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Molecular Sieving and Thin Film Transport by Molecular Materials Featuring Large Component Cavities

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The electrochemically measured sieving and transport properties for two new thin film materials composed of molecular squares featuring exceptionally large cavities, a salen-based zinc square **2** (23 Å metal to metal separation distance) and a porphyrin-based zinc square **1** (24 Å metal to metal separation distance) are described. Both materials are exceptionally porous with respect to smaller molecules but blocking toward larger permeants (*i.e.*, those larger than the square cavities). Electrochemical experiments reveal that the size cutoff for molecular sieving can be modified by incorporating difunctional ligands within the square cavity responsible for the observed porosity.
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We have been exploring the idea of using discrete, nanoscale-cavity-containing, supramolecular coordination complexes as building blocks for functional thin film materials.[1,2] The building blocks typically have been neutral molecular squares featuring rigid or semi-rigid difunctional ligand edges and cis-coordinated rhenium(I)chloro corners.[3,4] The resulting materials are generally characterized by high internal surface areas and excellent nanoscale porosity. By using redox-active probe molecules, we have been able to electrochemically characterize the molecular sieving properties of these materials, including molecular transport rates and size cutoffs for candidate permeant species.[5-9] For materials composed of squares with metal-to-metal (edge) separation distances ranging from *ca.* 7 to 20 Å and cavity sizes (minimum van der Waals cavity diameters) ranging from *ca.* 4.5 to 18 Å, we find that permeant-molecule size cutoffs correspond to sizes of cavities of the isolated molecular squares. We also typically find that permeant transport is faster than encountered for related metallopolymeric materials[10,11] featuring similar molecular size cutoffs. The thin film molecular materials featuring the largest cavities are disordered with no net orientation of cavities.

We now report on electrochemically measured sieving and transport properties for two new materials composed of molecular squares featuring exceptionally large cavities; a zinc salen based square, **2**, utilizing pyridyl linkages (*ca.* 21 Å estimated cavity diameter and 23 Å metal-to-metal separation distance) and a porphyrinic square, **1**, utilizing ethynylpyridyl linkages (*ca.* 22 Å estimated cavity diameter and 24 Å metal-to-metal separation distance). Metal salens are of particular interest because of their ability to function as chemical catalysts (manganese epoxidation catalysts,[12] aluminum ring opening polymerization catalysts,[13] etc.). Combining catalysis with molecular sieving opens the possibility of constructing membrane catalytic reactors. As we will report elsewhere,[14] dipyridyl(ethynyl)porphyrins are amenable to chemical functionalization (aryl thiols, phosphonate esters, carboxylates, etc.); advantage can be taken of the functionalization to create peptide-derivatized squares, self-assembled monolayers of squares, and polymeric square materials. As shown in Scheme 1, thin-film materials based on **2** and on the prototypical ethynyl(pyridyl)porphyrin square, **1**, display molecular sieving behavior that is consistent with a membrane permeation mechanism. In addition, the porphyrin-containing square material displays tunable size-cutoff behavior based on cavity derivatization.

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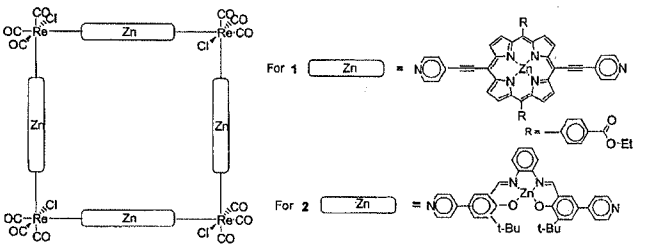


Scheme 1.

