

Luminescence response of the solid state polynuclear copper(I) iodide materials [CuI(4-picoline)]_x to volatile organic compounds

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Exposure of the polymeric solid [CuI(4-pic)]_∞ to either liquid or vapor toluene leads to disappearance of this material's characteristic room temperature blue emission (λ_{max} 437 nm) and the appearance of the yellow emission (λ_{max} 580 nm) indicative of the [CuI(4-pic)]₄ tetramer; the process is reversed when the latter is exposed to liquid or vapor *n*-pentane.

Polynuclear d¹⁰ metal complexes exhibit remarkably rich photoluminescent properties coupled in part to their diverse structural motifs.^{1–3} The copper(I) halide adducts CuXL (X = halide, L = a nitrogen donor ligand) are particularly fascinating for the variety of structural formats which can be altered by varying the reagent stoichiometry, crystallization conditions and the reaction medium.^{4–7} Many are brightly luminescent, even at ambient temperature, and the emission behavior varies markedly with structure and with environment. For example, the solid state luminescence spectrum of [CuIpy]_∞ (py = pyridine), a 'stair step' polymer [Fig. 1(a)], displays a broad blue emission band at room temperature (λ_{max} = 437 nm), which does not shift upon cooling, and is probably due to an excited state with iodide to pyridine charge transfer (XLCT) character.^{7,8} In contrast, the 'cubane' isomer [CuIpy]₄ [Fig. 1(b)] shows 'luminescence thermochromism'.⁹ Room temperature, solid [CuIpy]₄ displays a broad yellow emission (λ_{max} = 580 nm), but, at 77 K, two bands are seen (λ_{max} = 438, 618 nm);^{6,7} the higher energy one is largely XLCT in character, while that at lower energy has been assigned to a mixed halide to metal charge transfer (XMCT), d→(s,p) 'cluster centered' excited state.⁸ Here we report that, for the related material [CuI(4-pic)]_x (x = 4 or ∞, 4-pic = 4-picoline), exposure of the solid to the liquid or the vapor phase of certain volatile organic compounds (VOCs) reversibly induces structural changes readily seen in the luminescent behavior.

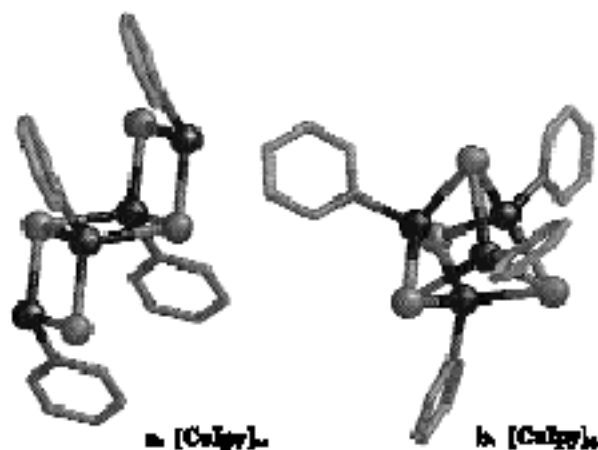


Fig. 1 Representations of the structures of the 'stair step' (a) and 'cubane' (b) forms of the compounds [CuIpy]_x, adapted from crystallographic data (refs. 5 and 6). Only a four copper fragment of the stair step chain of [CuIpy]_∞ is shown.

Addition of neat 4-picoline to an aqueous CuI–KI solution at room temperature results in the formation of [CuI(4-pic)]_∞ (A) as revealed by a single crystal X-ray structure study.¹⁰ Under UV illumination, the emission from this material is distinctly blue, and the room temperature luminescence spectrum displays a single broad band centered at 426 nm, which is shifted to slightly lower energy (λ_{max} 450 nm) at 77 K. Notably, similar addition of excess neat 3-picoline to aqueous CuI–KI solution gives the 'cubane' solid [CuI(3-pic)]₄ as confirmed by a single crystal X-ray structure determination.¹⁰ The luminescence spectrum of this solid displays a single, broad band centered at λ_{max} 614 nm at room temperature, but two bands at 77 K, one at 590 nm and one centered at 456 nm, as previously described.⁶ These results may explain the observation by Hardt and Pierre that, for solids of stoichiometry CuIL, the derivative with 3-picoline emits yellow while that with 4-picoline emits blue.¹¹ In this context, it is notable that dissolving 3-picoline in methanol before addition to the CuI–KI aqueous solution directs the reaction pathway toward formation of the blue emitting stair-step polymer [CuI(3-pic)]_∞ (λ_{max} 452 nm at room temperature) whose structure was confirmed by a single crystal X-ray study.

