Synthesis and Characterization of Electropolymerized Nanostructured Aminophenylporphyrin Films

Michael G. Walter and Carl C. Wamser*

Department of Chemistry, Portland State University, Portland, Oregon 97207-0751 Received: October 19, 2009; Revised Manuscript Received: February 23, 2010

Porphyrins substituted at meso positions with aminophenyl groups undergo oxidative electropolymerization in a process analogous to the formation of polyaniline. Porphyrins that successfully generate polymer films on the electrode include those tetrasubstituted with four *p*-aminophenyl groups, trisubstituted, or transdisubstituted, but not cis-disubstituted or monosubstituted. The polymerization process is monitored independently by cyclic voltammetry, absorption spectroscopy, and an electrochemical quartz crystal microbalance. The mechanism is considered analogous to aniline polymerization, except that attack of electrophilic nitrogens must occur at ortho positions of another aminophenyl group. Reflectance FT-IR and resonance Raman spectroscopy detect the presence of diphenylamine, dihydrophenazine, and phenazine linkages in the porphyrin polymer film from tetra(4-aminophenyl)porphyrin (TAPP). TAPP polymerized in dichloromethane (DCM) with added pyridine gradually passivates; i.e., electronic conductivity diminishes and polymer growth levels off (the films are light yellow). Without added pyridine, electronic conductivity is sustained and film growth continues to a thick black film. Diphenylamine and dihydrophenazine linkages were common in films whose electroactivity remained constant throughout the film growth process while phenazine linkages were prevalent in films where passivation and loss of electrochemical activity had occurred. It is proposed that overoxidation to the phenazine structures leads to loss of electronic conductivity, analogous to formation of pernigraniline in polyaniline. The morphology of poly-TAPP is a highly interconnected nanofibrous network, with fiber diameters in the range 40-100 nm, with somewhat different structures depending on polymerization conditions.

Introduction

Porphyrins continue to attract a great deal of attention for a variety of functions because of their versatile molecular framework, variable electronic and catalytic properties, and strong light absorptivity.¹ For example, porphyrins are frequently the basis of artificial photosynthetic systems designed to generate electricity directly²⁻⁴ or to drive the decomposition of water to H₂ and O₂.^{5,6} Porphyrins coupled to electron donors and/or electron acceptors have been designed for efficient photoinduced electron transfers suitable for a variety of optoelectronic applications.⁷ As a key component of the overall system design, innovative macromolecular or supramolecular architectures are typically required to optimize a wide variety of important steps, e.g., light harvesting, charge separation, charge mobility, and charge collection.⁸ Self-assembled porphyrin nanotubes, interfacial films, and other multiporphryin arrays have been developed and used to address these structural requirements.9,10

Electropolymerization of porphyrins offers the advantage of controlling film deposition and conductivity by judicious selection of the porphyrin monomer and/or potentiometric conditions.^{11,12} Electrochemically deposited porphyrin films have been investigated for a wide variety of applications including in electrocatalysis,¹³ as molecular sieves,^{14,15} in fuel cell cathodes,¹⁶ and in photovoltaic donor/acceptor heterojunction devices.^{17,18} The syntheses of these films typically have been carried out under oxidative conditions leading to polymeric porphyrins linked together with electropolymerizable substituents such as vinyl, amino, hydroxyphenyl, pyrrole, or thiophene.¹¹ Electrochemically polymerized porphyrins may also contain central metal cations whose redox peaks may be

detectable in the electrochemical polymerization window when they are not hidden by the peak currents of the porphyrin oxidation.¹⁹ Although the electrochemical polymerization of tetraphenylporphyrins is usually carried out using potentiometric three-electrode techniques such as cyclic voltammetry or fixed potentiometry, alternative polymerization methods have been reported such as the use of photochemically or radiolytically generated radicals to initiate porphyrin polymerization.²⁰

In the case of meso-substituted tetraaminophenylporphyrins, it has been concluded that the initial oxidation occurs primarily on the aminophenyl substituents, deduced from the cyclic voltammogram in which the first oxidation peak occurs at potentials 0.5-0.6 V less positive than is predicted to be required for porphyrin ring oxidation.²¹ Invoking a mechanism analogous to the oxidative polymerization of aniline, aminophenylporphyrin coupling is projected to occur by electrophilic nitrogen attack at the ortho position of another aminophenylporphyrin.²² Electrochemically generated polyporphyrin films exhibit absorbance spectra similar to those of the monomer in solution, indicating that the π -conjugated porphyrin macrocycle has remained intact throughout the polymerization process. It can be visualized that any of the four aminophenyl positions could undergo oxidation and coupling reactions to polymerize in a linear or angular fashion with additional branching and cross-linking between polymer chains.²² A variety of metallo and free base meso-substituted aminophenylporphyrins containing ortho-, meta-, and para-substituted amino groups have been reported to electropolymerize under a wide range of conditions using both organic and aqueous electrolyte solutions.²³⁻²⁵ A

linear porphyrin polymer with aminophenyl linkages has recently been prepared and shows good electronic conductivity.²⁶

Extending from the mechanism of aniline polymerization, it has been suggested that the structural connections between porphyrin units may contain diphenylamine, dihydrophenazine, or phenazine linkages,^{22,27} as have been suggested for polyaniline,²⁸ but specific structural evidence has been lacking. In addition, although several surface structure investigations of electrochemically deposited porphyrin films have been reported,²⁹⁻³¹ very little has been presented to suggest that these methods can deposit nanostructured film morphology with extremely high surface area. Here we report for the first time the synthesis and characterization of a nanofibrous poly[tetrakis(4-aminophenyl)porphyrin] (poly-TAPP) network electrochemically deposited from dichloromethane (DCM) solution using cyclic voltammetry. We demonstrate that by altering the solvent composition and electrodeposition method the porphyrin film network structure and optoelectronic properties can be adjusted. We identify some of the molecular connections linking the porphyrin monomers, and we propose a mechanism for the polymerization process and the effectiveness of the electronic conductivity.

