

{Tl[Au(C₆Cl₅)₂]}_n: A Vapochromic Complex

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Recently, synthetic efforts have been directed toward the preparation of polymeric materials with special optico-electronic properties.¹ Some of these materials are sensors for volatile organic compounds (VOC).² Materials that show appreciable selectivity and tunable changes of color or emission in the presence of VOCs are of particular interest.³ Here we report on a luminescent, polymeric, semiconducting gold–thallium complex with a solid-state structure that permits reversible interactions and related color changes with a variety of VOCs.

By reacting equimolar quantities of [NBu₄][Au(C₆Cl₅)₂] with TlPF₆ in tetrahydrofuran, the compound {Tl[Au(C₆Cl₅)₂]}_n, **1**, is obtained as a pale yellow solid.⁴

The X-ray structure⁵ of complex **1** consists of 1-D linear polymer chains parallel to the crystallographic *z* axis, with unsupported Au–Tl interactions between the [Au(C₆Cl₅)₂] anions and Tl(I) cations (Figure 1). The Au–Tl distances (3.0044(5) and 2.9726(5) Å) are shorter than the sum of Au(I) and Tl(I) ionic radii (2.96 Å)⁶ and Au–Tl distances in related systems (3.0161(2)–3.1887(6) Å)⁷ but similar to those observed in [TlAu(Pb₂P(S)CH₂)₂]_n⁸ [Au–Tl(intra) = 2.959(2) Å; Au–Tl(inter) = 3.003(2) Å] and longer than those found in the metallocryptate [TlAu₂(P₂-phen)₃](PF₆)₃ (P₂-phen = 2,9-bis(diphenylphosphino)-1,10-phenanthroline)⁹ [2.9171(5) and 2.9109(5) Å]. Each Au(I) atom is coordinated to two pentachlorophenyl groups with a normal Au–C distance (2.063(6) Å). The Tl center is not further coordinated, although this structure is stabilized by eight long Tl···Cl contacts (3.2441(15)–3.6786(15) Å). Four additional Au···Cl contacts (3.3388(15) and 3.3688(16) Å) may also contribute to the stability of the system. Finally, the crystal structure of **1** has channels that run parallel to the *z* axis (Figure 1) with interatom distances in the range 3.231–4.076 Å. There are holes with diameters as large as 10.471 Å (the static Au–Au distance between chains) which can accommodate the molecules which enter the lattice.

Solid complex **1** is luminescent at room temperature (RT) and at 77 K. UV excitation at 495 nm leads to an RT emission at 531 nm. The emission is shifted to 547 nm at 77 K. This observed thermochromism is similar to observations found in other gold–thallium extended linear chains^{7a,b,8} and is assumed to be a result of the thermal contraction that occurs when the temperature is lowered. The shortened Au–Tl distance at low temperatures in the absence of ligands coordinated to Tl causes the overlap between the Au(I) and Tl(I) orbitals to increase. This reduces the HOMO–LUMO gap, thereby lowering the energy of the emission band. Compound **1** is not luminescent when dissolved in THF.

The decay at 298 K of the emission centered at 531 nm has been fitted with two exponential functions giving lifetimes of 1039

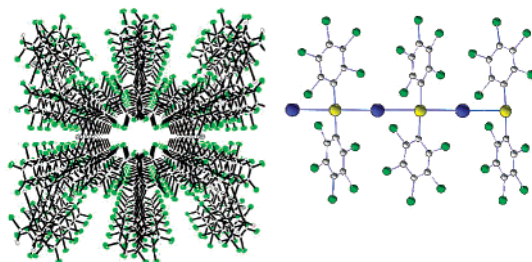


Figure 1. Crystal structure of **1** viewed down the crystallographic *z* axis. Inset: The polymeric molecular structure of **1**.

