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Monolayers as Models for Supported Catalysts: Zirconium Phosphonate Films Containing Manganese(III) Porphyrins

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Abstract: Organized monolayer films of a manganese tetraphenylporphyrin have been prepared and used as supported oxidation catalysts. Manganese 5,10,15,20-tetrakis(tetrafluorophenyl-4′-octadecyloxyphosphonic acid) porphyrin (**1**) has been immobilized as a monolayer film by a combination of Langmuir–Blodgett (LB) and self-assembled monolayer techniques that use zirconium phosphonate linkages to bind the molecule to the surface. Analysis by FTIR, XPS, UV–vis and polarized optical spectroscopy show that the films consist of noninteracting molecules effectively anchored and oriented nearly parallel to the surface. The monolayer films are stable to the solvent and temperature conditions needed to explore organic oxidations. The activity of films of **1** toward the epoxidation of cyclooctene using iodosylbenzene as the oxidant was compared to that of Manganese 5,10,15,20-tetrakis(pentafluorophenyl) porphyrin (**2**) and **1** under equivalent homogeneous conditions. The immobilized porphyrin **1** shows an enhanced activity relative to either homogeneous reaction. The main difference between **1** and **2** is the four alkyl phosphonate arms in **1** designed to incorporate the porphyrin within the films. The increased activity of immobilized **1** is a combination of the porphyrin structure, which prohibits the formation of μ-oxo dimers even in solution, and a change in conformation when anchored to the surface. The study demonstrates that careful monolayer studies can provide useful models for the design and study of supported molecular catalyst systems.

Introduction

There are several potential advantages to be derived from confining molecular catalysts at surfaces to form heterogeneous systems including easier product purification and catalyst recovery. Common strategies of immobilizing molecular catalysts include incorporating them into organic polymers,[1−10] high surface area carbon,[11,12] and inorganic frameworks such as zeolites,[13−15] silica,[16−21] or other metal oxides.[22,23] Immobilized catalysts can mirror their homogeneous behavior or the process can alter a catalyst's activity perhaps even changing the mechanism whereby it operates. Detailed understanding of catalytic behavior at interfaces is clearly desirable, but studies of supported catalysts can be riddled with uncertainties. Typical high-surface area supports are often not uniform, giving variation in catalyst binding sites, aggregation, and orientation with respect to the surface. It is often even difficult to determine if the structure of the molecular catalyst has remained intact upon adsorbing it to a surface. If catalytic activity is observed with a supported system, it is frequently impossible to know what species is responsible for the catalysis. Therefore, procedures for studying molecular catalysts at a uniform and reproducible interface could enhance the understanding of their behavior in heterogeneous environments.

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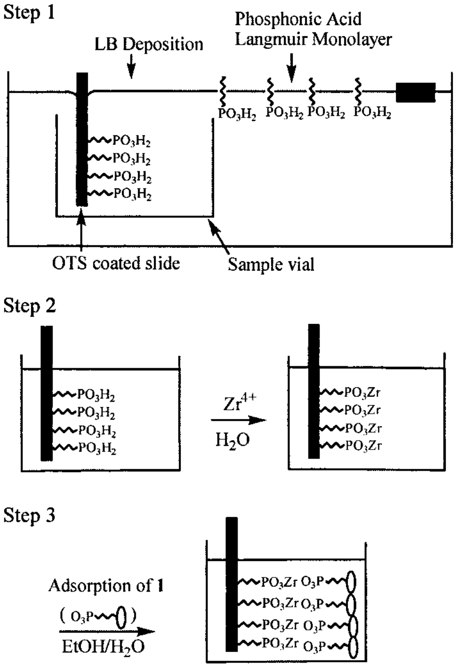
In this study, we take advantage of a well-understood surface modification process[24−30] to compare the activity of a monolayer film of a surface-confined manganese porphyrin oxidation catalyst with its homogeneous behavior. Through careful molecular design and controlled deposition, monolayers with known surface coverage, molecular orientation, and mode of binding to the interface are obtained. Using this controlled surface for the example of alkene epoxidation, we have observed increased activity with the surface-confined catalyst relative to homogeneous reactions under the same conditions. In contrast to many supported catalysts, all of the catalytic complexes present in the monolayer films are fully accessible, thus allowing accurate determination of the ratio of active site to substrate that is necessary to evaluate the effect of immobilization on catalytic activity. The monolayer films also allow careful monitoring of the state of the catalyst during the course of the reaction so that different behavior of the homogeneous and supported systems can be quantified. In addition to providing insight into the specific example of immobilized manganese porphyrins, the results demonstrate the utility of studying well-characterized molecular monolayers as models for supported molecular catalyst systems.

Methods for immobilizing metalloporphyrins in monolayer films frequently involve coordination bonds to the axial sites on the metal center.[31,32] However, under the conditions needed to catalyze organic transformations, a covalent linkage through the macrocycle ligand is preferred to free up the metal center to participate in the reaction and to guard against desorption that may result from labile coordination bonds. Our method of preparing monolayers of covalently confined molecules has been described previously, and is based on zirconium phosphonate linkages in combination with Langmuir−Blodgett and "self-assembled monolayer" adsorption.[24−30] It involves the initial formation a Langmuir−Blodgett monolayer of octadecylphosphonic acid (ODPA) on a hydrophobic support that after adsorption of a layer of Zr^{4+} ions provides a well-defined surface for the subsequent deposition of molecules containing phosphonic acid groups (Scheme 1).[24,25] The thin films are modeled after layered solid-state metal phosphonates, where organic layers separate continuous inorganic layers.[33−39] The practice of sequential adsorption of organophosphonates and tetravalent metal ions has frequently been used to build-up multilayered films.[38−42] However, the present study employs a single deposition cycle to afford a controlled monolayer. Films formed in this way are stable to solvents and reaction conditions commonly used for many organic transformations,[30] making it possible to use them in studies of supported catalysis.

