Molecular core–shell structure design: Facilitating delayed fluorescence in aggregates toward highly efficient solution-processed OLEDs

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Abstract
Light has been sought and explored by human since ancient times. As the most important form of light, fluorescence is significant to applications in bioimaging and optoelectronic devices. However, fluorescence quenching problem constitutes a serious bottleneck in materials creation. Inspired from the core–shell structure in nature, we report an effective strategy to overcome this long-standing problem by utilizing a molecular core–shell structure. With an emissive core and multifunctional shell fragments, these compounds show aggregation-induced delayed fluorescence (AIDF) properties by restricting singlet oxygen ($^1O_2$) generation and suppressing the triplet–triplet annihilation (TTA). Protected by the functional shell, the aggregation-induced emission luminogens (AIEgens) exhibit strong emission with high photoluminescent quantum yield and exciton utilization. Furthermore, because the shell materials can form exciplex with electron-transport materials, the fully solution-processed organic light-emitting diodes (OLEDs) based on these core–shell materials show low turn-on voltages, excellent device performance with current efficiency of 61.4 cd A$^{-1}$ and power efficiency of 42.8 lm W$^{-1}$, which is a record-breaking efficiency based on all-solution processed organic multilayer systems among the AIE-OLEDs so far. This simple visualization strategy based on molecular core–shell structure provides a promising platform for AIEgens used in the fully wet-processed optoelectronic field.

KEYWORDS
aggregation-induced emission (AIE), molecular core–shell structure, organic light-emitting diodes (OLEDs), triplet–triplet annihilation (TTA)

1 | INTRODUCTION

Core–shell structure is common in nature, ranging from the macroscopic galaxy in the universe to the mesoscopic cells in living body and even to the microscopic atomic nucleus surrounded by electrons. By learning from nature, humans designed various core–shell structure based materials through bionics including core–shell scaffolds, bone biomimetic composites, functionalized nanoparticles, and quantum dots.[1–5] Furthermore, these unique structural materials have exhibited extensive applications in different areas like tissue engineering, gene therapy, and optoelectronic devices.[6–10] Core–shell structures usually contain two or more layers with an inner core part and at least one outer layer to realize specific functions.[11] Taking the structure of virus as an example, the outer layer capsid of virus protects the inner layer nucleic acid and simultaneously interacted with surrounding environment to maintain the basic physiological functions.[12] Within the Au nanoparticles, the metal core is surrounded by ligand layers to stabilize the Au nanoparticles and endow

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them with versatile functionalities.[13] In addition, branched macromolecules with a multi-functional core unit and regular layers have provided a rich seam of research in terms of biological and photoelectric application.[14] In spite of the significant roles of those core–shell structures for both organism and functional materials, their preparation and application exploration are yet to be fully developed.[15] In particular, core–shell structures at the molecular level have scarcely been independently proposed and investigated although they may endow molecules with special properties and functions.

On the other hand, organic luminogens generally emit light through the deactivation of the first singlet excited state (S1), less often triplet state.[16] Although triplet excitons are limited by the spin forbidden nature, the photophysical processes that occur via the lowest triplet excited state (T1) have become important for a variety of bioscientific and optoelectronic technologies. These T1 excitons can not only react with triplet oxygen (3O2) to generate reactive oxygen species (ROS) for biomedical applications, but also can greatly improve the efficiency of electroluminescence device since 75% of triplet excitons can be generated during the electrical excitation process according to quantum statistics.[17–19] Recently, some strategies such as thermal activated delayed fluorescence (TADF), triplet–triplet energy transfer, and hot excitons have been developed to enhance the intersystem crossing (ISC) and reverse ISC (RISC) process and further increase the utilization efficiency of the triplet states.[20] However, in aggregate state, triplet excitons are prone to non-radiative transitions due to the aggregation-caused quenching (ACQ) effect and triplet–triplet annihilation (TTA).[21,22] Moreover, the collision between the long-lifetime triplet excitons and 3O2 species further aggravates the quenching of the triplet excitons.[19,23] Therefore, how to stabilize and protect the sensitive triplet excitons to improve the utilization efficiency of triplet excitons in aggregate state become significant for the corresponding applications involved triplet excitons especially for the application of electroluminescence devices.

