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# Inclusion of Organic Vapors by Crystalline, Solvatochromic [Pt(aryl isonitrile)<sub>4</sub>][Pd(CN)<sub>4</sub>] Compounds. "Vapochromic" Environmental Sensors

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The design and synthesis of environmental sensors have become an increasingly important area of research.<sup>1</sup> Particularly acute is the need to detect environmentally hazardous substances such as VOCs (volatile organic compounds) down to the part per million level and lower.<sup>2</sup> Many detection systems that consist of a chemically sensitive layer and a transducer device have been proposed: conducting polymers; Langmuir–Blodgett multilayers deposited on waveguide surfaces, a quartz crystal microbalance (QCM), or a surface acoustic wave (SAW) device; and lifetime sensing of fluorescence with phase modulated detection.<sup>3</sup> In general, the underlying data acquisition and analysis instrumentation of the transducer is in hand, but the design of rugged, well-characterized chemically sensitive layers has only more recently been addressed.<sup>4</sup>

We have set out to design, synthesize, and study crystalline host compounds that show a pronounced shift in visible absorption or emission spectra upon inclusion of organic vapor guest molecules ("vapochromism").<sup>5</sup> Host compounds of this type with the proper sensitivity and selectivity could easily find use as the chemically sensitive layer in optical detection schemes. Described here are the first mechanistic studies of the [Pt(aryl isonitrile)<sub>4</sub>][Pd(CN)<sub>4</sub>] compounds reported by Nagel<sup>5</sup> to change color reversibly when exposed to VOC vapors.

The [Pt(aryl isonitrile)<sub>4</sub>][Pd(CN)<sub>4</sub>] compounds (where aryl isonitrile = *p*-CN-C<sub>6</sub>H<sub>4</sub>-C<sub>n</sub>H<sub>2n+1</sub>; *n* = 6, 10, 12, 14,<sup>5</sup>

Figure 1) contain [Pt(CN-C<sub>6</sub>H<sub>4</sub>-C<sub>n</sub>H<sub>2n+1</sub>)<sub>4</sub>]<sup>2+</sup> dications and [Pd(CN)<sub>4</sub>]<sup>2-</sup> dianions.<sup>6</sup> They are brightly colored salts that are insoluble in most organic solvents.<sup>7</sup> The solids are dispersed by suspension in a suitable solvent, followed by dip coating on to filter paper or a microscope slide.<sup>8</sup> In Figure 2 are a sequence of solid state transmission UV–vis absorption spectra showing the time response of a [Pt(*p*-CN-C<sub>6</sub>H<sub>4</sub>-C<sub>10</sub>H<sub>21</sub>)<sub>4</sub>][Pd(CN)<sub>4</sub>] (compound 1) film when exposed to room temperature air, saturated with chloroform vapor. By eye, the film changes color from pink to blue; spectrally, the prominent visible absorption band at 548 nm rapidly shifts isospectically to 578 nm. Removal of the chloroform vapor results in the rapid regeneration of the initial spectrum. Repeating this cycle many times gives no apparent degradation. The time response is very rapid (*t*<sub>1/2</sub> ~ 350 ms). Spectral data presented in Table 1 indicate that 1 undergoes pronounced, reversible color changes when exposed to a variety of VOCs.  $\lambda_{\text{max}}$  is a function of the VOC, with chloroform resulting in the largest shift of those listed in Table 1. Surprisingly, even saturated hydrocarbons (hexanes) induce a measurable shift in  $\lambda_{\text{max}}$ . Shifts of slightly smaller magnitude occur in the emission observed from 1.<sup>9</sup> Studies with the complexes containing the C<sub>6</sub>, C<sub>12</sub>, or C<sub>14</sub> hydrocarbon chain substituents suggest that the selectivity and responsivity of the complex varies with the length of the hydrocarbon chain; qualitatively, the C<sub>10</sub> compound seems to have the highest responsivity, particularly for chlorinated solvents such as chloroform and dichloromethane.