Experimental Methods

Materials. Tetrakis-5,10,15,20-(4-aminophenyl)porphyrin (TAPP) was obtained from TCI America and used as received. Alternative aminophenylporphyrin monomers studied in electropolymerizations were prepared by a route previously reported starting with tetra-p-carboxyphenylporphyrin (TCPP) and converting some of the four carboxyl groups to amino groups via Lossen rearrangement.³² Workup using methanol (to generate methyl esters) followed by preparative thin-layer chromatography achieves the separation of the six statistical possibilities for mixed amino/carboxymethyl porphyrins. These are designated as $TA_n CM_{4-n} PP$ for *n* amino and the remaining 4 - ncarboxymethyl substituents. Solvents used in electropolymerizations (DCM, pyridine, 2,6-lutidine, acetonitrile) were purchased as HPLC grade from Aldrich or Fisher with less than 0.01% water content. Solvents were dried over activated 4 A molecular sieves, and electrolytes tetrabutylammonium perchlorate or hydroxide (TBAP/TBAH) were recrystallized from methanol/water and dried in vacuo for at least 24 h at 60 °C. Platinum flag counter electrodes were heated to red hot in a flame, and rinsed in concentrated nitric acid, water, and then DCM electrolyte solution immediately before use. Electrochemical cells were cleaned with concentrated KOH/2-propanol solution, rinsed with distilled water, and stored in a drying oven overnight at 110 °C. FTO (fluorine-doped tin oxide) or ITO (indium-doped tin oxide) electrodes obtained from Delta Technologies or Pilkington Glass were cleaned by sonication in dilute Micro electronic grade cleaner for 40 min followed by sonication in distilled water and then 3:1 electronic grade acetone:2-propanol solution. After drying in an oven and cooling, electrodes were used immediately for electropolymerization.

Instrumentation. Electropolymerizations were conducted using a Princeton Applied Research Model 263 Potentiostat with Win-Echem control and data analysis software. Electrochemical quartz crystal microbalance (EQCM) measurements were taken using single quartz crystal platinized electrodes (area 0.2 cm², 300 nm thick deposited Pt metal layer) in a Teflon mounting and electrochemical test tube cell mounted on the holder as the working electrode. A platinum wire was used as the counter electrode. A Princeton Applied Research Model QCA922 quartz

crystal analyzer was used with an operating frequency from 1 to 10 MHz (calibrated for a 9 MHz crystal). Typical scan ranges were 0.0-1.0 V vs Ag/AgCl or -0.3 to 0.7 vs Ag/AgNO₃ reference electrode using a 5.3 Hz current and 5.3 Hz voltage filter. A nonaqueous reference electrode Ag/AgNO₃ kit was purchased from Bioanalytical Systems and was prepared using Vycor frits and heat shrink tubing. Although an aqueous Ag/AgCl reference electrode was used for several of the organic solution electropolymerizations, its properties remained stable throughout the investigations with reproducible data within each set of films polymerized. After each electropolymerization experiment, ferrocene was added and the potential was calibrated against the ferrocenium/ferrocene redox couple.

Atomic force microscopy images were obtained with a Digital Instruments Multimode AFM operating in tapping mode and using silicon-tipped cantilevers from Veeco Metrology Group (f_0 , 281–319 kHz; k, 20–80 N/m). Scan sizes and speeds were adjusted and were recorded on the AFM images taken. Scanning electron micrographs were obtained using a FEI Sirion SEM operating at 2.0–5.0 kV accelerating voltage at a working distance of 5 mm. Transmission electron micrographs were obtained using a FEI Tecnai F-20 TEM operating at 200 kV with films electrochemically grown directly on gold TEM grids (400 mesh, 3.0 mm).

Spectroelectrochemical measurements were made in a quartz cuvette in which a freshly deposited poly-TAPP film on an FTO working electrode was immersed in a TBAP/acetonitrile electrolyte solution (0.01 M) along with a Pt wire counter electrode and Ag/AgNO₃ reference. Absorbance spectra of the films were measured in the UV-vis spectrophotometer (Shimadzu UV-260) at 50 mV increments (vs Ag/AgNO₃). Reflectance Fourier transform infrared spectroscopic (FT-IR) measurements were made at the University of Portland Department of Chemistry on a Thermo Nicolet 6700 FT-IR spectrometer operating in reflectance mode and evaluated using Grams 8.0 software. Resonance Raman spectra were obtained at the Caltech Department of Geology on a Renishaw M-1000 micro-Raman spectrometer using a 50× objective, $2-3 \mu m$ spot size, and 514 nm laser.

Electropolymerization. The following procedure was followed for TAPP electropolymerization and poly-TAPP deposition. Conditions that were varied include the concentrations of the aminophenylporphyrin, the aminophenylporphyrin derivative used, the quaternary ammonium electrolyte used, the concentration of pyridine in DCM, the concentrations of dissolved water in the primary solvents (pyridine and DCM), and the pyridine derivative used. The electropolymerization of tetrakis-5,10,15,20-(4-aminophenyl)porphyrin (TAPP) was carried out on a fluorinedoped SnO₂ glass electrode (FTO) in a three-probe electrochemical cell using a 1 cm² Pt foil counter electrode and Ag/ AgNO₃ reference electrode. The electropolymerization carried out for EQCM measurements was conducted in a QA-CL4 well type quartz crystal holder using a 0.2 cm² platinized quartz crystal working electrode and a platinum wire coil counter electrode. Typical solutions were prepared with 0.15 mM TAPP and 10 mM tetrabutylammonium perchlorate (TBAP) as supporting electrolyte in DCM deaerated solution (all solutions were purged with DCM-saturated argon for 20 min prior to electrodeposition). In some experiments, the electropolymerization solution also included pyridine or a pyridine derivative (5-15%)by volume). Cyclic voltammetry (-0.3 to +0.7 V vs Ag/ AgNO₃) was sometimes combined with fixed potentiometry by adding a 30 s vertex delay at +0.7 V within each cycle. The resultant polyporphyrin coated electrodes were rinsed with fresh



Figure 1. (a) Cyclic voltammograms (first eight cycles) of 0.15 mM TAPP in dichloromethane deposited onto Pt electrode with scan rate (ν) of 20 mV/s using 10 mM tetrabutylammonium perchlorate supporting electrolyte and Ag/AgCl reference. (b) Electrochemical quartz crystal microbalance measurements for the first eight cycles of TAPP oxidation under identical conditions. Dotted lines indicate identical conditions without TAPP.



