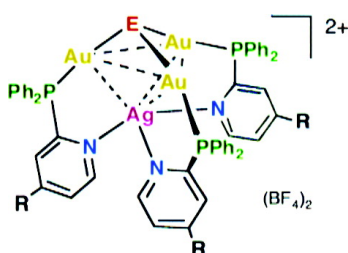


## Intensely Luminescent Gold(I)–Silver(I) Cluster Complexes with Tunable Structural Features

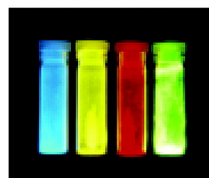
Quan-Ming Wang, Young-A. Lee, Olga Crespo, Joseph Deaton, Ching Tang, Henry J. Gysling, M. Concepcin Gimeno, Carmen Larraz, M. Dolores Villacampa, Antonio Laguna, and Richard Eisenberg

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- 1, E = O, R = H
- 2, E = S, R = H
- 3, E = Se, R = H
- 4, E = S, R = Me



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## Intensely Luminescent Gold(I)–Silver(I) Cluster Complexes with Tunable Structural Features

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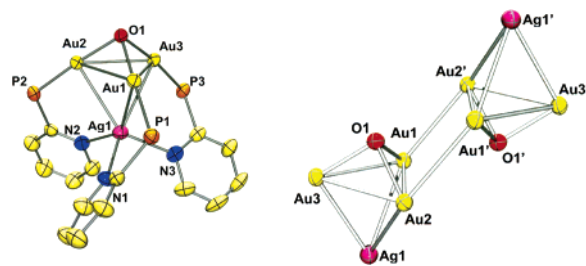
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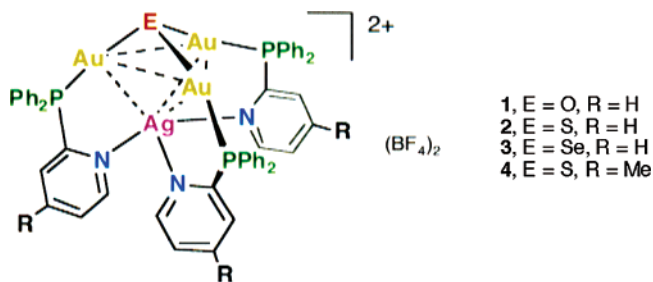
Recent interest in luminescent metal complexes has been driven by possible applications in OLED display technology as dopant emitters,<sup>1,2</sup> in solar photoconversion chemistry as chromophores,<sup>3</sup> and in sensor development for luminescence detection.<sup>4–6</sup> Potentially attractive in this regard are polynuclear Au(I) complexes that possess intense, long-lived luminescence in the solid state at ambient temperatures with emission energies spanning the visible spectrum.<sup>7–11</sup> Different excited-state assignments have been made for these systems including metal-centered or cluster-based (MC),<sup>10,12–14</sup> ligand-to-metal charge transfer (LMCT),<sup>13,15,16</sup> and intraligand (IL), with aggregation through aurophilic interactions<sup>17,18</sup> thought to play a key role in producing the emissive state. In these studies, however, systematic variation of an isolated electronic property without simultaneous alteration of another property (i.e., steric or structural) has generally not been done. The present study reports a new series of isostructural, brilliantly luminescent gold–silver complexes having a group-16  $\mu_3$ -bridging atom in which the emission energy changes strikingly from blue to yellow to orange in going from O to S to Se. While emission properties of Au(I) sulfide and selenide polynuclear complexes have been described previously,<sup>19</sup> this is the first report of luminescence from a gold(I) oxo system.