Although doping can reduce the quenching effect of organic luminogens in aggregate state to afford high electroluminescence efficiency, new problems emerge such as high cost of mass production, performance degradation by phase separation upon heating, and complexity of technology due to addition of dopants.[24,25] AIEgens provide an alternative strategy to address the solid-state quenching effect to some extent.[26] Additionally, the limited π–π stacking of AIE luminogens reduce the TTA effect. By integrating delayed fluorescence and AIE property, the efficiencies of electroluminescence device currently are comparable with the best TADF emitters with much lower roll-off effect.[27,28] However, the high device efficiencies of AIDF emitters are mainly achieved by vacuum deposition method, which generally is high-cost and unfavorable for large area preparation.[29] As a contrast, solution-process method has the advantage of low cost and large-area preparation, while the performance of solution-processed device mostly is disappointing.[30,31]

Inspired by the core–shell structure in nature, herein, we proposed and designed a molecular core–shell structure by introducing flexible-chain linked bulk fragments as a shell layer to protect the core emitter for electroluminescence device. Since the collision and energy transfer of triplet excitons (mainly Dexter energy transfer) are closely related to the distances, the shell layer of our design can effectively increase the intermolecular distance and spatial isolation to suppress the non-radiative attenuation of triplet excitons.[32] The luminescent behaviors of core–shell compounds were investigated by photoluminescence (PL) spectra, time-resolved photoluminescence spectra, theoretical calculations, electroluminescence measurement. Compared with core compound of 2,3,4,5,6-penta(9H-carbazol-9-yl) benzonitrile (5CzBN), the core–shell molecules hold the advantages of, (i) suitable to solution process due to the large molecular weight and the introduction of flexible chains, (ii) suppressing ACQ and exhibiting significant AIE property, (iii) weakening the influence of oxygen in the environment, then inhibiting the generation of singlet oxygen, (iv) suppressing the quenching of triplet excitons, increasing the exciton utilization rate, and improving the photoelectric efficiency, (v) reducing charge injection barrier by introducing functional shell units to form exciplex. These properties are not available for pure 5CzBN emitter, which demonstrates the superiority of the core–shell structure design in stabilizing and protecting the triplet excitons (Figure 1). Therefore, this core–shell strategy offers building blocks and templates for the rational design, understanding, and discovery of advanced optoelectronic materials.

2 RESULTS AND DISCUSSION

The core–shell molecules 5CzBN-SPhCz, 5CzBN-DPhCz, 5CzBN-TPhCz, 5CzBN-QPhCz, and 5CzBN-PPhCz were prepared through catalyst free aromatic nucleophilic substitution reactions.[33] Their synthetic routes are shown in Scheme 1 and in the Supporting Information. Core–shell materials with different degrees of encapsulation are composed of different numbers of phenylcarbazole (PhCz) branches, which were synthesized by substituent positioning effects and stoichiometric ratio control.[34] The new compounds have been fully characterized by 1H NMR, 13C NMR, MALDI-TOF, and elemental analysis with satisfied results.

2.1 Photoluminescent properties

The photophysical properties of 5CzBN and core–shell molecules were first investigated using UV-vis and PL spectra (Figures S1–S5). All compounds show strong absorption peaks at 280, 330 nm and a weak shoulder peak at around 420 nm in solution, which can be assigned to a π π* transition and intramolecular charge transfer (ICT), respectively. The fluorescence (Fluo) spectra of these compounds exhibit structureless and broad sky-blue emission with charge transfer (CT) characteristics in toluene solution.[35] The phosphorescence (Phos) spectra were measured in toluene at 77 K and showed characteristic vibrational band as a result of radiation transition of the vibrational energy level at low temperature.[36] Due to the introduction of shell structure and increased electron-donating ability, these 5CzBN derivatives exhibit gradually red-shifted Fluo and Phos emission as the number of branches increases. In addition, the Fluo and Phos spectra of these compounds in the film states were also measured. And all of these compounds show slightly
red-shifted emission compared to those in the solution state, which show that the $S_1$ and $T_1$ energy levels in aggregation state are decreased. Moreover, the core–shell materials exhibit smaller singlet-triplet energy differences ($\Delta E_{ST}$) (<0.1 eV) in aggregated state, especially for 5CzBN-PPhCz with $\Delta E_{ST} = 0.01$ eV (Table 1 and Table S1), which facilitates RISC and promotes the thermally activated up-conversion process. The theoretical calculations have been implemented to better understand these findings (Figures S6, S7, and Table S2). The electronic molecular orbital distribution demonstrated the electron cloud separation of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which is helpful to decrease the $\Delta E_{ST}$. Natural transition orbits (NTO) demonstrate the charge transfer characteristics of these 5CzBN derivatives. The small $\Delta E_{ST}$ values also benefit the TADF process.