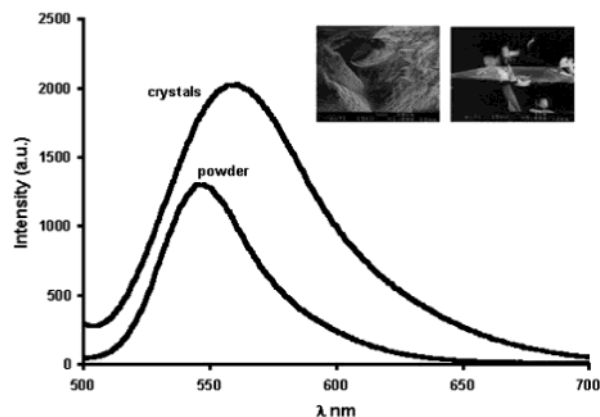


Figure 2. Comparison between emission spectra of crystals and powder of **1** at 77 K. Inset: SEM images of X-ray size crystals (left) and bulk powder (right) of **1** taken without coating with a conducting film.

and 123 ns. The longer lifetime₂ is suggestive of phosphorescence; however, the Stokes shift between the maxima of excitation and emission bands is only 1370 cm⁻¹. The emission spectrum is independent of the excitation wavelength in the range from 300 to 500 nm.

A very interesting spectral feature is the observed shift of the emission energy of **1** with particle size. At 77 K, the bulk powder shows an emission at 547 nm, while X-ray quality crystals display an emission at 560 nm (see Figure 2). In addition, when the crystals are gently crushed, the band shifts to higher energies. It is generally observed in semiconductors that a reduction in the spatial confinement of the electrons increases their kinetic energy. This produces a larger band gap, an effect known as the quantum size effect.¹⁰

The scanning electron microscope (SEM) images taken of the microcrystalline solid (Figure 2) and larger single crystals show clear SEM images without coating with a conductor. These data suggest that the material is not an insulator.¹¹ TD-DFT calculations carried out for Tl[Au(C₆Cl₅)₂]₂ (see the Supporting Information) show that the high oscillator strength transitions are between orbitals

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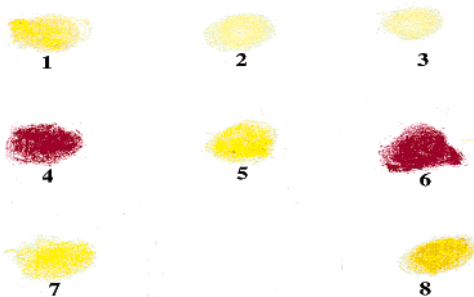


Figure 3. Powder samples of compound **1** deposited on filter paper and exposed to selected organic vapors: (1) 2-fluoropyridine, (2) THF, (3) acetone, (4) acetylacetone, (5) acetonitrile, (6) pyridine, (7) triethylamine, (8) THT.

located in the metal centers along the metal chain. Measurement for a single crystal failed to establish conductivity; hence semi-conductivity is suggested.

Complex **1** displays a vapochromic behavior with reversible changes¹² of color when the solid is exposed to a variety of organic vapors. Acetone, acetonitrile, triethylamine, acetylacetone, tetrahydrothiophene (THT), 2-fluoropyridine, tetrahydrofuran (THF), and pyridine vapors (see Figure 3) have been used. The color changes back to that of the starting material upon heating to 100 °C over a period that requires from a few seconds for acetone to 10 min for pyridine. In all cases, the process is found to be completely reversible with no detectable degradation of the starting material after 10 exposure/heating cycles. The exchange of color is even deeper under UV light, and the substances display a strong luminescence under these conditions (see the Supporting Information).

Exposure of solid complex **1** to the RT vapor pressure of the above VOCs shifts the RT emission band from 531 to 507 (THF, ex 473), 511 (NEt₃, ex 463), 513 (NCMe, ex 491), 532 (acetone, ex 444), 567 (THT, ex 485), 627 (2-fluoropyridine, ex 400), 646 (pyridine, ex 560), and 650 (acetylacetone, ex 550) nm, respectively. These shifts presumably are associated with a weak interaction of the Tl(I) centers with the VOCs. Each band shifts to the red when the measurements are made at 77 K. In addition, analysis of the UV–vis absorption and IR spectra is in accord with the presence of an interaction between VOCs and the metallic centers. A dilute solution (5×10^{-4} M) of complex **1** in THF displays only absorptions due to the [Au(C₆Cl₅)₂][−] units, centered in the pentachlorophenyl rings;^{7b} the UV–vis spectra in the solid state of both [NBu₄][Au(C₆Cl₅)₂] and **1** display a pattern similar to that of the bands at 217, 235, 288, and 311 nm for the Au material and 217, 240, 291, and 311 nm for Au–Tl complex **1**. Complex **1** shows an additional peak at 343 nm that can be assigned to a transition between levels formed as a consequence of the intermetallic interaction (see the Supporting Information).