Experimental

Materials.—Syntheses of **1** and **2** will be described in detail elsewhere. Briefly, however, the compounds were obtained by combining the difunctional salen[15] or porphyrin ligands (prepared by a method similar to that of Therien and co-workers[16,17]) stoichiometrically with $Re(CO)_5Cl$ in tetrahydrofuran and refluxing for 48 h until squares were obtained. Products were precipitated by concentrating the reaction mixtures to half their original volume, adding hexane, and cooling to 0°C, as previously described for related compounds.[3,4] Thin films were prepared by casting tetrahydrofuran (THF) or methylene chloride solutions on glassy carbon disk electrode surfaces and then slowly rotating the disks to facilitate uniform solvent evaporation. Average film thicknesses were determined via UV-vis absorption by dissolving films and determining the amount of material present from the molecular extinction coefficients, as described previously.[9]

Commercially available redox probe molecules (candidate permeants) used included ferrocene-methanol (**3**; diam (d) ~4.5 Å), $Ru(NH_3)_6^{3+}$ (**4**; d ~5.5 Å), $Ru(CN)_6^{4-}$ (**5**; d ~6 Å), and Fe(1,10-phenanthroline)$_3^{2+}$ (**6**; d ~13 Å). Permeants **7** (d ~23 Å) and **8** (d ~24 Å) (Scheme 2) were prepared and purified by literature methods.[5,18] Permeant **9** (d ~35 Å) (Scheme 2) which is a simple peptide derivative of **8** was obtained by reacting **8** with benzoic acid in freshly distilled THF in the presence of the following coupling reagents: benzotriazol-1-yloxytris(dimethylamino)phosphonium hexafluorophosphate, dimethylaminopyridine, 4-methylmorpholine, and 1-hydroxybenzotriazole. The reaction solution was stirred in air for 9 h and then added to acetonitrile. The precipitate was isolated by filtration and purified by recrystallization from THF/hexane.

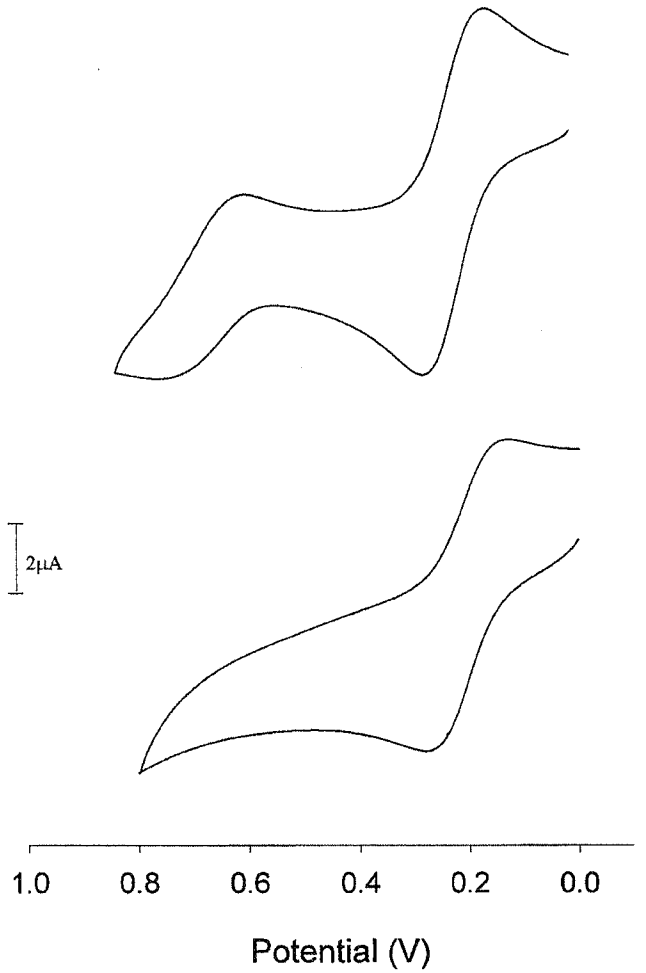
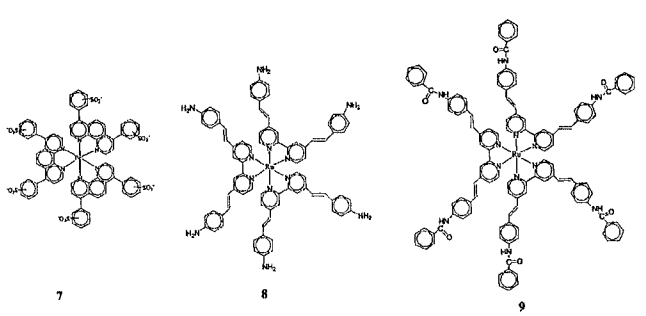


Figure 1. CVs (50 mV/s) of a naked electrode (top) and electrode coated with thin film of **1** (bottom) in the presence of **3** and **9**.