Figure 2. Peak current (I_p , μA) and forward/reverse peak separation (ΔE_p , mV) vs scan rate (ν , mV/s) for a poly-TAPP film deposited by 15 cyclic voltammetry scans.

solvent and then 2-propanol and dried under nitrogen. Films were used immediately for UV-vis, SEM, reflectance FT-IR, and AFM analyses.

Results

Electropolymerization in Dichloromethane. Electrochemical oxidation of TAPP was noted to be unusual even when

polymerization was not involved. In dimethyl sulfoxide (DMSO) solvent, oxidation is a reversible, one-electron process, apparently analogous to oxidation of other parasubstituted tetraphenylporphyrins (TPPs), except that the oxidation is about 0.5 V less positive than predicted by a Hammett correlation with other derivatives.²¹ This effect is ascribed to the location of the highest occupied molecular orbital (HOMO) of electron-rich TPPs, most notably with amino substituents, on the phenyl group rather than the porphyrin. The situation is analogous to protonation of aminosubstituted TPPs, where hyperporphyrin structures were proposed.33-36 In these cases, protonation occurs at the porphyrin nitrogens with charge delocalization out to the aminophenyl substituents. The hyperporphyrin spectrum includes strong near-IR bands indicative of increased conjugation between the porphyrin and the phenyl substituents.

In contrast, when TAPP is electrochemically oxidized in DCM solvent, the oxidation is irreversible and a polymer film slowly grows on the electrode. Figure 1 shows the first eight cycles of cyclic voltammetry, where the growth of polymer film is indicated by the increasing current waves as well as the increasing mass on the electrode detected by an electrochemical quartz crystal analyzer. Dotted lines in each graph show blank scans with the same electrolyte solution but without TAPP. Reversible oxidation of TAPP in DMSO occurs with $E_{1/2} \approx 515$ mV (vs Ag/AgNO₃) and small peak



Figure 3. (a) UV-vis spectra of poly-TAPP deposited by 15 CV scans in 95:5 (v:v) DCM:pyridine. (b) Surface coverage of poly-TAPP calculated from absorbance at 428 nm for 15 electrochemical cycles, with linear fit.



Figure 4. Mass deposition of poly-TAPP by EQCM/chronocoulometry at 0.4 V vs Ag/AgNO₃. (inset) UV–vis spectra of the growing (oxidized) poly-TAPP film after 50 and 75 s.

separation between oxidation and reduction waves (about 80 mV).²¹ In DCM, although $E_{1/2}$ is similar, about 531 mV, the peak separation is substantial ($E_{ox} = 728$ mV and $E_{red} = 334$ mV for $\Delta E_p = 394$ mV), indicating irreversibility. Subsequent scans show increasingly positive oxidation potentials and

increasing peak separations; these effects have been noted before for electropolymerization of TAPP and metallo derivatives.^{11,12,24,27}

The quartz crystal analyzer data in Figure 1b confirm that mass is accumulating on the electrode upon repeated scanning; calculation via the Sauerbrey equation³⁷ gives the amount of material deposited on the electrode. The oscillations observed in cyclic voltammetry (CV) are generally understood to represent the inclusion of counterions and solvent in the oxidized form, and expulsion of these (as well as possibly some unattached TAPP) during the reduction wave. The stages of the cyclic voltammetric scan can be correlated with the mass changes, as described later in Figure 6.

To further probe the reversibility of the redox processes of the poly-TAPP film, an electrode with a film deposited via 15 CV scans was reimmersed in a clean electrolyte solution (no TAPP) and subjected to different scan rates. Figure 2 illustrates that peak separation increases strongly up to 10 mV/s and then levels out, while peak current follows an approximate linear dependence at slow rates and a square root dependence at higher rates (above about 20 mV/s). These data indicate that there are slow kinetic processes within the poly-TAPP film that limit electronic conductivity in these time scales.^{12,24}

As the film grows, UV-vis absorbance spectroscopy clearly shows the increased absorbance that is readily detectable by



Figure 5. Mass deposition by EQCM for poly-TAPP electropolymerized in DCM, with and without 5% pyridine: (a) 15 cycles including a 30-s delay at +0.7 V; (b) 30 cycles without the 30-s delay.



Figure 6. (a) Cyclic voltammograms of the first three cycles of TAPP electropolymerization in 95:5 (v:v) DCM:pyridine, including a 30-s vertex delay at +0.7 V. (b) Combined CV (current, solid line, left axis) and EQCM (mass, dotted line, right axis) data for the first two cycles under standard conditions; the solid vertical lines indicate the 30-s vertex delay, and the dashed vertical line indicates the end of the first scan.



