Aggregation and luminescence in carbonized polymer dots

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Abstract
The aggregate luminescence behavior of organic luminescent materials has been studied extensively. As a new kind of luminescent nanomaterials, carbonized polymer dots (CPDs) not only inherit the stability and biocompatibility of carbon materials, but also possess the luminescence tunability, water solubility, and high photoluminescence quantum yield of organic luminescent materials, rendering them a strong candidate for the next generation of light-emitting materials. Previously, people mainly understood its luminescence from the perspective of carbon materials, but some luminescence mechanisms are still unclear. In this review, we discuss the luminescence mechanism by referring to organic luminescent materials with emphasis on their aggregation behavior. Firstly, three representative aggregate luminescence phenomena of organic luminescent materials are briefly introduced. Chromophores present in CPDs are elaborated to further discuss the potential interactions between them, with emphasis on the role of crosslinked polymer networks. On this basis, some special luminescence phenomena of CPDs in the aggregate state are summarized, and relevant mechanisms are discussed in detail to consolidate relevant statements.

KEYWORDS
aggregation-induced emission, carbon dots, carbonized polymer dots, crosslink-enhanced emission effect, luminescence

1 | INTRODUCTION

Organic luminescent materials that emit bright emission in their aggregate state have drawn considerable attention.[1–3] Traditionally, organic dyes with polycyclic aromatic hydrocarbons (PAHs) have been considered to be ideal luminescent materials, due to their good luminescence efficiency and high adjustability. Their luminescence wavelength can cover the whole range from the ultraviolet region to the near infrared region.[4] However, their large aromatic ring structure makes them extremely prone to π–π stacking to quench the luminescence, and it thus turns aggregation a detrimental thing.

Aggregation-induced emission (AIE) is an interesting luminescent phenomenon and also an effective strategy to modulate luminescence by tactfully utilizing aggregation.[1] In 2001, the concept of AIE was coined by Tang’s group during the investigation of the luminescence behavior of rotor-rich methylpentaphenylsilole.[5] In the past 20 years, AIE research has made great advances in many high-tech applications, such as biological imaging, environmental monitoring, optoelectronic devices, medical diagnosis and treatment, chemical sensing, and intelligent stimulus response.[1,2,6,7]

These achievements help researchers in various fields to try explain many other unknown luminescence phenomena from the perspective of aggregates.[3] These attempts have been largely successful and many other innovative mechanisms have been proposed to illustrate different phenomena, such as clusterization triggered emission (CTE), through-space interaction (TSI), and so on.[4,8]

Carbon dots (CDs) are typically defined as small carbon nanoparticles with size less than 10 nm. As a new type of luminescent nanomaterial, CDs have shown many excellent properties since their inception, such as water solubility, biocompatibility, tunable photoluminescence (PL), high thermal/photostability, low cost, high photoluminescence quantum yield (PLQY), environment-friendliness, and so on.[9–15] The simple synthesis methods have also attracted great attention.[11,16,17] However, while considering the diversity of CDs, the abundant precursors and varieties of synthesis methods available increase the difficulty to clarify the precise chemical structure and luminescence mechanism.
In accordance with different understandings of the structure and luminescence mechanism, researchers gradually formed three different perspective to comprehend CDs.\[^\text{18}\]\ The first point is to understand CDs from the perspective of quantum dots, which are regarded as a kind of semiconductor and believed that their luminescence comes from the quantum confinement effect and surface defects.\[^\text{19-22}\]\ The second approach is to understand CDs from the perspective of graphene, regarding CDs as nanoscale graphene fragments that emit through edge state (armchair and zigzag edges) and intrinsic state (graphene core).\[^\text{19,23-26}\]\ The third way is to understand the emission of CDs from the perspective of organic luminescence of crosslinked polymer, and it is believed that the emission of CDs is from the chromophores (conjugated \(\pi\)-domain, molecular fluorophore, and sub-lumiphore) inside the particle and strengthened by the crosslink-enhanced emission (CEE) effect of a highly crosslinked polymer network.\[^\text{9,10,18,27}\]\ However, due to the diversity of CDs, different synthesis paths would endow CDs with completely different characteristics. Therefore, CDs can be divided into carbon quantum dots (CQDs), graphene quantum dots (GQDs), and carbonized polymer dots (CPDs) according to the distinct structures and properties.

Obtained by polymerization, crosslinking, and carbonization of small molecules, polymers, or biomass via “bottom-up” methods, CPDs possess the characteristics of both carbon materials and organic luminescent materials with carbonized and crosslinked polymer hybrid nanostructures.\[^\text{28}\]\ However, due to the complex reaction process and the lack of appropriate characterization methods, there are still many controversies about the exact structure and luminescence mechanism of CPDs. In the past, more efforts have been made to understand CPDs from the perspective of carbon nanomaterials, and many progresses have been achieved.\[^\text{11,18,20,29}\]\ In this review, we attempt to evaluate the luminescence of CPDs from the perspective of the aggregate behavior of organic luminophores, or more specifically, nanoparticles of carbonized crosslinked polymer.\[^\text{30,31}\]\ Firstly, relevant discussions on aggregation and luminescence of organic luminescent materials will be overviewed, including aggregation caused quenching (ACQ), AIE, and CTE. Chromophores (conjugated \(\pi\)-domain, molecular fluorophore, and sub-lumiphore) inside the CPDs and the importance of the role of CEE will be studied in detail. Furthermore, some interesting phenomena existing in the aggregate state of CPDs will be summarized. Finally, future challenges and outlooks regarding CPDs are proposed. This review may provide a new perspective to understand the luminescence mechanism of CPDs from aggregates.

## 2 | AGGREGATION AND LUMINESCENCE OF ORGANIC LUMINESCENT MATERIALS

In this section, previous studies on the aggregate luminescence of organic luminescent materials will be reviewed to provide more insight into the luminescence mechanism of CPDs. Related contents including ACQ, AIE, and CTE will be mentioned. These contents have been summarized extensively elsewhere,\[^\text{1-3,6,7}\]\ so we will only provide a brief introduction to enlighten and inspire researchers more about the luminescence of CPDs.

