

Solvent- and Vapor-Induced Isomerization between the Luminescent Solids [CuI(4-pic)]₄ and [CuI(4-pic)]_∞ (pic = methylpyridine). The Structural Basis for the Observed Luminescence Vapochromism

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Exposure of the polymeric solid [CuI(4-pic)]_∞ (pic = picoline = methyl pyridine) to liquid or vapor toluene leads to disappearance of its room-temperature blue emission (λ_{\max} 437 nm) and the appearance of a yellow emission (λ_{\max} 580 nm) characteristic of the [CuI(4-pic)]₄ tetramer. The process is reversed when the latter is exposed to liquid or vapor *n*-pentane. Analogous transformations between the tetrameric and polymeric forms do not occur when the 3-picoline analogues [CuI(3-pic)]_x are similarly treated. Single-crystal X-ray diffraction studies on the compounds [CuIL]_∞ and [CuIL]₄ (L = 3-, 4-pic) indicate that the 4-pic tetranuclear isomer incorporates toluene into its solid phase to give a material with the composition [CuI(4-pic)]₄·2C₆H₅CH₃, but the other three phases are solvent-free. The chains in the two polymeric phases exhibit double-zigzag configurations, also commonly observed in zeolitic tetrahedral structures. In both polymeric phases, the chains propagate along the monoclinic *b* axis. The 3-pic tetrameric phase can be described as a close-packed structure of [CuIL]₄ units, whereas tetramers in the 4-pic phase form infinite columns along the unique tetragonal *c* axis segregated by four columns of toluene pairs. These structural differences explain the different behaviors during the phase transformation between tetrameric and polymeric polymorphs of the 3-pic and 4-pic compounds.

Introduction

Recently, there has been considerable interest in the photophysical properties of mono- and polynuclear complexes of transition metals in oxidation states having the d¹⁰ electronic configuration.^{1,2} Particularly interesting among these are the derivatives of Cu(I) which not only show a great variety of structural formats but also are often brightly luminescent even at ambient temperature and with an emissive behavior varying markedly with structure and environment. Copper(I) iodide adducts with bases show a relatively small energy difference between the various polymorphs, and a simple modification in the experimental conditions can vary the form of the copper complex obtained. For example, when crystallized from benzene, toluene, or dichloromethane, the {CuIpy}_n (py = pyridine) gives prismatic crystals of the tetramer [CuIpy]₄ while recrystallization from benzene/methanol results in a mixture of the polymer [CuIpy]_∞ and [CuIpy]₄.³ The solid-state luminescence spectrum of [CuIpy]_∞, a polymeric "stair" formed by an infinite chain of steps, displays a broad blue emission band at room tempera-

ture (λ_{\max} = 437 nm), which does not shift substantially upon cooling. This was assigned to radiative decay from an excited state with iodide to pyridine charge transfer (XLCT) character.^{4,5} In contrast, the luminescence of the isomer [CuIpy]₄, which has a "cubane" structure,⁶ is quite temperature dependent, a behavior described by Hardt as "luminescence thermochromism".⁷ At room temperature, this shows a broad yellow emission (λ_{\max} = 580 nm), but two emission bands (λ_{\max} = 438 and 618 nm) are displayed at 77 K.⁴ In the latter spectrum, the higher energy band was assigned to a XLCT excited state, while that at 618 nm was assigned to a "cluster-centered" (CC*) excited-state having mixed halide-to-metal charge transfer (XMCT), d → (s,p) character. The room-temperature emission spectrum of [CuIpy]₄ is also quite sensitive to the medium. In benzene, the dominant CC* emission is shifted to lower energy (λ_{\max} = 695 nm) from that of the solid, but when hydrostatic pressure was used to freeze the room-temperature solution, the color of emission shifted from red to yellow (λ_{\max} = 575 nm). Such sensitivity to the medium rigidity has been termed "luminescence rigidochromism"⁸ and can be

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attributed to the distortion of the CC* state relative to the ground state.⁹

In this context, the changes in the emissive behavior related to modifications of the crystal structure or of the environment offer some interesting possibilities for analytical sensors. For example, Hardt and co-workers have exploited the thermochromic luminescence properties of the CuIL adducts to identify various nitrogen-based ligands by reaction of their vapors with CuI-saturated papers.¹⁰ Furthermore, the rigidochromic behavior of [CuIpy]₄ may provide a sensitive means of probing the rigidity of the surrounding matrix.

Recently, compounds of the type [PtL₄][M(CN)₄] (M = Pt, Pd; L = arylisonitrile),¹¹ [Au₃(CH₃N=COCH₃)₃],¹² and [Au(S₂CN(C₅H₁₁)₂)₂]₂¹³ were reported to show emissive behaviors which are modified by exposure to vapors of volatile organic compounds (VOC). This behavior, which can be termed "luminescence vapochromism", offers some interesting possibilities for the construction of VOC sensors. Here, we report the luminescence vapochromism for the two [CuI(4-pic)]_n (**I**, n = 4; **II**, n = ∞) solids associated with the reversible interconversion of the two Cu(I) isomers by exposure to solvent vapors.¹⁴ The structures of these two forms are also reported as are the structures of the analogous tetranuclear and polynuclear complexes of 3-picoline which do not display a similar response to the solvents in question.

