Fabrication and Evaluation of Copper(I) Iodide Sensor Substrates

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College of William and Mary

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Copper(I) iodide and other copper(I) salts (CuX) react with amines and sulfides (L) in their gas phase to form luminescent rhomboid Cu$_2$(μ$_2$-X)$_2$L$_4$ and/or cubane Cu$_4$(μ$_3$-X)$_4$L$_4$ complexes. This work reports this spontaneous reaction occurring at the surface of CuI powder, pressed CuI pellets, CuI-impregnated polymer films, and CuI-embedded polypropylene plates. An LED fiber optic fluorimeter was used to monitor the reaction of gaseous pyridine (Py) or other nucleophile with CuI-impregnated PVC films. Known Py vapor pressures were established in a sealed chamber through gas-phase dilutions and correlated to luminescence emission response. Detectability of Py was established at vapor pressures as low as 0.001 Torr. Surface phases of CuI-Py were identified through X-ray powder diffraction. Initial formation of dimer Cu$_2$(μ$_2$-I)$_2$Py$_4$ (emission λ = 520 nm) quickly gives way to tetramer Cu$_4$(μ$_3$-I)$_4$Py$_4$ (emission λ = 580 nm).
INTRODUCTION

Volatile organic compounds (VOCs) can present a serious hazard to humans upon exposure. VOCs are characterized as organic chemicals with a high vapor pressure at standard, room temperature conditions. Until 2009, in the EPA’s definition of VOC, volatility was regarded as meaning having a vapor pressure greater than 0.1 Torr. In contrast, the current EPA definition of VOC refers to a specific list of designated compounds \[^1\]. VOCs are emitted as gases from commonly used products numbering in the thousands. Some examples of these are paints and lacquers, paint strippers, glues and adhesives, permanent markers, cleaning supplies, pesticides, office equipment including copiers and printers, correction fluids and carbonless copy paper, and photographic solutions. According to the EPA, VOCs can cause damage to liver, kidney, and central nervous system. Additionally, many VOCs are suspected or known to cause cancer. Since the concentrations of VOCs are generally low, symptoms can be slow to develop and can go unnoticed until the damage is already permanent. Due to the serious health risks, and increased understanding of prevalence of VOCs in such a wide variety of products within the past decades, there has been a push for practical VOC detectors in closed environments.

Current gas sensors function through the binding of molecules to a substrate surface in the device, and the measurement of a change in an observable substrate physical property resulting from that interaction. The analyte molecules can bind to the substrate in a variety of ways, such as adsorption, absorption, and chemisorption.
(Figure 1). While adsorption is simply the binding of liquid or gaseous molecules to the outside of a solid substrate, absorption is incorporation of the molecules into the crystal structure of the substrate. Neither of these sorption processes involve the formation of chemical bonds, whereas chemisorption is a sorption process by which the incorporated molecules are chemically bonded to the matrix material within the lattice.

Figure 1: Molecular depiction of adsorption versus absorption and chemisorption. Grey molecules represent solid substrate matrix, and red molecules represent liquid/gaseous species being sorbed onto/into the matrix.
For highly selective detection, stronger interactions between the molecules and the matrix are required, making chemisorption an ideal method of binding. However, the strong binding characteristics of chemisorption can cause poor reversibility. High reversibility can best be attained through weak interactions, associated with adsorption, but this tends to sacrifice selectivity. A compromise between these two situations is thus required. Other desirable traits for gas sensors include reliability, robustness, and sensitivity.\cite{2}

Conventional methods of detection of molecules on the substrate require measurement of differences in electrical conductivity. Optochemical sensors provide an improvement over these electricity-based sensors, given a lower sensitivity to electromagnetic noise, compatibility with fiber optics, and the ability to detect multiple gases through differences in intensity, wavelength, phase, and polarization of output signals. Many different methods of optochemical sensing exist, utilizing manipulations to absorbance and reflectance, refractive index, photoluminescence, and photothermal and photoacoustic properties. Of these, utilization of photoluminescence allows for rather simple and cost-effective sensing, yielding a relatively wide dynamic range of output signals.\cite{3}

**Copper(I) Iodide**

Copper(I) salts are inexpensive and known to exhibit luminescent properties similar to those of its fellow d\(^{10}\) group Au(I) and Ag(I) compounds. Copper exists commonly in three different oxidation states: 0, 1, and 2. Copper(0), a group 11 transition-metal, has the electron configuration \([\text{Ar}] \, 3d^{10}4s^1\). An electron is shifted from the 4s orbital to the
3d orbital such that the 3d subshell contains a full set of spin-paired electrons. Copper(I) has the electron configuration [Ar] 3d\(^{10}\), while copper(II) has the electron configuration [Ar] 3d\(^{9}\). This vacancy in the d-orbital allows for d-d transitions in copper(II), while these transitions are unavailable for copper(I) since the d-orbital is filled. The relatively electron-rich d-subshell in Cu(I) allows for \(\pi\)-backbonding to ligands, whereby the copper serves as both a \(\sigma\)-acceptor and a \(\pi\)-donor. d-Orbital electrons partially transfer from copper to the ligand, while electrons are received from the ligand to fill the lowest unoccupied \(\pi\) orbital (Figure 2).
Figure 2: Schematic of $\pi$-backbonding. For clarity, contributions to the $\sigma$-bond are colored blue and contributions to the $\pi$-backbond are colored red. The CO ligand is interchangeable with any ligand containing a $\sigma$ HOMO and a $\pi$ LUMO.

Furthermore, having a filled d-subshell limits the coordination number to no more than four, according to the 18 electron rule. Geometries commonly observed are two-coordinate linear, three-coordinate trigonal, and four-coordinate tetrahedral.

Iodide, a fifth-row halogen, is oxidized by copper(II) to form CuI$_2$.

$$\text{Cu(II)} + 2\Gamma \rightarrow \text{Cu(I)} + \text{I}_2$$
CuI$_2$ is unstable due to the strong reducing properties of iodide, which reduces Cu(II) to Cu(I).

\[
\text{Cu}^{II}I_2 \rightarrow \text{Cu}^I + \frac{1}{2} I_2
\]

CuI has three known solid phases at ambient temperature. Below 369°C it favors the zinc blende face-centered cubic crystal structure (γ-CuI). Between 369°C and 407°C it forms the wurtzite hexagonal close-packed structure (β-CuI), and above 407°C it forms a disordered face-centered cubic structure (α-CuI). These phases are seen in Figure 3.