### 2.1 | Aggregation-caused quenching

ACQ describes the phenomenon wherein luminophores can emit light efficiently in dilute solution, but be reduced or even disappear entirely in concentrated solution or solid state (Figure 1A).\[^\text{3,7}\]\ Most CPDs would also experience the same phenomenon, which considerably hinders their relevant applications. For example, using l-glutamic acid and \(\alpha\)-phenylenediamine as precursors, Xiong et al. prepared a series of CPDs with high PLQY across the entire visible spectrum and narrowed emission peak widths (Figure 1B).\[^\text{32}\]\ In solution they have good luminescence, but in solid state, they suffer from ACQ. There exists a unified description regarding the ACQ of small organic luminescent molecules with a planar aromatic ring. When these small organic luminescent molecules get closer, their large planar polycyclic aromatic structures prompt them to stack in an oriented way due to their intense intermolecular \(\pi-\pi\) stacking interactions. Such stacking will cause the excited state to return to the ground state in a nonradiative transition, generating luminescence quenching. It can allow us to reasonably infer that the chromophores inside the CPDs may possess the similar planar aromatic ring structure.

ACQ is an obstructive effect that needs to be resolved. In the past, researchers usually introduced steric hindrance or designed molecular conformation to prevent such aggregation. For example, bulky cyclics, spiral kinks, and dendritic wedges are covalently linked to aromatic cores to weaken the intermolecular \(\pi-\pi\) stacking interactions.\[^\text{13,34}\]\ These methods are instructive to realize solid emission in CPDs.\[^\text{22,35-37}\]\ Through chemically grafting polyhedral oligomeric silesquioxane (POSS), poly(ethylene glycol) (PEG), and hexadecylamine (HDA) at the edge sites of bare CPDs by carbodiimide coupling, Jeon et al. proposed surface functionalized CPDs to reduce ACQ (Figure 1C).\[^\text{35}\]\ Introducing a large number of long alkyl chains on the surface, Shen et al. prepared white-emitting CPDs via one-step carbonization of polyoxyethylene sorbitan monoooleate (Figure 1D).\[^\text{37}\]\ Through elaborately designing precursors and synthesis processes, Zeng et al.\[^\text{12}\]\ and Fan et al.\[^\text{36}\]\ sequentially achieved the fabrication of carbon nanorings that can effectively avoid ACQ.

### 2.2 | Aggregation-induced emission

Unlike ACQ luminophores, AIE luminogens (AIEgens) usually do not emit obviously in dilute solutions, but emit intensely in their aggregate states (Figure 1A).\[^\text{5}\]\ Basically, this is realized by designing molecular structures to get propeller-like or shell-like luminophores, such as hexaphenylsilole (HPS) and tetr phenylethene (TPE) or 10,10',11,11'-tetrahydro-5,5'-bidibenzo[a,d]7 annulenyldiene (THBA) (Figure 2A).\[^\text{38,39}\]\ For HPS and TPE, they would have high nonradiative decay rates in the solution state due to the rotor vibration. But in the aggregate state, aggregation limits intramolecular rotation and suppresses nonradiative transitions. Moreover, the highly twisted structure weakens the intermolecular \(\pi-\pi\) stacking interactions and avoids the formation of tightly packed structures, thus exhibiting strong fluorescence emissions. For THBA, it does not have any rotating components, but instead consists of two noncoplanar parts, each of which
has two phenyl rings connected to a flexible heptatomic ring. Thus, in the solution state, the phenyl rings can easily bend or vibrate to dissipate the excited states in a nonradiative transition. In the aggregate state, the intramolecular vibrations would be restricted due to the limitation of space, which would render THBA emissive in the aggregate state.

In the research on CPDs, people also discovered similar AIE phenomena.\(^{40-42}\) Hu et al. designed a kind of hydrophobic CPDs from melamine and dithiosalicylic acid/acetic acid through the solvothermal method (Figure 2B).\(^{41}\) They confirmed that the CPDs contain two potential luminescence centers, conjugated \(\pi\)-domains in the carbon core, and a fluorophore containing S–S bond on the surface. In the dispersed state, the surface fluorophores containing S–S bond do not have fluorescence emission due to intramolecular rotation of the S–S bond, and the emission of conjugated \(\pi\)-domains in the carbon core is dominated by blue light emission. But when the CPDs aggregate, the conjugated \(\pi\)-domains undergo \(\pi\)–\(\pi\) stacking due to their large conjugate structure with the spacing decreasing, quenching the blue light. And the surface fluorophore containing the S–S bond is limited by the aggregation of the CPDs, resulting in the emission in the red light, which is similar to AIE. Recently, by using molecular amines with different nitrogen numbers and dithiosalicylic acid as precursors, they prepared...
AIE–CPDs with different emission colors (Figure 2C). In the dispersed state, the AIE–CPDs all possessed the same blue emission from conjugated \( \pi \)-domains in the carbon core that will suffer from ACQ in the aggregate state. But in the solid state, the authors confirmed that the aggregation of surface fluorophores newly generated two luminescence centers, one for red emission corresponding to the structure containing C = O/C = N and the other for green emission corresponding to the structure containing the S–S bond. With the increase of nitrogen content in the precursor, the electron-withdrawing functional groups (C = N) make the intramolecular charge transfer from S–S to C = O/C = N increase gradually. The intensity of green emission decreases gradually, while the intensity of red emission increases gradually, resulting in different luminescence colors.

2.3 | Clusterization-triggered emission

Some organic materials with completely nonconjugated structures would also exhibit bright luminescence in their aggregate state. This phenomenon shows a lot of similarities to the luminescence origin of CPDs, in that many CPDs also have no obvious conjugated structure, but are with bright luminescence. Therefore, it may be helpful to elaborate this phenomenon.

Nonconjugated polyacrylonitrile (PAN) molecules could be a typical example to illustrate this phenomenon (Figure 3A). For the PAN molecule, it had almost no traditional chromophores, only some appended cyanos on the polymer chains (Figure 3B). Therefore, in dilute PAN/N, N-dimethylformamide (DMF) solutions, almost no luminescence could be observed. It was reasonable in that in dilute solution, appended cyanos in polymer chains were almost isolated without long conjugation to emit visible light. Meanwhile, the active intramolecular movement would dissipate the excited state energy, thus making the dilute solutions nonemissive. An exception phenomenon was that when the concentration of PAN increased, luminescence appeared and gradually became much brighter (Figure 3C). Researchers explained that when PAN molecules were in the aggregate state, the overlap of \( \pi \) and lone pair (n) of electrons from the cyano groups would promote the formation of cyano clusters with extended electronic conjugation and simultaneously rigidified conformations, thus generating noticeable emission. Moreover, dipole–dipole interactions and n–\( \pi \) interactions would also play a significant role (Figure 3D). The mentioned description is highly similar to our idea about
sub-luminophores in CPDs, which will be described in the next section. This is another powerful piece of evidence to rationally infer that sub-luminophores or such clusters are responsible for some luminescence behaviors in CPDs.