In order to explore how the photophysical properties of the materials change dynamically during the process from dispersion to aggregation, we further measured the PL intensity of 5CzBN derivatives in water (H$_2$O)/tetrahydrofuran (THF) mixtures with different water fractions ($f_w$). As shown in Figure S8, the PL intensity of 5CzBN first decreases and then increases as $f_w$ gradually increases. The fluorescence spectra undergo a certain degree of red shift at low $f_w$, and then when $f_w = 60\%$, nanoparticles are formed, and the spectra rapidly blue shift. After that, the proportion of water continues to increase, and the fluorescence spectra show red-shifted emission because of the increased intermolecular interactions. But the fluorescence intensity did not show a continuous upward trend. Overall, 5CzBN does not exhibit obvious AIE properties. Differently, these core–shell materials, especially 5CzBN-PPhCz, exhibit obvious aggregation-enhanced emission (AEE) phenomenon. Moreover, the AEE phenomenon of core–shell materials becomes more evident with the increase of the number of peripheral modified branches. Firstly, the FL intensity decreases and the wavelength increases as the water content increases from 0% to 40%. This phenomenon is attributed to the twisted intramolecular charge transfer (TICT) process. Then with the increase of $f_w$, the PL intensity and wavelength increases and decreases, respectively. This is a typical characteristic of AIE. Meanwhile, importantly, the wavelength changes of core–shell materials become smaller from dispersion to aggregation compared to 5CzBN, as shown in Figure S8. It suggested that these core–shell molecules, especially 5CzBN-PPhCz, show weak TICT nature and response to the environmental polarity owing to the encapsulation of the flexible branches. It was also confirmed by the solvatochroic effect measurement (Figures S1, S4, S5, and Table S3). It can be seen intuitively from the Lippert-Mataga plot (Figure S5) that with the increase of the number of flexible branches, the slopes of the curves become smaller and smaller, and the solvatochromism of the materials is weakened gradually. The results show that the dipole moment changes between the ground state and the excited state of the material get smaller, and the introduction of peripheral branches will stabilize the molecular configuration to a certain extent, and thereby weaken the solvation effect and aggregation-caused intermolecular interactions. Furthermore, the strong AEE phenomenon in core–shell system was investigated by measuring the PL transient decay spectra in H$_2$O/THF mixtures with different fractions of water (Figure 2C.E and Figure S9). Consistent with the fluorescence spectra, the PL lifetimes of core–shell materials first decreased and then increased as water content gradually increased. The PL lifetimes changed from the nanosecond to microsecond scale after the generation of nano-aggregates (Tables S4 and S5). In pure THF solutions, the photo-excited molecules at $S_1$ nonradiatively relax to $S_0$ because of active intramolecular motions and quenching of oxygen. While in the aggregate state, the molecular motions are restricted greatly by physical constraint, which blocks nonradiative decay of $S_1$, rendering strong fluorescence of the luminogens. Besides, the RISC process becomes dominative, owing to the unquenched $S_1$ and small $\Delta E_{ST}$, which results in delayed fluorescence enhancement. This phenomenon is also known as AIDF. As for the decreased lifetime of 5CzBN and the previously mentioned reduction in fluorescence intensity in 90% H$_2$O/THF mixture, we attributed it to TTA in the
aggregation states. This was also confirmed in subsequent experiments.

Not only that, the photoluminescence quantum yields ($\Phi_{PL}$) also show interesting phenomenon (Figure 2D, Table 1). First of all, the $\Phi_{PL}$ values of these compounds, especially 5CzBN, exhibit extremely low values (<20%) in toluene solutions under air condition. Then after bubbling N$_2$, it is remarkable all compounds showed outstanding $\Phi_{PL}$ enhancement in toluene solution. Taking 5CzBN-PPhCz as an example, the $\Phi_{PL}$ value (93%) increases by 5 times compared to the $\Phi_{PL}$ value (15%) before bubbling N$_2$. The exciting and interesting discovery attracted our attention, then prompted us to think about the influence of oxygen in the environment on the photophysical properties of these materials. And corresponding experiments were carried out, which will be described in the following section. Furthermore, we also compared the $\Phi_{PL}$ values in powder state and in toluene solution after bubbling N$_2$. The simultaneously increased
Table 1: Photophysical properties of 5CzBN and 5CzBN derivatives

