

## RESEARCH ARTICLE

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# Red-shift emission and rapid up-conversion of B,N-containing electroluminescent materials *via* tuning intramolecular charge transfer†

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Boron (B) and nitrogen (N)-based polycyclic aromatic hydrocarbons (PAHs) have been demonstrated as promising materials for building efficient thermally activated delayed fluorescent (TADF) emitters in blue and green regions, while red emission materials based on B,N systems are rare. Hence, to achieve a red-shifted emission peak over 600 nm by simply modifying the core of B,N-PAHs is a rewarding and challenging task. In this work, we demonstrate the *para*-D- $\pi$ -B strategy implementation of modulating the predominance of locally excited (LE)/charger transfer (CT) states by introducing peripheral electron-donating units in a boron-carbazole containing backbone (**BNCz**) to develop four TADF emitters, **BN-TC**, **BN-AC**, **BN-PXZ** and **BN-PZ**. Due to the effect of different donor strengths on the excited states of these materials, we obtain full-color emission and a high photoluminescence quantum yield ( $\Phi_{PL}$ ) of nearly 100%. Notably, the device employing **BN-PZ** as a dopant exhibits orange-red emission with an electroluminescence (EL) peak at 612 nm. Meanwhile, this compound realizes very fast reverse intersystem crossing (RISC) with a rate constant ( $k_{RISC}$ ) of  $1.8 \times 10^6 \text{ s}^{-1}$ , resulting in a device with a high external quantum efficiency (EQE) of 25.0% and low efficiency roll-off at high brightness.

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## 1. Introduction

Organic light-emitting diodes (OLEDs) are now the star product in the full-color display and solid-state lighting fields. The internal quantum efficiency (IQE) of OLEDs based on pure organic TADF emitters is up to 100%, as 75% of the triplet excitons can be transferred from the lowest triplet ( $T_1$ ) excited state to the lowest singlet ( $S_1$ ) excited state by the reverse intersystem crossing process.<sup>1–3</sup> In order to achieve an efficient RISC process, a small singlet-triplet splitting energy ( $\Delta E_{ST}$ ) between  $S_1$  and  $T_1$  in TADF materials is the critical point, which requires the overlap between the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) to be as small as possible.<sup>4–9</sup> The most widespread TADF molecular design strategy is the use of highly

distorted donor-acceptor (D-A) structures.<sup>10–13</sup> The twisted D-A framework accompanied by the intramolecular charge transfer (ICT) characteristic allows TADF materials to easily exhibit full-color emission, which is essential for color displays, white lighting, imaging applications, *etc.*<sup>14–16</sup>

In 2016, Hatakeyama and co-workers developed novel PAHs containing boron (B) and nitrogen (N) atoms. This B,N-based TADF material features outstanding blue emission with a high  $\Phi_{PL}$  and small  $\Delta E_{ST}$ .<sup>17</sup> B,N-based TADF materials emitting in blue and green regions are currently booming, owing to great efforts that have been made to modify and innovate this B,N-based core through different strategies. Duan *et al.* and Wang *et al.* both introduced acceptors at the *para*-carbon position of B-substituted phenyl rings (*para*-A- $\pi$ -B), which could modulate the LUMO distribution and excited state of the molecule to red-shift the emission wavelength, resulting in efficient green OLEDs.<sup>18,19</sup> Chou and co-workers reported a series of B,N-based TADF materials with green emission *via* the design approach of introducing sulfur atoms into the B,N-based core.<sup>20,21</sup> Yasuda's group and Yang's group obtained highly-efficient yellow devices by a peripheral decoration strategy on the B,N-based core (*para*-D- $\pi$ -N and *peri*-D- $\pi$ -N).<sup>22,23</sup> Recently, Duan and co-workers reported deep-red B,N-based TADF materials *via* the design approach of the *para*-B- $\pi$ -B method.<sup>24</sup> Regrettably, on the one hand, B,N-based TADF emitters in longer wavelength regions with emission peaks

