

Intensely Luminescent Gold(I)–Silver(I) Cluster with Hypercoordinated Carbon

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Metal complexes displaying intense phosphorescence have been of great interest due to their possible application in OLED, sensing, and biological labeling as emitters.¹ In this regard, much attention has been paid to polynuclear Au(I) complexes, because they usually possess intense, long-lived luminescence with emission energies in the visible range.² In many cases, aurophilic interactions³ are thought to be important in producing the emissive state. Because gold exhibits the highest spin–orbit coupling constant among metals, it favors the generation of the low-lying emissive triplet state by intersystem crossing. Consequently, the luminescence of gold complexes is normally phosphorescent in nature. Examples of gold(I) complexes intensely luminescent in solution at room temperature are known, such as the early work by Fackler and by Gray and the recent reports on heterometallic gold(I) alkynyl complexes with very high quantum yields (some higher than 0.9) by Koshevoy et al.^{4–6} However, most gold(I) complexes are only brightly emissive in the solid state at ambient temperature, due to the absence of gold–gold interaction and/or their suffering from quenching in solution.⁷

Inspired by the fact that strongly emissive gold *nanodots* showing high solution quantum yield can be attained by passivating the gold cluster with dendrimeric ligands,⁸ we envision that spherical *molecular* gold(I) clusters with peripheral phosphine ligands should be able to display phosphorescence of high quantum yield in solution. The novel hexaauriometane [(Ph₃PAu)₆C](BF₄)₂ (**1**) having an octahedral arrangement of Au₆ first reported by Schmidbauer et al.⁹ attracted our attention as an ideal candidate for solution emissive luminophore, because (a) hypercoordinated C compounds of gold have received very little study and its photophysical properties have not been investigated; (b) the presence of gold–gold interactions and its spherical shape with surrounding phosphines; and (c) it is quite stable in solution.

Complex **1** emits green light in the solid state when irradiated with UV light, but it is not emissive in solution at room temperature. The reason is probably that the terminal coordination of Ph₃P to Au(I) still makes possible the nonradiative relaxation pathways. To achieve the phosphorescence enhancement, it is necessary to close this nonradiative pathway by hindering the rotation of Au–P bonds. A facile approach is tying up the peripheral phosphines by introducing additional coordination, i.e. functionalizing [(Ph₃PAu)₆C]²⁺ by using diphenylphosphino-2-pyridine (dppy) in place of triphenylphosphine (Scheme 1) to form [Au₆(C)(dppy)₆](BF₄)₂ (**2**), which is followed by installing a silver atom, and thus the rigidity of the cluster is increased. Herein we report the synthesis, structure, and photophysical properties of a novel heteronuclear gold(I)–silver(I) cluster [Au₆Ag₂(C)(dppy)₆](BF₄)₄ (**3**) that is strongly emissive in solution at room temperature. While emission properties of Au(I) chalcogenide polynuclear complexes have been described previously,¹⁰ this is the first report on luminescence from a gold(I) carbonium system.¹¹

Scheme 1

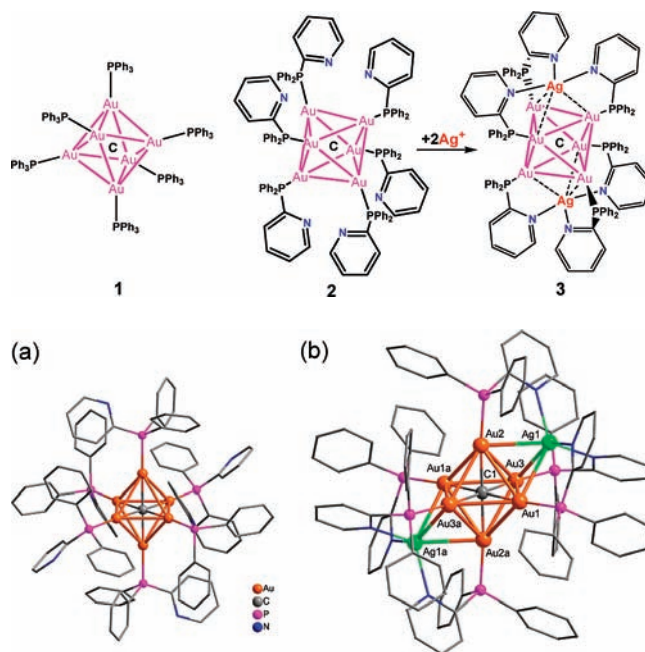


Figure 1. (a) Molecular structure of the cationic part of [Au₆(C)(dppy)₆](BF₄)₂ (**2**). Selected bond distances [Å]: Au(1)–C(1) 2.1053(2), Au(1)–Au(1)^a 2.9494(3), Au(1)–Au(1)^b 3.0049(2). Symmetry code: (a) *y*, *z* + 1, *x* – 1; (b) –*z* + 1, –*x* + 2, –*y* + 1. (b) Molecular structure of the cationic part of [Au₆Ag₂(C)(dppy)₆](BF₄)₄ (**3**). Selected bond distances [Å]: Au(1)–C(1) 2.1090(3), Au(2)–C(1) 2.0980(4), Au(3)–C(1) 2.1144(4), Au(1)–Au(2) 2.9406(5), Au(1)–Au(3) 2.9561(5), Au(1)–Au(2a) 3.0087(5), Au(1)–Au(3a) 3.0164(5), Au(1)–Ag(1) 2.9316(8), Au(2)–Au(3) 3.0100(5), Au(2)–Au(3a) 2.9469(5), Au(2)–Ag(1) 2.9134(8), Au(3)–Ag(1) 2.9218(8). Symmetry code: (a) –*x*, –*y* + 1, –*z*.

