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Luminescence Tribochromism and Bright Emission in Gold(I) Thiouracilate Complexes

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Over the past two decades, interest in gold(I) complexes has been stimulated by their tendency to aggregate through closed shell "aurophilic" interactions and their consequent luminescence properties.[1−7] Aurophilic interactions also play a key role in determining the solid-state structures that many gold(I) compounds exhibit.[4,8−13] The emissive properties of certain Au(I) compounds have been found to be sensitive to environmental factors such as volatile organic vapors,[14] making them of interest in possible sensor applications. The present study describes a new set of compounds that exhibit a unique property among metal complexes in which luminescence can be switched on under gentle grinding of a solid sample. This phenomenon, termed **luminescence tribochromism**,[15,16] leads to bright blue or cyan photoemission from the sample. In contrast with triboluminescence which represents transient emission upon sample grinding or crushing,[17,18] luminescence tribochromism is a sustained change in the *photo*emission spectrum upon the initial application of pressure. The process can be reversed through recrystallization, and the luminescence can be turned on or off through control of acidity as well. The compounds reported here are Au(I) thiouracilate complexes containing bis(diphenylphosphino)methane (dppm), and their luminescence relates to the different types and degrees of aurophilic interaction that the solid-state structures reveal.

The title complexes are prepared by the reaction of (μ-dppm)-$Au_2(CF_3COO)_2$ with 2-thiouracil (TU) and 6-methyl-2-thiouracil (Me-TU) to give **1a** and **1b**, respectively. Exchange of CF_3COO^- for other simple anions is accomplished readily by metathesis with NaY where $Y^- = NO_3^-$, ClO_4^-, $Au(CN)_2^-$ yielding colorless crystals exhibiting IR bands characteristic of Y^- as well as the dppm and thiouracilate ligands. The crystal structures of **1a** and **1b** have been determined and the cation of **1a** is shown in Figure 1a with selected bond distances and angles tabulated in Supporting Information.[19] In these structures, the thiouracilate and dppm ligands bridge two Au(I) ions, each having a linear coordination geometry and a Au···Au intramolecular distance of 2.8797 (4) Å. In **1a**, the CF_3COO^- anion refines satisfactorily but with large temperature factors and is H-bonded to the TU ligand protonated at the uncoordinated N atom. Most striking is the extended arrangement of the dinuclear cationic complexes that forms an aurophilic helix (Figure 1b) with hydrophilic thiouracilates stacked in the center of the helix and hydrophobic dppm ligands on the helix exterior. Neighboring dinuclear (i.e., Au_2) cations link in a head-to-tail arrangement based on the TU ligand with an *inter*molecular Au···Au distance of 3.3321 (5) Å. The basic structural arrangement for **1b** is similar but the aurophilic helix is discontinuous with one Au···Au separation of 4.344 Å for a head-to-head connection (the others are head-to-tail and average 3.236−3.354 Å).

The complexes [Au_2(μ-TU)(μ-dppm)]Y and the Me-TU analogues are either nonemissive or weakly photoluminescent. For **1a**, the weak emission is white in color indicative of multiple emissions. When solid samples of **1** are gently crushed under a spatula, a dramatic conversion occurs to give samples exhibiting bright blue or cyan photoluminescence at ambient temperature. The emission spectrum of this form, shown in Figure 2 for the R = Me derivative, exhibits a single band at 483 nm and a corresponding lowest-energy excitation maximum at 375 nm. However, powder X-ray diffraction patterns of polycrystalline and crushed samples of **1** reveal that no gross phase change transpires upon crushing (see Supporting Information). Derivatives with different Y-anions exhibit similar emission behavior upon crushing. For solid **1**, gentle heating (37 °C) for 5−6 h or sonication in a closed vial also gives conversion to the emissive form (**2**) with release of acid as detected using moist pH paper above the solid.