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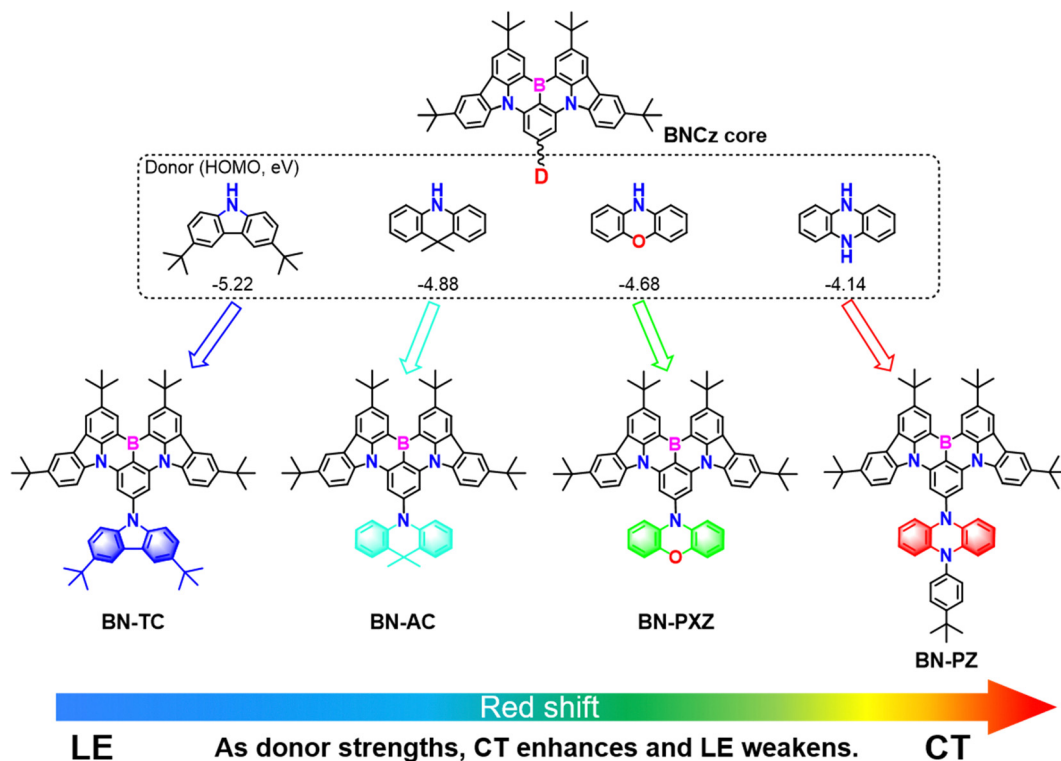


Fig. 1 Design for full-color TADF emitters based on boron–nitrogen embedded polycyclic aromatic hydrocarbon as well as chemical structures of BNCz, BN-TC, BN-AC, BN-PXZ and BN-PZ.

exceeding 600 nm remain scarce, while on the other hand, the up-conversion rates of these TADF materials are still limited to a magnitude order of  $10^4 \text{ s}^{-1}$ , leading to severe triplet–triplet annihilation (TTA) and triplet–polaron annihilation (TPA). Hence, developing new schemes for obtaining red-shifting B,N-containing PAHs with high up-conversion rates is in urgent demand for producing efficient and low roll-off red TADF-OLEDs.

Herein, we propose and practice a novel strategy of modulating the HOMO level and predominance of locally excited (LE)/charger transfer (CT) states by introducing a donor. In detail, we introduce donors with different HOMO energy levels at the *para*-position of the B atom in the BNCz core,<sup>25,26</sup> as shown in Fig. 1, namely, BN-TC, BN-AC, BN-PXZ and BN-PZ. It is worth noting that BNCz is not only an MR-TADF molecule,<sup>18,27,28</sup> but it can also act as an acceptor in the D–A skeleton. When increasing the interaction strength of the donors, the excited state properties gradually tend from LE towards CT. As a result, we have succeeded in achieving full-color emissions from 464 nm to 634 nm in toluene through donor engineering. These TADF emitters exhibit high  $\Phi_{\text{PLS}}$  of nearly 100% and a remarkably elevated RISC rate ( $10^6 \text{ s}^{-1}$ ) is obtained for BN-PZ. The corresponding blue and green devices achieve maximum external quantum efficiencies (EQE) of over 20%. Notably, the BN-PZ-based OLEDs display orange-red emission peaking at 612 nm, and a high maximum EQE of 25.0% with significantly low efficiency roll-off. A remarkable EQE of 17.6% at  $1000 \text{ cd m}^{-2}$  is the highest value reported for sensitizer-free TADF OLEDs with EL peaks over 610 nm so far. This work confirms that modulating the

predominance of the LE/CT state is an effective method to realize red-shifted emission in B–N-containing PAHs.

