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Chlorocarbon and Alcohol Vapor Discrimination by Electropolymerized Ultrathin Chromophore Films

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Metalloporphyrin containing thin film colorimetric sensors for volatile organic compounds (VOCs) have been synthesized and characterized. Electropolymerization has been employed to synthesize robust poly-tetrakis(4-aminophenyl)porphyrin films supported on indium tin oxide (ITO) electrodes. This fabrication method afforded fine control over film thickness, yielding rapid and reproducible responses to analytes. Several metalloporphyrins were studied for their sensory response based upon the affinity of particular transition metals for organic analytes. The sensors are capable of distinguishing between several alcohol and chlorocarbon vapors at a high level of statistical significance due to a modulation of film visible absorbance upon exposure to VOC vapors.
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Metalloporphyrins and related compounds, both naturally occurring and synthesized, are widely studied for a variety of applications, including use as photosensitizers, oxygen carriers, catalysts, and chemical sensors. The rich optoelectronic properties of porphyrin complexes are highly tunable by the addition of appropriate substituents and metal ions. The capability of porphyrins to ligate a variety of transition metals allows fine-tuning of chemical properties. Of interest in this study is the chemoselective interaction of metalloporphyrins with volatile organic compound (VOC) vapors due to interactions between the coordinatively unsaturated Lewis acidic metalloporphyrin and an analyte vapor. These interactions have been exploited to build chemical sensors based on the modulation of the porphyrin electronics upon exposure to organic vapors.

In the assembly of chemical sensors, immobilization of a thin film on a solid platform is one common approach for designing robust materials. Many methods of thin film assembly are based upon electrostatic interactions, including spin coating and Langmuir-Blodgett film deposition.[1,2] While electrostatically deposited thin films have demonstrated predictable and selective sensing upon the initial exposure of the sensor to an analyte, electrostatic attractions are easily overcome by exposing molecules to a suitable solvent, potentially resulting in reduced efficacy over repeated use in sensing VOCs. Recently, several reports have focused upon combating this limitation by use of various non-electrostatic deposition techniques including physical deposition methods,[3] incorporation of the sensor in a polymeric matrix,[4] and covalent bonding of monolayers to substrates.[5] We have recently reported on interfacially polymerized polyester metalloporphyrin membranes that are capable of discriminating amongst saturated VOC vapors.[6] However, the interfacial polymerization technique produces films that are on the order of several hundred nanometers thick, yielding a diffusion-limited sensory response that is not optimal.

In this study, we have synthesized covalently linked porphyrin containing thin films by electropolymerization of porphyrins with p-aminophenyl substituents in the meso positions, first reported by Murray and coworkers.[7] Electropolymerization of porphyrins has been extensively studied over the past three decades, with a variety of synthetic routes and porphyrin precursors deposited on electrode materials for wide ranging applications. While early studies focused on synthetic routes to porphyrin electropolymers,[7–10] more recent reports have focused on widely ranging applications, including use as sensors for a number of species.[11–14] In a recent report, Walter and Wamser have reported that the addition of small quantities of pyridine in the synthesis of aminophenyl porphyrin electropolymers yields a catalytic effect in the formation of high surface area nanofibrous polymers.[15] Film deposition by this method affords fine control over film optoelectronic properties, allowing film absorbance to be readily controlled by

number of voltammetric cycles. Further, the high surface area of films made by this method is attractive for chemical sensing applications since analyte-sensor contact can quickly occur on the film surface with minimal diffusion required. Finally, these polymer films are covalently linked, formed from an oxidative coupling reaction analogous to aniline polymerization, thus they are insoluble even upon prolonged submergence in organic solvents.

After electropolymerization of free-base porphyrin thin films, transition metals including Zn(II), Cu(II), and Co(II) were inserted into the porphyrin and the sensing capabilities for VOCs were studied. When considered as an array, the three sensors were found to discriminate amongst all analytes tested. By no means is the idea of an array of colorimetric sensors new; in the field of array-based colorimetric sensing, Suslick et al. have achieved outstanding discrimination amongst a vast variety of analytes using a 36-member disposable sensor array that typically includes a dozen commercially available metalloporphyrins.[16] However, in this study, the focus was upon covalently linked reusable sensor films that have the potential for future optimization by synthetically tailoring the sensing species. By controlling the film thickness and metal identity, selective sensors were fabricated to differentiate among VOCs including alcohols and several chlorocarbons identified by the Environmental Protection Agency (EPA) as harmful to public health when present in drinking water.

