Toward phosphorescent and delayed fluorescent carbon quantum dots for next-generation electroluminescent displays

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Featuring a combination of size-tunable emission wavelengths, high thermal stability, and low cytotoxicity, carbon quantum dots (CQDs) have opened up a new possibility for next-generation displays. However, the theoretically highest external quantum efficiency (EQE) limit of electroluminescent light-emitting diodes (LEDs) based on fluorescent CQDs is 5% due to the spin-forbidden nature of triplet state transitions. Comparatively, phosphorescent or delayed fluorescence CQDs are expected to overcome this limitation and allow the EQE of the devices to reach nearly 25%. At present, the preparation of CQDs with good solution processability, narrow bandwidth emission, and full-color phosphorescence or delayed fluorescence still faces great challenges. Herein, this review aims to offer a materials-chemistry perspective to tailor highly efficient phosphorescent or delayed fluorescence CQDs and present their applications in electroluminescent LEDs for the display technology. The mechanism and design principle of pure organic phosphorescence and delayed fluorescence as well as their recent advances in electroluminescent devices are summarized. Furthermore, we focus on the prospects and challenges for phosphorescent and delayed fluorescence CQDs in displays. We hope that this review will further stimulate the development of high-performance CQD-based electroluminescent displays with a combined effort from different disciplines.

1. Introduction

The world has entered the modern information age with abundant content. Display instruments have become the most important information carrier in daily life and are used in diverse media, including televisions, mobile phones, and other panels. Over the past decades, display technology based on electroluminescent light emitting diodes (LEDs), where electric current is used to directly excite emitters and generate photons leading to potentially higher efficiency in contrast to phosphor-converted LEDs (Fig. 1a and b), has advanced by leaps and bounds toward wide color gamut, high brightness, and long lifetimes.1–4 Generally, electroluminescent display technologies can be divided into two categories based on the types of emissions.
luminescent materials, i.e., organic LEDs (OLEDs) and quantum dot LEDs (QLEDs). OLEDs have demonstrated practical applications in flat panel displays for smartphones and televisions after three decades of development.\textsuperscript{5–8} So far, however, most OLED products have been fabricated by a vacuum deposition technology that requires high running cost, complicated device structures, and control preciseness, which greatly hinders their further large-area manufacturability.\textsuperscript{9–12} In contrast, QLEDs feature solution processability, bright photoluminescence, and narrow bandwidths, making them promising candidates for the fabrication of large-area displays and lightening devices through cost-effective ink-jet printing techniques.\textsuperscript{13–16} Giants in the display industry (e.g., Samsung, LG, TCL and BOE) worked together with start-up companies in the QD field (e.g., Nanjing Tech, QD Vision and Nanosys) to produce the so-called QLED television. However, the severe toxic and detrimental effects on humans and the environment are still crucial impediments to the use of Cd\textsuperscript{2+}/Pb\textsuperscript{2+}-based QDs as next-generation displays.\textsuperscript{17–19} Thus, it is of great significance to develop an ideal alternative.

Quantum-confined carbon quantum dots (CQDs), which represent a class of zero-dimensional (0D) carbon nanoparticles with sizes below 10 nm, exhibit superior properties to conventional semiconductor QDs, such as environment-friendliness, high stability, and low cost.\textsuperscript{20–30} Furthermore, CQDs show tunable bandgaps owing to their quantum confinement effect and high photoluminescence quantum yield (PLQY).\textsuperscript{31–36} The emission color of CQDs can be tuned by controlling their size and structure,\textsuperscript{37–39} providing access to solution-processable emitters covering ultraviolet, visible and near-infrared wavelength regions (Fig. 1c and d). Immense efforts have been made to develop CQD-based LEDs with intrinsic bandgap emission from deep-blue to near-infrared in the last few years.\textsuperscript{25,31,40,41} In particular, unprecedented narrow bandwidth emission was recorded for high color-purity multicolored LEDs,\textsuperscript{41} which opens up great prospects of CQDs for the next-generation display technology. It is well known that exciton formation under electrical excitation typically results in 25% singlet excitons and 75% triplet excitons. Unfortunately, 75% of the electrically generated energy is dissipated as heat by triplet excitons in fluorescent CQDs, leading to the theoretically highest external quantum efficiency (EQE) of 5% after considering a light outcoupling efficiency of \( \sim 20\% \) in the device. Therefore, to increase the efficiency of CQD-based electroluminescent devices,

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flourished for several years since the pioneering work by dispersing CQDs into a polyvinyl alcohol matrix in 2013.63 Then, CQDs with intrinsic RTP properties without the need for additional matrix compositing have also been demonstrated, indicating their potential for ISC and thus showing a new possibility for achieving CQD-based RTP optoelectronic applications.64–66

This review primarily aims to provide an illustrative account on recent progress of the mechanism and design of pure organic RTP and TADF emitters as well as their recent advances in electroluminescence to realize next-generation displays. The basic theories and fundamental properties of RTP and TADF of organic materials have been well described in a number of comprehensive reviews.8,67–74 Herein, we particularly focus on the current challenges and future prospects for RTP and TADF CQDs in displays. Finally, we hope that this review will further stimulate the development of high-performance CQD-based electroluminescent displays with a combined effort from different disciplines.

