

Manganese porphyrin multilayer films assembled on ITO electrodes via zirconium phosphonate chemistry: chemical and electrochemical catalytic oxidation activity

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A supported manganese porphyrin-based oxidation catalyst was prepared by zirconium-phosphonate multilayer assembly with [5,15-bis(4-phenylphosphonic acid)porphyrinato] manganese(III) chloride (**2**) and zirconium(IV) ions on indium–tin oxide electrodes. This assembly technique provided good control over the catalyst loading, which was confirmed by UV–Vis spectroscopy and cyclic voltammetry. Relative to its homogeneous counterpart, [5,15-bis(diethyl-4-phenylphosphonate)porphyrinato]manganese^{III} chloride (**1**), the film-based catalyst **2** showed moderately enhanced catalytic activity (up to 550 turnovers) for the oxidation of styrene by a soluble derivative of iodosylbenzene. Electrochemical oxidation of the film-based catalyst at pH 11 generated Mn^V(O)(porphyrin)(H₂O) intermediate at a potential of 1.20 V. The electrochemically generated active intermediate exhibited oxidative catalytic activity toward both the solvent (water) and an olefin substrate (CBZ) affording both hydrogen peroxide and epoxide products.

KEY WORDS: thin films; multilayer assemblies; metal phosphonates; manganese porphyrins; styrene epoxidation; supported catalysts; carbamazepine; electrochemical catalytic oxidation.

1. Introduction

Synthetic metalloporphyrins have been investigated extensively as both models and mimics of the oxidative catalytic behavior of cytochrome P-450 enzymes [1–4]. Iron and manganese porphyrins, in combination with a variety of oxidants, have served as models for P-450 activity in olefin epoxidation reactions [2,5]. While mechanistically instructive, studies of these particular metalloporphyrins reveal practical problems: low turnover numbers and catalyst lifetimes [3,6]. Under typical epoxidation conditions, the catalysts are prone to deactivation via porphyrin framework oxidation and/or the formation of inactive μ -oxo dimers. A common strategy to circumvent this problem is the immobilization of the catalyst on or within a solid support [7–9]. In addition to the enhanced stability engendered via site-isolation, heterogenizing the catalysts confers significant advantages in terms of product isolation and the potential for catalyst recyclability.

Methods for the immobilization of metalloporphyrins include adsorption into polymer matrices, entrapment in porous metal oxides, and chemical binding to polymer beads, ion exchange resins, or metal oxides [7–9]. Of these approaches, chemical binding has probably proven most effective. Immobilization based on catalyst/support bond formation typically yields

materials featuring good substrate and oxidant access, and therefore, comparatively high activity. Additionally, bond formation minimizes catalytic detachment [10,11].

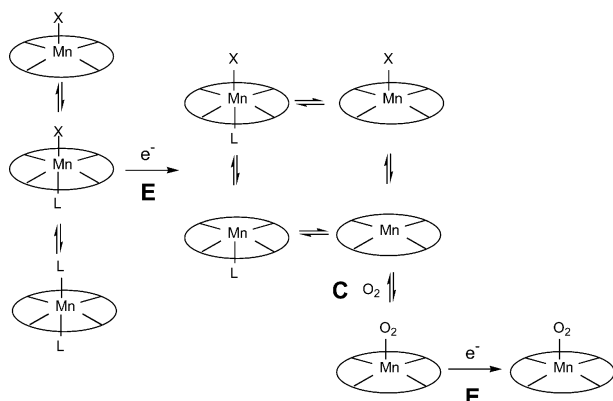
Numerous synthetic molecules bearing phosphonic acid groups have been attached to metal oxide surfaces [12,13]. Consistent with earlier reports [14–17], we have recently found that stable multilayer films based on a rigid 5,15-functionalized porphyrin bis-phosphonates and related supramolecular assemblies can be prepared on indium–tin oxide (ITO) coated glass slides [18,19]. This method involves the formation of a zirconium layer on the conductive surface and sequential adsorption of porphyrin bis-phosphonates and ZrOCl₂ providing multilayer films. This thin-film preparation has proven to be highly reproducible and allows outstanding control over the film thickness. The initial success of this approach has encouraged us to explore the construction of multilayers of catalytically active porphyrins and investigate their application as supported catalysts. Films formed in this way have several virtues as heterogeneous catalysts: first, they are mechanically stable and tolerant of various solvents and reaction conditions used for common organic transformations [20]; second, they are sufficiently well ordered that most or all of the catalytic centers are accessible, in contrast to some porous polymer- or zeolite-supported catalysts [21,22]; third surface-confined catalyst loading is easily controllable by layer-by-layer construction. Manganese