Experimental Section

Preparations. [CuI(4-pic)]₄·2C₆H₅CH₃ (**I**). This white compound was prepared by addition of toluene to solid [CuI(4-pic)]_∞ and stirring the mixture to give a saturated solution. After being filtered, pentane was added to precipitate the product as a powder showing a yellow emission under UV irradiation. By adding pentane to the point where precipitation just begins and cooling the mixture to 4 °C, needle-shaped crystals of the compound were obtained.

[CuI(4-pic)]_∞ (**II**). This was synthesized by adding excess 4-picoline ligand to a stirred solution of CuI in concentrated aqueous KI. The product precipitated immediately as a white powder and was collected by filtration and then washed successively as described above. **II** was recrystallized from dichloromethane/pentane to give needle-shaped crystals which were dried in vacuo. Yields were quantitative based on the amount of CuI used.

[CuI(3-pic)]₄ (**III**). This was synthesized by adding excess 3-picoline to a stirred solution of CuI in concentrated aqueous KI. The product precipitated immediately as a white powder, was separated by filtration, and then washed successively with saturated KI_(aq) to remove excess CuI, with H₂O to remove KI, with methanol to remove excess ligand, and then with hexanes. The [CuI(3-pic)]₄ was recrystallized from toluene/pentane to give cube-shaped crystals and then dried in vacuo. The yield was quantitative based on the CuI limiting reagent.

[CuI(3-pic)]_∞ (**IV**). Addition of 3-picoline dissolved in methanol to a stirred CuI solution in concentrated aqueous KI led to immediate, quantitative precipitation of this product as a white powder. This was filtered and washed as reported above. A few needle-shaped crystals of this compound were also obtained during the preparation of crystals of [CuI(3-pic)]₄ from toluene/pentane.

Luminescence Spectra. Solution samples were prepared in a four-window quartz 1-cm fluorescence cell, whereas solid samples for emission lifetime and spectra measurements were prepared in a 1.75-cm diameter quartz fluorimetry tube. The 77 K measurements were performed by using a quartz optical dewar filled with liquid N₂. Solvent-induced interconversions between the isomers were induced by adding liquid toluene and pentane directly to the solid sample in the 1.75-cm diameter quartz tube. The effect of vapors were checked by placing solid samples in an open small vial inside a bigger one filled with the solvent. The sealed system was then left at room temperature and the transformation was checked periodically qualitatively with an UV lamp and quantitatively by recording the powder's emission spectra using a SPEX Fluorolog 2 model III emission spectrometer interfaced with a SPEX Datamate II data station. Lifetimes were measured at 294 and 77 K using a Q-switched Nd:YAG pulsed laser operating at 10 Hz as the excitation source and techniques described previously.⁹

Single-Crystal Structure Analyses. A crystal of each sample was glued to a thin glass fiber with epoxy resin and mounted on a SMART CCD diffractometer equipped with a normal focus, 2.4 kW sealed-tube X-ray source (Mo Kα radiation, λ = 0.710 73 Å) operating at 50 kV and 40 mA. The temperature control was achieved with an Oxford Cryostream which provided a temperature range from 80 to 375 K with a stability of about 0.1 K. About 1.3 hemisphere of intensity data were collected in 1321 frames with ω scans (width of 0.30° and exposure time of 30 s/frame). The empirical absorption corrections were based on the equivalent reflections and other possible effects such as absorption by the glass fiber were simultaneously corrected. All structures were solved by direct methods followed by successive difference Fourier methods. The calculations were performed using SHELXTL running under Windows NT. Final full-matrix refinements were against F², and all reflections were included in the refinements. The crystallographic parameters for all four phases are summarized in Table 1.

Results and Discussion

Solvento- or Vapochromic Behavior. The luminescence vapochromism of solid {CuI(4-pic)}_n was demonstrated by the luminescence spectral changes which occurred slowly upon exposure of the solid polymeric material [CuI(4-pic)]_∞ (**II**) to toluene vapors and more rapidly upon exposure to toluene liquid. The new spectrum is characteristic of the tetranuclear isomer [CuI(4-pic)]₄ (**I**), so the spectral changes can be attributed to the **II** → **I** solid-state isomerization stimulated by exposure to toluene.

The blue-emitting compound **II** (as characterized by X-ray diffraction analyses, see below) was prepared by addition of excess neat 4-picoline to aqueous CuI/KI solution followed by washing with KI_(aq), water, methanol, and pentane. Its room-temperature luminescence spectrum displays an emission band at λ_{max} = 437 nm (best fit to a biexponential with τ = 0.4 and 2.7 μs) which is shifted to slightly lower energy (λ_{max} = 450 nm, τ = 12.7 μs) at 77 K. In analogy to the pyridine analog,⁴ assignment of this band as XLCT in nature appears appropriate.