Figure 7. SEM images of poly-TAPP films electropolymerized on FTO electrodes using three CV scans in DCM with variable amounts of pyridine: (a) no pyridine; (b) 5% pyridine; (c) 15% pyridine; (d) 15% pyridine, higher magnification.

eye (Figure 3). Using the Soret band absorbance and a reduced extinction coefficient of 67 000 M^{-1} cm⁻¹, as estimated for similar porphyrin polymer films,³⁸ the surface coverage can be calculated for the films. After 15 cycles, surface coverage of porphyrin units is about 13 nmol/cm². Integrating the charge under the CV oxidation wave using a general expression for



Figure 8. (a) SEM image of a poly-TAPP film electropolymerized on FTO electrodes using 15 CV scans in DCM with 5% pyridine, with a cross section shown on a small flake of FTO dislodged from the surface. (b) TEM image of a single nanofiber of poly-TAPP electrochemically grown directly on a gold TEM grid under identical conditions.

diffusionless electrochemical processes,³⁹ each oxidation wave corresponds to 0.87 electron passed per TAPP deposited (as measured by UV–vis). Surface coverage calculated from EQCM data generate significantly higher values, corresponding to only 0.3 electron per TAPP. This suggests that the mass registered by the EQCM includes significant amounts of solvent, counterions, or TAPP that ultimately does not end up in the completed film. This effect has been noted before with electrochemical growth of PEDOT.⁴⁰

Chronocoulometry was performed at a fixed potential of 0.4 V (vs Ag/AgNO₃), monitoring both the charge passed and the mass adsorbed on the electrode. Figure 4 shows that the adsorbed mass rises steadily; with continued oxidation the



Figure 9. AFM images of poly-TAPP films formed from three CV cycles in DCM (x and y units are micrometers) (a) without pyridine and (b) with 5% pyridine. (c) Cross-sectional analysis of (b).



Figure 10. SEM images of attempted electropolymerizations of variously substituted aminophenylporphyrins without pyridine catalysis: tetrakis-5,10,15,20-(4-aminophenyl)porphyrin (TAPP), 5,10,15-tris(4-aminophenyl)-20-(4-carbomethoxyphenyl) porphyrin (TA₃CMPP), and 5,15-bis(4aminophenyl)-10,20-bis(4-carbomethoxyphenyl)porphyrin (*trans*-TA₂CM₂PP).

adsorbed mass slowly levels off. The UV-vis spectra of the films in the oxidized state (Figure 4 inset) are distinct from the films in the reduced state, e.g., Figure 3a, where the usual final state after cyclic voltammetry was at 0 V.

Pyridine Catalysis. Traces of HCl are a common impurity in DCM, easily detectable while taking a UV-vis spectrum of a simple tetraphenylporphyrin. For example, we have noted that repeated scans of a UV-vis spectrum of tetratolylporphyrin in dilute DCM solution show increasing amounts of protonated porphyrin, indicated by the gradual rise of a new red-shifted Soret peak. Other TPPs have been noted to aggregate and precipitate from solution upon generation of HCl during irradiation in chloroform solution.⁴¹ Apparently the pulse of broad-spectrum light in a typical diode-array spectrophotometer is sufficient to generate traces of HCl from a chlorinated solvent, and the HCl can be sensitively detected as a rise in a new redshifted Soret peak attributable to protonated porphyrin. Thus we chose to examine the electropolymerizations in the presence of pyridine as a base to neutralize any HCl generated from photolysis of the DCM solvent. In addition, the oxidative electropolymerization was expected to release acid. We believed it would be desirable to maintain the porphyrin in neutral form, expecting that the protonated porphyrin would be less susceptible to continued oxidation and polymerization; i.e., the HOMO of the protonated porphyrin is lower in energy than the HOMO of the corresponding neutral porphyrin.

In fact, the presence of pyridine did have a strong catalytic effect on the growth of the poly-TAPP film, as indicated in the

EQCM traces shown in Figure 5. Although the early growth is significantly faster in the presence of pyridine, eventually the typical oscillations damp out and the growth levels off. CV traces show the corresponding effect: the oxidation wave has essentially disappeared by the 15th cycle, and the electrode film is nonconductive. The corresponding effects are not observed in the absence of pyridine; the oscillatory EQCM mass behavior and the growth of the oxidation waves in CV scans continue for extended scanning and do not significantly level off. Thus continued film growth (50 or more CV scans) in the absence of pyridine eventually overtakes the pyridine-catalyzed films in total amount of TAPP deposited. Note that the use of a 30-s vertex delay at the oxidizing end point (+0.7 V) allows for the comparable amount of mass to be deposited in about half as many cycles as without the delay.

The first CV scans were examined more closely, coordinating the electrochemical CV analysis with EQCM mass analysis (Figure 6). Mass accumulation occurs while the electrode is poised positively and anodic current is flowing, including during the constant-potential delay and continuing steadily even as the current slowly decreases. This suggests that even though current is limited by monomer diffusion, chemical processes such as coupling reactions continue to lead to sustained polymer deposition. In other words, monomer oxidation alone is not sufficient to lead to polymer deposition; higher oligomers are required in order to deposit onto the electrode surface, an effect cited in other conductive polymer depositions.^{42–44} The sharp transition to cathodic current flow at the reverse reduction wave



Figure 11. Mass deposition by EQCM for poly-TAPP prepared in DCM with 5% pyridine and varying concentrations of water: (a) anhydrous conditions; (b) <0.1% water; (c) \sim 1% water.

leads to an abrupt decrease in mass, which halts at the reversal of the potential scan direction. The new level of mass accumulated upon each successive scan rises gradually, indicating the permanent amount of material adsorbed onto the electrode.

During the course of studying the electropolymerization in pyridine/DCM, it was discovered that the two solvents react together, slowly forming a precipitate that was isolated and identified as methylenedipyridinium dichloride. Solutions that had been prepared in advance and allowed to react for 24 h did not support the growth of nanofibers very well. Thus, the mixed solvents were prepared just before use. It was noted that other pyridine derivatives such as 2,6-dimethylpyridine did not undergo the reaction, presumably due to steric hindrance, and were comparably effective in the catalysis of the electropolymerization.⁴⁵

Morphology of Poly-TAPP Films. The surface morphologies of the poly-TAPP films were examined with scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM). The catalytic effect of pyridine in the early stages of growth (three CV scans) is notable in comparing the diffuse structure of the polymer formed without pyridine to the well-defined nanofibers formed with 5% or 15% pyridine (Figure 7). Without pyridine, the nanostructures formed early in the process were extremely variable, possibly because of complications due to local generation of acid in the unbuffered solvent. With pyridine, well-defined nanofibers are formed early. Nanofiber thicknesses are about 25–75 nm and are strongly interconnected into a fibrous network. Pore sizes range from 10 to 500 nm.