In the past few years, researchers have identified a large number of similar unconventional luminophores that do not possess any classic chromophores but show obvious luminescence in the aggregate state, such as starch, cellulose, poly(amidoamine) (PAMAM) dendrimers, hyperplasmas, poly[(maleic anhydride)-alt-(vinyl acetate)] (PMV), and so on. These luminophores usually possess electron-rich heteratomic functional groups, such as tertiary amine, C=C, C=N, C=O, OH, ether, and imide. Researchers classified the phenomenon as CTE and named the chromophores responsible for it as clusteroluminogens (Figure 3E). An explanation for these clusteroluminescences was presented as through space conjugation (TSC), which refers to n-σ*, n-π*, π-π* orbital overlap, hydrogen bonding, and other weak interactions induced by these clusteroluminogens (Figure 3E). The presence of TSC can induce the formation of clusters with extended delocalization to generate a narrow band gap and rigidify molecular conformations to restrict vibrations and rotations, thus rendering these materials with unconventional luminescence. The earlier-mentioned mechanistic description inspired us to compare it with the CEE effect, which was a similar mechanism to illustrate the luminescence origin of CPDs (Figure 3F). They all emphasized the creation of new luminescence centers and the limitation of vibration and rotation. However, considering the extensive presence of covalently crosslinked polymer networks and noncovalent interactions, CEE could be a more suitable interpretation for the luminescence of CPDs which will be described later.

Furthermore, these clusteroluminescences exhibit many characteristics similar to CPDs. For example, their excitation spectrum may red shift relative to absorption spectrum; in
other words, the light of the exciting molecule is not in the range of the strong absorption peak. And they usually possess excitation-dependent luminescence, that is, emission red shift with increasing excitation wavelength. Moreover, with the increase of the size of cluster, the clusteroluminescence gradually red-shifts.\[4]\n
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Based on the earlier discussion about the luminescence behaviors of organic aggregates, many similar characteristics in the luminescence of CPDs can be identified. Therefore, it is necessary to analyze the structure of the CPDs and the internal chromophores in detail to provide a clear luminescence mechanism.

3.1 | Structural characteristics

In general, CPDs are considered to be a kind of CDs, undergoing the process of polymerization and incomplete carbonization by “bottom-up” methods, such as hydrothermal method, solvothermal method, microwave assisted method, and so on.\[55\]

In terms of structure, CPDs possess a core-shell structure with highly crosslinked and slightly carbonized hydrophobic core inside and hydrophilic polymer chains outside (Figure 4A). The precursors are usually multifunctional small molecules, polymers, or biomass rich in amino, hydroxyl, and carboxyl groups. At the initial stage of the reaction, the intense intermolecular collision caused by high temperature results in dehydration condensation between functional groups (Figure 4B).\[18\] Polymerization occurs between the precursors to form polymer chains. High temperature and high pressure cause the precursors to undergo intense thermal motion and open more reaction channels. Due to the disordered nature of the reaction and the multifunctional properties of the precursors, a certain degree of crosslinking also occurs in this process, resulting in entanglement between the polymer chains to form numerous crosslinked polymer clusters. Due to the shortening of space distance, further crosslinking occurs in the clusters, which make the structure more compact and stable. With the further dehydration reaction, the internal hydrophobicity gradually increases, and the water molecules are accelerated to discharge, which further accelerates the dehydration reaction, thus forming a hydrophobic core inside. Continuous collision with the precursors in aqueous solution results in hydrophilic polymer chains outside. With the prolongation of reaction time, the degree of carbonization of the core increases gradually and the micro-crystals and lattice appear in the interior of CPDs. As for the experimental observations, Xiong et al. used TEM to explore the formation mechanism of the CPDs through time-dependent experiments (Figure 4C).\[32\] The products with reaction time of 1, 2, 4, and 7 h were observed. As can be seen from TEM images, the precursors form an amorphous crosslinked polymer at the initial stage, and then gradually aggregate and nucleate, and finally carbonize to form CPDs.

Prato et al. systematically investigated the formation process of CPDs and its core–shell structure through a series of spectroscopic approaches (Figure 4D).\[55\] Using arginine and ethylenediamine (EDA) as precursors, they produced nitrogen-doped CPDs through microwave-assisted hydrothermal method and investigated reaction products ranging from 15 to 240 s. They tracked the structural characteristics during the synthesis using small- and wide-angle X-ray scattering (SAXS and WAXS, respectively), which were commonly used to characterize both crystalline and amorphous systems at the nanoscale. By analyzing the data of SAXS, the sticky hard-sphere interaction distance (hard-contact diameter) was found to be 1.8–2.4 nm, which is approximately 1 nm larger than the observed mean nanoparticle size (Figure 4D). This observation indicated the core–shell structure of CPDs for that the nanoparticle diameter derived from form-factor scattering relates to an electron-dense core of the CPDs, whereas the hard-contact diameter includes surface polymer chains that are transparent to X-rays (no scattering contrast due to solvent penetration).

A large number of retained amino, carboxyl, and hydroxyl groups, as well as newly formed amide bonds and carbonyl groups bring CPDs with plentiful sub-luminoophores inside. The existence of a highly crosslinked network structure, on the one hand, makes these sub-luminoophores contact closely with each other and serve as possible luminescence centers. On the other hand, crosslinking can restrict the vibration and rotation of the luminescence centers and reduce the nonradiative transition to enhance the luminescence.\[44,56\] In addition, intramolecular cyclization may occur in precursor molecules to produce luminescent organic molecule segments. These small molecule segments can be directly attached to the formed crosslinked polymer clusters as independent luminescent units or participate in subsequent crosslinking and carbonization reactions as new construction units. These dispersed \(sp^2\) conjugated domains generated during carbonization can serve as new luminescence centers. They are also likely to be the source of the lattice observed under transmission electron microscope.