In contrast to the 3-picoline analogue described below, **II** is only slightly soluble in most organic solvents. Despite this, addition of a small amount of liquid

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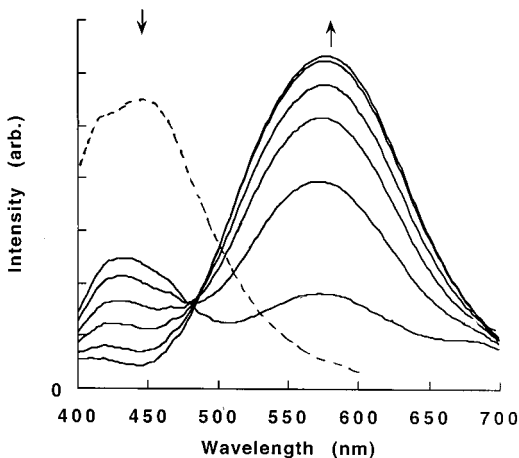
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Table 1. Crystallographic Parameters for $[\text{CuI}(3\text{-pic})_4]$ (III), $[\text{CuI}(3\text{-pic})]_\infty$ (IV), $[\text{CuI}(4\text{-pic})]_\infty$ (II), and $[\text{CuI}(4\text{-pic})_4] \cdot 2\text{C}_6\text{H}_5\text{CH}_3$ (I)^a

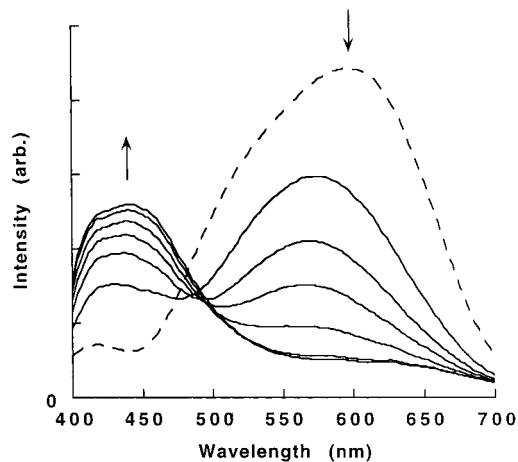
compounds	III	IV	II	I
formula	$(\text{CuIC}_6\text{NH}_7)_4$	CuIC_6NH_7	CuIC_6NH_7	$(\text{CuIC}_6\text{NH}_7)_4(\text{C}_7\text{H}_8)_2$
fw	1134.26	283.57	283.57	1318.53
habit	irregular block	needle	needle	needle
crystal size (μm)	$266 \times 266 \times 200$	$266 \times 27 \times 13$	$400 \times 10 \times 10$	$400 \times 20 \times 20$
space group	$P2_1/c$	$P2_1/n$	$C2/m$	$I-4c2$
a (\AA)	15.119(4)	9.1945(9)	20.0178(9)	16.1304(7)
b (\AA)	24.5144(6)	4.2514(4)	4.1460(2)	16.1304(7)
c (\AA)	18.3911(5)	20.471(2)	10.5935(5)	16.553(1)
β ($^\circ$)	92.495(1)	96.759(1)	118.966(1)	90
V (\AA^3)	6809.9(3)	794.6(1)	769.21(6)	4306.9(4)
Z	8	4	4	4
T ($^\circ\text{C}$)	20	20	-123	-123
ρ (calcd) (g cm^{-3})	2.213	2.370	2.449	2.033
μ (Mo, $\text{K}\alpha$) (mm^{-1})	6.110	6.545	6.762	4.846
max 2θ ($^\circ$)	50	50	56	50
no. of total data	33 287	3 705	2 559	10 790
no. of unique data	11 837	1 369	1 059	1 901
R_{int} (I)	0.073	0.082	0.035	0.100
no. of obsd data, $I > 2\sigma(I)$	7285	956	981	1693
no. of parameters	618	84	68	106
$R(F)$ (%)	4.01	6.57	2.74	4.13
$R_w(F^2)$ (%)	7.77	14.8	7.28	8.30
GOF	0.938	0.964	1.09	0.969

^a $R(F)$, $R_w(F^2)$, and GOF are based on reflections with $I > 2\sigma(I)$.

**Figure 1.** Emission spectral changes during the toluene-induced **II** \rightarrow **I** transformation.

toluene to the solid polymer at room temperature (far less than the quantity required for substantial dissolution) led to the disappearance of the characteristic blue luminescence and subsequent appearance of a yellow luminescence from the solid with an emission band centered at 580 nm ($\tau = 8.4 \mu\text{s}$) (Figure 1). The solid-state transformation from the blue- to the yellow-emitting compound is not accompanied by any visual macroscopic change in the appearance of the solid in the absence of UV illumination, and appeared to occur through formation of a nonemitting intermediate, readily formed by exposure of **II** to the liquid toluene, which gradually transformed into **I**.

The toluene supernatant solution isolated from the above experiment shows a room-temperature emission band at 684 nm, considerably different from the solid-state emissive behavior and consistent with that expected for solutions of **I**. Addition of pentane to this solution led to the formation of crystals of the yellow-emitting compound ($\lambda_{\text{max}} = 580 \text{ nm}$), which was demonstrated to be the tetramer **I** by low-temperature X-ray diffraction with toluene molecules incorporated in the crystal packing (see below). Notably, when these crys-

**Figure 2.** Emission spectral changes during the pentane-induced **I** \rightarrow **II** transformation.

tals were stored in vacuo, the emission maximum shifted to 600 nm, and the material became polycrystalline and was no longer suitable for single-crystal X-ray diffraction analysis. However, after 1 day in vacuo at room temperature, the blue emission switched on at the expense of the yellow one, a process which was shortened to a few minutes by heating the solid sample to 343 K. The **I** \rightarrow **II** transformation also occurred upon leaving **I** exposed to air for 2 days.

