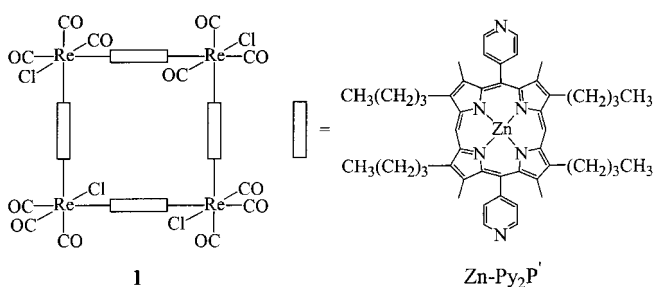


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Porphyrin-Based Thin-Film Molecular Materials with Highly Adjustable Nanoscale Porosity and Permeability Characteristics**

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We have recently reported that $[\text{Re}^{\text{I}}(\text{CO})_3(\text{Cl})(\mu\text{-L})]_4$ metallocyclophanes (“molecular squares”), where L = pyrazine, 4,4'-bipyridine, and 4,4'-bis(pyridyl)ethylene, can form mesoporous thin films, where the porosity of the materials allows for the selective permeation of molecules based on their size.^[1, 2] Notably, the observed permeation cutoffs correspond closely to the dimensions of individual molecular cavities. In addition, X-ray studies (albeit with single crystals rather than films) show that the cavities can align to form extended, one-dimensional, zeolite-like channels.^[1a,c] Atomic force microscopy studies, however, indicate that films typically comprises micron and submicron-sized crystallites; these presumably account for the well-defined sieving behavior.^[1d] We now report on the transport properties associated with thin films of a larger square (**1**; Re...Re edge distance approximately 20 Å) based on zinc 2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-bis(4-pyridyl)porphyrin (Zn-Py₂P') as a bridging ligand.^[1c]



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A key structural feature of **1**, exploited here, is the presence of multiple binding sites (Zn atoms) that allow for rapid chemical derivatization of walls and cavities.^[1c] Other important features include: a) the absence of channel-blocking counter ions, b) very good solubility in polar organic solvents, which thus permits film preparation by simple evaporative casting, and c) complete insolubility in water, which facilitates investigations and applications in aqueous environments. Derivatization of compound **1** could prove particularly effective for: 1) adjusting the size-cutoff for permeation, 2) modifying the shape of the cavity and inducing shape-selective transport, and 3) changing the chemical affinity of the cavity. The resulting materials would potentially be useful in sensing applications, where the sieving properties of the films could be used to exclude large interfering species, while the tailored cavity would induce preferential partitioning of specific target molecules. Additionally, the mesoporous nature of the material suggests applications in membrane-based separations and catalysis.

Electrochemical techniques (cyclic voltammetry (CV) and rotating disk electrochemistry (RDE)) can be used to determine the size cutoff for permeation through films of **1** (Figure 1). Briefly, a thin film is evaporatively cast at the surface of an electrode and then exposed to an aqueous solution of an electroactive probe molecule (permeant). If permeation takes place through the pores of molec-

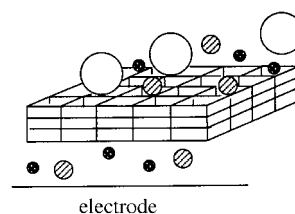


Figure 1. Schematic representation of film permeation studies using electrochemical techniques. (Note that the diagram is not meant to imply that all squares, channels, and domains within a given film are aligned normal to the electrode surface.)