Using conditions of 15 CV scans with 5% pyridine in DCM, where much thicker films are formed, typical film structure is further examined in Figure 8. The SEM cross section (Figure 8a) indicates a smaller, denser fiber structure observed at the film/FTO interface with larger fiber growth outward. A typical TEM image (Figure 8b) of a single poly-TAPP fiber does not indicate the presence of a tubular interior fiber nanostructure like those seen previously with self-assembled anionic/cationic porphyrins in solution.⁹ There are also no indications of porphyrin polymer crystallinity within individual fibers (no observed electron diffraction).

An approximate surface area of the nanofibers was calculated using a method successfully applied to polyaniline nanofibers.⁴⁶ Approximating the nanofibers as cylinders of 50 nm diameter (from SEM images) and the surface coverage as 4 nmol/cm² (after three CV scans, based on coulometry), the total surface area is 25 m²/g.

AFM images confirm the differences between the uncatalyzed and pyridine-catalyzed films (Figure 9). Nanofiber formation is significantly enhanced in the early stages of growth when pyridine is present. Cross-sectional analysis indicates a surface roughness of about 100 nm.

Alternative Monomers. Having available several other aminophenylporphyrin derivatives,³² the generality of the electropolymerization was investigated (Figure 10). Derivatives with fewer than four *p*-aminophenyl groups did not give extensive nanofiber structures as were observed with TAPP. However, thin films did form from derivatives with two or three *p*-aminophenyl groups (with the remaining groups *p*-carbometh-



Figure 12. Mass deposition by EQCM for poly-TAPP prepared in DCM without pyridine and with varying concentrations of water: (a) anhydrous conditions; (b) <0.1% water; (c) \sim 1% water.

oxyphenyl). The facility of formation and the quality of the films decreased from triamino to *trans*-diamino, and *cis*-diamino and monoamino did not form film at all. It is possible that hydrogen bonding between polymer chains is essential for successful nanofiber formation, as has been suggested for polyaniline.^{28,47} Thus it appears that at least two free *trans*-aminophenyl groups are required for polymerization and a third available aminophenyl group (as in the triamino derivative) significantly improves nanofiber growth.

Effects of Trace Water. Given the strong effect of pyridine on the electropolymerization, the significance of traces of water in the DCM solvent were studied. Most work was done with HPLC grade DCM, stated to contain less than 0.01% water. In conjunction with 5% pyridine (anhydrous), if the DCM was rigorously dried, the electropolymerization was distinctly slower, and if water was intentionally added (DCM can be saturated with about 1% water), the rate was distinctly faster with much larger mass oscillations during the initial CV scans. In every case, there was eventual passivation of the film, although at different limiting amounts. A greater amount of film was formed with more water present, but the nature of the nanofibers was also radically different (Figure 11). Anhydrous conditions led to thin smooth films, while the ultimate passivated films formed with water present showed thicker nanofibers in the uppermost layers of the films.

In the absence of pyridine, water itself, even at about 0.1%, served as a significant catalyst for the electropolymerization, and the resultant fibers are densely packed (Figure 12).

Other studies have recognized the role of trace water in electropolymerizations of porphyrins,⁴⁸ pyrrole,^{49,50} and thiophene.⁵¹ In general, water in organic media is a suitable base for deprotonation of oxidized intermediates. For formation

of polypyrrole in acetonitrile, about 1% water increased the polymerization rate, conductivity, and adherence to the electrode.⁵⁰ Incorporation of pyridine was noted to lead ultimately to loss of conductivity in the electrochemical polymerization of pyrrole or thiophene.^{52–54}

Molecular Structure. Oxidation and polymerization of the aminophenyl groups on TAPP are presumed to proceed in a manner analogous to aniline polymerization.^{55–57} Since the para positions of TAPP are occupied, ortho connections are expected, and linkages involving diphenylamine, dihydrophenazine, or phenazine have been proposed²⁷ (Figure 13). Comparable ortho connections are observed to occur in polyaniline under certain conditions.²⁸

Evidence for these types of linkages was sought using reflectance FT-IR and resonance Raman spectroscopies. The FT-IR spectrum of poly-TAPP formed either with or without pyridine strongly resembles that of a thin film of sublimed TAPP (Figure 14). For example, the N–H stretchings of both the aminophenyls $(3330-3470 \text{ cm}^{-1})$ and the pyrroles (3211 cm^{-1}) are clear. Broadening and shifting of the N–H aminophenyl peaks in the polymer spectrum suggest intermolecular H-bonding that is not observed in the TAPP monomer. Similar effects in polyaniline have been ascribed to interchain H-bonding.^{28,47}

For films formed in the presence of pyridine, the weak peak at 820 cm⁻¹ provides evidence for phenazine groups. This skeletal deformation vibration is one of the strongest absorptions in a phenazine spectrum, is present in all substituted phenazines, and does not appear in dihydrophenazines.^{58,59} Other new absorptions that match with phenazine vibrations are the peaks at 1625 and 1421 cm⁻¹, which have also been cited to support phenazine structures found in polyaniline.^{28,47} Figure 15 shows



Figure 13. Oxidative coupling possibilities for linking units of TAPP: o-aminodiphenylamine, dihydrophenazine, and phenazine linkages.



