Steplike Response Behavior of a New Vapochromic Platinum Complex Observed with Simultaneous Acoustic Wave Sensor and Optical Reflectance Measurements

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We report the synthesis and characterization of a new vapochromic platinum compound, [Pt(CN−cyclododecyl)$_4$][Pt(CN)$_4$]. This compound is stable to 120 °C and reversibly sorbs three water molecules per formula unit at room temperature when it is exposed to 100% relative humidity. Dramatic changes in absorption and emission spectra are observed in response to water uptake. The vapor response characteristics of this material were further investigated by simultaneous optical reflectance and quartz crystal microbalance (QCM) measurements, using water as the test vapor. The sensing film on the QCM consisted of a mixture of the solid vapochromic powder dispersed in a hydrophobic vapor permeable polymer. The polymer was incorporated as a binder to adhere the sensing material to the QCM surface. Reflectance measurements were taken from the film on the QCM surface using a bifurcated fiber optic bundle incorporated into the flow cell. The vapor sorption characteristics of the vapochromic compound as determined by the QCM were closely correlated with the observed spectral changes. In addition, an unexpected steplike response with increasing water vapor concentration was observed, with little water vapor uptake at low concentrations, followed by a large water uptake with corresponding spectral changes, and then little change with further increases in water vapor concentration. Water vapor uptake as measured by the QCM is in agreement with the bulk gravimetric measurements. The response behavior is rapid (minutes) and reversible. The distinctly nonlinear, steplike response is interpreted as a reversible transition from a nonhydrated form of [Pt(CN−cyclododecyl)$_4$][Pt(CN)$_4$] to a hydrated form with three water molecules per formula unit.

Introduction

Host materials consisting of stacked square planar complexes of platinum and/or palladium salts exhibit striking and reversible color changes upon suspension in solvents or upon exposure to volatile organic compounds and water vapor.[1−6] These spectroscopic changes in response to vapors have been called “vapochromism”. These types of materials are very promising for chemical vapor sensing applications. In general, the structures of vapochromic platinum compounds are similar to the cation/anion stacking motif adopted by Magnus Green Salt (MGS).[7−10] This structure produces the chromophore which arises from the “face to face” interaction of the d^8 cations and anions. In contrast to MGS, the vapochromic platinum compound structures are porous to solvent vapor molecules because of the inefficient packing produced by the sterically bulky ligands. The inefficient packing provides sorption sites and allows the analyte access to the solvatochromic chromophore.

Gravimetric studies have shown that guest−host stoichiometries can be much greater than 1, and they vary with the vapor sorbed. In one case, stoichiometries at room temperature of 12, 6, 8, and 4 have been found for water, chloroform, methanol, and trifluoroethanol, respectively.[4] It has also been observed that unit cell distances expand dramatically upon vapor sorption.[4] While most vapors producing color changes in these vapochromic compounds are capable of donating hydrogen bonds, vapochromic responses to nonpolar organic

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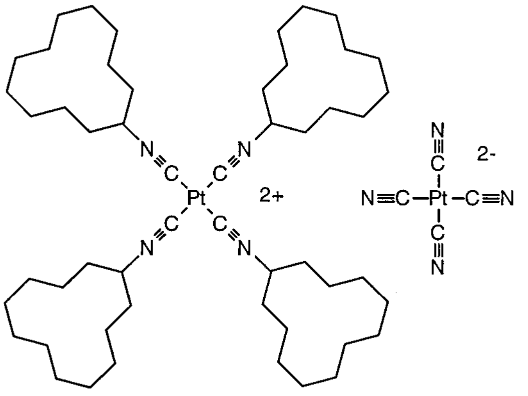

Figure 1. Chemical structure diagrams for the cation and anion in [Pt(CN−cyclododecyl)$_4$][Pt(CN)$_4$], **PtPt**.

vapors have also been found for certain vapochromic complexes.[3]

To date, most reported studies of these compounds describe the color changes observed when the solid is exposed to saturated solvent vapors. In these studies the compounds are either "off" under clean air or "on" in the presence of saturated vapors to which they respond. The responses of these materials at variable vapor concentrations below saturation have not been reported. Moreover, there is also limited information on vapor uptake and its relationship to the observed color changes. A more detailed understanding of the response behavior of these materials is of scientific interest and is also required to determine how best to apply them as sensors in analytical applications.

In the present paper, we describe vapor uptake and vapochromic behavior of the new vapochromic compound [Pt(CN-cyclododecyl)$_4$][Pt(CN)$_4$] (referred to as **PtPt** in this paper) over water vapor concentration ranges below saturation. The structures of the [Pt(CN−cyclododecyl)$_4$]$^{2+}$ cation and the [Pt(CN)$_4$]$^{2-}$ anion in this compound are shown in Figure 1. A method for simultaneous measurement of vapor sorption and spectral changes has been developed using a quartz crystal microbalance (QCM) configured with a bifurcated fiber optic probe that makes reflectance measurements from a film on the QCM surface. This measurement approach is shown schematically in Figure 2. The QCM is a type of acoustic wave device that detects changes in the mass of applied surface layers.[11−16] It was found that **PtPt** absorbs water vapor with spectral changes that correlate with vapor uptake. These studies show for the first time the response behavior of this type of vapochromic compound as a function of vapor concentration and reveal the simultaneous steplike vapor uptake and spectral changes that occur with increasing water vapor concentration.

