Aggregation-Induced Emission in Luminescent Metal Nanoclusters

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Leveraging on the well-defined molecular structures of metal nanoclusters, we provide in-depth discussions and future outlook on AIE-type luminescent metal nanoclusters, generating principles that can enhance the AIE properties of metal NCs from both in and beyond “single cluster” level.

Few- to hundred-atoms luminescent metal nanoclusters (NCs) protected by an organic monolayer have recently emerged as a novel class of chromophores because of their facile preparation, ultrafine size, low toxicity, high renal clearance, excellent photostability, and so on [1]. Luminescent metal NCs hold great promises for broad applications in lighting, imaging, sensing, and therapeutics [2]. However, the unsatisfactory emission intensity of metal NCs has constrained their further practical applications. In particular, the complexity, diversity, and mutability in terms of their total structures preclude an in-depth understanding of their emission origin [1, 3]. Therefore, there are very limited approaches and principles available for the desired improvements and tailoring of their luminescence performance.

In this context, inspired by the concept of aggregation-induced emission (AIE) first coined by Tang in 2001 to clarify the organic fluorophores involved photophysical variation upon aggregation [4], we have successfully designed a new family of ultrabright Au(0)@Au(I)-SR (SR: deprotonated thiol ligands) core-shell NCs in 2012, by preserving a high content of Au(I)-SR complexes in the protecting shell. Thereafter, AIE-type luminescent metal NCs are well-developed with markedly improved emission intensity, witnessing an increasing number of studies in both fundamental and practical sectors [5].

In sharp contrast to the structure of large-sized metal nanoparticles (> 3 nm in size), where the individual ligand is attached directly to the close-packed metal core substrate, the structure of metal NCs can be illustrated by a “divide-and-protect” model (Fig. 1a-c) with the “staple motifs” of metal(I)-ligand wrapping over the metal core [6, 7]. The composition and structure of metal(I)-ligand motifs are diverse (e.g., from monomeric ML₂ to heptameric M₇L₈ in the cases of Au NCs, where M and L denote the metal and ligand, respectively) and mostly determined by the curvature of the metal core. The AIE concept allows emission enhancement of metal NCs by effective restriction of intra-/intermolecular motion (i.e., vibration and rotation) of surface motifs, minimizing non-radiative decay [8]. Keeping these in mind, the AIE of metal NCs is, in essence, an affair closely related to their surface-emission state on the basis of ligand-to-metal charge transfer (LMCT) and/or
ligand-to-metal-metal charge transfer (LMMCT), generating radiative relaxation via a metal-centered triplet [1, 9]. Therefore, the AIE-type luminescent metal NCs feature long decay lifetime (μs-level), low emission energy (< 2.2 eV), large Stokes shifts (> 100 nm), and their emission intensity is highly dependent on the features of their surface and interface [5, 10].

This scenario imparts a fundamental principle for performance improvement of AIE-type luminescent metal NCs that is to positively affect the LMCT and/or LMMCT process dictated by the landscape of the surface (a synergy from ligand-centered charge transfer process). In this vein and at a single-cluster level, several efficient strategies have been identified: 1) to strengthen metal(I)-ligand contacts by i) endowing surface ligands with increased electron donation capability to the core; ii) introducing electron-rich atoms or groups into surface ligands; and iii) increasing the content of metal(I) species in the surface motifs to strengthen the charge transfer process of LMCT and/or LMMCT; 2) to improve rigidity of the surface shell by i) constructing long and/or interlocked surface motifs (polymeric chain-like or ring-like metal(I)-ligand compounds) (Fig. 1c); and ii) conferring ligands with multiple interaction sites to anchor the metal core, and to enhance the rates of radiative energy transfer by suppressing ligand-related nonradiative relaxation of excited states. All these cases are related to controlling the excited state relaxation dynamics of LMCT and/or LMMCT with different emphases in each other, thus allowing production of brighter AIE-type luminescent metal NCs.