The new complexes have the general formula  $[\text{Au}_3(\mu_3\text{-E})\text{Ag}(\text{PPh}_2\text{py})_3](\text{BF}_4)_2$  where E = O, S, Se and  $\text{PPh}_2\text{py}$  = diphenylphosphine-2-pyridine. Complex **1** (E = O) is synthesized directly by the reaction of  $\text{AuCl}(\text{PPh}_2\text{py})$  with excess  $\text{Ag}_2\text{O}$  and  $\text{NaBF}_4$  in wet acetone at ambient temperature (see Supporting Information). Complex **1** can also be prepared in two steps from  $\text{AuCl}(\text{PPh}_2\text{py})$  and  $\text{Ag}_2\text{O}$  with intermediate isolation of  $[\text{Au}_3(\mu_3\text{-O})(\text{PPh}_2\text{py})_3]^+$  (analogous to  $[\text{Au}_3(\mu_3\text{-O})(\text{PPh}_3)_3]^+$  originally reported by Nesmeyanov<sup>20</sup>). Syntheses of the sulfide complex **2** and the selenide complex **3** follow similar reaction paths from  $\text{AuCl}(\text{PPh}_2\text{py}) + \text{Li}_2\text{E}$  but proceed in two steps with intermediate isolation of  $\text{Au}_2(\mu\text{-E})(\text{PPh}_2\text{py})_2$  (E = S, Se) followed by reaction with a stoichiometric amount of  $\text{AuCl}(\text{PPh}_2\text{py})$  and two equivalents of  $\text{AgBF}_4$ . An attempt to prepare the analogous Te complex by reaction of  $[\text{Au}_3(\mu_3\text{-O})(\text{PPh}_2\text{py})_3]^+$  with  $\text{Te}=\text{P}(i\text{-Pr})_3$ , however, led to the formation of an unstable and uncharacterized product. For E = S, a derivative having a methyl substituent on the pyridyl ring,  $[\text{Au}_3(\mu_3\text{-S})\text{Ag}(\text{PPh}_2\text{-4-Mepy})_3](\text{BF}_4)_2$  (**4**), has also been prepared, structurally characterized and spectroscopically studied (see Supporting Information).

X-ray single-crystal structure analyses reveal that complexes **1–4**, while not isomorphous, are isostructural (**2** and **3** are isomorphous).<sup>21</sup> A perspective view of the cation of **1** is shown in Figure 1. The structural core is a  $\text{Au}_3\text{Ag}$  tetrahedron with an oxygen



**Figure 1.** (Left) Perspective view of the cationic part of **1**. (Right) View of the dimerization of  $\text{Au}_3\text{Ag}(\mu_3\text{-O})(\text{PPh}_2\text{py})_3^{2+}$  clusters through aurophilic interactions.



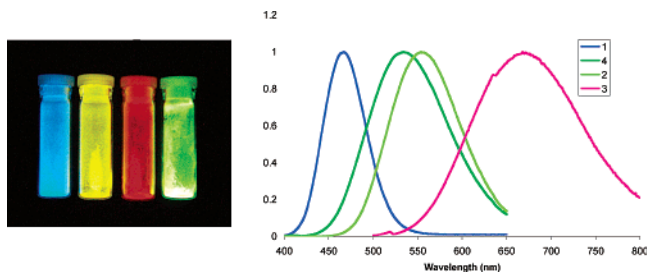
atom functioning as a  $\mu_3$ -ligand capping the three gold atoms. Each gold(I)···silver(I) edge is bridged by one  $\text{PPh}_2\text{py}$  ligand with the P atom attached to Au(I) and the pyridyl N atom coordinated to Ag(I). All of the metal ions are linked by metallophilic interactions as well as by bridging ligands. For **1**, the Au···Au contacts lie in the range of 2.9489(3)–3.0644(4) Å, whereas for **2–4** the respective ranges are 3.0661(3)–3.2096(3) Å, 3.1175(4)–3.2667(4) Å, and 3.1150(3)–3.4616(3) Å (the differences, while small, are statistically significant). The Ag···Au contacts in **1** (2.8985(5)–2.9690(5) Å) are similar in size to those found in complexes with appreciable metallophilic bonding, as for example, the sandwich silver(I) cluster  $[\text{Ag}\{\text{Au}_3(\text{bzim})_3\}_2]\text{BF}_4$  in which the silver(I) ion has metallophilic contacts with six gold atoms.<sup>22</sup> The triply bridging group-16 atoms exhibit E–Au bond lengths (2.053(4)–2.092(4) Å for **1**, 2.333(2)–2.337(1) Å for **2**, 2.4355(6)–2.4502(6) Å for **3**, and 2.333(2)–2.337(1) Å for **4**) that are similar to values for  $\mu_3$ -bridges reported previously.<sup>23–25</sup>

Aurophilic interactions also link two  $\text{Au}_3\text{Ag}$  tetrahedra together (see Figure 1) with a Au–Au distance of 3.0539(3) Å for **1**. Both **2** and **3** exhibit similar linking of  $[\text{Au}_3(\mu_3\text{-E})\text{Ag}(\text{PPh}_2\text{py})_3]^{2+}$  moieties, whereas the corresponding links for **4** are somewhat longer: 3.4616(3) Å. The metallophilic interactions and the bridging  $\text{PPh}_2\text{py}$  ligands confer greater structural rigidity and integrity to **1–4** as compared to trinuclear  $[\text{Au}_3(\mu_3\text{-E})(\text{PR}_3)_3]^+$  complexes in