2. Mechanism of pure organic RTP and TADF

2.1 Basic concepts of pure organic RTP and TADF

As compared to inorganic luminescence, light emission from organic counterparts is much more complicated due to their rich and highly flexible excited state structures, resulting in diverse luminescent phenomena, such as fluorescence, phosphorescence, TADF, etc., which depends on the multiple spin state during the radiative relaxation process. Fluorescence refers to the emission of light between energy states of the same spin multiplicity (from singlet excited states S1 to ground states S0) within nanoseconds, while phosphorescence is the emission of light between states with different spin multiplicities (from triplet excited states T1 to S0) with lifetimes in the microsecond to second regime. In addition, when T1 and S1 are close in energy, the singlet–triplet energy splitting (ΔE_{ST}) is small, and the endothermic RISC process can be overcome by the thermal motions of the molecular atoms. As a result, the nonradiative triplet excitons, due to a spin-forbidden T1 → S0 transition, are transformed to singlet excitons via RISC, leading to TADF emission (S1 → S0) with lifetimes in the range of hundreds of nanoseconds to dozens of milliseconds (Fig. 2).

In general, EQE is one of the most essential parameters for evaluating the performance of electroluminescent LEDs, which is defined as the ratio of the number of emitted photons outside the device to the number of charges injected into the device. However, only the radiative transition process of singlet excitons from S1 to S0 can be utilized for emitting light, i.e., fluorescence, which is quantum-mechanically allowed. Therefore, in organic fluorescent materials, the electrically generated 75% triplet excitons are emitted as heat rather than light. Even if the PLQY of conventional fluorescent molecules can reach nearly 100%, in theory, the EQE maximum (EQE_{max}) value may only reach roughly 5% due to the light out-coupling efficiency of ~20%
in the electroluminescence device. In contrast, the phosphorescent and TADF emitter capable of harvesting light from both triplet and singlet excitons allow a great break-through of the exciton statistical limit in fluorescent counterparts from 25% to 100% (Fig. 2), which is critically required for the enhanced efficiency. For instance, the theoretical EQE_{max} of the TADF devices can be estimated using eqn (1):

\[
\text{EQE} = \eta_{\text{int}}\eta_{\text{out}} = \gamma \eta g \eta_{\text{PL}} \eta_{\text{out}} \\
\quad = \sum_{k=0}^{\infty} \left( 0.75 \phi_{\text{PF}} \phi_{\text{RISC}} (\phi_{\text{ISC}} \phi_{\text{RISC}})^k + 0.25 \phi_{\text{PF}} (\phi_{\text{ISC}} \phi_{\text{RISC}}) \right) \eta_{\text{out}} \\
\quad = \gamma \left[ 0.25 \phi_{\text{PF}} + 0.75 + 0.25(1 - \phi_{\text{PF}}) \frac{\phi_{\text{DF}}}{1 - \phi_{\text{PF}}} \right] \eta_{\text{out}} \\
\quad = \gamma \left[ 0.25 \phi_{\text{PF}} + \phi_{\text{DF}} + 0.75 \frac{\phi_{\text{DF}}}{1 - \phi_{\text{PF}}} \right] \eta_{\text{out}} \\
\quad = \gamma \left[ 0.25 \eta_{\text{PL}} + 0.75 \frac{\phi_{\text{DF}}}{1 - (\eta_{\text{PL}} - \phi_{\text{DF}})} \right] \eta_{\text{out}} 
\]

where \(\eta_{\text{int}}\) is the IQE; \(\eta_{\text{out}}\) is the outcoupling constant; \(\gamma\) is the charge balance of injected holes and electrons (ideally \(\gamma = 1\)); \(\eta g\) is the excitation–production singlet-to-triplet ratio; \(\eta_{\text{PL}}\) is the photoluminescence efficiency; \(\phi_{\text{PF}}\) is the photoluminescence quantum yield of the prompt component; and \(\phi_{\text{DF}}\) is the photoluminescence quantum yield of the delayed component. If \(\phi_{\text{PF}} + \phi_{\text{DF}} = \eta_{\text{PL}} = 1\), then the IQE can be 100% according to eqn (1). In addition, it should be noted that a high degree of orientation of the transition dipole moment of emitters will effectively increase the \(\eta_{\text{out}}\), leading to a high EQE of the device.\(^8\)