Polymer characteristics endow CPDs with many excellent properties.\[57\] First of all, abundant amino, carboxyl, and hydroxyl groups on the surface make CPDs possess better water solubility and biocompatibility than organic dyes and inorganic quantum dots, thus rendering CPDs as potential replacement in the field of biology.\[57\] In addition, abundant functional groups endow CPDs with highly reactive sites that are easily functionalized. This good modifiability makes CPDs have a broad application prospect in many fields. For example, by combining with functional compounds, drug tracers, optical temperature sensing, and biological imaging can be realized.\[58-60\] In addition, the crosslinking points generated by the carbonization process would lead to closer aggregation between the internal chromophores, which can make CPDs have better stability.

3.2 | Chromophore

Although there was no unified understanding of the luminescence structure of CPDs, the extensive efforts of researchers have provided us with many inspirations.\[61-63\] From the perspective of organic luminescence, several chromophores can
be discovered in CPDs, including PAHs formed by carbonization, small molecular fluorophore segments derived from the reaction of the precursors and carbonyl groups, amide bonds, and other sub-luminophores on crosslinked polymer clusters.

3.2.1 Conjugated \( \pi \)-domain

Initially, numerous reports in literature pointed out that CDs have a quantum confinement effect.\(^{64,65}\) That is, the emission wavelength is longer as the size of particles increases, and this class of CDs was classified as CQDs. However, after systematically exploring multiple systems and summarizing a large amount of literature, many researchers declared that their CDs obtained by bottom-up methods did not show obvious and reliable quantum confinement effect, but exhibited classic polymeric characteristics.\(^{9,57,66–72}\) Even though some CDs would possess size-dependent luminescence, it was dominated by the size of the internal conjugated \( \pi \)-domain, rather than the quantum
confinement effect of the particle size. The conjugated π-domains just refer to these large sp² domains generated by incomplete carbonization of crosslinked polymer clusters.

The existence of conjugated π-domain was verified by theoretical simulation and calculation. Feldmann et al. developed a model system comprising only three PAH molecules, namely, anthracene, pyrene, and perylene, which were embedded in a polymer matrix, to simulate the luminescence behavior of conjugated π-domain (Figure 5A). By tuning the concentrations of the individual molecules, most of the luminescence properties of CPDs, such as large Stokes shifts and excitation-dependent emission could be reproduced, demonstrating conjugated π-domain was the main source of luminescence in the system. By DFT calculations, Jeon et al. confirmed that the energetically favorable formation of subdomains composed of four to seven carbon hexagons with lower formation energies (1.64–1.65 eV) was the intrinsic PL origin (Figure 5B).

Meanwhile, people gradually regulated the luminescence by controlling the size of the conjugated π-domains. Qu et al. proposed that DMF as solvent was a good strategy to form large-sized conjugated sp²-domain. Orange emissive CPDs with high PLQY were prepared via a solvothermal route from citric acid (CA) and urea using DMF as solvent. Subsequently, based on the idea that solvent can regulate the size of the conjugated sp²-domain, Qu et al. realized full-color emissive CPDs from CA and urea, employing three different solvents (water, glycerol, and DMF) (Figure 5C). Recently, by expending effective conjugated domains, Zhou et al. realized full-color CPDs with emission peaks of 435 nm, 495 nm (PLQY of 88.9%), 525 nm, and 595 nm (full width at half-maximum of 31 nm) (Figure 5D).

However, the characterization of conjugated π-domains was not very clear, due to the interference of the external polymer chain wrapping on the surface of CPDs. Therefore, greater attempts have been made to confirm its structure through theoretical methods. For example, based on both the experimental and theoretical results, Jamshidi et al. proposed that fullerene fragment structures might also be formed in CPDs under high temperature dehydration, except for nitrogen-doped aromatic ring structures (Figure 5E).
### Table 1 Molecular fluorophore in CPDs

| Starting materials                | Synthetic method       | Chemical structure of molecular fluorophore | $\lambda_{em, max}$ of molecular fluorophore | $\lambda_{em, max}$ of CPDs | PLQY of molecular fluorophore | Ref. |
|----------------------------------|------------------------|---------------------------------------------|---------------------------------------------|-----------------------------|-------------------------------|------|
| Citric acid, ethylenediamine     | Hydrothermal           | ![Chemical structure](image1)                | 443 nm                                     | 443 nm                      | 86%                           | [84] |
| Citric acid, L-cysteine          | Hydrothermal           | ![Chemical structure](image2)                | 418 nm                                     | 418 nm                      | 76%                           | [85] |
| Citric acid, hexamethylenetetramine | Hydrothermal          | ![Chemical structure](image3)                | 440 nm                                     | 415 nm                      | 32%                           | [86] |
| Citric acid, diethylenetriamine  | Hydrothermal           | ![Chemical structure](image4)                | 433 nm                                     | 434 nm                      | 98%                           | [130]|
| Citric acid, urea                | Microwave-assisted pyrolysis | ![Chemical structure](image5)              | 540 nm                                     | 540 nm                      | 15%                           | [87] |
| O-phenylenediamine               | Hydrothermal           | ![Chemical structure](image6)                | 605 nm                                     | 650 nm                      | 9%                            | [88] |

### 3.2.2 Molecular fluorophore

Molecular fluorophore is a small molecule intermediate formed during the dehydration condensation of precursor molecules.\[^{63,82}\] They are usually attached to the surface or embedded in the carbon core as relatively independent luminescent centers (Table 1).\[^{57}\]

Initially, Giannelis et al. investigated the formation mechanism of carbogenic nanoparticles by pyrolysis of CA and ethanolamine at different temperatures.\[^{83}\] They deduced that high PLQY was due to the forming of molecular fluorophores by dehydration of CA and ethanolamine. Moreover, they supposed that the carbogenic core started forming at higher temperatures at the expense of the molecular fluorophores with the decrease of PLQY. After that, Yang’s group verified the existence of the molecular fluorophore in CPDs for the first time.\[^{84}\] They reported the formation of a molecular fluorophore 5-oxo-1,2,3,5-tetrahydroimidazo[1,2-α]pyridine-7-carboxylic acid (IPCA) in the hydrothermal synthesis with CA and EDA as precursor. The structure of the molecular fluorophore IPCA was determined by using nuclear magnetic resonance (NMR) and mass spectrometry after carefully separating and purifying the reaction products by column chromatography.