Figure 3: Pressure/temperature phase diagram of CuI. [4], [5], [6], [7]
In the common $\gamma$-phase, the bridging iodine atoms occupy the corner positions, with tetrahedrally-coordinated copper atoms interstitially located. The copper and iodine atoms are separated by 2.338 Å. \[8\]

Figure 4: Crystal structure of $\gamma$-CuI. Miller indices of atomic planes are noted on the left hand side. \[9\]

Iodide, having four lone pairs, can potentially coordinate to four atoms. However, reducing the coordination number to two copper atoms allows for interaction between copper centers and additional ligands. Upon coordination of the copper atom to various ligands, four structures are commonly formed: rhomboid dimer, cuboid tetramer, and zigzag and staiirstep polymers. The staiirstep, and cuboid take on 1:1 CuI:L stoichiometries, whereas the rhomboid dimer or zigzag polymer take on a more ligand-rich 1:2 CuI:L stoichiometry.
Figure 5: Crystal structures of CuI-pyridine complexes, showing some commonly observed structures of CuI. (a) Rhomboid dimer \[^{[10]}\]. (b) Cuboid tetramer \[^{[11]}\]. (c) Stairstep polymer \[^{[12]}\].

Since coordination of copper(I) to four ligands is energetically favorable, the amount of ligand available to bond to copper has some influence in the structure of CuI. For instance, in a ligand-rich environment, the structure tends toward the ligand-rich dimer.
Luminescent Properties of Copper(I) Iodide

It is common for copper halides, CuX, to exhibit luminescence under UV excitation. The highest experimental quantum efficiency is achieved when X = I. \[^{[13]}\] Electrons are promoted from a 3d orbital to the 4s or 4p orbital, with a direct band gap of 3.1 eV. \[^{[14]}\] This results in peak emission near the UV/visible border. The emission is the result of a cluster-centered (CC) excited state. The term “cluster-centered” was coined to emphasize that the excited state is localized among the CuI cluster, thus independent of external ligands. The cluster-centered excited state, in the case of CuI, tends to be a combination of a halide-to-metal charge transfer (XMCT) and copper-centered d → s,p transitions. \[^{[13],[15]}\] Lifetime studies by Ford et. al, \[^{[16]}\] reveal that this excited state undergoes intersystem crossing before returning to the ground state, during which a photon is emitted. Upon initial excitation, one electron is promoted to an excited vibrational energy level, while maintaining its spin. That is to say, the singlet state is conserved, whereby electrons remain spin-paired. Immediate return of the excited electron to the ground state is accompanied by fluorescent emission of a photon. The lifetime of this electron is typically on the order of $10^{-9}$ seconds. An alternative pathway the electron can take from the excited singlet state is intersystem crossing. During intersystem crossing, the excited state electron flips spin to form an excited triplet state. The return of the electron from the excited triplet state to the ground state is coupled with the phosphorescent emission of a photon, illustrated in Figure 6. Typical lifetimes for electrons undergoing this pathway range from $10^{-6}$ to 1000 seconds.
Figure 6: Jablonski diagram illustrating fates of electrons excited to higher vibrational energy levels via absorption in the UV range.\textsuperscript{[17]}

Coordination of the copper to external ligands, yielding (CuI)\textsubscript{n}L\textsubscript{m}, results in a new emission peak in the visible region. The resultant emission, according to experimental data and density functional theory (DFT) calculations, results from cluster centered (CC), metal-to-ligand charge transfer (MLCT), or halide-to-ligand charge transfer (XLCT) excited states.

The most extensive photophysical studies of (CuI)\textsubscript{n}L\textsubscript{m} have been focused on the cubane tetramer, (CuI)\textsubscript{4}L\textsubscript{4}.\textsuperscript{[16]} Due to the prevalence of research on (CuX)\textsubscript{n}L\textsubscript{m} (L = pyridine (Py)) the remainder of this discussion will center around (CuI)\textsubscript{n}(Py)\textsubscript{m}. The tetramer, (CuI)\textsubscript{4}Py\textsubscript{4}, is known to exhibit luminescence thermochromism. That is, the emission band wavelength shifts with changes in temperature. At ambient temperature,
the dominant emission band is centered at 580 nm, with a weak, barely detectable band near the UV/vis region. Cooling to 77K results in a bathochromic (red) shift. The red shift results in two emission bands: a dominant high energy band at 438 nm and a lower intense low energy band at 619 nm.

Figure 7: Emission spectrum of (CuI)$_4$Py$_4$ demonstrating thermochromism. (a) Spectrum at 295 K ($\lambda_{ex} = 380$ nm). (b) Spectrum at 77 K ($\lambda_{ex} = 330$ nm). (c) Spectrum at 77 K ($\lambda_{ex} = 365$ nm).\[^{[13]}\]

By use of \textit{ab initio} calculations and ligand substituent studies\[^{[16]}\], the high energy band has been attributed to XLCT, while the low energy band results from a CC excited state. The high-energy band is only observed with $\pi$-unsaturated ligands, attributed to the presence of $\pi^*$ ligand orbitals. At ambient temperature, the lifetime ($\tau$) of the excited state of (CuI)$_4$Py$_4$ prior to the emission of a photon, has been measured at 11 $\mu$s, well
within the phosphorescent region. At 77K, the emission peaks for (CuI)$_4$Py$_4$ at 438 nm and 619 nm, respectively, have recorded lifetimes of 23.2 μs and 25.5 μs.\textsuperscript{[13]}

In contrast to the cubane tetramer, the dimer (CuI)$_2$Py$_4$, exhibits no thermochromism, having an emission centered around 502 nm at ambient temperature. At 77K, the emission shifts only slightly to 504 nm. The lifetimes of the excited state at ambient temperature and 77K, respectively, are 1.6 μs and 55 μs.\textsuperscript{[16]} Thus, all of the photon emissions studied seem to be phosphorescent in nature.

**Copper(I) Iodide as a Luminescent Sensor**

Metal-organics have been suggested for use in gas sensors as the substrate with which gaseous molecules interact. Their potential usefulness as sensor materials is due to properties such as photoactivity, chemical reactivity, redox activity, chirality, and porosity. The matrix is engineered with porosity in mind, with the higher surface area allowing for more interactions with gaseous molecules. More interactions between matrix material and these molecules allows for an increased luminescent response, causing a lower limit of detection.

Metal-organics have been shown to be potentially useful as detectors for O$_2$, CO$_2$, and H$_2$O. These molecules, in the gas phase, interact with the metal centers to quench metal luminescence. Examples of potential O$_2$ sensors, illustrated in Figure 8, include Ru(II)-tris(4,7-diphenyl-1,10-phenantroline) perchlorate in polysulfone and polyetherimide matrices\textsuperscript{[18]}, Pt(II) octaethylporphine in EC\textsuperscript{[19]}, and cationic complexes of Pt(II), Pd(II) and Rh(III) with water-soluble meso-tetrakis(N-methyl-4-pyridyl)porphyrin in perfluorinated ion-exchange membranes, such as Nafion\textsuperscript{[20]}. 
Figure 8: Metal-organics used for the detection of O\textsubscript{2}(g). (a) Ru(II)-tris(4,7-diphenyl-1,10-phenanthroline) perchlorate. (b) Pt(II)-octaethylporphine. (c) Pt(II)-(meso-tetrakis(N-methyl-4-pyridyl)porphyrin.
There are a similar variety of materials that can be used for the luminescent sensing of CO$_2$ and H$_2$O. Drew et al. \cite{21} reported the sensing of H$_2$O (g) using polycrystalline [(1,10-phenanthroline)Pt(CN-cyclohexyl)$_2$][Pt(CN)$_4$], providing experimental evidence for an attenuation of emission wavelength and intensity, rather than simply luminescent quenching. This compound is illustrated in Figure 9.

