An Electronic Nose Transducer Array of Vapoluminescent Platinum(II) Double Salts

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The development of environmental sensors continues to be an active area of research[2] especially the development of a practical "electronic nose."[3] Gardner and Bartlett define an electronic nose as "an instrument which comprises an array of electronic chemical sensors with partial specificity and an appropriate pattern recognition system, capable of recognizing simple or complex odors."[4] The chemistry associated with detection and signal transduction is of central importance in these types of devices. Electronic nose transducers reported to date include: semiconducting metal oxides,[3b,5] conducting polymer films,[6] acoustic wave devices,[7] field-effect transistors,[8] electrochemical sensors,[9] pellistors,[10] carbon-black loaded polymer film chemoresistors,[11] and conductometric sensors based on electrolyte/polymer composites.[12] Recent reports describe optical transducers with immobilized dyes such as Nile Red[13] or various metalloporphyrins.[14] Surface-modified semiconductor materials also show great promise as photoluminescent transducers for gas sensing.[15] In general, many optical transducers[13] depend as much on vapor/matrix interactions

Chart 1. Structures of Platinum(II) Double Salt Dications

1: R = $C_{12}H_{23}$ 3: R = $C_{14}H_{29}$ **2**
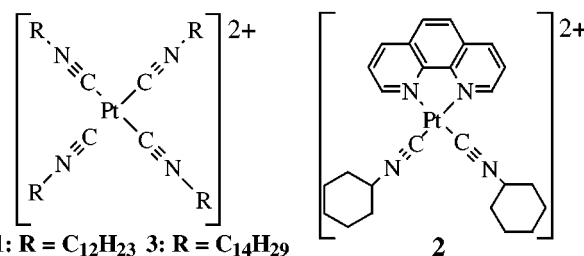
as on vapor/chromophore interactions for their discriminating power. Changes induced in the matrix/chromophore ensemble by the vapor are detected as a spectroscopic response of the chromophore that is usually analyzed by a multivariate statistical technique[16] to identify analyte vapors.

Our previous studies[17] suggested that pure vapochromic and vapoluminescent compounds[18] could be used as solid-state transducers without the complications of matrix/chromophore interactions. Vapochromism in crystalline [Pt(CNR)$_4$] [Pt(CN)$_4$] salts arises from highly anisotropic packing forces that enable solvent vapors to reversibly penetrate the interior of the material to form a new crystalline phase with precisely determined solvent−chromophore interactions.[17] The [Pt(CNR)$_4$][Pt(CN)$_4$] solids consist of infinite stacks of alternating [Pt(CNR)$_4^{2+}$] dications and [Pt(CN)$_4^{2-}$] dianions. The interionic metal−metal interactions produce the chromophore.[17] The vapor inclusion causes color changes that result from a combination of chemical interactions with the chromophore including: changes in the dielectric constant near the chromophore, hydrogen bonding between the solvent and coordinated cyanide, and expansion or contraction of the unit cell that is coupled to the Pt−Pt distance.

We now report the design and testing of a prototype electronic nose that uses an array of three new vapoluminescent salts (see Chart 1), [Pt(CN-cyclododecyl)$_4$] [Pt(CN)$_4$] (**1**), [(phen)Pt(CN-cyclohexyl)$_2$][Pt(CN)$_4$] (**2**) (phen = 1,10-phenanthroline), and [Pt-(CN-n-tetradecyl)$_4$][Pt(CN)$_4$] (**3**). The pure salts were synthesized and characterized by standard techniques.[19] Array elements are constructed by depositing submilligram quantities of a given salt from an ether suspension onto inert support disks, composed of platinum or carbon fibers. Qualitatively, the fibrous support material gave faster responses (milliseconds) than a layer on a platinum disk (seconds). Solvent vapors, generated by slowly bubbling nitrogen through a septum-capped flask containing the liquid of interest, were passed through a gas flow cell containing the three array elements. A separate fiber-optic excitation and emission channel for each array element allowed the collection of a luminescence spectrum from each salt.

Examples of simultaneous luminescence spectra of microcrystalline **1**, **2**, and **3** (Channels A, B, and C of the sensor array, respectively) in the presence of a set of solvent vapors that illustrate the chemical sensing diversity of the array elements are given in Figure 1. Compound **1** gives the largest shifts for the

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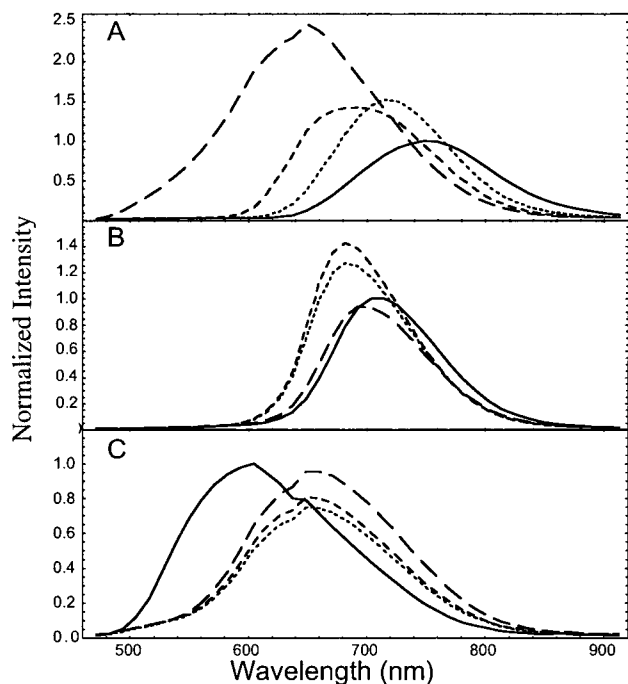
Figure 1. Luminescence spectra collected on Channels A, B, and C in the presence of acetone (—), 2-propanol (···), 1-propanol (---), and dichloromethane (— — —) Spectra are normalized relative to acetone. Excitation wavelength: 436 nm.