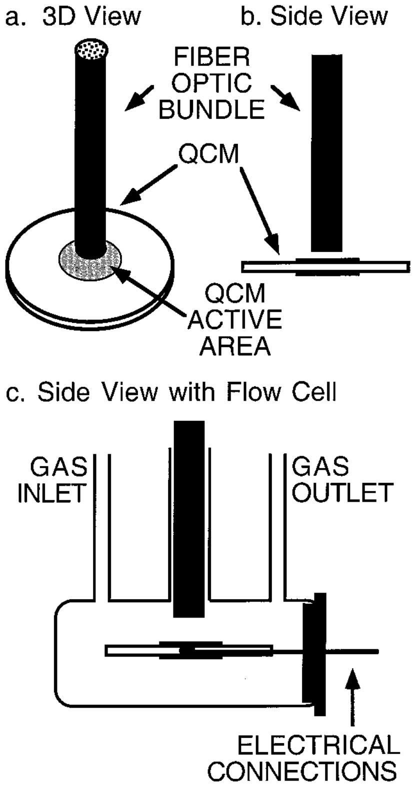

Figure 2. Schematic diagram showing the flow cell for simultaneous reflectance and vapor uptake measurements. The vapochromic film material is located on the top surface of the QCM facing the fiber optic probe. Crystals were $^{1}/_{2}$ in. in diameter with $^{1}/_{4}$-in. diameter electrodes. The fiber optic probe had an outside diameter of $^{1}/_{4}$ in. Gas inlet and outlet tubes were $^{1}/_{8}$-in. outside diameter.

Experimental Section

General Considerations. Acetonitrile was distilled under N_2 from P_2O_5. *cis*-Pt(CH$_3$CN)$_2$Cl$_2$ was prepared from K$_2$[PtCl$_4$] as previously reported.[17] [(*n*-C$_4$H$_9$)$_4$N]$_2$[Pt(CN)$_4$] was prepared from [(*n*-C$_4$H$_9$)$_4$N]Br (Aldrich) and K$_2$[Pt(CN)$_4$] (Strem) as previously reported.[18] Elemental analysis was performed by QTI Analytical Laboratories. All nonaqueous solvents were dried with activated molecular sieves. General procedures for gravimetric measurements have been previously described.[4] Infrared absorption spectra were obtained using the attenuated total reflectance (ATR) method on a Nicolet Magna-FTIR System 550 spectrometer equipped with a ZnSe trough HATR cell from PIKE Technologies. Sample films were coated on the ZnSe crystal from an ether suspension. Visible absorption (ATR method) and emission measurements were acquired under a dry nitrogen atmosphere (compressed nitrogen tank) and under a water-saturated nitrogen atmosphere. A dry nitrogen atmosphere was generated in this case by passing nitrogen gas from a liquid nitrogen tank through a liquid-nitrogen-cooled dewar. Sample films were coated onto a cubic zirconium ATR crystal from an ether suspension. Visible absorption spectra were recorded on an Ocean Optics CCD spectrophotometer equipped with an in-house-constructed ATR crystal holder with fiber optic mounts.

Polymer Analysis. ^{1}H NMR spectra were obtained on a Chemagnetics CMX 300 NMR spectrometer and IR spectra were recorded on a Nicolet 760 FT-IR. Thermal analysis was performed under nitrogen on a Seiko SSC/5200 equipped with DSC 220C and TA/DTA 320 modules. T_g is reported as the inflection point in the DSC trace. Refractive index was measured on a Leica Mark II Abbe Refractometer. Elemental

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analyses were obtained from Galbraith Laboratories, Inc., Knoxville, TN. Molecular weight determinations were made using a Waters gel permeation chromatography system using Waters Styragel HR 4E and HR 5E linear columns at 30 °C using THF as the mobile phase. Molecular weights are referenced relative to polystyrene standards. Molecular weights with a miniDAWN light scattering detector were in agreement with those determined with reference to polystyrene standards.

Cyclododecylformamide. Cyclododecylformamide was synthesized from cyclododecylamine (Aldrich) via the method described by Ugi and Meyer.[19,20] A solution of cyclododecylamine (Aldrich), c-$C_{12}H_{23}-NH_2$, (5.0 g, 27 mmol) and 90% formic acid (11 mL) in 75 mL of toluene was gently refluxed in a nitrogen-purged flask with a Dean−Stark water separator for 12 h. Partial evaporation of the solvent on the rotary evaporator produced a crop of white crystals (c-$C_{12}H_{23}-$NHCHO) that were collected via filtration. Further rotary evaporation yielded a second crop of product. Yield 69%; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.07 (d, $^3J_{HH} = 0.9$ Hz, 0.7H, *Z* isomer (H)CONHR), 8.03 (d, $^3J_{HH} = 12.0$ Hz, 0.3H, *E* isomer (H)CONHR), 5.66 (br d, 1H, *Z* and *E* isomers HCON(H)R), 4.09 (m, 1H), 1.63 (m, 2H), 1.36 (m, 20H). IR (ATR, solid, cm^{-1}) 1660 s.

Cyclododecylisocyanide. Cyclododecylisocyanide was synthesized from the cyclododecylformamide by a modification of the method described by Ugi and Meyer.[19,20] A solution of c-$C_{12}H_{23}-$NHCHO (4.0 g, 19 mmol) and triethylamine (13.2 mL, 94.7 mmol) in 78 mL of dichloromethane was added to a flask under nitrogen. The triethylamine was dried by passing it through an activated neutral alumina column prior to starting the synthesis. The solution was purged with nitrogen for 25 min and then a solution of $POCl_3$ (1.93 mL, 20.7 mmol in 10 mL dichloromethane) was added slowly to the reaction mixture over a 15-min period. The solution was allowed to stir for an additional hour. An aqueous solution of sodium acetate (25 g in 80 mL of H_2O) was then added to the reaction mixture and stirred for 35 min. The organic layer was separated and the aqueous layer was rinsed with 100 mL of dichloromethane. The combined organic layers were extracted with saturated aqueous sodium chloride (3 × 75 mL) and then dried with anhydrous calcium chloride. The liquid was decanted off the drying agent and the solvent removed by rotary evaporation. The resulting product (c-$C_{12}H_{23}-$NC) was an oily brown liquid. The c-$C_{12}H_{23}-$NC was then purified by chromatography with an activated alumina column with dichloromethane as the eluent. Yield 52%; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 3.66 (m, 1H), 1.79 (m, 2H), 1.66 (m, 2H), 1.55−1.25 (m, 18H); IR (ZnSe ATR film, cm^{-1}) ν(R−NC) 2136.

