

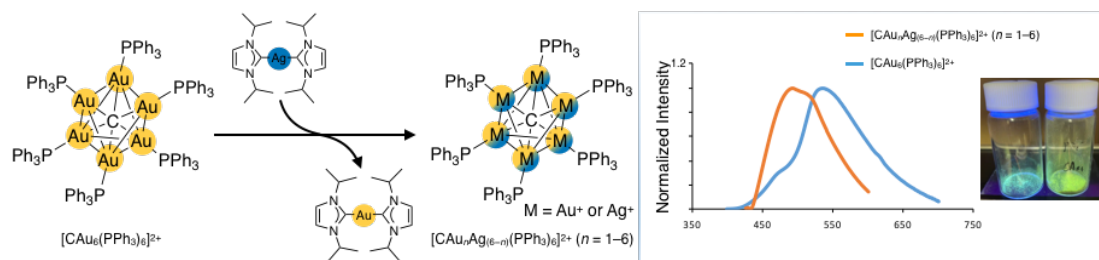
Transmetalation of a carbon-centered hexagold(I) cluster supported by triphenylphosphine ligands with silver(I) ions

(¹Graduate School of Science, The Univ. of Tokyo) ○Yiwei Wu,¹ Shun Sugimoto, Zhen Lei,¹ Xiaoli Pei,¹ Hitoshi Ube,¹ Mitsuhiko Shionoya¹

Keywords: Transmetalation Reaction; Gold(I) Cluster; N-Heterocyclic Carbene; Heterometallic Cluster; Luminescence

The construction of heterogeneous multinuclear metal complexes has a great potential for the expression of unique physical and chemical properties derived from heterometallic cooperativity and asymmetry specific to the metal arrangement. Since the first report by Schmidbaur in 1988,¹ C-centered hexagold(I) clusters have attracted much attention as promising building block for functional metal clusters.² For example, Wang reported C-centered clusters, CAu_6M_2 ($\text{M} = \text{Ag}^{\text{I}}, \text{Cu}^{\text{I}}$), in which the outer shell of the CAu_6 was modified using pyridylphosphine ligands.^{3,4} Here, we report the transmetalation reaction of a phosphine-supported C-centered hexagold(I) cluster with silver(I) ions to give heterometallic clusters, $[\text{CAu}_n\text{Ag}_{(6-n)}(\text{PPh}_3)_6]^{2+}$ ($n = 1-6$).

First, the transmetalation of $[\text{CAu}_6(\text{PPh}_3)_6]^{2+}$ by Ag^{I} complexes was examined. An excess amount of AgPPh_3OTf (30 eq.) was added to a CH_2Cl_2 solution of $[\text{C}(\text{Au}_6\text{PPh}_3)_6](\text{BF}_4)_2$. In the ESI-MS spectrum, peaks corresponding to the parent $[\text{CAu}_6(\text{PPh}_3)_6]^{2+}$ and $[\text{CAu}_5\text{Ag}_1(\text{PPh}_3)_6]^{2+}$ were observed. We found that the bis(*N,N*-diisopropylimidazolidene)silver complex, $(\text{I}^{\text{t}}\text{Pr})_2\text{Ag}^+$, effectively promoted transmetalation to give a mixture of heterometallic $[\text{CAu}_n\text{Ag}_{(6-n)}(\text{PPh}_3)_6]^{2+}$ clusters. The ^{31}P NMR spectrum also supported the formation of heterometallic clusters. A mixture of $[\text{CAu}_n\text{Ag}_{(6-n)}(\text{PPh}_3)_6]^{2+}$ clusters showed blue-shifted luminescence compared to the parent CAu_6 cluster in the solid state. The clusters showed stronger and red-shifted luminescence than at room temperature. In the presentation, we will discuss the details of their photophysical properties.



1) F. Scherbaum, A. Grohmann, B. Huber, C. Kruger, H. Schmidbaur, *Angew. Chem. Int. Ed. Engl.* **1988**, 27, 1544. 2) H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* **2008**, 37, 1931. 3) X.-Y. Liu, Y. Yang, Z. Lei, Z.-J. Guan, Q.-M. Wang, *Chem. Commun.* **2016**, 52, 8022. 4) J.-H. Jia, J.-X. Liang, Z. Lei, Z.-X. Cao, Q.-M. Wang, *Chem. Commun.* **2011**, 47, 4739.