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Detection of Volatile Organic Compounds Using Porphyrin Derivatives

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Seven different porphyrin compounds have been investigated as colorimetric gas sensors for a wide range of volatile organic compounds. The porphyrins examined were the free base and Mg, Sn, Zn, Au, Co, and Mn derivatives of 5,10,15,20-tetrakis[3,4-bis(2-ethylhexyloxy)phenyl]-21*H*,23*H*-porphine. Chloroform solutions of these materials were prepared and changes in their absorption spectra induced by exposure to various organic compounds measured. The porphyrins that showed strong responses in solution were selected, and Langmuir−Blodgett films were prepared and exposed to the corresponding analytes. This was done to determine whether they are useful materials for solid state thin film colorimetric vapor sensors. Porphyrins that readily coordinate extra ligands are shown to be suitable materials for colorimetric volatile organic compound detectors. However, porphyrins that already have bound axial ligands when synthesized only show a sensor response to those analytes that can substitute these axial ligands. The Co porphyrin displays a considerably larger response than the other porphyrins investigated which is attributed to a switch between Co(II) and Co(III) resulting in a large spectral change.

1. Introduction

There are increasing concerns about the impact of gaseous toxins released either maliciously or inadvertently as pollution from industry or combustion engines. Accurate information about the concentration of these toxins is required, so it is possible to determine their impact upon the environment and the health and safety of those living and working close to their sources. However, collecting such information is hindered because affordable, accurate, and reliable sensors capable of quantifying the presence of such toxins have not as yet been developed. Therefore, there is a strong motivation to develop more economical gas sensors for the monitoring of low concentrations of volatile organic toxic gases.

At present, readily available gas sensors include those that use semiconducting metal oxides such as tin, tungsten, or chromium titanium oxides.[1,2] These materials change conductivity when they interact with an oxidizing or reducing analyte. However, they do not respond well to humid conditions, and they require high operating temperatures of ∼150−600 °C. Other well-known sensor devices include liquid electrolyte fuel cells and infrared sensors.[3] Conducting polymers[4] have achieved limited success as "electronic nose" devices and phthalocyanines have attracted attention as semiconductometric sensors.[5] However, the majority of these organic sensors suffers from slow response times and incomplete recovery in the absence of the analyte vapor.

Porphyrins are highly stable and possess distinctive UV−visible absorption spectra due to their highly conjugated π-electron systems.[6] If the analyte under investigation has a sufficiently strong interaction with the porphyrin, the energies of the conjugated π-electrons in the porphyrin are shifted, and hence the absorption spectrum changes. Considerable work has already been performed to develop a porphyrin-based sensor system for NO_2,[7−10] and porphyrin-based sensors are also being incorporated into single use colorimetric sensor arrays to detect volatile organic compounds.[11,12]

This work is a study of seven different porphyrins (see Figure 1): EHO in its free base form and also when metalated with Mg, Sn, Zn, Au, Co, and Mn. We compare the reaction of these porphyrins with a broad range of different volatile organic compounds, and the aim of this work is to determine the suitability of these porphyrins for use as selective optical-based gas sensors for the different volatile organic analytes. Various metallo-porphyrins are known to form complexes with organic compounds and are therefore likely to result in strong optical changes upon exposure to the organic analytes. Their potential selectivity and ability to produce a visible optical change makes these materials very attractive as a low cost sensor system because the human eye could be used as the detection mechanism. Therefore, any high costs associated with fabricating a sophisticated detector are negated by making use of the high sensitivity of the human eye. The seven porphyrins were tested in solution for changes in their optical absorption upon exposure to the full range of analytes. These analytes were selected as they cover a wide range of volatile organic compounds that are typical of those commonly produced in industrial and biological processes; e.g., amines are a byproduct produced during the spoiling of seafood; organic acids are common products in spoilt wines; and ethyl acetate is a potentially explosive solvent common in many different industries where improved safety would be beneficial. Those porphyrin analyte pairs that showed a large spectral change upon exposure in the solution experiments were then selected for further investigation. The selected porphyrins were used to fabricate solid state Langmuir−Blodgett films which were subsequently exposed to the corresponding