## 2. Results and discussion

### 2.1. Molecular design and synthesis

Three designed boron-carbazole containing emitters, namely, BN-AC, BN-PXZ and BN-PZ, were synthesized by a nucleophilic aromatic substitution reaction and tandem electrophilic arene borylation (Experimental Section and Scheme S1 in the ESI<sup>†</sup>). These emitters have been characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and time of flight mass spectrometry (Fig. S1–S9, ESI<sup>†</sup>). All final products were purified by temperature-gradient sublimation under vacuum after recrystallization and the purity requirements of fabrication for OLEDs were achieved by vacuum deposition. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) indicated the excellent thermal stabilities of BN-AC, BN-PXZ and BN-PZ, with 5% weight-loss decomposition temperatures ( $T_d$ ) of 440 °C, 453 °C and 454 °C, respectively, and glass transition signals ( $T_g$ ) of 253 °C, 268 °C and 271 °C, respectively (Fig. S10, ESI<sup>†</sup>). Such excellent thermal stability of these emitters is consistent with their rigid configurations, which fulfills the requirement of thermal evaporation. The single crystal structure of BN-PZBN-PZ was obtained from a toluene/CH<sub>2</sub>Cl<sub>2</sub> mixed solution, as shown in Fig. S11 and S12 (ESI<sup>†</sup>) (CCDC number: 2241686<sup>†</sup>), revealing a highly distorted molecular geometry with a large dihedral angle of 84.9° between

the B,N-core and phenazine. The twisted D–A structure and the strongest PZ donor could strengthen the ICT state, enabling the simultaneous realization of long-wavelength emission.

## 2.2. Theoretical calculations

To understand the effect of different *para*-donor units of the backbone on molecular geometry and optoelectronic properties, density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were performed using the B3LYP functional with the 6-31G(d) basis set in the Gaussian 16 program. The frontier orbital distributions and energy levels of these compounds are depicted in Fig. 2. The dihedral angles of the twisted D–A structure are estimated to be 52°, 84°, 74° and 77° for **BN-TC**, **BN-AC**, **BN-PXZ** and **BN-PZ**, respectively. The large dihedral angles are beneficial for enhancing the ICT character and lowering  $\Delta E_{ST}$ . **BN-TC** shows a delocalized HOMO–LUMO distribution, whereas the HOMO and LUMO orbitals of **BN-AC**, **BN-PXZ** and **BN-PZ** are separated. In addition, the energy gap ( $E_g$ ),  $S_1$  and  $T_1$  all decrease as the donor strength increases, which could cause spectral red-shifts. They also exhibit large oscillator strengths ( $f$ ) of 0.3912, 0.4139, 0.4163 and 0.3444, indicating a fast-radiative decay and high  $\Phi_{PL}$ .

Furthermore, the natural transition orbitals (NTOs) of  $S_1$  and triplet ( $T_n$ ) excited states of these materials were calculated and are shown in Fig. 3. The  $S_1$  excited states of all three molecules show completely separated “holes” and “particles” respectively located on the donor and **BNCz** core, but their  $T_n$  excited states are distinguishing. For **BN-AC**, the  $\Delta E_{ST}$  between the  $S_1$  and  $T_1$  excited state is 0.110 eV, while  $\Delta E_{ST}$  between the  $S_1$  and second triplet ( $T_2$ ) excited state is 0.010 eV, which seems