| Emitters       | λ<sub>em</sub> | S<sub>T1</sub>/T<sub>1</sub><sup>b</sup> | Φ<sub>PL</sub><sup>c</sup> | τ<sub>p/τ</sub><sub>d</sub><sup>d</sup> | k<sub>nr</sub> (10<sup>5</sup>)<sup>g</sup> | λ<sub>em</sub> | S<sub>T1</sub>/T<sub>1</sub><sup>f</sup> | Φ<sub>PL</sub> | τ<sub>p/τ</sub><sub>d</sub><sup>e</sup> | k<sub>nr</sub> (10<sup>5</sup>)<sup>g</sup> |
|----------------|---------------|---------------------------------|-----------------|-----------------|-----------------|---------------|---------------------------------|-----------------|-----------------|-----------------|
| 5CzBN          | 461           | 2.94/2.77                        | 5/70            | 0.11/2.64       | 1.13            | 479           | 2.78/2.67                        | 36              | 0.30/1.93       | 3.32            |
| 5CzBN-SPhCz    | 471           | 2.88/2.77                        | 5/72            | 0.16/3.23       | 0.86            | 503           | 2.68/2.60                        | 46              | 0.29/3.90       | 1.38            |
| 5CzBN-DPhCz    | 474           | 2.88/2.77                        | 7/83            | 0.17/5.28       | 0.51            | 505           | 2.74/2.68                        | 55              | 0.11/4.17       | 1.09            |
| 5CzBN-TPhCz    | 482           | 2.85/2.75                        | 10/88           | 0.21/3.80       | 0.31            | 505           | 2.71/2.64                        | 58              | 0.09/4.81       | 0.86            |
| 5CzBN-QPhCz    | 485           | 2.84/2.78                        | 12/90           | 0.10/4.05       | 0.24            | 506           | 2.70/2.67                        | 60              | 0.24/5.07       | 0.78            |
| 5CzBN-PPhCz    | 489           | 2.81/2.75                        | 15/93           | 0.16/4.12       | 0.17            | 507           | 2.71/2.70                        | 73              | 0.32/5.51       | 0.49            |

<sup>a</sup>In toluene solution (10<sup>-5</sup> M) at room temperature.
<sup>b</sup>Calculated from the onset of the fluorescence and phosphorescence spectra in toluene.
<sup>c</sup>Measured in toluene before/after bubbling N<sub>2</sub>.
<sup>d</sup>In degassed toluene without O<sub>2</sub>.
<sup>e</sup>In pure film.
<sup>f</sup>Calculated from the onset of the fluorescence and phosphorescence spectra in neat films.
<sup>g</sup>Measured in pure films. k<sub>nr</sub>: the nonradiative decay rate constants, k<sub>RISC</sub>: the rate constant of reverse intersystem crossing.

Values indicate that the AIE mechanism is not only due to restriction of intramolecular motion in aggregated states, but also the inhibition of oxygen erosion by aggregation. It should be emphasized that this is a new AIE mechanism, which has not been studied in previous studies. Moreover, the Φ<sub>PL</sub> value differences of these 5CzBN derivatives in the powder state are also intriguing. For example, 5CzBN have 37% photoluminescence quantum yield. Then the Φ<sub>PL</sub> values of core–shell materials gradually increased as the numbers of branches increased, finally 5CzBN-PPhCz showed strong fluorescence emission with Φ<sub>PL</sub> = 82%. The Φ<sub>PL</sub> values in film states also demonstrate the same trend (Table 1). This indicates that in addition to oxygen effect, the molecular structure also has an important effect on the PLQY of the materials. Therefore, these results preliminarily confirm the superiority of our core–shell molecular design. Owing to the protection of the shell, these core–shell materials can protect the triplet excitons and achieve efficient up-conversion, especially in the aggregated states.

2.2 Effect of reactive oxygen species

For above speculations, we undertook experimental demonstrations showing the influence of oxygen to triplet excitons and verified that molecular core–shell design circumvents...
concentration quenching. First, the PL transient decay spectra of these materials in toluene before/after bubbling N2 were measured and shown in Figure 3A,B. The PL decay curves of all compounds only showed transient lifetimes with dozens of nanoseconds under air condition. After bubbling N2, the PL lifetimes significant change from ns to μs scale, prominent delayed fluorescence is observed for all luminogens with long lifetimes in microsecond scale (2.6–4.1 μs). The delayed fluorescence is mainly derived from the up-conversion of triplet excitons through RISC process. Therefore, triplet excitons are very sensitive to oxygen. By bubbling nitrogen, the interaction between the triplet excitons and oxygen is suppressed. So that the triplet excitons can emit delayed fluorescence with a higher probability. According to the ΦPL and lifetime in degassed toluene, the kinetic constants associated with photophysical properties were calculated and shown in Table 1 and Table S6. The RISC processes are promoted in core–shell system as the numbers of branches increases, thus the ratio (Φdelayed) and lifetime of delayed component (τd) rise progressively, further validating the core–shell design advantage.