Figure 9: Structure of [(1,10-phenanthroline)Pt(CN-cyclohexyl)$_2$][Pt(CN)$_4$].
Copper(I) halides offer an advantage over the aforementioned sensing materials, insofar as a new and unique, strongly emissive peak is observed under UV light as a result of coordination to these gaseous Lewis bases. The appearance of a new peak is preferable to modulation or attenuation of existing peaks insofar as it is more obvious and allows for a lower degree of uncertainty in qualitative and quantitative determinations. Additionally, copper(I) and other d^{10} transition metals experience weak crystal field effects, increasing the likelihood of a reversible interaction with potential ligands.
EXPERIMENTAL

Materials

All reagents and solvents were purchased from Fisher, Aldrich or Acros. Gas-tight syringes were Hamilton brand 1000 and 1700 series. All water used was deionized and degassed with argon.

Analysis

Fluorimetry: All emission measurements were taken on an Ocean Optics Maya 2000Pro spectrometer. Fiber optics were fabricated in-house, whereby six 1000 µm fiber optics, bundled around a single central 1000 µm fiber optic, were directed towards the sample. The six outside fibers carried excitation light to the sample cell from a filtered 365 nm LED light source. The central fiber optic carried emission light from the sample cell into the spectrometer. Figure 10 illustrates the cross section of this configuration. This “fiber optic probe” allowed for in situ measurements, where the excitation light source came through the six outside fibers, and the emission spectrum was read by the spectrometer through the central fiber.

Figure 10: Cross section of fiber optic probe used for fluorimetry.
In order to create a consistent, reproducible surface, the face of the fiber optic probe was cut flat, orthogonal to the length of the probe. According to Snell’s law of refraction,

$$\sin \theta_1 n_1 = \sin \theta_2 n_2$$

where $\theta_1$ and $\theta_2$ are the angles of incidence of a ray crossing the boundary between two media with refractive indices $n_1$ and $n_2$. The two media in this case are air and the fiber optics, with refractive indices of 1.000 and 1.492, respectively. Given the flat-cut probe, $\theta_1 = 90^\circ$. According to Snell’s law of refraction, the angle of refraction for light originating from the fiber optics, $\theta_2$, is therefore $42.08^\circ$. In order to maximize the efficiency of the fiber optics, the entire sample must be illuminated under UV light from the excitation fibers, while keeping the sample as close to the probe as possible in order to maximize throughput of the emissive photons into the detector fiber. This idea is illustrated in Figure 11.
Using simple trigonometric operations, the minimum height of the probe above the sample at which the entire sample is illuminated is 0.45 cm. Thus, for all measurements, the sample was located approximately 0.45 cm below the fiber optic probe.

The $x$-axis of the output from the spectrometer (the emission wavelength) was calibrated using an Ocean Optics HG-1 Mercury/Argon line source. The $y$-axis (emission intensity) was calibrated using an Ocean Optics HL-2000CAL blackbody light source.
**Thermogravimetric Analysis:** All thermogravimetry measurements were taken on a TA Instruments Q500 TGA in the high resolution mode (variable heating rate). Maximum heating rate, occurring while little mass change was detected by the instrument, was 50 °C/min., with 60 mL/min. N₂ flow rate. Measurements were taken up to 300 °C.

**X-Ray Diffraction:** Powder X-ray spectra were taken using a Bruker SMART Apex IIdiffractometer using graphite-monochromated Cu Kα radiation. Well-ground samples were suspended in Paratone N oil. Experiments collected four frames, with 2θ ranging from 5° to 100°. Processing of data was carried out with DIFFRAC-Plus and EVA software. [22]

**Optical Microscopy:** Optical micrographs were taken using a Nikon SMZ800 microscope with capability of capturing images of the field and sending them to a computer.
Syntheses

Synthesis of \((\text{CuI})_2\text{Py}_4\)\[^{[23]}\]

A 0.285 g sample of CuI was dissolved in 0.22 mL pyridine, resulting in a yellow solution. Hexanes were added in excess of the point where the solution became colorless, separating from it a pale yellow-green powder. This precipitate was held under the solvent until analysis, due to its air sensitivity (avoiding conversion to \((\text{CuI})_4\text{Py}_4\)). Immediately before analysis, the precipitate was collected in a fritted glass funnel via vacuum-filtration.

Synthesis of \((\text{CuI})_2\text{Py}_4\)\[^{[23]}\]

A 16.301 g sample of KI was completely dissolved in 10.0 mL water, creating a saturated solution. 2.359 g of CuI was stirred in, and 1.000 mL pyridine added. The precipitate was collected in a fritted glass funnel via vacuum filtration, and thoroughly washed sequentially with water, ethanol, and hexanes.

Fabrication of CuX Pellets \((X = \Gamma, \text{CN}^-, \text{SCN}^-)\)

Pellets were pressed using a pellet-press fabricated in-house. Approximately 0.170 grams of CuX powder was placed between two 0.75 cm rods butting up against each other, with approximately 2000 lbs force applied to the rods to push them together, pressing the CuI into a pellet. The pellet press is shown in Figure 12.
CuX Pellet Drop Tests

One drop (approximately 0.014 mL) of volatile nucleophile (L) was placed on a pre-prepared CuX pellet at ambient temperature and pressure conditions. Experiments were performed on the exposed pellet once all visible traces of liquid on the CuX surface had disappeared.
CuX Pellet Vapor Exposure

**Saturated Atmosphere:** A 225 mL glass jar was modified for this experiment, in order to create a closed chamber in which a pellet would be exposed to vaporous L without being exposed to the liquid. The lid, lined with Teflon on the inside, was drilled and a 3.5 cm rubber stopper placed through the middle. A glass tube with an inner diameter of 5 mm and an outer diameter of 9 mm was placed through the middle of the stopper and secured with epoxy cement. The bottom of the glass tube (inside the chamber) was slightly flared inward with an oxygen/propane torch, to create a shelf-like intrusion. This allowed for the fiber optic probe to be fed through the glass tube, with the end resting on the shelf. A septum was incorporated around the probe to seal against the top of the glass tube. The base from the pellet press was placed inside the reaction vessel, with a CuX pellet on the top. Six drops of L were placed in the reaction vessel, around the outside of the base holding the pellet. Immediately upon introducing the L to the reaction vessel, the vessel was sealed, and data collection began, at ambient temperature and pressure conditions. Temperature was controlled by immersion of the reaction vessel in a controlled-temperature water bath.
Figure 13: Illustration of reaction vessel used to expose CuI pellets to pyridine (L), via saturated pyridine vapor pressure.