### 2.2 Factors affecting pure organic RTP

Notably, high quantum efficiencies and short lifetimes (dozens of microseconds) are a prerequisite to realize efficient RTP or TADF emitters for high-performance electroluminescent devices. Promoting ISC to generate triplet excitons and suppress its nonradiative decay is key to achieving enhanced phosphorescence emission. Specifically, according to the first-order perturbation theory and Marcus semiclassical approach in the room-temperature region, the rate constant \(k_{\text{ISC}}\) of ISC can be expressed using eqn (2):\(^73\)

\[
k_{\text{ISC}} = \frac{2\pi}{\hbar} (S|\hat{H}_{\text{SOC}}|T)^2 \sqrt{\frac{\pi}{2k_B T}} \exp \left[ -\frac{(\Delta E_{\text{ST}} - \lambda)^2}{4k_B T} \right] 
\]

where \(\langle S|\hat{H}_{\text{SOC}}|T \rangle\) is the SOC matrix element between \(S_s\) and \(T_s\), \(\hbar\) is the reduced Planck constant, \(\lambda\) is the total reorganization energy, \(k_B\) is the Boltzmann constant, and \(\Delta E_{\text{ST}}\) is the energy gap between the singlet and triplet states. This expression indicates that a large SOC and a small \(\Delta E_{\text{ST}}\) will lead to a high \(k_{\text{ISC}}\). Heavy atoms such as Br and I can enhance SOC to increase \(k_{\text{ISC}}\). For example, it is found that directed halogen bonding in a co-crystal can activate efficient ISC to realize materials with bright RTP and quantum yields of up to 55%.\(^19\) Furthermore, SOC between \(S_s\) and \(T_s\) is favored when they have different electronic configurations such as \(1n\pi^*\) and \(1n\pi^*\) or \(1\pi\pi^*\) and \(1\pi\pi^*\), respectively, according to El-Sayed’s rule (Fig. 3).\(^51\)\(^67\)\(^68\) and hence the proportions of hybrid \((n, \pi^*)\) and \((\pi, \pi^*)\) configurations can be tuned to facilitate a strong SOC for promoting the ISC.\(^52\)

Consequently, incorporating a carbonyl group or heteroatoms (N, S, and P) with lone pair electrons into organic emitters can generate an \(n\pi^*\) transition to enhance SOC. For example, Chi and coworkers proposed that the intermolecular electronic coupling of \(n\) and \(\pi\) units in a crystal can promote ISC to achieve persistent RTP with a lifetime of 0.49 s.\(^51\) An excited state with hybrid configurations of \(\pi\pi^*\) and \(n\pi^*\) in appreciable proportions is desired to achieve a balanced lifetime (up to 0.23 s) and efficiency (up to 36.0%).\(^69\) According to

Fig. 2 Electroluminescence processes in phosphorescent and TADF materials. The transition process of electrically generated excitons for fluorescence (0), phosphorescence (2→3) and TADF (0→3). \(\dagger\): fluorescence, \(\ddagger\): intersystem crossing (ISC), \(\ddagger\ddagger\): phosphorescence, \(\ddagger\ddagger\ddagger\): reversible intersystem crossing (RISC).

Fig. 3 Schematic illustration of El-Sayed’s rule for ISC and its utilization for controlling the phosphorescence decay rate based on the molecular-orbital hybridization of the lowest triplet states. Reprinted with permission from ref. 69. Copyright 2016 Cell Press.
eqn (1), an alternative way to considerably strengthen ISC is to reduce $\Delta E_{ST}$, which has been applied successfully in designing TADF emitters. A design principle based on the realization of small $\Delta E_{ST}$ via structural isomerism was used to obtain efficient and ultralong pure organic phosphorescence with a quantum yield of 2.1%.