Furthermore, we tried our best to experimentally confirm the involvement of oxygen in the triplet quenching process more intuitively. Triplet oxygen (1O2) is easily reacted with the excited triplet (T1) states to generate reactive oxygen species (ROS), which is widely applied in photodynamic therapy (PDT).[41] Many fluorescent probes have been reported to specifically detect the presence of ROS.[42,43] Therefore, we measured the ROS generation of 5CzBN derivatives in UV irradiation by using 1,3-diphenylisobenzofuran (DPBF) as a singlet oxygen (1O2) monitoring agent (Figure 3). In the presence of these 5CzBN derivatives, noticeable decreases in DPBF absorption are observed. Especially 5CzBN causes the fastest drop in DPBF absorption (Figure 3E). The photos in Figure 3D clearly show the color change of the DPBF solution in the presence of 5CzBN, from initial blue emission of the DPBF indicator to quenching. Finally, the solution shows green color in UV lamp, which is derived from the fluorescent emission of 5CzBN. The results indicate that 5CzBN can generate 1O2 effectively. On the contrary, the triplet excitons of 5CzBN-PPhCz generate less 1O2 in oxygen environment. Such weak 1O2 generation ability may be due to the smaller ΔE_ST and enhanced RISC process. But overall, the triplet excitons of these materials are easily quenched by oxygen in dilute solutions. Furthermore, the PL intensity of these materials in the 2-methyl tetrahydrofuran (2-Me-THF) solution gradually increased after UV irradiation, which is because oxygen was gradually consumed by capturing singlet oxygen in 2-Me-THF in a covered container (Figure S10). The measurement provided further evidence that the singlet oxygen can generate after light excitation by interacting with triplet excitons.

Subsequently, we also measured the change trend of the 1O2 generation rate of these 5CzBN derivatives during the aggregation process. As shown in Figure 3C,F and Figures S11–S15, we used dichloromethane (DCM) as a good solvent and methanol (MeOH) as a poor solvent. I is the absorption intensity of DPBF after irradiation for a certain time, I0 is the absorption intensity of DPBF before irradiation. So the curves of I/I0 values versus UV light irradiation time can

**Figure 3** (A) PL transient decay curves of 5CzBN derivatives at 300 K before N2 bubbling; (B) PL transient decay curves of 5CzBN derivatives at 300 K after N2 bubbling; (C) The decomposition rates of DPBF in the presence of 5CzBN in MeOH/DCM (v:v) = 0%, 20%, 80%, 100% and light irradiation for different times, where I0 and I are the absorbance of DPBF in the presence of 5CzBN derivatives at 410 nm before and after irradiation, respectively; (D) The photo of 5CzBN and DPBF mixture in DCM solution before and after irradiation (left side: UV lamp and right side: sunlight); (E) UV–vis absorption spectra of DPBF in the presence of 5CzBN; (F) The decomposition rates of DPBF in the presence of 5CzBN-PPhCz in MeOH/DCM (v:v) = 0%, 20%, 80%, 100% and light irradiation for different times.
reflect the reduction of absorption intensity of DPBF. The larger the slope of the curve is, the faster the decomposition of DPBF is. As the volume ratio of MeOH ($f_{\text{MeOH}}$) increases in MeOH/DCM mixtures, it can be found that the slope of the curve gets smaller and smaller, and the rate of $^{1}\text{O}_2$ generation obviously decreases. In the insoluble methanol solution, the almost constant absorption intensity is in sharp contrast with those in pure DCM solution. This shows that the generation of molecular aggregates isolates the oxygen and inhibits triplet exciton quenching. Therefore, through the continuous increase of doping ratio, the increase of $f_{\text{MeOH}}$, and the same is true for 5CzBN-PPhCz. And secondly, in MeOH/DCM mixtures of same $f_{\text{MeOH}}$, the decomposition rates of DPBF in presence of 5CzBN-PPhCz became lower significantly than that in 5CzBN. We observed benefits accrued in molecular core–shell structure and further shell package led to significant restriction of $^{1}\text{O}_2$ generation. Thus, the $^{1}\text{O}_2$ generation efficiency of these 5CzBN derivatives is closely associated with the AIE mechanism and it became lower during the aggregation and shell packaging. These results demonstrated the quenching pathway of triplet excitons in aggregated states is suppressed by restriction of $^{1}\text{O}_2$ generation.