Non-saturated Atmosphere: A reaction vessel, similar to the one used for saturated VOC atmosphere, was used. This reaction vessel had a septum on the lid, to allow for delivery of L via syringe. The experiment was set up in a fashion similar to that with a saturated atmosphere, but without the presence of liquid L in the bottom of the chamber. Instead, air with a predetermined vapor pressure of L was delivered through the septum via a gas-tight syringe at ambient temperature and pressure conditions, in order to establish a target vapor pressure, according to Table 1. The vapor pressure inside the gas-tight syringe was established by establishing a saturated atmosphere of L in a closed 225 mL jar. The vapor pressure of L was controlled by placing the jar in a controlled-temperature water bath, and maintaining temperature at 23.0 °C. The vapor pressure of a pure volatile substance varies with temperature according to the Antoine equation. [24]
This is predicated on the assumption that L acts as an ideal gas. Data collection was commenced immediately upon introduction of L to the reaction vessel.

Table 1: Volumes of L introduced into reaction vessel to produce target vapor pressures.

<table>
<thead>
<tr>
<th>L P_{vap} in chamber</th>
<th>Vol. injected</th>
<th>L P_{vap} injected</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00 Torr</td>
<td>12.16 mL</td>
<td>18.51 Torr</td>
</tr>
<tr>
<td>0.50 Torr</td>
<td>6.078 mL</td>
<td>18.51 Torr</td>
</tr>
<tr>
<td>0.10 Torr</td>
<td>1.216 mL</td>
<td>18.51 Torr</td>
</tr>
<tr>
<td>0.05 Torr</td>
<td>0.6078 mL</td>
<td>18.51 Torr</td>
</tr>
<tr>
<td>0.01 Torr</td>
<td>0.1216 mL</td>
<td>18.51 Torr</td>
</tr>
</tbody>
</table>
Figure 14: Illustration of reaction vessel used to expose CuI pellets to pyridine (L), via unsaturated pyridine vapor pressure.

Fabrication of CuX-impregnated PVC films

50 mL of THF (47.0 g, 0.65 mol) was heated to 40 °C on a hotplate with vigorous stirring. 8.0 g of PVC was slowly added until completely dissolved, forming a 15% by mass stock solution. 10 mL of this PVC stock solution was transferred to a beaker and stirred vigorously on a hotplate at 40 °C. 6.0 g CuX was suspended in this solution to form a 9.8% by mass CuX suspension. This resulting suspension was poured onto a glass plate and pulled to a thickness of 0.381 mm by placing a doctor blade on the plate above the suspension and drawing it down the length of the suspension. The suspension was left to dry overnight and collected the next day using a small razor blade to peel up
the edges of the dried film. The dried film was sanded with 1500 grit sandpaper before use in experiments.

**CuX-impregnated PVC film drop tests**

A square of CuX-impregnated PVC film was cut out with an area of 4 cm². A drop of L was placed on this film at ambient temperature and pressure conditions. Experiments were performed on the exposed film once all traces of liquid on the CuX surface, visible to the naked eye, had disappeared.

**CuX-impregnated PVC film vapor exposure**

**Saturated L Atmosphere:** The reaction vessel from the CuX pellet saturated vapor exposure was utilized, but without the base from the pellet press. Instead, a 25 mL beaker was inverted, and a square of CuX-impregnated PVC film cut to 4 cm² was taped on top with double-stick tape. After this, the procedure for vapor exposure mirrored that used for exposure of a CuX pellet to a saturated L atmosphere.

**Unsaturated L Atmosphere:** The reaction vessel from the CuX pellet unsaturated vapor exposure was utilized, but with the same changes made from the PVC film saturated vapor exposure. After this, the procedure for vapor exposure mirrored that used for exposure of a CuX pellet to a nonsaturated L atmosphere.
Fabrication of CuX-embedded polypropylene (PP) plates: Procedure A

A 1.0 cm thick polypropylene plate was cut into 4 cm$^2$ squares using a reciprocating saw with a wood blade. The upper face of the PP plate was then sanded with 1500 grit sandpaper to ensure uniformity on the surface. The upper heating plate on a heated press was set at 200 ºC. The 4 cm$^2$ PP plate was placed in the heated press, with the top of the PP plate 2.0 mm from the upper heating plate. After ten minutes, the heated polypropylene was pressed, heated side down, into a mound of finely-ground CuX. The PP plate, with the CuX that clung to it, was returned to the heated press at the same distance from the upper heating plate, and heated for 30 min. The PP plate was then removed from the press and dusted off with a brush to remove excess CuX. This heating process allowed for partial melting of the plate, thus partially absorbing a thin layer of CuX into the surface.

Fabrication of CuX-embedded polypropylene (PP) plates: Procedure B

A 1.0 cm thick polypropylene plate was cut into 4 cm$^2$ squares using a reciprocating saw with a wood blade. The upper face of the PP plate was then sanded with 1500 grit sandpaper to ensure uniformity on the surface. The upper heating plate on a heated press was set at 200 ºC. Finely ground CuX was suspended in acetone, in concentrations of 0.150 g/mL, 0.750 g/mL, and 1.850 g/mL. The sanded surface of the PP plate was then placed into the solution and immediately removed, with a given amount of CuX/acetone suspension stuck to it. The PP plate, along with the CuX that clung to it, was placed in the heated press with the upper face 2.0 mm from the upper heating plate, and heated for 30
min. The PP plate was then removed from the press and dusted off with a brush to remove excess CuX.

**CuX-embedded polypropylene plate drop tests**

A drop of L was placed on a CuX-embedded PP plate at ambient temperature and pressure conditions. Data collection and subsequent experiments were performed on the exposed PP plate once all visible traces of liquid on the surface had disappeared.

**CuX-embedded polypropylene plate vapor exposure**

**Saturated L Atmosphere:** The procedure for vapor exposure mirrored that for exposure of a CuX-embedded PVC film to a saturated L atmosphere, with the exception that a 10 mL beaker was used in order to accommodate for the extra thickness of the PP plate.