2.3 Factors affecting TADF

The key process in efficient TADF emitters is the facilitated RISC ($T_1 \rightarrow S_1$), and the dependence of the rate constant of RISC ($k_{RISC}$) can be expressed as a Boltzmann distribution relation (3):

$$k_{RISC} \propto \exp \left( \frac{-\Delta E_{ST}}{k_BT} \right)$$

where $k_B$ is the Boltzmann constant, $T$ is the temperature, and $\Delta E_{ST}$ is the singlet–triplet energy splitting; a small $\Delta E_{ST}$ is particularly important according to eqn (3). In principle, $\Delta E_{ST}$ is equal to twice the exchange energy $J$ as presented in the following eqn (4):

$$\Delta E_{ST} = E_S - E_T = 2J$$

In eqn (4), $E_S$ and $E_T$ are the energies of $S_1$ and $T_1$, respectively. For a typical emitter, the two electrons of $S_1$ and $T_1$ states are mainly distributed on the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively, and the exchange energy $J$ of these two electrons at the HOMO and LUMO can be calculated by the overlap integral of their wave functions as presented in eqn (5):

$$J = \int \phi_{HOMO}(r_1)\phi_{LUMO}(r_2)\frac{1}{|r_2 - r_1|}\phi_{HOMO}(r_1)\phi_{LUMO}(r_2)dr_1dr_2$$

where $\phi_{HOMO}$ and $\phi_{LUMO}$ represent HOMO and LUMO wave functions, respectively. As clearly demonstrated in eqn (5), a small $\Delta E_{ST}$ can be realized by minimizing the overlap between the HOMO and LUMO, i.e., spatial wave function separation of the HOMO and LUMO. Therefore, the design of TADF emitters involves spatial separation of the electron-rich (donor) and electron-deficient (acceptor) moieties to separate the HOMO and LUMO distributions and create a small $\Delta E_{ST}$ between the $S_1$ and $T_1$ states (Fig. 4a). Several molecular design methods have been presented, including physical separation of donor and acceptor units, X-shaped molecular structures, and dual acceptor/donor units. In addition, notably efficient TADF emitters based on the multiple resonance (MR) effect of boron and nitrogen/oxygen atoms have been designed, in which the HOMO and LUMO are separated onto different atoms without the need for electron-rich or electron-deficient substituents (Fig. 4b).

3. Design of pure organic RTP and TADF emitters

Continuous efforts have been devoted to formulating rational rules for designing bright pure organic RTP and TADF in recent years. In general, a unique class of organic RTP emitters can be designed systematically through major strategies based on halogen bonding, H-aggregation, and n–π transitions, aiming at strengthening the ISC transitions from $S_1$ to $T_1$ and simultaneously depressing the unfavourable non-radiative relaxations of $T_1$ states. As mentioned above, a small $\Delta E_{ST}$ to aid the RISC from $T_1$ to $S_1$ is critically required for designing an efficient TADF emitter.

3.1 Design of pure organic RTP emitters

One of the earliest attempts in realizing pure organic phosphorescence relied on the crystallization-induced restriction of intramolecular motions, which can be categorized into pure organic single crystals, ionic crystals, co-crystals and self-assembled crystals based on their packing modes. Furthermore, they are mainly connected by intermolecular interactions, including hydrogen bonding, halogen bonding, ion bonding, CH–π interactions and π–π interactions. For example, a facile strategy of heavy atom-participated anion–π interactions is proposed to construct RTP-active organic salt compounds (1,2,3,4-tetraphenylloxazoliums with different counterions), and the film of TPO-Br exhibited white light emission by simply tuning the degree of crystallization (Fig. 5a–c). Another increasingly explored strategy to design organic RTP with a long lifetime is the stabilization of triplet excitons through molecular H-aggregation, which can be achieved by controlling the...
intermolecular interactions in the crystalline state or constructing a small energy gap of $\Delta E_{ST} < 0.3$ eV due to the existence of an energy trapping state $T_1^*$ in organic luminophores. A series of single-component organic crystals featuring colour-tunable ultra-long phosphorescence with lifetime and phosphorescence quantum efficiency of up to 2.45 s and 31.2%, respectively.\(^{59}\)