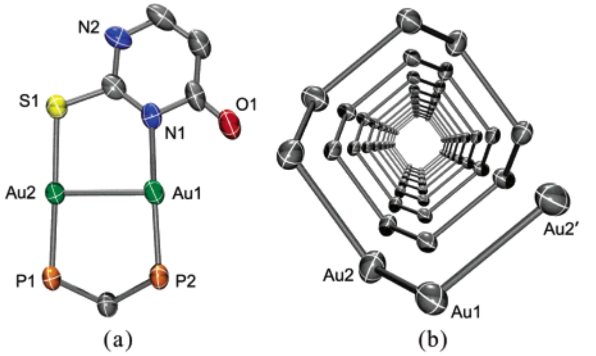

Figure 1. (a) View of cationic **1a** (phenyl rings omitted) and (b) helical arrangement of Au(I) ions with ligands omitted for clarity.

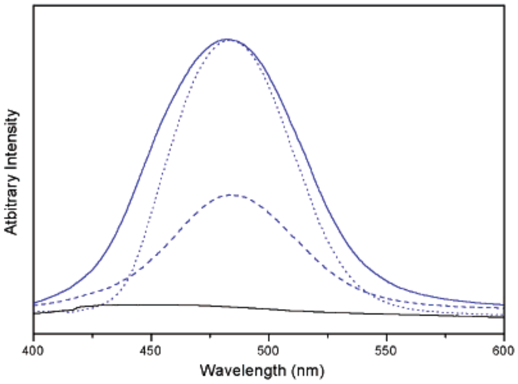

Figure 2. Emission spectra of nonemissive (black line) and crushed crystals (blue line) of **1b**, CH_2Cl_2 solution (- - -) of **1b** and crystals (······) of **2b** (blue form) at room temperature (at $\lambda_{ex} = 375$ nm).

Brightly emissive **2** can be prepared directly by stirring CH_2Cl_2/MeOH solutions of **1** over Na_2CO_3 followed by filtration and crystallization to yield pale yellow crystals of X-ray quality. Analytical and spectroscopic data support the formulation of **2** as the neutral dinuclear complex in which the thiouracil is doubly deprotonated. The structure of **2b** (Figure 3) shows the same μ-thiouracilate, μ-dppm pattern as that for **1a** and **1b** but a vastly different packing arrangement. The intermolecular arrangement is that of dimers held together by a strong aurophilic interaction of

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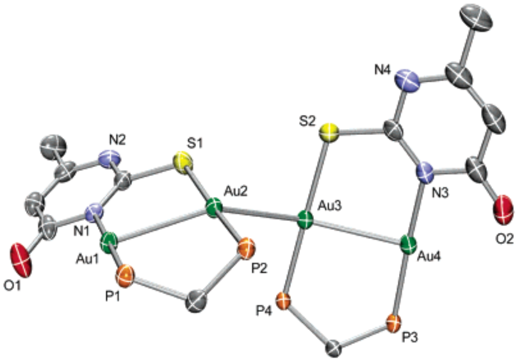

Figure 3. Perspective view of **2b**. The phenyl rings on phosphorus atoms are omitted for clarity.

2.9235 (4) Å and a head-to-head orientation of the thiouracil groups. The thiouracil carbonyl groups serve to block further aggregation along the Au···Au direction. The emission spectra of **2a** and **2b** obtained as above show single bands at the same λ_{em}^{max} as those seen for the crushed samples of **1**, albeit with slightly narrower band profiles (fwhm = 58 and 73 nm for the Me derivative). Excited-state lifetimes for **2a** and **2b**, synthesized directly or by crushing **1**, are 2−4 μs at 298 and 77 K. Conversion back to **1** is achieved by recrystallization of **2** from solutions to which trifluoroacetic acid is added, while exposure of solid **2** to CF_3COOH vapor leads very slowly to loss of luminescence. The latter process is reversed upon exposure to NEt_3 vapor.

