

“On–Off” Au(I)⋯Cu(I) Interactions in a Au(NHC)₂ Luminescent Vapochromic Sensor

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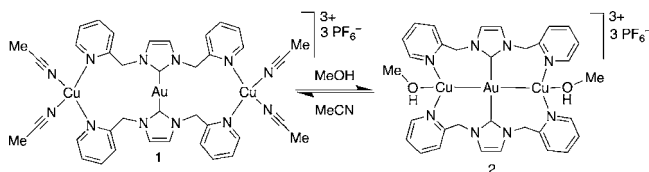
Abstract: Reaction of the Au(I) N-heterocyclic carbene (NHC) compound [Au(im(CH₂py)₂)₂]₂PF₆ with 2 equiv of [Cu(MeCN)₄]₂PF₆ affords the tricationic compound [Au(im(CH₂py)₂)₂(Cu(MeCN)₂)₂]₂(PF₆)₃ (**1**), which exhibits blue luminescence (λ_{max} = 462 nm). Reaction of **1** with either liquid MeOH or MeOH vapor affords [Au(im(CH₂py)₂)₂(Cu(MeOH))₂]₂(PF₆)₃ (**2**), which produces green luminescence (λ_{max} = 520 nm) under UV excitation. The molecular structures of **1**·2MeCN and **2**·2MeOH·2Et₂O were determined by single-crystal X-ray diffraction. Compound **1** contains a linearly coordinated [Au(NHC)₂]⁺ core in which each picolyl side arm bridges a [Cu(MeCN)₂]⁺ center. The Au⋯Cu separations are long at 4.596 Å. Compound **2** exhibits two short Au⋯Cu interactions of 2.7195(7) Å, with the Au(NHC)₂ core acting as an additional ligand toward each copper center to complete its tetrahedral coordination mode. Exposure of **2** to atmosphere produces a partial loss of MeOH accompanied by a luminescence color change to yellow (λ_{max} = 543 nm). The uptake and loss of MeOH vapor is rapid and reversible. Exposure of **2** to vacuum affords complete loss of MeOH, and the luminescence changes to yellow-orange (λ_{max} = 573 nm). Treatment of **2** with MeCN vapor regenerates **1**. The interconversion of **1** and **2** was confirmed by powder X-ray diffraction. Compound **1** also reacts with acetone and H₂O vapors, leading to species that produce yellow-orange (λ_{max} = 591 nm) and green (λ_{max} = 519 nm) emission, respectively. Compounds **1** and **2** are examples of molecular vapochromic materials that exhibit large changes in the emission through ligand substitution reactions between the solid complex and solvent vapors. The dramatic color change likely results from the “on–off” Au⋯Cu interactions induced by the ligand exchange reaction.

Vapochromic materials suitable for sensing volatile organic compounds (VOCs) by the alteration of auro-¹ and metallophilic attractions have attracted considerable attention.² Whereas these systems often comprise metallophilic Pt⋯Pt,³ Au⋯Tl,⁴ Au⋯Au,⁵ and Au⋯Ag^{2,6} interactions, compounds with Au⋯Cu contacts are generally less common,⁷ and such vapochromic compounds have not been reported to date. The mechanism associated with the vapochromic response typically involves reversible *rearrangements* catalyzed by solvent vapor or interstitial solvation of transition-metal complexes.⁸ Additionally, solid–vapor reactions involving the *exchange* of ligands coordinated to metal centers are quite rare.⁹ However, solvents are known to reversibly replace H₂O at Fe^{9f} and Co^{9a,c} centers, and HCl(g) adds reversibly to [CuCl₂L₂] (L = 3-Clpy, 3-Brpy) to afford [HL]₂(CuCl₄).^{9c,d} Leznoff and co-workers^{9b} demonstrated the viability of ligand exchange in polymers having the general formula [CuL_n](Au(CN)₂)₂ utilizing solvent vapors with different functional groups. As part of our continuing study^{7h,10} of metallophilic interactions between closed-shell metal

ions, we report a N-heterocyclic Au^I carbene complex that modulates its vapochromic response through changes in ligation and subsequent formation or cleavage of short Au⋯Cu interactions, depending on the ligand offered.