Scheme 1. Three-step Deposition Procedure for the Formation of Films of **1** (The Film Is Present on Both Sides of the Slide)



Manganese 5,10,15,20-tetrakis(tetrafluorophenyl-4′-octadecyloxyphosphonic acid) porphyrin, **1**, was prepared for this study. The fluorinated tetraphenylporphyrin has four alkylphosphonic acid arms intended for binding and orienting the porphyrin at the surface. Previous studies on the Pd^{2+} [29] and free-base analogues[43] of **1** have shown that the ligand structure indeed leads to monolayer coverage with the porphyrin macrocycle oriented parallel to the surface. Another important feature is that the molecules do not aggregate on the surface.[29] The phosphonate groups bind strongly to the zirconated LB layer to reach a high surface coverage of noninteracting molecules.

Natural metalloporphyrins are known oxidation catalysts, and there has been a great deal of investigation of synthetic analogues[44−55] since the early reports that an iron porphyrin

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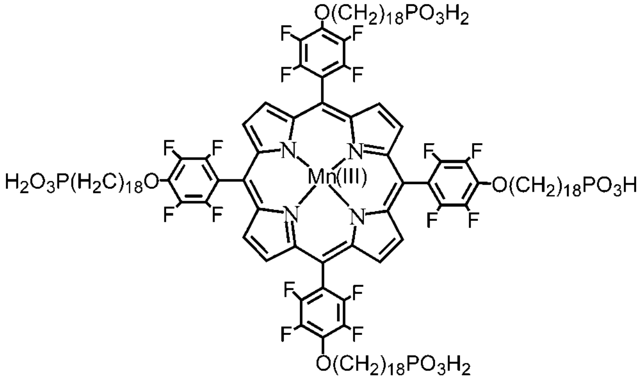

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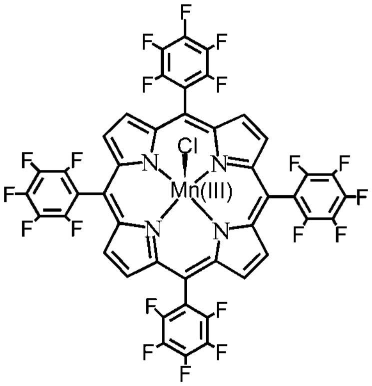

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with iodosylbenzene could oxidize a number of alkenes and alkanes.[44] The ability of porphyrins to efficiently serve as oxidation catalysts unfortunately leaves them as potential substrates. In addition to oxidative degradation of the ligand, metalloporphyrins deactivate through oxidation of the metal center to form μ-oxo dimers. One way of avoiding deactivation is through immobilization of the chromophore.[56] Attempts at immobilizing porphyrin catalysts within supports such as organic polymers,[3,57] silica,[3,57−60] zeolites,[61,62] and metal phosphonates[63,64] have also been reported.

The monolayer studies reported here represent an attempt to better understand the behavior of surface-confined porphyrins. The activity of a monolayer of porphyrin **1** was carefully compared to its homogeneous reaction and that of catalyst **2,** an equivalent molecule without the alkylphosphonic acid arms. Catalyst **2** is manganese 5,10,15,20-tetrakis(pentafluorophenyl) porphyrin. Catalyst **2** was chosen for its ease of preparation and because its geometry is likely to mimic the one found in **1** once the alkylphosphonate chains are employed in the immobilization. We find that the films of **1** offer higher yields and have a longer lifetime than either of the catalysts **1** or **2** in solution. The principal difference is that **2** deactivates through the formation of μ-oxo dimers. On the surface, molecule **1** cannot dimerize, but in solution the alkylphosphonic acid arms also protect the metalloporphyrin core from dimerization. However, **1** still shows increased catalytic activity in the monolayer relative to in solution. In both cases, the molecule oxidatively degrades with time, but the monolayer deactivates more slowly, leading to a higher number of turnovers. Confining the bulky molecule to the surface alters the conformation of the porphyrin, changing the steric environment around the metal center. This feature along with the density of the catalytic sites resulting from the monolayer deposition technique may also play a role in the observed increase in activity.

Experimental Section

Materials. Reagents were obtained from commercial sources and used as received unless indicated. Bicyclohexyl 99%, purchased from Acros (Pittsburgh, PA), was purified by percolation through basic alumina. Teflon (fluoro(ethylene-propylene)) sheets were purchased from American Durafilm (Holliston, MA). Single-crystal silicon wafers (1 0 0) were purchased from Semiconductor Processing Company (Boston, MA). Germanium attenuated total-reflectance (ATR) crystals (45°, 50 mm × 10 mm × 3 mm) were purchased from Wilmad Glass (Buena, NJ).