Synthesis and Characterization of [Pt(CN−cyclododecyl)$_4$][Pt(CN)$_4$], PtPt. The method of Keller and Lorenz[21,22] with slight modification was used as described below. To a solution of *cis*-$Pt(CH_3CN)_2Cl_2$ (0.102 g, 0.29 mmol) a solution of c-$C_{12}H_{23}-$NC (0.235 g, 0.12 mmol) was added via a syringe and stirred under argon for 30 min. Then, $[(n\text{-}C_4H_9)_4N]_2[Pt(CN)_4]$ (0.227 g, 0.29 mmol) in 25 mL of freshly distilled acetonitrile was added and the solution was stirred under an argon atmosphere for 8 h. The bright yellow precipitate that formed was collected by filtration and rinsed with 10 mL of distilled acetonitrile. The yellow solid gradually turned red on the frit as the residual acetonitrile evaporated. Drying under vacuum results in an additional color change to the purple anhydrous material. Yield 46%; IR (ZnSe ATR film, cm^{-1}) ν(R−NC) 2276, ν(CN) 2122; Vis−NIR (cubic zirconium ATR film, nm) $\lambda_{max} = 614$. Anal. Calcd for $C_{56}H_{92}N_8Pt_2$: C, 53.06; H, 7.32; N, 8.84. Found: C, 52.39; H, 7.20; N, 8.64.

Synthesis of CSPH Polymer. A *c*arbosiloxane polymer with *ph*enyl groups that we have abreviated CSPH was prepared as follows. Silanes and catalyst were obtained from Gelest, Inc. (Tulleytown, PA). Tetraphenyldisiloxane was prepared by hydrolysis of chlorodiphenylsilane; its structure and purity were verified by NMR.[23] Diphenylsilane (1.7253 g, 0.0093608 mol) and one drop of platinum-1,3-divinyltetramethyldisiloxane complex were added to a magnetically stirred solution of 1,3-dimethyl-1,3-diphenyl-1,3-divinyldisiloxane (3.0537 g, 0.009833 mol) in 4 mL of toluene. This gave a molar ratio of reacting functional groups, $r = [\mathrm{SiH}]/[\mathrm{CH_2{=}CH}]$, equal to 0.95. The solution was heated to 103−110 °C in an oil bath for 88 h until FTIR analysis of reaction mixture indicated that the Si−H peak was barely distinguishable from the baseline. Upon cooling, the reaction mixture solidified and an additional 10 mL of toluene was added to redissolve the polymer. The solution was treated with activated charcoal and filtered. Most of the solvent was removed by rotary evaporation. The residue was poured into 150 mL of methanol to precipitate the polymer. The recovered polymer was heated under vacuum at 66 °C for 17 h. The temperature was then raised to 142−148 °C for 3 h. The product (4.1496 g, 87%) was a thick, colorless gum. GPC $M_w = 50\,000$ and $M_n = 19\,600$ ($M_w/M_n = 2.6$). Anal. Calcd: C, 72.82; H, 6.92. Found: C, 71.77; H, 6.98. $n^{25} = 1.583$. ^{1}H NMR ($CDCl_3$) δ 7.38−7.21 (m, 20H), 0.83 (m, 4H), 0.54 (m, 4H), 0.21−0.18 (m, 6H). ^{13}C NMR ($CDCl_3$) δ 138.7, 135.9, 135.2, 133.5, 129.5, 129.2, 127.9, 9.2, 3.4, −1.5. T_g(DSC): 4 °C.

Microbalance Measurements. Ten megahertz QCM devices of AT-cut quartz (Colorado Crystal) were operated with an oscillator card originally built at the University of Washington. The frequency signal was measured using a Hewlett-Packard 53131A High Performance Universal Counter with a medium stability time base, with data transferred to a microcomputer by GPIB. The frequency counter was controlled and data were logged using LabVIEW software (National Instruments, Austin, TX).

Sensing Film Application and Characterization. A suspension of **PtPt** in a 3% solution of CSPH was prepared in dichloromethane. The **PtPt**:CSPH ratio was 80:20. This suspension was spray-coated onto one side of a gold-coated 10-MHz AT-quartz QCM (Colorado Crystal Co., Loveland, CO) using an air brush, while monitoring frequency changes to determine the amount of film applied. An effort was made to keep the **PtPt** suspended in the polymer solution by swirling the suspension between sweeping the air brush spray over the crystal surface. The film application changed the crystal frequency by 24 kHz. Scanning electron microscope images of the sensing film were obtained using a LEO 982 Field Emission Scanning Electron Microscope. A Hewlett-Packard 4194A Impedance Analyzer was used to check motional resistance changes[24,25] after coating crystals.

Sensing Film Spectral Measurements. The absorption spectrum of the vapochromic compound was monitored in reflectance mode using a fiber optic bundle (Ocean Optics, Dunedin, FL) combined with a diode array spectrometer (American Holographic Rainbowmeter, Littleton, MA) configured for a spectral range of 350−700 nm. An Osram mercury lamp with automated shutter was used as a source. Data acquisition and control were performed using LabVIEW on a Gateway 486 laptop computer. Spectral data as a function of time were processed using MATLAB software. The Rainbowmeter images sample and reference spectra onto a single 256 element diode array such that each recorded spectrum contains both sample and reference data. Raw diode array data were processed to remove spikes, ratio the sample channels to the reference channels, and convert channels to wavelengths using calibration on a measured mercury line spectrum. The spike removal routine consisted of deleting data from the channel with a spike and using a cubic spline fittting technique on the 10 data points to the left and the right of the spike-containing

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channel to find a fitted value to replace the deleted point. Finally, reflectance changes relative to the initial reflectance spectrum under dry nitrogen were determined as I/I_0, where the average of the first 10 spectra under dry nitrogen prior to water vapor exposures was taken as the I_0 spectrum. Finally, the average of the first 10 reflectance intensity spectra under dry nitrogen was divided into each of the test spectra during alternating dry nitrogen/test vapor exposures. This procedure yields spectral data as the ratio of the reflectance intensity of the sample spectrum divided by the reflectance intensity of the sample under dry nitrogen.