We have begun to address the mechanistic details of the vapochromic effect exhibited by these solid state complexes. By analogy to previously characterized compounds conforming to the [M(L)<sub>4</sub>][M(X)<sub>4</sub>] stoichiometry,<sup>10</sup> we believe that [Pt(aryl isonitrile)<sub>4</sub>][Pd(CN)<sub>4</sub>] solids consist of infinite stacks<sup>11</sup> of alternating [Pt(CN-C<sub>6</sub>H<sub>4</sub>-C<sub>n</sub>H<sub>2n+1</sub>)<sub>4</sub>]<sup>2+</sup> dications and [Pd(CN)<sub>4</sub>]<sup>2-</sup> dianions with considerable metal–metal interactions along the chains propagated through interionic *d<sub>z</sub><sup>2</sup>* and *p<sub>z</sub>* interactions. Conversely, the specific interchain interactions are probably due to relatively weak, van der Waals type forces. We suggest that the large mismatch in size between the [Pt(CN-C<sub>6</sub>H<sub>4</sub>-C<sub>n</sub>H<sub>2n+1</sub>)<sub>4</sub>]<sup>2+</sup> dications and [Pd(CN)<sub>4</sub>]<sup>2-</sup> dianions produces a structure with a relatively large free volume, facilitating the rapid and reversible sorption of the VOC in and out of the lattice<sup>12,13</sup> with minimal disruption of the crystallinity. Interactions between the guest solvent molecules and the [Pt(aryl isonitrile)<sub>4</sub>][Pd(CN)<sub>4</sub>] linear chain chro-

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(1) A literature search produced several thousand references in the general area of sensors published between 1991 and 1994.

(2) The U.S. EPA Environmental Technology Initiative for FY 1994 includes monitoring VOC's as a critical need.

(3) (a) Rabolt, J. F.; Santo, R.; Schlotter, N. E.; Swalen, J. D. *IBM J. Res. Dev.* **1992**, *26*, 209–216. (b) Yang, L.; Saavedra, S. S.; Armstrong, N. R.; Hayes, J. *Anal. Chem.* **1994**, *66*, 1254–1263. (c) Mirkin, C. A.; Valentine, J. R.; Ofer, D.; Hickman, J. J.; Wrighton, M. S. *ACS Symp. Ser.* **1992**, *487*, 218–236. (d) Hillman, A. R.; Loveday, D. C.; Swann, M. J.; Bruckenstein, S.; Wilde, C. P. *ACS Symp. Ser.* **1992**, *487*, 150–163. (e) Zellers, E. T.; Zhang, G.-Z. *Anal. Chem.* **1992**, *64*, 1277–1284. (f) Szmazinski, H.; Lakowicz, J. R. *ACS Symp. Ser.* **1993**, *538*, 196–226. (g) DeQuan, L.; Buscher, C. T.; Swanson, B. I. *Chem. Mater.* **1994**, *6*, 803–810.

(4) Dickert, F. L.; Haunschild, A. *Adv. Mater.* **1993**, *5*, 887–895.

(5) (a) Nagel, C. C. U.S. Patent 4,834,909. (b) Nagel, C. C. U.S. Patent 4,826,774. Related compounds have also been synthesized: (c) Isci, H.; Mason, W. R. *Inorg. Chem.* **1974**, *13*, 1175–1180. (d) Keller, H. J.; Lorentz, R. *J. Organomet. Chem.* **1975**, *102*, 119–122. (e) Keller, H. J.; Lorentz, R. *Z. Naturforsch. B.* **1976**, *31B*, 565–568.

(6) Slow addition of [(*n*-butyl)<sub>4</sub>N]<sub>2</sub>[Pd(CN)<sub>4</sub>] to an acetonitrile solution of (CH<sub>3</sub>CN)<sub>2</sub>PtCl<sub>2</sub> and RNC. Details and characterization data are in the supplementary material.

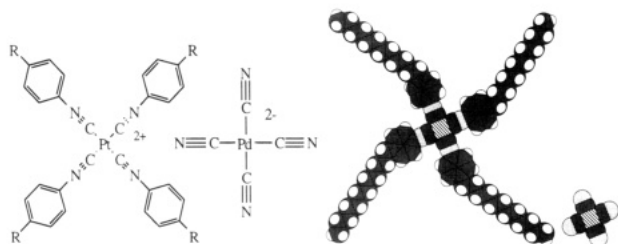
(7) Notable exceptions are dichloromethane and chloroform, in which these compounds are freely soluble but undergo a slow decomposition reaction.

(8) Details are given in the supplementary material.

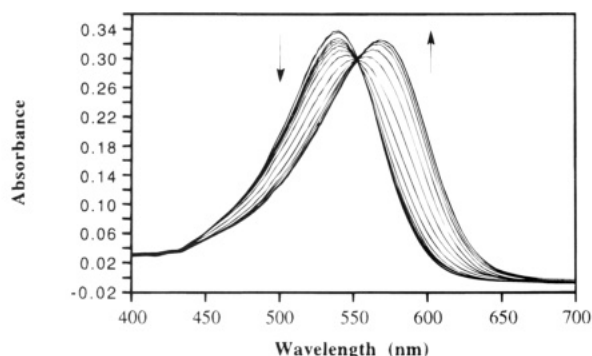
(9) Excitation was at the isosbestic point observed in the corresponding absorption experiment.