Manganese 5,10,15,20-tetrakis(tetrafluorophenyl-4′-octadecyloxy-phosphonic acid) porphyrin (1). Synthetic procedures are included in the Supporting Information.

Manganese 5,10,15,20-tetrakis(pentafluorophenyl)-porphyrin (2). This compound was prepared according to published methods.[65,66]

Substrate Preparation. Glass microscope slides were used as substrates for UV−vis and catalysis studies. These were cleaned by the RCA procedure[67] and blown dry with a nitrogen stream. To make them hydrophobic, they were immersed in a 5 mM solution of OTS in bicyclohexyl for 2 min and dipped in toluene for a few seconds. The slides were dried with a nitrogen stream and the process repeated.[68] Single-crystal silicon wafers (1 0 0), were cut using a diamond glass cutter to 25 mm × 15 mm × 0.8 mm for XPS substrates. The substrates were cleaned using the RCA procedure then sonicated for 15 min each in methanol, 50/50 by volume methanol/chloroform, and chloroform. The substrates were then sonicated in a 2% OTS solution in hexadecane and chloroform (50/50 by volume) for 2 h. Finally, the substrates were sonicated for 15 min each in chloroform, 50/50 by volume methanol/chloroform, and methanol.[69] Germanium attenuated total-reflectance (ATR) crystals were washed with hot chloroform by placing them in the thimble of a Soxhlet extractor. They were made hydrophobic by soaking them in the above OTS solution for an hour, and then rinsed again with hot chloroform.

Film Formation. KSV Instruments (Stratford, CT) Langmuir−Blodgett systems KSV 2000 and 3000 were used in combination with a homemade, double barrier Teflon trough for the LB film preparation. A platinum or filter paper Wilhelmy plate, suspended from a KSV microbalance, measured the surface pressure. Subphases were prepared with pure water, with a resistivity of 17.8−18.0 MΩ cm^{-1} produced from a Barnstead NANOpure (Boston, MA) purification system.

Zirconium phosphonate films were prepared using a three-step deposition technique (Scheme 1).[24,25] The aqueous subphase was 2.6 mM in $CaCl_2$ adjusted to pH 7.8 with a 0.10 g/L KOH solution.[26] A glass sample vial was placed in the subphase in the well of the trough. ODPA was spread from a 0.3 mg/mL chloroform solution and

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compressed at 10 mm/min on the water surface to a target surface pressure of 20 mN/m. The hydrophobic substrate was dipped down through the monolayer surface and into the sample vial at 8 mm/min, transferring the ODPA layer. The substrate and the vial were then removed from the trough and an amount of zirconyl chloride was added to the vial to make the solution ca. 3 mM in Zr^{4+}. After at least 36 h in the zirconium solution, the hydrophilic substrate was removed from the vial and rinsed with water.

To deposit the porphyrin layer, the hydrophilic substrate was submerged in a solution of **1** at about 10^{-5} M in 9/1 ethanol/water, and the porphyrin was allowed to adsorb for 2 h. The substrate was then rinsed with methylene chloride or chloroform for 30 min to remove any physisorbed chromophores. UV−vis and ATR−IR were used to monitor the completeness of the deposition.

Film Characterization. Methods for attenuated total-reflectance FTIR, X-ray photoelectron spectroscopy, and transmittance UV−vis experiments were the same as we have reported in the past.[25,29]

Catalytic Oxidations. Iodosylbenzene (PhIO) was synthesized from the diacetate precursor using NaOH.[70] Its purity was confirmed using catalyst **2** in a test reaction of the epoxidation of cyclooctene by PhIO where the published results were obtained.[63]

The PhIO compound is only slightly soluble in carbon tetrachloride, so 27.5 mg were diluted in 20 mL and sonicated for 30 min. After sonicating, 13 μL of cyclohexanone, the internal standard, and 130 μL of cyclooctene were added. The mixture was stirred for about 1 min and solvent was added to complete 25 mL of solution. Samples of 1 mL of this mixture were used for the "blank," "homogeneous," and "heterogeneous" runs in Teflon bags. The heterogeneous bag contained a microscope slide (34 mm × 26 mm × 1 mm) with the adsorbed catalyst, while the blank and homogeneous reactions contained a clean slide of the same dimensions. In all reactions, catalyst:oxidant:substrate ratios were near 1:5000:40 000. For the homogeneous reactions, 10 μL of a 0.1-mM (1 nmol) solution of **1** or **2** were added, while coverage on the glass slides was measured as 1.0 ± 0.2 nmol for the heterogeneous reactions. For the reactions with ethylphosphonic acid ($EtPO_3H_2$), 5.2 μL of 1.9×10^{-4} M or 1.9×10^{-5} M $EtPO_3H_2$ were added for a **2**:acid ratio of 1:10 or 1:1.

The Teflon bags were made by sealing sheets with a Technaseal (Livermore, CA) thermal impulse heat sealer. The sealed bags, with dimensions of approximately 40 mm × 30 mm, were placed in a closed beaker and tumbled with a mechanical arm at ca. 100 rpm.