ular dimensions then faradaic current will flow only if the electroactive probe is small enough to pass through the available pores (since the film thickness is much larger than the maximum achievable charge transfer distance). We find that thin films of **1** are permeable to small organic molecules (hydroquinone and nitrobenzene), small main group ions (for example, I^- ; diameter (d) ≈ 2.4 Å), and small and intermediate-size metal complexes, such as ferrocenemethanol (FcCH_2OH ($d \approx 4.5$ Å), $[\text{Fe}(\text{CN})_6]^{3-}$ ($d \approx 6.0$ Å), $[\text{Ru}(\text{NH}_3)_5(4\text{-picoline})]^{2+}$ ($d \approx 6.7$ Å), $[\text{M}(\text{LL})_3]^{2+}$ ($\text{M} = \text{Co}$ or Fe , $\text{LL} = 2,2'$ -bipyridine (bpy; $d \approx 11$ Å), 1,10-phenanthroline (phen; $d \approx 13$ Å), or 3,4,7,8-tetramethyl-1,10-phenanthroline ($d \approx 15$ Å)). However, the films are impermeable to $[\text{Fe}(\text{bphenSO}_3)_3]^{4-}$ ($d \approx 24$ Å; $\text{bphenSO}_3 =$ disulphonated bathophenanthroline (4,7-diphenyl-1,10-phenanthroline), Figure 2), which is consistent with an estimated minimum van der Waals cavity diameter of about 18 Å for **1**.

Modification of the molecular square can be done in solution, prior to film casting, in cases where the Zn/guest binding constant is high. For example, the binding constants between 5,15- H_2 -tetrapyrrolylporphyrin ($\text{H}_2\text{-Py}_4\text{P}$) and **1**, and between $\text{H}_2\text{-Py}_2\text{P}'$ and **1** are on the order of 10^6 – 10^7 M^{-1} in CH_2Cl_2 .^[1c] Previous studies have indicated that $\text{H}_2\text{-Py}_2\text{P}'$ and $\text{H}_4\text{-Py}_4\text{P}$ bind to the interior of the square cavity through two- and four-point binding, respectively.^[1c] Thus, upon incorpo-

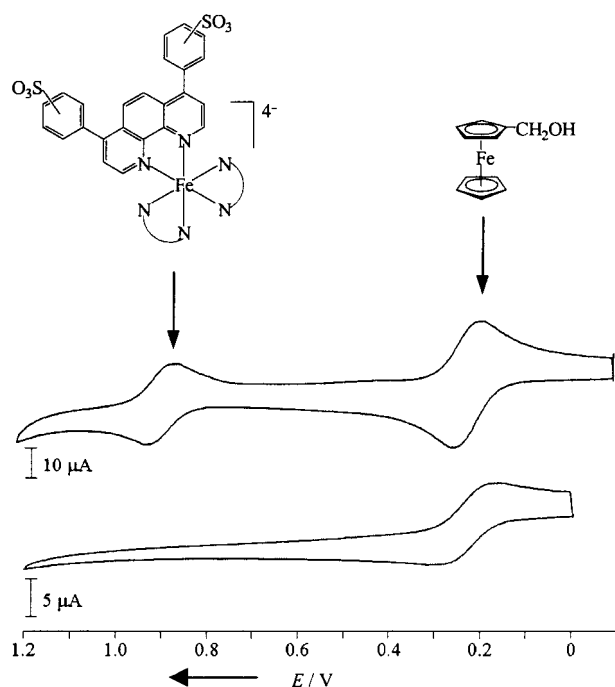


Figure 2. Cyclic voltammogram showing molecular sieving on a 190 nm thick film of **1** at the surface of a 3 mm diameter glassy carbon (Gc) electrode versus the saturated standard calomel electrode (SSCE). The permeant solution is a mixture of FcCH_2OH ($E_{1/2} \approx 0.2 \text{ V}$, $c = 1.1 \text{ mM}$, $d \approx 4.5 \text{ \AA}$) and $[\text{Fe}(\text{bphenSO}_3)_3]^{4+}$ ($E_{1/2} \approx 0.9 \text{ V}$, $c = 1.0 \text{ mM}$, $d \sim 24 \text{ \AA}$). Top: bare electrode, bottom: electrode covered with a film.

ration of $\text{H}_2\text{-Py}_4\text{P}$ four small cavities with $d \approx 6 \text{ \AA}$ replace the single large cavity initially present. We find from electrochemical transport measurements (Figure 3) that I^- readily