Remarkably, when **I**, obtained as reported above and dried in vacuo, was exposed to a small amount of liquid pentane, it completely reverted to the blue-emitting polymer **II** within 2 h (Figure 2). The emission at $\lambda_{\text{max}} = 600 \text{ nm}$ first shifted to 580 nm then gradually switched off with concomitant growth of the 437 nm band characteristic of **II**.

These observations prompted examination of the solid-state behavior of the two $[\text{CuI}(4\text{-pic})_n]$ oligomers in the presence of toluene and pentane vapors to see if interconversion between the two structures could also be affected by the solvent vapors. In this context, when the blue-emitting solid $[\text{CuI}(4\text{-pic})]_\infty$ was left in a sealed vial in contact with toluene vapors at ambient temper-

Table 2. Photophysical Properties of Compounds I–IV

compound	$\lambda_{\max}^{\text{em}}$ (nm)	τ (μs)	$\lambda_{\max}^{\text{exc}}$ (nm)
Room Temperature			
[CuI(3-pic)] ₄	614	8	310
[CuI(3-pic)] _∞	454	0.38, 3.8	330
[CuI(4-pic)] ₄ ·2C ₆ H ₅ CH ₃	580	8.4	350
[CuI(4-pic)] _∞	437	0.4, 2.7	360
77 K			
[CuI(3-pic)] ₄	590, 456	9.3, 10	323
[CuI(3-pic)] _∞	454	0.57, 4.2	350
[CuI(4-pic)] ₄ ·2C ₆ H ₅ CH ₃	564, 452	9.8, 0.9, 22	325
[CuI(4-pic)] _∞	450	12.7	370

ature partial pressure, the transformation to the yellow-emitting **I** was complete within 2 days. The reverse process, the transformation from **I** to **II**, can be carried out by exposing [CuI(4-pic)]₄ solid to pentane vapors for 3 h. Remarkably, in the presence of pentane vapors, the transformation **I** → **II** is at least 1 order of magnitude faster than the analogous process when the solids are exposed only to dry air. The transformations proved to be fully reversible and were carried out many times on individual samples.

The tetranuclear complex of 3-picoline **III** analogous to **I** was prepared by addition of neat 3-picoline to an aqueous KI saturated solution of CuI (see Experimental Section). A single-crystal X-ray diffraction study gave the molecular structure consistent with that previously reported for [CuI(3-pic)]₄.¹⁵ The room-temperature luminescence spectrum of this material displays a single, broad emission band at $\lambda_{\max} = 614$ nm ($\tau = 8$ μs). Furthermore, solid **III** shows the thermochromic behavior typical of many other [CuI(py-*x*)]₄ derivatives,² so at 77 K, two emission bands, one somewhat narrower and shifted to the blue ($\lambda_{\max} = 590$ nm, $\tau = 9.3$ μs) from that seen at room temperature, and one at higher energy ($\lambda_{\max} = 456$ nm, $\tau = 10$ μs) are present in its luminescence spectrum. In analogy with [CuIpy]₄ these emissions can be suggested to be from the CC* excited state and the XLCT excited state, respectively. A slight modification of the synthetic procedure, involving the dissolution of the 3-picoline in methanol before the addition to the CuI/KI aqueous solution, gave instead the blue-emitting polymer [CuI(3-pic)]_∞ (**IV**), selectively. The room-temperature emission spectrum of **IV** displays a band at $\lambda_{\max} = 454$ nm (best fit to a biexponential with $\tau = 0.38$ and 3.78 μs) which is not shifted but somewhat narrowed by lowering the temperature to 77 K. This band can be suggested to derive from a XLCT state in analogy with the luminescence spectrum of [CuIpy]_∞.

Both [CuI(3-pic)]_n isomers are very soluble in most organic solvents. The emission spectra were the same for the ambient-temperature toluene solutions of both compounds with a single broad band centered at 682 nm. This suggests that dissolution of **IV** leads to reassembly of the molecular fragments to the tetranuclear species [CuI(3-pic)]₄ in solution as was seen above for the 4-pic analogue. Pentane addition to the toluene solution of **IV** gave solid **III** as characterized from its emission spectrum.

Despite the ready reorganization of **IV** to **III** in solution, these two isomers show a very different behavior from that described above for the 4-picoline

