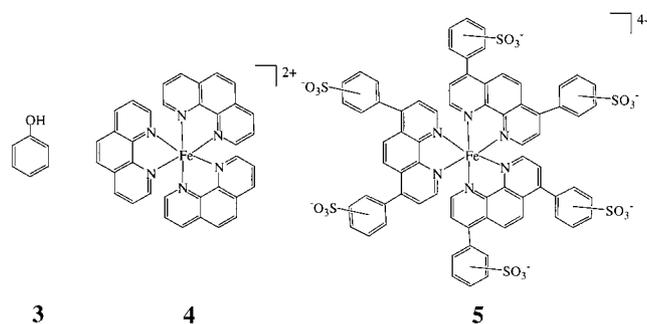


Fig. 2. Schematic representation of size-selectivity in U-tube experiment.

line)<sub>3</sub><sup>2+</sup> (**4**;  $d \sim 13$  Å; sulfate salt), and Fe(4,7-phenylsulfonate-1,10-phenanthroline)<sub>3</sub><sup>4+</sup> (**5**;  $d \sim 24$  Å; sodium salt). Film transport was monitored via ultraviolet-visible (UV-vis) absorption in both sections. Thin films of **1** displayed a strong preference



(two orders of magnitude) for transport of the small phenol molecule versus the larger iron complex, **4**. Given that the dimensions of the internal cavities of **1** are smaller than the size of the phenol molecules, it is unlikely that phenol permeated the films via an intra-square transport mechanism. What then accounts for the preferential transport of phenol versus **4**?

To investigate this question, molecular simulations of a similar system were performed, and the results illustrate the channel structure present in a single crystal of **1**. The simulation system consisted of an atomistic representation of **1** where the coordinates of the atoms were taken from single crystal X-ray diffraction results.<sup>[20]</sup> A benzene molecule was

used as a probe (Lennard-Jones parameters:  $\sigma = 5.27$  Å,  $\epsilon/k = 440.0$  K), and the potential energy of interaction between the probe and the atoms of **1** was calculated at all points in a single unit cell.<sup>[22,23]</sup> The gray region of Figure 3 represents a contour inside which the potential energy of the probe is less than

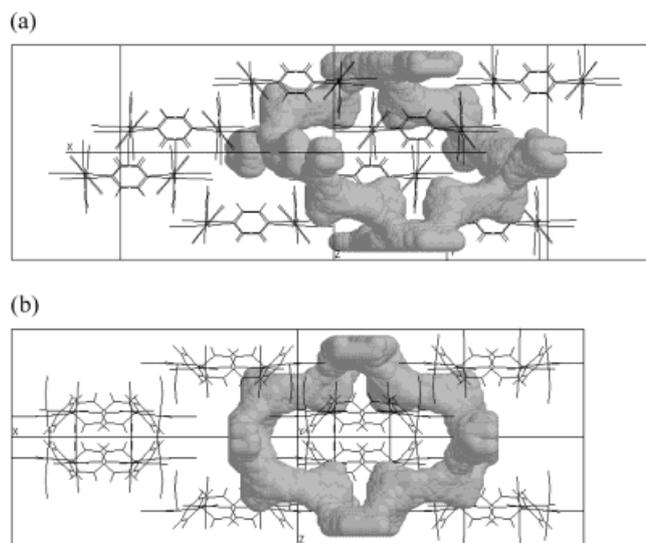


Fig. 3. Inter-square channels representing the portion of the unit cell of **1** accessible by a spherical benzene probe molecule during a molecular simulation. a) The image shows two unit cells of **1** in black and one unit cell of the channel structure shown in gray. The aromatic rings of **1** are shown from the side along with the channels that weave around the molecules of **1** but do not penetrate the center cavities. b) The same image as (a) is shown, now slightly rotated about the  $z$ -axis to better reveal the continuity of the channels.

$-39.0$  kJ/mol. Points lying outside the gray region have a higher energy and are not likely to be occupied by the probe molecule. The contour shows that there are three-dimensional intermolecular channels that weave between the molecules of **1**. The smallest dimensions of these channels are  $5.7 \times 6.3$  Å, suggesting that phenol would be able to diffuse through this intermolecular pore network found in **1** but that **4** would not. That **4** is detectably transported at all in films of **1** is attributed to film cracks and/or pinhole defects, a problem that also was encountered in electrochemical studies of transport through thin films of the pyrazine-bridged square.

