

Synthesis and Characterization of Electropolymerized Porphyrin Nanofibers

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ABSTRACT

Electrochemical oxidation of tetrakis-5,10,15,20-(4-aminophenyl)porphyrin (TAPP) on fluorine-doped tin oxide electrodes leads to a conductive polymeric film (poly-TAPP) with a nanostructured fibrous morphology. The nanofiber structure and growth rate are enhanced by the addition of pyridine (5 - 15%) to the dichloromethane electrochemical solution. Electropolymerization in the absence of pyridine leads to a more highly bundled poly-TAPP structure with a spectrum indicative of protonated porphyrin units. Testing of poly-TAPP electrodes in an electrochemical iodide cell and in a 1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C₆₁ (PCBM) integrated solid state photovoltaic cell indicates modest photoactivity.

INTRODUCTION

Porphyrins and porphyrin-containing materials continue to attract a great deal of attention for organic photonic devices because of their versatile molecular framework, varied optoelectronic properties, and strongly light-absorbing chromophores.¹ The electropolymerization of porphyrins offers the advantage of controlling the film deposition and conductivity through varying porphyrin monomer, the potential window, and the electrolytic conditions.² Figure 1 depicts the oxidative linkage of two TAPP monomers to the dihydrophenazine/phenazine structures proposed in poly-TAPP. We report a method to obtain a

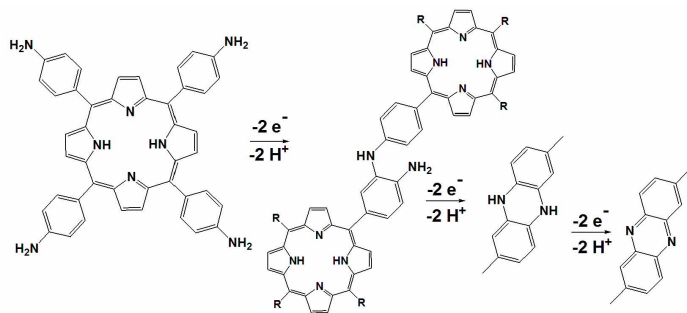


Figure 1. Oxidative coupling of TAPP to diphenylamine, dihydrophenazine, or phenazine linkages.

nanofibrous poly-tetrakis(4-aminophenyl)porphyrin (poly-TAPP) network electrochemically deposited from a dichloromethane/pyridine solution using cyclic voltammetry with a 30 s vertex delay. We demonstrate that by altering the solvent composition and electrodeposition method

the porphyrin film network structure and optoelectronic properties can be adjusted. Film morphology was studied using SEM/AFM microscopy while the porphyrin film deposition rates were studied using an electrochemical quartz crystal microbalance. The photoactivity of the films was measured in an iodide/triiodide electrochemical cell and in a bilayer PCBM integrated solid-state cell for determining their potential role in an organic/inorganic solar cell.

EXPERIMENTAL

The electropolymerization of tetrakis-5,10,15,20-(4-aminophenyl)porphyrin (TAPP) is carried out on a fluorine-doped SnO₂ glass electrode (FTO, Pilkington North America, TEC 15) in a three-probe electrochemical cell using a 1 cm² Pt foil counter electrode and Ag/AgNO₃ reference electrode. Solutions were prepared with 0.15 mM TAPP used as received from TCI America with 10 mM tetrabutylammonium perchlorate (TBAP) as supporting electrolyte in a 95:5 or 85:15 (v:v) dichloromethane:pyridine deaerated solution. A combination of cyclic voltammetry (-0.3 to +0.7 V vs. Ag/AgNO₃) and fixed potentiometry is used with a 30 s vertex delay at +0.7 V within each cycle. The resultant polyporphyrin coated electrodes were rinsed with dichloromethane:pyridine and 2-propanol then dried under nitrogen. Electrochemical quartz crystal microbalance (EQCM) measurements were performed on a Pt quartz crystal resonator (AT-cut) operating at 9 MHz controlled with an EG&G PAR 263 potentiostat. Photovoltaic properties were measured illuminating (100 mW/cm²) the active area (0.3 cm²) of a liquid electrochemical cell consisting of the electropolymerized poly-TAPP film, redox electrolyte (0.1 M KI, 0.05 M I₂ in a 80:20 (w:w) solution of ethylene carbonate and propylene carbonate), and FTO glass counter electrode. The bilayer PCBM cell was constructed by drop casting a 2% chlorobenzene solution of PCBM on top of the poly-TAPP electrode followed by Al/LiF metal evaporation.

