Walljet Electrochemistry: Quantifying Molecular **Transport through Metallopolymeric and Zirconium Phosphonate Assembled Porphyrin Square Thin Films**

Aaron M. Massari, Richard W. Gurney, Craig P. Schwartz, SonBinh T. Nguyen, and Joseph T. Hupp*

Department of Chemistry and the Institute for Nanotechnology, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113

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By employing redox-active probes, condensed-phase molecular transport through nanoporous thin films can often be measured electrochemically. Certain kinds of electrode materials (e.g. conductive glass) are difficult to fabricate as rotatable disks or as ultramicroelectrodes-the configurations most often used for electrochemical permeation measurements. These limitations point to the need for a more materialsgeneral measurement method. Herein, we report the application of walljet electrochemistry to the study of molecular transport through model metallopolymeric films on indium tin oxide electrodes. À quantitative expression is presented that describes the transport-limited current at the walljet electrode in terms of mass transport through solution and permeation through the film phase. A comparison of the film permeabilities for a series of redox probes measured using the walljet electrode and a rotating disk electrode establishes the accuracy of the walljet method, while also demonstrating similar precision for the two methods. We apply this technique to a system consisting of zirconium phosphonate assembled films of a porphyrinic molecular square. Transport through films comprising three or more layers is free from significant contributions from pinhole defects. Surprisingly, transport through films of this kind is 2-3 orders of magnitude slower than through films constructed via interfacial polymerization of nearly identical supramolecular square building blocks (Keefe; et al. *Adv. Mater.* **2003**, *15*, 1936). The zirconium phosphate assembled films show good size exclusion behavior. The details of the observed dependence of permeation rates on probe molecule size can be rationalized with a model that assumes that the walls of the squares are slightly tilted from a strictly vertical geometry, consistent with atomic force microscopy measurements, and assumes that the individual wall geometries are locked by rigid interlayer linkages.

Introduction

Molecular transport through thin films can be of considerable importance in the areas of heterogeneous catalysis,¹ chemical separations,² sensing,³ and excitonic transport.⁴ The *rate* at which substrates, analytes, or redox-active molecules diffuse through a film phase, for example, has obvious consequences for system response time and even functionality. If oxidizable or reducible probe molecules are used, electrochemical methods can be enlisted to determine thin-film diffusion coefficients (D_f) or, more typically, permeabilities (i.e. products of D_f and solution-to-film partition coefficients, \hat{P}). From Fick's laws of diffusion, the Faradaic current (molecular flux) measured at a planar working electrode (in the absence of charge migration or slow interfacial kinetics) is determined by the concentration gradient generated by depletion of half of a redox couple (and formation of its complementary half) at the electrode surface.⁵ Indeed,

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the flux scales directly with the concentration gradient at the electrode surface and with a technique-dependent function of the diffusion coefficient.

Cyclic voltammetry and chronoamperometry at filmcovered planar macroelectrodes (radii greater than tens of micrometers) report on molecular transport through the solution and film phases. Because these are transient techniques, however, the diffusion behavior is dynamic and quantitative evaluation often requires comparison to simulated data. Nevertheless, careful comparisons of experimental data to numerical simulations have been shown to provide reasonable measures of diffusion coefficients.⁶ Generally though, it is simpler to extract solution and film diffusion coefficients from electrochemical methods which inhibit the temporal evolution of the diffusion layer and therefore the Faradaic current. Under these conditions, eq 1 describes the relationship between the overall measured diffusion-limited current (i_{lim}) and the current due to mass transport through solution ($\mathit{i_{MT}}$) and permeation through the film (i_{perm}) .⁵

$$\frac{1}{i_{\rm lim}} = \frac{1}{i_{MT}} + \frac{1}{i_{perm}}$$
(1)

Three-dimensional diffusion to an ultramicroelectrode (UME) ensures that diffusive transport to the naked

^{*} Corresponding author. Telephone: +1-847-491-3504. FAX: +1-847-491-7713. E-mail: jthupp@chem.northwestern.edu.

