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Abstract: Copper(I) iodide films were cast onto glass from solution. The CuI films absorb vapor-phase amine and sulfide molecules, producing a range of photoluminescent emission colors. Spectroscopic data suggest the presence of low energy CuI cluster-centered transitions.

Real-time sensing of amine and sulfide pollutants in the environment is a matter of great importance [1]. These compounds are commonly found as contaminants in water [2], air [3], and food [4]. Although a multitude of sensor strategies have emerged in recent years, the plethora of relevant compounds provides on-going motivation for the discovery of new rapid, *in situ* sensing techniques. One real-time sensing strategy involves the spontaneous formation of photoemissive adducts on an inorganic or metal-organic substrate (Fig. 1) [5]. The unexposed detector film should be dark under UV irradiation and become emissive only after exposure to a volatile organic compound (VOC) as depicted in Fig. 1. Irradiation is not necessary for adsorption of the VOC, merely to visualize the product response. For such a device to be viable, the inorganic substrate must be cast as a film; in addition, the response to VOCs should ideally be sensitive, rapid, discriminating, and reversible [1].
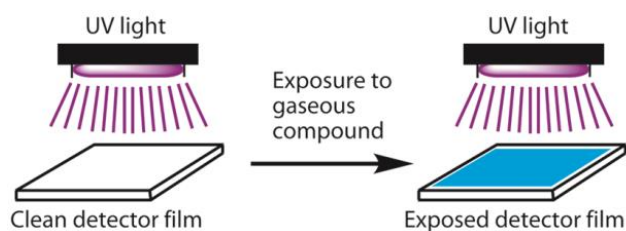

Figure 1. Design of potential luminescence VOC detector.

Copper(I) compounds are potentially ideal substrates for luminescence detection of nucleophilic VOCs, as suggested in Fig. 1. We have shown that inexpensive and stable salts, such as CuCN [6], CuSCN [7], and CuI [8] spontaneously react with amines and other nucleophiles to make weakly-bound complexes that often show photoluminescence. The photophysics of the CuI-amine cubane and related clusters has been studied experimentally and computationally by Ford and others [8-10]. The results have revealed a variety of photophysical processes, including metal-centered (MC) and cluster-centered (CC) transitions which, although modulated by the amine, do not require amine acceptor orbitals (such as π^*). Although the vapochromic behavior of the CuI system has been noted [11], no research has yet demonstrated the facile casting and use of CuI films as viable VOC sensors. The objective of the current study is the development of CuI film surfaces for real-time

photoluminescence detection of amine and sulfide vapors in the environment. It was anticipated that CuI films cast onto glass would enable us to exploit the facile formation and the known photoluminescence behavior of CuI-nucleophile adducts, offering facile visual detection of nucleophilic VOCs. Being a soft d^{10} Lewis acid, Cu(I) is not especially subject to coordination of water or formation of surface oxide. Furthermore, it is indefinitely stable in air.