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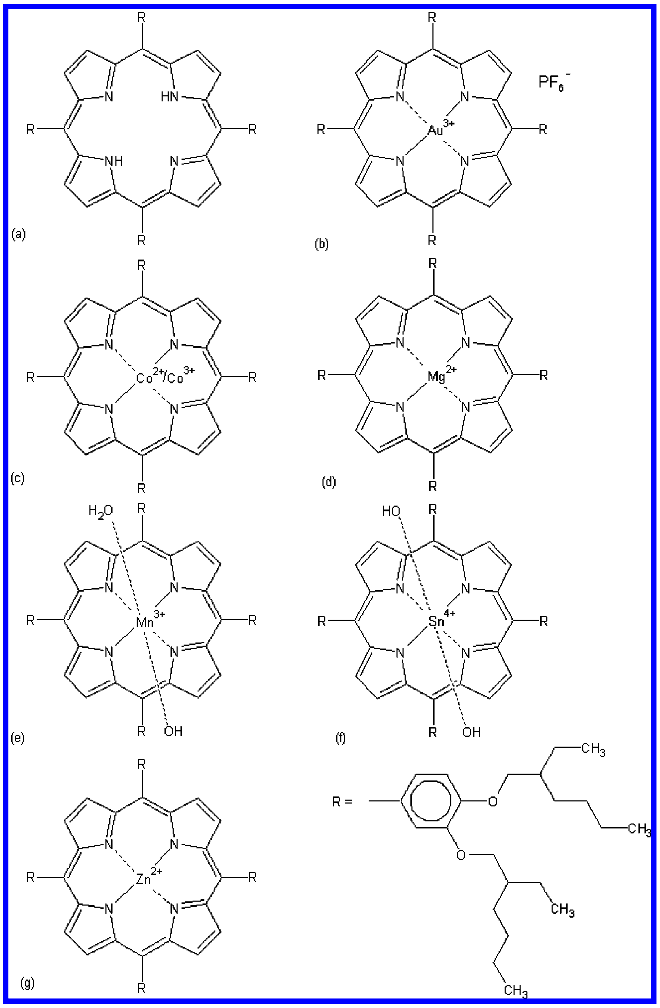

Figure 1. Molecular structure of the porphyrins used in this study.

analyte. The morphologies similar to the Langmuir−Blodgett films after transferring to a solid substrate are presented in ref 13. The materials and experimental procedures used are described in the next section, followed by discussion of the results, and finally some conclusions are stated.

2. Materials and Experimental Methods

2.1. Synthesis of the Porphyrins and Analyte Details. The synthesis of 5,10,15,20-tetrakis[3,4-bis(2-ethylhexyloxy)phenyl]-21*H*,23*H*-porphine (EHO) is described elsewhere,[8] and its chemical structure is shown in Figure 1(a). Upon metalation, the two hydrogen atoms in the center of the porphyrin ring are replaced with the corresponding metal ion. The metal derivatives of 5,10,15,20-tetrakis[3,4-bis(2-ethylhexyloxy)phenyl]-21*H*,23*H*-porphine were prepared in accordance with literature methods.[14] To prepare the Au(III) porphyrin, free base EHO was refluxed with excess potassium tetrachloroaurate(III) and sodium acetate in glacial acetic acid. After 48 h, the reaction mixture was cooled and treated with 10% sodium carbonate solution before being extracted with dichloromethane. This organic solution was washed with 10% potassium hexafluorophosphate and then concentrated (see Figure 1(b)). Co was inserted into the free base EHO by adding an excess of cobalt(II) acetate to a solution of the free base EHO dissolved in dichloromethane and methanol (7:3) at room temperature. Mg EHO was prepared at room temperature in dichloromethane using magnesium bromide ethyl etherate and triethylamine (see Figure 1(d)). Mn EHO was prepared by refluxing the free base EHO with excess manganese acetate in glacial acetic acid. Following a basic workup with dilute sodium hydroxide, the Mn(II)porphyrin initially formed is rapidly oxidized to Mn(III) EHO (see Figure 1(e)). To insert tin, the free base porphyrin was refluxed with tin(II) chloride in pyridine followed by stirring with sodium hydroxide solution (see Figure 1(f)). Zinc was inserted into the free base EHO by using excess zinc acetate in dichloromethane at room temperature (see Figure 1(g)). All six metalloporphyrins upon reaction completion were purified using column chromatography. The analytes used are 1-octanol, hexylamine, octanal, acetic acid, 1-hexanethiol, 2-butanone, ethyl acetate, trimethyl phosphite, octylamine, and triethylamine. They were all provided by Sigma Aldrich and used as supplied.

