Aggregation-induced emission of copper nanoclusters

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Abstract
Copper nanoclusters (Cu NCs) have recently emerged as promising luminophores, featuring ultra-small size, reasonable photostability, large Stokes shift, and long emission lifetimes. Aggregation-induced emission (AIE) has been often used to further improve both the emission intensity and stability of these clusters, with plenty of potential applications in the fields of chemical sensing and bioimaging. This review starts with a summary of the current understanding of emission mechanisms of Cu NCs and proceeds with the analysis of contributions from the Cu metal core and the organic ligands. We summarize the recent research progress on the design of ligands, and the ways on how to induce aggregation of the Cu NCs through electrostatic charge neutralization, host-guest interactions, and the use of templates. We also discuss the current understanding of emission mechanisms of Cu NCs experiencing AIE, such as the often-cited restriction of intramolecular motion and contributions from Cu(I) molecular complexes. We finish this review by providing concluding remarks and offering our own perspective on the active field of AIE of Cu NCs, with a hope to further promote the research on the fundamental aspects of this useful phenomenon.

KEYWORDS
aggregation-induced emission, copper nanoclusters, surface ligands

INTRODUCTION
Copper (Cu), one of the most abundant metals on the earth, possesses excellent electrical, thermal, and mechanical properties and has been widely used in the fields of machinery and electronics. Upon decrease of size resulting in the tiny Cu nanoparticles, many interesting phenomena start to appear. Various Cu-based nanomaterials have been reported, with attractive optical, catalytic, and antimicrobial properties. Among them, there are also few-atomic Cu nanoclusters (NCs), which typically comprise molecular-like Cu cores surrounded by organic ligands. Similar to the well-studied Au and Ag NCs, they possess discrete electronic states and show rather efficient photoluminescence (PL). At the same time, the use of Cu in this case offers several advantages, in particular, because it is an earth-abundant, cheap, and non-toxic element. The light-emitting Cu NCs have already attracted plenty of attention as summarized in several recent reviews. The emission of Cu NCs is indeed an attractive property, as it offers an avenue to further develop them into luminescent components for such diverse applications as chemical sensing, bioimaging, anticounterfeiting, and even optoelectronic devices. Compared with conventional luminescent materials, such as organic dyes and semiconductor quantum dots, Cu NCs possess advantages of ultra-small size combined with reasonable...
photostability, large Stokes shift, and long emission lifetimes. However, their PL quantum yields (QY) are still not competitive with those conventional luminescent materials, and their wider applications have been limited by poor stability caused by the easy oxidation of Cu. Fortunately, the aggregation-induced emission (AIE) phenomenon has provided a powerful approach to enhance the emission efficiency (and to some extent improve the stability) of Cu NCs. The restriction of intramolecular motion (RIM) is the widely accepted reason for the AIE phenomenon to occur. Hydrophilicity, electrostatic charges, and length of the organic ligands can all affect the intramolecular motions of clusters both in isolated and aggregated states, which makes ligands on the surface of Cu NCs critical for their AIE behavior. Several physical, chemical, and engineering strategies have been suggested to control the aggregation behavior of Cu NCs, such as making use of viscosity and polarity of solvent mixtures, modifying surface charge, and confining clusters within templates. Understanding the principles of the synthesis strategies, modulation of aggregation, and PL mechanisms of Cu NCs are important for a large number of researchers active in this field.

While there have been several reviews mostly focused on the synthesis and applications of Cu NCs, little in-depth discussion has been offered on the origin of their AIE-related features so far. This review is aimed at closing this gap, by providing specific consideration on the nature of ligands to be selected for the synthesis of Cu NCs experiencing AIE, the approaches to modulate their aggregation behavior, and the mechanisms of their AIE. The review starts with a summary on the current understanding of PL mechanisms of Cu NCs and proceeds with the analysis of contributions of Cu metal core and organic ligands to AIE-related properties. Note that we do not consider in detail practical applications of Cu NC AIEgens, as those are already available in a number of topical reviews but some examples of those are provided. We end this review by offering some concluding remarks and our own perspective on the active field of AIE of Cu NCs, with a hope to promote further research on the fundamental aspects of this useful phenomenon.

THEORETICAL AND EXPERIMENTAL UNDERSTANDING OF EMISSION MECHANISMS OF CU NCs

To understand the PL mechanism of Cu NCs, a combination of data from their structural and optical characterizations and theoretical calculations is often needed. During the early stages of research on this matter, so-called “naked” Cu NCs, which were unprotected by any surface ligands, were synthesized through gas-phase fabrication and electrochemical methods. Some of those naked Cu NCs showed rather intensive PL, which suggested that their emission originated from the Cu core. For example, Huseyinova et al. reported surfactant-free Cux NCs produced in water, which showed strong PL in the UV.