The solids resulting from the exposure of **1** to VOCs display this new absorption band in the range 455–600 nm, at energies similar to the maxima observed in the excitation spectra, suggesting that these bands give rise to the luminescence. This observation supports the premise that the luminescence observed has its origin in the Au–Tl interactions.

These preliminary results illustrate the potential applications of Au(I)–Tl(I) compounds as candidates for the detection of various VOCs.

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Supporting Information Available: X-ray crystallographic files for **1** (CIF); luminescence, absorption data, and TD-DFT results (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum Press: New York, 1982; Vols. 1–3.
- (2) Buss, C. E.; Mann, K. R. *J. Am. Chem. Soc.* **2002**, *124*, 1031 and references therein.
- (3) (a) Mansour, M. A.; Connick, W. B.; Lachicotte, R. J.; Gysling, H. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1998**, *120*, 1329. (b) Beauvais, L. G.; Shores, M. P.; Long, J. R. *J. Am. Chem. Soc.* **2000**, *122*, 2763. (c) Cariati, E.; Bu, X.; Ford, P. C. *Chem. Mater.* **2000**, *12*, 3385. (d) Evju, J. K.; Mann, K. R. *Chem. Mater.* **1999**, *11*, 1425.
- (4) Anal. Calcd (found) for C₁₂AuCl₁₀Tl: C, 16.1 (16.0). Λ_M (acetonitrile) = 109 Ω^{-1} cm² mol^{−1}. Yield: 65%.
- (5) Crystallographic data were obtained using a Nonius Kappa CCD diffractometer, Mo K α radiation ($\lambda = 0.71073$ Å), $T = -100$ °C. Crystal data: orthorhombic, *Pccn*, $a = 14.7106(8)$, $b = 10.4709(4)$, $c = 11.9540(6)$ Å, $V = 1841.31(15)$ Å³, $Z = 4$, $d_{\text{calc}} = 3.246$ Mg/m³, 3371 measured reflections, 1870 independent reflections ($R_{\text{int}} = 0.0306$), $R1 = 0.0282$ and $wR2 = 0.0571$, goodness-of-fit on $F^2 = 1.055$.
- (6) Pauling, L. *The Chemical Bond*; Cornell University Press: Ithaca, New York, 1967. Lide, D. R. *CRC Handbook of Chemistry and Physics*, 73rd ed.; CRC Press: Boca Raton, FL, 1993.
- (7) (a) Crespo, O.; Fernández, E. J.; Jones, P. G.; Laguna, A.; López-de-Luzuriaga, J. M.; Mendía, A.; Monge, M.; Olmos, E. *Chem. Commun.* **1998**, 2233. (b) Fernández, E. J.; Jones, P. G.; Laguna, A.; López-de-Luzuriaga, J. M.; Monge, M.; Olmos, E.; Pérez, J. *Inorg. Chem.* **2002**, *41*, 1056. (c) Fernández, E. J.; Laguna, A.; López-de-Luzuriaga, J. M.; Monge, M.; Olmos, E.; Pérez, J. *J. Am. Chem. Soc.* **2002**, *124*, 5942.
- (8) (a) Wang, S.; Fackler, J. P., Jr.; King, C.; Wang, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 3308. (b) Wang, S.; Garzón, G.; King, C.; Wang, J. C.; Fackler, J. P., Jr. *Inorg. Chem.* **1989**, *28*, 4623.
- (9) Catalano, V. J.; Bennett, B. L.; Kar, H. M.; Noll, B. C. *J. Am. Chem. Soc.* **1999**, *121*, 10235.
- (10) Blasse, G.; Grabmaier, B. C. *Luminescent Materials*; Springer-Verlag: New York, 1994; pp 216–218. A similar, but somewhat more complex, emission has been observed for the linear chain complex, [Au(TPA)₂Au(CN)₂]_n. See: Assefa, Z.; Omary, M. A.; McBurnett, B. G.; Mohamed, A.; Fackler, J. P., Jr.; Patterson, H. H.; Staples, R. J. *Inorg. Chem.* **2002**, *41*, 6274–6280.
- (11) *Scanning Electron Microscopy and X-ray Microanalysis*; Goldstein, J. I., et al., Eds.; Plenum Press: New York, 1992.
- (12) Crystallizations from different solvents give different structures and different coordination of the ligands to Tl.

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