Vapor Response Measurements. The flow cell containing the QCM sensor with fiber optic reflectance probe (see Figure 2) was placed in a brass box suspended in a refrigerated circulating water bath (Neslab). Good thermal contact was maintained between the flow cell and the box walls, and the temperature was maintained at 298 K. Test vapors were generated from bubbler sources with dry nitrogen carrier gas. Bubblers were maintained at 288 K in a machined aluminum block with water circulating from another water bath. Carrier gas flows for the bubbler and additional dilution gas mixed downstream were controlled with electronic mass flow controllers. The entire vapor blending system was automated. The sensor probe was exposed to alternating 10-min intervals of dry nitrogen and diluted water vapor. QCM data and spectral data were collected with separate microcomputers running separate Labview programs. QCM data were collected every 12 s and spectra were recorded every 15 s.

Results and Discussion

Synthesis and Characterization of [Pt(CN−cyclododecyl)$_4$][Pt(CN)$_4$]. We synthesized [Pt(CN−cyclododecyl)$_4$][Pt(CN)$_4$] by the reaction of Pt(CH_3CN)$_2$$Cl_2$ with cyclododecylisocyanide in acetonitrile to produce the [Pt(CN−cyclododecyl)$_4$]$^{2+}$ cation, which was then precipitated by adding [(n-C_4H_9)$_4$N]$_2$[Pt(CN)$_4$] to the solution. [Pt(CN−cyclododecyl)$_4$][Pt(CN)$_4$] was isolated from the reaction mixture by filtration. The resulting yellow solid that contains sorbed acetonitrile gradually turns red (a hydrated form) and finally gives a purple solid after drying under vacuum, heating, or long-term storage under a dry nitrogen purge. The solid was distinctly sensitive to water (purple to red) and to some other organic solvents as well.[26] This organometallic solid material is stable to laboratory air indefinitely and thermally stable up to 120 °C for at least 15 h.

The compound was characterized by elemental analysis, IR, visible absorption, and emission spectroscopies. The infrared spectrum displayed one cyanide and one isocyanide stretch as expected for platinum(II) double salt materials.[5] The visible absorption band shifts reversibly from 614 to 517 nm upon exposure to nitrogen saturated with water vapor, as measured using the ATR method described in the Experimental Section. In addition, the emission spectrum also shifts reversibly from 787 to 707 nm and increases in intensity by a factor of 3 upon exposure to nitrogen saturated with water vapor. These changes are reversible and reproducible over many cycles.

The gravimetric behavior of a bulk sample of [Pt(CN−cyclododecyl)$_4$][Pt(CN)$_4$] under dry conditions and at 100% relative humidity was investigated. The solid material handled in laboratory air was found to be partially hydrated. An anhydrous sample was obtained by drying at 100 °C for 15 h in an oven; the cooled dry samples were stored at room temperature in a desiccator. A sample of this dry material under a dry nitrogen atmosphere was placed on the pan of a balance under computer control and the mass was monitored as a function of time. Under these conditions the mass was stable. Exposure of this sample to 100% relative humidity resulted in a rapid (<1 min) mass gain step followed by a slower step that ultimately resulted in the uptake of 3 ± 0.1 water molecules per formula unit. Reduction of the relative humidity to the dry condition resulted in a similar fast and then slow mass loss to the original value. The slow phase of the drying cycle occurred after the loss of about 0.5 water molecules per mole of sample. All of these mass changes are reproducible with no apparent degradation over several days and multiple cycles. The high chemical stability, reversibility, and color changes observed for this system suggested that more detailed studies with simultaneous QCM and reflectance measurements would be useful.

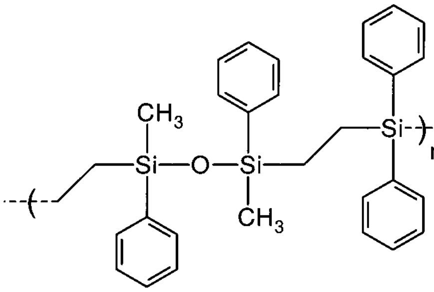

Figure 3. The repeat unit structure of the carbosiloxane polymer, CSPH.

Measurement Approach. The QCM was used to monitor vapor uptake by the vapochromic complex as a function of time and vapor concentration. The application of thin adherent films of the vapochromic **PtPt** complex to a QCM surface was problematic because **PtPt** has negligible solubility in most solvents. Therefore, conventional solvent casting techniques are not applicable. Initial attempts to apply films from suspensions of **PtPt** in organic solvents were met with little success. Spin coating left nonuniform films with scattered crystallite aggregates. Spray coating was more successful in obtaining a film on the active sensing surface, but crystal oscillation was typically unstable after coating. Impedance analyzer measurements showed that the motional resistance increase after spray coating was substantial, indicating that the sensing film was not moving synchronously with the device surface and energy was being dissipated.

To improve adhesion, the vapochromic compound was prepared as a suspension in a polymer solution and spray-coated on one side of a QCM crystal as described in the Experimental Section. The use of the polymer as a binder to produce a composite film resulted in stable crystal oscillation and no significant change in motional resistance by impedance analyzer measurements. The motional resistance of the coated crystal was 10 Ω, compared to 5−8 Ω for clean crystals. These results indicate that the film is adherent and moves synchronously with the device surface and hence will function as a gravimetric sensor.