2.2. Solution Absorption Measurement. Solutions of the free base and metalated EHOs were prepared at concentrations of 4.0×10^{-6}, 3.2×10^{-6}, 2.6×10^{-6}, 4.0×10^{-6}, 4.0×10^{-6}, 4.0×10^{-6}, and 4.0×10^{-6} M for the free base, Mg, Sn, Zn, Au, Co, and Mn EHO, respectively, using chloroform as the solvent (used as supplied by Sigma-Aldrich). Quantities of 2 mL of each of these EHO solutions were placed in quartz cuvettes, and initial absorption spectra of the solutions were recorded using an Ocean Optics USB2000 spectrometer with a Mikropack Mini D2 UV−vis−IR light source. The absorbance spectra for each porphyrin solution were measured across the range 350−850 nm with respect to a reference taken of chloroform. Then 20 μL of the analyte to be investigated was added and the mixture stirred before repeating the absorption measurement. More analyte was added 20 μL at a time and the absorption recorded each time until no further spectral changes were observed. This process was repeated for the seven EHOs with each of the ten different analytes described in the materials section 2.1. Absorbance spectra of each of the analytes mixed with chloroform (i.e., no porphyrin present) were also recorded with respect to a chloroform filled quartz cuvette reference, to confirm the range of optical transparency of each analyte.

2.3. Langmuir−Blodgett Film Preparation and Absorption Measurement. Langmuir−Blodgett (LB) films of each of the porphyrins selected on the strength of their corresponding solution interactions, i.e., free base, Mg, Zn, Co, and Mn EHO, were prepared from concentrated chloroform solutions (~0.3 mg/mL). Typically, 150 μL of the EHO solution (~0.3 mg/mL) was spread on a clean water (Elga PURELab Option >15MΩcm) subphase surface in a NIMA model 611 Langmuir−Blodgett trough. After evaporation of the solventm the film was compressed to and then held at a surface pressure of 15 mN/m while deposition onto a glass plate (rendered hydrophobic by exposure to 1,1,1,3,3,3-hexamethyldisilazane vapors for 12 h) was carried out. Deposition was performed by inserting and withdrawing the glass plate vertically at a rate of 10 mm/min. Ten excursions were performed for each plate resulting in the deposition of 20 layers (one layer for each of the up and down strokes). If necessary, so as to maintain the surface pressure at 15 mN/m, the deposition was halted, while the trough barrier was retracted and more of the solution added to the subphase before recompressing to 15 mN/m again and continuing the deposition.

A purpose built sensor testing chamber was used to expose the solid state sensor films to the analyte vapors (see ref 12 for more details). The delivery of clean dry nitrogen to a chamber containing the analyte was controlled with a Tylan FC-260 mass flow controller. The temperature of the analyte was maintained at 0 °C by submerging the analyte chamber in iced water, therefore mixing the N_2 gas with the analyte at a known vapor pressure. For the analytes used, this method of producing analyte