Another major strategy to promote singlet–triplet ISC in order to produce triplet states and achieve long-lived organic RTP is the enhancement of SOC based on $n$-$\pi$ transitions (Fig. 5d–k).\(^{51,52}\) Specifically, the inclusion of a heavy halogen atom (i.e., Br, Cl, or F), a carbonyl group, and a $\pi$-extended dibenzothiophene subunit, etc., is also beneficial in triggering SOC to strengthen the rate of ISC from $S_1$ to $T_1$, as well as the rate of radiative relaxation from $T_1$ to $S_0$.\(^{46}\) Furthermore, by varying the $\pi$-conjugated units, the ($n$, $\pi^*$) and ($\pi$, $\pi^*$) molecular orbitals could be mixed to generate tunable $T_1$ state with distinct $^3(\pi, \pi^*)$ configuration and energy levels, which in turn enabled the tuning of phosphorescence colour and quantum yield.\(^{51}\) Additionally, apart from achieving efficient ISC, the other key factor for enhancing $\phi_P$ is suppressing the non-radiative deactivation pathways and reducing the quenching of $T_1$. These mainly include co-crystal assembly,\(^{49}\) rigid matrix host–guest systems,\(^{83}\) structurally modified host–guest systems,\(^{84}\) and dopant-based systems.\(^{54}\) By dissolving 1,8-naphthalic anhydride in certain organic solid hosts, purely organic phosphorescence with a lifetime of over 600 ms and an overall quantum yield of over 20% were realized,\(^{55}\) where it was proposed that a cluster exciton spanning the host and guest forms as a transient state before the guest acts as an energy trap for the RTP state. Overall, the key to achieving efficient phosphorescence lies in enhancing $k_{ISC}$ accelerating phosphorescent decay and minimizing the non-radiative decay rate and quenching rate. By satisfying these three crucial requirements, the efficiency of pure organic systems exhibiting RTP can be maximized through rational molecular-design principles and aggregation-modulation strategies.

3.2 Design of TADF emitters

Compared to RTP emitters, studies about the design of TADF counterparts are relatively extensive. A small $\Delta E_{ST}$ is the dominant driving force for RISC and can be realized through the electron-donating and electron-accepting interactions from intramolecular or intermolecular charge transfer, greatly reducing the overlap of the HOMO and LUMO of the molecules. Various rational design strategies, such as the introduction of a large steric hindrance structure,\(^{78,79}\) or a donor–acceptor system with twist/spiro/bulky connection reducing the overlap between the HOMO and LUMO to enhance the charge transfer state,\(^{80,85}\) have thus been geared towards generating efficient TADF emission. Despite the significant improvement in EL efficiency, however, the enhanced structural relaxation in the excited states results in broad emission (FWHM of 80–100 nm) with a large Stokes shift in TADF emitters. Thus, to achieve narrowband emission, the HOMO and LUMO can be significantly separated without the need for electron-rich or electron-deficient substituents for a small $\Delta E_{ST}$ via the MR effect. The strategic introduction of electron-donating amine and electron-donating amine moieties into a versatile boron-embedded 1,3-bis(carbazol-9-yl)benzene skeleton, enabling the systematic hypsochromic and bathochromic shifts of narrowband emissions, respectively, has been demonstrated, achieving a wide visible range from deep blue to yellow (461–571 nm) (Fig. 6).\(^{86}\)

4. Application of pure organic RTP and TADF emitters in electroluminescent displays

Electroluminescence (EL) based on pure organic RTP and TADF emitters provides an attractive route to harness the non-emissive triplet excitons for display applications.
4.1 Pure organic RTP LEDs

Despite the great potential for display applications, the dependence of ISC and phosphorescence efficiency on efficient SOC as well as the prominent effect of oxygen quenching on the triplet excited state in organic molecules has rendered the realization of pure organic RTP extremely challenging. Additionally, the lifetimes of pure organic phosphorescent emitters are too long (usually at the millisecond level), which will inevitably result in a severe efficiency roll-off at high current densities in electroluminescence due to triplet–triplet exciton annihilation or triplet–polaron annihilation, and thus the applications of pure organic RTP are greatly limited to anti-counterfeiting, optical sensing, biochemistry and security systems. There-
color purity that complies with the Commission Internationale de L’Eclairage (CIE) coordinates requirements defined by the broadcasting standards, is highly important.

In the past few years, TADF with MR effect induced HOMO–LUMO separation has shown great potential to deliver a narrow EL band.91–94 For example, Hatakeyama et al. first reported two MR-TADF compounds with a B–N-containing core skeleton, which exhibited blue EL with a small FWHM of only 28 nm, a high maximum EQE of 20.2%, and high color purity with CIE coordinates of (0.13, 0.09) which are close to the National Television System Committee (NTSC) blue light standard (CIE: (0.14, 0.08)).95 The as-synthesized compounds with tert-butyl and carbazolyl units were subsequently modified and achieved blue OLEDs with a FWHM of only 27 nm, a high EQE of 32.1%, and low efficiency roll-off.96 Later, excellent electroluminescence performance with a high EQE of up to 34% and a narrowband emission with a FWHM of 14 nm was achieved for deep-blue OLEDs by incorporating a state-of-the-art MR-TADF emitter (n-DABNA).97 However, thus far, the available emission colors in MR-TADF have been restricted to the blue spectral region owing to the intrinsic difficulties associated with the bathochromic shifts of the MR-induced emissions while retaining TADF characteristics. Therefore, the realization of long wavelength or even full-color MR-TADF emitters with narrowband emissions for next-generation full color displays remains a great challenge.5,101 Benefiting from the abundant energy levels, the emerging quantum-confined CQDs have shown huge prospects in RTP and TADF for exploring the possibilities of implementing the next-generation displays.106,107 In the last few years, steady efforts have been made to develop phosphorescent and delayed fluorescence CQDs through host–guest complexation strategies to prevent unnecessary triplet energy dissipation, in which isolated guest CQDs are homogeneously dispersed in hosts such as crystalline frameworks,108 SiO2,109 boric acid110 and inorganic crystalline nanocomposites.111 However, this strategy