The reaction of [OAu₃(dppy)₃]BF₄ with Me₃SiCHN₂ in CH₂Cl₂ solution led to the isolation of **2** as colorless crystals. Further treatment of **2** with 2 equiv of AgBF₄ resulted in the formation of a red complex **3**. Complexes **2** and **3** have been characterized by NMR, ESI-MS, and elemental analysis (see Supporting Information). The incorporation of silver(I) into the cluster was clearly confirmed by the change of ³¹P NMR value from 28.24 for **2** to 32.96 for **3**.

Single crystal X-ray structural analysis¹² revealed that the structure of the cationic part of **2** is similar to that of **1** (Figure 1a). A carbon atom is located at the inversion center of the hexagold octahedron, and the Au–C and Au...Au distances are comparable to those in **1**.

The skeleton of **3** is a Au₆Ag₂ bicapped octahedron as shown in Figure 1b. Six gold atoms form an octahedron with two silver atoms each capping one of the two opposite Au₃ triangles. All the Au...Au and Au...Ag distances lie in the range 2.9134(8)–3.0164(6) Å,

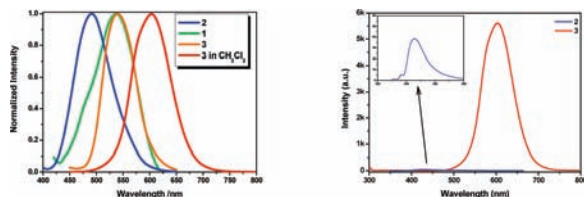


Figure 2. (Left) Normalized emission spectra of **1–3** in the solid state and **3** in solution at room temperature. (Right) Comparison of solution emissions of **2** and **3** at room temperature.

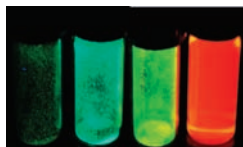


Figure 3. From left to right: photo of emissions from **1–3** in the solid state and **3** in CH_2Cl_2 solution at room temperature (365 nm excitation).

which suggests the presence of metallophilic interactions. A carbon atom sits in the middle of the cluster with Au–C bond lengths from 2.0980(4) to 2.1144(4) Å. Each gold(I)–silver(I) edge is bridged by one dpvy ligand with the P atom bound to Au(I) and the pyridyl N atom coordinated to Ag(I). Compared with **2** in which the dpvy ligands act as terminal ligands only, extra rigidity and integrity are conferred to **3** with the binding of the silver atom to the pyridyl of dpvy and the additional $\text{Au}^{\text{I}} \cdots \text{Ag}^{\text{I}}$ metallophilic interactions thus formed.

Interestingly, the structure of **3** can be viewed as the fusion of two Au_3Ag tetrahedral moieties sharing a carbon center, and each moiety is quite similar to the heterometallic clusters $[\text{Au}_3(\text{E})\text{Ag}(\text{dpvy})_3](\text{BF}_4)_2$ (E = O, S, or Se) reported by Eisenberg and Laguna.^{10c} These tetrahedral clusters are bright emitters in the solid state and frozen glass but are weakly emissive in solution.

Complex **2** is brightly emissive in the solid state at room temperature with the λ_{em} maximum at 495 nm, but its weak luminescence in solution is almost negligible. Complex **3** is strongly green emissive in the solid state, and a distinctive feature of **3** is its extremely bright room-temperature solution luminescence. The quantum yield was measured to be 0.29 with Rhodamine B in absolute ethanol as the standard (0.69).¹³ As shown in Figures 2 and 3, complex **3** exhibits red emission with a $\lambda_{\text{em}}^{\text{max}}$ value of 625 nm in dichloromethane. The emission shows single-exponential behavior with a lifetime of 5.7 μs at room temperature. The lifetime at microsecond scale and the large Stokes shift indicate that the emission is phosphorescence. The nature of the emission for **3** is tentatively assigned to a cluster-based metal-centered excited state.

Complex **3** is soluble in polar solvents such as methylene chloride, chloroform, and acetonitrile, and it is quite stable in solution. A CH_2Cl_2 solution of **3** was still brightly emissive after being kept in the dark for months. Furthermore, a preliminary study showed that **3** has very good photostability: no significant emission intensity decrease was observed after the solution had been exposed under a strong UV light (300 W Hg lamp) for 30 min.

The unusual luminescence from **3** is probably attributed to two reasons: the enhanced rigidity provided by additional coordination of silver that prevents the dpvy ligands from moving around; and the peripheral dpvy ligands protect the cluster from quenchers in

solution. Stronger enhancement of phosphorescence can be anticipated via the modification of dpvy ligands with bulkier substituents.

In summary, complex **3** has been rationally synthesized through the hold by an interstitial carbon and peripheral dpvy ligands, and it is highly phosphorescent both in solution and in the solid state at room temperature because of the enhancement of rigidity. The high quantum yield and good photostability make it a novel luminophore that may be useful in practical applications.

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Supporting Information Available: Detailed experimental procedures, characterization data and cif files for **2** and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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