**Unsaturated L Atmosphere:** The procedure for vapor exposure mirrored that for exposure of a CuX-embedded PVC film to an unsaturated atmosphere, but again using a 10 mL beaker to accommodate for the extra thickness of the PP plate.
RESULTS AND DISCUSSION

Previous research in the Pike group\textsuperscript{[25], [26], [27]} has focused on interactions between copper(I) cyanide and various neutral donor ligands and characterization of the product luminescent properties. All syntheses were direct in nature, involving exposure of CuCN to liquid amine or sulfide with the product being suspended in the neat liquid nucleophile. The current work represents the next step for us: testing our potential sensory substrate’s ability to interact with gaseous volatiles, and examining the resultant changes in luminescent properties. Volatiles used for this work are shown in Figure 15. Additionally, various CuX compounds were examined for their viability as potential sensory devices, with the intention of identifying a substrate with preferable properties over those of CuCN. Various supporting media for nucleophile exposure were explored, with the intention of finding a durable, easy-to-fabricate, and sensitive medium upon which to expose our substrate to the aforementioned volatile nucleophiles (L). The ultimate goal in finding a suitable exposure medium, for the purpose of this study, was to use the supported CuX to study the potential correlation between vapor pressure of the particular volatile nucleophile and the luminescent response of CuX:L under UV excitation. We also hoped to get an idea of the limit of detection using this system.
Figure 15: Volatile nucleophiles used in this work as ligands (L), coordinating to copper centers.
Selection of Sensory Substrate

The copper(I) salts CuCN, CuSCN, and CuI were selected as candidate compounds for our sensory substrate, based on their relative stability, the softness of the ligand, their low expense, and their demonstrated ability to pick up nucleophiles.\textsuperscript{[25],[26],[27]} All three compounds are known to exhibit luminescent properties in association with their tendency for the copper(I) center to take on one to two incoming ligands. Along with pure CuCN, CuSCN, and CuI, various mixtures of these compounds were prepared for testing by grinding together. These ground mixtures included CuCN/CuSCN, CuCN/CuI, CuSCN/CuI, and CuCN/CuSCN/CuI, all in equimolar proportions. The three pure compounds and four ground mixtures were each pressed into pellets and then exposed to various volatile nucleophiles via direct addition of a drop of the liquid (the “drop test”), according to reaction (1).

\[
\text{CuX (s)} + \text{L (l)} \rightarrow (\text{CuX})_n\text{L}_m \text{(s)}
\]  

Nucleophiles used for these drop tests included Py, 2-Pic, Pipd, MeMorph, EtPipd, MePyrrol, and Quin. Based on the visually-estimated intensity of emission and variety of colors observed, CuI and 1:1 CuSCN/CuI were picked out of the group of candidate substrates for further evaluation. These two compounds were exposed to a variety of amines, sulfides, and phosphorus-containing volatiles via the pellet drop test method, in order to determine which one displayed the most favorable properties, namely emissive intensity. Additionally, powder X-ray diffraction was utilized to determine whether the ground CuSCN/CuI mixture created a new phase upon being pressed into a pellet, or if it remained a mixture of the constituent CuI and CuSCN phases. As can be seen in Figure 16, the diffractogram for the pressed CuSCN/CuI proved to be a mixture of the peaks for
CuI and CuSCN. Based on this data, it is evident that, under the conditions used, the CuSCN/CuI mixture maintained distinct CuI and CuSCN phases.

Figure 16: Powder X-ray diffraction overlay for CuI, CuSCN, and CuSCN/CuI.
Figure 17: Pellet drop tests on both CuI and CuI/CuSCN. Photos taken under 365 nm irradiation.
As shown in Figure 17, CuI generally displayed a higher intensity of emission and a wider variety of emission colors. Additional favorable properties of CuI include a simple unit cell, not having to mix it with another material to make the substrate, and lack of toxicity. Based on these criteria, CuI was selected as the sensory substrate.
Products from Direct Syntheses

Direct synthesis of \( (\text{CuI})_2\text{Py}_4 \) via dissolution of CuI in pyridine and washing with hexanes \(^{[23]}\) resulted in a bright yellow-luminescent product with an emission band centered at 520 nm. The product was sensitive to the air, losing pyridine to form \( (\text{CuI})_4\text{Py}_4 \) within half an hour of exposure to air. To remedy this, the product was kept under solvent until analysis. Characterization of the product was performed using thermogravimetric analysis (TGA), see Figure 18. Two mass losses are observed on the plot: one between 58 °C and 81 °C, and another between 115 °C and 162 °C. The initial mass loss resulted in a 78.4% mass percent, closely matching the expected 77.3% expected after an initial loss of pyridine to form the pyridine-poor \( (\text{CuI})_4\text{Py}_4 \). The final mass percent after the mass loss at 140 °C was 55.3%, closely matching the 54.7% expected following the loss of the remaining pyridine to form CuI. These results are summarized in Reactions (2) and (3).

\[
2 \ (\text{CuI})_2\text{Py}_4 \ (s) \rightarrow (\text{CuI})_4\text{Py}_4 \ (s) + 4 \text{ Py (g)} \quad (2)
\]

\[
(\text{CuI})_4\text{Py}_4 \ (s) \rightarrow 4 \text{ CuI (s)} + 4 \text{ Py (g)} \quad (3)
\]
Figure 18: TGA of (CuI)$_2$Py$_4$.

Synthesis of (CuI)$_4$Py$_4$ via addition of CuI and pyridine to a solution of KI in water$^{[23]}$ resulted in a bright-green luminescent product with an emission band centered at 580 nm. The identity of the product was confirmed again using thermogravimetric analysis. As seen in Figure 19, a single mass loss was observed between 111 °C and 141 °C. This mass loss resulted in a mass percent of 71.8%, closely matching the 70.7% expected upon loss of pyridine.
Initial Vapor Exposure Experiments

Initial experiments conducted by exposing CuI pellets to pyridine vapor revealed that CuI was indeed capable of adsorbing Py from the gas phase. A saturated Py atmosphere was established in a sealed reaction vessel, and a CuI pellet exposed for a period of ten minutes, at 30.0 °C. A series of emission measurements was taken using the LED fiber-optic fluorimeter every minute following the beginning of the experiment, seen in Figure 20. Initially, a peak was observed at 580 nm, indicating that CuI had interacted with the gas-phase pyridine to form (CuI)$_4$Py$_4$, via Reaction 4.

\[
CuX(s) + L(g) \rightarrow (CuX)_nL_m(s) \quad (4)
\]

Within two minutes, a shoulder was observed at 520 nm, and three minutes into the experiment the peak at 520 nm had overtaken that at 580 nm, indicating that (CuI)$_2$Py$_4$
had displaced (CuI)$_4$Py$_4$ as the dominant emissive species. This came as no surprise, since one would expect the pyridine-rich dimer to form by way of the pyridine-poor tetramer upon initial exposure. Reactions 5 and 6 demonstrate this proposed sequence.

$$4 \text{CuI} (s) + 4 \text{Py} (g) \rightarrow (\text{CuI})_4\text{Py}_4 (s) \quad (5)$$

$$(\text{CuI})_4\text{Py}_4 (s) + 4 \text{Py} (g) \rightarrow 2 (\text{CuI})_2\text{Py}_4 (s) \quad (6)$$