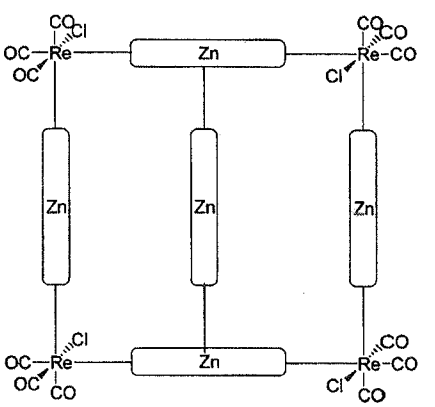
Scheme 2.

Measurements.—All electrochemical measurements were performed in aqueous solutions containing 0.5 M KNO_3 as electrolyte. A standard three-electrode, one-compartment cell was employed. The working, counter, and reference electrodes were a 3 mm diam glassy carbon disk in a 6.35 mm diam Teflon shroud, a platinum wire, and Ag/AgCl, respectively. A CH Instruments model potentiostat, and in some cases, a Pine Instruments model electrode rotator, were employed. Electronic absorption measurements were performed using an HP model 8452A diode-array spectrophotometer.

Results and Discussion

Qualitative molecular transport and sieving studies.—Figure 1 shows the cyclic voltammetric (CV) responses of a naked electrode and an electrode coated with a thin film of **2** to a solution containing both small (**3**) and large (**9**) redox-probe molecules. The experiments indicate that the film is permeable to the smaller probe, but blocking with respect to the larger probe. Additional measurements established that films of **1** are also permeable to probes **3-8** where the largest of these is *ca.* 24 Å diam. The combined results are consistent with sieving behavior that is governed by transport through the cavity defined by isolated molecules of **1**, assuming slight outward bowing of the molecule's porphyrin-ligand edges. As expected, given the charge-neutrality of the molecular assemblies comprising the films, no discrimination on the basis of charge is observed.

Similar studies with thin films of the slightly smaller salen square revealed that it likewise is permeable to probes **3-7**, but is blocking toward the two largest probes (**8** and **9**). These experiments establish a size cutoff of *ca.* 23 Å, again consistent with the cavity size obtained by modeling isolated molecules of **2**, assuming slight bowing of the edges. Returning to assembly **1**, the availability of multiple Lewis acid sites (Zn(II) sites) suggests the possibility of cavity tuning via axial binding of Lewis bases.[9] The free dipyridyl(ethynyl)porphyrin species comprises a difunctional Lewis-basic ligand of precisely the right length to span and bisect the square cavity; see assembly **10** (Scheme 3).



Scheme 3. Assembly 10.

Following an approach used previously with a smaller porphyrin square, **11**,[19] solution-phase UV-vis absorption measurements were used to establish that the ligand binds to the square with 1-to-1 host-to-guest stoichiometry. (Binding is accompanied by an 8 nm red shift of the intense Soret absorption band of **1**.) Electronic absorption measurements of thin films obtained by evaporatively casting **10** show a similar red shift in the Soret region, indicating that the cavity-bisecting ligand is retained upon film formation. Consistent with modulation of the cavity size, films of **10** exclude probes **6** and **7**, compounds that do permeate films of the empty square. Films of **10** are readily permeated, however, by smaller probe molecules such as **3** and **4**.

