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Reversible Mechanochromic Luminescence of $[(C_6F_5Au)_2(\mu\text{-}1,4\text{-Diisocyanobenzene})]$

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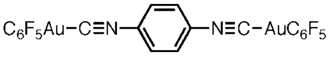
Mechanochromism is the phenomenon of color change due to mechanical grinding or pressing of a solid sample, and the subsequent reversion to its original color through treatment such as heating or recrystallization.[1] Photoluminescent compounds that possess mechanochromic properties in their solid-state emissions can provide unique recording or sensing materials that involve luminescence detection. Unfortunately, reports that describe such mechanochromic, photoluminescent compounds have been limited.[2,3] Herein, we report the mechanochromic luminescence behavior of $[(C_6F_5Au)_2(\mu\text{-}1,4\text{-diisocyanobenzene})]$ (**1**)—the photoluminescence of the solid, upon grinding, undergoes a drastic change and, upon exposure to solvents or its vapor, is restored to its original color.[4–6] Optical properties, powder X-ray diffraction (XRD), IR measurements, and X-ray crystallographic analysis strongly suggest that the mechanochromic property is attributable to changes in the molecular arrangement, rather than molecular structure, of the Au(I) complexes in the solid state.[7] Presumably, intermolecular aurophilic interactions are responsible for the altered emission of the ground samples.[5] Our studies help establish **1** as a notable example of a Au(I) complex with solid-state photoemission that can be reversibly switched by external stimului.[6,8]

The synthesis of **1** involved the reaction of $C_6F_5Au(tht)$ (tht: tetrahydrothiophene) with 1,4-diisocyanobenzene in dichloromethane. The resulting precipitate was collected by filtration and dried under reduced pressure to give analytically pure **1** as an air-stable white powder (92% yield), which is sparingly soluble in common solvents.



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To our surprise, upon gentle grinding of **1** using a spatula or a pestle, the blue luminescence that results from UV irradiation at 365 nm changes to an intense yellow luminescence (Figure 1a). Under ambient light, however, color changes were not detected (Figure 1b). Upon treatment of the ground powder with drops of dichloromethane, the yellow luminescence reverted to the original blue color (Figure 1c,d). Evaporation of the solvent afforded the original blue luminescent solid (Figure 1e). Repetitions of the blue-to-yellow conversion by subsequent regrinding (Figure 1f) did not exhibit any degradation in the luminescence, even after 20 cycles. Furthermore, reversion from the yellow- to the blue-emitting solid was achieved by the addition of various solvents such as ethyl acetate, diethyl ether, and chloroform, as well as exposure to the vapor of dichloromethane.

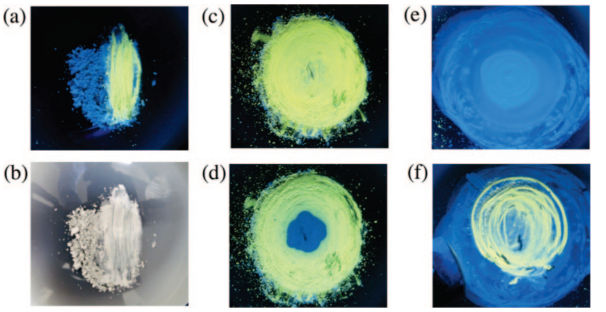

Figure 1. Photographs showing Au(I) complex **1** on an agate mortar under UV irradiation with black light (365 nm), unless otherwise noted: (a) Au(I) complex **1** powder after grinding the right-half with a pestle, (b) a same sample under ambient light, (c) entirely ground powder of **1**, (d) partial reversion to the blue luminescence by dropwise treatment using dichloromethane onto the center of the ground powder, (e) powder after treatment with dichloromethane, and (f) repetition of the yellow emission by scratching the powder with a pestle (see video 1 for a movie of the grinding process).

ⓦ video 1 shows the grinding process.

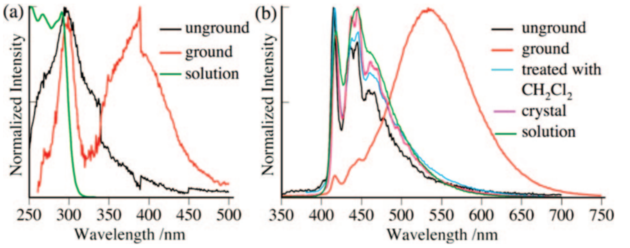

Figure 2. (a) Absorption and (b) emission (excited at 260 nm) spectra of **1** in various states.

Absorption and emission spectra of **1** in various states are shown in Figure 2.[9,10] The absorption spectrum of the unground sample of **1** was observed as a broadband, ranging from 250 to 350 nm, whereas the emission spectra showed a structured profile with a maximum wavelength ($\lambda_{em}{}^{max}$) at 415 nm, accompanied by weaker vibronic bands at ca. 437, 445, and 459 nm [$\Phi^{em} = 0.09$, lifetime: $\tau_1 = 9.7\ \mu s$ ($A_1 = 0.32$), $\tau_2 = 71.2\ \mu s$ ($A_2 = 0.68$)]. Thorough grinding of the sample gave a yellowish gray powder, which exhibited a new red-shifted absorption band ranging from 340 to 450 nm and a broad structureless emission band with $\lambda_{em}{}^{max}$ at 533 nm. Compared to the unground sample, the emission of the ground sample exhibited an increase in the quantum yield, along with a shorter lifetime [$\Phi^{em} = 0.19$, $\tau_1 = 0.18\ \mu s$ ($A_1 = 0.54$), $\tau_2 = 0.45\ \mu s$ ($A_2 = 0.46$)]. The solid resulting from treatment with dichloromethane followed by drying under reduced pressure exhibited an emission band similar to that of the unground sample. A dilute solution of **1** in dichloromethane (0.025 mM) exhibited a broad absorption below 320 nm and an emission band (418, 445, 464 nm, $\Phi^{em} = 0.01$, $\tau = 6.1\ \mu s$) comparable to those of the unground sample.