CuI films were cast by evaporation of 100 mM CuI/CH$_3$CN solution on clean microscope cover glasses. The CuI/glass films were exposed for 5−15 min. to saturated atmospheres of amine or sulfide vapors in sealed containers. Steady-state photoluminescence spectra of the CuI/glass films were measured immediately after exposure at both ambient and liquid nitrogen temperatures. Scanning electron microscopy (Fig. 2) and optical microscopy (Fig. 2, Supporting Information) of unexposed and pyridine (Py) exposed CuI films showed film thicknesses of approximately 1 μm, and nearly continuous film coverage. As seen in Fig. 2, there is a difference in CuI surface morphology before and after exposure to Py vapor. Some degree of crystallinity is lost, but more complete coverage of the glass is realized, presumably due to recrystallization upon CuI-Py binding. Powder X-ray diffraction (PXRD) of fresh films confirmed the expected cubic γ-CuI phase (see Fig. 3). After Py exposure PXRD revealed the formation of an additional phase corresponding to the Py adduct (Fig. 3).
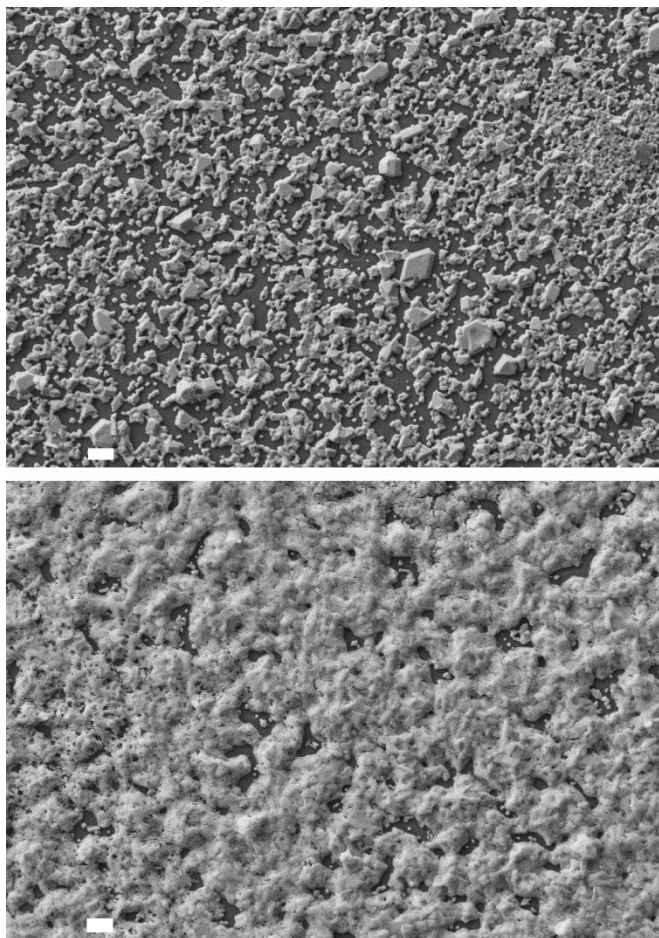
Figure 2. Scanning electron micrograph of unexposed (top) and pyridine-exposed (bottom) CuI film/glass sample (scale bar = 2 μm)
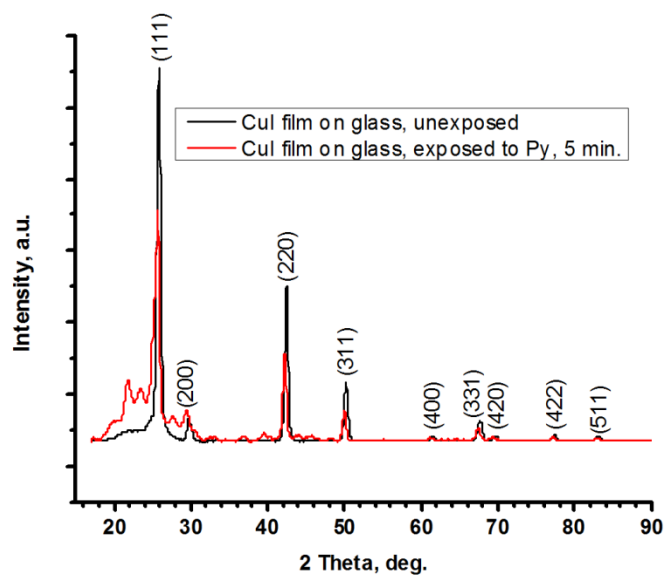
Figure 3. Powder diffraction trace of CuI film on glass before and after 5 min. pyridine (Py) exposure. Indexed peaks for γ-CuI noted.

The luminescence activity of the exposed films was measured under ambient or reduced temperature conditions (see Fig. S3-S7). The unexposed CuI film on glass displayed a sharp narrow emission peak at 414 nm with a corresponding excitation peak at 390 nm. This emission has been ascribed to the exciton band gap recombination of γ–CuI crystals [12]. This peak yields a very faint purple emission which remains detectable upon vapor exposure, but is no longer visible to the eye. A wide range of luminescence behavior is observed when the CuI films are exposed to amine vapors, as seen in Fig. 4. Table 1 displays the maximum excitation and emission energy and Stokes shift at ambient and liquid nitrogen temperatures for select amine and sulfide compounds. Maximum excitation of emissive adducts occurs in the UV (277−357 nm), varying fairly widely. Emission wavelength varied from blue to orange and was often distinctive even for chemically similar VOCs, demonstrating the potential selectivity of CuI detection. Aromatic amines tended to have higher emission energies than aliphatic amines or sulfides. Blue-shifts were noted for Py when substituted as various isomers of MePy, BrPy, and ClPy. Overall, emission maxima ranged from 447 nm (3-BrPy) to 620 nm (tetrahydrothiophene, THT) with relatively large Stokes shifts occurring in all cases. It was noteworthy that the 2-MePy, morpholine (Morph), and THT adducts showed pairs of emission peaks at room temperature.
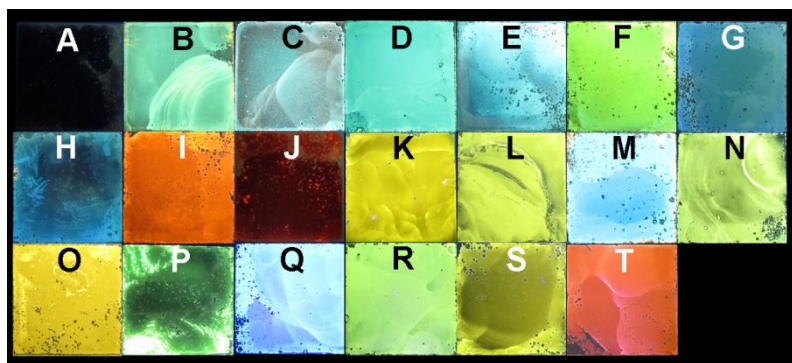