The permeability of phenol ( $PD_f$ ) in films of **1** was evaluated via a simple one-dimensional diffusion model (Eq. 1) that assumes rapid partitioning of permeants from solution to film and vice versa:

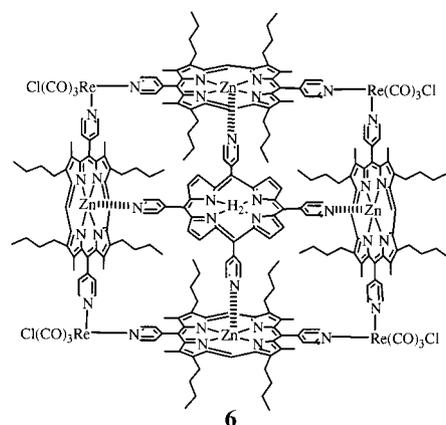
$$J = (PD_f)\Delta C/l \quad (1)$$

In this equation,  $J$  is the permeant flux,  $P$  is the solution-to-film partition coefficient,  $D_f$  is the film-based diffusion coefficient,  $\Delta C$  is the difference in permeant concentration between feed and permeate solutions, and  $l$  is the film thickness measured above ( $8 \mu\text{m}$  for **1** and  $25 \mu\text{m}$  for **2**). The changes in feed and permeate concentrations as functions of

time were relatively small compared to the initial feed concentration, allowing this steady-state model to be used. We verified that the concentration gradient and flux remained essentially constant throughout the time of the experiments over which Equation 1 was used to calculate the  $PD_f$  values. Application of the equation to phenol transport through **1** yielded a  $PD_f$  value of  $8 \pm 2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ . Control experiments revealed that naked polyester membranes offer negligible mass transport resistance in comparison to the molecular films.

Transport studies based on thin films of the much larger square, **2**, established that **3** and **4** readily permeate ( $PD_f$  values of  $5.6 \pm 0.6 \times 10^{-8}$  and  $7 \pm 3 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ ), but that **5** is essentially completely blocked (i.e., only trace amounts detected in the receiving solution even after 70 h of exposure)—consistent with a molecular-square-cavity based size cutoff of ca. 18 to 20 Å. (That size, rather than charge, is the controlling factor was established by showing that the films are permeable to the small anionic complex,  $\text{Fe}(\text{CN})_6^{3-}$ .)

One of the desirable features of this system is that the size cutoff can be further manipulated by chemically functionalizing the square interior.<sup>[18,21,24]</sup> Axial ligation of the four available  $\text{Zn}^{\text{II}}$  sites of **2** with tetrapyrrolyl porphyrin, **6**, followed by film formation, yielded materials that had a similar degree



of crystallinity and film thicknesses as **2**. These films blocked the intermediate-sized permeant, **4** (only trace amounts detected after 250 h of exposure), but remained highly permeable with respect to **3** ( $PD_f = 8 \pm 2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ ). This result provides strong evidence that transport through films of **2** is governed by the diffusion of the penetrants through the interior square cavities rather than through inter-square voids as in films of **1**.

In conclusion, novel molecular square membranes have been fabricated and the size-selective transport of various probe molecules through them has been demonstrated. With these demonstrations of sized-based nanofiltration in hand, we are currently pursuing functionalized thin-film molecular-square transport studies for chiral discrimination and for embedded-catalyst transformation of selected permeants in a membrane catalytic reactor.

## Experimental

Molecular squares **1** and **2** were synthesized as described previously [20,21]. It was necessary to cast films of **1** from a suspension and not a solution so that enough material was deposited on the membrane to bridge the membrane pores. Approximately 4–6  $\mu\text{L}$  drops of a 1.0–1.5 mM suspension of **1** were applied to the polyester membrane support. The solvent was allowed to evaporate from each drop in a fume hood before subsequent drops of the suspension were applied to the polyester membrane support. The solubility of **2** was much greater than **1**, and therefore casting films of **2** from solution was possible. Approximately 2–3 drops, each  $5 \mu\text{L}$  of a 5.0–7.5 mM solution of **2** in chloroform, were added to the polyester membrane support. The drops were allowed to evaporate in the room before additional drops were added. Axial ligation of **2** with tetrapyrrolyl porphyrin was achieved by mixing together  $\sim 200 \mu\text{L}$  of 10 mM solutions of **2** and tetrapyrrolyl porphyrin in chloroform. This solution was then added dropwise to the polyester membrane support in the same manner as **2**. The polyester membranes (Osmonics, Minnetonka, MN, USA) are characterized by a uniform thickness (9  $\mu\text{m}$ ) and a high density of cylindrical pores oriented normal to the membrane face (3  $\mu\text{m}$  diameter pores;  $2 \times 10^6$  pores/ $\text{cm}^2$ ).

Phenol (**3**) and tetrapyrrolyl porphyrin (**6**) were purchased from Aldrich, and  $\text{Fe}(1,10\text{-phenanthroline})_3^{2+}$  (**4**; sulfate salt), and  $\text{Fe}(4,7\text{-phenylsulfonate-1,10-phenanthroline})_3^{3+}$  (**5**; sodium salt) were purchased from GFS Chemicals.

The cross sections of the films were obtained by mounting the membranes in an epoxy embedding medium (Epon, from Aldrich), heating at 70 °C overnight, and using an LEO/Reichert Ultracut S Ultramicrotome to take 1  $\mu\text{m}$  thick cross sections. The cross sections were then placed on a glass slide and brightness and luminescence images were taken using a digital camera (Princeton Instruments, Inc.). Atomic force microscopy measurements were made in air using a Digital Instruments Multimode Nanoscope IIIa with single etched silicon (TESP) Nanoprobe SPM tips (cantilever length 125  $\mu\text{m}$  and resonance frequency 307–367 Hz).

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