small enough to establish a feasible RISC channel. However, the  $S_1$  and  $T_2$  excited states have highly similar CT features, which forbids spin–orbital coupling (SOC) between them, and therefore invalidates  $T_2 \rightarrow S_1$  RISC.<sup>28</sup> In addition, the simulated SOC matrix element ( $\langle S_1 | \hat{H}_{SOC} | T_1 \rangle$ ) between the LE-predominant  $T_1$  excited state and  $S_1$  excited state of **BN-AC** reaches 0.436  $\text{cm}^{-1}$  ( $\langle S_1 | \hat{H}_{SOC} | T_1 \rangle = 0.436 \text{ cm}^{-1}$ ), which is one order of magnitude higher than that between  $T_2$  and  $S_1$  ( $\langle S_1 | \hat{H}_{SOC} | T_2 \rangle = 0.0283 \text{ cm}^{-1}$ ). The  $T_2$  excited state of **BN-PXZ** is mainly centralized on the **BNCz** core, corresponding to LE-predominance. Despite a smaller energy gap between its  $T_1$  and  $S_1$ ,  $T_1$  can also not support RISC to  $S_1$ , because its CT feature induced vanishing of SOC. Meanwhile, SOC of the  $S_1 \rightarrow T_1$  excitation sharply decreases by several times, compared to that of  $S_1 \rightarrow T_2$  excitation ( $\langle S_1 | \hat{H}_{SOC} | T_1 \rangle = 0.071 \text{ cm}^{-1}$ ,  $\langle S_1 | \hat{H}_{SOC} | T_2 \rangle = 0.312 \text{ cm}^{-1}$ ). The  $T_1$  excited state of **BN-PZ** exhibits a similar “hole” and “particle” distribution to  $S_1$ , while  $T_2$  is unable to establish a transition channel with  $S_1$ , due to an unbridgeable energy gap. In a word, both **BN-AC** and **BN-PXZ** simultaneously contain CT-predominant  $S_1$  and LE-predominant  $T_n$  excited states, while **BN-PZ** only has the CT feature, demonstrating that excited states convert from LE-predominant to CT-predominant with increasing donor strength, in which a limit that determines the role of the BN core as an emitter or an acceptor probably exists. More specifically, on connecting a *para*-donor with a shallower HOMO energy level than that of PXZ, the molecule will exhibit a CT-predominant excited state, while the **BNCz** core will act as an

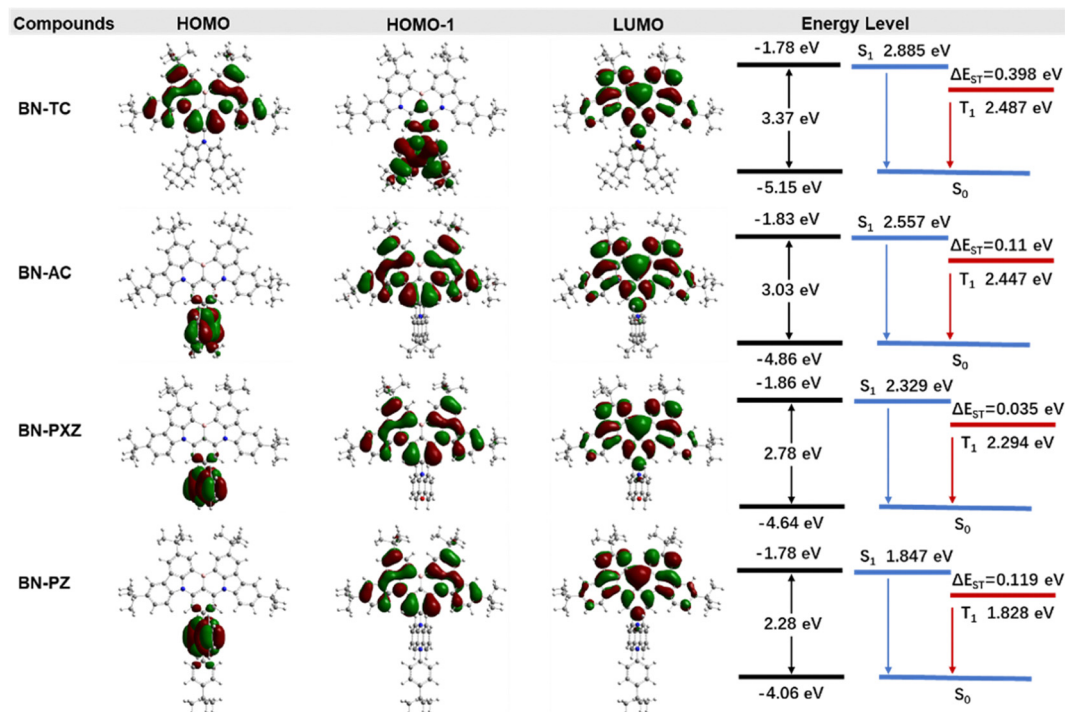


Fig. 2 Distributions of frontier molecular orbitals, calculated energy gaps and energy-level diagrams for the singlet and triplet excited states of **BN-TC**, **BN-AC**, **BN-PXZ** and **BN-PZ**.