Figure 20: Emission spectra of CuI:Py, collected via LED fiber optic fluorimeter. Measurements were taken in one minute intervals, starting at the point in time during which the CuI was first exposed to pyridine vapor. $\lambda_{ex} = 365$ nm.
Identifying a supporting medium for exposure of CuI to volatile Lewis bases

Once the feasibility of CuI as a luminescent sensor material had been confirmed, we set out to find a medium onto which we could coat CuI for exposure to the Lewis bases in question. Desirable characteristics for the support medium included durability, ease of fabrication, resistance to volatiles in the atmosphere, and formation of a consistent CuI surface. The pressed CuI pellet was the first medium tested, however several problems quickly became evident with the use of pellets. They were brittle, making handling difficult without destroying them. Additionally, the surface was fairly un-controlled, resulting in inconsistent irradiance spectra. While the relative peak height was consistent for each trial, the absolute peak height varied greatly. We attributed this inconsistency to inconsistent distribution of CuI on the surface, which resulted in variable surface area. Further discussion on this topic is found later in this section. In an effort to remedy these problems we sought a method to create a very thin layer of CuI on a solid support, thus reducing surface-level inconsistencies. The solution we devised involved distributing a thin layer of CuI on a polypropylene plate, and heating up the plate such that the CuI would become embedded in the surface, creating a permanent thin layer of CuI in the surface. Additionally, we experimented with CuI-impregnated PVC films based on previous work done in the group.\cite{28} In fabricating CuI-impregnated PVC films, we wanted to ensure that the solvent conditions in the processes did not alter the phase of the CuI. To do this, powder X-ray diffraction was utilized. Figure 20 shows that diffraction peaks for both the CuI pellet and CuI-impregnated PVC film match one another very closely, confirming that they are in fact the same phase. In order to determine which medium would best fit our needs, drop tests and vapor exposure
experiments were performed to determine which medium yielded the most favorable results.

**X-ray Diffractometry**

Powder X-ray diffractometry was utilized to compare compounds to one another. Powder diffraction is a valuable technique for comparing compounds for which other characterization methods may not be viable. For instance, determining the stoichiometry of \((\text{CuI})_n\text{Py}_m\) via TGA is only possible when the product is homogeneous in nature. When a reaction has only occurred on the surface, such as in a drop test or vapor deposition on a substrate, powder diffraction can be used to compare the product pattern to those of authentic compounds in order to identify the phases present. Powder diffraction was also used to compare CuI in different media, to ensure that the CuI phase was conserved. Given the thickness of CuI-embedded polypropylene plates, powder X-ray diffraction was not a viable technique for characterization. However, it seems a reasonable assumption that the spectra for the CuI-embedded polypropylene plates would match those for the CuI pellets, since the substrate itself was not dissolved, exposed to solvents, or otherwise potentially modified.

As seen in Figure 21, vapor deposition of pyridine onto CuI pellets and CuI-impregnated PVC films yielded the same product, which powder diffraction revealed to be \((\text{CuI})_2\text{Py}_4\). In both instances, pyridine was lost in the absence of Py vapor at ambient temperature within one hour to form \((\text{CuI})_4\text{Py}_4\).
Figure 21: Powder X-ray diffractogram of pyridine vapor deposition on CuI pellet and CuI-impregnated PVC film, overlaid on spectrum of authentic CuI. Disproportionately large peaks at $2\theta = 25.5, 29.5, 42,$ and $50^\circ$ represent $\gamma$-CuI.

Additionally, comparison of powder diffractograms for vapor deposition and drop tests for both media revealed that the same product was formed whether by liquid drop test or vapor deposition, shown in Figure 22 and Figure 23.
Figure 22: Overlay of powder X-ray diffractograms of CuI pellets exposed to pyridine via drop test and vapor deposition methods.
Figure 23: Overlay of powder X-ray diffractograms of CuI-impregnated PVC films exposed to pyridine via drop test and vapor deposition methods.
Irradiance Spectra

Irradiance spectra were taken of all three CuI/media combinations exposed to pyridine via both the drop test and the vapor exposure methods. As is evident in Figure 24, all three media yielded similar emission peaks. Comparison of emission intensity between different media is difficult since the intensity detected by the fluorimeter is dependent on how far the fiber optic probe is from the sample, and it is impossible using our system to get the same sample-probe tip distance from three different sized media. Due to the fixed height of the probe however, it is possible to compare emissive intensity among species of the same media, with identical thickness. In doing this, it is apparent that vapor deposition of pyridine onto the CuI substrate yields emission higher than do the liquid drop tests. The reason for this self-quenching effect of excess Py has yet to be determined.
Figure 24: Emission spectra for CuI exposed to pyridine via drop tests and vapor depositions. Vapor depositions were carried out in a saturated Py vapor pressure (18.51 Torr). (A) Exposure medium: CuI pellet, (B) Exposure medium: CuI-impregnated PVC film, (C) Exposure medium: CuI-embedded polypropylene plate. $\lambda_{\text{ex}} = 365$ nm.
The data summarized above, combined with observations made regarding the physical properties of the different exposure media, helped us to decide on which medium was best suited to our needs.

**CuI Pellets**

The first experimental medium investigated was the CuI pellet, shown under magnification in Figure 25. CuI pellets were by far the simplest of the viable candidates, being pure substrate. In any molecular device, the simplest solution is often the best one, for reasons of reliability and/or ease of production. However, there proved to be many disadvantages to the pellets.

Figure 25: Optical micrograph of CuI pellet. Field of view is 1.67 mm across.
Fabrication of CuI pellets, despite the simple pressing procedure, was quite difficult, owing to the brittleness of the pellet. The pellet would often break upon removal from the pellet press. This brittleness is an unappealing trait for a detector, since it makes handling of the substrate difficult. We obtained inconsistent pellet data on the fluorimeter, getting widely varied emissive intensities. We attribute this to an inconsistent surface on the molecular level; however, this is difficult to prove without surface characterization techniques. That being said, different surface compositions would explain our inconsistent data. A pellet with a higher surface area would have more molecules on the surface to absorb UV light, thus resulting in a greater number of photons being emitted, giving a higher emissive intensity.

Furthermore, chemisorption of pyridine onto the substrate proved to be irreversible for the CuI pellets. The idea of reversibility is to allow for the substrate to release the ligand after uptake, as seen in Reaction 6 and Figure 26. This is advantageous because a substrate can be recycled if the nucleophile uptake is reversible, allowing for repeated reuse of the substrate, rather than needing to replace it every time a slight shift in luminescence is observed.

\[(\text{CuI})_4\text{Py}_4 \text{(s)} \rightarrow 4 \text{CuI (s)} + 4 \text{Py (g)} \quad (6)\]
Figure 26: Suggested means for uptake and release of ligand by CuI and resultant change in luminescence.