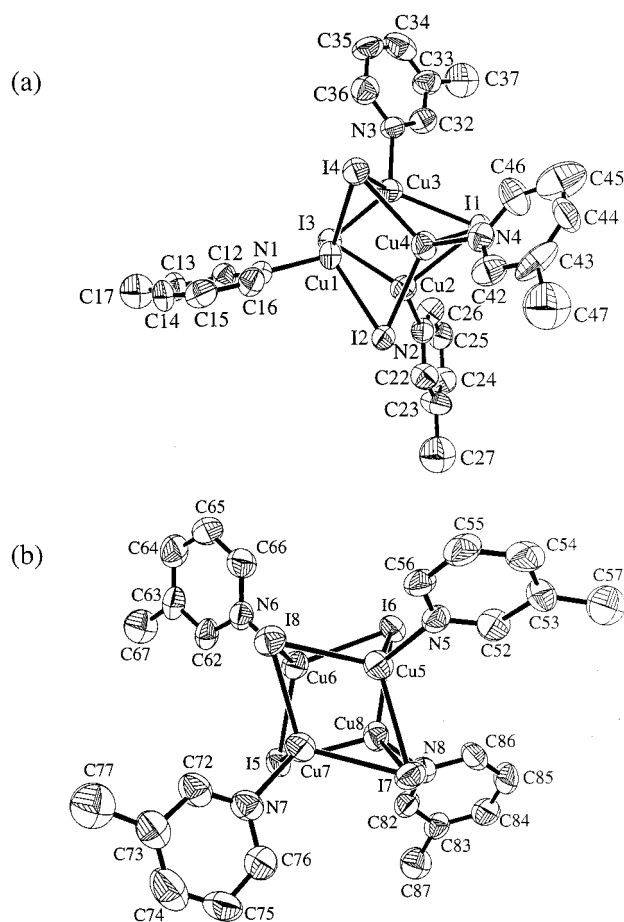


Figure 3. Molecular structure and numbering of atoms for [CuI(3-pic)]₄. There are two crystallographically independent molecules. Thermal ellipsoids are drawn at the 50% level.

analogues with regard to the solid-state reactivities. Heating **IV** at 358 K for a few hours leads to the formation of **III**, a solid state [CuIL]_∞ → [CuIL]₄ conversion in the opposite direction from that seen for L = 4-pic for which the polymeric material appeared to be the more stable in the solid, at least in the absence of toluene. Moreover, there was no interconversion between the two oligomers in either direction by exposure to toluene or pentane vapors.

Luminescence Spectra of Oligomers. The emission maxima of the [CuI(3-pic)]_x and [CuI(4-pic)]_x ($x = 4, \infty$) solids are summarized in Table 2 along with the excitation data and the luminescence lifetimes. Our observations are in agreement with previous results by Hardt¹⁶ who reported that the derivatives of stoichiometry CuIL 1:1:1 with L = 4-, 3-, and 2-pic emit at room-temperature blue, yellow, and orange, respectively. The first two of these observations are explained by noting that the synthetic procedures used lead to formation of the "stairstep polymer" product **II** when L = 4-pic, but the tetranuclear isomer **III** when L = 3-pic. In preliminary studies, we found that a similar preparation by adding neat 2-picoline to a saturated KI solution of CuI gave a white solid which displayed an orange emission ($\lambda_{\max} = 656$ nm) compound. This is suggestive of formation of the tetranuclear product [CuI(2-pic)]₄. The same product was also formed upon the analogous

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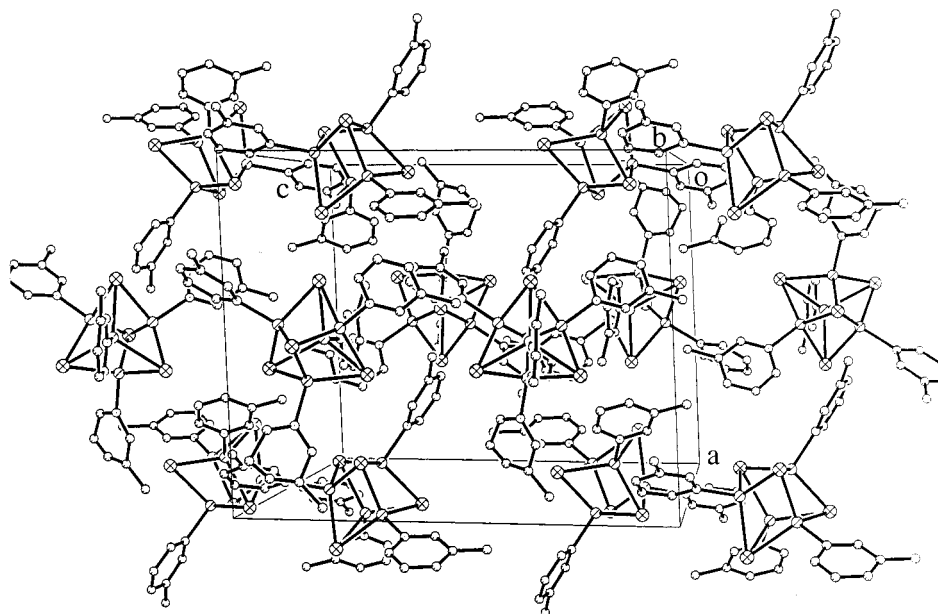


Figure 4. Unit cell packing diagram for $[\text{CuI}(3\text{-pic})_4]$.

reaction of 2-pic dissolved in methanol, i.e., the procedure which gave the polymer **IV** for $L = 3\text{-pic}$.¹⁷ Exposure to liquid toluene had no effect on the emission properties of this solid.

Crystal Structures. Structures were solved for all four compounds (**I–IV**) described in this article. Positional coordinates for all four structures solved as well as bond lengths and bond angles are listed in the Supporting Information, Tables 1s–19s.