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porphyrins are attractive candidates for this application because they have been shown to be active catalysts for olefin epoxidation and improvement of their catalytic activity via immobilization on solid supports has some precedent [23,24]. Since manganese porphyrins are electrochemically active, we have also assessed their electrochemical properties on the electrode surface – including their ability to function as *electrocatalysts* for olefin oxidation, specifically in water as solvent. Most earlier studies on electrocatalytic epoxidation by manganese porphyrins have been focused on an “electron transfer–chemical step–electron transfer” (ECE) process that entails binding and activation of molecular oxygen upon reduction of manganese to oxidation state II [25–27]. These studies typically have been done in non-hydroxylic solvent. An interesting alternative strategy, especially from the perspective of green chemistry, is to utilize reaction pathways that use water as both a solvent and an oxygen source. Water, of course, is an abundant and inexpensive (albeit low energy) source of oxygen atoms. Because of their insolubility in water, catalysts immobilized by phosphonate coordination of zirconium are potentially very well suited for this purpose [12].

We describe herein manganese porphyrin multilayer films assembled via zirconium phosphonate chemistry on a conductive surface and their activity as supported catalysts and electrocatalysts. [5,15-Bis(4-phenylphosphonic acid)porphyrinato] manganese(III) chloride (**2**) was prepared for this purpose, while [5,15-bis(diethyl-4-phenylphosphonate)porphyrinato] manganese(III) chloride (**1**) was used as both a synthetic precursor and a homogeneous catalyst counterpart of complex **2**. We found that for the epoxidation reaction of styrene with an organic oxidant, films of **2** displayed somewhat higher yields and somewhat longer lifetimes than the homogeneous catalyst **1**. The films of **2** also showed electrocatalytic epoxidation activity in aqueous solutions at high pH when high potentials (1.0–1.5 V) were applied.



Scheme 1. The proposed ECE mechanism by R.W. Murray *et al.*

2. Experimental

2.1. Materials

The free-base version of **1** was prepared according to published methods [18,19]. 2-(*tert*-butylsulfonyl)iodosylbenzene (soluble PhIO) was synthesized by a literature method [28]. Carbamazepine-10,11-oxide was synthesized as an authentic epoxide standard according to the published method [29]. Dichloromethane (CH_2Cl_2) was distilled over calcium hydride. Water was purified using a Millipore filtration and ion-exchange system and had a resistivity of 18 M Ω . Commercially available styrene (Aldrich) was passed through a plug of inhibitor remover (Aldrich) and checked by GC for purity before use. Carbamazepine (5*H*-dibenzo[*b,f*]azepine-5-carboxamide, CBZ) was purchased from Aldrich and its purity was checked by high-performance liquid chromatography (HPLC) prior to use. A basic solution (pH 11) was made by dissolving NaOH (4 mg, 0.10 mmol) in deionized water (100 ml). Inductively coupled plasma (ICP) calibration standard solution of manganese (1000 $\mu\text{g}/\text{ml}$ Mn) was purchased from Aldrich. Indium–tin oxide coated glass was obtained from Delta Technologies, Ltd. All other reagents were purchased from Aldrich and used as received unless indicated.

2.2. Instrumentation

Electronic absorption spectra were obtained on a Varian Cary 5000 spectrophotometer. Electrochemical measurements were performed with a CH Instruments Model potentiostat using a three-electrode configuration with an ITO working electrode, a Pt wire counter electrode, and a silver wire electrocoated with silver chloride (pseudo-Ag/AgCl) as the reference electrode. Bulk electrolysis was performed with EG&G Princeton Applied Research potentiostat (model 273). Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA). ICP spectrometry was conducted with a Thermo Jarrell Ash Atomscan Model 25 Sequential ICP spectrometer, equipped with vacuum optics covering the spectral range from 160 to 850 nm. A calibration curve for manganese was made using 5% piranha aqueous solution (2:1, $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2$) and same solution containing manganese calibration standard solution (1 ppm). GC analyses of styrene epoxidation were carried out on Hewlett Packard 5890A gas chromatograph equipped with a FID detector and HP3396A integrator. The column used was a 30-m HP-5 (Crosslinked 5% PH ME Siloxane) capillary column with 0.32 mm inner diameter and 0.25 μm film thickness. Product concentrations were determined relative to undecane internal standard. Column head pressure was 15 psi. The column temperature was ramped from 50 to 100 $^\circ\text{C}$ at a rate of 5 $^\circ\text{C}/\text{min}$. A second ramp of 30 $^\circ\text{C}/\text{min}$ was applied to a temperature of 250 $^\circ\text{C}$ and held for 1 min. Quantitative analyses of electrochemical epoxidation were conducted on a Hewlett