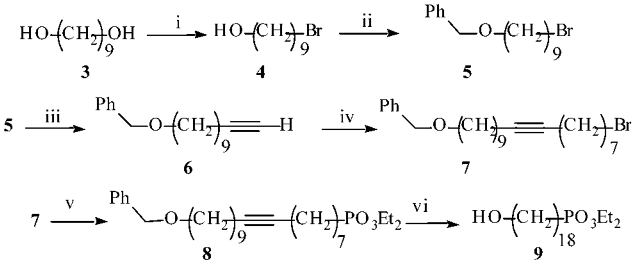
Product concentrations were determined relative to cyclohexanone, which was used as the internal standard. The gas chromatograph was a Hewlett-Packard 5890 Series II equipped with a hydrogen flame ionization detector. A 0.4-μL portion of the reaction solution was injected onto the 25-m, 0.33-μm film thickness, 0.20-mm ID HP-5 column (Cross-linked 5% PH ME Siloxane). The column was held at 80 °C for 1 min and then ramped at 5 °C/min to a temperature of 95 °C. A second ramp of 70 °C/min was applied to a temperature of 200 °C for 1 min. To avoid evaporation of the solvent, the syringe hole was sealed after each sampling with a self-adhesive label of a size similar to the bag. The average solvent loss for each reaction was less than 6%.

After completion of the reaction, films were continuously rinsed with chloroform in a Soxhlet extractor for at least 1 h to remove any remaining PhIO. Optical spectra of the slides were then recorded.

Results

Porphyrin Synthesis. The key reaction in the preparation of the porphyrin **1** is an aromatic nucleophilic substitution between the 5,10,15,20-tetrakis(pentafluorophenyl) porphyrin with the alcohol spacer **9** (Scheme 2). The preparation of compound **9** follows our previous work[29] describing the immobilization of palladium porphyrins, except that a benzyl group now replaces the tetrahydropyrannyl protecting group of the alcohol used previously. The benzyl moiety makes this spacer easy to characterize by TLC (with UV light) and one step is saved in the synthesis of the spacer, since it can be cleaved during the palladium catalyzed hydrogenation of the alkyne group (Scheme 2).

Scheme 2. Synthesis of the Alkyl Spacer **9**



i) HBr/ bz; ii) NaH-THF, then $PhCH_2Br$ 89%; iii) LiC≡CH, DMSO 78%; iv) nBuli/ THF, $Br_2C_7H_{14}$, HMPA 80%; v) $NaPO_3Et_2$/ THF 82%; vi) H_2-Pd/ C, EtOAc 78%

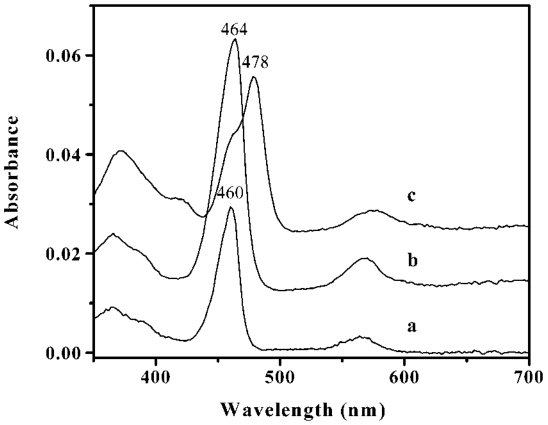


Figure 1. Optical spectra of **1** as (a) 1×10^{-6} M in CH_2Cl_2 (b) monolayer film after deposition from ethanol/water and (c) the same film rinsed in methylene chloride for 30 min. Soret bands near 460−464 nm are assigned to phosphonate coordinated to the Mn^{3+} while the peak position at 478 nm is attributed to Cl$^-$ coordination.

After preparing the substituted porphyrin (Supporting Information), the usual harsh conditions for manganese insertion ($Mn(OAc)_2$ in refluxing DMF) were modified in order to prevent phosphonate ester hydrolysis. Metalation was preferably performed in DMF at 50 °C using manganese iodide and sodium acetate and gave the manganese porphyrin in 84% yield. Finally, the phosphonic ester groups were hydrolyzed in quantitative yield with bromotrimethylsilane in DMF using triethylamine as a base to avoid demetalation caused by the formation of hydrogen bromide.

Optical Properties of the Porphyrins. The optical spectrum of **1** in a 1×10^{-6} M methylene chloride solution shows a Soret band at 460 nm ($\epsilon = 2.9 \times 10^4$ M^{-1} cm^{-1}) (Figure 1a). This peak position is attributed to intramolecular phosphonate binding to the Mn^{3+} ion based on studies of the parent compound, **2**. Chloroform solutions of **2** in the concentration range 10^{-5} to 10^{-8} M consistently exhibit the Soret band near 476 nm ($\epsilon = 4.5 \times 10^4$ M^{-1} cm^{-1}). Optical spectra reveal no tendency for the chromophore **2** to aggregate in these dilute solutions. The porphyrin is axially bound by chloride ligands either from the porphyrin synthesis or present in low concentration from the solvent.[71] Purposeful addition of chloride does not change the optical spectrum. However, when 1×10^{-4} M ethylphosphonic

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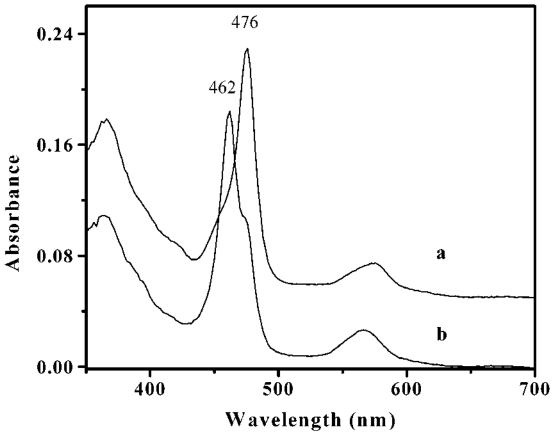