Researchers attempted to explain the appearance of this PL by drawing an analogy to the well-studied semiconductor quantum dots, where it is the quantum confinement effect that results in the size-dependent emission color. In a line with this view, Vázquez-Vázquez et al. reported size-dependent optical properties of a series of Cu NCs with an increasing number N of Cu atoms (N varying from less than 10 to several hundreds) in the metal core where “magic size” of the Cu core increased with increasing the amount of reducing agent NaBH4 amount used in their synthesis (Figure 1). They observed that only the smallest clusters (N < 10) showed PL, while the larger NCs (Cu15, Cu25, and Cu147) and—as expected—larger “plasmonic” Cu nanoparticles were non-luminescent. These results indicated the possibility to unravel the size-dependent PL properties of Cu NCs and suggested that their electronic structure was closely defined by the number of free electrons within clusters. A simple spherical jellium model described by an expression $E_g = E_{\text{fermi}}N_1^{1/3}$ was used to describe the relationship between the emission energy $E_g$ and the number $N$ of metal atoms in the NCs, where $E_{\text{fermi}}$ is the Fermi energy of bulk Cu metal. Several follow-up publications have claimed that indeed Cu NCs followed this simple spherical Jellium model. Vilar-Vidal et al. reported Cu NCs stabilized with tetrabutylammonium salt and determined their core as Cu14 by the laser desorption/ionization time-of-flight mass spectrometry; their PL peak located at 410 nm could indeed be correlated to the number of Cu atoms in their core following the jellium model. The same group has also prepared a series of Cu NCs with varying core sizes using tetrabutylammonium salt as ligands as shown in Figure 2A. These clusters displayed a redshift of the first absorption maximum (corresponding to decreasing optical band gap) and a concomitant redshift of the PL peak (Figure 2B) in the order of Cu5, Cu13, and Cu20, which matched well with the jellium model. The core size of glutathione (GSH)-stabilized Cu NCs with PL peak at 430 nm was measured to be Cu15, which was very close to the calculated result by the spherical jellium model. The PL peak at 410 nm of the bovine serum albumin (BSA)-protected Cu15 could also be described by this model.

However, the jellium model could not be applied for several other types of Cu NCs, in particular, for the orange- or red-emitting clusters. Thus, the PL peak position at 615 nm of the Cu NCs protected by 2-phenylethanol (PET) with a formula of Cu38(PET)25 as reported by Pradeep’s et al. could not be described by the jellium model. Needless to say, the simple jellium model also cannot explain the differences in the PL peak positions of Cu NCs with the same size of the metal core stabilized by different ligands. It is rather clear that the number of metal atoms in the Cu core cannot be the only factor that determines the PL peak position of Cu NCs. Several other factors, such as the nature of stabilizing ligands, their surface density, and the valence state of Cu (zero vs. one) should also be responsible for their PL properties. It appears that “naked” (ligand-free) Cu NCs, or those stabilized by weakly bound ligands, such as tetrabutylammonium, BSA, and polyethyleneimine, tend to follow the simple spherical jellium model; these clusters mostly have emission in the UV/blue spectral region, and they possess a short PL lifetime on the scale of nanoseconds, which can be attributed to the singlet excited state of the Cu core. On the other hand, Cu NCs stabilized by strongly bound ligands, such as those with thiolate, amino, and carboxyl groups usually show PL in the orange and red spectral range and have a much longer PL lifetime on the scale of microseconds. The relationship between the emission energy
AGGREGATE

FIGURE 1 Evolution of the number of atoms per cluster accompanied by the disappearance of fluorescence while changing the $\alpha$ value (which is the volume fraction of the reducing agent NaBH$_4$) used for the synthesis of a size series of copper nanoclusters (Cu NCs). Reproduced with permission.[35] Copyright © 2009, American Chemical Society

and the size of those clusters cannot be described by the simple spherical jellium model. The luminescent center of these clusters is rather a Cu(I)-ligand complex, and the emission here can be attributed to a ligand-to-metal-metal charge transfer (LMMCT) mechanism.[19,21] Thus, the content of Cu(I) in this complex and the number of ligands on the surface of the Cu core will be the most important factors that determine PL properties in this case.

AIE OF Cu NCs

Since the discovery of AIE by Tang et al.[22,49] plenty of researchers have engaged in the design, synthesis, and application of highly luminescent AIE materials.[24,27] Cu NCs stabilized by strongly bound ligands can also experience the AIE effect, as it was first reported for GSH-stabilized Cu clusters. Different from the organic AIEgens, interactions between the metalcore and surface ligands of Cu NCs render them rather unusual as will be considered further on in this review. Compared with the well-dispersed Cu NCs, the PL QY of AIE Cu NCs can be significantly enhanced. In this section, we will summarize the influence of ligands on the PL characteristics of the AIE Cu NCs, approaches that are used to induce their controlled aggregation, and the suggested AIE mechanisms.

Influence of ligands

Most of the reported Cu NCs have been produced under stabilization and protection of organic ligands, which also allows us to control their composition and the core size.[48] Because of the ultra-small size of the Cu core in such clusters, ligands play a dominant role in determining their properties. A large variety of ligands with different chemical functional groups and polarity were applied to produce Cu NCs; the most common of them are listed in Figure 3. Most of these ligands are thiolates, owing to their strong binding ability with Cu.[46] We note that weakly bound ligands are rarely used for the stabilization of the AIE Cu NCs, which is eventually related to the insufficient protection of the Cu core from oxidative species.