**Figure 1.** Schematic illustration of the typical structure model of organic layer-protected (a) metal nanoparticles (NPs) and (b, c) metal nanoclusters (NCs). In metal NPs, individual ligand is attached independently and directly to the close-packed metal core, while in metal NCs, unique staple-like metal(I)-ligand motifs (short and long/interlocked motifs for b and c, respectively) are wrapping over the metal(0) core of metal NCs, following a “divide-and-protect” model. (d) and (e) are the corresponding aggregates of (b) and (c), respectively. (ligands: pink patches; metal(I): golden patches; metal(0): golden spheres; all hydrocarbon tails of ligands are omitted for clarity).
In addition, beyond the single-cluster level, treating metal NCs as building blocks to direct their aggregation is another well-recognized and effective strategy for rendering metal NCs strong luminescence (Fig. 1d, 1e). The aggregation of NCs is capable of altering the ligand-ligand (e.g., restraining molecular vibrations), ligand-metal (e.g., varying conformation of interfaces), and metal-metal (e.g., forming metallophilic bonding) interactions, which will further influence the excited state relaxation dynamics. At present, the most widely used methods are the solvent- and cation-induced aggregation of metal NCs triggered by the disturbance of solvent polarity and introduction of electrostatic/coordination interactions, respectively. However, both of these approaches are challenging for homogeneity control over the NC aggregates, which in general leads to a poor color purity. In contrast, exploring the directed self-assembly of metal NCs is more advanced for aggregating component metal NCs into ordered, customizable and versatile patterns, thus giving rise to their enhanced emission properties with high controllability. Besides, it also provides a platform to unravel the relationship between cluster luminescence and their packing attributes (e.g., spatial distribution and inter-NCs interactions). In parallel to self-assembly, continuous progress on the crystallization and the scaffold (e.g., zeolites, metal/covalent-organic frameworks) confinement of metal NCs to attain excellent AIE properties have also been made [11, 12]. Of particular note, some fundamental inspirations are obtained in these exquisite systems. For example, the metal(I) species related metal defect state is evidently responsible for the unexpected enhancement of emission intensity of metal NC ensembles. In the crystalline state, metal NCs can show red shift of the emission band, which is caused by a combined effect of the electronic coupling and lattice-originated, nonradiative decay pathways occurring through electron-photon interaction. Moreover, a positive influence of host-guest interaction, polarization effect, and the localization of excitons on metal NCs’ emission intensity is observed in a surface confinement system imposed by layered double hydroxide nanosheets.

It is notable that although the surface engineering is the most immediate breakthrough in the investigation of AIE-type luminescent metal NCs, the contribution of metal(0) core is also important and deserves further attention. The metal(0) core can act as the substrate to anchor the surface motifs for their condensation. And, with an oxidation agent, it is able to increase the content of metal(I) species in sacrifice of metal(0) core. In some cases, large metal(0) core (i.e., 2-5 nm) dictated surface plasmon resonance (SPR) could induce a strong coupling effect with the metal(I) involved surface emitter, thus leading to remarkable emission enhancement of AIE-type metal NCs. Most importantly, the emission states derived from the metal(0) core and the metal(I) surface, in general with a fluorescence and phosphorescence feature, respectively, are possible to coexist or to transform each other in the scheme of AIE-type luminescent metal NCs [1].

To sum up, the AIE mechanism has been widely accepted and continuously improved in the research community of luminescent metal NCs. However, the current development of cluster chemistry has not yet reached an unambiguous agreement on the AIE fundamentals of metal NC luminescence. In the near future, it is foreseeable that studies on AIE-type metal NCs bound to remain a research hotspot, which could include but is not limited to:

- Nailing down the relationship between the structures and the AIE properties of metal
NCs to their molecular-level precision, which will greatly add to human being’s capability of rational prediction, tailoring, and thus customization of highly luminescent metal NCs.

- Tapping the potential of AIE-type metal NCs in applications of the related biological systems. The development of water-soluble, small-sized, highly luminescent AIE-type metal NCs, especially with the near-infrared (NIR-I and NIR-II regime) absorption and/or emission, is still in its infancy.

- Adding high conductivity, thermostability, and processability, etc. to AIE-type metal NCs, thus allowing construction of the metal NC-based photoelectric devices.

- Beyond the most investigated noble metals (Au, Ag and their alloys), the earth-abundant, low-cost metals (e.g., Cu, Zn and other transition metals) also deserve extensive exploration. For instance, it is worth exploring AIE properties in Cu NCs, not only due to its electronic configuration (d^{10}s^1) which is similar to Au/Ag, but also due to its wide range of accessible oxidation states (Cu^0, Cu^I, Cu^{II} and Cu^{III}) [13].

- The understanding of AIE concept has been deepened with the increasing structural recognition of luminescent metal NCs. For example, it is more appropriate to use “aggregation-induced emission enhancement (AIEE)” to describe the cases that involve the isolated metal NCs with weak emission instead of non-luminescence. Most recently, the AIE of metal NCs is also well-categorized as clusterization-triggered emission (CTE) in consideration of their totally nonconjugated structures, where the chromophores in clusteroluminogens are attributed to the significant through-space conjugation (TSC) built in the inter-/intra-NCs [14].

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Conflict of interest statement.
None declared.

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