Figure 14. Reflectance FT-IR spectra of TAPP evaporated onto an FTO electrode compared with poly-TAPP prepared by electropolymerization in pure DCM (\bigcirc , peaks attributable to dihydrophenazine) and in DCM with 5% pyridine (\times , peaks attributable to phenazine).

the Raman spectrum of a poly-TAPP film formed in the presence of pyridine. Absorptions characteristic of phenazine units are found at 820 cm⁻¹ (skeletal deformation) and 1420 cm⁻¹ (symmetric phenazine ring stretching) and have been found in the Raman spectra of polyaniline and polymerized phenosafranines.^{60–62}

For films formed in the absence of pyridine, the presence of dihydrophenazine units can be inferred from the FT-IR spectrum (Figure 14, middle) based on the peak at 1294 cm⁻¹, which is a very strong peak in dihydrophenazine representing a C–NH–C

stretching vibration.⁵⁸ A peak at 1230 cm⁻¹ is also characteristic of dihydrophenazine and is absent in the spectra of TAPP and poly-TAPP films formed with pyridine present.

Discussion

Electronic Conductivity. The data indicate that the presence of pyridine, although it initially catalyzes the rate of polymerization, ultimately leads to a film that loses conductivity. We propose that conductivity in poly-TAPP requires that the linkages between TAPP units include both dihydrophenazine



Figure 15. Reflectance resonance Raman spectrum of poly-TAPP

(the reduced form) and protonated phenazine (the oxidized form). This is analogous to the situation in polyaniline, where optimum conductivity is achieved with a balance of neutral diphenylamino groups and oxidized (and protonated) imino quinoid forms.⁶³ The availability of both forms facilitates the movement of electron pairs (bipolarons) through the chain (Figure 16).

electropolymerized from solutions containing 5% pyridine in DCM.

The conductivity mechanism proposed for poly-TAPP is similar to that of polyaniline, in that there are reduced diamino (aromatic) units that can be interconverted with oxidized diimino (quinone) units (Figure 17).

Effectively the oxidation may be localized on the phenazine linker unit (Figure 17, form b), in which case it is independent of the porphyrins and need not be coplanar with the porphyrin rings, or it may be delocalized in either direction into a porphyrin ring system (c or d), in which case coplanarity is required to extend through to both sides of the porphyrin involved in the oxidized form. Note that the delocalized oxidized form resembles an extended *p*-quinoid form similar to that in polyaniline, while the adjacent porphyrin takes on the corresponding reduced form of extended aromatic *p*-diamines. We are initiating calculations to determine the relative energetics of the localized and delocalized oxidized forms and the energies required to convert between twisted and coplanar structures.

We propose that the catalytic function of pyridine in the early stages of polymerization is simply to keep the porphyrin monomers unprotonated, since protonated forms would be expected to be less reactive toward oxidation. Later in the polymerization, pyridine deprotonates the growing polymer, which leads to loss of conductivity, since unprotonated phenazine units cannot maintain the conductivity mechanism we propose; this is analogous to the deprotonation of polyaniline from emeraldine salt to emeraldine base, which is nonconductive. Polymerization in the absence of pyridine generates acid stoichiometrically during the oxidation processes, so the polymer is able to maintain its state of protonation and maintain its conductivity.



Figure 17. Proposed conductivity mechanism in poly-TAPP.



Figure 18. (a) Reversible spectroelectrochemistry of a poly-TAPP film held at various potentials (vs Ag/AgNO₃). (b) Spectra of monomeric TAPP in DMSO solution oxidized by ammonium persulfate (APS). (c) Hyperporphyrin resonance forms for oxidized forms of TAPP with charges delocalized either cis or trans.

The delocalized quinoid form effectively extends the conjugation outside the porphyrin ring system, in an effect often referred to as a hyperporphyrin. The extended conjugation creates a long-wavelength absorption characteristic of hyperporphyrins. Spectroelectrochemistry of a poly-TAPP film held at oxidizing potentials reveals growth of a strong, broad absorption at about 750 nm (Figure 18a); the same phenomenon is observed on oxidation of TAPP with ammonium persulfate in DMSO (Figure 18b). These absorptions are attributed to oxidized quinoid forms, which conceivably extend through the porphyrin ring either cis or trans (Figure 18c). Although trans conjugation was cited in the conductivity mechanism (Figure 17), the polymer could certainly include cis linkages, which would be equally plausible as quinoid oxidized forms and conduits for electronic conductivity. Hyperporphyrin spectra have been noted from TAPP upon protonation.33-36 Like protonation, oxidation creates a dipositive form of TAPP that has similar delocalization opportunities to the *p*-amino groups. Hydroxyphenylporphyrins have also been well studied; these generate hyperporphyrin spectra upon deprotonation⁶⁴ or oxidation⁶⁵ and they can be electropolymerized.⁶⁶

Applications. We propose that poly-TAPP can be an electronically conductive polymer so long as a number of structural conditions are satisfied. The phenazine linker units need to remain protonated, both reduced (dihydrophenazine) and oxidized (protonated phenazine) units need to be present (probably approximately equally), and conjugation through the porphyrin rings needs to be possible, involving minimal energy barriers between twisted and coplanar conformations. Given these structural conditions, poly-TAPP could show promise in a variety of applications, since it is a strong visible light absorber



Figure 19. Current-voltage curves for a representative solar cell composed of a thin film of poly-TAPP on FTO created by three CV scans in DCM without pyridine, a spin-coated layer of PCBM (from a 2% solution in chlorobenzene), and a top electrode of evaporated LiF/ Al, illuminated with visible light of 100 mW/cm² simulating an AM 1.5 solar spectrum.

and a good electronic conductor, and it has a very high surface area. For example, as a solar cell in which the poly-TAPP serves as the light harvester and hole conductor, an electron acceptor such as PCBM can be spin-cast into the pores to create a bulk heterojunction (BHJ) solar cell in which the nanostructure is created in advance, rather than by phase separation as in typical BHJ solar cells.⁶⁷ A preliminary attempt at creating such a cell gave a distinctive photocurrent but low overall efficiency (Figure 19). Additional work in this area is underway.