### 2.3 Effect of TTA

Further, $T_1$ excitons can be utilized to achieve delayed fluorescence through RISC process due to restriction of triplet sensitization. Although 5CzBN showed low $^{1}\text{O}_2$ generation rate in the aggregated state, it is worth noting that 5CzBN aggregates exhibited reduced PL intensity (Figure S8), small delayed lifetime (1.61 $\mu$s, Figure 2C) and lower powder $\Phi_{\text{PL}}$ (Figure 2D). Therefore, the effect of oxygen on the triplet state cannot fully explain the fluorescent decrease of 5CzBN and the AIDF process of core–shell materials. We suspect that the TTA plays a role in the process of aggregation because the delayed lifetime is mainly related to long-lived triplet excitons. In order to confirm our guess, these materials were doped in poly (methyl methacrylate) (PMMA) with different proportions, and the mixtures were prepared as doped thin films. Due to the small polarity (dielectric constant $\varepsilon = 2.6$ at 1 MHz) of PMMA and the restricted molecular motion in the doped films, it was thought that different ratios of doped films only affect the distance and interaction between these molecules and other factors will not be considered here. Therefore, through the continuous increase of doping ratio, the interaction distance between molecules is getting closer and closer, and the quenching pathways of triplet excitons in this process are basically affected by the TTA process. The fluorescence spectra and transient PL decay curves of different doping ratios are displayed in Figure 4 and Figures S16, S17. As the doping ratios increase, the fluorescence spectra of 5CzBN small molecule undergo a significant red shift, and the fluorescence lifetime is gradually reduced. It clearly demonstrates that intermolecular interactions make triplet excitons more prone to collision and quenching with the occurrence of aggregation, thereby weakening the RISC process and reducing the fluorescence quantum yield. However, for the core–shell system, as the shell package and the number of branches increases, the degrees of red shift in the fluorescence spectra gradually weaken. 5CzBN-PPhCz, which is in the fully encapsulated form, shows basically unchanged fluorescence spectra. At the same time, the transient delay curve of 5CzBN-PPhCz also shows basically unchanged PL delay emission in pure film compared to that in low-doped film. Furthermore, we compared the rate constants of 5CzBN and its derivatives in the low-doped film and pure film states, and the calculated rate constants of the TADF materials are summarized in Figure 4E and Table S7. First of all, compared with 1% doped films, the nonradiative decay rate constant ($k_{\text{nr}}$) is greatly increased in the pure film. It shows that the nonradiative process is seriously affected by concentration, the intermolecular interaction will lead to the long-lived triplet exciton collision quenching. In particular, the $k_{\text{nr}}$ value of 5CzBN changed from $1.08 \times 10^4$ s$^{-1}$ to $3.33 \times 10^5$ s$^{-1}$ with increasing an order of magnitude. The core–shell materials also show the same law, but at the same time we also noticed that compared with 5CzBN, the $k_{\text{nr}}$ values of 5CzBN-PPhCz has been greatly reduced with $4.37 \times 10^3$ s$^{-1}$ in 1% doped films (1 times smaller) and $4.92 \times 10^4$ s$^{-1}$ in pure films (5 times smaller). It indicated the nonradiative decay pathways can be suppressed efficiently by the core-dendron molecular design. Secondly, the $k_{\text{RISC}}$ values gradually increase as the number of branches increases. It shows that the introduction of shell units is sufficient to inhibit the TTA process to a large extent, and then achieve efficient TADF and enhanced fluorescence emission.

Overall, by constructing the core–shell structures, these 5CzBN derivatives achieve efficient AIDF. They show weak or even quenched emission in dilute solutions, but strong emission in the aggregated state. On one hand, the movements in AIDF luminophores are restricted so that the nonradiative transition is suppressed. The aggregation can also protect luminophores from the surrounding polar environment, which weakens the charge-transfer character of $S_1$ state (weaker solvent effect) and helps to improve the radiative transition. On the other hand, the aggregation of AIDF luminophores can protect its $T_1$ state from the surrounding triplet oxygen and TTA process, which suppresses the triplet state quenching pathway and results in more efficient RISC process for realizing longlived delayed emission in an oxygenic environment (Figure 5A).