$[\text{CuI}(3\text{-pic})_4]$ (**III**) and $[\text{CuI}(3\text{-pic})]_\infty$ (**IV**). There are two crystallographically unique tetrameric units per the asymmetric unit in the cubane phase **III** (Figures 3 and 4), whereas in the polymeric phase **IV** there is only one unique 3-picoline molecule (Figures 5 and 6). Thus, this tetranuclear phase has an 8-fold supercell as compared to the isomeric polymer phase. Because of the formation of chains, the polymeric phase is slightly more dense than the molecular cubane phase. For the two tetrameric units of **III**, the six Cu–Cu distances all fall in the 2.68–2.74 Å range while the eight Cu–N(pic) and the 24 Cu–I metal-adjacent ligand distances fall into the 2.037–2.062 Å and 2.66–2.79 Å ranges, respectively. For **IV**, the corresponding Cu–Cu, Cu–N(pic), Cu–I distances are 2.911(2), 2.650–2.694, and 2.063–(10) Å, respectively. A key feature in the latter is the longer Cu–Cu distance, since the presence of the relatively low energy CC* emission has been correlated with the very short Cu–Cu distances found in the $[\text{CuIL}]_4$ tetramers.²

In the polymeric phase, the inorganic species, Cu and I, form infinite chains in the double-zigzag configuration (also called a stairstep polymer). The chain propagates along the shortest unit cell axis, the *b* axis (Figure 6). Each iodine is bonded to three copper cations, and each copper ion is tetrahedrally coordinated, to three iodine ions and to a nitrogen atom of the 3-picoline molecule. Thus, despite very different crystal structures, the local coordinations (3 and 4, respectively) of copper and iodine

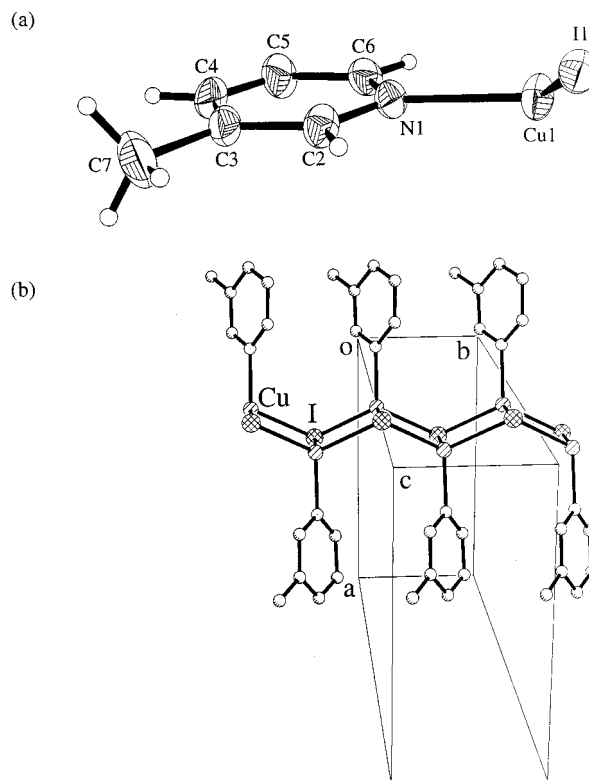


Figure 5. (a) Molecular structure and numbering of atoms for $[\text{CuI}(3\text{-pic})]_\infty$. Note that there is one unique 3-picoline molecule per asymmetric unit. Thermal ellipsoids are drawn at the 50% level. (b) Infinite polymeric chain in the stair configuration propagating along the crystallographic *c* axis in $[\text{CuI}(3\text{-pic})]_\infty$.

in the cubane and polymeric phases are essentially the same.

$[\text{CuI}(4\text{-pic})]_4 \cdot 2\text{C}_6\text{H}_5\text{CH}_3$ (**I**) and $[\text{CuI}(4\text{-pic})]_\infty$ (**II**). Among adducts of copper halides with Lewis bases, the 4-picoline cubane phase **I** is rare because it requires the inclusion of the solvent molecule (toluene) to stabilize its configuration. The loss of the solvent molecules (either through heating or solvent extraction with

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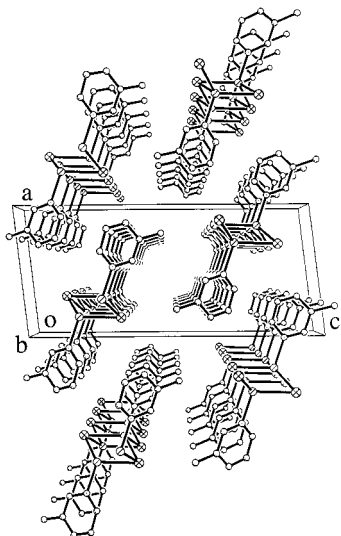


Figure 6. Unit cell packing diagram projected down the crystallographic *b* axis for $[\text{CuI}(3\text{-pic})]_{\infty}$ showing relative orientations of six polymeric chains.

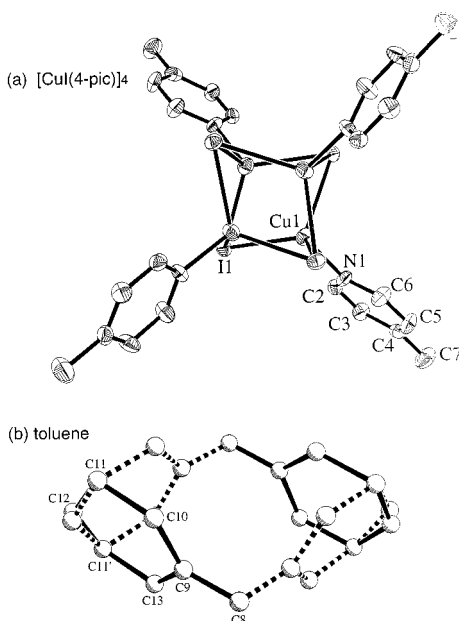


Figure 7. (a) Molecular structure and numbering of atoms for **I**. Note that there is one crystallographically unique 4-picoline molecule per asymmetric unit. Thermal ellipsoids are drawn at the 50% level. (b) Two possible orientations for the distribution of the toluene pair in $[\text{CuI}(4\text{-pic})]_4 \cdot 2\text{C}_6\text{H}_5\text{CH}_3$.