Experimental

Materials.— All reagents were used as received unless specified otherwise. Spectrochemical grade solvents (acetonitrile and pyridine) were purchased from Fisher or VWR. Tetrabutylammoniumtetrafluoroborate (TBABF$_4$), zinc acetate dihydrate, and copper(II) acetate monohydrate were obtained from Aldrich. Cobalt(II) chloride was purchased from Baker Chemical Company and 5,10,15,20-tetrakis-(4-aminophenyl)porphyrin (TAPP) was purchased from TCI. Indium tin oxide (ITO) electrodes were obtained from Delta Technologies and cleaned by sonication in ethanol and drying in a stream of nitrogen.

Film preparation.— Electropolymerizations were performed similarly to literature methods,[7,15] using a CH Instruments (Austin, TX) Model 410A Time-Resolved Electrochemical Quartz Crystal Microbalance. All voltammetry experiments were run in acetonitrile with TBABF$_4$ supporting electrolyte with a Pt counter electrode, a Ag/AgNO$_3$ or a pseudo-Ag/AgCl reference electrode, and an ITO working electrode. Typically, 0.10 – 0.20 mM TAPP was dissolved by sonication in 95% acetonitrile/5% pyridine with 10 mM TBABF$_4$ supporting electrolyte. At a scan rate of 20 mV/s, the cell potential was cycled between 0 V and 1.4 V. Post-deposition, the film-modified ITO electrode was rinsed in acetonitrile, dried under a stream of nitrogen and stored in the dark.

Vapor sensing measurement and analysis.— Electronic absorption spectra of ITO supported films were recorded on a Perkin Elmer Lambda 35 UV/Vis Spectrometer in a glass cuvette. For vapor sensing measurements, the cuvette was equipped with a coil of copper wire to keep the slide elevated from the bottom of the cuvette to prevent the liquid analyte from contact with the film. When testing the sensing of a given analyte, the cell was sealed with a rubber septum and an initial spectrum of the film was collected. Then, a 100 μL aliquot of the VOC analyte was added to the cuvette via syringe injection and allowed to equilibrate for three minutes. A second spectrum was then obtained. The VOC was subsequently removed via syringe and the cuvette containing the slide was dried under nitrogen purge for three minutes before collecting the next spectrum then reintroducing the analyte. This procedure was repeated for four trials for each VOC studied.

For each sensor-analyte pair, film absorbance was tabulated at analytical wavelengths of 425 nm and 550 nm both in air and in saturated analyte vapor for each trial. After averaging absorbances for all trials and computing standard deviations, percent differences in absorbance at both analytical wavelengths for each pair were calculated. The responses of each sensor-analyte pair were classified by solvent type for comparisons, breaking the seven solvents studied in to two classes, alcohols and chlorocarbons. Data for the analyte classes were subjected to a two-tailed Student's t-test. The sensors were considered to be weakly discriminating between two analytes if the responses were found to be different at the 95% confidence interval and strongly discriminating when different at the 99.9% confidence interval.