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electrode surface quickly reaches a steady state; thus, evaluation of the diffusion-limited current with and without a film-covered electrode provides information about molecular diffusion through the film phase. More accurate diffusion coefficients can be obtained by using rotating disk electrode (RDE) voltammetry. In this approach, the rotation of the working electrode generates solution convection to the electrode surface, which effectively compresses the diffusion layer and limits its growth. In this manner, higher rotation speeds produce smaller diffusion layer thicknesses, with higher Faradaic currents resulting from the correspondingly steeper concentration gradients. Within the limits of the mem-brane diffusion model,^{5,7} an analytical expression exists which describes the relationship between disk electrode rotation speed (ω) and diffusion-limited current for a filmcovered electrode:^{7,8}

$$\frac{1}{i_{\rm lim}} = \frac{\nu^{1/6}}{0.620 \, nFAD_s^{2/3} \omega^{1/2} C} + \frac{d}{nFA(PD_f)C} \qquad (2)$$

In this equation, d is the film thickness, P is the partition coefficient, C is the concentration of the permeant in solution, ν is the kinematic viscosity of the solution, D_s is the coefficient for diffusion through the solution phase, F is the Faraday constant, *n* is the electron stoichiometry for the reaction, and A is the electrode area.⁵ As it is difficult, though not impossible,⁹ to separate P from D_f in electrochemical measurements (especially if *P* is small), their product is typically reported as a measure of molecular transport. According to eq 2, a plot of $1/i_{lim}$ as a function of $1/\omega$ should be linear with a slope that is dependent on the solution-phase transport properties and a *y*-axis intercept that is dependent on the film thickness and the rate of molecular permeation through the film.

Recently, we reported on the permeabilities of a number of evaporatively cast and polymerized films of molecular squares.^{10–13} These materials exhibit remarkable size selectivity and, in some instances, enhanced permeability likely attributable to the alignment of square cavities. Recent synthetic work in our laboratories has yielded the porphyrinic "molecular square", 1a. This square, which features a cavity diameter slightly greater than 20 Å, is nearly identical to squares used previously for evaporatively cast or polymer film formation-the difference being the replacement of either copolymerizable substituents (**1b**)¹¹ or esters (**1c**)¹² with phosphonic acids. We and others have previously demonstrated that diphosphonic acid derivatized porphyrins are amenable to assembly into ultrathin films using established zirconium phosphonate (ZrP) chemistry.^{14,15} For nanoporous thin films of molecular

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squares, the primary advantages of the ZrP approach over casting or polymerization are greatly enhanced control over film thickness, especially in the ultrathin film limit, and bond-directed orientation of the square cavity opening normal to the platform surface.

For a number of reasons, measuring molecular transport through ZrP films has proven more challenging than measuring transport through polymeric or cast films. First,

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the assembly procedure for ZrP materials has been optimized for transparent conductive indium tin oxide (ITO) electrode surfaces. Preliminary macroelectrode electrochemical measurements (cyclic voltammetry and chronoamperometry) of these thin films were qualitatively informative but quantitatively ambiguous. Unfortunately, neither UME's nor RDE's are commercially available with ITO as their active electrode surface. Fabrication of ITO UME's is a difficult undertaking and is impractical if film thicknesses or optical densities are to be correlated with individual film behavior. Limited literature precedent exists for the preparation of rotatable ITO disk electrodes;¹⁶ however, many of the fabrication materials (glues, epoxies, and polymers) are soluble in the organic solvents used in our thin-film assembly procedures.