Because elemental analysis of the thoroughly ground solid and the solid after treatment with dichloromethane gave expected values (based on the formula of **1**), the evaporation step in our process was able to completely remove all traces of the solvent, which is in contrast to other common solvato- or vapochromism.[11] Both unground and thoroughly ground samples, after heating at 100 °C for 10 min, exhibited comparable emission spectra. Differential scanning calorimetery (DSC) measurements, over the

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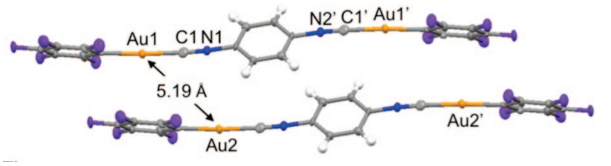

Figure 3. Partial view of the crystal packing of a blue luminescent crystal of **1**. Thermal ellipsoids were drawn at 50%-probability level. Crystal data: monoclinic, $P2_1/c$ (No. 14), $a = 5.190(2)$ Å, $b = 17.154(6)$ Å, $c = 10.861(4)$ Å, $\beta = 90.83(3)°$, $V = 966(2)$ Å^3, $Z = 2$. $T = 296.2$ K. $2\theta_{max} = 55.0+$, $R = 0.0355$ ($I > 2.00\sigma(I)$), $Rw = 0.0976$, GOF = 1.007.

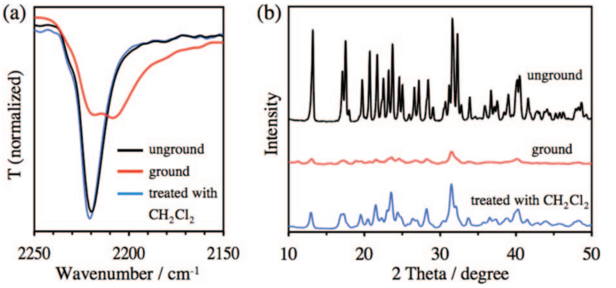

Figure 4. IR and XRD spectra of **1** in various states.

temperature range of 25−200 °C, did not indicate any phase transitions. Upon heating at 200 °C for 10 min, however, the color of both samples turned into pale red (under ambient light), indicating thermal decomposition. The emission spectra of the pale red unground sample remained unchanged, whereas that of the ground sample showed partial reversion to the blue emission.

Recrystallization of **1** from chlorobenzene afforded single crystals suitable for X-ray structure analysis (Figure 3). Because the shortest Au−Au distance of 5.19 Å was beyond the range of significant aurophilic bonding (2.7−3.3 Å),[5] aurophilic interactions were absent within the crystal. The emission spectrum of the crystals was nearly identical to that of the unground powder (Figure 2b).

The blue and yellow emissions are attributable to distinct mechanisms. Similarity among the emission spectrum of the unground powder, the single crystal, and the dichloromethane solution of **1** suggests that the solid-state blue emissions from these samples occurred from single molecules. On the basis of the long emission lifetime, and the structured profile of the emission band, this blue luminescence can be attributed to the phosphorescence from the intraligand-localized $\pi-\pi^*$ excited state.[12] On the other hand, the broad and red-shifted emission from the ground sample appears to arise from an amorphous material in which aurophilic interactions may be responsible for the new emissive state.[4,5,8]

The IR spectrum of the unground solid exhibited a single absorption (2220 cm^{-1}) that corresponds to the isocyanide N≡C stretching (Figure 4a). In contrast, two absorbances (2218 and 2208 cm^{-1}) were observed for the ground solid, which indicate that, upon grinding, considerable changes occur in the coordination mode of the isocyanide ligand to the Au(I) atom, presumably due to the formation of aurophilic bonds.[13] As observed in the emission properties, the IR spectrum of the sample, upon treatment with dichloromethane, reverted to that of the unground solid.

The powder X-ray diffraction (XRD) pattern of the unground sample showed clear reflection peaks, in good agreement with the simulated pattern of the single crystals of **1** (Figure 4b). In contrast, the XRD pattern of the ground sample showed significant decreased peak intensities with increased peak widths, which indicates that the grinding causes crystal-to-amorphous phase conversion. Upon treatment of the ground sample with dichloromethane, the reflection peaks were restored,[14] which indicates reversion from the amorphous to the crystalline phase.

On the basis of our results, the mechanism of the mechanochromic process of **1** can be summarized as follows: First, the grinding transforms the blue luminescent microcrystalline powder into a metastable amorphous phase, with aurophilic interactions that are responsible for the lower energy emission. Next, upon treatment of the ground sample with a solvent, the amorphous phase rearranges into the more stable crystalline phase via a partial dissolution and recrystallization process. Within the crystals of **1**, the planarity of the molecular structure and the lack of strong intermolecular forces (such as C−H···π interaction) would allow slipping of the molecular stacks by mechanical stimulus.

Detailed studies into the mechanism of the reversible mechanochromic luminescence along with the optical properties of structural variants of **1** are currently underway.

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Supporting Information Available: Experimental procedures for the synthesis of **1**, compound characterization data, and crystallographic data in CIF format are available free of charge via the Internet at http://pubs.acs.org.

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