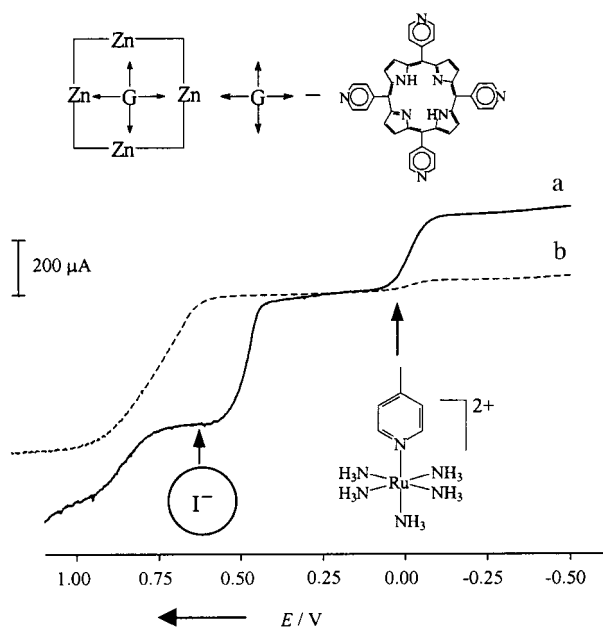


Figure 3. RDE voltammogram of a mixture of I^- ($d \approx 2.4 \text{ \AA}$) and $[\text{Ru}(\text{NH}_3)_5(4\text{-picoline})]^{2+}$ ($d \approx 6.7 \text{ \AA}$) on a) a bare 3 mm diameter GC electrode versus SSCE, and b) on the same electrode covered with composite **1**: $\text{H}_2\text{-Py}_4\text{P}$. Note the smaller molecular size cutoff compared to that of films of underivatized **1** (cutoff $> 15 \text{ \AA}$), through which $[\text{Ru}(\text{NH}_3)_5(4\text{-picoline})]^{2+}$ permeates.

permeates films of **1**: $\text{H}_2\text{-Py}_4\text{P}$, but that the larger $[\text{Ru}(\text{NH}_3)_5(4\text{-picoline})]^{2+}$ ion is almost completely blocked. In a related experiment a **1**: $\text{H}_2\text{-Py}_2\text{P}'$ assembly was investigated. Inclusion of the dipyridyl ligand in the square cavity yields two $20 \times 10 \text{ \AA}$ rectangular cavities, as defined by the metal centers. Electrochemical sieving experiments show that the modified material is highly permeable to smaller species, such as $[\text{Ru}(\text{NH}_3)_6]^{3+}$ and FcCH_2OH , while blocking toward the larger $[\text{Co}(\text{bpy})_3]^{2+}$ entity (Figure 4). Compound **1** can also be