Initial efforts at reversing the adsorption of pyridine onto the CuI substrate involved simply leaving the \((\text{CuI})_4\text{Py}_4\) product in open atmosphere at ambient temperature for the duration of a week to see whether the pyridine would spontaneously desorb. When this proved to be unsuccessful, the product was put into a vacuum oven, pulling a vacuum of under 5 Torr at 30 ºC. This too was unsuccessful. The last attempt at reversibility for the CuI pellets with pyridine was an HCl acid wash. The idea was pyridine would be protonated via Reaction 7. Thus, the pyridine could be removed from the substrate via a simple wash with water. The concentrations of HCl used varied from 1 \(M\) to 18 \(M\). Not even concentrated 18 \(M\) HCl proved successful in removing pyridine from CuI.

\[
(\text{CuI})_4\text{Py}_4 (s) + 4 \text{HCl (aq)} \rightarrow 4 \text{CuI (s)} + 4 \text{HPy}^+\text{Cl}^- (\text{aq}) \quad (7)
\]
CuI-Embedded Polypropylene Plates

Embedding some sort of polymer plate with CuI seemed to be a promising idea. Creating a very thin layer of CuI would provide for consistent emissive intensity, allowing us to study the effects of varying the vapor pressure of pyridine on emissive intensity of the substrate. Furthermore, once consistent, reliable data were accessible, we could then undertake efforts to determine the limit of detection for our device. Additionally, having a thin layer of CuI would theoretically allow for a reversible chemisorption, since there would be fewer physical barriers to the desorption of pyridine from the substrate surface.

We decided to use polypropylene for our polymer support, given its relatively low melting temperature and the low cost. The low melting temperature enabled the material to soften sufficiently through heating to re-solidify around CuI particles on the surface, thus holding them in place. The first difficulty encountered with the embedded-polymer method was fabrication of the material. In order to be able to collect consistent data on our fluorimeter, the fiber optic probe had to be held at a consistent distance from the substrate during every experiment. Thus, the substrate-support had to remain the same thickness for all experiments. However, partial melting of the support surface tended to cause the surface to swell. Eventually, a compromise was found between overheating the material (causing it to melt), and not heating it sufficiently for it to hold the CuI. Once we had found the proper temperature and duration during which to heat the polymer in order to embed CuI on the surface without swelling the material, we attacked the next problem. Since the goal was to have a consistent, reproducible CuI surface on the support material, close attention was paid to the distribution of CuI on the
surface. The initial fabrication method involved heating the polypropylene plate until the surface became tacky, pressing the tacky side down into a mound of CuI powder, reheating the polypropylene with the CuI on top, and then brushing off the excess CuI from the surface. However, CuI proved to have a high affinity for itself upon heating; thus, it tended to clump on the surface and either completely pull off of the support surface, or remain fixed to the surface in a clump. Grinding the CuI with a mortar and pestle prior to heating did not remedy this problem. It became clear that a more consistent CuI surface must be attained on the polymer surface prior to the heating step.

To do this, we experimented with suspending the CuI in acetone. The concentration of CuI suspended in the acetone was varied from that of a highly fluid, sparsely distributed suspension to that of a thick paste. The polypropylene plate, following initial heating, was pressed tacky-side down into the suspension, and then reheated. As with the previous method, the excess CuI was brushed off the surface after removal of the sample from the heat source. The methods involving the thicker (0.750 g/mL and 1.850 g/mL) suspensions were subject to the problems seen before, with the CuI clumping together upon volatilization of the acetone under the heat source. However, the use of less concentrated 0.150 g/mL suspension was found to be quite successful for creating a thin layer of CuI on the surface. An optical micrograph of the CuI surface created on the polypropylene plate using the thin suspension of acetone method is found in Figure 27.

Although a thin layer of CuI was successfully created on the polypropylene plate, the distribution of CuI on the plate was still found to be non-reproducible, with replicate fabrications yielding variable CuI distributions. In addition, the size of the particles exerted an effect on the uniformity of the surface. Since the size of the particles was not
successfully regulated, we found uneven distributions of variably sized particles on the polypropylene surface. This made for widely variable surface areas of CuI substrate on the polypropylene support surfaces, making it impossible to collect reliable quantitative data using several different samples.

Figure 27: Optical micrograph of CuI-embedded polypropylene plate. Field of view is 1.67 mm across.
Sorption of pyridine onto the CuI-embedded polypropylene plates proved to be irreversible as well. Luminescent properties indicative of the presence of pyridine on the substrate were observed after leaving the plates exposed to ambient air overnight. Additionally, these properties were observed upon removal of the plates from a vacuum oven pulling 5 torr at 30 ºC. However, a wash with 2.0 M HCl did remove the luminescence indicative of CuI:Py interaction, returning it to the weak pink luminescence indicative of CuI. Luminescence was reestablished by exposing the CuI-embedded polypropylene plate to pyridine. Thus, reversibility was possible for this medium, without destroying the substrate.

Despite the drawbacks, the CuI-embedded polypropylene plates showed promise insofar as they proved to be very durable and easy to handle.

**CuI-Impregnated PVC Films**

In the past year, members of the Pike Group had experimented with CuCN-impregnated PVC films as a means of exposing CuCN to volatile nucleophiles. The advantages noted were that they were easier to handle, and less toxic than crystalline CuCN. Drawbacks of this system were that the sorption of the nucleophiles was irreversible, and fabrication of the material was a lengthy process involving multiple starting materials. Even though the sorption had earlier been shown to be irreversible for CuCN-impregnated films, we decided to experiment with CuI-impregnated films to see if these too formed interactions with nucleophiles irreversibly. Thus, CuI-impregnated PVC films were formed by suspending CuI in a PVC solution in THF before casting the film, in a fashion similar
that used in the fabrication of CuCN/PVC films. [28] The CuI-impregnated PVC film is shown under magnification in Figure 28.

There were some readily evident drawbacks to the CuI-impregnated PVC films upon initial experimentation. Liquid drop tests destroyed the medium, whereby the pyridine acted as a solvent, dissolving the PVC. This made collection of drop test data impossible. Exposure of CuI/PVC films to saturated pyridine atmospheres resulted in condensation of pyridine onto the surface of the film, causing noticeable swelling and eventual dissolution of the support. Quantitative fluorimetry was not reliable for this medium even before the film had begun to dissolve, since the swelling of the film caused it to move closer to the fiber optic probe, resulting in more intense detection of luminescent emission. Additionally, fabrication of the films was a long process, involving multiple starting materials and several steps. Finally, the nucleophile uptake was found to be irreversible under vacuum and acid wash with HCl concentrations as high as 6 M. Beyond 6 M, the acid wash did remove the ligand, but it subsequently destroyed the film, defeating the goal of reversibility.