Results and Discussion

Synthesis and metalation.— Films were deposited from 19:1 acetonitrile:pyridine onto ITO coated glass slides. As films deposited, decreasing anodic current was observed with increasing scan cycles, Figure 1. This current attenuation was similar to that observed by Guo et al. for films deposited from sulfuric acid,[13] suggesting that these films are likely of either very low or no conductivity. The decreasing current observed is indicative of a diffusion limitations to current flow, as electron hopping must occur for electronic communication as layers are added.[10,17]
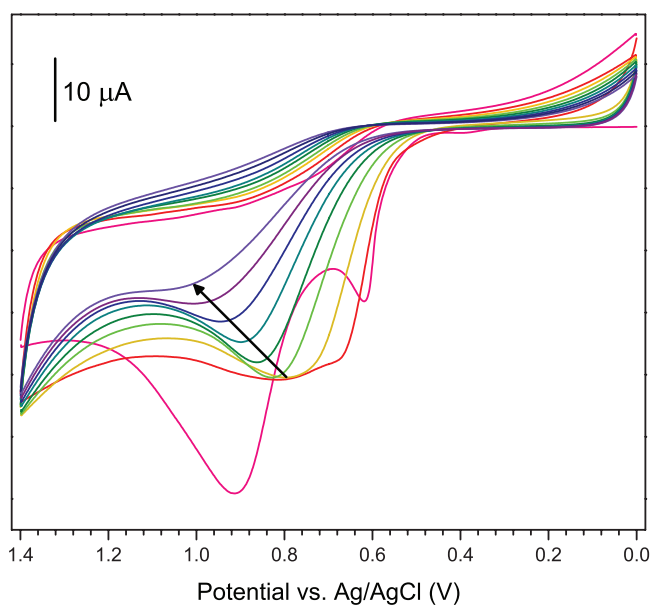

Figure 1. (Color online) Cyclic voltammetric polymerization of 0.10 mM TAPP on ITO by repeated anodic cycles in 19:1 acetonitrile:pyridine with 10 mM TBABF$_4$ supporting electrolyte. The first cycle shows two distinct oxidations at 0.6 V and 0.9 V which begin to coalesce in the second and remaining cycles as indicated by the arrow.
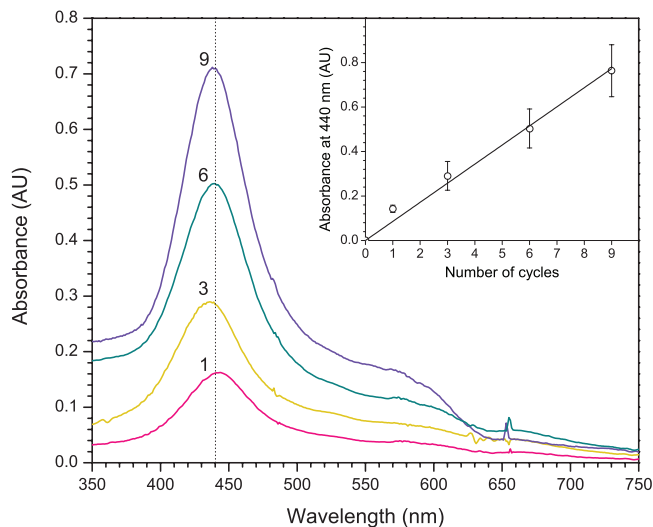

Figure 2. (Color online) Absorption spectra in air of ITO supported TAPP electropolymer generated at 1, 3, 6 and 9 cycles. Inset: Absorbance at the Soret peak (440 nm) increases in a linear fashion for the first 9 cycles.

Examination of visible absorption spectra of films indicate that deposition occurs in a controlled fashion, with linear increases in absorbance with cycle number for up to nine voltammetric cycles as shown in Figure 2. The reproducibility of film fabrication by this method is highly attractive for sensor applications, as numerous sensing platforms with very little deviation in optoelectronic properties can be produced and studied over a period of time. Our previous studies have suggested that fine control over film thickness is critical for rapid and full response to analytes, as thicker films will display diffusion limited responses.[6]