Quantitative transport studies.—Rates of probe-molecule transport through thin films of the meso- and microporous compounds **1**, **2**, and **10**, were measured by rotating disk electrode (RDE) voltammetry, following a well established procedure.[10,20] Briefly, for simple sequential transport through a solution and then a film, the overall RDE flux or limiting current, i_{total}, is given by a reciprocal sum of the component fluxes or currents

$$i_{total}^{-1} = i_{soln}^{-1} + i_{film}^{-1} = [0.602nFAD_s^{2/3}\omega^{1/2}\nu^{-1/6}C_s]^{-1} + i_{film}^{-1} \quad [1]$$

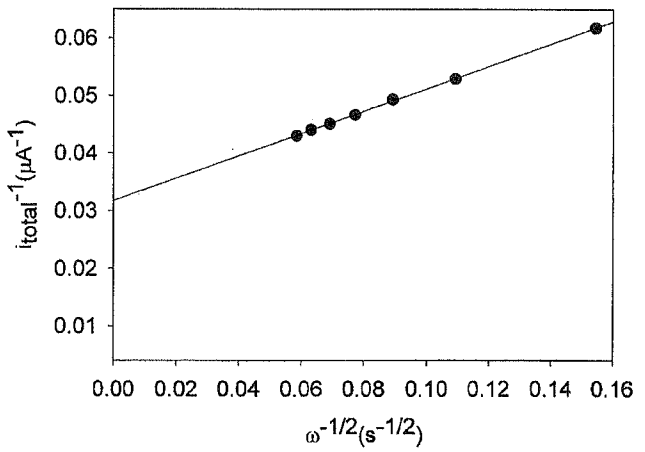


Figure 2. Inverse limiting current *vs.* inverse square root of rotation rate for permeation of a thin film of **1** by ferrocenemethanol.

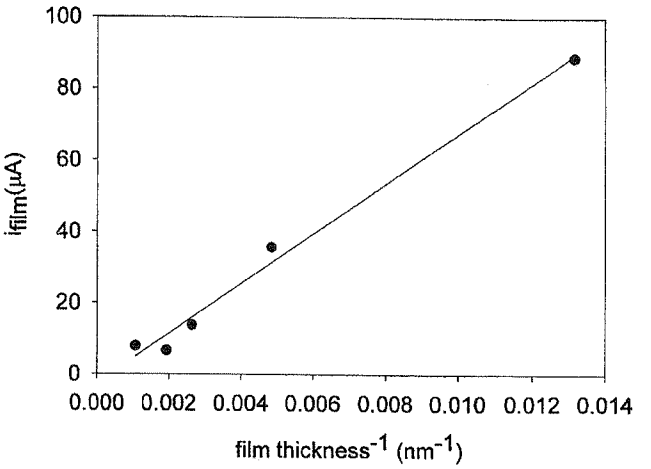


Figure 3. Limiting film flux (i_{film}) *vs.* inverse of film thickness for permeation of **1** by ferrocenemethanol.

In Eq. 1, n is the number of electrons transferred during the oxidation or reduction process, F is the Faraday constant, A is the electrode area, ω is the angular frequency of rotation, ν is the solvent's kinematic viscosity, C_s and D_s are the redox probe's solution concentration and solution diffusion coefficient, respectively, and d is the film thickness. By plotting i_{total}^{-1} *vs.* $\omega^{-1/2}$, the desired rate of molecular transport through the film can be obtained from the y intercept, as illustrated experimentally in Fig. 2.

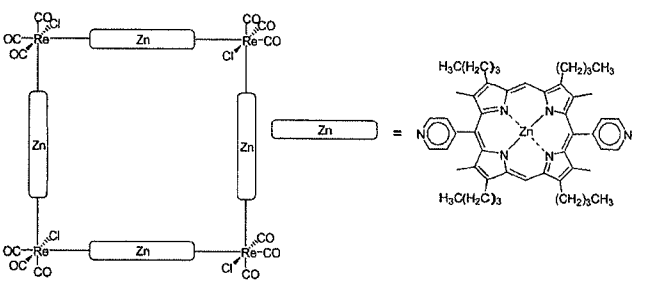
If the film transport rate is controlled by diffusion through the film itself rather than by the rate of partitioning from the solution to the film, the rate will vary directly with the molecular probe's film-diffusion coefficient, D_f, and equilibrium solution-to-film partition coefficient, P. In addition, as indicated in Eq. 2, it varies inversely with the film thickness, d

$$i_{film} = nFAPD_fC_s/d \qquad [2]$$

Figure 3 shows a representative plot of film flux *vs.* film thickness for transport of ferrocenemethanol through thin films of **2**, confirming that film diffusion is rate determining. With this mechanistic information in hand, a composite PD_f value of $3.3 \pm 0.1 \times 10^{-7}$ cm^2 s^{-1} was extracted from the data. In principle, counterion motion can also measurably influence electrochemically determined permeabilities. This problem has been explored in some detail in reports involving related thin-film materials.[5,7]