The repeat unit structure of the polymer binder, which we call CSPH, is shown in Figure 3. This material

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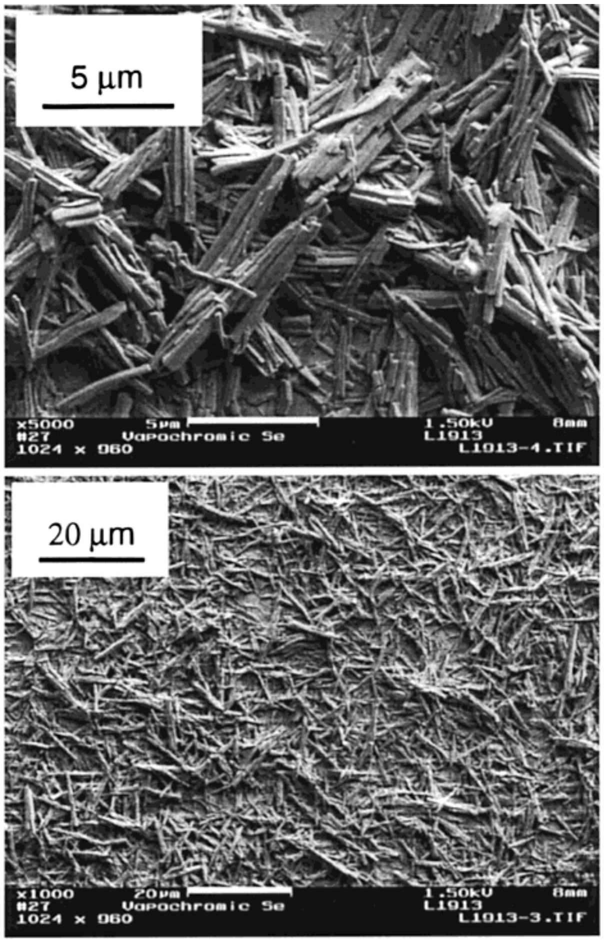

Figure 4. SEM images of the composite sensing film showing crystallites of the **PtPt** complex.

has a glass transition temperature below room temperature, affording rapid vapor diffusion in and out of thin films. The presence of polarizable phenyl groups was considered advantageous for adhesion to surfaces and for adhesion with crystallites. The mass ratio of **PtPt** to polymer in the composite sensing film was 80:20 and the response behavior was dominated by the vapochromic material (vide infra).

Scanning electron microscope (SEM) images of the composite film are shown in Figure 4. The sensing film consists of needle-shaped crystallites and crystallite agglomerates, with individual crytallites typically a fraction of a micrometer in width and one to several micrometers long. For reference, a 10-MHz crystal with a uniformly deposited film of a material with a density of 1 g/mL would have a thickness of 1.06 μm if coated to a thickness yielding a 24-kHz frequency change. The film structure consists of crystallites adhering to one another and to the surface, not as crystallites embedded in a polymer film. This film structure allows a large surface exposure of the vapochromic compound and accommodates unit cell volume changes that result from vapor sorption/desorption steps that would disrupt a continuous homogeneous film.

The composite film coated QCM was mounted in the flow cell shown in Figure 2. A fiber optic bundle positioned normal to the surface over the active sensing surface enabled reflectance measurements to monitor spectral changes in response to vapors delivered by inlet and outlet ports.

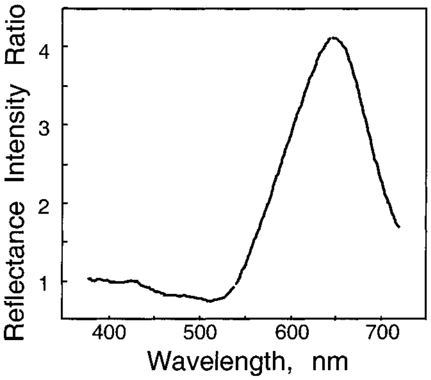

Figure 5. Ratio of the reflectance intensity spectral data obtained in response to water vapor at a concentration above the step response at 6000 mg/m^3 to the reflectance intensity spectral data under dry nitrogen.

Steplike Responses to Increasing Vapor Concentration. At the outset of this investigation, it was not known how these inorganic solid vapochromic compounds would respond to variable vapor concentrations below the saturated vapor pressure. We were surprised to find a steplike change in both vapor sorption and spectral properties in response to increasing concentrations of water vapor. Thus, the calibration curves (response as a function of concentration) are not simple linear relationships. The largest reflectance intensity changes relative to the dry film reflectance intensity occurred around 650 nm, as shown in Figure 5. This figure shows the ratio of the reflectance intensity spectrum in the presence of a high water vapor concentration to the reflectance intensity spectrum obtained under dry nitrogen (see Experimental Section). Note that this spectrum contains essentially no contribution of emitted light, which would be of much lower intensity. The increase in reflectance intensity at the higher wavelengths correlates with a decrease in absorbance at these wavelengths as the absorbance spectrum shifts to lower wavelengths with water uptake. The same spectral changes were observed from reflectance measurements on neat films containing no polymer binder. Therefore, the spectral behavior is due to the vapochromic chromophore and it is not perturbed by the presence of the polymer.

Response behavior as a function of time upon exposure to several intervals of water vapor exposure over a wide concentration range are shown in Figure 6. The top plot, Figure 6a, shows the optical signal at 650 nm. The middle plot, Figure 6b, shows the signal from the QCM, while the lower plot, Figure 6c, shows the profile of vapor concentrations as a function of time. Neither the optical signal nor the QCM signal follow the vapor concentration profile. Instead, the responses of both the optical and QCM measurements are small until a certain water vapor concentration is exceeded. At that point, there is a large increase in the QCM response, indicating water vapor absorption, and a corresponding large change in the optical response. The responses are rapid and reversible, although noticeably slower in the range where the transition in sorbed water content occurs. As seen in the figure, tests against low vapor concentrations after high vapor concentrations are in agreement with tests at those low vapor concentrations prior to the high concentrations.