Figure 2. Optical spectra of (a) 2.4 × 10^{-6} M solution of **2** in chloroform (b) solution of 2.4 × 10^{-6} M of **2** with 1 × 10^{-4} M ethylphosphonic acid and 1 × 10^{-4} M triisobutylamine in chloroform.

acid ($EtPO_3H_2$) and 1 × 10^{-4} M triisobutylamine were added, the Soret band shifts to 462 nm (Figure 2). The amine is necessary to deprotonate the phosphonic acid and it was found not to bind the porphyrin in the absence of $EtPO_3H_2$. The peaks at 462 nm for **2** and at 460 for **1** are therefore assigned to axial coordination of the Mn^{3+} center by phosphonate.

Self-Assembled Monolayers. Monolayers of **1** were prepared by adsorbing the porphyrin from solution onto zirconated LB monolayers of octadecylphosphonic acid according to Scheme 1. A key to the process is that the LB layer generated after step 2 provides a flat, uniform surface allowing detailed analysis of the subsequently adsorbed porphyrin layer. The deposited porphyrin layer is clearly observed in optical spectroscopy. Films of **1** deposited from ethanol/water (9/1 mixture) show a λ_{max} at ca. 463−464 nm (Figure 1b), which corresponds to the peak in solutions of **1** and can be attributed to nonaggregated metalloporphyrins with coordinated phosphonate. Evidently, not all of the phosphonate groups on each porphyrin bind the surface. When self-assembled films of **1** are rinsed in methylene chloride or chloroform, the red shoulder associated with a change in the ligand environment grows in significantly, indicating that chloride can displace phosphonate ligation (Figure 1c). However, as the films dry, the chloride ion is displaced by the phosphonate group.

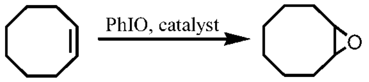
Additional evidence for porphyrin adsorption is seen in FTIR and XPS studies. An ATR-FTIR spectrum of a monolayer of **1**, referenced to the zirconated LB layer, clearly shows the presence of the alkyl chains associated with the four alkylphosphonic acid substituents (Supporting Information). Bands at 2926 and 2855 cm^{-1} corresponding to the $\nu_a(CH_2)$ and $\nu_s(CH_2)$ modes, respectively, are consistent with a disordered, liquidlike arrangement of the alkyl substituents. The size of the porphyrin prohibits the alkyl substituents from organizing to any extent. A complex pattern centered near 1050 cm^{-1}, due to the phosphonate P−O stretches, is also observed. An XPS survey scan of the film (Supporting Information) shows the presence of Mn, F, O, and N, corresponding to the porphyrin, as well as Zr, P, and O from the metal phosphonate network.

The orientation of the porphyrin in the films can be determined from polarized absorbance of the Soret band, according to a procedure described by Möbius.[72] Optical spectra were recorded using polarized light at an incident angle of 45°. The ratio of s- and p-polarized absorbance for the band at 464 nm corresponds to the porphyrin having an orientation where the ligand plane is tilted from the substrate, normally in the range of 72° to 76°. No in-plane anisotropy was observed. Therefore, the porphyrin molecules are arranged nearly parallel to the surface, as was found previously for the Pd^{2+} and free-base analogues of **1**.[29] The slight deviation from laying exactly parallel to the surface may be a consequence of the altered molecular geometry caused by one of the alkylphosphonate arms coordinating the metal center.

The porphyrin coverage in the films was measured by etching the metal phosphonate layer off of the glass slides and measuring the optical spectra of the porphyrin in the resulting solutions. The films do not wash off with water or organic solvents because of the insolubility of the zirconium phosphonate network. However, zirconium phosphonates are soluble in HF, so films prepared on glass coverslips were rinsed off with a solution of 50% HF and water. Transmittance optical spectra of the glass slide after rinsing revealed that porphyrin **1** was entirely removed. Application of Beer's law to the washings indicates a coverage of (6 ± 1) × 10^{-11} mol/cm^2 (an average of four films). The measured coverage can be compared with that observed for a Langmuir monolayer of **1** on water. A compression isotherm of **1** (Supporting Information) on a water subphase at room temperature shows an increase in surface pressure near a mean molecular area of 250 Å^2/molecule. This value can be taken as the surface area per molecule in the absence of constraints on the organization of the alkyl substituents and corresponds to a coverage of 6.6 × 10^{-11} moles/cm^2. Therefore, the observed coverage for the metal phosphonate layers is consistent with a model whereby the porphyrin molecules adsorb from solution to give a complete monolayer of noninteracting chromophores laying approximately parallel to the surface.

To show that **1** does not desorb from the film under the conditions used in the catalysis studies, a slide with a monolayer of porphyrin was stirred in 1 mL of CCl_4 for 24 h. Afterward, the optical spectrum of the solvent did not show the presence of **1**. For the slide, a decrease of less than 10% in the area of the Soret band was observed.

Catalysis. We chose to investigate the catalytic properties of the films using the epoxidation of cis-cyclooctene with iodosylbenzene (PhIO) as an oxygen donor (1).