### 2.4 Thermal stability and electrochemical properties

AIDF luminophores have shown great potential in the application for high efficient non-doped organic light-emitting diode (OLED) devices owing to the excellent luminous properties of AIDF luminophores in the aggregated state. Before applying these novel dendrimers to OLED devices, their thermal stability, and electrochemical properties need to be measured to ensure device stability and charge transporting balance. The thermal stability properties of 5CzBN derivatives were characterized by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere at a heating rate of 10°C min$^{-1}$. With the increase of flexible branches, the thermal decomposition temperatures $T_d$ gradually decrease from 422°C.
FIGURE 4 (A) Normalized PL spectra of 5CzBN doped in PMMA films with different concentrations; (B) Normalized PL spectra of 5CzBN-PPhCz doped in PMMA films with different concentrations; (C) PL decay curves of 5CzBN doped in PMMA films with different concentrations. (D) Kinetic parameters of these compounds in 1% doped PMMA and neat films, respectively. $k_F$: the radiative decay rate constant of fluorescence; $k_{nr}$: the nonradiative decay rate constants. $k_{ISC}$: the rate of intersystem crossing, $k_{RISC}$: the rate constant of reverse intersystem crossing; (E) PL decay curves of 5CzBN-PPhCz doped in PMMA films with different concentrations.

FIGURE 5 (A) The device configurations and aggregation-induced emission (AIE) mechanism of the emissive layer material; (B) Current density–voltage–luminance (J–V–L) characteristics of devices A–E; (C) Current efficiencies and the external quantum efficiencies versus brightness; (D) Electroluminescence spectra at 10 V.
for 5CzBN-SPhCz to 406°C for 5CzBN-PPhCz. 5CzBN core has high glass transition temperature (318°C), which has been reported by Duan et al.[45] And the glass transition temperature dramatically drops after adding flexible alkyl chains. And as the flexible branches increase, \( T_g \) values of these core–shell molecules gradually decrease (Figure S18). Furthermore, the cyclic voltammetry (CV) measurements of the compounds were performed to assess the contribution of the peripheral dendron on the HOMO and LUMO energy levels of 5CzBN derivatives. As shown in Figure S19, according to the onset potential, the HOMO energy levels of 5CzBN-SPhCz, 5CzBN-DPhCz, 5CzBN-TPhCz, 5CzBN-QPhCz, and 5CzBN-PPhCz are calculated to be \(-5.31, -5.31, -5.30, -5.32, \) and \(-5.34 \) eV, respectively. The results are further verified by DFT calculations, the peripheral dendrons make little effect on the oxidation potential and HOMO energy levels. Based on the energy band-gaps calculated by the absorption spectra, the LUMO energy levels of 5CzBN-SPhCz, 5CzBN-DPhCz, 5CzBN-TPhCz, 5CzBN-QPhCz, and 5CzBN-PPhCz are calculated to be \(-2.51, -2.51, -2.52, -2.55, \) and \(-2.58 \) eV, respectively (Table 1), which match well with the theoretical simulations (Table S1). In a word, the shallower HOMO levels of these 5CzBN derivatives are close to the energy level of hole transport layer PEDOT: PSS (\(-5.2 \) eV), which would facilitate the hole injection into the emitter.

### 2.5 Electroluminescence properties

Therefore, the fully solution-processed OLEDs based on these AIDF materials are fabricated and evaluated. Figure 5A shows the device structure and AIE mechanism of these core–shell molecules. The optimal device architecture consists of ITO/PEDOT: PSS (40 nm)/AIDF emitters (5CzBN-SPhCz for Device A, 5CzBN-DPhCz for Device B, 5CzBN-TPhCz for Device C, 5CzBN-QPhCz for Device D and 5CzBN-PPhCz for Device E)/PO-T2T (40 nm)/Cs2CO3 (2 nm)/Al (100 nm), where the AIDF dendrimers are used as non-doped emitters to investigate their electroluminescence (EL) performance. The PEDOT: PSS is used as a hole injection layer (HIL) to decrease the energy barrier between the emission layer (EML) and the ITO anode (indium tin oxide). In order to optimize the carrier balance, PO-T2T is introduced as the electron transport layer (ETL). It should be noted that all the functional organic layers (HIL, EML, and ETL) in the devices are fabricated through solution-process. The OLEDs containing each of the five core–shell materials, 5CzBN-SPhCz, 5CzBN-DPhCz, 5CzBN-TPhCz, 5CzBN-QPhCz, and 5CzBN-PPhCz, are denominated as Device A–E, respectively.