Packard 1100 series HPLC instrument equipped with a multiple wavelength photodiode detector. Separation was performed on a Hypersil ODS (C18) column (200 × 4.6 mm, 5 μ m particle size) using a mixture of methanol and water (1:1, v:v) at 1 ml/min flow rate. Detection was done at 230 nm.

2.3. Synthesis

2.3.1. [5,15-Bis(diethyl-4-phenylphosphonate)porphyrinato] manganese(III) chloride (1)

5,15-Bis(diethyl-4-phenylphosphonate)porphyrin (150 mg, 0.203 mmol) was dissolved in a mixture of chloroform (15 ml) and acetic acid (10 ml) in a 50 ml Schlenk flask equipped with a magnetic stir bar and a reflux condenser. Mn(OAc)₂ · 4H₂O (224 mg, 0.914 mmol) and NaCl (46 mg, 1.1 mmol) were then added and the solution was heated to reflux for 12 h. After completion of the reaction, the solvent was removed by rotary evaporation to give a brown solid. CH₂Cl₂ (20 ml) was then added to the solid, which was subsequently precipitated by dropwise addition to stirring hexanes (50 ml). The brown suspension was then filtered, washed with water, and dried under vacuum to give a brown solid (130 mg, 0.158 mmol, 78% yield). UV-Vis (CH₃OH): λ_{max} nm (log ϵ) 371 (4.66), 392 (4.63), 412 (4.37), 458 (4.84), 547 (4.03), 580 (3.73). ESI-MS (CH₂Cl₂): m/z Calcd. for C₄₀H₃₈MnN₄O₆P₂ (M-Cl): 787.16. Found: 787.42. EA: Calcd. for C₄₀H₃₈ClMnN₄O₆P₂ · 1/2 H₂O: C, 57.74; H, 4.72; N, 6.73. Found: C, 57.36; H, 4.62; N, 7.20.

2.3.2. [5,15-Bis(4-phenylphosphonic acid)porphyrinato] manganese(III) chloride (2)

In a 50 ml Schlenk flask equipped with a magnetic stir bar and a reflux condenser, **1** (112 mg, 0.136 mmol) was dissolved in freshly distilled CH₂Cl₂ (30 ml). The resulting solution was deoxygenated with N₂ for 5 min. Bromotrimethylsilane (538 μ l, 4.08 mmol) was added via syringe and the mixture was stirred overnight at 40 °C under N₂. Next, the solvent was removed from the reaction mixture by rotary evaporation to give a dark brown solid that was then stirred in water (30 ml) for 2 h. The reaction mixture was filtered and the resulting crude product was washed with cold water (50 ml) and hexane (50 ml) to give a brown solid (89.1 mg, 0.125 mmol, 92% yield). UV-Vis (DMSO): λ_{max} nm (log ϵ) 370 (4.51), 391 (4.53), 410 (4.43), 458 (4.79), 557 (4.21), 587 (4.07). ESI-MS (CH₃OH): m/z Calcd. for C₃₂H₂₁ClMnN₄O₆P₂ (M-H⁺): 709.28. Found: 709.00. EA: Calcd. for C₃₂H₂₂ClMnN₄O₆P₂ · 2H₂O: C, 51.46; H, 3.51; N, 7.50. Found: C, 51.55; H, 3.37; N, 7.24.