(10) The prototype is [Pt(NH<sub>3</sub>)<sub>4</sub>][PtCl<sub>4</sub>], Magnus' green salt: Magnus, G. *Pogg. Ann.* **1828**, *11*, 242. Atoji, M.; Richardson, J. W.; Rundle, R. E. *J. Am. Chem. Soc.* **1957**, *79*, 3017.

(11) Upon cooling a "dry" film of 1 from room temperature to 77 K, the absorption maximum shifts from 548 to 602 nm, and the emission maximum shifts from 640 to 719 nm. This red shift is diagnostic for metal–metal stacked complexes because of thermal lattice contraction, which results in shorter metal–metal distances. See: Gliemann, G.; Yersin, H. *Struct. Bonding* **1985**, *62*, 87. Miskowski, V. M.; Houlding, V. H. *Inorg. Chem.* **1991**, *30*, 4446.



**Figure 1.** Line drawings and space-filling models of [Pt(aryl isonitrile)<sub>4</sub>]<sup>2+</sup> and [Pd(CN)<sub>4</sub>]<sup>2-</sup>.



**Figure 2.** Solid-state absorption spectra (transmission mode) of **1** dispersed on a microscope slide. Spectra recorded as air saturated with chloroform is admitted into the sample compartment. Spectra are recorded at approximately 50 ms intervals. Arrows indicate the direction of change.

**Table 1. Absorption and Emission  $\lambda_{\text{max}}$  for Solid-State Films of **1** When Exposed to VOCs<sup>a</sup>**

solvent	abs max (nm)	vapochromic shift (nm) <sup>b</sup>	emission max (nm) <sup>c</sup>	vapochromic shift (nm) <sup>b</sup>
none	548		640	
MeOH	544	-4	621	-19
EtOH	554	6	<i>d</i>	<i>d</i>
2-PrOH	554	6	<i>d</i>	<i>d</i>
Et <sub>2</sub> O	558	10	<i>d</i>	<i>d</i>
CH <sub>3</sub> CN	559	11	642	2
hexanes	561	13	640	0
acetone	562	14	650	10
benzene	567	19	642	2
CH <sub>2</sub> Cl <sub>2</sub>	569	21	653	13
CHCl <sub>3</sub>	578	30	658	18

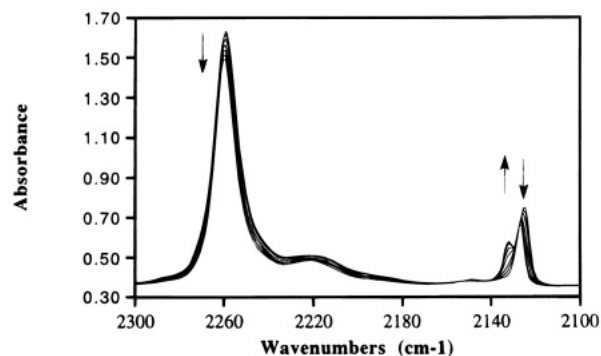
<sup>a</sup> See supplementary material for details of sample preparation.

<sup>b</sup> Vapochromic shift is  $\lambda_{\text{max}}(\text{VOC}) - \lambda_{\text{max}}(\text{none})$ . <sup>c</sup> Films were excited at the isosbestic points determined from vapochromic absorption data. <sup>d</sup> No data collected.

mophore in the ground and/or excited state then result in the observed shift in the visible absorption band. Our physical measurements support these basic ideas.

The sorption of organic solvent vapors is detected gravimetrically. When a solid sample of **1** on the pan of an analytical balance is exposed to acetone saturated air, the solid reversibly gains  $0.60 \pm 0.05$  molecules of acetone/formula unit. The sorption of benzene ( $0.75 \pm 0.05$ /formula unit) is also reversible. More sensitive<sup>12</sup> QCM (quartz crystal microbalance) measurements of these processes are currently in progress.