Since then, more and more similar molecular fluorophores have been discovered in CA based CPDs (Table 1). Via systematic analyses, Zhang et al. attributed the organic fluorophores 5-oxo-3,5-dihydro-2H-thiazolo[3,2-a]pyridine-3,7-dicarboxylic acid (TPDCA) and 5-oxo-3,5-dihydro-2H-thiazolo[3,2-a] pyridine-7-carboxylic acid (TPCA) as the main ingredients and fluorescence origins of the N,S-CPDs from CA and L-cysteine.\[^{85}\] Rogach et al. studied three CPDs produced by hydrothermal reactions of CA with three different amine precursors: EDA, hexamethylenetetramine, and triethanolamine and further emphasized the effect of molecular fluorophore on the luminescence of CPDs.\[^{86}\] Identically, Kasprzyk et al. revealed 4-hydroxy-1H-pyrrolo[3,4-c]pyridine-1,3,6(2H,5H)-trione (HPPT) as the molecular origin of the luminescence of CPDs prepared from CA and urea.\[^{87}\]

Similar molecular fluorophores were also found in CPDs using another well-known precursor, O-phenylenediamine. Recently, Nandi et al. revealed the presence of molecular fluorophore, quinonaxino[2,3-b]phenazine-2,3-diamine.
(QXPDA) in red emissive CPDs synthesized from o-
phenylenediamine by performing systematic purification and
characterization.\textsuperscript{[88]} Although only few articles explicitly reported the existence of
molecular fluorescent species (Table 1), it can be pre-
picted that similar fluorescent molecular species may exist
in many CPDs.\textsuperscript{[63,82]} They may not be complete molecules,
but a part of the crosslinked polymer networks that was
difficult to isolate and verify, which play the same role.\textsuperscript{[69]}
It was generally believed that CPDs containing molecular
fluorophores may exhibit the following characteristics: high
PLQY; low photo-stability; excitation-independent lumines-
cence; absorption peaks with Gaussian characteristics in
UV–vis absorption spectra, and the inverted shape between
PL emission spectra and PL excitation spectra. Meanwhile,
although most-reported CPDs experienced high temperature
and long reaction time to achieve carbonization, molecular
fluorophore can still be retained and notably influence the
optical properties of the resulting products.\textsuperscript{[86]}

The molecular fluorophore and most conjugated \(\pi\)-domain
have planar aromatic ring structures like those of organic
dyes. But differently, the molecular fluorophore was pro-
duced by dehydration and cyclization of the precursors, usu-
ally possessing five-membered ring or six-membered ring
structure, while the conjugated \(\pi\)-domain was the PAHs pro-
duced by carbonization under high temperature and high
pressure. With the increase of the size of PAHs , the emission
wavelength gradually red-shifted. Furthermore, it is common
sense to assume that luminescence quenching can occur in
such nano-aggregates as CPDs due to \(\pi–\pi\) stacking between
such chromophores. However, due to the effective barrier of
the crosslinked polymer network, it still shows good lumine-
scence performance. Furthermore, considering the com-
mon phenomenon of intramolecular charge transfer in the
fluorescence process of dye molecules, there may also exist
various potential interactions between these chromophores
inside the CPDs, resulting in a variety of inexplicable lumine-
scence phenomena, such as excitation-dependent lumines-
cence and wide half-peak width. Besides, utilizing charge
transfer between chromophores, the control of the lumines-
cence can be realized. Through a series of comparative exper-
iments, Hu et al. verified that the increase of the nitrogen
content in CPDs can induce intramolecular charge transfer
between S–S-based symmetrical fluorescent molecules and
C–N-based conjugated structures. Based on the principle,
tunable AIE multicolor CDs were prepared.\textsuperscript{[40]}

3.2.3 Sub-luminophore

The concept of sub-luminophore was first proposed in the
summary of nonconjugated polymer dots in 2015 (Figure 6A).\textsuperscript{[89]} Initially, people discovered a class of CPDs that
did not have any typical chromophores but showed obvious
luminescence emission. For example, through a moderate
hydrothermal treatment of nonconjugated poly-
poly(vinyl alcohol), Yang et al. prepared CPDs with blue
fluorescence.\textsuperscript{[90]} Normally, it was not realistic to obtain flu-
orescent materials only from such simple polymers without
photoluminescent centers. Therefore, researchers proposed
that some chemical groups such as heteroatom-containing
double bonds (C = O, C = N, N = O) and single bonds
(amino-based groups, C–O) can be potential PL groups as
sub-luminophores.\textsuperscript{[89]} Due to the lack of effective long
conjugate structures, these sub-luminophores usually emit in the
ultraviolet region. However, in the structure of the crosslinked
polymer network, the energy level structure of these sub-
luminophores can be changed, causing the luminescence to
red shift to the visible light region. Meanwhile, nonradia-
tive transition is suppressed, resulting in the phenomenon of
enhanced emission. For example, amide-like structures have
been confirmed to be a kind of sub-luminophores in CPDs.
Yang et al. achieved metal-free room temperature phospho-
rescence (RTP) in CPDs from polyacrylic acid and EDA
through hydrothermal treatment and confirmed amide/imide
structures as the origin of luminescence.\textsuperscript{[71]} Moreover, simi-
lar amide structures have also been shown to be the origin of
luminescence in polyacrylamide systems obtained by addi-
tion polymerization.\textsuperscript{[72]}

3.3 Crosslink-enhanced emission effect

The crosslink-enhanced emission (CEE) effect was originally
proposed in conjunction with sub-luminophores to explain
the strong emission of nonconjugated polymer dots only with
sub-luminophores. Its basic function includes immobilization
and generation of new energy levels.\textsuperscript{[144,91]} Effective immo-
bilization can greatly suppress the vibration and rotation of
chromophores, inhibit nonradiative transitions, and enhance
luminescence emission. The tight fixation also prevents chro-
morphores in the CEE not only exists in
polymer and secondary, and tertiary amines as sub-luminophores
(Figure 6B).\textsuperscript{[56]} Different synthetic methods were used to
immobilize the PEI chains to decrease the vibration and rota-
tion of these sub-luminophores, including carbon tetra-
chlo-
rside crosslinking with branched PEI, the hydrothermal of PEI,
connecting the PEI on the surface of the amorphous CDs, and
connecting the PEI on the surface of the CQDs. Femtosecond
transient absorption (TA) spectroscopy confirmed that all the
samples possess obvious transient signals with the same PL
centers, while bare PEI molecules have no obvious transient
signals, which implied that the enhanced PL originated from
the decreased vibration and rotation of crosslinking. Maser
et al. investigated hydrogen bond-mediated supramolecular
interaction CEE in CPDs (Figure 6C).\textsuperscript{[92]} They synthesized
blue fluorescent model CPDs from CA and EDA as well as
from tricarballylic acid and EDA by microwave irradiation
and from CA and EDA by a novel coupling-agent-mediated
condensation at room temperature. Detailed structural char-
acterizations revealed that the presence of hydrogen bond and
electrostatic interactions resulted in the high conformational
rigidity of the polymeric chains, which hindered vibration
and rotation and facilitated the radiative relaxation process.