2.4. Thin film preparation

Thin films of **2** were prepared and characterized analogously to the published procedure [1]. To summa-

rize, phosphorylated ITO slides were immersed in 25 mM ZrOCl₂ (aq) overnight. The slides were then immersed in a 0.10 mM DMSO solution of **2** in the dark for 4 h. Additional layers were assembled through successive treatment with ZrOCl₂ (25 mM) for 30 min and **2** (0.10 mM) for 4 h. Films prepared in this manner were assembled on both sides of the ITO/glass substrates. Successive growth of the films after each layer deposition cycle was monitored by both electronic absorption spectroscopy and cyclic voltammetry.

2.5. Styrene epoxidation using soluble PhIO

For the homogeneous reactions, a stock solution of 0.10 mM **1** in CH₂Cl₂ (30 μ l) was added to a 5-ml vial equipped with a magnetic stir bar. A stock solution in CH₂Cl₂ (4.0 ml) containing styrene (14 μ l, 0.12 mmol) and undecane (1.0 μ l, 4.8 μ mol) was then added to the vial. Soluble PhIO, (24 mg, 0.072 mmol) was added to start the reaction. Aliquots (50 μ l) of the reaction mixture were removed via syringe and passed through a plug of silica (60 mg). The crude product mixture was rinsed through the plug of silica with CH₂Cl₂ (1.0 ml) and the combined filtrate was analyzed via GC to obtain the catalytic turnover number. For the heterogeneous reactions, a slide (10 × 30 mm) of an ITO electrode containing 5 layers of **2** on both sides (3.0 ± 0.3 nmol) was placed in a 5-ml vial equipped with a magnetic stir bar. The CH₂Cl₂ stock solution above was then added to the vial and the reaction started with addition of the soluble PhIO (24 mg, 0.072 mmol). Aliquots of the reaction mixture were taken and prepared for GC analysis in a same manner as homogeneous reaction. Oxidation of styrene afforded a mixture of products (styrene oxide, phenyl acetaldehyde, and benzaldehyde) which were identified by gas chromatography/mass spectrometry (GC/MS). Product concentrations were determined by all three products corresponding to response factors of each relative to undecane.

2.6. Electrochemical epoxidation of CBZ

A 5-ml vial equipped with a magnetic stir bar was charged with an aqueous solution (pH 11) containing CBZ (0.38 mg, 1.6 μ mol) as the substrate and 0.10 M KNO₃ as a supporting electrolyte. A slide (10 × 40 mm) of ITO electrode containing 5 layers of **2** on both sides was placed into the vial covering 10 × 30 mm of its surface with the solution. Bulk electrolysis was conducted at $E_{\text{appl}} = 1.1$ V versus Ag/AgCl reference electrode with stirring, under an atmosphere of air, at room temperature. Aliquots (100 μ l) were taken and acetophenone was added. Without any further preparation, the sample was analyzed by HPLC. The conversion of CBZ and the yield of CBZ-10,11-oxide were determined using the corresponding calibration curves by acetophenone internal standard, at the detection wavelength of

230 nm. Control experiments were performed with a clean ITO slide of the same dimensions by the same method.

3. Results and discussion

3.1. Optical properties of the thin films of **2**

Figure 1(a) shows the electronic absorption spectrum of a dilute (7.5×10^{-7} M) DMSO solution of complex **2**. The Soret band is observed at 458 nm and a pair of bands at 391 and 370 nm is also observed along with a shoulder at 410 nm. The absorption spectrum of complex **2** closely resembles the reported absorption spectrum of tetraphenyl porphyrinato manganese(III) chloride [30]. Upon immobilization of **2** on glass and ITO, the Soret band shifted from 458 to 463 nm. Given the prior reports on zirconium phosphonate multilayers (quarterthiophene [31], poly(phenylenevinylene) [13], and free-base porphyrin [18]), it is reasonable to assume that this red-shift is caused by nearest neighbor interactions. Figure 1(b) shows a series of electronic absorption spectra of thin films of **2** (1–5 layers). Each spectrum was taken by placing an ITO slide (optically transparent) covered with a thin layer of **2** in a 1-cm cuvet containing water and subtracting a blank ITO spectrum. Linear growth in absorbance as a function of the number of assembly cycles from 1 to 5 is clearly observed, underscoring the usefulness of the layer assembly method for controlling surface-confined catalyst loading. The number of moles of catalyst immobilized per cm^2 is 1.0×10^{-10} mol per assembly cycle based on assessments of the absorbance at 463 nm (Soret band) by the method reported previously [18]. This estimate is consistent with the results from ICP spectroscopy ($1.1 \pm 0.1 \times 10^{-10}$ mole/ cm^2) whereby the manganese concentration in acid solution is measured.