X-ray diffraction<sup>8</sup> studies of **1** reveal broad peaks in the powder pattern that undergo small, reversible shifts when the sample is exposed to chloroform vapor; similar



**Figure 3.** ATR-FT-IR spectral study in the region 2100–2300 cm<sup>-1</sup> of a film of **1** as air saturated with chloroform is admitted into the sample compartment. Arrows indicate the direction of change.

changes occur with benzene as the VOC.<sup>14</sup> The patterns before and during vapor exposure illustrate that the changes occur through out the bulk sample. Further, they indicate that the material is probably disordered,<sup>15</sup> but the degree of crystallinity is maintained in the presence of chloroform vapor.

Reversible changes are also observed in the <sup>13</sup>C CPMAS NMR spectrum<sup>8</sup> of **1**. Exposure of the solid to chloroform causes a doublet (12.4, 14.4 ppm assigned to the  $\omega$ -carbon methyl group) to collapse to a singlet (14.2 ppm). This change could result from averaging the environments of two different methyl site symmetries to one equivalent site. A small shift is also observed in the quaternary aromatic N-bound ipso carbon (initially observed at 144.9 ppm; shifts to 145.9 ppm).

IR spectroscopy was used to determine the site of VOC interaction with the solid. The IR spectra in the  $\nu(\text{CN})$  region (2100–2300 cm<sup>-1</sup>) of a film<sup>8</sup> of **1** deposited on the surface of an ATR crystal as chloroform vapor is admitted are shown in Figure 3. Bands at 2259 and 2219 cm<sup>-1</sup> due to  $\nu(\text{CN})$  of the coordinated isonitrile ligands are essentially invariant to the presence of chloroform vapor. Slight shifts are observed in an arene ring vibrational centered at 1170 cm<sup>-1</sup>. Much more significant changes are observed for the  $\nu(\text{CN})$  of the coordinated cyanide ligand<sup>16</sup> (initially at 2125 cm<sup>-1</sup>) which splits into two bands (2127 and 2132 cm<sup>-1</sup>). Vibrations observed for the chloroform guest (C–H at 2988 cm<sup>-1</sup> and C–Cl at 750 cm<sup>-1</sup>) are also shifted from their free values.<sup>17</sup> These data indicate that a primary, ground-state interaction occurs between the Pd(CN)<sub>4</sub><sup>2-</sup> anion and the chloroform lattice guest.

In summary, we have studied the reversible sorption of VOCs by [Pt(aryl isonitrile)<sub>4</sub>][Pd(CN)<sub>4</sub>] compounds with para-substituted hydrocarbon chains. The complexes exhibit significant shifts in  $\lambda_{\text{max}}$  for absorption and emission. The VOC guest changes the lattice parameters of the host slightly but does not significantly disrupt the crystallinity. <sup>13</sup>C CPMAS NMR and ATR FT IR spectroscopy suggest that chloroform guests

(14) A powder pattern of the sample after exposure to chloroform vapor is superimposable on the original.<sup>8</sup>

(15) Zheng, H.; Chung, K. L.; Swager, T. M. *Chem. Mater.* **1994**, *6*, 101–103.

(16) The  $\nu(\text{CN})$  of Pt(CN)<sub>4</sub><sup>2-</sup> has been reported to be sensitive to interstitial water: Kiernan, P. M.; Ludi, A. *J. Chem. Soc., Dalton Trans.* **1978**, 1127.

(17) Chloroform IR data: Neat liquid: 3019, 759 cm<sup>-1</sup>; vapor 770 cm<sup>-1</sup>.

(12) Reinbold, J.; Buhlmann, K.; Cammann, K.; Wierig, A.; Wimmer, C.; Weber, E. *Sens. Actuators B*, **1994**, *18–19*, 77–81. Schierbaum, K. D. *Sens. and Actuators B* **1994**, *18–19*, 71–76.

(13) Hinsberg, W. D.; MacDonald, S. A.; Clecak, N. J.; Snyder, C. D. *Chem. Mater.* **1994**, *6*, 481–488.

interact primarily with the  $\text{Pd}(\text{CN})_4^{2-}$  anion and to a lesser extent with the N-bound ipso carbon of the arene ring and the  $\omega$ -methyl group of the isonitrile ligand. Further experiments are in progress to investigate the mechanism of the vapochromic effect and to synthesize other complexes with higher sensitivity and selectivity for specific VOCs.

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**Supplementary Material Available:** Compound synthesis and characterization, sample preparation, X-ray powder diffraction measurements,  $^{13}\text{C}$  CPMAS NMR measurements, and ATR-FT-IR measurements (12 pages). Ordering information is given on any current masthead page.

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