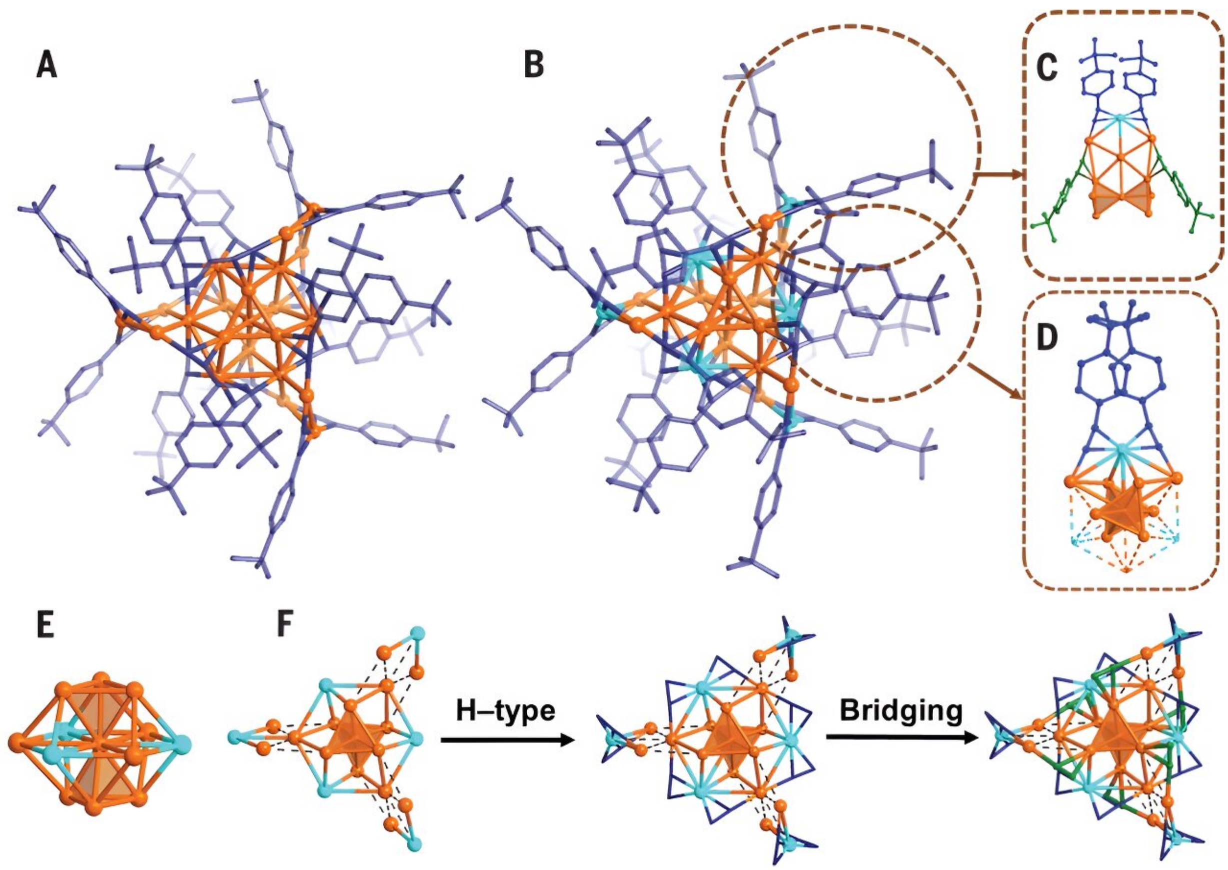
Researchers achieve >99% photoluminescence quantum yield in metal nanoclusters

March 18 2024



Molecular structures of Au_{22} and $Au_{16}Cu_6$ and structure anatomy of $Au_{16}Cu_6$.
Credit: Prof. Zhou's team

A research team has achieved near-unity room-temperature photoluminescence quantum yield (PLQY) (>99%) in the near-infrared (NIR) emission of metal nanoclusters in solution. Their work is published in *Science*.

Gold nanoclusters (Au NCs) as NIR-emissive materials hold potential in biomedical applications. However, the PLQY of Au NCs in the NIR region is typically low, often less than 10%. To address this problem, researchers synthesized $Au_{22}(^{t}BuPhC{\equiv}C)_{18}(Au_{22})$ and its copper-doped counterpart, $Au_{16}Cu_6(^{t}BuPhC{\equiv}C)_{18}$ $(Au_{16}Cu_6)$, to study their photophysical properties.

Single-crystal X-ray diffraction analysis revealed that Au_{22} and $Au_{16}Cu_6$ share similar structures. Au_{22} showed an emission peak at 690 nm and $Au_{16}Cu_6$ at 720 nm. The absolute PLQY of Au_{22} and $Au_{16}Cu_6$ in air were 9% and 95%, respectively.

In the deaerated solution, the PLQY of $Au_{16}Cu_6$ reached 100%, measured by both absolute and relative methods. Time-correlated single-photon counting measured the photoluminescence lifetimes of Au_{22} and $Au_{16}Cu_6$ to be 485 ns and 1.64 μs, respectively.

Further investigation of NCs' excited-state dynamics through transient-absorption spectroscopy revealed that both NCs' luminescent states originated from the triplet state (T_1), with distinct dynamic processes observed in femtosecond transient-absorption spectroscopy. Under 380 nm excitation, Au_{22} showed a slow rise of 148 ps, while $Au_{16}Cu_6$ showed a rapid relaxation of 0.5 ps.

Triplet sensitization experiments confirmed that these processes are attributed to ultrafast intersystem crossing (ISC) from singlet state (S_1) to T_1. Due to copper doping, $Au_{16}Cu_6$ has a smaller ΔE_{st}, significantly accelerating its ISC rate. As a result, $Au_{16}Cu_6$ ultimately showcases PLQY close to 100%.

The approach to achieve near-unity PLQY could enable the development of highly emissive metal cluster materials. Specifically, this work demonstrates that near-unity PLQY can be attained with an alloy of gold-copper nanoclusters even in solution at room temperature, which will enable applications ranging from biological imaging to luminescent devices.

The research team included Prof. Zhou Meng's group from the University of Science and Technology of China of the Chinese Academy of Sciences (CAS), collaborating with Prof. Wang Quanming's team from Tsinghua University.

More information: Wan-Qi Shi et al, Near-unity NIR phosphorescent quantum yield from a room-temperature solvated metal nanocluster, *Science* (2024). DOI: 10.1126/science.adk6628

Provided by University of Science and Technology of China