ICP experiments were conducted by cautiously dissolving films from ITO slides in 2:1 (v/v) $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2$ solution and carefully diluting the solution with deionized water to reach a 5% acid concentration.

3.2. Electrochemical studies of multilayers of **2** on ITO

The electrochemical behavior of electrode immobilized **2** was investigated in a deoxygenated DMSO solution containing 0.10 M tetrabutylammonium hexafluorophosphate (TBAPF₆). Representative cyclic voltammograms (CVs) of a monolayer of **2** on an ITO electrode (2 cm^2) at several scan rates (25–300 mV/s) under a N_2 atmosphere are shown in figure 2. Well-defined pairs of anodic and cathodic current peaks of essentially equal area are observed at all scan rates. The waves are assigned to a chemically reversible Mn(III)/Mn(II) redox couple ($E_{\text{eq}} = -0.25$ V versus pseudo-Ag/AgCl) [32]. Consistent with spectral measurements (figure 1(b)), CVs of the thicker films show uniform increases in peak current with increasing number of layers (figure 3). In contrast to solution-phase redox couples, surface-immobilized couples often display mean-zero voltammetric peak separations. The somewhat different observation here of finite peak separation that increases with increasing scan rate and increasing number of catalyst layers may well be indicative of kinetic limitation on electrode/catalyst electron exchange [33]. We cannot rule out the possibility, however, that the splitting arises from uncompensated electrochemical cell resistance. Notably, a chemically reversible Mn(III/II) response was observed only when oxygen was excluded. In the presence of oxygen, the amplitude of Mn(III) reduction wave was increased and the wave for Mn(II) oxidation was lost (figure 4). Such behavior is characteristic of electrochemical processes involving a coupled chemical reaction. Similar behavior has been

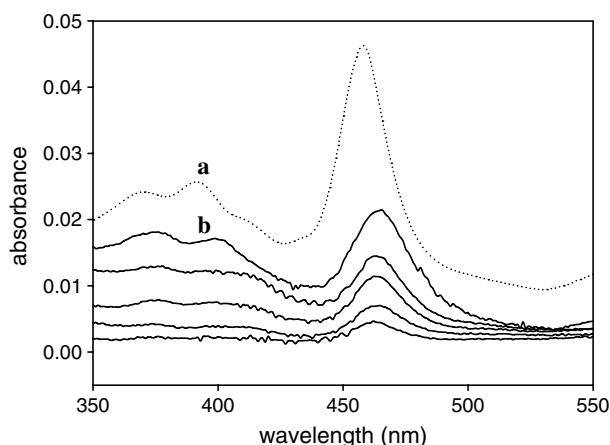


Figure 1. (a) Electronic absorption spectrum of **2** in DMSO solution (7.5×10^{-7} M) (dotted line); (b) electronic absorption spectra of thin films (1–5 layers, from lowest to highest amplitude) of **2** on ITO (solid lines).

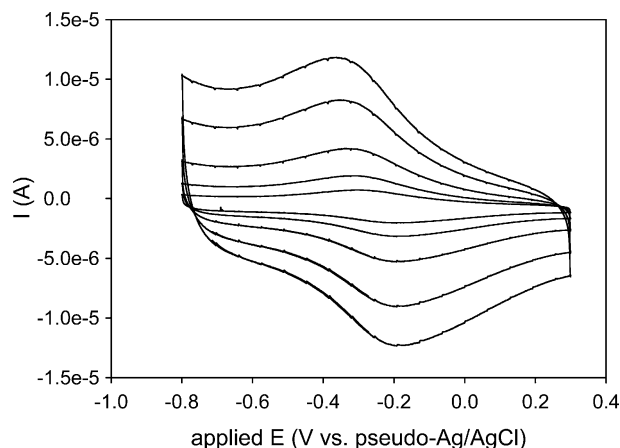


Figure 2. CVs of a thin film (monolayer) of **2** on an ITO electrode in DMSO solution containing 0.1 M TBAPF₆ under N_2 atmosphere at scan rates of 25, 50, 100, 200, and 300 mV/s (from lowest to highest amplitude).