Figure 5 shows current density voltage luminance (J-V-L) curves, current efficiency/external quantum efficiency (EQE) versus luminance curves. Table 2 summarizes the electroluminescent (EL) data of the devices. All devices show efficient green electroluminescence, their EL peaks are similar to the device based on 5CzBN. It indicates that the EL emission is mainly derived from the 5CzBN core. With the enhanced encapsulation of PhCz shell, the device performances improve significantly. Device E based on 5CzBN-PPhCz exhibits a low turn-on voltage of 3.2 V at the luminance of 1 cd m\(^{-2}\). The maximum current efficiency (CE), power efficiency (PE), and EQE of Device E are 61.4 cd A\(^{-1}\), 42.8 lm W\(^{-1}\), and 21.8%, respectively. The maximum luminance of Device E is above 30,000 cd m\(^{-2}\). Moreover, the efficiencies still remain as high as 41.2 cd A\(^{-1}\), 25.8 lm W\(^{-1}\), and 19.0% at the high luminance of 1000 cd m\(^{-2}\), which fully demonstrate the superiority of AIDF materials with molecular core–shell structures in solution-processed OLEDs. And the functional shells PhCz also decrease the turn-on voltage by forming exciplex with the electron-transporting materials PO-T2T. Figure S20 shows the EL spectra of PhCz and PO-T2T mixture with 1:1 molar ratio, the excited PhCz donor (D\(^*\)) can interact with the ground state PO-T2T acceptor (A) to form exciplex state. As can be seen from the EL of 1:1 blend film, the emission spectra are broad and redshifted to 468 nm, which is different from the emission from single molecule PhCz and PO-T2T. Therefore, it indicates the exciplex is formed between EML and ETL at interfaces. Then, the interface exciplex will transfer the energy to the emissive core 5CzBN. Owing to this efficient energy transfer process, all the excited excitons gather in TADF emissive core without energy leakage through other low-energy states, which is also the key point of the high efficiencies of these core–shell molecules. To the best of our best knowledge, these device efficiencies are among the best efficiency of solution-processed AIE-OLEDs.[46-55] Admittedly, the device stability of core–shell molecule may be poor since the introduction of solubilized flexible chains. However, the design of core–shell structure holds the advantages of simplicity and compatibility. We believe this work would provide critical guidelines for design of efficient

| Device | \( V_{on} \) \( ^a \) | \( \lambda_{EL} \) \( ^b \) | \( CE_{max} \) \( ^c \) | \( PE_{max} \) \( ^d \) | \( EQE_{max} \) \( ^e \) | \( I_{max} \) \( ^f \) | CIE\((x,y)\) \( ^g \) |
|--------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| A      | 2.9             | 532             | 41.6            | 34.1            | 14.0            | 26,500          | (0.32,0.55)     |
| B      | 3.0             | 532             | 43.4            | 34.2            | 14.5            | 26,500          | (0.32,0.54)     |
| C      | 3.1             | 524             | 49.3            | 36.4            | 15.7            | 27,800          | (0.32,0.54)     |
| D      | 3.5             | 524             | 53.7            | 37.5            | 17.1            | 36,800          | (0.32,0.54)     |
| E      | 3.2             | 512             | 61.4            | 42.8            | 21.8            | 32,100          | (0.26,0.50)     |

\( ^a V_{on} \) = turn-on voltage at 1 cd m\(^{-2}\).

\( ^b \) The wavelength of electroluminescence peak at 10 V.

\( ^c CE_{max} \) = maximum current efficiency.

\( ^d PE_{max} \) = maximum power efficiency.

\( ^e EQE_{max} \) = maximum external quantum efficiency.

\( ^f I_{max} \) = maximum luminance.

\( ^g \) CIE = The Commission Internationale de L’Eclairage coordinates at 10 V.
AIE-TADF materials used in wet-processed optoelectronic field.

3 | CONCLUSION

Core–shell molecules are a novel class of materials that offer bright prospect to AIDF emitters. This core–shell structure can be prepared by following general design rules to produce spatial isolation and functional integration. The spatial isolation can be achieved by connecting a range of sterically hindered shell materials to a variety of fluorescent cores with flexible chain. Thus, the excellent AIDF performance can be suppressed by increasing the distance between the cores. Furthermore, the core–shell materials are suitable to solution process due to the large molecular weight and the introduction of flexible chains. Thus, the excellent AIDF characteristic and efficient exciton utilization make it suitable to fabricate non-doped OLEDs. Finally, the fully solution-processed OLEDs using these core–shell materials as lighting-layers have demonstrated great resistance to isopropyl alcohol and achieved outstanding performance with maximum lumiance of 30,000 cd m⁻², excellent EL efficiencies of up to 21.8%, 61.4 cd A⁻¹ and 42.8 lm W⁻¹ (based on 5CzBN-PPh2Cz). The results eloquently demonstrate the feasibility and versatility of the presented molecular design, and novel AIDF lumogenes with core–shell structures have the great potential for high-performance non-doped OLED, even solution-processed fabrication.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest that could be perceived as prejudicing the impartiality of the research reported.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are openly available in the Supporting Information at the end of this document.

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