(1)

The monolayer films were deposited to cover 17.7 cm^2, resulting in approximately 1 nmol of catalyst on each slide. The small amount of catalyst imposed the condition of a small solvent volume, chosen to be 1 mL in this study. Significantly larger volumes would lead to low epoxide concentration and inaccurate detection. Thermally sealed Teflon bags, formed in the shape of the slides, served as reaction vessels for the small-volume reactions. Similar bags have been used by other groups for solvatothermal solid-state synthesis.[73,74] We adapted the

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(71) Chloride coordination is reduced or eliminated by rinsing the film with solvent filtered trough basic alumina.

(72) Möbius, D.; Orrit, M.; H., G.; Meyer, H. *Thin Solid Films* **1985**, *132*, 41.

(73) Harrison, W. T. A.; Nenof, T. M.; Gier, T. E.; Stucky, G. D. *Inorg. Chem.* **1993**, *32*, 2437.

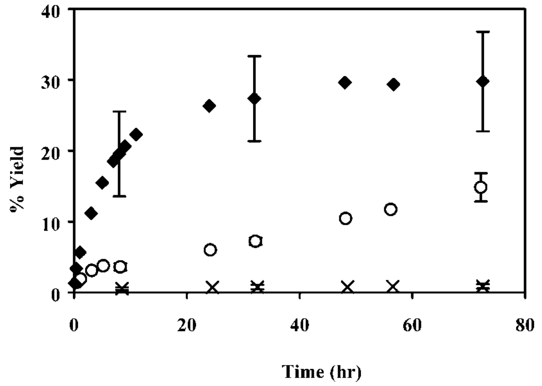

Figure 3. Extent of the epoxidation of cyclooctene with PhIO oxidant over 72 h with catalysts: films of **1** (♦), **2** in solution (○), and no catalyst (×).

Table 1. Epoxidation of Cyclooctene by PhIO and Catalyzed by Manganese Porphyrins in Monolayer Films and in Solution[a]

catalyst	reaction time (hr)	yield of epoxide[d]	turnover number[e]
monolayer of **1**	8	20 ± 6%	893 ± 268
1 homogeneous[b]	7	4.9%	245
2 homogeneous[b]	8	3.6 ± 0.5%	180 ± 25
2 homogeneous[b] with 1 nmol $EtPO_3H_2$	8	4.1%	205
2 homogeneous[b] with 10 nmol $EtPO_3H_2$	7.5	6.1%	305
blank[c]	8	0.5 ± 0.2%	
monolayer of **1**	72	30 ± 7%	1340 ± 350
2 homogeneous[b]	72	15 ± 2%	750 ± 100
blank[c]	72	0.9 ± 0.3%	

[a] Molar ratios of catalyst:PhIO:cyclooctene were 1:5000:40000 in CCl_4. Uncertainties are based on standard deviations from at least three runs. [b] 1 nmol of catalyst used. [c] Conditions identical to homogeneous reactions but no catalyst used. [d] Calculated using on PhIO as the limiting reagent. [e] Calculated as moles of cyclooctene oxide produced over moles of catalyst.

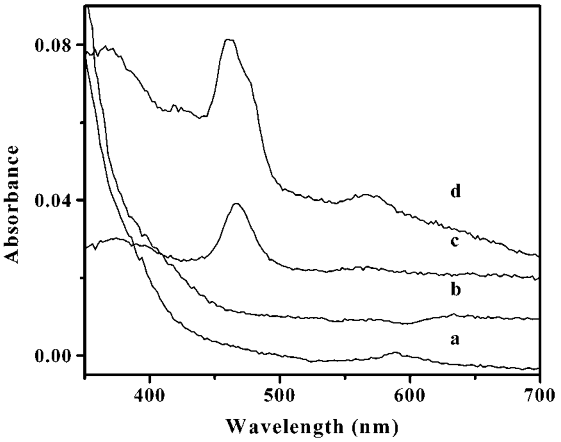

Figure 4. Optical spectra of (a) the supernatant solution of an oxidation with a monolayer film of **1** after 72 h, (b) a homogeneous reaction of **1** after 7 h, (c) a film of **1** after 11 h of reaction, and (d) a film of **1** immersed in the oxidative conditions after 10 min of tumbling.

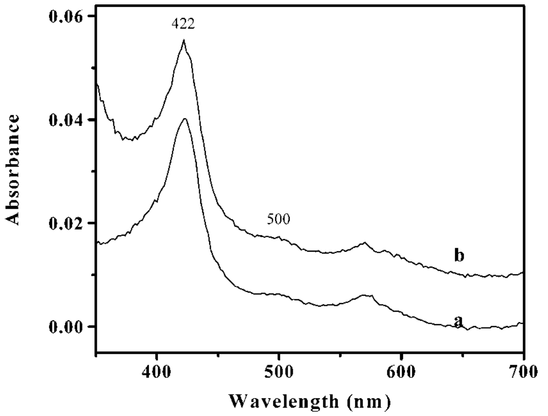

Figure 5. Optical spectrum of homogeneous reaction of **2** after (a) 1 h and (b) 72 h of tumbling.

approach to prepare reactors to hold the glass slides. The bags allow a small solvent volume to wet the slides and eliminate solvent evaporation during the course of the reaction.