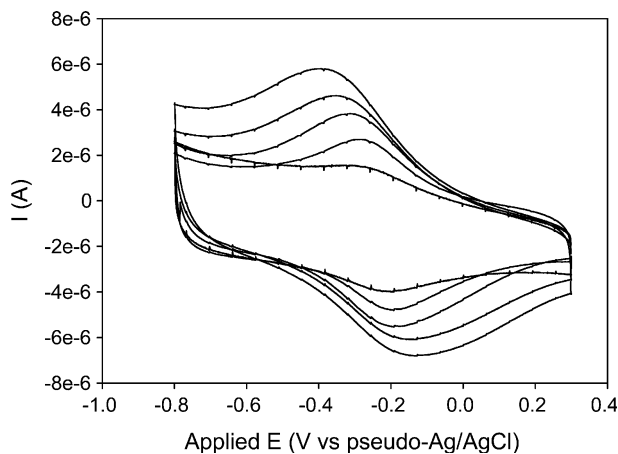


Figure 3. CVs of thin films (1 ~ 5 layers, from lowest to highest amplitude) of **2** on an ITO electrode in DMSO solution containing 0.1 M TBAPF₆ at a scan rate of 50 mV/s under N₂ atmosphere.

reported for manganese porphyrins in solution [25,26] and is well described by an ECE mechanism where reduction of Mn(III) by one electron (E) is followed by chemical steps involving binding of molecular oxygen (C) and then transfer of a second electron (E) (see scheme 1) [34].

The electrochemistry of monolayer films **2** on ITO was also examined in aqueous solution. At pH 11, [Mn(III)(porphyrin)(H₂O)₂] undergoes a two-electron oxidation to [Mn(V)(O)(porphyrin)(H₂O)] [35]. A large oxidative peak at ca. 1.0–1.5 V is indicative of such reactivity (figure 5(a)). This oxidation process is chemically irreversible and becomes progressively more difficult as the pH is decreased (figure 5(b)). At pH 11, the oxidative peak appears at 1.20 V versus pseudo-Ag/AgCl, but is shifted to 1.36 V at pH 10. The absence of the return peak for reduction of Mn(V) to Mn(III) points to its disappearance by a non-electrochemical pathway, probably by reaction with water to give

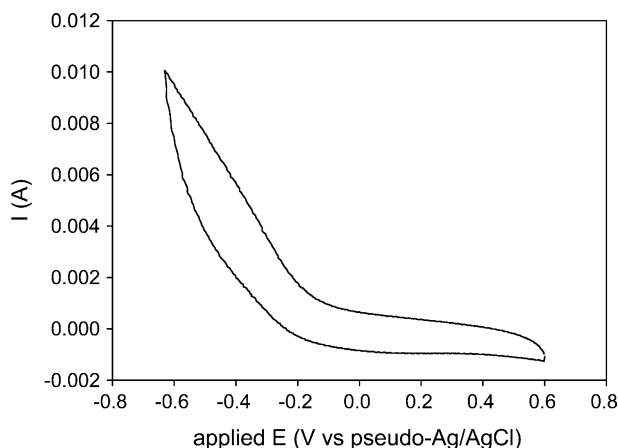


Figure 4. CV of a thin film (monolayer) of **2** in air-saturated DMSO containing 0.1 M TBAPF₆ at an ITO electrode at a scan rate of 100 mV/s.

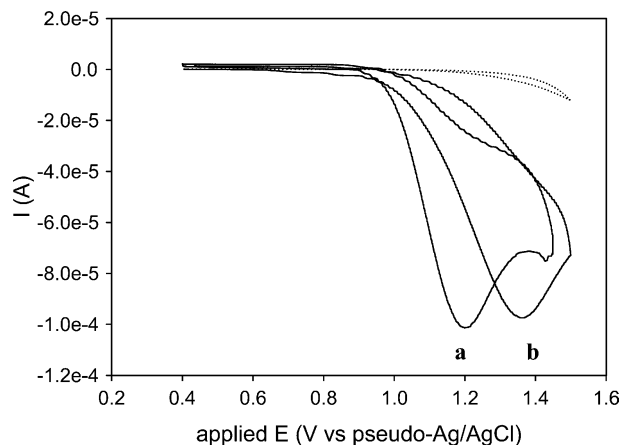


Figure 5. CVs of a thin film (monolayer) of **2** on an ITO electrode in aqueous 0.1 M KNO₃ solution (solid line) at (a) pH 11; (b) pH 10. Also shown is a CV using an ITO electrode lacking the catalyst layer (dotted line).