To circumvent these issues, we have constructed a simple, yet effective, walljet electrode.¹⁷ As implied by the nomenclature, this apparatus consists of a planar electrode of known area (wall) and an impinging flow of solution (jet) that provides well-defined hydrodynamics normal to the electrode. As in rotating disk voltammetry, a stagnant layer exists in the region closest to the electrode. In this region, transport is controlled by diffusion. The thickness of the layer, and therefore the rate of diffusion, can be manipulated by adjusting the volume flow rate, V-faster flow leading to a thinner layer and a greater limiting current. Yamada and co-workers quantitatively described the behavior as18

$$i_{\rm lim} = \frac{1.38nFCD_s^{2/3}V^{3/4}r^{3/4}}{v^{5/12}\alpha^{1/2}}$$
(3)

where *a* is the diameter of the solution jet and *r* is the radius of the wall electrode. Combining eq 3 with eqs 1 and 2 produces an equation that can be used to describe the behavior of a film-covered walljet electrode:

$$\frac{1}{i_{\rm lim}} = \frac{\nu^{5/12} \alpha^{1/2}}{1.38 nFCD_s^{2/3} V^{3/4} R^{3/4}} + \frac{d}{nFA(PD) C}$$
(4)

Using eq 4, $1/i_{lim}$ for a film-covered electrode can be plotted against $V^{-3/4}$, and the *y*-axis intercept will yield information about the permeation processes.

Herein, we first report the application of walljet electrochemistry for the measurement of molecular transport through previously studied metallopolymeric films. A comparison of permeabilities for a series of redox probes measured using the walljet electrode to those measured with a rotating disk electrode demonstrates the accuracy of the walljet technique and reveals comparable precision. We then use the walljet electrode to measure the permeability of ZrP-assembled thin films of 1a with respect to a series of redox probe molecules and describe the observed permeation trends based on probe size.

Experimental Section

Ferrocenemethanol (FcMeOH), hexammineruthenium(III) chloride ([Ru(NH₃)₆]Cl₃), ammonium hexachloroosmate ((NH₄)₂-[OsCl₆]), phosphorus oxychloride (POCl₃), 2,4,6-collidine, (3aminopropyl)trimethoxysilane (3-APTMS), anhydrous 1-octanol, zirconyl chloride octahydrate (ZrOCl₂·8H₂O), phenosafranin (PS⁺), Azure A, and ethanolamine were used as received from Aldrich. Potassium ferrocyanide (K₄[Fe(CN)₆]) was used as received from J. T. Baker. tris-(5-amino-1,10-phenanthroline)iron(II) hexafluorophosphate ([Fe(phenNH₂)₃](PF₆)₂) and tris-(2,2'-bipyridine) cobalt (II) nitrate $([Co(bpy)_3](NO_3)_3)$ were prepared as described in the literature.^{10,19,20} Sodium iodide, dimethyl sulfoxide (DMSO), concentrated sulfuric acid, concentrated hydrochloric acid, 30% hydrogen peroxide, hexanes, and "Optidri" acetonitrile (ACN) were obtained from Fisher Scientific. Electrochemical grade potassium nitrate (KNO₃) was obtained from Fluka. All water used was purified with a Millipore system (18 M Ω). Indium tin oxide coated soda glass (ITO) (10 Ω /square) was obtained from Delta Technologies, Ltd.

All electrochemical measurements and polymerizations were performed with a CH Instruments 1202 Bipotentiostat in a threeelectrode configuration using a bare or film-covered ITO working electrode, an aqueous Ag/AgCl reference electrode, and a platinum foil auxiliary electrode. All redox solutions were prepared in 0.1-0.2 M KNO₃ to eliminate current contributions due to migration.

ITO for metallopolymer-covered samples was carefully cut into 0.9 cm \times 4 cm pieces and cleaned for 15 min in an aqueous ethanolamine (20% (v/v)) solution under reflux. These pieces were rinsed with copious amounts of water and dried in a stream of nitrogen. Metallopolymeric thin films of Fe(phenNH₂)₃ⁿ⁺ were deposited on the cleaned ITO by electrochemical cycling at 100 mV/s between 0.5 and 1.2 V in an aqueous 0.2 M KNO₃ and 0.5 mM Fe(phenNH₂)₃ solution. Previous work showed that the growth of this metallopolymer is self-limiting at ca. 50 nm thick after 100 electrochemical cycles.¹⁰ Samples used here were polymerized for 150 electrochemical cycles to ensure 50 nm film thicknesses.