Many phenomena indicate that CEE not only exists in
CPDs, but widely exists in various polymer systems, which
has been discussed by our research group recently (Figure
6D).\textsuperscript{[144]} The CEE effect can be divided into covalent
CEE and noncovalent CEE (supramolecular interaction CEE,
ionic-bonding CEE, and confined domain CEE). Covalent-bond CEE is a stable and powerful bonding interaction formed by condensation of carboxyl, hydroxyl, and amine groups of multifunctional precursors. It can not only form a covalent crosslinked network to fix the chromophores, but also generate new luminescent structures due to the formation of new chemical bonds. Noncovalent bond interactions are more extensive, including supramolecular interaction CEE, ionic-bonding CEE, and confined domain CEE. Hydrogen, van der Waals interactions, and \(\pi-\pi\) stacking can all be classified as supramolecular interaction CEE, which is widely present in CPDs. Due to the dynamic and reversibility of such interactions, it is a good tool for realizing responsive luminescence properties of CPDs. Ionic-bonding CEE builds ionic crosslinking network by the electrostatic interaction of opposite charges. Confined domain CEE refers to a deeper orbital interaction that exists inside the CPDs.

4 | SPECIAL PHENOMENA OF LUMINESCENCE ORIGINATED FROM AGGREGATION OF CPDs

In the last section, we simply established the luminescence model of CPDs from the perspective of organic luminescent materials. When the aggregation of particles occurs, the interaction between chromophores will also cause many special phenomena of the luminescence. Therefore, we hope to further consolidate our theory based on the discussion of the luminescence mechanism of these special phenomena originated from aggregation of CPDs.

4.1 | Aggregation-induced fluorescence

4.1.1 | Concentration-dependent fluorescence

Generally, due to the reabsorption effect and quenching effect at high concentration, the luminescence intensity of CPDs decreases with increasing the concentration to a high level, which is similar to most of organic luminescent materials. However, many researchers have caught a special phenomenon named concentration-dependent fluorescence occurring in some CPDs [93–100]. That is, except for the decrease of luminescence intensity, the emission wavelength will also red-shift with the increase of the concentration. To a large extent, concentration-dependent fluorescence is a reflection of AIE in CPDs. The luminescence changes gradually with the occurrence of aggregation.

It was initially thought that the red shift of emission wavelength was due to the decrease of particle distance, which implied that CPDs were still uniformly dispersed,
but with closer distance. Nanda et al. synthesized boron-doped CPDs with concentration-dependent fluorescence by the hydrothermal reaction of boric acid and sucrose, and the luminescence can be regulated from blue to red by adjusting the concentration.\cite{99} They believed that at higher concentration, the decrease of the interparticle distance could enhance the interactions between the particles resulting in the red-shift. Wang et al. had similar observations.\cite{101} They obtained nitrogen-doped CPDs by microwave pyrolysis of CA and ammonium hydroxide. Simply by increasing the concentration of nitrogen-doped CPDs in aqueous solution, the emission peaks could be tuned from blue to red region.

Regarding the decrease of particle distance as an explanation was indistinct and insufficient. More experimental phenomena showed that with the increase of concentration, the aggregation of particles has taken place, and the emergence of aggregates led to the red shift of luminescence. An intuitive and common phenomenon was that the apparent color of solution became darker as the concentration increased, which implied the formation of large aggregates.\cite{94,101} Moreover, Peng et al. illustrated the formation of aggregates by performing dynamic light scattering (DLS) measurements.\cite{106} The average particle sizes of three different CPDs samples with concentration of 0.22, 0.71, and 2.26 OD were found to be 145, 305, and 740 nm, and the corresponding emission wavelengths were 434, 483, and 525 nm, respectively. Zheng et al. confirmed the appearance of aggregates resulting in luminescence red-shift by synthesizing Zr–CPDs with no concentration-dependent emission.\cite{102}

Furthermore, the reason why aggregation can lead to the red-shift of luminescence was still not clear. Researchers have come up with many theories. For example, Shao et al. proposed that resonance energy transfer between multiple luminescence centers lead to concentration-dependent fluorescence (Figure 7A).\cite{68} Using maleic acid and EDA as precursors, they prepared CPDs exhibiting yellow, green, and blue fluorescence in different concentrations through a microwave-assisted method and attributed the extra-large red-shift to three luminescence centers existing in CPDs. State I was originated from sub-luminophores existing on the surface, possessing blue luminescence in dilute solution and quenching in concentrated solution. State II (the green emission band gap) and State III (the yellow emission one) were derived from close sub-luminophores with the protection of the polymer network, exhibiting resonance energy transfer between them and dominating the luminescence sequentially as the concentration increases.

