COMMENTARY

Near-infrared phosphorescence from metal nanoclusters with nearly unity quantum yield

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Cluster molecules are composed of metallic nuclei containing several to dozens of atoms, e.g. Au, Cu or Pt, and counter-ions, respectively, which are stabilized with organic ligands through coordination, giving rise to core-shell molecular aggregate structures. Consequently, as a typical organic-inorganic hybrid systems, clusters combine the advantages of both metallic cores and organic ligands, leading to their unique physical properties, especially comprehensive optoelectronic and magnetic properties, unusual photo- and thermo- stability, high catalytic activity, and excellent biocompatibility.

Luminescence is one of the most important merits and functions for cluster materials. The ligand incorporation and metal-ligand coupling result in discrete energy level distributions, molecular electronic structures, and diverse excited states of clusters. Strong metal-metal interactions in metallic

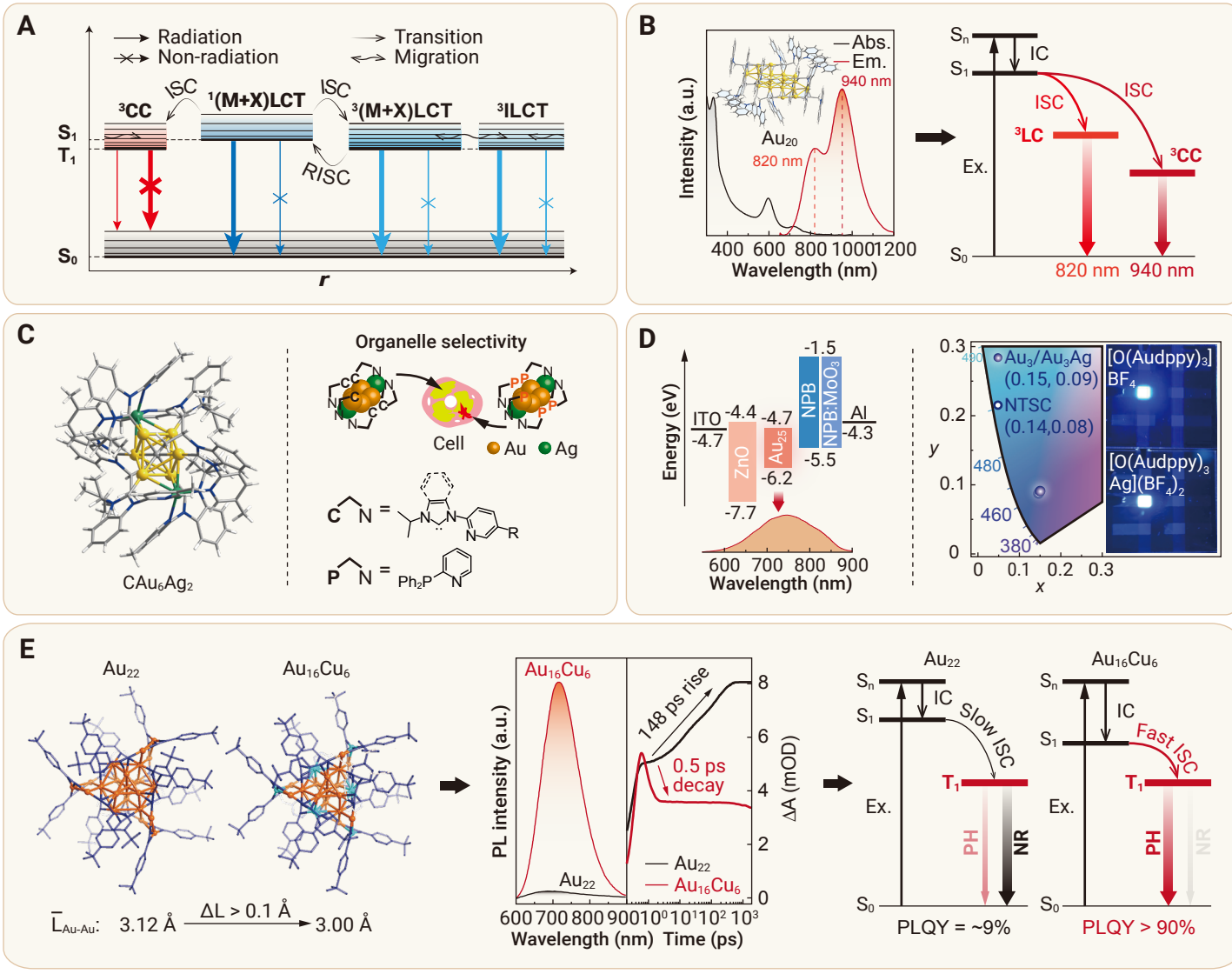

Figure 1. Optimization of luminescent properties for clusters (A) Excited state composition of common ligand-stabilized clusters. Reproduced with permission. Copyright 2019, American Association for the Advancement of Science. (B) Absorption (abs.) and emission (E_m) spectra of an Au_{20} cluster and the mechanism of dual emissions based on energy transfer process. S0, S1 and Sn are ground state, the first singlet and the high-lying singlet excited states, respectively. ^{3}LC and ^{3}CC are ligand and cluster centered triplet states, respectively. IC and ISC refer to internal conversion and intersystem crossing. Reproduced with permission.[1] Copyright 2023, American Association for the Advancement of Science. (C) Single-crystal structure of CAu_6Ag_2 and its application in cell imaging. Reproduced with permission.[2] Copyright 2022, Nature publishing group. (D) Device energy level diagram and electroluminescence spectrum of Au_{25} based light-emitting diodes (left), and the chromatic panel and device pictures of Au_3 and Au_3Ag based diodes (right). Reproduced with permission.[3,4] Copyright 2014 and 2022, Wiley-VCH. (E) Single-crystal structures, and photoluminescence and ultrafast transient absorption (TA) spectra of Au_{22} and $Au_{16}Cu_6$, and their different transition mechanisms of emission processes. Reproduced with permission.[5] Copyright 2024, American Association for the Advancement of Science.