Thin films of **1a** were prepared using an assembly procedure that will be described in greater detail elsewhere. Briefly, ITO was cut into 0.9 cm \times 4 cm pieces and cleaned in a 2:1 H₂SO₄: H₂O₂ mixture, which has been immersed in a cold water bath for 15 min (Caution: reacts violently with organics). The samples were then rinsed with copious amounts of water and placed into a 2 M HCl solution for 5 min. After rinsing with water, the samples were oven-dried for 15 min at 80 °C. The hydroxy-terminated surface was then amine-terminated by refluxing in a 1:100 (v/v) solution of 3-APTMS in anhydrous octanol for 10 min, followed by rinsing with hexanes, rinsing with water, and oven-drying for 15 min. The surface was then phosphorylated by soaking in a 10 mM POCl₃ and 10 mM 2,4,6-collidine solution in dry ACN for 15 min. The samples were rinsed with ACN and water and then subjected to zirconation in an aqueous 25 mM ZrOCl₂ solution for at least 2 h. The first layer of 1a was then assembled onto the zirconated surface by soaking in a 0.02 mM solution of 1a in DMSO under vacuum for at least 3 h. The resulting films were rinsed by soaking in DMSO and water for 15 min each and then exposed to ZrOCl₂ for 30 min. As shown schematically in Scheme 1, subsequent layers were assembled by repeated exposure to 1a and ZrOCl₂, as described above. To facilitate consistent film preparation, a computer-controlled robotic arm was built within a vacuum desiccator to perform the repeated dipping cycles.²¹

Film growth was monitored by UV-visible spectroscopy using a Varian Cary 5000 spectrophotometer. Film thicknesses were determined via atomic force microscopy (AFM) performed with a Digital Instruments Bioscope with a Nanoscope III controller in contact mode.

To achieve an imageable "step" between the film and the bare surface, the glass side of a ZrP-assembled sample (assembled layers of 1a are grown on both the glass and ITO sides of the sample) was deliberately scratched with a razor blade and rinsed vigorously with water to remove debris.10 The AFM tip was positioned at the scratched region on an inverted optical microscope (Nikon Eclipse TE300).

The walljet instrument is shown schematically in Chart 1. A 75 mL solution reservoir was fabricated from Plexiglas and sealed with silicone adhesive (GE Sealants and Adhesives, Silicone II). The sample was positioned at one face of the reservoir with an aluminum plate and stainless steel bolts, and the bolts and sample

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Scheme 1. Zirconium Phosphonate Assembly Procedure: (1) A Cleaned and Phosphorylated Surface Exposed to an Aqueous Zirconium Solution, Followed by (2) Soaking in a Solution of Molecule 1a; (3) Steps 1 and 2 Repeated To Assemble Multiple Layers of 1a



3. Repeat steps 1 and 2 for subsequent layers

Chart 1. Schematic Representation of the Walljet Apparatus^a



^{*a*} A motor-driven syringe is fixed through one face of the redox solution reservoir, normal to the active electrode surface, which is attached to the opposite wall. ITO, platinum foil, and an aqueous Ag/AgCl electrode are the working (WE), counter (CE), and reference electrodes (RE) in this apparatus. Additional details are provided in the text.

were sealed with O-rings and gasket material. The gasket material was cut to expose a 0.25 cm^2 disk-shaped area of the ITO to the redox solution.