Conclusions

Thin films of polymeric porphyrin are readily created by electrochemical oxidation of aminophenylporphyrin monomers. The films are electronically conductive, with the individual monomer units linked by bridging groups that facilitate electron conductivity. The film morphology features nanofibers, offering a very high surface area for a variety of potential applications.

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References and Notes

(1) *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000.

(2) Campbell, W. M.; Burrell, A. K.; Officer, D. L.; Jolley, K. W. Coord. Chem. Rev. 2004, 248, 1363–1379.

- (3) Campbell, W. M.; Jolley, K. W.; Wagner, P.; Wagner, K.; Walsh, P. J.; Gordon, K. C.; Schmidt-Mende, L.; Nazeeruddin, M. K.; Wang, Q.;
- Graetzel, M.; Officer, D. L. J. Phys. Chem. C 2007, 111, 11760–11762.
- (4) Cherian, S.; Wamser, C. C. J. Phys. Chem. B 2000, 104, 3624– 3629.

(5) Alstrum-Acevedo, J. H.; Brennaman, M. K.; Meyer, T. J. *Inorg. Chem.* **2005**, *44*, 6802–6827.

- (6) Gust, D.; Moore, T. A.; Moore, A. L. Acc. Chem. Res. 2000, 34, 40-48.
- (7) Vail, S. A.; Schuster, D. I.; Guldi, D. M.; Isosomppi, M.; Tkachenko, N.; Lemmetyinen, H.; Palkar, A.; Echegoyen, L.; Chen, X.; Zhang, J. Z. H. J. Phys. Chem. B 2006, 110, 14155–14166.
- (8) Spanggaard, H.; Krebs, F. C. Sol. Energy Mater. Sol. Cells 2004, 83, 125–146.
- (9) Wang, Z.; Medforth, C. J.; Shelnutt, J. A. J. Am. Chem. Soc. 2004, 126, 15954–15955.
- (10) Holten, D.; Bocian, D. F.; Lindsey, J. S. Acc. Chem. Res. 2002, 35, 57-69.
- (11) Bedioui, F.; Devynck, J.; Bied-Charreton, C. Acc. Chem. Res. 1995, 28, 30–36.
- (12) White, B. A.; Murray, R. W. J. Electroanal. Chem. 1985, 189, 345–352.
- (13) Trevin, S.; Bedioui, F.; Villegas, M. G. G.; Bied-Charreton, C. J. Mater. Chem. 1997, 7, 923–928.
- (14) Pressprich, K. A.; Maybury, S. G.; Thomas, R. E.; Linton, R. W.; Irene, E. A.; Murray, R. W. J. Phys. Chem. **1989**, 93, 5568–5574.
- (15) O'Donnell, J. L.; Thaitrong, N.; Nelson, A. P.; Hupp, J. T. Langmuir 2006, 22, 1804–1809.
- (16) Bettelheim, A.; Soifer, L.; Korin, E. J. Electroanal. Chem. 2004, 571, 265–272.
- (17) Maree, C. H. M.; Roosendaal, S. J.; Savenije, T. J.; Schropp, R. E. I.; Schaafsma, T. J.; Habraken, F. H. P. M. *J. Appl. Phys.* **1996**, *80*, 3381–3389.
- (18) Wamser, C. C.; Bard, R. R.; Senthilathipan, V.; Anderson, V. C.; Yates, J. A.; Lonsdale, H. K.; Rayfield, G. W.; Friesen, D. T.; Lorenz,
- D. A.; et al. J. Am. Chem. Soc. **1989**, 111, 8485–8491.
- (19) Macor, K. A.; Spiro, T. G. J. Am. Chem. Soc. **1983**, 105, 5601–5607.
- (20) Kajiwara, A.; Kamachi, M. Polym. J. (Tokyo) 1989, 21, 593–595.
 (21) Ransdell, R. A.; Wamser, C. C. J. Phys. Chem. 1992, 96, 10572–10575.
- (22) Bruti, E. M.; Giannetto, M.; Mori, G.; Seeber, R. *Electroanalysis* **1999**, *11*, 565–572.
- (23) Cornejo, G.; Ramirez, G.; Villagran, M.; Costamagna, J.; Trollund, E.; Aguirre, M. J. J. Chil. Chem. Soc. **2003**, 48, 49–55.
- (24) Huang, S.; Tang, H.; Li, B. Microchim. Acta 1998, 128, 37-42.

(25) Chen, S.; Chen, Y.; Thangamuthu, R. J. Solid State Electrochem. 2007, 11, 1441–1448.

- (26) Liddell, P.; Gervaldo, M.; Bridgewater, J.; Keirstead, A.; Lin, S.; Moore, T.; Moore, A.; Gust, D. *Chem. Mater.* **2007**, *20*, 135–142.
- (27) Bettelheim, A.; White, B. A.; Raybuck, S. A.; Murray, R. W. *Inorg. Chem.* **1987**, *26*, 1009–1017.
- (28) Trchova, M.; Sedenkova, I.; Konyushenko, E.; Stejskal, J.; Holler, P.; Ciric-Marjanovic, G. J. Phys. Chem. B 2006, 110, 9461–9468.
- (29) Holmes-Smith, A.; Zheng, X.; Uttamlal, M. Meas. Sci. Technol. 2006, 17, 3328–3334.
 - (30) Bennett, J. E.; Malinski, T. Chem. Mater. 1991, 3, 490-495.

(31) Armijo, F.; Goya, M. C.; Gimeno, Y.; Arevalo, M. C.; Aguirre, M. J.; Creus, A. H. *Electrochem. Commun.* **2006**, *8*, 779–784.