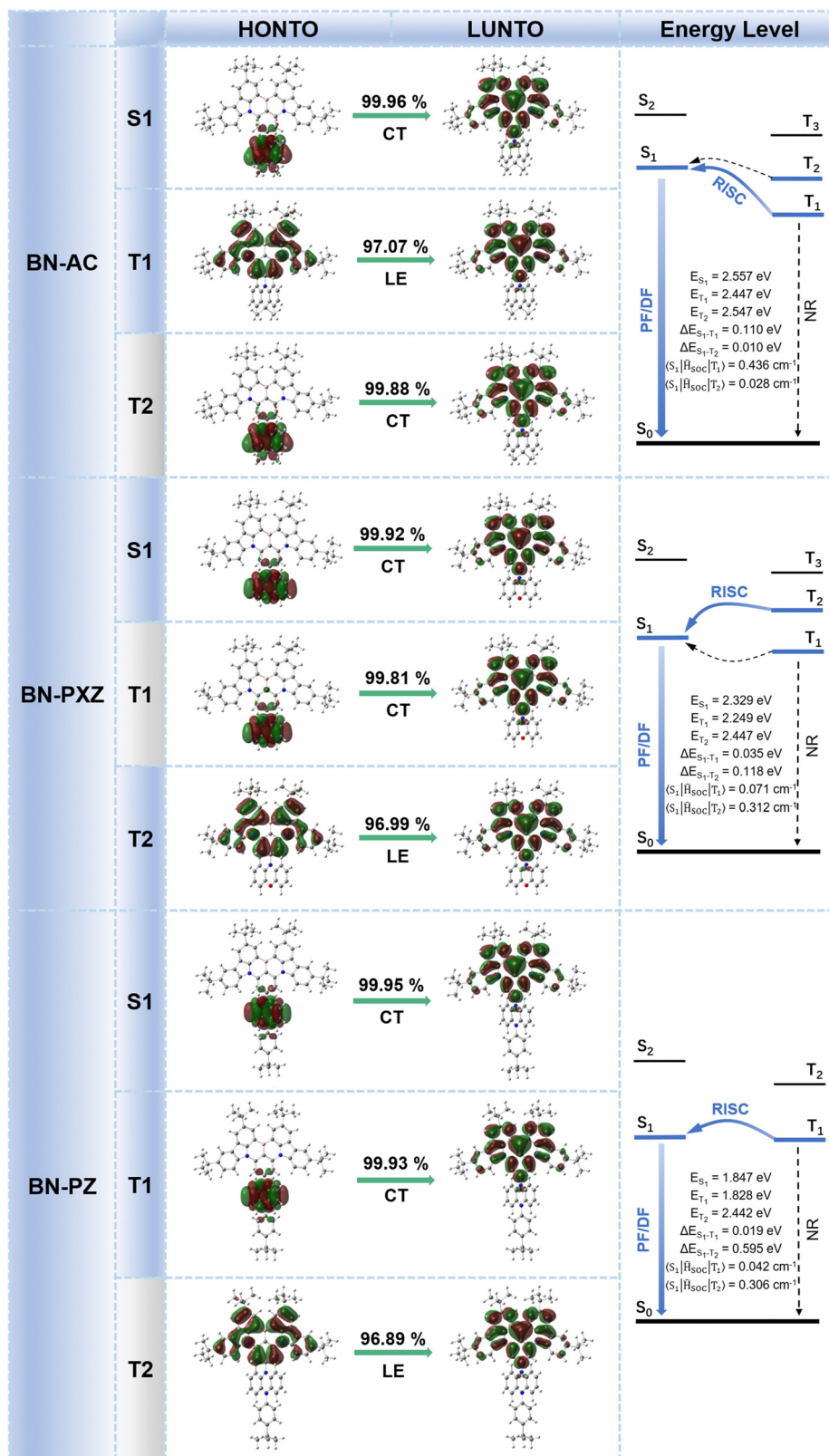


Fig. 3 Energy-level diagrams and related NTOs for the singlet and triplet excited states of **BN-AC**, **BN-PXZ** and **BN-PZ**. Transition energies for  $S_1$  and  $T_n$  ( $n = 1, 2$ ) and the SOC matrix elements were calculated at the B3LYP/6-31G(d) levels of theory, respectively.

acceptor. In this case, we predict that **BN-AC** and **BN-PXZ** should exhibit narrow-band emissions combined with the CT feature, while **BN-PZ** is identical to common D-A type molecules with broad emission.