The gasket material and Plexiglas openings to the active electrode disk were beveled (ca. 30°) to facilitate unobstructed flow across the wall electrode surface. A syringe needle was cut to a square point and inserted through the reservoir face opposite to the sample with the tip positioned 3 mm from the sample surface. Care was taken to center the syringe needle within the sample opening where it was permanently attached with 5 min epoxy. The geometry of the solution jet and electrodes was in accordance with other reported walljet electrodes.^{17,18,22} A motor-driven 10 mL disposable syringe (Fisher) was used to propel the redox solution to the sample surface through the syringe needle. A Newport 860 Motorizer with a Newport 860SC-C variable-speed controller provided consistent volume flow rates (*V*) from 0.007 to 0.065 cm³/s.

All walljet experiments were performed chronoamperometrically with several volume flow rates measured in each trial. The dispensed volume was monitored visually on the syringe wall, and the elapsed time for each flow rate was determined from the chronoamperometry data after the trial was finished. For film diffusion coefficient calculations, redox probe concentrations were determined by either absorbance spectroscopy (FcMeOH, ϵ_{438} nm = 100 M⁻¹ cm⁻¹;²³ PS⁺, ϵ_{521} nm = 36 280 M⁻¹ cm⁻¹;²⁴ Azure A, ϵ_{634} nm = 56 000 M⁻¹ cm⁻¹;²⁵ OsCl₆²⁻, ϵ_{370} nm = 7300 M⁻¹ cm⁻¹ ²⁶) or by measuring a cyclic voltammogram with a freshly polished platinum UME of known radius (FcMeOH, $D_{\rm s}$ = 7.8 \times 10⁻⁶ cm²/s;¹⁰ I⁻, $D_{\rm s}$ = 6.4 \times 10⁻⁶ cm²/s;¹⁰ Ru(NH₃)₆³⁺, $D_{\rm s}$ = 14.7 \times 10⁻⁶ cm²/s;¹⁰ I⁻, $D_{\rm s}$ = 19.9 \times 10⁻⁶ cm²/s²⁸), prior to each experiment. All redox probe concentrations were found to be

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Figure 1. Representative chronoamperometric trace demonstrating the walljet electrode behavior at several volume flow rates (*V*) for a 2 mM solution of FcMeOH at a bare ITO electrode.

approximately 2 mM. Solution-phase diffusion coefficients for Azure A ($D_s = 4.2 \times 10^{-6} \text{ cm}^2/\text{s}$), $OsCl_6{}^{2-}$ ($D_s = 4.9 \times 10^{-6} \text{ cm}^2/\text{s}$), and $Co(bpy)_3{}^{3+}$ ($D_s = 3.4 \times 10^{-6} \text{ cm}^2/\text{s}$) were determined by cyclic voltammetry using a freshly polished platinum UME of known radius in solutions of known concentration. For all concentration and D_s calculations, the number of electrons transferred, *n*, is 1, except PS⁺ and Azure A, which are known to be n = 2 processes.²⁹



Azure A



Results and Discussion

Walljet Calibration: Metallopolymeric Thin Films. Typical chronoamperometric walljet data are shown in Figure 1 for a bare ITO electrode in FcMeOH-containing solution. After the initial potential step past the formal potential of the redox probe (at time = 0), the diffusion layer was allowed to evolve, as evidenced by the exponential decrease of the current toward zero. This period of time (usually 20-30 s) allowed the Faradaic and non-Faradaic currents to stabilize. After this stabilization period, the solution jet was turned on at a low flow rate producing a stable, diffusion-limited current. After a known volume of solution was propelled to the electrode, the flow rate was increased incrementally. For all experiments, 0.4 mL was expelled during the first and slowest flow rate, and all subsequent flow rates expelled a total volume of 1.0 mL of solution. As shown in Figure 1, the increased flow rates produce higher limiting currents, as expected. By using this chronoamperometric method, the



Figure 2. $1/i_{lim}$ versus $V^{-3/4}$ for solutions of (a) FcMeOH and (b) Fe(CN)₆⁴⁻ at a bare (solid points) and polymer-covered (open points) walljet electrode.