The colorless compound [Au(im(CH₂py)₂)₂(Cu(MeCN)₂)₂]₂(PF₆)₃ (**1**) is formed by the simple addition of 2 equiv of [Cu(MeCN)₄]₂PF₆ to [Au(im(CH₂py)₂)₂]₂PF₆¹⁰ in acetonitrile. The X-ray crystal structure of **1**·2MeCN (Figure 1) reveals a nearly linear Au^I center coordinated to two NHC ligands whose picolyl arms bridge two [Cu(MeCN)₂]⁺ moieties with long and presumably repulsive Au^I⋯Cu^I separations of ~4.6 Å. Additionally, compound **1**·2MeCN crystallizes as an acetonitrile disolvate with acetonitrile molecules positioned collinear to the C–Au–C vector 3.8–5.4 Å from the Au^I center. These two lattice MeCN molecules are lost upon evacuation of the crystals or prolonged exposure to air, affording blue-emitting **1** (λ_{max} = 462 nm; see Figure 3).

Scheme 1. Complexes **1** and **2**



As shown in Scheme 1, solid samples of **1** or **1**·2MeCN react with MeOH vapor to produce a green luminescent species (λ_{max} = 520 nm) presumed to be [Au(im(CH₂py)₂)₂(Cu(MeOH))₂]₂(PF₆)₃ (**2**). Alternatively, **1** is sparingly soluble in liquid MeOH but reacts to form **2**. This process can be facilitated by gentle heating. Crystallization from MeOH/Et₂O mixtures produces the bluish-green luminescent species **2**·2MeOH·2Et₂O (depicted in Figure 2), where, relative to **1**, the two MeCN ligands on each Cu^I center are replaced by a single MeOH molecule. Remarkably, this simple ligand substitution reaction induces a significant metal reorganization. In the absence of a second coordinating solvent molecule, each Cu^I center completes its tetrahedral coordination geometry through ligation to the Au^I center with short (and attractive) Au⋯Cu contacts of 2.7915(7) Å. Unlike **1**·2MeCN, the lattice solvates of **2**·2MeOH·2Et₂O reside away from the metal centers. It is also noteworthy that the picolyl arms on each NHC ligand in **2** twist to alternate faces of the complex.

Exposure to air or vacuum red-shifts the luminescence color of crystalline **2**·2MeOH·2Et₂O (λ_{max} = 502 nm) to 520 nm, reinforcing the assigned composition depicted in Scheme 1. More conclusively, the powder X-ray diffraction (XRD) pattern obtained from a vacuum-dried sample of **2**·2MeOH·2Et₂O matches the pattern obtained by exposing **1** to dry MeOH vapor [see the Supporting Information (SI)]. Both **1** and **2** were additionally characterized by several methods (see the SI), and their spectroscopy and analyses are consistent with their proposed formulation.

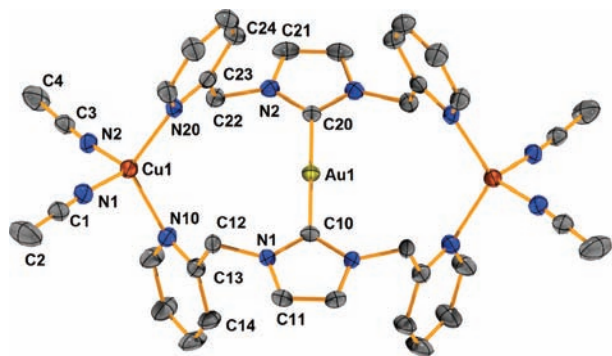


Figure 1. Molecular structure of **1**·2MeCN; lattice solvent, anions, and hydrogen atoms have been omitted for clarity. Selected distances (Å): Au1···Cu1, 4.591; Cu1–N1, 2.996(4); Cu1–N2, 2.986(4); Cu1–N10, 2.058(4); Cu1–N20, 2.044(4).

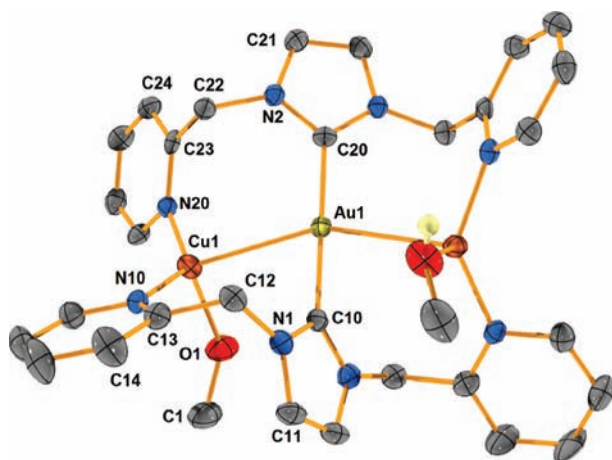


Figure 2. Molecular structure of **2**·2MeOH·2Et₂O; lattice solvents, anions, and C–H hydrogen atoms have been omitted for clarity. Selected distances (Å): Au1–Cu1, 2.7915(7); Cu1–N10, 1.956(4); Cu1–N20, 1.965(4); Cu1–O1, 2.120(4).