nuclei not only improve the stability and suppress non-radiative structural relaxation, but also generate metal-metal-ligand charge transfer to enhance spin-orbit coupling and reduce singlet-triplet splitting energy for facilitating intersystem crossing (ISC) and reverse ISC (RISC), leading to phosphorescence (PH) and thermally activated delayed fluorescence (TADF), respectively. As a result, excited states of cluster molecules are composed of ligand-centered (^{n}LC*, n = 1 for singlet and 3 for triplet, respectively) and cluster-centered (^{3}CC) components. The former contain metal-to-ligand (^{n}MLCT), counterion to ligand (^{n}XLCT), and intra-ligand (^{n}ILCT) transitions, and ligand local excited (^{n}LLE) components (Figure 1A).

This feature endows cluster emitters with the unique luminescent properties, e.g. dual Near infrared (NIR) emissions from both LC* and ^{3}CC states of a Au_{20} cluster respectively at 820 and 940 nm (Figure 1B).[1] But, its photoluminescence quantum yield (PLQY) was only 6.26% in ambient solution, since ^{3}CC states commonly suffered from nonradiative recombination. Nonetheless, gold clusters were already used in diverse optical applications, e.g. bioimaging and light-emitting diodes. It is worth noting that, compared to homogeneous Au_n clusters, heteroatom doping can markedly improve the optical performances. For example, yellow emissive CAu_6Ag_2 clusters with PLQY of 88% were used for selective cytoplasm imaging (Figure 1C).[2] NIR electroluminescence at 750 nm from Au_{25} cluster was demonstrated. Unfortunately the external quantum efficiencies (EQE) of the device was less than 0.1%.[3] In contrast, most recently, an Au_3Ag based light-emitting diode achieved the maximum EQE beyond 2% (Figure 1D).[4] These results indicated that heteronuclear clusters revealed different optical properties. Compared with homogenous analogs, some of heteronuclear clusters could realize the markedly improved performance.

PLQY values of most of gold clusters with NIR emissions were very low, commonly less than 10% under ambient conditions, because the narrow bandgaps for NIR emissions induce nonradiation through internal conversion, which is known as "energy gap law". Recently, through doping copper atoms into gold cluster core, Wang et al. reported a highly luminescent $Au_{16}Cu_6(^t$BuPhC≡C$)_{18}$ ($Au_{16}Cu_6$) stabilized with 4-(tert-butyl)phenylacetylene ligands, in comparison to the homogenous $Au_{22}(^t$BuPhC≡C$)_{18}$(Au_{22}) (Figure 1E).[5] It showed that the incorporation of Cu atoms reduced Au-Au bond lengths to shrink the metallic nucleus and strengthen Au-Au interactions, leading to the deepened lowest unoccupied (LUMO) and the increased highest occupied molecular orbital (HOMO) energy levels, and the narrowed energy gap of $Au_{16}Cu_6$ as further demonstrated by time-dependent density functional theory analysis. Consequently, in accord to the red-shifted absorptions of $Au_{16}Cu_6$, compared to the peak of deep-red emissive Au_{22} at 690 nm, the peak wavelength of NIR emission from $Au_{16}Cu_6$ was red-shifted by 30 nm to 720 nm. More importantly, PLQY of $Au_{16}Cu_6$ in solution reached 95%, which was ten folds of that of Au_{22} (9%). In deaerated solution at room temperature, PLQY of $Au_{16}Cu_6$ was nearly 100%.

Ultrafast transient absorption (TA) analysis showed that under excitation at 380 nm, the excited-state absorption spectrum of Au_{22} consisted of a weak ultrafast attenuation at the first 1 ps, but a continuous rise at 1-300 ps, corresponding to a slow ISC for ~150 ps. $Au_{16}Cu_6$ also displayed an ultrafast ISC in the first 0.5 ps. Then its decay remained constant until 2 ns. Since Au_{22} and $Au_{16}Cu_6$ were isostructural, copper doping did not change spin-orbital coupling. Nonetheless, the ultrafine relaxation of $Au_{16}Cu_6$ indicated an internal transition occurred simultaneously with ISC, making triplet population more efficient. In this sense, copper doping made main contribution to the markedly increased intersystem crossing rate (k_{ISC}). In addition, copper doping decreased the singlet-triplet splitting (ΔE_{ST}) and Marcus reorganization energy (λ), resulting in an increase of Franck–Condon weighted density (ρ). Consequently, compared with that of Au_{22}, k_{ISC} of $Au_{16}Cu_6$ was increased by ~300-fold, leading to a rapid triplet radiative decay.

In consequence, copper doping in gold clusters rendered a more compact structure and stronger metal-metal interactions for $Au_{16}Cu_6$. The geometric effect suppressed non-radiation by ~60 folds, and the corresponding electronic effect increased k_{ISC} by ~300 folds. The synergy of these two effects resulted in the nearly unity PLQY. Obviously, "heteroatom doping" is an effective strategy to improve the luminescent efficiencies of nanocluster molecules, establishing the solid basis for their practical applications.

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DECLARATION OF INTERESTS

The authors declare no competing interests.