Table 1. Comparison of Metallopolymer PDf Values AsDetermined by Walljet Electrochemistry versus RotatingDisk Electrochemical Methods

redox	molec diam (Å)	$10^9 imes PD_f$ (cm²/s)	
permeant		RDE ^a	walljet
FcMeOH [Ru(NH ₃) ₆] ³⁺ [Fe(CN) ₆] ⁴⁻	4.5 5.5 6.0	$\begin{array}{c} 61\pm7\\ 8.6\pm1.5\\ 2.6\pm1.0\end{array}$	$\begin{array}{c} 65\pm21\\ 9.4\pm1.6\\ 4.1\pm1.3 \end{array}$

^{*a*} Values reported in ref 10.

known solution volume expelled and the time required to expel it allow for the calculation of Vat each motor speed.

The observed linear relationship between i_{lim}^{-1} and $V^{-3/4}$ for bare (filled circles) and poly-Fe(phenNH₂)₃-covered (open circles) ITO electrodes points to the validity of eq 4 for our walljet apparatus (Figure 2a,b). The slopes of the data plots with and without the polymer coating are identical, as expected, since they report exclusively on mass transport in the solution phase.

Consistent with eq 4, the presence of the polymer coating produces *y*-axis data offsets with larger offsets corresponding to slower film permeation. Table 1 lists permeabilities calculated from the offsets, together with permeabilities obtained previously via rotating disk voltammetry. Clearly the agreement is excellent. The table additionally indicates that the precision of permeabilities measured by walljet electrochemistry is similar to that obtained using rotating disk voltammetry.

ZrP-Assembled Thin Films. ZrP-based films of **1a** covering a range of thicknesses were prepared on ITO using the procedure described above. A plot of AFM-determined film thickness versus the number of assembly cycles (Figure 3) is linear and indicates an average

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Figure 3. AFM heights for ZrP films of 1a assembled on glass.



Figure 4. Geometry-optimized structure of a portion of **1a**. The vertical distance from the top oxygen to an oxygen below the zirconium is 25 Å, and the horizontal rhenium to rhenium distance is 24 Å.

thickness of 19 Å/layer. A geometry-optimized model of the square wall coordinated to a zirconium oxide fragment (Figure 4) gives a height of 25 Å.³⁰ Assuming this geometry for each wall in the square, the AFM heights imply an average porphyrin tilt angle of around 40°. Previous work has shown that ZrP linkages are not linear;³¹ therefore, it is likely that the tilt angle is directed to some degree by the coordination bonds around the zirconium centers. However, with each successive assembly cycle, the tilt angles of the molecular square walls in the previous molecular layers are locked by the coordinate bonding scheme.

Although ZrP films of **1a** are extremely thin, their permeabilities are measurable by walljet electrochemistry as evidenced by nonzero *y*-axis intercepts in plots of i_{lim}^{-1} versus $V^{-3/4}$ (see Supporting Information). From eqs 1 and 4, the intercepts equal the inverse of the permeation current. In Figure 5, values for i_{perm} are plotted versus 1/dwhen using FcMeOH as the redox probe. With the exception of the point for the thinnest film (not shown), the data fall (admittedly with some scatter) near a line of constant slope, indicating that (a) the permeability changes little as the film thickness increases and (b)



Figure 5. Permeation current (i_{perm}) for FcMeOH as a function of inverse film thickness for films of **1a**. A thickness of 19 Å/layer was assumed (see text). The corresponding number of layers of **1a** is shown on the top axis.