Often, porphyrins are first metalated and then polymerized in the generation of metalloporphyrin electropolymers and other thin films.[18–21] In order to streamline the fabrication of a variety of metalloporphyrin films without modifying the electropolymerization scheme to account for variations in monomer solubility and redox potentials upon metalation, free base films were formed and then post-synthetically metalated as described previously.[6] Spectra taken after metalation indicate the coalescence of the four Q-bands to two, indicating successful metalation, Figure 3. In this study, TAPP films were metalated with zinc(II), copper(II), and cobalt(II). All three
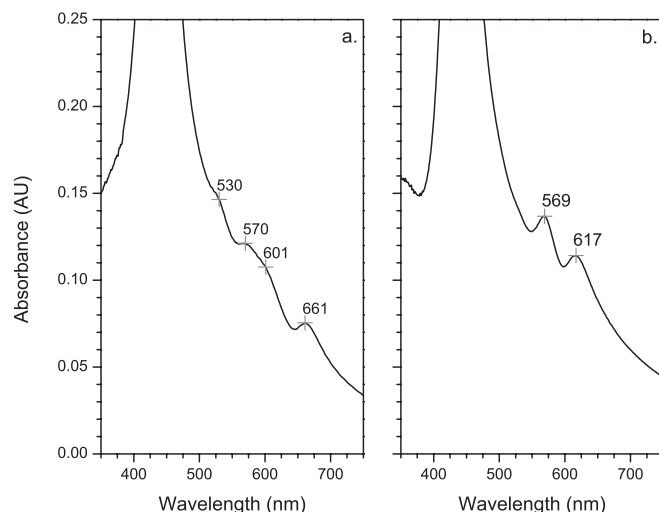
Figure 3. Absorption spectra in air of ITO supported TAPP electropolymer (a.) before and (b.) after zinc metalation.
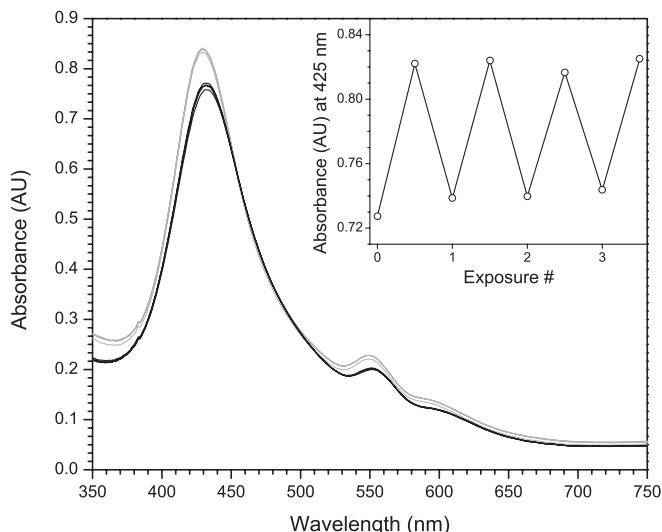
Figure 4. Absorption spectra for a Cu(II) porphyrin polymer before (black) and after (gray) exposure to ethanol vapor. Inset: absorbance at 425 nm as a function of analyte addition-removal cycles.

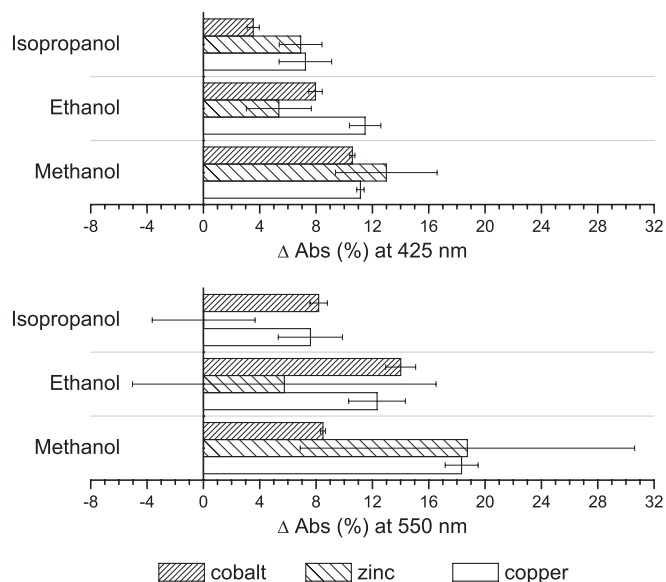**Figure 5.** Sensor response to alcohol vapors at 425 nm (top) and 550 nm (bottom).

metals were observed to alter the optoelectronic properties of the films in a manner suggesting that complete or near complete conversion of the free base porphyrin monomers to metalloporphyrins occurred. These three metals were chosen to complement previous studies.[6] Briefly, all three metals form stable coordinatively unsaturated complexes with the porphyrin and all three have previously shown to have weak affinities for binding with the analytes of interest in this study. The weak affinities are particularly important, as reversible sensing can be achieved if the analyte is easily unbound.[22–24]

Vapor sensing.— As previously reported,[25] films were exposed to analyte vapor for three minutes, followed by the removal of the analyte and drying of the cuvette and film under a stream of nitrogen. A glass cuvette in which the slide was elevated by being pressed against the glass by a spring facilitated the testing of numerous analytes with one sensor film, as the slide was held in place between trials. While the film thickness was very consistent across the electrode surface, immobilization of the sensor in this fashion further increased sensing reproducibility.