In a pioneered system involving self-assembly induced emission enhancement of metal NCs, Wu et al. used 1-dodecanethiol (DT) as both the ligand and reducing agent to synthesize Cu NCs with a claimed composition of Cu$_{10}$Cu(I)$_{10}$DT$_{10}$.[52] While no emission could be detected for the well-dispersed Cu NCs, PL appeared upon aggregating them into the ribbons with twisted or bent structures, or nanosheets through thermal annealing, with a PL QY reaching 6.5%. DT has a long and soft carbon chain facilitating its long-range mobility, which allows for ease of modulation.
of the morphology and density of the resulting aggregates. Their emission color could be tuned from cyan to yellow by controlling the annealing temperature. However, the solubility of these nanostructures in aqueous solution was severely limited due to the hydrophobic nature of DT. Stimulus-response PL properties, commonly observed for AIEgens, were rarely reported for such alkyl thiol-stabilized Cu NCs due to the lack of functional groups on the carbon chains.

Later on, a variety of chemical functional groups such as -SH, -COOH, and -NH₂ were introduced onto the carbon chain of alkyl thiols used as ligands for Cu NCs. Ai et al. used hexanethiol (Figure 4A), hexanedithiol (Figure 4B), and mercapto-1-hexanol (Figure 4C) as ligands to synthesize Cu NCs-exhibiting AIE. Both the morphology of the resulting agglomerated clusters and their PL color could be tuned over to a rather broad spectral range from blue to red by altering those ligands as illustrated in Figure 4D. Alkyl thiols with shorter carbon chains and diverse functional groups, such as GSH, D-penicillamine, and L-cysteine, were also used as ligands for Cu NCs. These alkyl thiols are hydrophilic and provide functional sites for designing stimulus-response AIEgens for biological applications. In particular, GSH-bearing thiol, amino, and carboxyl groups have become the most frequently used ligand for Cu NCs experiencing AIE. GSH-capped Cu NCs are easily dispersible in aqueous solution, and based on the varying binding affinity of GSH with various molecules, such as glucose, trinitrotoluene, p-nitrophenol, and different metal ions sensors for these substances have been developed. Dutta et al reported L-cysteine-stabilized Cu NCs, with a claimed core structure of Cu₆, which presented a faint red emission in the dispersed state; changing the pH of the system from 3.0 to 7.4 led to their aggregation and appearance of intense green emission (Figure 5). This AIE-related effect was further used to probe the intracellular uptake of the clusters by MCF-7 cells and HEK-293 cell lines (Figure 5). Wang et al. reported GSH-capped Cu NCs with a strong orange emission in the powdered state, with a PL QY reaching 23%.

The presence of N-heterocycles on organic ligands of Cu NCs provides an effective way to tailor the morphology and AIE characteristics of their aggregates. Venkatesh et al. reported 2-mercaptopimidazole (MI)-stabilized Cu NCs, where the morphology and photophysical properties of aggregated clusters could be modulated by changing the substituents on the N-heterocycles. Aggregates of original MI-stabilized Cu NCs showed intense yellow emission peaked at 540 nm, while bluish-green (peaked at 480 nm) and a rather weak blue (peaked at 380 nm) emission was observed for aggregates obtained using ligands with a methyl group introduced on N₁ nitrogen atoms, or substituting both N₁ and N₃ nitrogen atoms of MI with methyl groups. AIE of MI-stabilized Cu NCs was used to monitor the pathways of cellular uptake of these clusters under confocal laser scanning microscopy.

Aromatic thiols with different substituents, such as halogen, -NH₂, -CH₃, -OCH₃, and boronic acid, were also used as ligands for Cu NCs experiencing AIE. The electronic structure of such aromatic thiols could be easily tuned through modulation of functional groups, which offered an
FIGURE 4  (A–C) Transmission electron microscopy (TEM) images of the aggregated Cu NCs stabilized by different thiol-containing ligands, shown in insets on the left. Insets on the right provide photographs of light-emitting NCs under excitation with UV light. (D) PL spectra of those aggregated Cu NCs stabilized by three different ligands, namely, hexanethiol, hexanedithiol, and mercapto-1-hexanol. Reproduced with permission.[53]

FIGURE 5  Synthetic pathway toward Cu NCs stabilized by L-cysteine and chitosan, which change their emission color from red to green upon changing pH (from 4.5 to 7.4), and experience AIE phenomenon upon aggregation in buffer and cell lines. Reproduced with permission.[59] Copyright © 2018, American Chemical Society
efficient way to change emission color and improve PL QY of Cu NCs. Wang group reported 2,3,5,6-tetrafluorothiophenol-stabilized Cu NCs, which showed PL QY as high as 43% in the aggregated state.\[59\] Zhang et al. studied optical properties of Cu NCs stabilized by aromatic thiols with different functional groups\[60\] and found out a redshift of their PL as a result of the presence of electron-rich groups on the aromatic ring. The electron-donating ability was later related to the degree of orbital hybridization between the Cu core and the ligands.\[61,62\] Aromatic rings of such ligands provided a rigid platform for reactions between their functional groups and external molecules, which endowed them with stimulus-responsive and recognition ability toward metal ions and biomolecules. As an example, Lei et al. synthesized \(p\)-mercaptophenylboronic (MBA) acid-stabilized Cu NCs, which could be linked together by D-glucose through forming cyclic boronate ester bonds with boronic acid (Figure 6).\[63\] This led to the aggregation of Cu NCs and the appearance of a strong red emission. Then, MBA-stabilized Cu NCs were modified with D-glucose 6-phosphate (P-Glu), forming the complex of P-Glu/CuNCs, which showed a rather weak emission. Introducing alkaline phosphatase into the system resulted in the cleavage of the phosphate group on P-Glu, which led to the activation of 5,6-diol unit. The activated P-Glu linked with MBA on the surface of Cu NCs to induce their aggregation and PL enhancement (Figure 6).\[63\] This stimuli-responsive AIE strategy was further used for in-situ localization of alkaline phosphatase activity in HepG2 cells and HCT116 cells. Notably, aromatic thiols contain a large number of \(\pi\) bonds, while \(\pi-\pi\) interactions are considered as a negative factor because they may contribute to PL quenching of the AIEgens. Thus, the chemical structure and functional groups on aromatic thiols need to be carefully designed, in order to achieve highly luminescent AIE Cu NCs.