But more researchers accepted that aggregation increased the conjugation degree of surface luminophores, resulting in the decrease of band gap. Hence, the usual phenomenon was that the emission wavelength was gradually red shifted, but rarely blue shifted with increasing the concentration. Peng et al. obtained phosphorus-doped CPDs that own aggregation-caused red-shift of emission, which can be tuned in the range from 455 to 595 nm by changing the solution concentration.\cite{106} They believed that after aggregation, the particle sizes increased, which may cause the extension of electron system. The extension of electron system, similar to the increase in π–π conjugation, will result in the red shift of emission wavelength. Using CA monohydrate and ammonium hydroxide as precursors, Liu et al. synthesized CPDs that own concentration-dependent PL emission accompanied by self-assembly behavior in solution (Figure 7B).\cite{93} Based on the characterization results, they proposed that with the concentration of CPDs rising in solution, π–π stacking interaction was restrained while electron redistribution was induced. Consequently, a localized state caused by electron rearrangement gradually became the predominant emission state, resulting in the PL emission shifting to long-wavelength region. Recently, Lu et al. offered more concrete evidence.\cite{103} They synthesized CPDs with concentration-dependent fluorescence using CA and ethanolamine as precursors and DMSO as solvent (Figure 7C). Through theoretical calculations, they confirmed that the molecular fluorophore located on the surface of CPDs resulted in the concentration-dependent fluorescence. As shown in Figure 7D, with the concentration increasing, the fluorophore monomer formed dimers and trimers through hydrophobic interactions and π–π stacking. The emission wavelength of the radiative transition from \( S_1 \) to \( S_0 \) significantly red-shifted to 460.6 and 469.6 nm for the dimer and trimer, respectively. According to the earlier discussion, a clear picture can be depicted (Figure 7E). As the concentration increases, the particles gradually aggregate into larger particles. The molecular fluorophores and sub-luminophores on the surface of the CPDs will interact with each other and the conjugation degree will increase, resulting in a longer emission wavelength.

In the last few years, concentration-dependent CPDs have drawn considerable interest for their excellent capacity to obtain multicolor luminescence by simply adjusting the concentration of the solution. This excellent performance has great application values in many fields, especially identification of microorganisms.\cite{105,106} It is also an efficient way to obtain CPDs with long wavelength emission. Therefore, it is very valuable to summarize the related progress and elucidate the luminescence mechanism in this review.

4.1.2 Quench-resistant solid-state fluorescence

Ordinarily, CPDs face the challenge of fluorescence quenching in solid state,\cite{105–107} since the main chromophores (conjugated π-domain and molecular fluorophore) inside are planar aromatic ring structures. The distance between them is reduced in such a highly aggregated state. Hence, they are easy to influence each other through π–π stacking interactions or resonance energy transfer, resulting in fluorescence quenching. For example, from the hydrothermal of CA and EDA, our group prepared highly fluorescent CPDs with molecular fluorophore IPCA.\cite{58} They can emit intense blue fluorescence in solution, but show no fluorescence under solid state due to strong π–π stacking interaction between IPCA. Based on this principle, Zboril et al. realized the reversible detection of the water–ice phase transition using the same CPDs. In the liquid aqueous environment, molecular fluorophore IPCA attributed to the bright PL. But in the solid phase (ice), its emission was severely quenched, so that phase transition can be monitored.\cite{108}

Similarly, in the conjugated π-domain produced from carbonization, there also exists severe quenching in the solid state due to their polycyclic aromatic structure. Accordingly, controlling the degree of carbonization can achieve solid luminescence.\cite{109} Through precisely manipulating the microwave reaction conditions, Zhou et al.
prepared solid-state luminescent CPDs with light carbonization and solid-state nonluminescent CPDs with excessive carbonization from identical precursors (CA and urea). By designing molecular fluorophores and avoiding carbonization, Kim et al. achieved the same fluorescence performance in solid-state as that in solution state (Figure 8A). They used CA and diethylenetriamine through a hydrothermal reaction at 70°C for 48 h to synthesize CPDs. With CA and diethylenetriamine as the precursor, molecular fluorophore 1-(2-aminoethyl)-5-oxo-1,2,3,5-tetrahydroimidazo[1,2-a]-pyridine-7-carboxylic acid (AEIOP) (Table 1) can be produced. Suspended amino and carboxyl groups of AEIOP made it well fixed on the crosslinked polymer network. The low temperature avoided carbonization, so that the CPDs retained many polymer characteristics, which prevent the π–π stacking of molecular fluorophore in the solid state. Thus, it can disperse uniformly in the crosslinked polymer network and emit normally in the solid state. Moreover, synthesizing from high temperature carbonization, RCPDs showed red-shifted emission and decreased fluorescence intensity in the solid state, very similar to those solid emissive CPDs with concentration-dependent fluorescence. The excessive carbonization driving the crosslinked polymer network tighter and reducing polymer chains rendered molecular fluorophores tend to π–π stacking and quench the blue light. But some aggregates of molecular fluorophores showed increased conjugation, resulting in red shift of fluorescence. Consequently, regulating molecular structure and carbonization degree can be an effective strategy to realize quench-resistant solid-state fluorescence of CPDs. And more significantly, the presence of crosslinked polymer network is imperative to protect chromophores from fluorescence quenching.

Many solid-state luminescent CPDs show obvious concentration-dependent fluorescence in solution state. They usually have remarkable red-shift wavelengths in solid state relative to that in solution state. As discussed in the previous section, such solid-state luminescence is usually due to the increased conjugation degree of surface fluorophore while aggregation, thus realizing long wavelength emission in solid state. Yang et al. prepared quench-resistant solid-state fluorescent CPDs from maleic
Quench-resistant solid-state fluorescence in CPDs. (A) Schematic illustration of the synthetic method and mechanism for solid-state luminescence with the emission color consistency compared to carbon dots with multiple emissive states. Reproduced with permission. [111] Copyright 2019, Wiley-VCH. (B) The formation process of CPDs with quench-resistant solid-state fluorescence induced by polymer-like structure. Reproduced with permission. [69] Copyright 2017, Wiley-VCH. (C) TEM image and schematic diagram of PVA-chain induced quench-resistant solid-state fluorescence and the schematic of construction of dual-fluorescence morphologies emitting white light in organic solvents or matrices. Reproduced with permission. [114] Copyright 2015, Wiley-VCH.

Acid and EDA (Figure 8B). [69] The prepared CPDs show concentration controlled emission with emissions at 460, 510, 575 nm at concentrations of 0.8, 6.5, and 16.5 mg mL$^{-1}$, respectively. In the solid state, the wavelength red-shifts to 625 nm. Liu et al. synthesized nitrogen-doped CPDs by one-pot hydrothermal treatment of poly(vinyl alcohol) and EDA (Figure 8C). [114] The produced CPDs exhibited strong yellow-green fluorescence in aggregate state as well as blue fluorescence in water and solid matrices. The fluorescence of solution also showed concentration-dependent fluorescence, which can change from blue to yellow-green followed by the increase of the solute concentration, and approach that of the powder when the concentration was up to 30 mg · mL$^{-1}$. Moreover, as the polarity of the solvent increased, the yellow-green fluorescence turned white and then blue. Because the emergence of yellow-green aggregates lead to white-light emission together with blue CPDs in the dispersed state.