Figure 4. Previously VOC-exposed CuI films on glass placed under 365 nm irradiation. A, no exposure, B, Py; C, 2-MePy; D, 3-MePy; E, 4-MePy; F, 2-BrPy; G, 3-ClPy; H, 3-BrPy; I, 2-PhPy; J, 4-AcPy; K, Pipd; L, N-MePipd; M, N-EtPipd; N, Morph; O, N-MePyrr; P, N,N'-Me$_2$Pipz; Q, N,N'-Et$_2$Pipz; R, Me$_2$S, S, Et$_2$S; T, THT. (see Table 1 for abbreviation key.)

Table 1. CuI-Adduct Luminescence Results

Adduct[a]	298 K Data			77 K Data		
	Ex λ, nm	Em λ, nm	Stokes, cm^{-1}	Ex λ, nm	Em λ, nm	Stokes, cm^{-1}
Py	344	552	11000	365	500	7400
2-MePy	347, 308	488, 575	8390, 15100	–	–	–
3-MePy	357	491	7980	320, 360	463, 497	9660, 7660
4-MePy	336	482	9020	–	–	–
2-BrPy	300	451	11200	–	–	–
3-ClPy	330	460	8560	316	461	9950
3-BrPy	325	447	8400	–	–	–
2-PhPy	277	495	15900	–	–	–
4-AcPy	327	594	13700	422	588	6690
Pipd	322	586	14000	311	593	15300
MePipd	305	553	14700	–	–	–
EtPipd	312	472	10900	–	–	–
Morph	305, 337	414, 615	8630, 13400	278, 334	506, 660	16800, 14800
MePyrr	324	584	13700	–	–	–
Me$_2$Pipz	308	532	13700	–	–	–
Et$_2$Pipz	308	442	9840	–	–	–
Me$_2$S	308	546	14200	–	–	–
Et$_2$S	326	590	13700	–	–	–
THT	336	530, 620	10900, 13600	330	582	13100

[a]Py = pyridine, Ac = acetyl, Pipd = piperidine, Morph = morpholine, Pyrr = pyrrolidine, Pipz = piperazine, THT = tetrahydrothiophene. Aliphatic amines substituted at N position.

In general, small thermochromic shifts were seen between room temperature and 77 K luminescence experiments. A second, higher energy peak appeared for the 3-MePy adduct. Both Morph adduct peaks red-shifted at 77 K. THT exhibited interesting behavior, displaying blue-green and orange emission at room temperature, and only a strong green-yellow peak at 77 K. Variable temperature excitation and emission spectra for 3-MePy and THT are shown in Fig. 5.
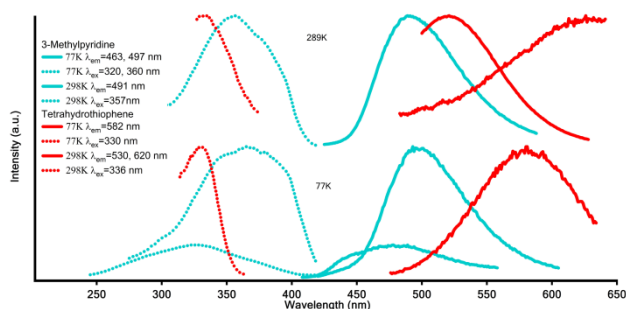

Figure 5. Ambient (298K) and liquid nitrogen (77K) temperature excitation and emission spectra of 3-MePy and THT.