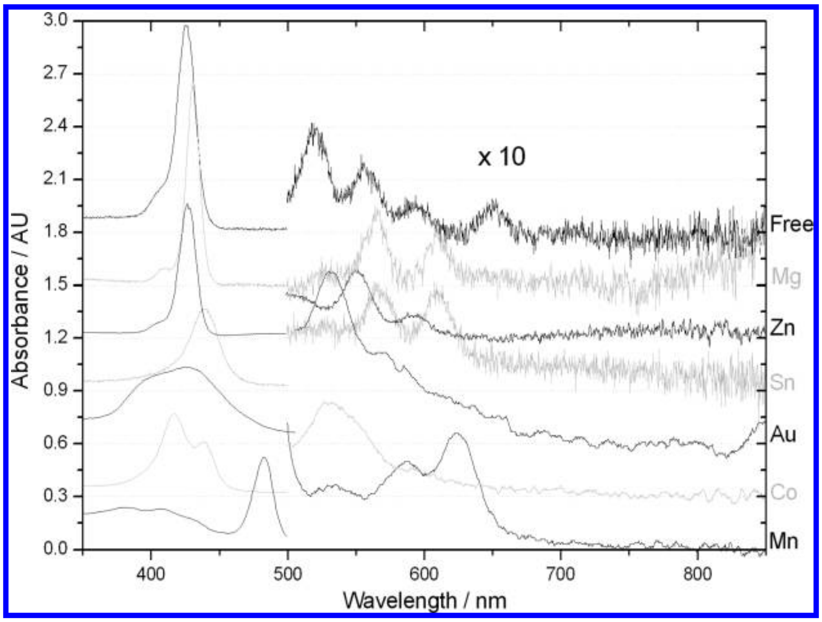

Figure 2. Absorbance spectra of the seven porphyrin solutions prior to exposure. Each spectrum is offset by 0.3 au from the previous for clarity, and the data at wavelengths longer than 500 nm have been multiplied by ten. Note the double peak observed for the Co EHO solution at 417 and 439 nm.

TABLE 1: Absorbance Peak Positions for Each of the Seven Porphyrins Prior to Exposure to the Analytes

	absorbance peak positions			
	solution		Langmuir−Blodgett film	
porphyrin	Soret	Q bands	Soret	Q bands
free base	426 nm (405 nm shoulder)	519, 556, 592, and 652 nm	439 nm (asymmetric)	521, 555, 597, and 652 nm
Mg EHO	430 nm (409 nm shoulder)	567 and 610 nm	435 nm (vague shoulder)	571, 613, and 657 nm
Zn EHO	426 nm (408 nm shoulder)	550 and 593 nm	436 nm	560 and 604 nm
Sn EHO	440 nm	566 and 610 nm	-	-
Au EHO	428 nm (398 nm shoulder)	532 nm (570 nm shoulder)	-	-
Co EHO	417 and 439 nm	531 nm (550 nm shoulder)	427 nm (single broad peak)	546 nm
Mn EHO	483 nm (broad feature, 350−450 nm)	533, 588, and 625 nm	480 nm (broad feature, 350−450 nm)	none observed

vapor at a known vapor pressure results in concentrations of approximately 2600 ppm (acetic acid), 32 000 ppm (butanone), 32 000 ppm (ethylacetate), 940 ppm (hexane thiol), 2200 ppm (hexylamine), 670 ppm (octanal), 3 ppm (octanol), 180 ppm (octylamine), 15 000 ppm (triethylamine), and 5900 ppm (trimethyl phosphate) for each of the different analytes correspondingly (further details are provided in Supporting Information). The main purpose of this study was to determine the ability of the different porphyrins to sense different analytes, and therefore the exact concentration of each analyte used was not crucial provided it was reasonably high, as they were. Further studies are required to determine the sensitivity, stability, reversibility, and dynamics of each sensor action for each sensor−analyte pair. The cooling of the gas also helped to reduce cross contamination problems due to condensation of the analytes onto the walls of the delivery pipes which were at room temperature and therefore warmer than the analyte vapors. Light was delivered and collected from the chamber by optical fibers connected to a World Precision Instruments Spectromate spectrophotometer which incorporates a tungsten white light source and a multichannel photodiode detector allowing the absorption spectra of the film under test to be recorded in situ every 3 s over the spectral range 350−850 nm. The exhaust gas passes through an activated charcoal filter to absorb the toxic vapor before being vented to the atmosphere. The presence of analyte vapors in the test chamber was found to cause increased scattering and therefore increased the optical absorbance at all wavelengths. In these experiments, such effects were accounted for by subtracting a reference absorbance (measured at 700 nm where all the samples investigated are transparent) from the recorded experimental data. The before and after exposure spectra and the calculated difference spectrum for each of the thin film analyte pairs studied are included in the Supporting Information.