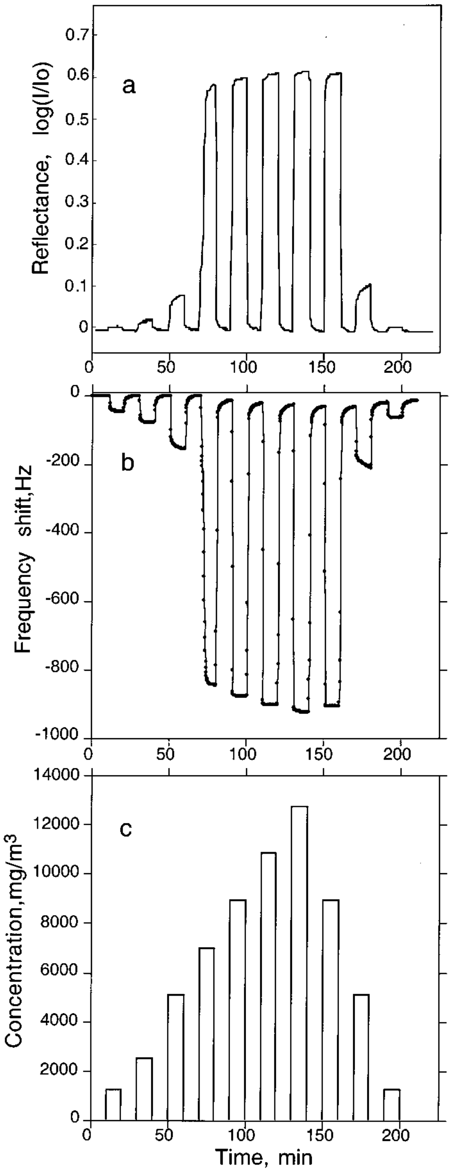

Figure 6. Response behavior observed over a large water vapor concentration range: (a) optical response at 650 nm, (b) QCM response, and (c) test vapor concentration profile.

Additional experiments were conducted over a much narrower water vapor concentration range that bracketed the concentration where the large signal changes were observed. Results are shown in Figure 7, using the same format as Figure 6 for plots a, b, and c in Figure 7. These results show that the film exists in essentially two compositions over this concentration range, with conversion from one composition to another occurring near a concentration of 6000 mg/m^3. At concentrations near the conversion concentration the responses are notably slower than those at higher concentrations.

Further information can be gained by examining the full spectral data, shown in Figure 8. These data correspond to the experiment shown in Figure 6. The spectral changes observed at the low initial water concentrations have a different peak wavelength than the changes observed at the higher water concentrations. Thus, the initial responses below 6000 mg/m^3 shown in Figure 6 at 650 nm are due to a spectrally distinct process from the major change at concentrations above 6000 mg/m^3.

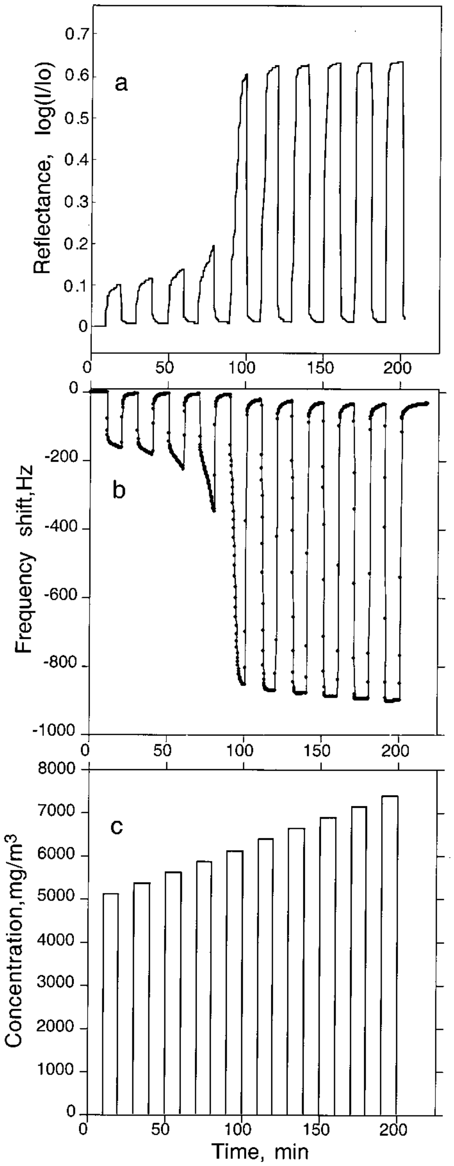

Figure 7. Response behavior observed over a narrow water vapor concentration range around the step change in film composition: (a) optical response at 650 nm, (b) QCM response, and (c) test vapor concentration profile.

QCM calibration curves from these experiments are shown in Figure 9. The separate runs demonstrate good agreement where the test concentrations overlap and show good reproducibility. The dramatic step change in vapor sorption at about 6000 mg/m^3 (about 26% relative humidity at 25 °C) is evident in this plot. Up to this concentration, there is a linear sorption process indicated in the QCM data, and there is additional apparently linear sorption with smaller slope after the step change in composition.

A control experiment was conducted with a QCM coated with CSPH polymer to give a frequency change of 12.3 kHz. These results are also presented in Figure 9. This control represents a combination of water vapor absorption by the polymer material and surface adsorption at any mass-sensitive location, including the uncoated underside of the device. The responses to water even at the highest concentrations, about 30 Hz, are negligible compared to frequency shifts of nearly 900 Hz when the composite vapochromic film takes up

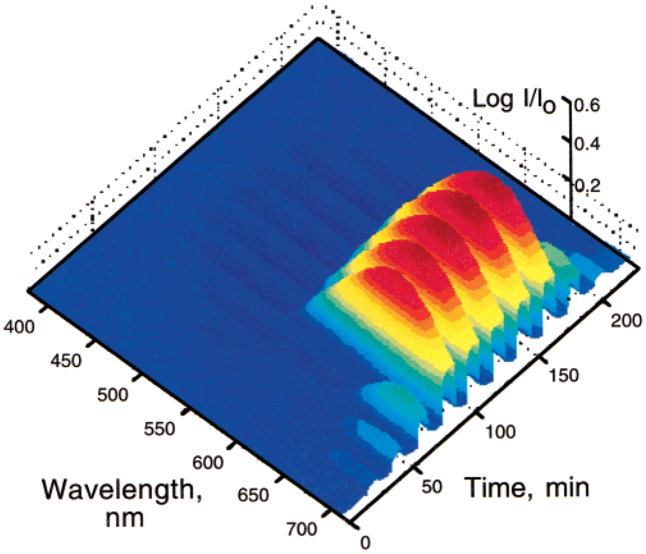

Figure 8. Full spectral response as a function of time for the experiment shown in Figure 5. The log I/I_0 scale shown in the upper right is placed at 650 nm, corresponding to the peak maximum at high water concentrations.