The polymeric [CuI(4-pic)]_∞ solid is only very slightly soluble in most organic solvents. Despite this, we found that the addition of a small amount of toluene (far less than that needed for substantial dissolution) to a vial containing solid A leads to disappearance of the characteristic room temperature blue luminescence and subsequent appearance of yellow luminescence from the solid with an emission band centered at 578 nm (Fig. 2). This band corresponds to that of the tetranuclear 4-picoline complex [CuI(4-pic)]₄ (B) which was independently prepared as described below and confirmed by a single crystal X-ray diffraction study. Notably, there appears to be an intermediate non-emitting species formed rapidly upon exposure of A to liquid toluene which more gradually undergoes

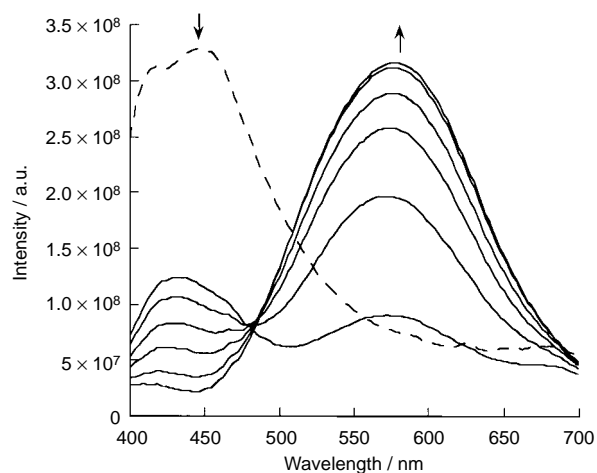


Fig. 2 Temporal emission spectra of solid [CuI(4-pic)]_∞ at ambient temperature before (---) and after (—) exposure to liquid toluene. Spectra were collected every 5 min (arrows indicate sequence of data collection).

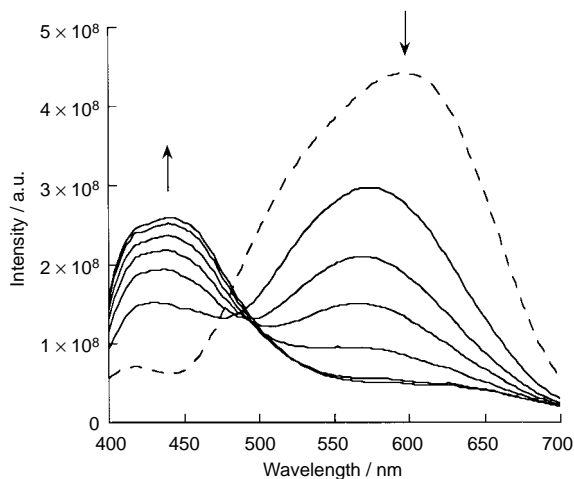


Fig. 3 Temporal emission spectra of solid $[\text{CuI}(4\text{-pic})]_4$ at ambient temperature before (---) and after (—) exposure to liquid pentane. Spectra were collected every 15 min (arrows indicate sequence of data collection).

transformation into **B** in a few minutes. We are attempting to characterize the non-emitting intermediate.

The toluene supernatant solution isolated from the above experiment shows a room temperature emission band at 684 nm, considerably different from the solid state emission behavior, as previously observed in the case of $[\text{CuIpy}]_4$.⁷ Addition of pentane to this solution led to the isolation of trace amounts of **B**. However, exposure of the room temperature cubane solid to a small amount of liquid pentane caused it to revert to the blue emitting polymer over the course of 2 h (Fig. 3).

These surprising observations prompted us to examine the solid state behavior of the two $[\text{CuI}(4\text{-pic})]_x$ derivatives **A** and **B** in the presence of toluene and pentane vapors to test whether the same transformations could be effected by exposure to the vapors as well as to the liquids of these two solvents. This indeed turned out to be the case. When the blue emitting solid $[\text{CuI}(4\text{-pic})]_\infty$ was left in a sealed vial in contact with toluene vapors at the room temperature partial pressure, the transformation to the yellow emitting cubane solid was complete within two days. The reverse process, transformation back to **A**, was effected by exposing this sample to pentane vapors for 3 hours. Remarkably, while transformation **B** to **A** can be carried out in a few minutes by heating the sample to 343 K and appears to occur thermally over several days when simply left standing in air, the process is at least an order of magnitude faster at ambient temperature under pentane vapor. The analogous transformations between the cubane and polymeric forms do not occur when the 3-picoline analogs $[\text{CuI}(3\text{-pic})]_x$ are similarly treated with liquid or vapor toluene or pentane.

In conclusion, an unusual chromic photoluminescent behavior linked to a solid state structural change induced by exposure to the liquid or vapor phase of two VOCs has been demonstrated. This behavior is strongly ligand dependent, as revealed by our analogous studies with 3-picoline. X-Ray

crystal structure determinations currently in progress¹⁰ indicate that the cubane form of $[\text{CuI}(4\text{-pic})]_x$ displaying the yellow emission band at 578 nm has incorporated toluene into the crystal packing, and it is likely that this plays an important role in effecting the solid state isomerization from the blue emitting stair-step polymer. We have not detected analogous pentane incorporation into the structure of **B**, and are uncertain as to what role pentane plays in reformation of the more stable polymer. A recent study by Eisenberg and coworkers has described a similar 'luminescent switch for the detection of volatile organic compounds' using gold(I) dimers¹² following pioneering work by Mann and coworkers on absorption and emission spectra vapochromic Pt^{II} and Pd^{II} compounds.¹³ The present work demonstrates the greater generality of such behavior, as well as the extension of this to much less expensive copper compounds, expense being a possible consideration in the design of practical sensors. An advantage of the present system is the very distinctive differences in the emission colors of the polymeric and cubane forms of $[\text{CuI}(4\text{-pic})]_4$, although the relatively slow response times would not be acceptable in the design of a practical sensor. Ongoing studies are concerned with defining the mechanisms of these structural transformations induced by exposure to VOCs as well as the photophysical mechanisms responsible for the differing luminescence responses.

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