3. Results and Discussion

Porphyrins possess a delocalized π-electron system associated with the highly conjugated porphyrin ring. Upon exposure with light with a photon energy greater than the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) energy gap, photons are absorbed causing excitation of electrons from the HOMO to the LUMO. The energy separation between the HOMO and LUMO levels is such that the photons absorbed are in the visible wavelength range giving the molecules their colorful appearance. The spectra generally consist of a strong Soret absorbance at shorter wavelengths (between 350 and 500 nm) and a number of Q-band absorbance features at longer wavelengths (>500 nm). The initial absorption spectra for the seven different EHO solutions are shown in Figure 2, and their peak positions are recorded in Table 1. There are four Q bands for the free base EHO, but for the metalated EHOs there are only two or three Q bands. This is because the metalated EHOs have increased symmetry, therefore making the energy levels involved in the Q-band absorption degenerate and thus reducing the number of visible absorption bands.

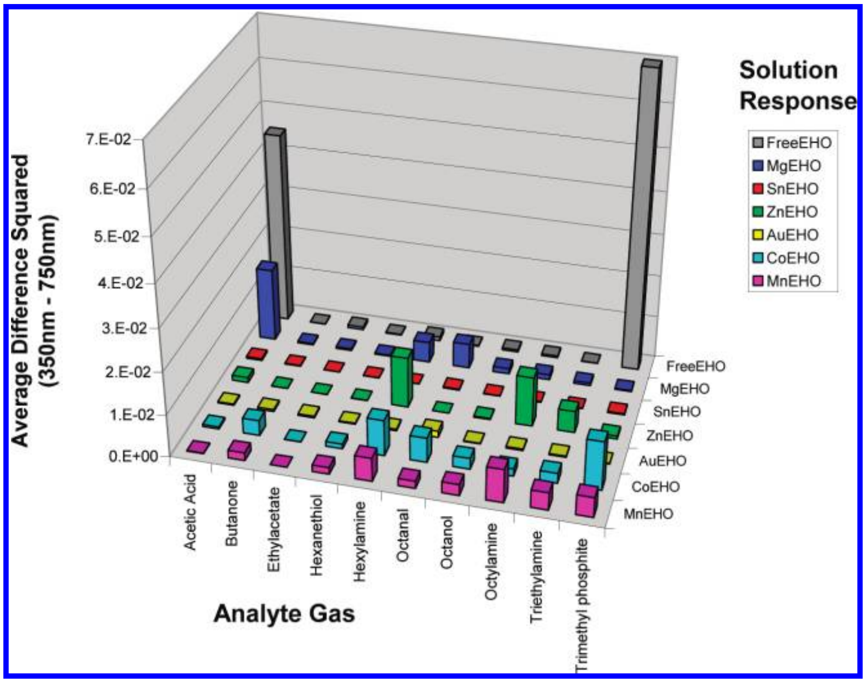

Figure 3. Summary of the sensor response for the seven porphyrins in chloroform solution with various organic analytes.

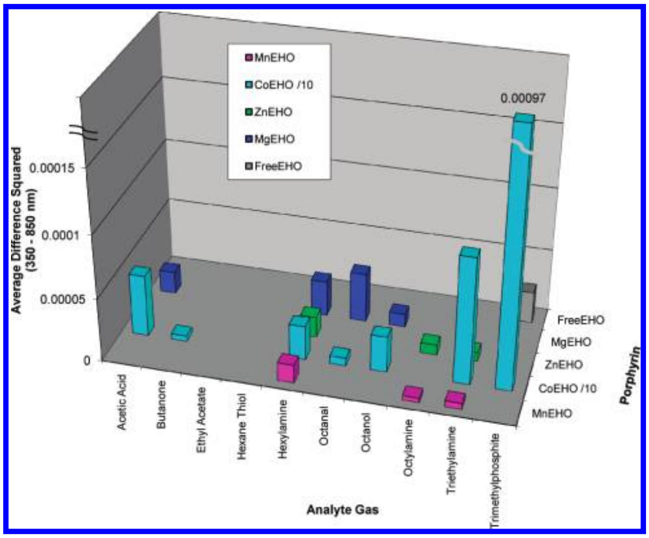

Figure 4. Summary of the sensor response for LB films of the porphyrins with various organic analytes. Only the sensor−analyte pairs which generated strong responses in the solution experiments were conducted (in some cases the acetic acid result is not reported since it destroyed the LB films). NB. the Co EHO responses are very strong and therefore have been reduced by an order of magnitude so all the data can all be presented on the same chart. The Co EHO response to trimethyl phosphate has also been truncated.