hydrogen peroxide and the Mn(III) form of the immobilized porphyrin. This occurrence is supported by detection of hydrogen peroxide by potassium permanganate titration [36]. Such a pathway would be redox catalytic in an electrochemical sense. In other words, at sufficiently positive electrode potentials the chemically regenerated Mn(III) would be re-oxidized to Mn(V) which, in turn, could be converted again to Mn(III) via reaction with water. Such behavior would be manifest electrochemically by the loss of the reductive wave and amplification of the oxidative wave. Notably, addition of olefin to the electrolyte solution does not appreciably alter the voltammetry under these conditions, implying that oxygen transfer to olefin is too slow to be strongly competitive with water oxidation to hydrogen peroxide.

3.3. Olefin epoxidation using soluble PhIO

The *non*-electrochemical catalytic activity of the thin films was tested on a model epoxidation reaction using styrene as a substrate and 2-(*tert*-butylsulfonyl)iodosylbenzene (soluble PhIO) as an oxidant. The use of soluble derivative of iodosylbenzene is essential, since iodosylbenzene itself is sparingly soluble in CH₂Cl₂, thereby limiting the reaction rate in this heterogeneous catalytic system. The extent of epoxidation as a function of time in the presence of the films (10 × 30 mm) containing five layers on each side is reported as total turnover numbers (figure 6(a)). Homogeneous reactions were also monitored using 3.0 nmol of **1** in CH₂Cl₂, over the same period of time (figure 6(b)). All the turnover numbers are given after subtracting the amount of product formed from the reaction without catalyst. Both the homogeneous and heterogeneous catalysts are active, but the number of turnovers of the latter (measured after 8 h) was double than that of the homogeneous version. Consistent with this finding, the lifetime of film-based catalyst was found to be significantly greater than

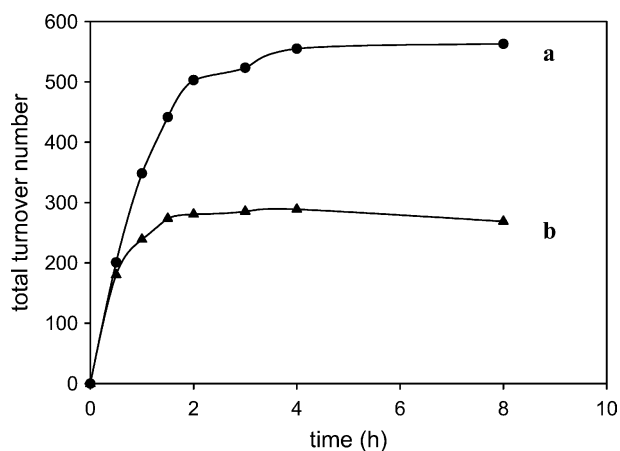
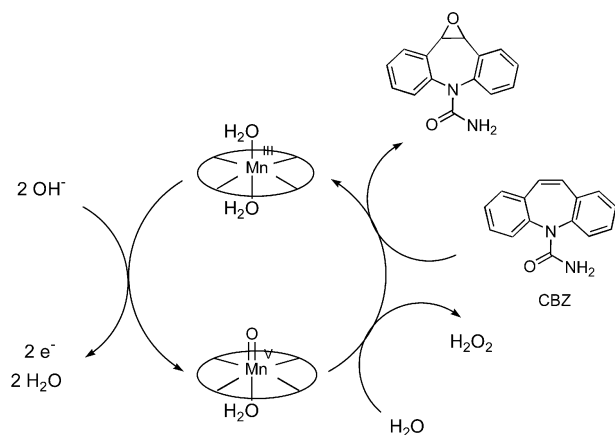


Figure 6. Extent of oxidation of styrene with soluble PhIO over 8 h with (a) thin films of **2**; (b) **1** in CH_2Cl_2 solution.

that of the solution phase catalysts. Catalytic activity for **1** ceased within 2 h whereas the film-based catalyst was still measurably active, but decreasing, after 4 h, with no further product forming after 8 h. Consistent with the observed activity and lifetime differences, the homogeneous catalyst **1** easily deactivates through μ -oxo dimer formation. However, the immobility of the surface-confined catalyst **2** prevents all but a small fraction from deactivating in this way. Nonetheless, both catalysts deactivate fairly rapidly, presumably primarily by oxidative degradation of the porphyrin ligand. Consistent with this notion is the complete disappearance of the originally intense B-band absorbance of both the homogeneous and heterogeneous catalysts after 8 h.