The extent of epoxidation as a function of time in the presence of the films, and for homogeneous reactions with **1** or **2**, is reported in Figure 3 and Table 1. The yields are calculated relative to the limiting reagent, which is the oxidant in each case. Small variations in the amount of catalyst present from one slide to another were accounted for by normalizing the result for the amount of catalyst, determined from the area under the Soret band. Each point is an average of at least three runs and representative error bars, calculated at the 95% confidence level, are included. Figure 3 also shows the epoxide yield in the absence of catalyst (blank reaction). Homogeneous reactions containing 1 nmol of **1**, 1 nmol of **2** with 1 nmol of $EtPO_3H_2$, and 1 nmol of **2** with 10 nmol $EtPO_3H_2$ were also monitored over time and their yields and turnovers after 7 to 8 h are also included in Table 1.

Characterization of the Catalyst Systems. Heterogeneous and Homogeneous Reactions with 1. The optical spectra of the films used in oxidations were recorded after they were rinsed to remove adsorbed PhIO. The spectra have the same bands as before use, with a Soret band consistently found near 464 nm (Figure 4c), although the intensity is decreased by 70 ± 10% after 11 h (average of 4 films) and 99% after 72 h (average of 3 films). Optical spectra of the supernatant reaction solutions show no dissolved porphyrin (Figure 4a). For comparison, the spectrum of the solution of a homogeneous reaction of **1** shows similar degradation of the porphyrin, but at an even faster rate (Figure 4b).

As the spectra in Figure 4a-c were taken after catalysis runs and after the slides have been removed from the reaction conditions, it is possible that they do not represent the state of the film during the course of the reaction. Therefore, a slightly different experimental setup was used to monitor the porphyrin film under the reaction conditions. A film of **1** was prepared on a thin glass coverslip and placed in an optical cuvette containing cyclooctene and PhIO in the same concentrations used in the quantitative runs. The cuvette was tumbled by a rotating arm and then stopped to record the electronic spectra of the film while still immersed in the reaction conditions. The spectrum, shown in Figure 4d, is similar to the ex situ spectrum and no μ-oxo or other higher oxidation state porphyrin species are observed.

Homogeneous Reactions with 2. The optical spectra of the homogeneous reaction solutions of **2** showed at all times the Soret band shifted to 422 nm with a shoulder at 500 nm (Figure 5). This species has been identified in related porphyrins as a Mn(IV) μ-oxo dimer.[75] The intensity of the Soret band does

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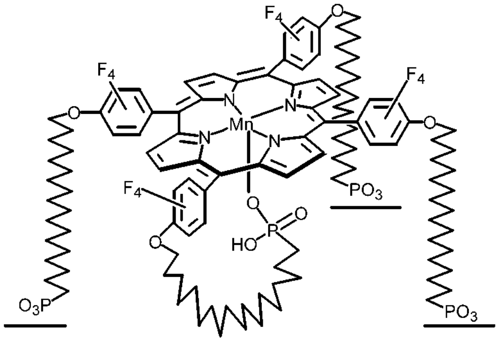
(74) Norquist, A. J.; Welk, M. E.; Stern, C. L.; Poeppelmeier, K. R. *Chem. Mater.* **2000**, *12*, 1905.

(75) Smegal, J. A.; Schardt, B. C.; Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 1983.

Scheme 3. Representation of the Orientation of the Porphyrin **1** in the Monolayer Films



not change even after 72 h of reaction, suggesting that this species is stable under the oxidative reaction conditions. When $EtPO_3H_2$ is added to a solution of **2** in a 1:1 ratio, the optical spectrum taken after 8 h is similar to that of the reaction without the acid. On the other hand, a ten-fold excess of the acid causes a significant inhibition of the μ-oxo dimer with a Soret band at 478 nm.

Discussion

Analysis of how the catalyst **1** is organized in the zirconium phosphonate films is consistent with a near monolayer coverage of noninteracting porphyrins, with their macrocycle plane oriented almost parallel to the substrate. A combination of optical spectroscopy, XPS, and FTIR spectroscopy confirms that **1** adsorbs to the surface, and the orientation of the molecule is supported by measurements of surface coverage together with dichroism of the optical spectra. This result was expected since the position of the phosphonic acids on the periphery of the chromophore was designed to allow the porphyrin to stand like a table on the surface, and a similar monolayer arrangement was found for the Pd^{2+} analogue of **1**.[29] However, not all of the phosphonate arms of **1** bind to the zirconated surface, as the Soret band at 464 nm (Figure 1c) indicates that at least one arm participates in axial binding of the Mn^{3+} center. Therefore, our view of the porphyrin on the surface is similar to that depicted in Scheme 3, with molecules chemisorbed to the surface such that the porphyrin plane tilts slightly from parallel.