Table 2. Comparison of Permeabilities of ZrP-Assembled, Evaporatively Cast, and Interfacially Polymerized Films of Porphyrinic Molecular Squares

-				-
redox permeant	$10^6 imes D_{ m s} \ ({ m cm}^2/{ m s})^a$	$10^9 imes PD_f({ m cm^2/s})$		
		ZrP, 1a ^b	polym., 1b ^c	evap., 1c ^d
I-	19.9	12 ± 4	_	_
PS^+	9.95	4.2 ± 3.6	-	_
FcMeOH	7.8	3.6 ± 2.5	1380 ± 350	330 ± 10
$[OsCl_6]^{2-}$	4.9	1.3 ± 1.2	-	-
Azure A ⁺	4.2	1.1 ± 0.9		
[Co(bpy) ₃] ³⁺	3.4	0.10 ± 0.13	630 ± 120^{e}	24 ± 1^{e}

^{*a*} Experimental section contains references for these values. ^{*b*} Values measured through ZrP-assembled films of three or more layers of **1a** in the present study. ^{*c*} As measured through interfacially polymerized molecular square films in ref 11. ^{*d*} As measured through evaporatively cast molecular square films in ref 12. ^{*e*} This value represents Co(1,10-phenanthroline)₃³⁺, which has similar redox kinetics, identical charge, and a comparable, though slightly larger (13 Å instead of 12 Å), molecular diameter.

diffusion through the film phase, rather than partitioning from the solution to film, is rate-determining. The deviation of the thinnest film from the line implies that the initial layer is poorly packed and/or contains some bare regions or pinholes. However, it appears that any pinhole defects initially present are "overwritten" in subsequent assembly cycles—their population generally becoming negligible once three or more layers are formed.

Table 2 lists the permeabilities of the ZrP molecular square films for a series of roughly spherical redox probes of varying diameter.³² Also included for comparison are previously reported transport data for evaporatively cast¹² and interfacially polymerized films.¹¹ The squares comprising these films feature cavities that are (in isolation) of identical size to those of the phosphonated squares. In contrast to the phosphonated porphyrin square films, however, the cast and polymerized porphyrin square films lack net orientation of square cavities. It is surprising, therefore, that transport through ZrP molecular square films, after normalization for thickness differences, is considerably slower than through polymerized and cast

⁽³⁰⁾ The height of this structure is the distance from the top oxygen atom to an oxygen located below the zirconium atom.

⁽³¹⁾ Clearfield, A.; Wang, Z. J. Chem. Soc., Dalton. Trans. 2002, 23, 2937.

⁽³²⁾ The reported permeabilities and standard deviations reflect the average of at least 10 PD_r measurements on films with three or more layers of 1. The standard deviations also reflect the standard deviations of the AFM thickness measurements. The geometry optimization was performed using HyperChem version 6.0.



Figure 6. *PD_f* values for ZrP-assembled (right axis) and interfacially polymerized (left axis) films of porphyrinic molecular squares **1a** ($\mathbf{\nabla}$) and **1b** ($\mathbf{\Theta}$), respectively, as a function of the inverse radius of the permeant. Results shown for **1b** are taken from ref 11.

films (although it is closer to that found for cast films). Figure 6 illustrates a further difference: *PD_f* values become progressively smaller as the size of the probe molecule increases, culminating, in the polymer case, in a sharp size cutoff at ca. 22 Å-the approximate diameter of the molecular cavity defined by the tetrarhenium framework. *PD_f* values for ZrP molecular square films similarly decrease with increasing probe size, but a sharp size cutoff is absent. Instead, the tapering is gradual, with complete size exclusion occurring around 13 Å-slightly more than half of the cavity diameter for an isolated square. Cast films of 1c exhibit the tapering behavior observed with ZrP molecular square films (data not shown). In contrast, earlier work with electropolymerized films of polypyridyl ruthenium complexes showed that transport through these are characterized by sharp size cutoffs.33

The reduced size cutoff is consistent with a tilted orientation of the ZrP square's walls with respect to the tetrarhenium framework. As mentioned above, the coordinate bonding of the phosphonic acid functional groups and zirconium directs the location of each subsequent layer of 1a. Unlike interfacially polymerized squares (1b) connected via flexible propyl-diester units,¹¹ in which the linkages presumably permit unfavorably tilted porphyrin square walls to untilt sufficiently to allow larger probe molecules to permeate, the ZrP linkages are rigid. Using the simple geometric model shown in Chart 2, and assuming rigid linkages, an average tilt angle of around 28° would be needed to produce the exclusion of permeants exceeding 13 Å in diameter observed in Figure 6. If a range of tilt angles exists, however, tapered rather than sharp size exclusion behavior would be expected.