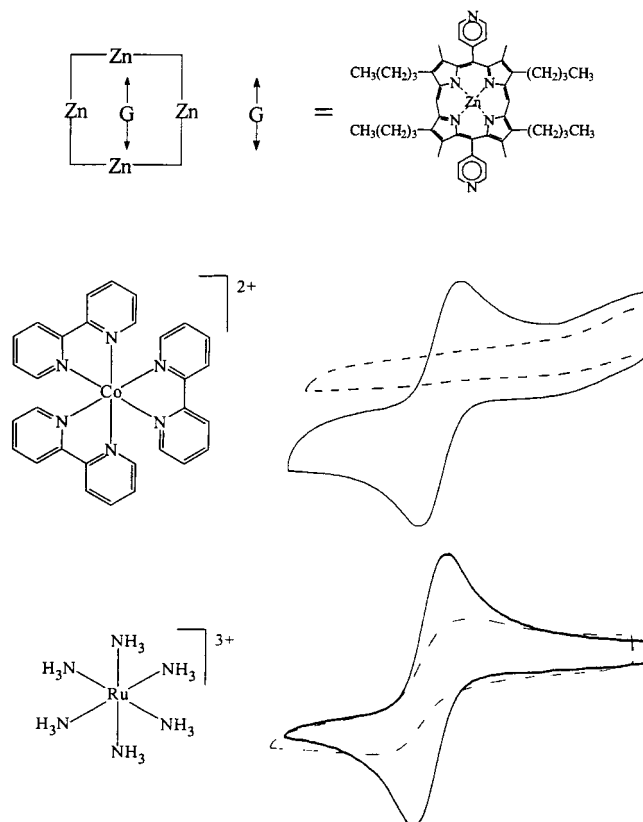


Figure 4. Cyclic voltammograms on a bare electrode (solid line) and on an electrode covered with **1**: $\text{H}_2\text{-Py}_2\text{P}'$ (dashed line) for $[\text{Ru}(\text{NH}_3)_6]^{3+}$ (bottom, $d \approx 6.5 \text{ \AA}$), and $[\text{Co}(\text{bpy})_3]^{2+}$ (top, $d \approx 13 \text{ \AA}$). The resulting cavity after modification of the square is about $10 \times 20 \text{ \AA}$.

derivatized after film formation by exposing the film (typically for 12 hours) to an aqueous solution of the desired ligand. Indeed, more than 30 such variants or derivatives have already been prepared.^[1] In a representative study thin films of **1** were functionalized with 4-phenylpyridine. The modification selectively inhibits permeation by $[\text{Fe}(\text{bpy})_3]^{2+}$, but not by $[\text{Ru}(\text{NH}_3)_6]^{3+}$. While inhibition in this case almost certainly is steric, one could envision that with different ligands chemical discrimination of candidate permeants would be possible. Ligand-modifiable membranes of a somewhat different kind—gold plated polymeric membranes^[3]—have recently been described and have indeed been shown to display chemically selective permeant partitioning.^[3b]

Finally, quantitative permeability studies (Koutecky–Levich type RDE studies^[4]), primarily with films of **1**, revealed that: a) rates of transport through the film systematically decrease with increasing film thickness, as expected if a simple permeation model is appropriate, b) film permeabilities, as

measured by the composite quantity PD_f (where P is the solution–film partition coefficient and D_f is the film-based diffusion coefficient), systematically decrease with increasing permeant size, and c) permeabilities with films of **1** somewhat exceed those obtained with related electropolymerized materials. For example, the PD_f value for the passage of $[\text{Fe}(\text{bpy})_3]^{2+}$ through **1** is $(4 \pm 2) \times 10^{-8}$, but is only $(1.4 \pm 0.2) \times 10^{-8}$ for passage of the related compound $[\text{Os}(\text{bpy})_2\text{Cl}_2]$ through poly-(orthoamino)tetrphenylporphyrin (or 3.6×10^{-9} for passage through “annealed” polymer films).^[5] Other values of PD_f measured with **1** are: $[\text{Fe}(\text{CN})_6]^{3-}$: $(1.3 \pm 0.5) \times 10^{-7}$, $[\text{Co}(\text{phen})_3]^{2+}$: $(2.4 \pm 1.9) \times 10^{-8}$, $[\text{Fe}_2(\text{CN})_{10}(\mu\text{-4,4-bipyridine})]^{6-}$: $(6.5 \pm 5.0) \times 10^{-9}$. We hope to exploit the sieving characteristics, the tailorability, and the high permeability of thin films of **1** and related compounds in applications-oriented membrane catalysis, sensing, and transport investigations.