pentane) transforms the cubane phase into the one-dimensional "step polymer" phase. Toluene molecules in the 4-picoline cubane phase are present in pairs, and each pair is disordered over two statistical sites (Figure 7). The 4-picoline polymeric phase **II** is also unique because it is the only phase reported here that contains orientationally disordered ligand molecule. Similar to the 3-picoline polymeric, the chain in the 4-picoline polymeric phase has a double-zigzag configuration and propagates along the shortest crystallographic axis, the *b* axis (Figure 8). For **I**, the Cu–Cu, Cu–I, and Cu–N(pic) distances are 2.651–2.735, 2.671–2.714, and 2.031(7), respectively. For **II**, the corresponding Cu–Cu, Cu–I, and Cu–N(pic) distances are 2.8087(8), 2.640–2.662, and 2.057(4), respectively. Again, the shorter Cu–Cu distances in the former are consistent

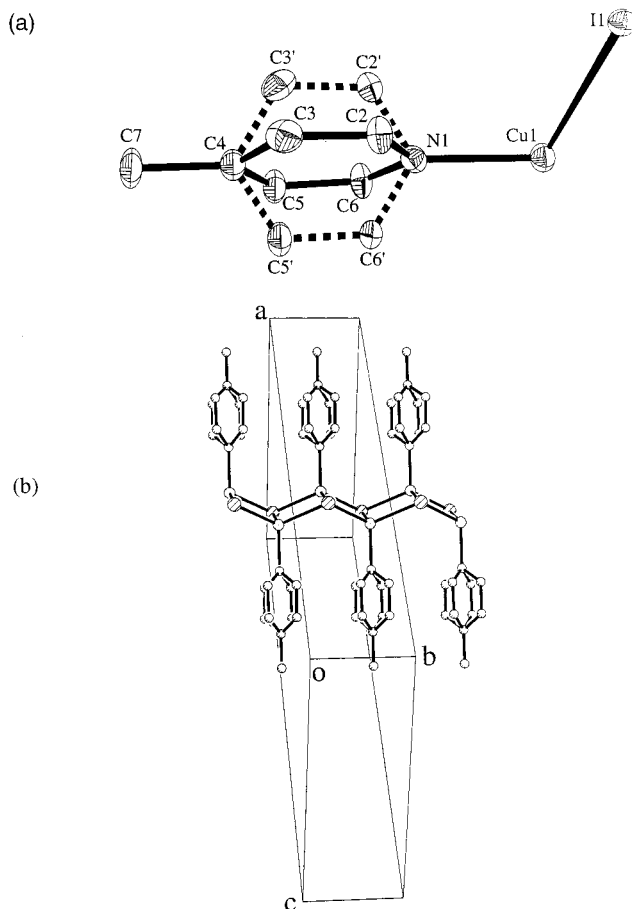


Figure 8. (a) Molecular structure and numbering of atoms for $[\text{CuI}(4\text{-pic})]_{\infty}$. Note that there is only half of the 4-picoline molecule per asymmetric unit because of the mirror symmetry. Two statistical orientations of the aromatic ring are illustrated. Except orientationally disordered C2, C3, C5, and C6 atoms, all other atoms are located on the mirror plane. Thermal ellipsoids are drawn at the 50% level. (b) Infinite polymeric chain in the stair configuration propagating along the crystallographic *b* axis in $[\text{CuI}(4\text{-pic})]_{\infty}$.

with the appearance of a CC^* emission band with this material.

There is only one crystallographically unique 4-picoline molecule in the cubane phase. As a comparison, there are eight crystallographically unique 3-picoline molecule in the corresponding 3-picoline cubane phase. This is undoubtedly due to the relatively higher molecular symmetry of 4-picoline molecules leading to the more symmetric tetrameric unit. For the same reason, there is only half of a 4-picoline molecule per asymmetric unit in the 4-picoline polymeric phase as compared to one unique 3-picoline molecule in the 3-picoline polymeric phase.

It is likely that the inclusion of the toluene pairs in solid **I** is because that more symmetrical 4-picoline tetrameric units cannot be stacked in an efficient manner. The large voids generated between adjacent tetrameric units need to be filled with suitably shaped molecules. This is illustrated by comparing the unit cell packing diagram for **I** in Figure 9a in which the included toluene molecules are shown with Figure 9b where they are not shown. In contrast, the tetrameric 3-picoline units pack reasonably well given that its density (2.213 g cm^{-3}) is only slightly less than that of the polymeric phase (2.370 g cm^{-3}).