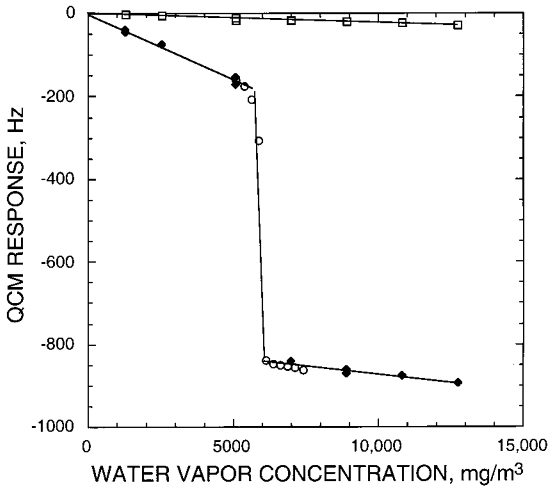

Figure 9. Calibration curves for the responses of the **PtPt**/CSPH composite film to water vapor concentrations. The frequency shifts from the wide concentration range experiments are shown in solid diamonds with the narrow concentration range data plotted as open circles. The open squares show responses of a CSPH-coated QCM device as a control.

water. It should also be noted that the CSPH-coated QCM has more CSPH material on it than the QCM coated with composite vapochromic film to a 24-kHz change, CSPH being ≈20% of that total. Therefore, the responses observed with the composite vapochromic film, and particularly the large sudden response in the QCM signal that correlates with large sudden changes in optical signal, can be attributed entirely to the sorption behavior of the inorganic vapochromic solids in the composite film.

The magnitude of the QCM response can be used to estimate the number of water molecules involved. On the basis of the film amount of 24 kHz of which 19.2 kHz is attributed to **PtPt**, the frequency change of 690 Hz at the steplike phase of water uptake indicates the addition of 2.5 water molecules per formula unit. The total frequency change from the dry film to the completion of the steplike uptake of water molecules represents 3 water molecules per formula unit, in agreement with the bulk gravimetric measurements. These calculations assume the QCM functions purely as a mass sensor, that the composition of the film material is the same as the composition of the suspension used to apply it, and that all the solid inorganic material is **PtPt** in the host structure.

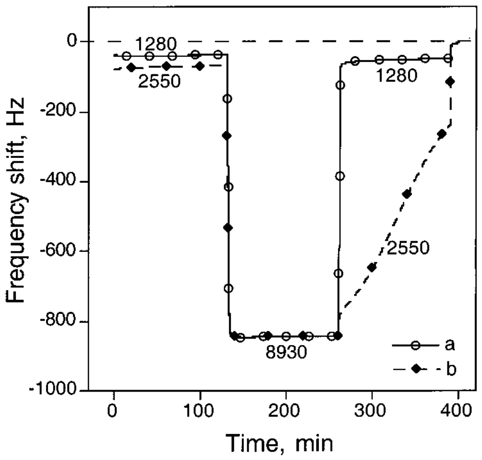

Figure 10. Vapor uptake and release from QCM measurements with long vapor exposure times and changes from higher to lower water vapor concentrations without zero water vapor concentrations in between. Numbers in the figure correspond to water vapor concentrations in mg/m^3. The two traces overlap during the high water vapor concentration.

The response data described above are for 10-min exposures with each exposure followed by a return to dry carrier gas. A second set of experiments was carried out with longer exposure times and returns to non-zero water concentrations. Figure 10 shows the results from these experiments. Results from two such experiments are shown, one (a) starting at 1280 mg/m^3 water vapor concentration, changing to 8930 mg/m^3, then back to 1280 mg/m^3, and finally down to zero water vapor concentration, with exposure times of 120, 140, 130, and 10 min, respectively. (The water vapor concentration was zero just prior to the beginning of data collection at the low water vapor concentration.) The other experiment (b) substitutes 2550 mg/m^3 water vapor concentration for the 1280 mg/m^3 concentration. It is evident that 2-h exposures to water vapor concentrations below the steplike uptake concentration does not result in a transition, suggesting the steplike behavior observed is not due to a kinetic barrier that is only overcome at sufficiently high concentrations. Furthermore, on transition from the exposure at 8930 mg/m^3 to the lower concentrations, the water content of the sensing film decreases. It does so quite rapidly when the exposure changes from 8930 down to 1280 mg/m^3 and much more slowly upon a decrease from 8930 to 2550 mg/m^3. These results show that the hydrated form of the complex obtained at 8930 mg/m^3 is not thermodynamically stable at the lower vapor phase water concentrations. The steplike response behavior from the composite sensing film has been observed repeatedly over time. The initial experiments shown in Figures 5−9 were followed by experiments 3 months later with the same sensor again showing steplike behavior, with little water vapor uptake at 1280 and 2550 mg/m^3 and substantial uptake at 5100 mg/m^3.[27] Forty-six months after coating, the sensor was tested again and again displayed steplike behavior.

A separate film of the complex prepared with no polymer was also investigated using reflectance measurements. The reflectance intensity spectra were the same as those of the composite film, as described above. Reflectance changes indicated little water vapor uptake at 1280 and 2550 mg/m^3 and substantial uptake at 5100 mg/m^3, in agreement with the composite film. Thus, the steplike behavior is not an artifact of a single-coated sensor or the presence of a polymer binder. It is a characteristic of the vapochromic complex.