Exposure of CuI-impregnated PVC films to non-saturated pyridine atmospheres yielded much better results, with the film remaining intact, and no detectible swelling of the medium. Initially the intensity of the luminescent response varied slightly between samples, but this was corrected by sanding the CuI-impregnated films to ensure a uniform surface across samples. Thus, data collected on the fluorimeter was consistent in nature, yielding predictable luminescent intensities upon UV excitation. Another advantage was that the medium allowed for us to control the amount of CuI on the surface simply by varying the ratio of CuI to PVC solution prior to casting the film. For
exposure of these films to pyridine vapor pressures of down to 0.001 Torr, reversibility was still not observed.

Figure 28: Optical micrograph of sanded CuI-impregnated PVC film. Field of view is 1.67 mm across.

Based on the observations outlined above, CuI-impregnated PVC films were selected as the exposure media for this work. The films were the only media through which we could control the consistency of the CuI surface (by means of sanding), allowing for the collection of reliable quantitative data in particular environments. The benefits of being able to collect reliable data for non-saturated pyridine atmospheres outweighed the disadvantage found in the fact that we could not collect reliable data for
liquid drop tests or saturated pyridine atmospheres using the films. This was a reasonable compromise, since the goal of this study was to detect low vapor pressures of volatile nucleophiles in the atmosphere. The exposure media would never be exposed to any sort of saturated atmosphere during practical use as we intended it. For the sake of collecting data over varied vapor pressures and determining the low vapor pressure limit of detection, the CuI-impregnated PVC films best suited our needs at this point.

**Vapor Pressure Versus Luminescent Response**

The final goal of this work was to examine a correlation between vapor pressure of the volatile nucleophile and the luminescent intensity of the CuX substrate. This work took the form of varying the vapor pressure of pyridine in the reaction vessel via serial gas dilutions, as described in the Experimental Section, and using the LED fiber optic fluorimeter to obtain an emission spectrum for the CuI/PVC substrate under 365 nm excitation. Pyridine vapor pressures were established in the reaction vessel according to Table 2. Real-time emission data were collected on the fluorimeter, and the emission spectrum retained once the peak height had stabilized (Figure 29).
Table 2. Unsaturated vapor pressures of pyridine in reaction vessel, and associated maximum emission peak heights from CuI substrate.

<table>
<thead>
<tr>
<th>Vapor Pressure (Torr)</th>
<th>Max Peak Height (µW/cm²/nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>0.00435</td>
</tr>
<tr>
<td>0.01</td>
<td>0.01207</td>
</tr>
<tr>
<td>0.1</td>
<td>0.02258</td>
</tr>
<tr>
<td>1.0</td>
<td>0.03037</td>
</tr>
<tr>
<td>2.0</td>
<td>0.03632</td>
</tr>
<tr>
<td>3.0</td>
<td>0.04259</td>
</tr>
<tr>
<td>5.0</td>
<td>0.05824</td>
</tr>
<tr>
<td>10.0</td>
<td>0.09468</td>
</tr>
</tbody>
</table>

Figure 29: Emission spectra of CuI-impregnated PVC films exposed to variable pyridine vapor pressures. $\lambda_{ex} = 365$ nm.
A direct correlation was observed between vapor pressure of pyridine and the maximum peak height from the emission of CuI, whereby higher pressures of pyridine yielded greater peak heights in the emission spectrum of CuI. In performing the real-time experiments, it was noted that the peak height would increase with the uptake of pyridine by CuI, but it would eventually stabilize and stop increasing, as if reaching an asymptote. This stabilization would take anywhere from four hours for the vapor pressure of 10 Torr, to three full days for the vapor pressure of 0.001 Torr. Two immediately evident explanations exist to explain this. The first explanation is that an equilibrium is reached, whereby the rate of uptake of pyridine from the gas phase would match the rate of loss of pyridine from CuI to the atmosphere. The alternate explanation is that uptake of pyridine is continued by CuI until the pyridine is depleted from the atmosphere, either due to complete deposition onto the substrate, or leaking from the reaction vessel into the external environment. Since our experiments regarding reversibility suggest that CuI-impregnated PVC films do not release pyridine in the presence of air under ambient conditions, the alternate explanation seems more likely. No experiments have been done to confirm this, but if it is indeed correct, then we would have to measure the rate of pyridine uptake from the atmosphere in order to accurately measure the quantity of pyridine in the atmosphere. This is assuming the device is being used in a large system and that it will continue the uptake of pyridine until there is no pyridine left in the atmosphere. The lowest vapor pressure we were able to establish with our gas-tight syringes, and without a complex serial dilution scheme, was 0.001 Torr. As seen in Figure 29, there was still a substantial emission peak
indicating the presence of pyridine at this vapor pressure, so a limit of detection was not determined in this work.
CONCLUSION

We have evaluated several candidate substrates for our potential luminescent sensing device, and concluded that copper(I) iodide best fulfills our needs. Various supporting media were prepared, including CuI pellets, CuI-embedded polypropylene plates, and CuI-impregnated PVC films. Based on their ability to yield reproducible data, the CuI-impregnated PVC films were selected as the sensory substrate through which to examine interactions with gas-phase pyridine in this work. CuI-embedded polypropylene displayed promise insofar as it was the only medium examined in this work that displayed any reversibility in its uptake of pyridine, a highly desirable characteristic. However, reproducible data were not obtained using this medium. Further research into the feasibility of CuI-embedded polypropylene plates is recommended, with the goal of embedding CuI-nanoparticles into the plates. We believe that the nanoparticles may provide for more reproducible data collection, since the size of the particles is controlled.

CuI pellets were exposed to a saturated pyridine vapor pressure, and the uptake of pyridine observed closely. Based on an early emission peak at 580 nm, later giving way to a strong peak at 520 nm, it was determined that the first product formed is (CuI)$_4$Py$_4$, giving way to a more pyridine-rich (CuI)$_2$Py$_4$ as more pyridine is deposited on the substrate.

The CuI-impregnated PVC films were exposed to variable vapor pressures of pyridine in an in-house-built reaction vessel, and data collected via the in-house-built LED fiber optic fluorimeter. Vapor pressures of pyridine ranged from 0.001 Torr to 10.0
Torr. Through these experiments, we confirmed the hypothesis that exposure to higher vapor pressures of pyridine leads to a stronger luminescent response from CuI. Due to limitations in our experimental method, a limit of detection has not yet been determined for this system.

Further investigation into the viability of CuI as a sensory device in the Pike group will deal with the introduction of various ligands to the system, rather than solely pyridine. Additionally, simultaneous uptake of multiple ligands is a potential area for further research.
REFERENCES

1. California Air Resources Board. Definitions of VOC and ROG.