Equation 2 assumes that the only contributor to D_s is diffusion of the permeant. In principle, however, an additional contribution could arise from permeant-to-permeant electron hopping, *i.e.*, the "Dahms-Ruff" effect.[21-23] Indeed, enhancement of apparent molecular diffusion rates in thin film electrode coatings has been well documented by Buttry and Anson.[24] To test whether electron-exchange phenomena might contribute to the apparent transport rates measured here, we examined a transport of a representative permeant, $Fe(CN)_6^{4-}$, as a function of its concentration. Because electron exchange is a second-order process, elevating the concentration of the permeant should increase the apparent permeability (PD_f value) if exchange contributions are significant. Experimentally, however, we find that PD_f is insensitive to a tenfold variation of C_s.

Table I summarizes measured permeabilities (PD_f values) for several probe-molecule/mesoporous-molecular-film combinations. Included for comparison are permeabilities measured previously for films of a smaller porphyrinic square, **11** (Scheme 4).[5]



Scheme 4.

Briefly, the new large-cavity materials are characterized by permeabilities that are roughly equivalent to those observed with **11**, but up to 30 times larger than seen with thin films composed of a representative amorphous metallopolymer, poly-[Fe(5-amino-1,10-phenanthroline)$_3^{2+}$](X$^-$)$_2$.[11] We have previously ascribed enhanced transport through films of molecular materials to the existence of less tortuous pathways than found in amorphous metal-

Table I. Film permeabilities.

Permeant (charge)(d(Å))	Film **1** $PD_f \times 10^7$ (cm^2/s)	Film **2** $PD_f \times 10^7$ (cm^2/s)	Film **10** $PD_f \times 10^7$ (cm^2/s)	Film **11**[a] $PD_f \times 10^7$ (cm^2/s)
3 (0)(4.5)	3.3 ± 0.1	3.18 ± 0.05	2.1 ± 0.1	1.45 ± 0.1
4 (3+)(5.5)	2.30 ± 0.05	2.21 ± 0.06		2.5 ± 0.1
5 (4−)(6)	1.95 ± 0.04	3.7 ± 0.1	0.89 ± 0.04	11.1 ± 0.04[b]
6 (2+)(13)	0.24 ± 0.01	0.46 ± 0.02		0.19 ± 0.03

[a] Data from Ref. 5.
[b] $Fe(CN)_6^{4-}$ used in place of $Ru(CN)_6^{4-}$.

lopolymers. As with films of **11**, increasing the permeant size decreases the permeant transport rate. Finally, reducing the cavity dimensions of **2** from *ca.* 24 × 24 Å to *ca.* 24 × 11 Å by forming assembly **10** diminishes permeabilities by factors of 1.5 to 4.

Conclusions

Two new mesoporous materials composed of large-cavity "molecular squares" have been configured as thin films on electrode surfaces. Both exhibit molecular sieving with respect to redox-active probe molecules. The size cutoff for **1** is about 23 Å. The cutoff for **2** is greater than 24 Å. When the size of the cavity of compound **2** is altered by introduction of a difunctional ligand capable of bisecting the cavity, the size cutoff for probe transport is decreased to less than 13 Å. The observed cutoffs are broadly consistent with model-based estimates of cavity sizes for assemblies **1**, **2**, and **10** in isolation. RDE measurements of probe-molecule transport rates as a function of film thickness establish that transport is limited by the rate diffusion of the probe, rather than the kinetics of entry into the film from the solution. As with other molecular square derived materials featuring smaller cavities, rates of permeation by appropriately sized probe molecules are significantly greater for the new materials than for related amorphous metallopolymers.

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