Responses to Other Vapors. In addition to the response of **PtPt** to water described in this paper, **PtPt** shows interesting vapochromic response behavior to a number of organic vapors. In reflectance measurements on neat films (i.e., no polymer mixed with the inorganic vapochromic solids), spectral changes provide evidence for the formation of multiple discrete compositions as concentrations of dichloromethane and chloroform are increased, although the steps are not as abrupt as those shown above for water vapor. Thus, it appears that compounds capable of hydrogen bonding give rise to optically distinct species. On the other hand, vapochromic responses to benzene, toluene, and xylene are also observed with **PtPt**.[28] In these cases spectral changes appear to grow gradually with increasing concentration. It has also been observed in preliminary investigations that **PtPt** emission is modulated by varying concentrations of dichloromethane.[28] These results also showed the transition from one sorption state to another, with a fairly broad transition range. The concentration at which transitions occur can be shifted by changing the temperature. It is apparent that these vapochromic materials can display a number of intriguing behaviors worthy of further investigation under conditions other than simple saturated vapor exposures.

Discussion. One could imagine a number of possible behaviors for vapochromic materials as a function of vapor concentration. There could be gradual spectral changes as concentration increases, yielding linear calibration curves over useful concentration ranges. For example, Dickert has demonstrated that crystal violet lactone in bisphenol A forms an intensely colored film whose absorbance decreases upon absorption of basic organic vapors.[29] Linear calibration curves were obtained for solvent vapors in air, indicating gradual continuous spectral changes with changing concentration.

In contrast, the **PtPt** inorganic vapochromic material displays strikingly nonlinear behavior to varying concentrations of water, with a steplike change in response. This behavior was not previously known for this class of vapochromic compounds. A gradual uptake of water vapor molecules was observed at low water vapor concentrations, leading to 0.5 water molecules per formula unit. This behavior was followed by a sudden uptake of 2.5 water molecules per formula unit at water vapor concentrations around 25% relative humidity, for a total of 3 water molecules per formula unit. Little further water uptake was observed in the QCM measurements, and bulk gravimetric measurements indicate 3 water molecules per formula unit at 100% relative humidity. The QCM measurements further showed that the fully hydrated compound loses waters of hydration if exposed to finite water vapor concentrations lower than the concentration at which the 3 water molecules per formula unit are absorbed.

Several lines of evidence establish that the behavior we have observed is real and is due to the vapochromic material. The combination of independent optical and QCM measurements on the same film provided unequivocal evidence that the sorptive and optical properties of **PtPt** changed in a correlated fashion. The fact that these measurements were made simultaneously lends certainty to the conclusion that the change in composition is associated with the observed color changes. The change in composition of the complex on the QCM cannot be an artifact of the QCM measurement because it is confirmed by the spectral changes. The spectral changes observed involve distinct spectral bands, rather than some vague overall change in reflectance; therefore, the spectral changes are related to the chromophore of the complex. Steplike behavior has been observed with both polymer/**PtPt** composite films and neat films of **PtPt**. The results in Figure 10 show that low vapor uptake at low water concentrations is not simply due to slow kinetics; it is based on thermodynamic properties of **PtPt** and its hydrates. Finally, the QCM results found are consistent with gravimetric and spectroscopic studies performed with the bulk material.

Mechanisms for steplike vapor sorption have also been discussed previously in studies of Werner-type clathrates involving the β phases of M(II)(4-methylpyridine)$_4$(SCN)$_2$, where M is typically Co or Ni.[30] These complexes have also been used as chemical sensing materials on QCM devices.[25,31] Under appropriate conditions, these compounds yielded sorption isotherms of gases and vapors with inflections or steps. Steplike isotherms may involve the generation of new sites created during the sorption process, for example, through phase changes or lattice expansions. Diffraction studies on vapochromic complexes with and without sorbed vapor have shown that lattice expansion does occur. The present study at subsaturated water vapor concentrations indicate that sorption of more than one vapor molecule per formula unit occurs at the concentrations where a large vapor uptake step is observed.

It is the stoichiometric ratio that determines the shape of the isotherms observed. A ratio of unity results in the commonly observed linear response at low concentrations followed by saturation at higher concentrations (e.g., a Langmuir sorption isotherm). Ratios >1

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[27] Each test involves a new vapor sample generated for those tests. Hence, drifts in observed behavior, in this case the specific concentration at which a large vapor uptake is observed, may be due to either drift in sensor material behavior or drift in the accuracy of the generated test vapor sample, with the latter being most likely. The precision of vapor generation involves an uncertainty of at least 6−15% (depending on the specific concentration generated) based solely on error propagation of the 1% full-scale precision of the electronic mass flow controllers involved. Further uncertainties exist in the accuracy with which electronic mass flow controllers are periodically calibrated and adjusted (which depends on the skill of the experimenter).

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result in steplike behavior with a region of low uptake, a dramatic uptake region, and another region of low uptake. As the ratio becomes larger, the dramatic response region becomes sharper and more sudden. We suggest that the crystalline structure of the vapochromes requires a specific number of vapor molecules per formula unit that defines the intrinsic stoichiometry of the vapor uptake.

The new analytical approach described herein, providing simultaneous optical and mass uptake data, offers the opportunity to resolve and elucidate matters that could not be determined from spectral changes alone. This can be useful both in chemical understanding and in designing analytical approaches with these compounds. The agreement of the QCM mass uptake measurements with stiochiometry found in bulk gravimetric measurements confirms the validity of using a QCM device for sorptive studies. This approach is faster and more convenient than bulk experiments provided that (a) adherent films can be obtained and (b) motional resistance measurements by impedance analysis are used to confirm that the coated QCM is in a gravimetric sensing regime. We will present the detailed response behaviors of **PtPt** and other vapochromic complexes upon exposure to organic vapors at subsaturated vapor concentrations in future papers. The present study has, for the first time, demonstrated a method for simultaneous measurements of the sorptive and optical properties of these sensing compounds, shown data for optical response as a function of vapor concentrations below saturated vapor, and shown steplike response behavior that has not been previously reported for these stacked d^8 metal complex salts.

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