DISCUSSION

The poly-TAPP films deposited from 3 and 15 CV cycles (with 30 s vertex delay) using dichloromethane solutions containing 15% pyridine form a well-connected, continuous porous network (Figure 2a,b). Film thickness was about 80 nm for 3 to 5 CV cycles and up to 300 nm for films deposited with 15 electrochemical cycles. In general, the film thickness varied (\pm 50 nm) over the surface area of the electrodes (1 cm²); however, comparable nanofibrous structural features were observed throughout the polyporphyrin film. A lower concentration of pyridine results in decreased fiber structure/spacing and decreased pore size (Figure 2c,d).

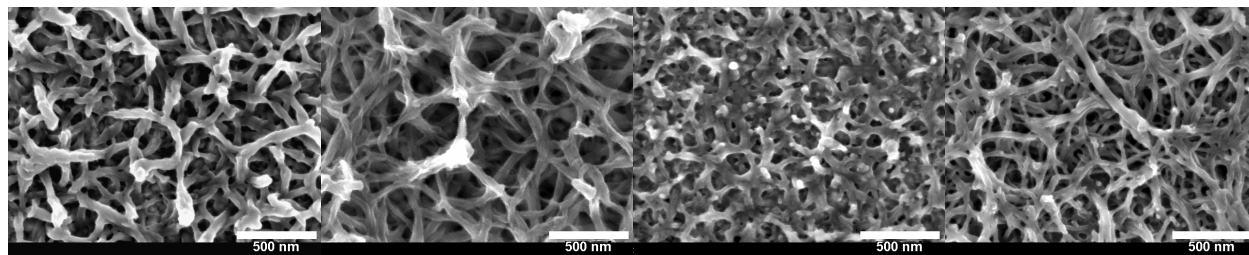


Figure 2. SEM (all at 64K magnification) for poly-TAPP electrochemically grown from CH₂Cl₂:pyridine (85:15) for (a) 3 cycles and (b) 15 cycles. Poly-TAPP electrochemically grown from CH₂Cl₂:pyridine (95:5) for (c) 3 cycles and (d) 15 cycles.

Poly-TAPP films made using the same potentiometric method but without pyridine in the electrochemical solution using 3 or 15 electrochemical cycles have a complex fibril structure with larger fiber dimensions and porosity as seen in Figure 3. The films created without pyridine have a more bundled fiber structure with significantly larger (0.5-1.0 μm) open pores. The structural features of these films are non-uniformly distributed across the electrode surface.

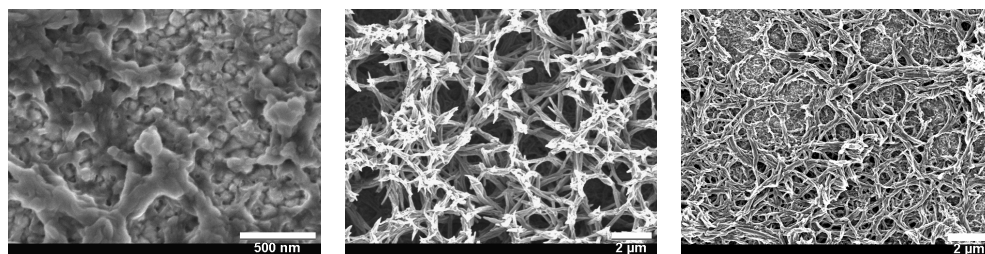


Figure 3. SEM images for poly-TAPP electrochemically grown from a dichloromethane solution at 20 mV/s for (a) 3 cycles and (b, c) 15 cycles.

Cyclic Voltammetry/Quartz Crystal Microbalance Analysis

Cyclic voltammograms of the first three CV cycles are shown for poly-TAPP films electrodeposited from dichloromethane solutions containing 5% pyridine (Figure 4a). At the vertex of each scan (+0.7 V) the potential was held for 30 s to enhance the amount of porphyrin deposited during each cycle. The delay depicted as the flat vertical line at +0.7 V indicates polymerization slowing during the delay time. This behavior suggests diffusion limitations for further porphyrin oxidation.