3.4. Electrochemical epoxidation of CBZ

The electrocatalytic oxidation of olefin by thin films of **2** on an ITO electrode has been assessed in epoxidation of carbamazepine (CBZ) in basic aqueous solution using water as an oxygen source. Epoxidation



Scheme 2. The proposed electrochemical catalytic cycle of **2** and CBZ in pH 11 aqueous solution.

in aqueous media has attracted interest because of its biological significance, but studies have been limited by the availability of comparatively few water-soluble catalysts and substrates [37]. However, several reports exist on catalytic oxidation of CBZ in aqueous media using water-soluble metalloporphyrins and various oxidants such as KHSO_5 , H_2O_2 , *m*-chloroperbenzoic acid, and NaOCl [29,38–40]. CBZ, first introduced in epoxidation studies by Meunier in 1994 and since then commonly used as a substrate for epoxidation in various aqueous media [29,37], is moderately water soluble. The electrocatalytic epoxidation reaction was carried out with 5 layers of **2** on an ITO electrode in pH 11 aqueous solution (4 ml) containing 0.10 M KNO_3 and 0.4 mM CBZ, while holding potential at 1.1 V. We observed significant oxidation within 30 min, providing a turnover number of 63, with CBZ-oxide as the sole product. However, longer reaction times yielded the diol derivative, possibly due to epoxide hydrolysis, and other non-identified by-products. A control reaction with a blank ITO electrode was performed under the same reaction condition. No product or by-products were found over a reaction time of 24 h.

Initially, we expected that upon addition of olefin substrate, the electrochemically formed Mn(V)(O) species would oxidize the substrate to the corresponding epoxide yielding Mn(III) to start a new catalytic cycle. In view of the electrochemical experiments above, however, we were concerned that the CBZ reaction might be unable to compete with the catalytic oxidation of water to hydrogen peroxide. Consistent with that concern, we found that the addition of CBZ to the electrolyte solution did not appreciably alter the voltammetry. An increase in electrocatalytic current would be expected if olefin epoxidation occurred more rapidly than water oxidation. Product analysis reveals, however, that both CBZ oxide and hydrogen oxide are produced (see scheme 2). We surmise that oxygen transfer from Mn(V)(O) to water occurs competitively with the oxygen transfer to CBZ, i.e., the system generates both hydrogen peroxide and CBZ oxide (scheme 2). The presence of hydrogen peroxide is detrimental to the catalytic system due to its propensity to oxidatively degrade the porphyrin ligand under basic conditions [39,41–43]. Indeed, within 1 h of the start of the film-based electrolysis, porphyrin bleaching was easily observable. Repeating the experiment at a range of potentials between 0.8 and 1.5 V failed to improve the activity of the catalyst with respect to epoxidation. Finally, the ability of hydrogen peroxide to degrade the surface-bound catalyst was confirmed in a non-electrochemical control experiment. Placement of an ITO-supported film of **2** into a pH 11 aqueous solution containing CBZ (0.4 mM) and 5% hydrogen peroxide for 1 h, yielded no detectable CBZ oxidation product but did bleach the film.

4. Conclusions

Consistent with earlier reports for free-base porphyrins [18,19], manganese(III) bis-phosphonate porphyrin, an active epoxidation catalyst, was successfully incorporated into multilayer films via zirconium phosphonate chemistry on the surface of ITO electrodes. This multilayer assembly technique gave good control over the catalyst loading on the surface as evidenced by the consistent growth of the deposited porphyrin layers. When manganese porphyrin catalysts are supported on ITO, they are somewhat more resistant to degradation than their homogeneous counterpart, displaying longer lifetimes and higher turnover number for the epoxidation of styrene. Attempts to exploit the film-based catalysts electrochemically, using the solvent (water) as the source of oxygen for olefin epoxidation were only partially successful. Epoxide product was indeed obtained electrocatalytically, but in competition with the electrocatalytic conversion of water to hydrogen peroxide – which, in turn, inactivates the catalyst by irreversibly oxidizing the porphyrin ligand.

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