**Approaches to induce aggregation of Cu NCs**

In order to induce a controlled aggregation of ligand-protected Cu NCs in colloidal solution (which is a prerequisite for AIE), a proper external stimulus is required. The existing strategies to trigger aggregation of NCs can be classified into those governed by electrostatic interactions, host-guest interactions, and template effects. The aggregation can also promote the stability of Cu NCs by diminishing the possibility of the diffusion of oxidative species towards the Cu core. We will discuss these approaches in the following section.

**Electrostatic interactions**

**Solvent-induced charge neutralization**

The solvent-induced charge neutralization involves destabilization of NCs dispersed in a high polar solvent by addition of a relatively weak polar solvent.\[64\] In this respect, Wang et al. studied GSH-stabilized Cu NCs synthesized by etching

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**FIGURE 6** Schematics of (A) glucose-linked, mercaptophenylboronic-stabilized Cu NCs, and (B) the AIE strategy for imaging the alkaline phosphatase activity in cells using these Cu NCs. Reproduced with permission.\[63\] Copyright © 2020, American Chemical Society
of bigger-sized Cu nanoparticles into ultra-small clusters.[50] These NCs were well dispersed in water (polarity: 10.2), where they showed very weak red emission. Upon introduction of ethanol (polarity: 4.3) or methanol (polarity: 6.6), the hydration shell on Cu NCs was disrupted, leading to the charge neutralization and aggregation of the clusters. Almost 15-fold enhancement of their PL QY was achieved, and the emission color changed to intense orange due to the AIE phenomenon.[50] Such solvent-induced charge neutralization can also be conveniently applied to process solution-based AIEgens into powders or films. Wang et al. applied ethanol treatment to GSH-capped Cu NCs, which improved their PL QY from 0.5% in the dispersed state to 43% in the powder form; they were subsequently used as phosphors to fabricate white light-emitting devices.[57] Thus, solvent-induced charge neutralization offers a straightforward and effective approach to induce aggregation of Cu NCs. We note that in order to achieve the maximum degree of aggregation, an overdose of a weak polar solvent is usually mixed with Cu NCs, which are dispersed in a small amount of highly polar solvent.[31,65] As a result of this procedure, the final concentration of cluster agglomerates is typically rather low, which may limit some of their applications.

**Cation-induced charge neutralization**

Cu NCs with charged functional groups at the surface show a behavior similar to multivalent ions. The presence of counterions in solution may lead to the neutralization of surface charge of Cu NCs, or even to the inter-cluster cross-linking, which would then trigger assembly and aggregation of clusters.[66] Lin et al. reported how the aggregation of GSH-stabilized Cu NCs with a PL QY of 1.3% was driven by electrostatic interactions between introduced Zn$^{2+}$ cations and GSH at the surface of the clusters, promoting their PL QY to 6.2%.[42] This allowed them to apply GSH-stabilized Cu NCs for Zn$^{2+}$ imaging in living cells.[42] Following this study, several other researchers reported aggregation of GSH-stabilized Cu NCs triggered by other cations, such as Al$^{3+}$, Pb$^{2+}$, Zr$^{4+}$, and Pb$^{2+}$.[67,68] You et al. have shown that the AIE performance of Cu NCs induced by the synergistic effect of Pb$^{2+}$ and Zr$^{4+}$ cations was superior to that triggered by Zr$^{4+}$ or Pb$^{2+}$ alone (Figure 7).[69] An obvious increase of the
PL intensity was observed after introducing Pb$^{2+}$ to the GSH-stabilized Cu NCs, and further promotion of intensity happened using the synergistic effect of Zr$^{4+}$ as schematically illustrated in Figure 7A and quantitatively presented by the corresponding PL spectra (Figure 7B). TEM images shown in Figure 7C–E also confirmed more effective aggregation of the Cu NCs in the presence of a mixture of Pb$^{2+}$ and Zr$^{4+}$ ions. Improved stability was also observed for Cu NCs aggregated with the use of mixed ions.

Apart from the inorganic cations, positively charged organic molecules were also used to induce the aggregation of Cu NCs. Wang et al. used a positively charged copolymer of Hyprimellose-grafted chitosan to neutralize the negative surface charge of Cu NCs, which led to the formation of spherical agglomerates. Highly luminescent films could be obtained from this composite material after evaporation of the solvent, with a high PL QY of 42%. Importantly, cation-induced charge neutralization can be conveniently conducted by adding appropriate cations into the original solution of Cu NCs without the need of diluting the samples or using the second solvent, which makes it possible to obtain AIEgens with a high concentration. Moreover, the cation-induced change of optical properties and the related AIE effects on Cu NCs can be used for monitoring positively charged species, such as metal ions, polypeptides, and amino acids in various environments. On the detrimental side, morphology, size, and density of agglomerates could hardly be controlled using this method because of the fast and rather nonselective nature of the interactions between Cu NCs and introduced cations.