Upon exposure to VOCs, films typically showed a Soret blue shift of 2–4 nm with an accompanying increase in absorbance, Figure 4. The Q-bands also blue shifted 2–4 nm, however the relative increase in absorption varied with respect to that observed for the Soret band. Analytical wavelengths of 425 nm and 550 nm were used for all sensors-analyte combinations. These two wavelengths are in the proximity of all three sensor Soret and higher energy Q-band maximum absorbances. By choosing consistent points at which to monitor all sensors, eventual construction of a high-sensitivity sensor array is possible.

After confirmation that the sensors responded reversibly to a given analyte, Cu(II), Co(II) and Zn(II) TAPP electropolymers were exposed to saturated vapors of alcohols and chlorocarbons and visible absorption spectra were collected for each exposure as described above. The sensors were successively exposed to each analyte four times; films showed no spectral degradation or change during testing and complete reversibility of the sensory response between trials, Figure 4. The films responded with tremendous consistency between trials, and all returned to their initial states when the analyte was removed. Even after dozens of trials using multiple analytes, the films showed no degradation.

Alcohol vapor sensing.— The responses of the three sensors to methanol, ethanol and isopropanol are shown in Figure 5. For each

sensor, the response to each analyte is presented as a percent change in absorbance at the two analytical wavelengths 425 nm and 550 nm, in close proximity to the Soret and higher-energy Q-bands respectively. The most effective of the three sensors for the alcohols was the cobalt(II) sensor. This sensor was found to strongly discriminate amongst all three vapors when compared at 425 nm, that is, differentiation between all three alcohols at the 99.9% confidence interval was observed. Additionally, when monitored at 550 nm, strong discrimination between ethanol and both methanol and isopropanol was observed, although methanol and isopropanol did not yield statistically significantly different results. The other two sensors showed much wider standard deviations in their responses to the alcohols, not allowing either of them to strongly discriminate amongst all three of the analytes at either analytical wavelength. However, each of the other two sensors are effective at differentiation for two of the three alcohols at the 95% confidence interval, considered in this study to be weakly discriminating. The zinc(II) sensor is able to weakly discriminate methanol from ethanol and methanol from isopropanol but cannot distinguish between ethanol and isopropanol at 425 nm. Data collected at 550 nm for the zinc(II) sensor showed a very high level of variation, with standard deviations so significant that discrimination amongst all alcohol vapors was poor, yielding only weak discrimination between methanol and isopropanol. The copper(II) sensor was unable to differentiate methanol from ethanol, although it could weakly discriminate isopropanol from both of the other two at 425 nm and strongly discriminate isopropanol from methanol at 550 nm.

Most notable of the alcohol sensing results is the ability of the cobalt(II) sensor to discriminate all three analytes at the highly rigorous 99.9% confidence interval at 425 nm. While the zinc(II) and copper(II) sensors were not outstanding for discrimination amongst all three alcohol vapors, they can be used in the fabrication of an array sensor in which two or three sensing elements are observed at a common analytical wavelength leading to redundancy and higher level discrimination than any one sensor alone.