Experimental Section

Compound **1** was prepared as described earlier.^[1c] $[\text{Fe}(\text{bpy})_3](\text{SO}_4)$ was purchased from GFS chemicals as a 0.025 M solution. $[\text{Ru}(\text{NH}_3)_5(4\text{-picoline})](\text{PF}_6)_2$, the various $[\text{M}(\text{LL})_3](\text{NO}_3)_2$ species, $\text{Na}_4[\text{Fe}_2(\text{CN})_{10}(\mu\text{-4,4-bipyridine})]$, and $[\text{Fe}(\text{bphenSO}_3\text{Na})_3](\text{NO}_3)_2$ (mix of meta and para sulphonates) were prepared by minor adaptations of literature methods.^[6] All other permeants and chemicals were obtained from Aldrich or Mallinckrodt. Films were prepared by the slow evaporation of a drop hanging from a glassy carbon disk electrode spinning at ≈ 100 rpm. Thicknesses (typically ≈ 40 nm, but up to 1000 nm) were manipulated by changing the concentration of the casting solution and/or by applying a second coat after a drying time of 10 min; all films were subjected to a final drying of at least 30 min to ensure strong surface adhesion. The casting solutions, which were first filtered through a 0.1 μm polytetrafluoroethylene membrane (Whatman), were: CHCl_3 (**1**), 2:1 CHCl_3 : CH_3CN (**1**· $\text{H}_2\text{-Py}_4\text{P}$), and 2:1 CH_3Cl : $\text{CH}_3\text{CH}_2\text{OH}$ (**1**· $\text{H}_2\text{-Py}_2\text{P}$).

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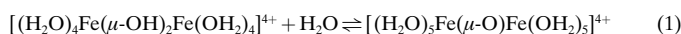
Keywords: electrochemistry • mesoporosity • metallacycles • nanostructures • supramolecular chemistry

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Supramolecular Complexation of Polynuclear Aqua Ions: A Crown Ether Adduct of a μ -Oxo-Bridged Iron(III) Aqua Dimer**

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The hydrolysis and polymerization of iron(III) in aqueous solution has been the subject of intense investigation since before the turn of this century^[1, 2] owing to the relevance of iron(III) hydrolytic processes to, for example, aquatic systems, the storage of iron by ferritin, and industrial processes such as alumina production. Although various products were proposed to form in the early stages of polymerization, the constitution and structure of even the simplest oligomers is still open to conjecture. For example, the structure of the binuclear iron(III) aqua ion has proved elusive, and there is considerable debate whether the two metal atoms are linked by two hydroxo bridges, $[(\text{H}_2\text{O})_4\text{Fe}(\mu\text{-OH})_2\text{Fe}(\text{OH}_2)_4]^{4+}$, or by a single μ -oxo bridge, $[(\text{H}_2\text{O})_5\text{Fe}(\mu\text{-O})\text{Fe}(\text{OH}_2)_5]^{4+}$.^[1–5] The two forms are related by the equilibrium shown in Equation (1). The latter form is favored according to magneto-



chemical and spectroscopic evidence, but it is noteworthy that a different structural assignment is preferred in two leading textbooks.^[4, 5] Moreover, although binuclear Fe^{III} complexes with hydroxo and oxo bridges are both common, with the latter predominant, they provide little insight into the structure of the binuclear aqua ion.

Previous X-ray structural studies on binuclear aqua ions of Al^{III} ,^[6] Cr^{III} ,^[7] Sc^{III} ,^[8] and Rh^{III} ,^[9] as well as on a heterometallic $\text{Cr}^{\text{III}}\text{Rh}^{\text{III}}$ aqua ion,^[10] showed that the bis(μ -hydroxo) M_2 core is preferred in all these cases. However, the existence of a μ -oxo-bridged Cr^{III} dimer was proposed on spectroscopic grounds. With the exception of the Al^{III} dimer,^[6] aromatic sulfonates were a key factor in the crystallization of these aqua ions. Such anions assist in the assembly of a superlattice in which layers of aqua ions are separated by layers of the anions. The superlattice is stabilized by an extensive hydrogen-bonding network involving the aqua ions, water solvate molecules, and anions, and by interactions between the anion themselves. In a further elaboration of this approach, crown ethers were introduced to modify the hydrogen-bonding array that surrounds these ions in aqueous solution. This led

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