Host–guest interactions

Host–guest interactions involve two components that can form a complex through non-covalent bonding; they are widely used in the assembly of polymers and nanoparticles into supermolecules or superstructures. The morphology of the resulting structures can be relatively well-controlled by designing the shape, binding sites, and chemical functional groups of host and guest. This approach can be used to induce AIE of Cu NCs and to better control the morphology of agglomerates. In addition, the interactions between host and guest could provide useful clues for designing chemical sensors. Huang et al. prepared mono-(6-mercapto-6-deoxy)-beta-cyclodextrin (SH-βCD)-stabilized Cu NCs, which showed typical AIE features such as increased PL intensity after dispersing into a mixed solvent with increasing volume fraction of methanol/water. Di(adamantan-1-yl) phosphine (Ad–Ad) was then used to form an inclusion complex with these Cu NCs, through the host–guest interactions between Ad-Ad and SH-βCD. As schematically illustrated in Figure 8A, well-dispersed and uniform spherical agglomerates with a size of about 65 nm (Figure 8D) were formed upon addition of Ad-Ad, whose PL QY reached 14.9%, much higher than of initial Cu NCs (2.6%), as shown in Figure 8C. The agglomerates were stable, owing to the encapsulation effect of Ad-Ad, and could thus be employed for long-term bioimaging of MUC1 protein in MCF-7 cells (Figure 8B). Qian et al. utilized the host–guest interactions to modulate the PL properties of penicillamine-stabilized Cu
Cu NCs were first forced to aggregate by adjusting the pH from 7.4 to 3.0, which resulted in bright red emission. P-nitrophenol was then absorbed on the surface of these aggregates, driven by the hydrophobic interactions, which switched off the PL signal through a static quenching mechanism. P-nitrophenol could then be removed by adding α-cyclodextrin, through the strong host–guest interaction between α-cyclodextrin and p-nitrophenol. This resulted in the recovery of PL signal of the aggregated Cu NCs, and the switch on/off of emission occurred in a reversible way, which was used to develop assays for the acid phosphatase.

Template confinement

Templates can provide a protective matrix for Cu NCs, which helps to prevent the access of oxidative species to the Cu cores and thus to improve their stability. A large variety of available templates is advantageous for the control of morphology, size, and density of Cu NC agglomerates. Polymers and proteins can be seen as soft templates, while hydroxy double salts and metal-organic frameworks—as hard templates; all of them have been used to modulate the AIE properties of Cu NCs as will be discussed below. Template confinement can effectively isolate the Cu NCs from oxidative species, which ensures the high stability of aggregates or assembly of Cu clusters.

Polymer-based films were often used as a soft template to confine Cu NCs and thus trigger their AIE. Liu et al. incorporated GSH-stabilized Cu NCs into the chiral nematic structure of cellulose nanocrystals (CNC), where polyethylene glycol (PEG) was also added to ensure flexibility of the resulting composite films (Figure 9). Cu NCs were entrapped within the lamellar structure of the CNC-based liquid crystal domains, and multiple hydrogen bonds were formed between the chemical groups on PEG, GSH, and cellulose. The resulting PEG-CNC-CuNC composite films had a strong orange emission with a PL QY of 16.1%. Our group reported several kinds of polymer films with confined Cu NCs, using polyurethane,[77] cross-linked polyvinyl alcohol and polyvinylpyrrolidone,[78] and hyromellose grafted chitosan.[79] In the latter study, chitosan was copolymerized with hyromellose, forming a negatively charged polyelectrolyte, which was subsequently mixed with Cu NCs to generate a hydrogel (Figure 10A). This hydrogel was poured onto a substrate followed by water evaporation in an oven, which resulted in the formation of transparent (Figure 10B) and at the same highly luminescent composite films with an orange emission (Figure 10C), whose PL QY reached as high as 42%; these films were used as a down-conversion layer for light-emitting devices.[70] Cu NCs formed spherical agglomerates of several tens of nm within these composite films (Figure 10D), which was used to develop assays for the acid phosphatase.[75]

![Figure 9](image_url)

**Figure 9** Schematic illustration of the fabrication of luminescent polyethylene glycol (PEG) cellulose nanocrystals (CNC) CuNC (PEG-CNC- CuNC) composite films (CNS stays for CNC). Reproduced with permission.[76] Copyright © 2021, Elsevier
FIGURE 10  (A) Schematic illustration showing fabrication of composite films of Cu NCs and Hypromellose-copolymerized chitosan. Photographs of these composite films were taken under daylight (B) and UV light (C). (D) TEM image of the aggregated Cu NCs, triggered by the charge neutralization. Reproduced with permission. Copyright © 2018, Wiley

FIGURE 11  Schematic illustration of the in-situ method to synthesize chitosan-templated Cu NCs, their optical spectra, as well as fluorescence quenching induced by lysozyme. Reproduced with permission. Copyright © 2020, Elsevier
Chemistry

