Toward an intensely phosphorescent tetrahedral Au_6Ag_4 cluster with hypercoordinated carbon

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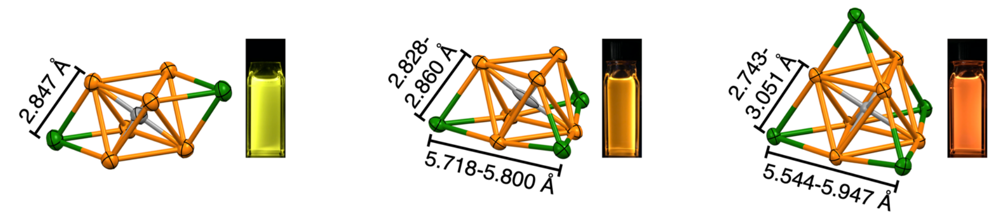
Tetrahedral gold clusters (e.g. Au_4, Au_{10}, Au_{20}) have long been pursued because they can be considered fragments of bulk gold, but were found or predicted to exhibit very different properties such as wide energy gap and spherical aromaticity.[1-3] Despite Au_4 being reported, the structure information for the latter two clusters is not yet available. By functionalizing the N-heterocyclic carbene ligands with one picolyl group, instead of pyridyl,[4,5] a moderately phosphorescent cluster $C@Au_6Ag_3$ in a shape of *triangular frustum* (monorectified tetrahedron) was first assembled. Compared to the outstanding photophysical properties of bicapped octahedral $C@Au_6Ag_2$ stabilized by ligands with pyridyl pendant,[5] $C@Au_6Ag_3$ has a red-shifted emission, but exhibited a much lower quantum yield (QY = 0.04) and a shorter lifetime (0.23 μs). The use of picolyl group allows for coordination of one more silver ion around the octahedral $C@Au_6$, thus resulted in the red-shift in emission. Meanwhile, the introduction of a methylene linker into the picolyl group that leads to a rather loose coordination sphere is responsible for the low QY and short lifetime.

To recover the phosphorescence, two picolyl groups were then installed on the carbene ligand, which allows the formation of a fuller protection for $C@Au_6$ with the aid of silver ions.[4] As a result, a novel cluster $C@Au_6Ag_4$ with a *tetrahedral* geometry and intense phosphorescence was constructed. The edges of the $C@Au_6Ag_4$ tetrahedron are between 5.544-5.947 Å, which are comparable to the predicted Au_{10}.[2] More interestingly, it emits strong red phosphorescence in CH_2Cl_2 with a QY of 0.40 and a lifetime of 1.41 μs, both of which were significantly improved as compared to $C@Au_6Ag_3$. This work indicates that both rigidity and coverage of the protection sphere are vital for intense and long-lived phosphorescence of metal clusters. It also shed light on the rational synthesis of tetrahedral Au_{10} and Au_{20}, and highlights their potential luminescence properties.



$C@Au_6Ag_2$, bicapped octahedron, λ_{em}^{max} = 562 nm, QY: 0.86, lifetime: 1.66 μs in CH_2Cl_2

$C@Au_6Ag_3$, triangular frustum, λ_{em}^{max} = 612 nm, QY: 0.04, lifetime: 0.23 μs in CH_2Cl_2

$C@Au_6Ag_4$, tetrahedron, λ_{em}^{max} = 634 nm, QY: 0.40, lifetime: 1.41 μs in CH_2Cl_2

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