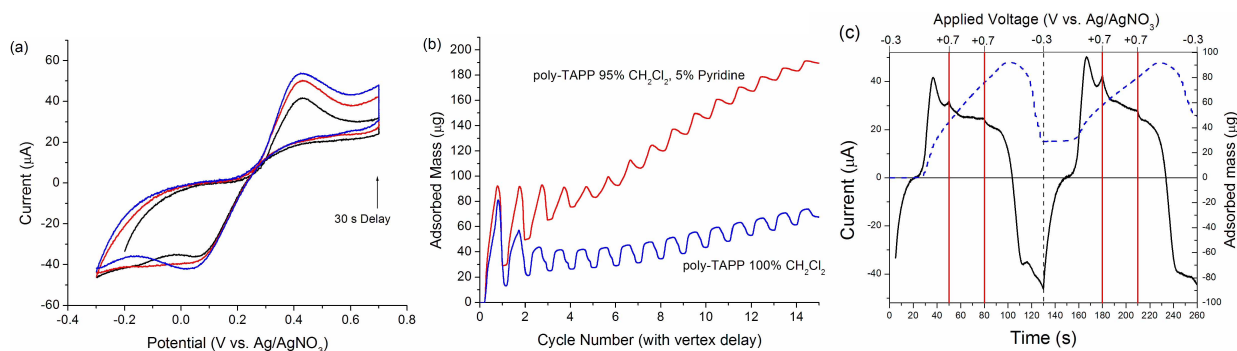


Figure 4. (a) Cyclic voltammogram of the first three cycles of TAPP electropolymerization with 5% pyridine; (b) electrochemical quartz crystal microbalance (EQCM) data for 15 cycles of growth with and without 5% pyridine; (c) combined CV (current, solid line) and EQCM (mass, dotted line) data for the first two cycles of electropolymerization of TAPP with 5% pyridine; the solid vertical lines show the 30 s constant potential delay at +0.7 V.

Film growth was also monitored using an electrochemical quartz crystal microbalance (EQCM) by electrochemically depositing poly-TAPP directly on the platinum-coated quartz crystal electrode while measuring the resonant frequency (Figure 4b). The oscillations in the EQCM graphs correspond to adsorbed mass variations of the poly-TAPP film as

cations/anions/solvent are adsorbed/desorbed from the electrolyte solution as the charge on the film changes during oxidation/reduction.³ As shown in Figure 4b, the presence of pyridine enhances the initial poly-TAPP electrodeposition process. The magnitude of the mass change per cycle decreases as the number of electrochemical cycles increases. The poly-TAPP film apparently reaches a point where monomer diffusion is hindered (film passivation) after which growth of fibrous poly-TAPP film begins leveling off. Films grown from solutions with no pyridine exhibit an initial variation in adsorbed mass but eventually exhibit characteristics of a nonpassivating electroactive polymer film.

The electrochemical and microbalance data are combined in Figure 4c to reveal the stages of growth during the first two cycles. Mass growth begins at the onset of the TAPP oxidation wave and continues through the constant potential delay and the reverse scan as long as potentials remain positive. Mass is lost abruptly when the potential moves negative, suggesting ejection of counterions (perchlorate) and solvent as the oxidized film returns to neutral. Each cycle plateaus at an increased mass, presumably corresponding to the adherent poly-TAPP film.

UV-Vis Spectroscopy

The electronic absorption spectrum of the poly-TAPP electrodeposited from dichloromethane:pyridine solutions (Figure 5a) appears much broader but similar to the monomer in solution indicating that the porphyrin chromophore remains intact during the electropolymerization.⁴ The Soret band is broadened and red-shifted from 425 nm for TAPP in solution to 439 nm in the polymer, which is consistent with excitonic interactions between densely packed porphyrins.⁵ By following the λ_{\max} absorbance at 439 nm, the growth of poly-TAPP films from pyridine-containing solutions are in close agreement with EQCM data for film growth during 15 CV cycles (Figure 5b). The lowered absorbance is consistent with the broadening effect ascribed to porphyrin-porphyrin interactions in the film.