The catalytic activity reported in Table 1 and in Figure 3 clearly shows that the film catalyzes alkene epoxidation, demonstrating that monolayers prepared in this way can be used to investigate supported catalysis. To better understand the monolayer catalyst and its activity, homogeneous studies were performed using **1** and the related compound **2** under conditions similar to those used in the heterogeneous studies. The homogeneous reaction conditions were not chosen to optimize reaction yields, but rather to allow useful comparisons of the catalyst behavior. Therefore, homogeneous reactions used the same amount of catalyst, substrate, oxidant, and solvent as were used with the monolayer reactions. It is for this reason that reaction yields reported here are lower than those of other studies using similar porphyrins but with larger catalyst:substrate ratios.[3,58,60,63,64]

Comparing Homogeneous Reactions of 1 and 2. The activity of catalysts **1** and **2** are very similar after 7 to 8 h (Table 1) resulting in ca. 200 turnovers. However, the mechanisms of deactivation of the molecules are very different. Porphyrin **2** forms a μ-oxo dimer shortly after the reaction starts and perseveres over a period of 72 h (Figure 3). Epoxidation continues over this time, but the rate of conversion is low. Inclusion of the sterically hindering alkyl phosphonate chains on **1** prevents the formation of μ-oxo dimers and a band at ca. 420 nm, typical of these species,[75] is not seen in optical spectra of the reaction mixture. On the other hand, the molecule **1** has been completely destroyed after 7 h as evidenced by the absence of any Soret band at all (Figure 4b). The two homogeneous catalysts generate epoxide at similar rates early on in the reaction, perhaps via the same mechanism, but then deactivate differently. Compound **1** is destroyed by the reaction conditions, while **2** forms the less active μ-oxo dimer.

Films of 1 versus the Homogeneous Reactions. The films of **1** show a significant improvement in catalyst turnovers over the first few hours relative to the homogeneous reactions (Figure 3). The turnover numbers are five times higher for the films relative to either **1** or **2** in solution after 8 h. Similar to the homogeneous reaction, the immobilized catalyst **1** does not form μ-oxo derivatives (Figures 4c and 4d), as its structure combined with surface immobilization prevents dimer formation. Nevertheless, the films of **1** degrade during the reaction and there is no increase in the epoxide yield after about 30 h. The degradation mechanism is probably the same as in the homogeneous reaction of **1**, as optical spectra of the reaction solutions are similar (Figures 4a and 4b). However, immobilization offers some protection toward porphyrin degradation since 30% of the porphyrin is still present on the film after 11 h, as compared to the homogeneous reaction with **1** where no porphyrin is present in solution after 7 h. In addition, the remaining film continues to catalyze with the same rate of turnover (corrected for the amount of remaining porphyrin) as the starting film. This result, plus the comparison with the homogeneous reactions of **2**, clearly shows that immobilization of the catalyst, and not only its modified structure, have an important influence on its activity.

Effect of Phosphonate. Another set of control reactions was performed to investigate the role of phosphonate. Ethylphosphonic acid was added to a homogeneous reaction with **2** to investigate the potential role of the phosphonate as a cocatalyst in the films. A molar ratio of 1:1 **2**:$EtPO_3H_2$ gives turnovers comparable to the reaction without the acid (Table 1). Increasing the amount of phosphonic acid to a molar ratio of 1:10, however, gives a slightly higher turnover. Optical spectra of these reaction solutions show that the 1:1 ratio does not affect μ-oxo dimer formation, while a significant inhibition is observed when a tenfold excess of the phosphonic acid is included. The phosphonic acid appears to stabilize the porphyrin in the oxidation conditions, but the activity is still significantly less than for the immobilized porphyrin.

Monolayers as Models for Supported Catalysts. While monolayers on flat surfaces have limited utility as practical catalysts due to the difficulty of achieving large surface areas, the present study shows that they can be useful tools in the study of heterogeneous reactions. An important feature is that a flat surface, prepared under controlled conditions, allows for uniform adsorption. Deposition of the catalyst then results in monolayers that contain essentially a single type of catalytic site. This feature of monolayers is important when attempting to correlate structure with properties. Chemical and structural characterization is easier if only a single species is present, which then allows catalytic activity to be correlated with a specific, characterized site. These points are in contrast with the situation for high surface area supports, where different surface features and a variety of pore shapes and sizes lead to a dispersion of catalyst environments. Activity must then be assigned to an ensemble of sites, making it difficult to correlate behavior with surface structure. The monolayer films can then serve as models for specific types of molecular sites on high surface-area supports. Changes in molecular design and deposition procedures can be used to explore different molecular arrangements.

It should also be noted that new phenomena might arise from the ability to organize molecular catalysts into controlled assemblies. The recent example of Töllner et al. showed that an LB film of an amphiphilic rhodium bipyridine complex presented a largely improved catalytic efficiency with respect to the same complex in solution.[76] The authors attributed the increase to the influence of the assembly of sites at the interface. In the case of the monolayer films of **1**, the observed increase in activity can be attributed to a combination of enhanced catalyst lifetime and the altered conformation that the molecule adopts upon adsorption. However, effects due to the local concentration of sites cannot be ruled out.

Finally, monolayer deposition techniques provide special opportunities for arranging molecular components into "supramolecular assemblies" at solid supports.[77] Organized structures can present different or enhanced properties compared to those of the individual molecules. For example, with respect to the present system, the deposition process might be extended to include surface-bound ligands to axially coordinate the porphyrin **1**. The axial coordination would complement covalent linkage, but might also be used to direct surface adsorption. In addition, axial ligands as cofactors can improve the catalytic performance of the porphyrin and can also extend the array of useful oxidants. Efforts to explore the possibilities of using monolayers to build multicomponent catalytic assemblies are underway.

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Supporting Information Available: Synthetic procedures and full characterization of all new molecules as well as compression isotherm of **1**, ATR−IR spectrum and XPS spectrum of a film of **1** has been provided for this journal article (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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