AIE features of Cu NCs,\textsuperscript{[50]} in agreement with the classical view of AIE proposed by the Tang et al.\textsuperscript{[81,82]} Ligands that are anchored on individual well-dispersed Cu NCs can experience free movement, with a little restriction imposed on their molecular motions. In the aggregates of Cu NCs, those intramolecular motions are supposed to be restricted by the physical confinement,\textsuperscript{[46,83]} which reduces the probability of nonradiative recombination and activates radiative decay, leading to enhanced PL QY. This explanation is in line with the prolonged PL lifetime of aggregated Cu NCs. Alongside with the enhancement of the PL QY, spectral shifts of the PL maxima have also been observed for aggregated Cu NCs. Both blueshift and redshift were reported, which suggests the presence of different kinds of luminescent centers in the Cu NCs. There are two theories that are presently used to explain the PL shift, namely, inter-cluster interactions and metal defects. Very often, a PL shift to higher energy, mostly accompanied by emission color change from red to orange, has been reported for the GSH-stabilized Cu NCs.\textsuperscript{[42,50,57,76]} The reason for this blueshift is that the inter-cluster interactions become stronger through the formation of Cu(I)\textperiodcentered\textperiodcenteredCu(I) bonds after processing the Cu NCs into the aggregated state, which simultaneously leads to the weakening of the intra-cluster Cu(I)\textperiodcentered\textperiodcenteredCu(I) bonds. This leads to the PL shift toward higher energy as observed for the system of GSH-stabilized Cu NCs. At the same time, a redshift for the DT-stabilized Cu NCs has been observed after adding ethanol into the system.\textsuperscript{[53]} These observations could not be explained just by implying the theory of RIM related to the surface ligands.

One remarkable aspect in the area of luminescent metal NCs was emphasized by Wu et al., namely, the significant contribution of metal defects on the AIE-type Cu NCs.\textsuperscript{[43]} In their view, ethanol could coordinate with Cu atoms in the aggregated clusters, which results in the coexistence of several triplet states. The PL decay curves at the different detection wavelengths (from 500 to 600 nm) suggested that the PL lifetime increases with the increase of detection wavelength (Figure 13A). An obvious time lag when the detection wavelength comes to the range from 570 to 590 nm suggested the presence of parallel or equative states. To better reveal these triplet states, PL decays of aggregated Cu NCs for different delay times were recorded under an excitation wavelength of 365 nm (Figure 13B). An obvious peak could be observed at 490 nm, with a relatively short delay time of 1.3 μs, which shifted to 550 nm with the increase of delay time to 1.7 μs. Thus, two triplet states existed in the relaxation dynamics, located at 490 and 550 nm, which were denoted as $T_1$ and $T_2$ states, respectively. Figure 13C schematically illustrates recombination dynamics over these two states, where $T_1$ was ascribed to the LMMCT-determined triplet state, while the $T_2$ was ascribed to metal defects of the aggregated clusters. Series of control experiments and results of the natural bond orbital analysis confirmed that the metal defects in these clusters were mainly related to Cu(I).\textsuperscript{[43]} The existence of $T_2$ states influenced the emission color by providing a lower energy level for the charge transfer process. Cu NC aggregation created additional metal defects, which enhanced charge transfer to $T_2$ states and resulted in higher PL QY alongside the redshift of the PL maximum. The d$^{10}$ electronic structure of Cu(I) complexes endowed them with a strong PL, alongside a relatively long PL lifetime of several microseconds.

We note that the AIE phenomena were also reported for Cu(I) complexes, whose emission color typically lie in the orange-red region.\textsuperscript{[84,85]} For example, Xin et al. reported a series of binuclear mixed-ligand Cu(I) complexes such as Cu$_2$(BrphenBr)$_2$(P$_2$PH$_2$(CH$_2$)$_n$PPh$_2$)$_2$][ClO$_4$]$_2$, which showed strong PL peaked in the yellow region after processing into powders. In the above complex, BrphenBr stands for 3,8-dibromo-1,10-phenanthroline; P$_2$PH$_2$(CH$_2$)$_n$PPh$_2$ is a bridging diphophine ligand, and $n$ varies between 1, 4, 5, and 6. These complexes showed AIE in CH$_2$Cl$_2$/hexane mixed solvents, which was in line with the RIM-related mechanism.\textsuperscript{[86]} Zang et al. reported AIE from the Cu(I) complex made from dBuSCu as a Cu source (‘Bu is short for tertiary butyl) and 2,2-bis(diphenylphosphino)-1,1-binaphthyl as a ligand.\textsuperscript{[87]} As shown in Figure 14A, the motion of the phenyl groups of this ligand was restricted in the aggregated state, as well as in a

\textbf{FIGURE 12} (A) Schematic illustration of the fabrication of Zn-HDS templated Cu NCs. (B) Accumulation of electron-hole pairs within Cu NCs surrounded by “energy wells” of layered double hydroxide and Zn-HDS. Reproduced with permission.\textsuperscript{[80]} Copyright © 2020, Royal Society of Chemistry.