5. Prospects and challenges for RTP and TADF CQDs in displays

Benefiting from the abundant energy levels, the emerging quantum-confined CQDs have shown huge prospects in RTP and TADF for exploring the possibilities of implementing the next-generation displays.106,107 In the last few years, steady efforts have been made to develop phosphorescent and delayed fluorescence CQDs through host–guest complexation strategies to prevent unnecessary triplet energy dissipation, in which isolated guest CQDs are homogeneously dispersed in hosts such as crystalline frameworks,108 SiO2,109 boric acid110 and inorganic crystalline nanocomposites.111 However, this strategy
using CQD composites to achieve triplet-excited-state-involved emission is more vulnerable to phase segregation, poor thermal stability and conductivity, which severely impedes their practical applications,\textsuperscript{112} and thus, undoubtedly, single-component CQDs with intrinsic RTP and TADF properties are highly desired. For example, a gram-scale method for the preparation of ultralong RTP CQDs (1.46 s)\textsuperscript{113} and the hydrothermal treatment of levofloxacin for synthesizing time-dependent phosphorescent CQDs exhibiting a change in phosphorescence color from orange to green and blue-green self-protective RTP emission based on fluorine and nitrogen codoped carbon dots\textsuperscript{114} have been demonstrated, indicating the intrinsic ability of ISC in CQDs. Previously, we reported the first successful demonstration of single-component white emission derived from blue-yellow fluorescence–phosphorescence dual emission with an overall PLQY as high as 25% and a relatively high yellow phosphorescence with a $\Phi_P$ of 6% under ambient conditions based on W-CNQDs (Fig. 9a–e).\textsuperscript{65} Experimental and theoretical investigations revealed that the key role of the carbonyl groups at the rim of W-CNQDs is in assisting the ISC arising from the carbonyl (n\textsuperscript{\pi}p\textsuperscript{\*}) mediated intermolecular (p\textsuperscript{\pi}p\textsuperscript{\*}) electronic coupling. In addition, some efforts have been made to explore CQD-based multicolor phosphorescence. For instance, a universal approach based on efficient radiative energy transfer was designed to obtain NIR-excited multicolor phosphorescent carbon dots.\textsuperscript{115}

In contrast, studies about CQD-based TADF emitters are relatively rare due to their planar configurations.\textsuperscript{116} Recently, a new design approach was reported to control $\Delta E_{ST}$ in graphene quantum dots/graphene oxide quantum dots by varying the ratio of oxygenated carbon to sp\textsuperscript{2} carbon ($\gamma_{OC}$) (Fig. 9f–h).\textsuperscript{117} It was demonstrated that $\Delta E_{ST}$ decreases from 0.365 to 0.123 eV as $\gamma_{OC}$ increases from 4.63% to 59.6%, which in turn induces a dramatic transition from RTP to TADF. Calculations based on time-dependent density functional theory elucidate that such behavior with the changing afterglow characteristics is attributed in part to the distorted molecular geometry and to the change of the SOC matrix element (SOCME) value with the increase of oxygen functional groups, providing a new approach to the engineering of $\Delta E_{ST}$ in GQDs for controlled realization of smart multimodal afterglow materials.

Despite the intensive work on CQD-based RTP and TADF emitters, the research of CQD-based triplet state modulation is still at an early stage with extremely low phosphorescence quantum efficiencies and long lifetimes (hundreds of milliseconds) compared with well-developed transition metal complexes. Furthermore, narrow-band (FWHM $< 50$ nm) and color-tunable RTP emissions are of great necessity and significance for the realization of a full-color electroluminescent display with high color purity. Therefore, the following problems need to be solved for applications in electroluminescence.

