Post-Synthesis from Carbon-Centered Hexagold(I) Clusters to Pentagold(I) Clusters with Controlled Geometry and Luminescence Behaviors

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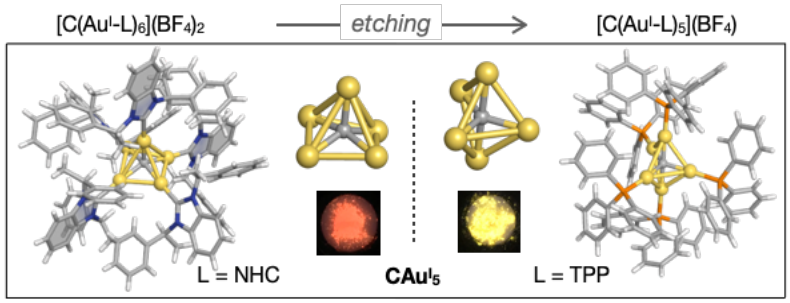
In recent years, there has been a growing interest in the field of gold chemistry to tune the size and structure of gold clusters at the atomic level.[1] Post-synthetic reactions such as etching/degradation reactions using free ligands to obtain smaller gold nanoclusters have made significant progress,[1] but the development of the underlying chemistry has only just begun.[2] Our carbon-centered hexagold(I) (CAu^{I}_{6}) clusters with *N*-heterocyclic carbene (NHC) ligands[3] are promising as starting materials for the synthesis of smaller CAu^{I}_{n} ($n < 6$) clusters, which are difficult to synthesize directly. Recently, we have reported the synthesis of $[(C)(Au^{I}\text{-NHC})_6](BF_4)_2$ and the ligand effects on their chemical and physical properties.[3] With the CAu^{I}_{6} clusters in hand, we set out to precisely tune the smaller carbon-centered gold clusters by an etching process *via* degradation with the addition of phosphine ligands.

By adding two equivalents of 1,2-bis(diphenylphosphaneyl)benzene to a solution of $[(C)(Au^{I}\text{-L})_6](BF_4)_2$ (L = NHC, TPP: triphenylphosphine) in CH_2Cl_2, a series of pentagold(I) clusters $[(C)(Au^{I}\text{-L})_5](BF_4)$ were successfully obtained in 79%-93% yield. To our best knowledge, this work is the first example of phosphine-etching in NHC-protected gold(I) clusters. Single-crystal X-ray analyses revealed that the NHC and TPP ligands ensure the distorted trigonal-bipyramidal and square-pyramidal geometries of the pentagold(I) motifs, respectively. The NHC-CAu^{I}_{5} cluster showed an orange-red luminescence in the solid state, while the TPP-CAu^{I}_{5} cluster showed a bright yellow luminescence. This structure-dependent luminescence behaviors is a noteworthy result.



1) M. Zhu et al., *Chem. Mater.* **2019**, *31*, 9939. 2) J. Xie et al., *Nat. Commun.* **2021**, *12*, 3212. 3) a) M. Shionoya et al., *Organometallics* **2018**, *37*, 2007. b) M. Shionoya et al., *J. Organomet. Chem.* **2020**, *917*, 121271. c) M. Shionoya et al., **2021**, *submitted*.