The absorption spectra of the different analytes were measured, and it was found that all the analytes are highly transparent from 350 to >850 nm. Short wavelength (<350 nm) absorption features which were observed in some of the interaction experiments (data not shown) containing octanal, butanone, and triethylamine are simply due to absorption by unreacted analyte in the solution rather than due to any interaction with the porphyrin, as observed by measuring the analyte and solvent (without any porphyrin) references.

To be useful as an optical sensor, the absorption spectrum of the sensor material must change upon exposure. The interaction upon exposure of 2 mL of the seven different porphyrin solutions to the different analytes is summarized in Figure 3. The difference between the unexposed and exposed spectra was calculated and then squared (such that all differences are positive). The data plotted in Figure 3 are the average of the squared difference in the range 350−750 nm.

For the porphyrin−anaylte pairs that showed strong responses in solution, LB films of the porphyrin were produced and tested with the corresponding analyte. Upon transferring them to a solid substrate to form an LB film, the optical absorption peaks broaden considerably. In some instances, there are also significant shifts in the peak absorption wavelength, usually to longer wavelengths. These changes are assumed to be due to either the removal of solvent effects or aggregation of the porphyrins upon transferring them to a solid substrate or both. Details of the LB film absorption peaks for the LB films studied are given in Table 1. When using solid state LB films rather than solution, in general the color change upon exposure to the various anayltes is more difficult to detect since the absorption peaks are now broader. However, to function as practical gas sensing elements, it is advantageous to have a solid state sensor. Therefore, despite the reduction of the spectral changes observed for the solid state films it is still worthwhile studying their behavior as gas sensors. Figure 4 shows the sensor response for the selected porphyrin−analyte pairings that had a strong response in solution, and again the difference between the unexposed and exposed spectra was calculated and squared.

In the case for the free base EHO when exposed to acetic acid and trimethyl phosphite, the Soret peak is replaced by a broader, lower intensity peak at longer wavelength (∼465 nm), and the four Q bands initially present are replaced with a single broader but more intense absorbance band at much longer wavelength (∼700 nm). A similar reaction for free base EHO upon exposure to NO_2 is reported in ref 15. No other significant responses were observed for the free base EHO in solution. When the free base EHO was fabricated into a solid LB film, its response to trimethylphosphite is considerably weaker than in solution. Therefore, gas sensors made from the free base EHO are highly selective, only responding significantly to NO_2 as reported elsewhere.[15]

Magnesium(II) porphyrins have the tendency to axially bind a fifth and sixth ligand sequentially. It is clear in the literature that hard ligands (such as oxygen and nitrogen) are greatly favored over soft ligands.[19] This may explain the occurrence of responses for Mg EHO exposed to hexylamine and octanal. It was noted that for Mg EHO exposed to acetic acid there was a slow interaction during which the absorbance spectrum changed from that which is characteristic of Mg EHO to that which is typical for the free base EHO before then partially undergoing a further change similar to that observed for free base EHO upon exposure to acetic acid. It has been well documented that Mg (II) porphyrins are demetalated by acids to form the corresponding free base porphyrin.[18] It is therefore likely that exposure to acetic acid causes the conversion of Mg EHO back to the free base EHO. When transferred to a solid LB film, Mg EHO has strong responses to hexylamine and octanal implying that Mg EHO has promise as a sensor material; however, demetalation of the Mg EHO upon exposure to acetic acid as occurs in solution is observed, therefore the chemical stability of Mg EHO films may not be sufficient to make robust sensors. This is also thought to be the reason why the LB film of Mg EHO displays 3 Q bands (Table 1); i.e., the as-formed film may actually be a blend of free base EHO and Mg EHO and as such has a broad Soret, and 3 Q bands can be distinguished.