AIE mechanisms for Cu NCs

As outlined in multiple examples offered above, Cu NCs with an enhanced PL QY and improved stability can be aggregated with the purpose of achieving AIE; this has naturally motivated researchers to explore the origins of AIE mechanisms for Cu NCs. As early as 2013, Jia et al. made a statement that it is the RIM of ligands that should be responsible for the AIE features of Cu NCs,\textsuperscript{[50]} in agreement with the classical view of AIE proposed by the Tang et al.\textsuperscript{[81,82]} Ligands that are anchored on individual well-dispersed Cu NCs can experience free movement, with a little restriction imposed on their molecular motions. In the aggregates of Cu NCs, those intramolecular motions are supposed to be restricted by the physical confinement,\textsuperscript{[46,83]} which reduces the probability of nonradiative recombination and activates radiative decay, leading to enhanced PL QY. This explanation is in line with the prolonged PL lifetime of aggregated Cu NCs. Alongside with the enhancement of the PL QY, spectral shifts of the PL maxima have also been observed for aggregated Cu NCs. Both blueshift and redshift were reported, which suggests the presence of different kinds of luminescent centers in the Cu NCs. There are two theories that are presently used to explain the PL shift, namely, inter-cluster interactions and metal defects. Very often, a PL shift to higher energy, mostly accompanied by emission color change from red to orange, has been reported for the GSH-stabilized Cu NCs.\textsuperscript{[42,50,57,76]} The reason for this blueshift is that the inter-cluster interactions become stronger through the formation of Cu(I)\textperiodcentered\textperiodcenteredCu(I) bonds after processing the Cu NCs into the aggregated state, which simultaneously leads to the weakening of the intra-cluster Cu(I)\textperiodcentered\textperiodcenteredCu(I) bonds. This leads to the PL shift toward higher energy as observed for the system of GSH-stabilized Cu NCs. At the same time, a redshift for the DT-stabilized Cu NCs has been observed after adding ethanol into the system.\textsuperscript{[53]} These observations could not be explained just by implying the theory of RIM related to the surface ligands.

One remarkable aspect in the area of luminescent metal NCs was emphasized by Wu et al., namely, the significant contribution of metal defects on the AIE-type Cu NCs.\textsuperscript{[43]} In their view, ethanol could coordinate with Cu atoms in the aggregated clusters, which results in the coexistence of several triplet states. The PL decay curves at the different detection wavelengths (from 500 to 600 nm) suggested that the PL lifetime increases with the increase of detection wavelength (Figure 13A). An obvious time lag when the detection wavelength comes to the range from 570 to 590 nm suggested the presence of parallel or equative states. To better reveal these triplet states, PL decays of aggregated Cu NCs for different delay times were recorded under an excitation wavelength of 365 nm (Figure 13B). An obvious peak could be observed at 490 nm, with a relatively short delay time of 1.3 μs, which shifted to 550 nm with the increase of delay time to 1.7 μs. Thus, two triplet states existed in the relaxation dynamics, located at 490 and 550 nm, which were denoted as $T_1$ and $T_2$ states, respectively. Figure 13C schematically illustrates recombination dynamics over these two states, where $T_1$ was ascribed to the LMMCT-determined triplet state, while the $T_2$ was ascribed to metal defects of the aggregated clusters. Series of control experiments and results of the natural bond orbital analysis confirmed that the metal defects in these clusters were mainly related to Cu(I).\textsuperscript{[43]} The existence of $T_2$ states influenced the emission color by providing a lower energy level for the charge transfer process. Cu NC aggregation created additional metal defects, which enhanced charge transfer to $T_2$ states and resulted in higher PL QY alongside the redshift of the PL maximum. The d$^{10}$ electronic structure of Cu(I) complexes endowed them with a strong PL, alongside a relatively long PL lifetime of several microseconds.

We note that the AIE phenomena were also reported for Cu(I) complexes, whose emission color typically lie in the orange-red region.\textsuperscript{[84,85]} For example, Xin et al. reported a series of binuclear mixed-ligand Cu(I) complexes such as Cu$_2$(BrphenBr)$_2$(P$_2$PH$_2$(CH$_2$)$_n$PPh$_2$)$_2$][ClO$_4$]$_2$, which showed strong PL peaked in the yellow region after processing into powders. In the above complex, BrphenBr stands for 3,8-dibromo-1,10-phenanthroline; P$_2$PH$_2$(CH$_2$)$_n$PPh$_2$ is a bridging diphophine ligand, and $n$ varies between 1, 4, 5, and 6. These complexes showed AIE in CH$_2$Cl$_2$/hexane mixed solvents, which was in line with the RIM-related mechanism.\textsuperscript{[86]} Zang et al. reported AIE from the Cu(I) complex made from dBuSCu as a Cu source (‘Bu is short for tertiary butyl) and 2,2-bis(diphenylphosphino)-1,1-binaphthyl as a ligand.\textsuperscript{[87]} As shown in Figure 14A, the motion of the phenyl groups of this ligand was restricted in the aggregated state, as well as in a

\textbf{FIGURE 12} (A) Schematic illustration of the fabrication of Zn-HDS templated Cu NCs. (B) Accumulation of electron-hole pairs within Cu NCs surrounded by “energy wells” of layered double hydroxide and Zn-HDS. Reproduced with permission.\textsuperscript{[80]} Copyright © 2020, Royal Society of Chemistry.
Figure 13 (A) PL decays of aggregated Cu NCs at different detection wavelengths. (B) PL decays of aggregated Cu NCs for different delay times, recorded under excitation wavelength of 365 nm. (C) Schematic diagram showing S\textsubscript{1} and T\textsubscript{1} states and metal defect states, and the corresponding charge carrier relaxation dynamics of Cu NCs aggregated in the presence of ethanol. Reproduced with permission.\textsuperscript{[43]} Copyright © 2017, American Chemical Society