Emission measurements in room-temperature fluid solution contrast with the solid state observations and exhibit distinct behavior as a function of acidity. Specifically, CH_2Cl_2 solutions of **1** are blue emissive ($\lambda_{em}^{max} = 489$ nm) whereas corresponding solutions of **2** are nonemissive. Upon exposure to NEt_3 vapor, the blue-emissive solutions of **1** become nonemissive as acidity decreases, but a further decrease yields a modest return of emission at the same λ_{em}^{max}. The process is reversed when CF_3COOH is used and can be carried out repetitively with no loss of emission intensity. The probable site of protonation/deprotonation in **1** and **2** is the uncoordinated pyrimidine nitrogen atom as evidenced by H-bonding in the structures and similar thiouracil carbonyl bond lengths in **1** and **2**. Variation of the complex concentration from 1×10^{-2} to 1×10^{-5} M in CH_2Cl_2/toluene (v/v = 1/1) shows that emission intensity does not increase linearly with concentration, suggestive of a possible equilibrium between emissive and nonemissive forms.

In CH_2Cl_2/toluene frozen glass at 77 K, complex **1b** exhibits dual emission bands at λ_{em}^{max} at 440 and 486 nm. The lower-energy band is more sensitive to concentration than the higher-energy band and is attenuated in dilute frozen solution (see Supporting Information). Despite differences in the fluid solution emission, qualitatively similar emission results are obtained for **2b** in frozen glass at 77 K with emission bands at $\lambda_{em}^{max} = 450$ and 485 nm.

The emission properties of **1** and **2** in the solid state are clearly affected by the interplay of thiouracilate protonation and the different aurophilic interactions exhibited by these systems. We propose that the latter leads to the unique luminescence tribochromism reported here. In nonemissive **1** with its helical structure, the intermolecular Au···Au interactions are weak, and the extended Au···Au interactions are severely kinked, whereas in emissive **2** with its dimeric structure, the *inter*molecular interaction is strong, and the Au···Au···Au···Au arrangement, more linear. Application of pressure to **1** appears to induce cleavage of the weakest links of the Au_n helix, rearrangement to dimers, and release of volatile acid. The systems reported here thus represent an interesting and exquisite balance of aurophilic interactions and acid−base properties that confer on these systems their unique luminescence tribochromism. Other related systems exhibiting this property will be reported separately.

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Supporting Information Available: X-ray crystallographic data in CIF format for **1a**, **1b** and **2b**. Tables of crystallographic parameters and selected distances and angles for **1a**, **1b** and **2b**; characterization and photophysical data for **1** and **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) X-ray data were collected at 193 K on a standard Siemens SMART CCD diffractormeter with Mo Kα radiation. Crystal data for **1a** (colorless form): tetragonal $I4(1)/a$, $a = 33.3063(15)$ Å, $b = 33.3063(15)$ Å, $c = 13.8485(9)$ Å, $V = 15362.3(14)$ Å^3, $Z = 16$, d(calcd) = 1.891 Mg/m^3, no. of independent data = 9162, no. of variables = 442, R1 = 0.0516 [$I > 2\sigma(I)$], wR2 = 0.1441. **1b** (colorless form): triclinic $P\bar{1}$, $a = 13.8976(12)$ Å, $b = 21.5548(19)$ Å, $c = 26.928(2)$ Å, $\alpha = 84.383(2)$, $\beta = 77.259(2)$ °, $\gamma = 83.480(2)$, $V = 7794.9(12)$ Å^3, $Z = 2$, d(calcd) = 1.822 Mg/m^3, no. of independent data = 31312, no. of variables = 1720, R1 = 0.0556 [$I > 2\sigma(I)$], wR2 = 0.1472. **2b** (blue form): monoclinic $P2(1)/c$, $a = 12.3737(6)$ Å, $b = 29.1208(14)$ Å, $c = 17.4858(8)$ Å, $\beta = 93.6570(10)$ °, $V = 6287.9(5)$ Å^3, $Z = 4$, d(calcd) = 2.031 Mg/m^3, no. of independent data = 14818, no. of variables = 729, R1 = 0.0424 [$I > 2\sigma(I)$], wR2 = 0.0795.

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