

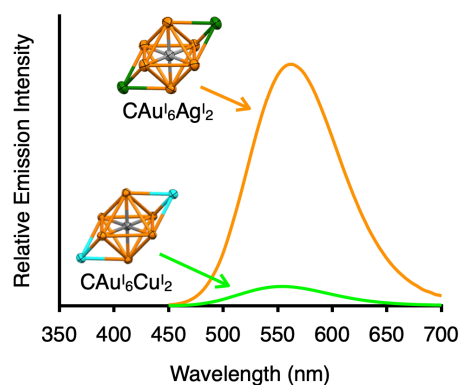
A Luminescent C-centered Au(I)-Cu(I) Cluster Protected by *N*-Heterocyclic Carbene Ligands

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Gold clusters are inorganic materials that are advantageous for the study of structure-property relationship because they have atomically precise molecular structures and usually exhibit interesting luminescent properties.^{1,2} The phosphine ligand-protected carbon-centered hexagold(I) clusters (CAu^I₆) are the most representative group of molecules.^{3,4} We have recently unsealed a parallel world of CAu^I₆ clusters protected by *N*-heterocyclic carbene (NHC) ligands.⁵⁻⁸ The NHC ligands were found to have significant effects on the luminescence behavior of the CAu^I₆ clusters in the solid state, without changing the core octahedral CAu^I₆ structures. More interestingly, very strong luminescence was obtained in solution due to the synergetic effect of additional silver(I) ions and NHC ligands. The obtained CAu^I₆Ag^I₂ clusters exhibited high quantum yields (QYs) up to 0.88 in CH₂Cl₂, almost three times higher than that of phosphine-protected analogues.

To better understand the role of secondary metal ions, a similar NHC-protected C-centered Au(I)-Cu(I) cluster CAu^I₆Cu^I₂ was synthesized. Single-crystal X-ray diffraction analysis confirmed that CAu^I₆Cu^I₂ and CAu^I₆Ag^I₂ have almost the same bicapped octahedral structure. The emission maxima in CH₂Cl₂ were also found to be comparable (554 and 562 nm, respectively). However, the introduction of copper(I) as an adatom on the surface of CAu^I₆ dramatically decreased the QY from 0.86 to 0.06, and emission lifetime from 1.66 to 0.03 μs. In other words, in CAu^I₆Cu^I₂, the non-radiative rate constant (*k*_{nr}) was amplified by more than two orders of magnitude, from 1.0 × 10⁵ s⁻¹ to 3.4 × 10⁷ s⁻¹, and the nonradiative decay became more dominant. These results suggest that the type of secondary adatoms is one of the most important factors for tuning the luminescence properties of heterometallic clusters.



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