The correlation in Figure 7 of molecule size-dependent PD_f values with the solution-phase diffusion coefficients of the same molecules is reminiscent of the Einstein–Stokes relation:

$$D_{\rm s} = k_B T / 6\pi \eta r \tag{5}$$

According to this equation, for a given solution the product of D_s and r, the permeant radius, should be a constant whose value depends on the solution viscosity, η . It is tempting to interpret the correlation as a measure of the effective viscosity of the solvent within the nanoporous film, relative to its bulk value. On this basis

Chart 2. Geometric Model of 1a (Side View), Where L Is the Re-to-Re Distance, h Is Half of the Wall Height, and θ Is the Average Tilt Angle^a



 $x = L - 2[h \cdot \cos(90 - \theta)]$

^a For simplicity, only two opposing walls are shown.



Figure 7. PD_f values for ZrP-assembled films of **1a** as a function of permeant D_s .

(choosing FcMeOH as the permeant and assuming Pdoes not differ appreciably from unity) a several-thousandfold difference in effective viscosity is implied by the solution- and ZrP-film-phase permeabilities. However, if the interpretation is applicable to polymerized films as well, a nearly 400-fold difference in effective viscosity is implied for the solvent within ZrP squares versus polymerized-square films. A more prosaic interpretation for the correlation of ZrP film permeability with D_s may be the tilt-angle-distribution-defined size exclusion and tapering effect proposed above. The extraordinary differences in permeability for polymerized versus ZrPassembled films of essentially identical supramolecular building blocks is conceivably related to the polymer's ability to swell, where swelling could either eliminate structural bottlenecks or engender favorable dynamics of some kind. Left unexplained, however, would be the transport advantage of unswellable nanoporous square films obtained simply by casting from solution.¹² The role of polymer dynamics, if any, might be revealed by impedance spectroscopy. Also likely to be instructive would be a study of flexible ZrP-assembled films-for example, films comprising alternating layers of porphyrin square and short alkanes.

Conclusions

Walljet electrochemistry provides a simple method of determining film permeabilities on otherwise difficult to study electrode materials such as ITO. Permeabilities measured in this way agree well with values obtained via alternative techniques like rotating disk voltammetry. The precision of the walljet technique is similar to that of the RDE method. Application of the walljet method to zirconium phosphonate assembled films of a porphyrinic molecular square reveals that molecular transport through the films is (a) controlled by diffusion-limited permeation rather than rates of partitioning and (b) nearly 3 orders of magnitude slower than transport through closely related polymeric films. Films comprising three or more layers are largely free of pinhole defects and exhibit good size exclusion when confronted with probe molecules of varying radius. Size exclusion occurs at just over half of the maximum diameter of the cavity of an isolated square, with a gradual tapering of transport rate with increasing probe molecule size. In contrast, interfacially polymerized films have previously been shown to display sharp size cutoffs at a diameter matching the molecular square cavity diameter. The differences likely arise from differences in torsional mobility of the walls of the squares comprising the two types of films. Polymerized films are characterized by flexible alkane linkages that should permit torsional motion. Both the reduced size cutoff and the absence of

a discontinuity at a critical permeant size in a PD_f /size plot can be rationalized if the walls of the squares of ZrPassembled films are tilted on average about 28° from a vertical geometry with respect to the squares' tetrarhenium framework. In this manner, the cavity width at the interlayer linkage point governs cavity access. AFM measurements of "per layer" film thickness support the contention that moderate tilting exists.

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Supporting Information Available: Representative plots of the inverse limiting current versus $V^{-3/4}$ for FcMeOH permeation of ZrP films of varying thicknesses. These materials are available free of charge via the Internet at http://pubs.acs.org.

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