The complex showed no PL when it was dispersed in a mixed DMSO/water solvent with a water fraction (f\textsubscript{w}) lower than 40%, while the red emission appeared when the f\textsubscript{w} was higher than 50% (Figure 14B). A 17-fold PL enhancement has been observed after the change of solvent from DMSO to water, which was attributed to the RIM effect (Figure 14C).\textsuperscript{[87]}

These studies imply that the AIE of Cu NCs may be related to the presence of Cu(I) complex, which is associated with the Cu core. Emission of the AIE Cu NCs originates from the Cu(I) complexes, occurring through LMMCT. The LMMCT is usually observed in luminophores with relative narrow energy gaps, which results in their orange/red emission. This view was further confirmed by a recent study on bimetallic NCs, where the Cu(I) complex was aggregated on the Au(0) core.\textsuperscript{[88,89]} Zhu et al. proposed an ingenious strategy by producing core-shell-like Cu(I)@Au(0) clusters through in-situ selective reduction of Au(I) into Au(0) in the presence of Cu(I)-SC\textsubscript{10}H\textsubscript{15}.\textsuperscript{[88]} The movement of the Cu(I) complex was limited by its strong binding ability with a gold atom, resulting in the increase of the PL QY (Figure 14D). Jin et al. reported bright orange emissive Au@Cu\textsubscript{14} NCs, with a PL QY as high as 71%,\textsuperscript{[89]} which were composed from a single-Au-atom kernel and an exterior cage of [Cu\textsubscript{14}SR\textsubscript{12}(BCPP)\textsubscript{6}]. Each exterior cage was composed from an inner Cu\textsubscript{8} cube and an outer Cu\textsubscript{6} octahedron, which were linked together by thiolate ligands. Such a cross-linked structure could effectively limit the intramolecular motion and reduced the probability of nonradiative recombination pathways.\textsuperscript{[89]} Thus, we conclude that the AIE effect in Cu NCs can also be attributed to the presence of Cu(I) complex attached to the Cu(0) metalcore. RIM effect of this Cu(I) complex in an aggregated state restricts its intramolecular motion and reduces the probability of nonradiative path, resulting in the enhancement of the PL QY.

Conclusions and Outlook

Luminescent Cu NCs attracted a lot of attention due to the earth-abundant nature of Cu, ease of their synthesis, large Stokes shift, and long PL lifetime. These NCs often exhibited the AIE phenomenon in their aggregated state, which significantly improved their PL QY. Typically, the PL QY of GSH-stabilized Cu NCs could be improved from less than 0.5% to higher than 40%,\textsuperscript{[57]} and a PL QY of as high as 71.3% was achieved by aggregation Cu(I) complex onto the Au atom core.\textsuperscript{[89]} Several approaches such as the solvent and cation-induced charge neutralization, host-guest interactions, and template confinement have been used to modulate the
aggregation and PL properties of Cu NCs, which also helped to improve the stability of those clusters. The AIE effects on Cu NCs severely boosted their potential applications in the fields of chemical sensing, bioimaging, and even light-emitting devices.

Despite the impressive progress already achieved in the field of Cu NCs as AIEgens, there are still several challenges that remain to be addressed. PL QY of reported AIE Cu clusters, in general, is often lower than that of other competing luminescent materials, such as organic dyes, semiconductor quantum dots, and other kinds of reported AIEgens. While RIM of ligands of Cu NCs or associated Cu(I) complexes were widely considered to be the origin of their AIE, the molecular motion of ligands in those clusters might still remain active in the aggregated states. Confining Cu NCs in soft or hard templates may further help to inhibit this molecular motion to a larger extent, thus further improving their PL QY. At the same time, further strategies should be developed to better control the aggregation of Cu NCs in solution, in order to achieve higher PL QYs.

Various organic ligands have already been used to synthesize and stabilize Cu NCs, with various kinds of functional chemical groups, such as -SH, -COOH, -NH₂, and N-heterocycles. However, in most of the present studies, the choice of ligands is still mostly limited to thiolates due to their ability to form a strong bond with Cu. Selecting some other suitable ligands may enrich our ability to further modulate PL properties of Cu NCs. An in-depth understanding of
the exact structure of Cu NCs would also allow us to pursue their purposeful design and synthesize Cu NCs with attractive AIE properties.

AIE mechanisms of Cu NCs have been mostly considered within the framework of the classical theory of ligands’ RIM, while more recently possible contributions of metal defects and Cu(I) complexes have also been put forward. There is still a lack of a general theory that would be able to explain the relationship between the PL properties of Cu NCs before and after aggregation. Elucidation of the structure of the dispersed Cu NCs and their aggregated counterparts is critical for the development of such a theory. When all the above-mentioned pieces of knowledge will come together, it would allow us to offer better-designed synthetic approaches toward highly luminescent Cu NCs. Cu NCs with AIE properties could then find a wider acceptance for applications in several fields, particularly for chemical sensing and bioimaging.

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CONFLICT OF INTEREST
The authors declare no conflict of interest.

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