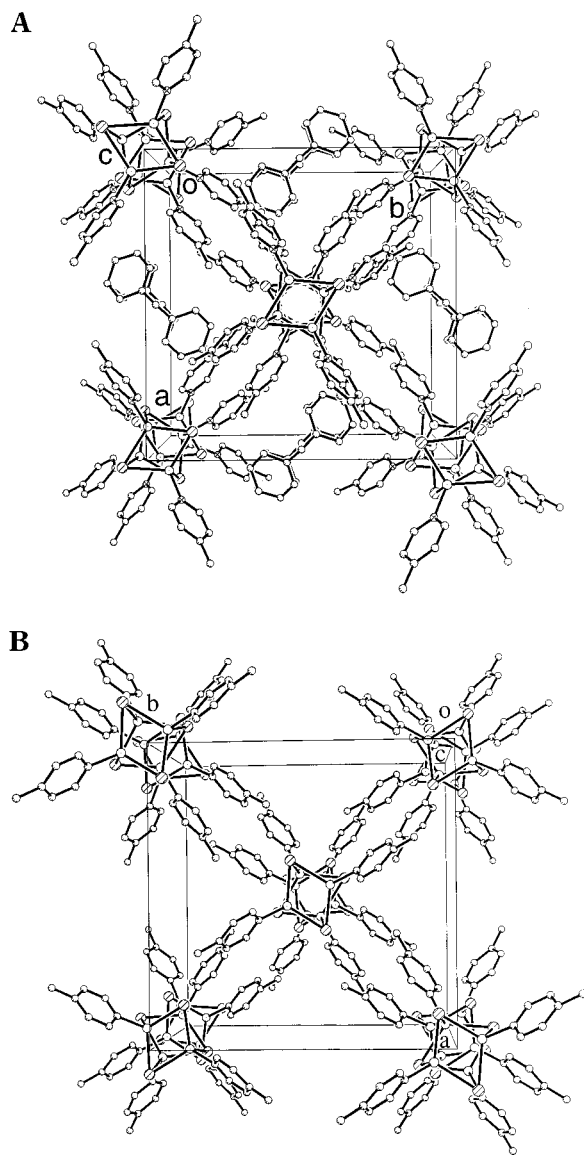


Figure 9. (A) Unit cell packing diagram projected down the crystallographic c axis for $[\text{CuI}(4\text{-pic})]_4$ showing five columns of tetramers and four columns of toluene pairs. Note that the shortest distance between centers of two tetramers (or toluene pairs) is only half of the c axis. (B) Same structure with toluenes removed to illustrate the channels occupied by the included solvent molecules.

Phase Transformation. Both the tetrameric units and the toluene pairs are located on crystallographic special positions in the 4-picoline cubane form **I**. The tetramers are located at unit cell origins, body centers, centers on the c axis and ab face centers, whereas the toluene pairs are located at centers of a and b axes and ac and bc face centers. The number of tetramers is equal to the number of the toluene pairs. Columns of tetramers are separated by columns of toluene pairs along the c axis (Figure 8). Each tetramer column is surrounded by four toluene columns and vice versa. It should be noted that the mass centers of the tetramers and toluene pairs have the same z height so that tetramers along the a or b axis are separated by toluene pairs. However, along the c axis, there are no toluene pairs separating tetrameric units. Thus, the incorporation of toluene pairs helps the organization of tetrameric units into chains. This may facilitate the transformation of

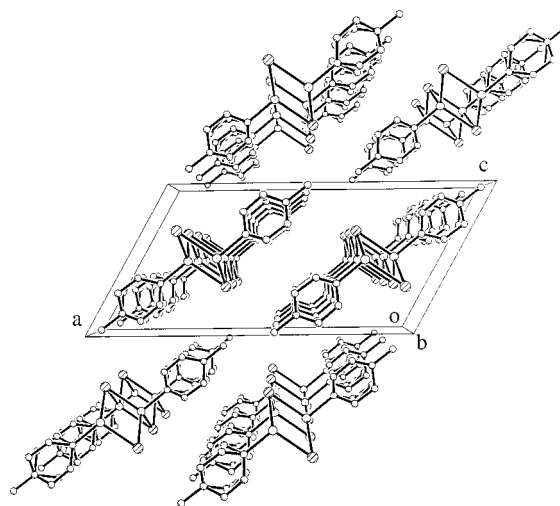


Figure 10. Unit cell packing diagram projected down the crystallographic b axis for $[\text{CuI}(4\text{-pic})]_\infty$ showing relative orientations of six polymeric chains.

the tetrameric phase **I** to the toluene-free polymeric form **II** (Figure 10), since the tetramers are already prearranged into a chain configuration. Similarly, the reverse transformation can be brought about by relatively small orientational changes of 4-picoline molecules, and no extensive migration of molecular units are needed.

In contrast, the tetramers in the 3-picoline cubane structure are closely packed, and there are no voids for the inclusion of the solvent molecules. Furthermore, there are no isolated chains of tetramers that can help in promoting the phase transformation between two different 3-picoline polymorphs.

In summary, the dramatic and reversible color changes in the emission spectra reported here make the two $[\text{CuI}(4\text{-pic})]_x$ compounds interesting candidates as sensors of VOCs. An advantage in the application of the Cu(I) compounds in this field is their relatively low cost, expense being a possible consideration in the design of practical sensors. However, the slow response times of these compounds would not be acceptable in the design of practical devices. Notably, the interconversion between the two phases is apparently dependent on the dimensions of the solid particles; e.g., the **II** \rightarrow **I** interconversion is faster for samples which have been pulverized into fine powders. In this context, ongoing work is focused on the preparation and testing of thin films.

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Supporting Information Available: Tables of crystal data, atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and crystallographic details for all four compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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