Sn(IV) porphyrins are known to bind strongly to oxygen-containing ligands (such as alcohols) forming 6-coordinate complexes.[20] Therefore, a response to octanol was expected. However, in our experiments no response is observed for Sn EHO upon exposure to any of the analytes. The Sn EHO when synthesized already has two axial hydroxyl ligands to satisfy the +4 oxidation state of the Sn metal atom. The presence of these ligands may explain the longer wavelength of the Soret peak observed in the unexposed Sn EHO absorbance spectrum. Upon exposure, either the analytes do not exchange with these hydroxyl ligands or if they do this may not affect the absorption spectrum significantly and hence no appreciable optical response is observed. Since our experiments showed no interesting responses for the Sn EHO in solution, Sn EHO LB films were not produced and tested.

Zinc(II) porphyrins are well-known to coordinate nitrogen ligands to form 5-coordinate complexes[16] with an associated change in the Soret absorption spectrum because the metal is pulled slightly out of the plane of the porphyrin in the complex that is formed. The trend for Zn EHO upon exposure to amines is for the Soret absorbance band to both shift slightly to longer wavelength (from 426 to ~433 nm) and and increase in intensity. Meanwhile, the two Q bands shift to longer wavelengths, and often a third Q bands appears. The magnitude of the Soret band shift and the intensity change appear to be dependent upon the amine used during the exposure. Zn EHO initially is thought to have no ligands but upon exposure forms coordinates with the amines, and therefore the particular amine involved will determine the change in symmetry that the porphyrin experiences. Upon transferring to an LB film, the Zn EHO continues to respond to the amines, albeit weakly to the presence of amines. LB films of Zn EHO as an amine detector were the focus of further investigations.[17,21]

The Au EHO when synthesized is a salt with PF_6^- counterion. This may explain the broad features observed in the absorbance spectrum for unexposed Au EHO. The Au porphyrin was expected to exhibit an interaction with hexanethiol since it is known that Au readily forms complexes with sulfur-containing compounds. However, no interactions were observed with any of the analytes. Therefore it is assumed that the Au EHO salt is similar to the Sn EHO in that it does not readily exchange ligands and therefore forms new complexes with any of the analytes. For this reason, LB films of Au EHO were not fabricated and tested.

The absorption spectrum for the Co EHO solution is more complicated than the other EHOs. It has two Soret peaks which are attributed to the presence of both Co(II) EHO and Co(III) EHO in the solution. Stirring the solution tends to cause a shift toward the longer wavelength peak. The absorption spectrum of the Co EHO in solution has two Soret peaks as shown in Figure 2, and upon exposure one of these two peaks becomes dominant. Which peak becomes dominant depends upon whether the analyte used is oxidizing or reducing. Therefore, Co EHO is a very promising material for further development of gas sensing materials. Upon exposure to ethyl acetate no change is observed, and both Soret peaks remain. For butanone, hexylamine, octanol, octanal, octylamine, and triethylamine, the Soret peak at 417 nm reduces or disappears, and the Soret peak at 439 nm increases in intensity. However, for hexanethiol and acetic acid, the opposite occurs; i.e., the 417 nm peak increases in intensity, and the 439 nm peak disappears. The different groups of analytes cause a shift in the balance of the mixed Co(II)/Co(III) to become either Co(II) or Co(III). Upon exposure to trimethylphosphite, the 417 nm peak remains unchanged, but the 439 nm peak shifts to 453 nm, presumably due to a complex occurring for only one of the two oxidation states of Co EHO, presumably Co(III) as the +3 oxidation state will not be completely satisfied by complexing to the porphyrin. When transferred to an LB film and exposed to the various analytes, the response of Co EHO is considerably larger than for any of the other porphyrins (the scale for the Co data in Figure 4 is reduced by an order of magnitude, and the trimethylphosphite column is truncated). The strength of absorbance change for Co EHO upon exposure is thought to be due to the mixed Co(II)/Co(III) system switching to become either Co(II) or Co(III) upon exposure. This allows the Co EHO to coordinate different numbers of ligands depending upon its oxidation state which results in a significant change in the symmetry of the porphyrin ring and hence a large spectral change. Therefore, utilizing this change of oxidation state and the corresponding changes in the absorption spectra holds great promise for the development of highly sensitive toxic gas sensors.