The electronic absorption spectrum of TAPP in CH_2Cl_2 is not affected by the presence of pyridine. However, what is most striking from the resulting films is an increased visible absorbance of films synthesized using 100% dichloromethane, with a shifted Soret absorbance

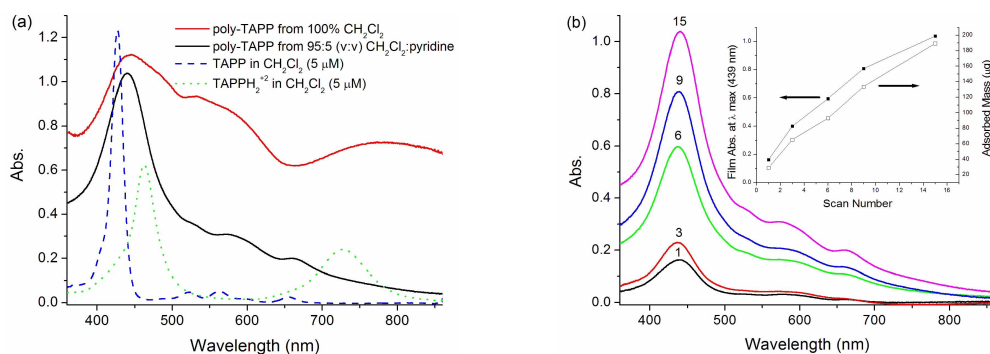


Figure 5. (a) Spectra of TAPP and diprotonated TAPP in solution, poly-TAPP electropolymerized from 100% dichloromethane, and electropolymerized from 95:5 (v:v) dichloromethane:pyridine. (b) Electronic absorption spectra of poly-TAPP deposited on FTO from 1-15 cycles from pyridine-containing solution. Inset: Absorbance at λ_{\max} and mass (from EQCM data) as a function of scans.

and two broad absorbances centered around 550 nm and 775 nm. This effect has been well documented for free-base porphyrins and is called a hyper-porphyrin absorbance spectrum, attributed to the protonation of the pyrrole rings within the macrocycle of the porphyrin resulting in an altered porphyrin geometry with possible extended chromophore and J-aggregation.⁶ The source of the excess acid is attributed to the oxidative polymerization process, in which coupling the porphyrins, presumably at the ortho-aminophenyl locations, leads to loss of two protons per linkage. Protonation of the porphyrin would be expected to hinder the continued oxidative electrochemical growth of the polymer film. A pH dependency has been observed with the oxidation of a poly-TAPP film in aqueous buffers.⁴ Rate acceleration using pyridine has been reported with the electrooxidative polymerization of tetra(p-hydroxyphenyl)porphyrins; however, that effect was attributed to the deprotonation of hydroxyphenyl groups enhancing the oxidation process.⁷

Photovoltaic Properties

The photovoltaic activity of poly-TAPP films was tested using an electrochemical solar cell with a liquid redox agent (I/I_3^-) as well as a solid-state cell constructed using the n-type fullerene (PCBM) to fill the porous porphyrin film with an electron acceptor. In the liquid electrochemical cell, photogenerated excitons are dissociated at the FTO/polyTAPP interface with the liquid electrolyte providing electrons back to the oxidized porphyrin film. To observe photoactivity, thick films of poly-TAPP (~500 nm) were required for sufficient light absorption. These cells exhibited low photocurrent densities ($3 \mu A/cm^2$) and photovoltages (100 mV) (Figure 6a), due in part to low hole mobilities reported for porphyrin films ($1 \times 10^{-8} \text{ cm}^2 V^{-1} s^{-1}$).⁷ The PCBM solid state cell provides the opposite current directionality by using electrodes with two different work functions (FTO/Al). This directs exciton diffusion and dissociation to occur at the poly-TAPP/PCBM interface. The solid state devices exhibited photoactivity when a thin poly-TAPP film (70 nm) was used with a thick PCBM layer (200 nm) drop cast onto the surface of the poly-TAPP film followed by Al/LiF metal evaporation. This device exhibited current densities up to $180 \mu A/cm^2$ and open circuit voltages of 300-500 mV (Figure 6b).