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**Figure 2.** (a) Photo of solid-state emissions from compounds **1–4**, from left to right (365 nm excitation). (b) Normalized emission spectra of compounds **1–4** at ambient temperature in the solid state.

which the phosphine ligands coordinate as terminal ligands only.<sup>23–25</sup> The PPh<sub>2</sub>py ligands thus play a key role in assembling and buttressing the Au<sub>3</sub>Ag tetrahedra, a notion that has been utilized previously in synthesizing [Pt<sub>2</sub>(μ<sub>3</sub>-E)<sub>2</sub>(PPh<sub>2</sub>py)<sub>4</sub>Ag<sub>2</sub>(dppm)](PF<sub>6</sub>)<sub>2</sub> from the reaction of [Pt<sub>2</sub>(μ-E)<sub>2</sub>(PPh<sub>2</sub>py)<sub>4</sub>] (E = S, Se) with [Ag<sub>2</sub>(dppm)<sub>2</sub>(MeCN)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>.<sup>26</sup>

A distinctive feature of complexes **1–4** is their room-temperature solid-state luminescence, which for **1**, **2**, and **4** is extremely bright. As shown in Figure 2, complexes **1–3** exhibit a large variation in λ<sub>em</sub><sup>max</sup> as a function of the μ<sub>3</sub>-E capping ligand with values of 466, 554, and 670 nm for E = O, S, Se, respectively. At 77 K, the solid-state emission maxima shift to 482, 565, and 696 nm, respectively. For **1**, the bright-blue emission shows single-exponential behavior with lifetimes of 7 and 49 μs at 295 and 77 K, respectively, indicating that the emission is phosphorescence. Corresponding room temperature and 77 K excited-state lifetimes for **2** are 3.5 and 5.8 μs, respectively, while for **3** the respective values are 1.6 and 23.4 μs. The effect of methyl substituent in going from **2** to **4** is to increase the emission energy with a decrease in λ<sub>em</sub><sup>max</sup> in the solid from 554 to 534 nm.

The nature of the emission for **1–4** can be assigned on the basis of the luminescence data outlined above and literature reports. The emission for **1** is found at significantly higher energy than that of **2**, which in turn occurs at higher energy than that from **3**. The large change in λ<sub>em</sub><sup>max</sup> between **1**, **2**, and **3** clearly indicates involvement of the group-16 capping atom in the excited state. Based on the fact that lone pair orbitals lie lowest in O, next in S, and highest in Se, an assignment consistent with the emission results is that of a ligand-to-metal–metal-charge-transfer (<sup>3</sup>LMMCT). In fact, assignments of this type have been made by Fackler for thiolate-coordinated gold(I) compounds<sup>13</sup> and by Yam and co-workers for the high nuclearity cluster [Au<sub>12</sub>(μ-dppm)<sub>6</sub>(μ<sub>3</sub>-S)<sub>4</sub>](PF<sub>6</sub>)<sub>4</sub>, which contains four “μ<sub>3</sub>-S(Au–P)<sub>3</sub>” units.<sup>19</sup> In these assignments, the LUMO is said to be a cluster-based orbital rather than one localized on a single metal center, a view we support.

When cast into PMMA films, both **2** and **3** exhibit single bands in accord with the solid-state results, but at 9 K dual emission is observed from these samples with the high-energy shoulder at 480 nm. This high-energy band is also observed in the emission spectra of **1–4** in frozen dichloromethane at 77 K, which does not change with capping ligand E. These results lead to the conclusion that multiple emitting states exist for these compounds. On the basis of the constancy of the blue emission at 480 nm and literature reports describing energetically similar emission from aggregated gold complexes,<sup>12,27,28</sup> we conclude that the high-energy emission for **1–4** observable at low temperature is metal-centered. Accordingly,

the solid-state emission of **1** could be either LMMCT or metal-centered cluster-based emission.

The brightness of the solid-state emissions for **1**, **2** and **4** make these systems of interest for possible application as dopant emitters in OLED displays and the variation of λ<sub>em</sub><sup>max</sup> for **1–4** suggests ways of systematically tuning the excited states of these (μ<sub>3</sub>-EAu<sub>3</sub>M)<sup>2+</sup> heterobimetallic clusters through capping atom, bridging phosphine, and M<sup>+</sup> variation.

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**Supporting Information Available:** X-ray crystallographic data in CIF format for **1**, **2**, **3**, and **4**; experimental procedures, characterization data and photophysical data for **1–4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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