5.1 Chemical functionalization

The chemical functionalization of CQDs is a potential strategy to regulate their chemical, electronic, and photophysical properties.\textsuperscript{118,119} Generally, CQDs prepared from either “top-down” or “bottom-up” synthetic approaches are indigenously functionalized with abundant surface groups, especially oxygen related functional groups, such as carboxyl and hydroxyl, which impart suitable chemically reactive groups for surface passivation and functionalization.\textsuperscript{120} For instance, bandgap narrowing
can be tailored by grafting GQDs with electron-donating/withdrawing functionalities.\textsuperscript{121} Specifically, different polyaromatic compounds through the condensation reaction between -COOH/C\text{O} and -NH\text{2} to form N-C\text{O} or C-N amide bonds can be synthesized under solvothermal conditions. White-light-emitting GQDs through oxidative-cutting and post-synthesis functionalization with bulky Fréchet’s dendritic wedges were synthesized,\textsuperscript{122} which are soluble in common organic solvents, such as dichloromethane, tetrahydrofuran, and acetonitrile (Fig. 10a). Narrow emission (FWHM < 40 nm) was achieved through post-synthetic modifications of surface functional groups in which a boron-dipyrromethene dye was integrated into the carbon dots under solvothermal conditions (Fig. 10b-d).\textsuperscript{123} The increased solubility of the large colloidal GQDs prepared from solution chemistry with a uniform and tunable size, e.g., samples 1–3, is achieved by multiple 2',4',6'-trialkyl phenyl groups covalently attached to the edges of the graphene moieties.\textsuperscript{124}

5.2 Efficient full-color phosphorescent and delayed fluorescence CQDs with short lifetimes

For next-generation electroluminescent displays, high-performance RTP and TADF CQDs with short lifetimes are highly demanded for breaking through the 5% limit of the traditional fluorescence devices. However, to date most of the reported triplet-excited-state-involved emissions of CQDs relying on host-guest systems generally exhibit dim luminescence because of inefficient SOC with lifetimes in the second regime\textsuperscript{21,112} and, strictly speaking, persistent afterglow, which severely impede their practical applications. Accordingly, from a fundamental perspective, the most critical way to develop efficient CQD-based RTP or TADF emitters is to reduce $\Delta E_{ST}$ by manipulating the separation of the HOMO and the LUMO for boosting the ISC or RISC according to eqn (2) and (3). In fact, CQDs possessing dominant ($\pi$, $\pi^*$) characteristic in singlet and triplet states normally have a large $\Delta E_{ST}$ due to their plane sp$^2$ $\pi$-conjugation domains and, consequently, a slow $k_{ISC}$. Following the design principle of pure organic RTP or TADF emitters using donor–acceptor systems, with CQDs regarded as either the donor or acceptor, after the incorporation of acceptor or donor subunits, intramolecular charge-transfer states are generated, serving as intermediate states for minimizing $\Delta E_{ST}$, and, thus, in theory, accelerating $k_{ISC}$. For instance, electron-donating aromatics, (donor) such as carbazole, diphenyl amine, phenoxazine, etc., can be grafted into CQDs containing electron-donating groups (acceptor) through one-pot reactions or post-synthetic modification for achieving efficient $k_{ISC}$. In addition, the RTP emission wavelengths of those CQDs were constrained to the blue or green region below 540 nm, and color-tunable RTP emissions are of great necessity and significance for full-color displays. On the basis of the enhancement of SOC based on $\pi$-$\pi$ transitions, by varying the $\pi$-conjugated units and edged functional group ratio in CQDs, the ($n$, $\pi^*$) and ($\pi$, $\pi^*$) molecular orbitals could be mixed to generate tunable $T_1$ state with distinct $^3(\pi$, $\pi^*)$ configuration and energy levels, which in turn enabled the tuning of phosphorescence color, lifetime, and quantum yield.\textsuperscript{125}

Notably, when $\Delta E_{ST}$ is relatively small ($\sim$0.37 eV), a RISC process can occur, which may contribute to TADF emission.\textsuperscript{86,99,117,126} Noteworthy, MR-TADF emitters with planar boron- and oxygen (or nitrogen)-containing arene compounds can be taken as an example for designing efficient CQD-based TADF emitters. Specifically, it is likely to select polycyclic aromatic hydrocarbons (PAHs) containing boron, nitrogen, phosphorus, and sulfur to prepare nanographenes, which is potentially advantageous for the production of complementary resonance effects of the electron density distributions on the HOMO and LUMO orbitals leading to a small $\Delta E_{ST}$ (Fig. 11).\textsuperscript{127,128}
5.3 Tailored design of CQDs for narrow emission