Figure 2. PCA scores plot. Solvent vapors: acetone (○), cyclohexane (△), *n*-hexane (+), benzene (×), chloroform (●), 2-propanol (◇), 1-propanol (□), water (◆), ethanol (*), methanol (▼), dichloromethane (■).

vapors studied: dichloromethane gives the most blue-shifted spectrum and acetone the most red-shifted.

The intensity for **1** increases as the luminescence maximum shifts to shorter wavelength. In contrast, **2** shows smaller shifts, but it nonetheless provides distinct and reproducible spectra for the different solvent vapors. Compound **3** behaves as a nearly binary sensor, with two distinct states: a blue-shifted state for hydrocarbons and acetone and a red-shifted state for chlorinated hydrocarbons, alcohols, and water. Further details of the vapoluminescence mechanisms of **1**, **2**, and **3** will be communicated in a separate report. The analysis of these three distinctive behaviors with the principal component analysis (PCA) method efficiently captures the variance inherent in the complete data set and allows discrimination of the solvents tested.

A data set of at least three equilibrium spectra for each solvent vapor were obtained in the presence of acetone, cyclohexane, *n*-hexane, benzene, chloroform, 2-propanol, 1-propanol, ethanol, methanol, water, and dichloromethane. Half the data set was obtained by changing the solvent exposure to the array in random order, while the other half used an acetone exposure "cleaning" step of 1 or 2 min between different solvent vapors. The cleaning step was implemented because the exposure order affected the rate and the final equilibrium state of the luminescence spectrum in some cases. In general, strong hydrogen-bonding molecules displaced hydrocarbons to reach equilibrium faster compared to the opposite order of exposure. Additionally, three replacement order combinations were discovered to give unusual spectra, especially with **1**: dichloromethane followed by acetone, methanol followed by ethanol, and 2-propanol followed by 1-propanol. We believe that the sensitivity of **1** to order is reasonable, as it displays
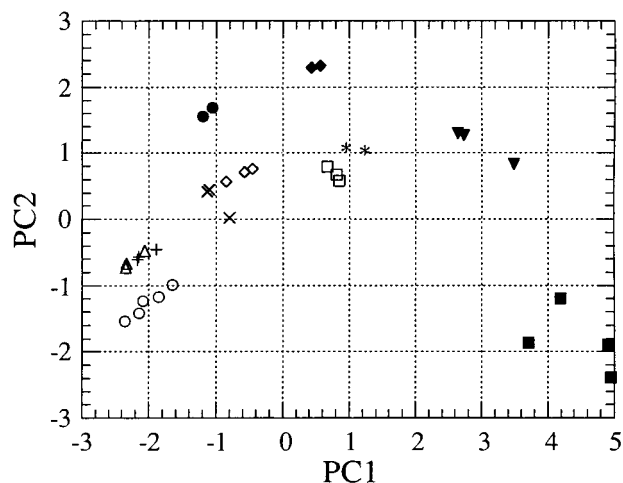
the highest degree of spectral shift in the presence of different solvent vapors. We speculate that the unusual spectra are generated from meta-stable mixed solvate crystalline phases.

The complete set of spectra were preprocessed[19] and examined with PCA. Principal components (PC's) 1 and 2 describe 84% of the variance in the data set.[19] The loading plot[19] indicates that PC1 is highly dependent on Channel A, while PC2 has a loading with nearly equal weighting of all three channels. The scores plot in Figure 2 shows that the projection of the data onto the PC1−PC2 plane allows the reliable identification of most of the solvents tested. Chloroform, water, methanol, and dichloromethane occupy distinct regions in the PC1−PC2 plane and are easily differentiated from the other solvent vapors studied. The hydrocarbons and acetone also occupy a unique region of PC space that differentiates them from the alcohols, water, and chlorinated hydrocarbons. Acetone and benzene occupy distinctly different regions of this "non-polar" PC space, but *n*-hexane and cyclohexane are not well-resolved from each other by this array. Finally, the higher alcohols, ethanol, 1-propanol, and 2-propanol, occupy unique locations in a third region of PC space. Surprisingly, this array is able to differentiate between isomeric 2-propanol and 1-propanol.

In conclusion, we have shown that a simple vapoluminescent array of only three pure compounds is able to reproducibly identify a range of solvent vapors. Studies are in progress to investigate the interferences that are peculiar to this array, to determine if quantitative measurements of concentration are possible, and to synthesize and characterize additional vapochromic compounds.

Supporting Information Available: Details of the prototype electronic nose instrumental configuration and PCA calculation (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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