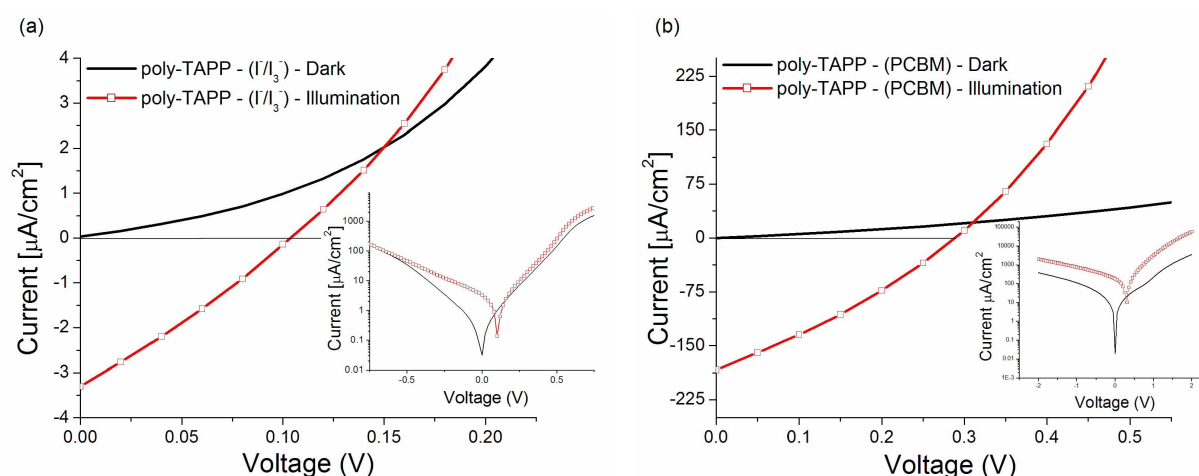


Figure 6. Current-voltage characteristics of (a) poly-TAPP nanoporous electrochemical cell with (I/I_3^-) liquid electrolyte and (b) poly-TAPP/PCBM solar cell in the dark and under 100 mW/cm^2 illumination. Insets - log plots of the same data.

CONCLUSIONS

We have demonstrated the synthesis of an electrochemically deposited, nanofibrous poly-tetrakis(4-aminophenyl)porphyrin film from dichloromethane:pyridine solutions. Electrochemical quartz crystal microbalance measurements show that pyridine enhances the initial electrochemical growth rate of the poly-TAPP films. The films deposited from dichloromethane:pyridine show the absorption spectrum of a neutral porphyrin while those deposited from dichloromethane indicate a partially protonated hyperporphyrin structure. A liquid electrochemical cell with I/I_3^- based electrolyte was used to show the photovoltaic response of these films under AM 1.5 illumination. A solid-state device was constructed using the n-type fullerene derivative PCBM incorporated into the film demonstrating the possibility of a heterogeneous bilayer poly-TAPP photovoltaic device. We are optimistic that these nanofibrous poly-TAPP films will be useful building blocks for the construction of an organic/inorganic solar cell using the electrodeposited high surface area poly-porphyrin film as a photoactive, structure-directing layer.

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REFERENCES

1. K. M. Kadish, K. M. Smith, R. Guilard, *The Porphyrin Handbook*. (Academic Press: San Diego, 2000).
2. B. A. White, R. W. Murray, *J. Electroanal. Chem.* **189** (2), 345-352 (1985).
3. W. Plieth, A. Bund, U. Rammelt, S. Neudeck, L. Duc, *Electrochim. Acta* **51** (11), 2366-2372 (2006).
4. A. Bettelheim, B. A. White, S. A. Raybuck, R. W. Murray, *Inorg. Chem.*, **26**, 1009-1017 (1987).
5. T. J. Savenije, R. B. M. Koehorst, T. J. Schaafsma, *Chem. Phys. Lett.*, **244**, 363-370 (1995).
6. J. R. Weinkauff, S. W. Cooper, A. Schweiger, C. C. Wamser, *J. Phys. Chem. A*, **107** (18), 3486-3496 (2003).
7. T. J. Savenije, R. B. M. Koehorst, T. J. Schaafsma, *J. Phys. Chem. B*, **101**, 720-725 (1997).