4.2 Aggregation-induced room temperature phosphorescence

Another interesting phenomenon, RTP, can also be observed when some kind of CPDs aggregate. [71,115–125] Generally, phosphorescence is more difficult to achieve than fluorescence because it usually undergoes triplet exciton transitions with spin-forbidden nature. [126,127] The long lifetime of triplet exciton is easy to be dissipated by nonradiative decay process at room temperature. [119] To achieve RTP, effective intersystem crossing (ISC) and suppression of non-radiative transitions are required. Thus, RTP of CPDs is usually achieved in their aggregate state which can strongly fix luminophores and facilitate the radiative relaxation. Moreover, new triplet states can be generated by aggregation which can induce the emergence of RTP. Via hydrothermal treatment of trimellitic acid, Lin et al. prepared a kind of TA-CPDs exhibiting unique white prompt and yellow RTP emissions in solid state (Figure 9A). [128] The yellow RTP emission was verified to be resulted from the formation of a new excited triplet state due to the aggregation of TA-CPDs through comparing the low temperature (77 K) afterglow spectra of TA-CPDs in dispersion state and solid state. They deduced that the aggregates of large conjugated structures contributed to the formation of another triplet excited state which produced the aggregation-induced RTP.

Sub-luminophore and crosslinked polymer networks play a key role in the realization of RTP of CPDs. [129] Abundant sub-luminophores such as C=O and C = N provide sufficient energy levels contributing to the generation of triplet states and ISC. Crosslinked polymer networks can effectively protect luminophores from ambient air and inhibit non-radiative transitions. Liu et al. hydrothermally synthesized
self-quenching-resistant nitrogen-doped CPDs powder using PVA and EDA as carbon and nitrogen sources, respectively.\textsuperscript{115} They reported PVA chains can not only suppress nonradiation by obstructing the moisture, but also act as oxygen-barriers to prevent the triplet excitons from being quenched by triplet oxygen. Yang et al. indicated that the covalent crosslinking occurring in the interior of CPDs can restrict their vibration and rotation, thus providing favorable conditions for effective ISC (Figure 9B).\textsuperscript{71} Through selecting small molecules, EDA, and linear polymers polyacrylic acid as precursors, they prepared CPDs with abundant amides and imides as sub-luminophores and a covalently crosslinked framework as inhibitor, they thus achieved long-lifetime RTP. Moreover, through hydrothermal addition polymerization with acrylamide as monomer, they prepared ultrahigh-yield acrylamide-based N-doped CPDs with ultralong RTP lifetime (Figure 9C).\textsuperscript{72,129} By changing the carbonization degree, the RTP lifetimes of CPDs can be regulated in the range of 61.4–466.5 ms, while the RTP emission wavelengths can be regulated from 485 to 558 nm. Carbonization will change the degree of crosslinking and make the sub-luminophores form aggregates to increase the degree of conjugation, thus resulting in the luminescence red shift. Similarly, inspired by the concept of CEE, Lin et al. converted certain structured CPDs from fluorescence to RTP emission through further carbonization by heating to achieve a more compact structure (Figure 9D).\textsuperscript{117} Choosing EDA and phosphoric acid as starting materials, they prepared fluorescence CPDs (F-CPDs) exhibiting blue emission with PLQY of 5.17% in water but with no phosphorescence. After further heating treatment of the F-CPDs powder at a higher temperature (280°C for 2 h), an ultralong RTP phenomenon could be observed.

5 | SUMMARY AND PERSPECTIVE

As a new kind of luminescent nanomaterial, CPDs have been studied a lot in the past few years. Its structure is considered to be a core-shell structure with a highly crosslinked and slightly carbonized hydrophobic core inside and hydrophilic polymer chains outside. With respect to its luminescence, there still exist some mysteries. In this review, we carefully distinguish the different types of
luminescence centers present in CPDs, including conjugated \(\pi\)-domain, molecular fluorophore, and sub-lumophore. By comparing with organic luminescent aggregates, the interactions between different luminescence centers are mentioned, especially emphasizing the importance of the highly crosslinked polymer network. On this basis, we summarized some special luminescence behavior of CPDs in the aggregate state, including concentration-dependent fluorescence, quench-resistant solid-state fluorescence, and aggregation-induced RTP.

Regarding the luminescence origin of CPDs, although great progress has been made, some critical issues remain to be resolved. For the presence of luminescent centers, direct evidence from experimental characterization analysis and theoretical calculations or indirect evidence through ingenious experimental design are required. As for the conjugated \(\pi\)-domain, although it is a recognized existence, it still needs direct observation through experiments. Also the relationship between its structure and luminescence and their potential interactions need to be further studied. For molecular fluorophores, we need to know more precisely about its distribution, whether they are evenly distributed in the particle or just connected to the surface of the particle. The concept of sub-lumophore remains vague, but experimental verification will be a meaningful work that could help explain many confusing luminescence phenomena of CPDs, including excitation-dependent luminescence, excitation spectral red-shift, and so on. Furthermore, given the diversity of CPDs, an in-depth understanding of luminescence origin requires the combination of lucubrating the individual representative example and systematically analyzing and comparing different systems to conclude the universal luminescence mechanism.

With respect to the aggregation of CPDs, relevant research could be instructive with both theoretical significance and practical value. On the one hand, the aggregate luminescence behaviors of CPDs can provide researchers with different perspectives to explore the luminescence centers. On the other hand, CPDs usually exist in the form of aggregates in practical applications, which exhibit many different properties from that in the dispersed state. For example, some CPDs emit phosphorescence when they are aggregated, but only fluorescence when they are dispersed, which can be applied in the field of anticounterfeiting; some quench-resistant solid-state fluorescence CPDs can be applied in the field of organic light-emitting diodes without the need of the assistance of matrix. The reason why some CPDs can exhibit aggregation-induced luminescence still needs a clear structure description and mechanism analysis. If the mechanism can be well explained, CPDs with quench-resistant solid-state fluorescence and multicolor luminescence, or even RTP, could be easily prepared for use in organic light-emitting diodes, anticounterfeiting, identification of microorganisms, and so on.

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CONFLICT OF INTEREST
The authors declare no conflict of interest.

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