In order to understand the photophysical behavior of CuI-nucleophile (CuI-L) films, structural models for the adducted CuI surface must be considered. The most relevant models are the L-coordinated cubane tetramer ($Cu_4I_4L_4$) and stair step polymer ($Cu_nI_nL_n$), see Chart 1. Both polymorphs have been found for certain L (e.g. Py), and both are emissive; however, $Cu_4I_4L_4$ has been more widely studied (L = amines, sulfides, phosphines) [8-10]. Two emission bands have been identified: a high energy (HE) and low energy (LE) band. The HE band has been ascribed to halide to ligand charge transfer (^{3}XLCT) transition having a *ca.* 90% I-based HOMO and π^* LUMO. The HE band is seen only when L has π^* acceptor orbitals; it shows relatively small Stokes shifts and is thermochromic. The LE emission band is seen regardless of ligand type, shows very little change in emission with temperature, and has a large Stokes shift. The LE band has been assigned to a ^{3}CC transition of the type $I_4 \rightarrow Cu_4$ in which increased Cu−Cu excited state bonding distorts the cluster. This reorganization produces the large Stokes shift.

As is evident from Chart 1, the presumptive arrangement of L bonded to surface Cu(I) sites on γ-CuI must be very different from that of the cubane $Cu_4I_4L_4$ or stair step $Cu_nI_nL_n$. Nevertheless, it is reasonable to expect that the surface Cu atoms are bonded to three networked I atoms, as well as to L. The resulting clusters are larger than Cu_4I_4, and thus are apt to exhibit even more facile CC transitions.

Chart 1

cubane
$Cu_4I_4L_4$

stair step
$Cu_nI_nL_n$

γ-CuI-L adduct

● = Cu   ● = I   ● = L
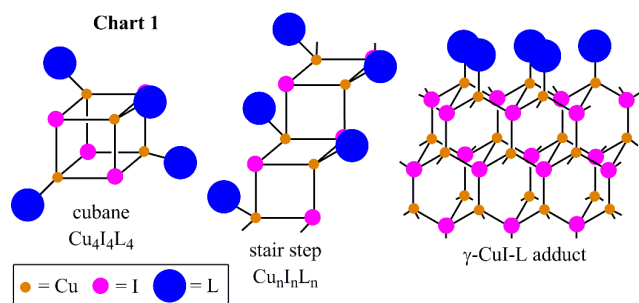
The emissive behavior of the compounds listed in Table 1 appears to be consistent with the LE band noted for $Cu_4I_4L_4$. Firstly, emission is observed for both aliphatic and aromatic ligands. Secondly, Stokes shifts are uniformly large for all ligands. And thirdly, emission energies show almost no thermochromism between 77 K and room temperature. Therefore, we hypothesize that emission from the CuI nucleophile-adducts arise from CC transitions. Nevertheless, a weak temperature-dependent HE peak was noted for 2- and 3-MePy, possibly representing the ^{3}XLCT noted for the cubane species. Of interest in the current data is the strong ligand

dependence of emission energy. This suggests that the donor orbital of the amine or sulfide ligands exerts a substantial effect on the cluster HOMO and/or LUMO energy. Computational studies aimed at understanding this effect are underway.

In prior work [8], we reported that N,N'-dimethylpiperazine (Me$_2$Pipz) forms a linked 3D network of Cu$_4$I$_4$ cubane units. Like other (Cu$_4$I$_4$)(LL)$_2$ networks (LL = bridging diamine or bis(sulfide)) [13,14], (Cu$_4$I$_4$)(Me$_2$Pipz)$_2$ shows a relatively low energy and large Stokes shifted emission (λ = 525 nm, Stokes = 12100 cm^{-1}). On the other hand, the CuI-Et$_2$Pipz network consists of chains of Et$_2$Pipz-linked 3-coordinate Cu$_2$I$_2$ dimers, and emits in the blue (λ = 444 nm, Stokes = 7780 cm^{-1}) [8]. Similar distinction between N-methyl (longer λ, higher Stokes) and N-ethyl (shorter λ, lower Stokes) was observed in the CuI film adducts for both the piperazines and piperidines. These results further support the notion that the ligands exert significant structural influence upon the cluster center, much as they do in isolated Cu$_n$I$_n$ clusters.

In summary, we have reported that CuI films cast onto a glass surface can act as vapochromic sensors for amine and sulfide VOCs (L). Because of the distinctive luminescence emission of the CuI-L adducts, CuI films show potential as environmental sensors. Photophysical analysis of the CuI-L adducts show behavior related to that of the known Cu$_4$I$_4$L$_4$ clusters. Quantitative studies of response factors versus VOC partial pressures are on-going.

Supporting information available: (1) Visible light photograph and photomicrograph of CuI/glass film and (2) luminescence spectra for exposed film samples.

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