(32) Walter, M. G.; Wamser, C. C.; Ruwitch, J.; Zhao, Y.; Braden, D.; Stevens, M.; Denman, A.; Pi, R.; Rudine, A.; Pessiki, P. J. J. Porphyrins Phthalocyanines **2007**, *11*, 601–612.

(33) Ojadi, E. C. A.; Linschitz, H.; Gouterman, M.; Walter, R. I.;
 Lindsey, J. S.; Wagner, R. W.; Droupadi, P. R.; Wang, W. J. Phys. Chem.
 1993, 97, 13192–13197.

(34) Weinkauf, J. R.; Cooper, S. W.; Schweiger, A.; Wamser, C. C. J. Phys. Chem. A 2003, 107, 3486–3496.

(35) Vitasovic, M.; Gouterman, M.; Linschitz, H. J. Porphyrins Phthalocyanines 2001, 5, 191–197.

(36) Walter, R. I.; Ojadi, E. C. A.; Linschitz, H. J. Phys. Chem. 1993, 97, 13308–13312.

(37) Paolesse, R.; Natale, C. D.; Dall'Orto, V. C.; Macagnano, A.;

- Angelaccio, A.; Motta, N.; Sgarlata, A.; Hurst, J.; Rezzano, I.; Mascini, M.; D'Amico, A. *Thin Solid Films* **1999**, *354*, 245–250.
 - (38) Li, W.; Wamser, C. C. Langmuir 1995, 11, 4061-4071.

(39) Laviron, E. J. Electroanal. Chem. Interfacial Electrochem. 1979, 101, 19–28.

(40) Seshadri, V.; Wu, L.; Sotzing, G. Langmuir 2003, 19, 9479–9485.
(41) Okada, S.; Segawa, H. J. Am. Chem. Soc. 2003, 125, 2792–2796.

(41) Okada, S., Segawa, H. J. Am. Chem. Soc. 2005, 125, 2192–2190.
 (42) Heinze, J.; Rasche, A.; Pagels, M.; Geschke, B. J. Phys. Chem. B

2007, 111, 989–997.
(43) Carrillo, I.; Sanchez de la Blanca, E.; Gonzalez-Tejera, M. *Polymer*2001, 9447–9453.

(44) Baba, A.; Tian, S.; Stefani, F.; Xia, C.; Wang, Z.; Advincula, R.; Johannsmann, D.; Knoll, W. J. Electroanal. Chem. **2004**, *562*, 95–103.

(45) Rudine, A. B.; Walter, M. G.; Wamser, C. C. J. Org. Chem. 2010, in press.

- (46) Huang, J.; Kaner, R. Chem. Commun. 2006, 2006, 367-376.
- (47) Zujovic, Z.; Zhang, L.; Bowmaker, G.; Kilmartin, P.; Travas-Sejdic,
 J. *Macromolecules* 2008, 41, 3125–3135.
- (48) Milgrom, L. R.; Hill, J. P.; Flitter, W. D. Tetrahedron 1993, 49, 507-513.
 - (49) Zhou, M.; Heinze, J. J. Phys. Chem. B 1999, 103, 8451-8457.

(50) Downard, A.; Pletcher, D. J. Electroanal. Chem. Interfacial Electrochem. 1986, 206, 139–145.

(51) Downard, A.; Pletcher, D. J. Electroanal. Chem. 1986, 206, 147–152.

(52) Morse, N. J.; Rosseinsky, D. R.; Mortimer, R. J.; Walton, D. J. J. Electroanal. Chem. Interfacial Electrochem. **1988**, 255, 119–141.

(53) Rosseinsky, D. R.; Morse, N. J.; Slade, R. C. T.; Hix, G. B.; Mortimer, R. J.; Walton, D. J. *Electrochim. Acta* **1991**, *36*, 733–738.

(54) Qian, R.; Pei, Q.; Huang, Z. Makromol. Chem. 1991, 192, 1263-1273.

(55) Phillips, S. D.; Yu, G.; Cao, Y.; Heeger, A. J. Phys. Rev. B: Condens. Matter 1989, 39, 10702–10707.

(56) Luzny, W.; Banka, E. Macromolecules 2000, 33, 425-429.

(57) Wei, X. L.; Wang, Y. Z.; Long, S. M.; Bobeczko, C.; Epstein, A. J. J. Am. Chem. Soc. **1996**, 118, 2545–2555.

- (58) Wheaton, G.; Stoel, L.; Stevens, N.; Frank, C. Appl. Spectrosc. 1970, 24, 339–343.
- (59) Stammer, C.; Taurins, A. *Spectrochim. Acta* 1963, *19*, 1625–1654.
 (60) Ćirić-Marjanović, G.; Trchová, M.; Stejskal, J. *J. Raman Spectrosc.* 2008, *39*, 1375–1387.
- (61) Li, X.-G.; Huang, M.-R.; Duan, W.; Yang, Y.-L. Chem. Rev. 2002, 102, 2925–3030.
- (62) Ciric-Marjanovic, G.; Blinova, N. V.; Trchova, M.; Stejskal, J. J. Phys. Chem. B 2007, 111, 2188–2199.
- (63) Nalwa, H. S. Handbook of Organic Conductive Molecules and Polymers; John Wiley & Sons Ltd.: New York, 1997; Vol. 2.
- (64) Guo, H.; Jiang, J.; Shi, Y.; Wang, Y.; Wang, Y.; Dong, S. J. Phys. Chem. B 2006, 110, 587–594.
- (65) Milgrom, L. R.; Hill, J. P.; Yahioglu, G. J. Heterocycl. Chem. 1995, 32, 97–101.
- (66) Savenije, T. J.; Koehorst, R. B. M.; Schaafsma, T. J. J. Phys. Chem. B 1997, 101, 720–725.
- (67) Hoppe, H.; Sariciftci, N. S. J. Mater. Chem. 2006, 16, 45-61.
- JP910016H