Presumably, other metal ions which can exist in more than one oxidation state should also hold great promise as gas sensors when incorporated into the porphyrin system. Mn can also adopt more than one valence state. When it is incorporated into the porphyrin ring, it rapidly oxidizes to Mn(III) and takes on two different ligands, namely, a water molecule and an OH^- ion. These asymmetric ligands mean that the Mn atom is slightly pulled out of the plane of the porphyrin ring before interaction with any analytes. It is this asymmetry that is thought to result in Mn EHO's atypical absorption spectrum (see Figure 2). In solution, when exposed to amines a small spectral change is observed. The Soret band and the Q-bands shift to slightly shorter wavelengths. It is assumed in this case that the Mn EHO exchanges ligands upon exposure to amines, and this exchange causes a small perturbation of the Mn ion position resulting in an optical change. For Mn EHO, it is thought that the Mn remains in the Mn(III) state unlike the case of Co EHO where a transition from Co(II) to Co(III) is thought to occur. When transferred to an LB film, the Mn EHO continues to show small but significant absorption changes when exposed to amine analytes, and as such Mn EHO holds considerable potential to be used as an amine sensor.[22]

The response of all the selected porphyrin−analyte pairs shown in Figure 4 are comparable to, or stronger than, that of the Zn EHO–amine response. Previous studies of Zn EHO have shown that it can be successfully used to fabricate an alkylamine detector.[17,21] Therefore, all these porphyrin–analyte pairs highlighted in Figure 4 have sufficiently strong responses to be used to develop toxic gas sensors.

4. Conclusions

The responses of several different metallo-porphyrins to a broad range of analytes have been investigated to determine their suitability as optical-based thin film sensors. Those porphyrins that showed changes in their absorbance spectra upon exposure hold considerable potential to be used as gas sensors for the corresponding analyte. It is the process of gaining a ligand or ligand exchange which results in a change of the porphyrin symmetry that results in the spectral changes observed and therefore is a necessary condition to make an effective optical-based gas sensor.

Upon transferring the porphyrins to solid state Langmuir–Blodgett films, spectral changes similar to those observed in solution occurred most of the time. Therefore, porphyrins that readily exchange or coordinate extra ligands in solution are shown to be suitable materials for solid state colorimetric detectors for volatile organic gases. However, porphyrins that already have strongly attached axial ligands when synthesized only show a sensor response to those analytes that can substitute these axial ligands, and as such Au EHO and Sn EHO showed no response to any of the anaytles.

In particular, the response of Co EHO was very strong upon exposure to acetic acid, butanone, hexylamine, octylamine, triethylamine, octanol, octanal, and trimethyl phosphate. This is attributed to switching between the Co(II) and Co(III), resulting in the formation of either fewer or more axial ligands, respectively, with large associated spectral changes. However, not all metallo-pophyrins that can exist in more than one oxidation state showed such strong responses; for example, it is proposed that Mn EHO did not switch oxidation state but merely exchanged ligands therefore displaying considerably smaller spectral changes. While the spectral changes displayed by Mn EHO were considerably smaller than those for Co EHO, they are comparable to those observed for Zn EHO as an amine sensor.[17,21] Therefore, it is concluded that all of the porphyrin–analyte pairs reported in Figure 4 (apart from Mg EHO which was readily demetalated and therefore not sufficiently stable) are sufficiently strong to be used as effective toxic gas sensors.

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Supporting Information Available: The analyte vapor concentration for each of the analytes held at 0 °C in the iced water bath was estimated by extrapolating the data found in the *CRC handbook of chemistry and physics: a ready reference book of chemical and physical data*, 58th ed.; editor Robert C. Weast; Cleveland (Ohio): CRC Press, 1977. The results are shown in table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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