Complexes **1** and **2** (and their solvates) respond reversibly to solvent vapor, although **2** responds much more dramatically. Vapor experiments were conducted by passing a stream of N₂ saturated with the respective solvent onto powdered samples of **1** or **2**. Methanol, H₂O, or Me₂CO vapor effected changes in the luminescence wavelength, while CH₂Cl₂ and tetrahydrofuran vapors had no effect over the course of days. All of these species react with MeCN to regenerate **1**. As shown in Figure 3, when **1** is exposed to MeOH vapor, the solid-state luminescence changes from blue to green ($\lambda_{\max} = 520$ nm), and the emission intensity notably decreases. Notably, *all* of the MeCN molecules are completely exchanged, and no residual MeCN was detected in the material by either IR or ¹H or ¹³C{¹H} NMR spectroscopy, despite the nitrile's stronger affinity for Cu^I in comparison with that of MeOH. Integration of the methanol signal suggested that one MeOH is added per copper center, along with some trace H₂O incorporation. Upon exposure to air, some of the MeOH is quickly lost, producing a compound with faint yellow emission ($\lambda_{\max} = 543$ nm). Re-exposure to dry MeOH vapor rapidly restores the green luminescence. The reversibility of this process is documented in the video files in the SI. Exposing the MeOH-containing species to vacuum produces a unique and fast luminescence change to yellow-orange ($\lambda_{\max} = 573$ nm) that can be reversed by MeOH(g) to restore the species emitting at 520 nm. The ¹H NMR analysis showed that this evacuated species is devoid of MeOH, suggesting a coordinatively unsaturated Cu^I center. Using vapor from commercial, undried

MeOH also produces a green emission with incorporation of H₂O (see the SI); however, removal of the incorporated water by acetonitrile or vacuum takes more time or gentle warming.

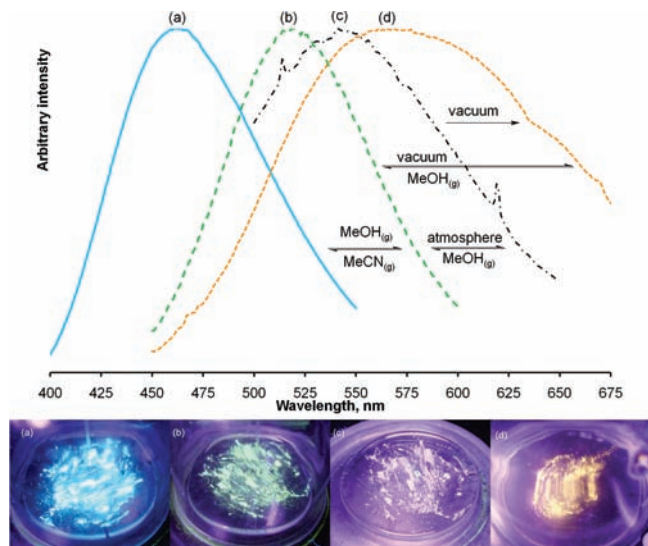


Figure 3. (top) Normalized solid-state emission spectra ($\lambda_{\text{ex}} = 365$ nm) showing transformations and (bottom) photographs of (a) **1**, (b) compound **2** formed by treating **1** with MeOH(g), (c) MeOH-treated **1** exposed to atmosphere, and (d) MeOH-treated **1** exposed to vacuum.

Treatment of **1** with Me₂CO vapor changes the solid-state luminescence color from blue to yellow-orange ($\lambda_{\max} = 591$ nm), a maximum wavelength distinct from that of the evacuated MeOH(g) sample, indicating the presence of a different species. This luminescence change can also be brought about by a quantity of Me₂CO(l) insufficient to dissolve all of the compound. The ¹H and ¹³C{¹H} NMR analyses showed the presence of both Me₂CO (0.9 equiv) and residual MeCN (0.1 equiv) in the converted sample. The structural makeup of this species has yet to be determined.

We have demonstrated that compounds **1** and **2** exhibit reversible luminescent vapochromic behavior through ligand exchange reactions, allowing the sensing of MeCN, H₂O, MeOH, and Me₂CO vapors. The interchange between MeCN and MeOH exposure induces a profound change in Au···Cu bonding depending on the coordination number at the copper centers. Expansion of the concept could present new approaches to molecular materials that exhibit fast and reversible response to VOCs.

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Supporting Information Available: Experimental details, characterization of the compounds, powder XRD and fluorescence spectra of all compounds, videos of the vapor experiments (QT), and single-crystal XRD data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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