Chlorocarbon vapor sensing.— The responses of all three sensors to chlorocarbon vapors are shown in Figure 6. The cobalt(II) sensor, which had been the most effective with the alcohols, responded strongly to all chlorocarbon vapors, but was the least discriminatory of the three. It was only capable of strongly discriminating dichloromethane from both trichloroethane isomers at 425 nm and dichloromethane from 1,1,2-trichloroethane at 550 nm. The
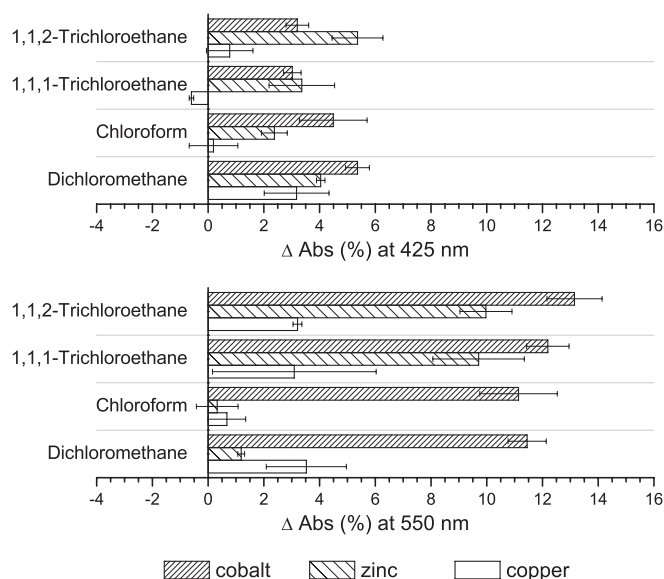
Figure 6. Sensor response to chlorocarbon vapors at 425 nm (top) and 550 nm (bottom).

copper(II) sensor showed weak discrimination between chloroform and dichloromethane at both analytical wavelengths. Further, at 425 nm, there was discrimination between the two isomers of trichloroethane. The zinc(II) sensor yielded the most notable results for sensing of chlorocarbon vapors. Like the copper(II) sensor, it was capable of discrimination of the two trichloroethane isomers at 425 nm. This sensor also showed outstanding results when comparing dichloromethane to chloroform, yielding strong discrimination between them at both analytical wavelengths. Further, at 550 nm, it showed strong discrimination of each chloroform and dichloromethane from both trichloroethane isomers.

While none of the sensors on their own were able to discriminate amongst all four chlorocarbon vapors, when considered as an array, discrimination at the 95% confidence interval for all four is achieved. These electropolymerized sensors showed much stronger interactions with the chlorocarbons across the board when compared to our previous studies using the much thicker interfacially polymerized sensors. Further, in previous studies, results for trichloroethane isomer sensing were not included, as the previous generation of sensors was unable to distinguish between these remarkably structurally similar analytes while these sensors could do so.

Conclusions

Porphyrin multilayer thin films have been synthesized via electropolymerization of 5,10,15,20-tetrakis-(4-aminophenyl)porphyrin onto ITO-coated glass substrates. The formation of these films occurs in a controlled fashion, with linear increases in porphyrin absorbance with each voltammetric cycle, allowing for fine control over film thickness and optoelectronic properties. The films were metalated with Co(II), Cu(II), and Zn(II) and the metalloporphyrin films were exposed to alcohol and chlorocarbon vapors to test their efficacy as VOC sensors. Upon VOC exposures, reversible changes in

the visible absorbance of the films occurred with specific responses recorded for each sensor/analyte pair. Discrimination was shown between alcohol and chlorocarbon vapors with zinc, copper and cobalt films, with excellent reversibility. Most notably, the Co(II) sensor was able to strongly discriminate amongst all three alcohol vapors while the Zn(II) sensor and Cu(II) sensors could distinguish between 1,1,1-trichloroethane and 1,1,2-trichloroethane and the Zn(II) sensor strongly discriminated between chloroform and dichloromethane. As an array, the three sensors are more highly selective than each standing alone and we envision that a catalog of polymeric sensors could be generated, further enhancing the selectivity for these and other analytes.

Ongoing studies are addressing sensitivity upon submergence in dilute aqueous solutions of target analytes. Upon sensor exposure to step-wise additions of analyte, discernable and incremental changes in visible absorbance occur. For example, the copper(II) porphyrin sensor senses methanol in water with a detection limit of one percent. To further enhance sensitivity, we are also optimizing electropolymerization on quartz crystals, with a goal of simultaneously sensing dilute VOCs with spectroscopic and QCM-based methods.

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