Narrowband emission is critically vital for achieving energy efficiency and a wide color gamut.128–130 Some advances have been made in preparing narrow bandwidth CQDs ranging from blue to red with high PLQYs.131–135 Particularly, the development of multicolored narrow bandwidth emission (FWHM of 30 nm) from triangular CQDs for high color-purity full-color LEDs opens up great prospects for the next-generation display technology.41 Yet, the greatest challenges concern the rational synthesis of efficient phosphorescent and delayed fluorescence CQDs with a narrow bandwidth and their correspondingly intrinsic mechanism at the molecular level. Recently, a variety of B, N-PAHs such as DABNA-analogues have been developed as narrow bandwidth TADF emitters possessing planar and conjugate structures instead of the separation between donor and acceptor moieties for improved color purity (Fig. 12).136 Therefore, a simple and versatile approach that enables the implementation of multiple boron centers and the modulation of their arrangement and electron-accepting nature is highly desirable to systematically investigate the structure–property relationship of nanographenes as actual functional π-conjugated materials. Choosing precursors with a B–N-containing skeleton to enlarge planar π-systems may become a feasible strategy for the development of novel CQD-based RTP or TADF emitters. For instance, triphenylboron, diphenylamine or triphenylamine combines neighboring phenyl groups to construct a rigid π-conjugated plane framework. Moreover, the nitrogen atom exhibits the opposite resonance effect of the boron atoms, and para-substitution relative to it can enhance the resonance effect and significantly separate the HOMO and LUMO without introducing donor or acceptor groups, resulting in a small $\Delta E_{\text{ST}}$. Additionally, narrowband emissive CQDs can be developed using various modification agents, including small molecules and polymers.

5.4 Enhancing the organic solubility of CQDs

Solution processes, such as spin coating and ink-jet printing, show great potential in enabling low-cost and large-area manufacturability of QLEDs129,130 and hence good solubility of CQDs is indispensable for easily forming uniform thin films with low surface roughness. Undoubtedly, the good solution processability requirement increases the design difficulty of TADF emitters. On one hand, these molecules must have good enough solubility in common organic solvents to make a solution process feasible. On the other hand, these molecules...
should form high quality and pinhole-free uniform films without aggregation and phase separation in the solution process. Furthermore, these films are expected to exhibit excellent morphological and thermal stabilities during device operation at high current densities.137 Generally, CQDs prepared from “bottom-up” synthetic approaches are functionalized with abundant groups, such as carboxyl, amidogen and hydroxyl groups, indigenously endowing them with good solubility.22 And the precursors chosen often determine the solubility of the resulting CQDs; alkyl precursors are ideal for the synthesis of CQDs. For example, the synthesis of three red-emitting electron-donating group passivated CQDs R-EGP-CQDs showing high solubility in o-dichlorobenzene (4.4–5.0 mg mL⁻¹) has been demonstrated.31 Furthermore, the post-synthesis modification of CQDs is another potential strategy to regulate their solubility. The edge-functionalized GQD-2 and GQD-3a–c through the reaction of edge-oxidized GQDs with 4-propynoxybenzylamine were synthesized,122 endowing them with high solubility and good film-forming ability. By the introduction of tert-butyl substitution units into the molecular frameworks of NAI_R1, NAI_R2 and NAI_R3, the solubility in chlorobenzene was gradually enhanced as the number of tert-butyl substitution units was increased from 17.5 to 200 mg mL⁻¹.138,139 Intriguingly, a general edge chlorination protocol for atomically precise functionalization of nanographenes at different scales from 1.2 to 3.4 nm was presented, showing enhanced solution processability associated with decreases in the optical bandgap and frontier molecular orbital energy levels via the structure-correlated property modulation (Fig. 13).139

Fig. 11 The designed boron-doped and nitrogen-doped π-extended nanographene structures and oscillator strength, fosc, as a function of ΔEST for 3–6. Reprinted with permission from ref. 128. Copyright 2020 John Wiley and Sons.

Fig. 12 (a) Two-step synthesis of B4. (b–d) Normalized absorption (blue), fluorescence (red), and phosphorescence (green, 77 K, 25 ms delay) spectra, with absorption/emission maxima, absolute fluorescence quantum yields (Φf), and FWHM of PMMA films of B2, B3, and B4 (1 wt%, excited at 360 nm). Reprinted with permission from ref. 136. Copyright 2018 American Chemical Society.

Fig. 13 Chlorinated nanographenes (1–7): (a) structural formulae; (b) mass spectra; and (c) photos of the toluene solutions of 1–7. Reprinted with permission from ref. 139. Copyright 2013 Springer.
Conflicts of interest

There are no conflicts to declare.

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Notes and references

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