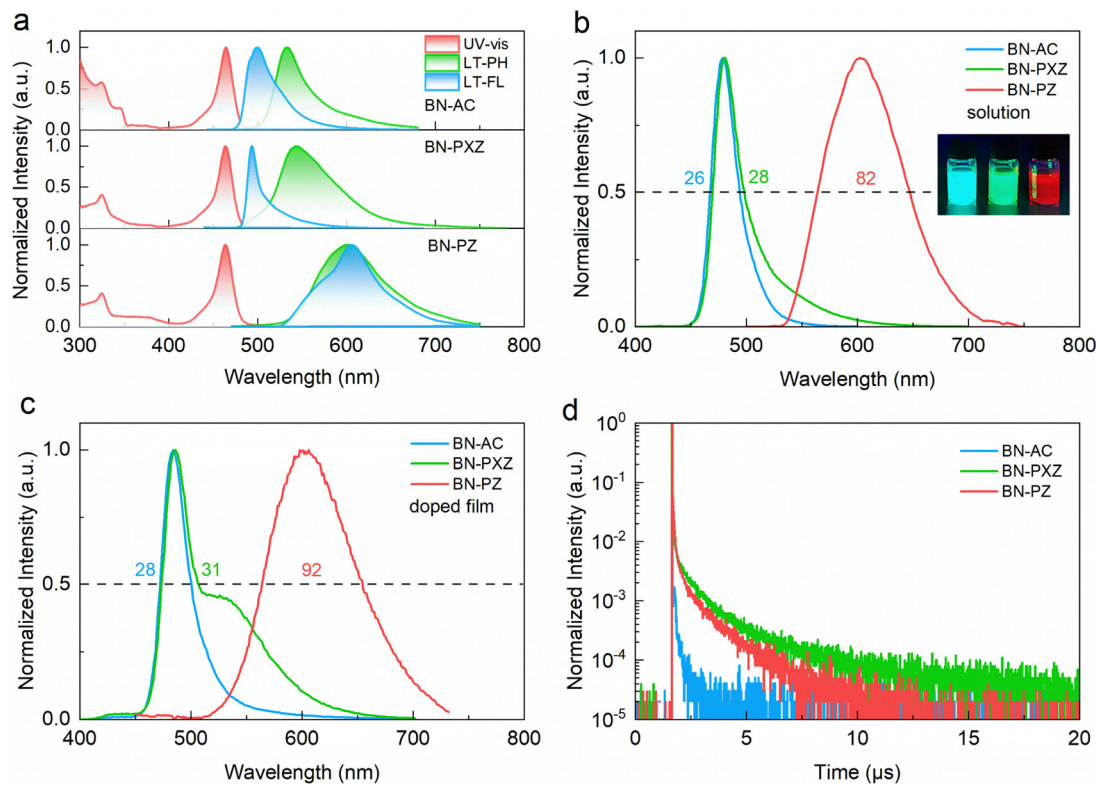


Fig. 4 (a) UV-vis absorption (Abs., in  $1 \times 10^{-5}$  M toluene), steady-state fluorescence (LT-FL, 77 K in neat films) and phosphorescence (LT-Ph, 77 K in neat films) spectra. (b) Photoluminescence spectra in toluene ( $1 \times 10^{-5}$  M). (c) Photoluminescence spectra in 15 wt% doped films (host: mCBP). (d) Transient photoluminescence decay profiles (doped films *in vacuo*).

### 2.3. Photophysical properties

The photophysical spectroscopic properties of **BN-AC**, **BN-PXZ** and **BN-PZ** are shown in Fig. 4, and the key data are summarized in Table 1. As predicted by DFT calculations, the UV absorption of these materials shows a strong MR characteristic peak at  $\sim 464$  nm, which originates from the B,N-containing framework. Due to the shallowest HOMO energy level of the donor PZ, **BN-PZ** has an additional low energy ICT absorption band at 490–550 nm (Fig. S13, ESI<sup>†</sup>) and exhibits red emission with a peak at 634 nm in a dilute toluene solution (Fig. 4b). The  $S_1$  and  $T_1$  energy values are obtained from the onset wavelength of low-temperature fluorescence and phosphorescence spectra, based on which the  $\Delta E_{ST}$  values are calculated to be 0.14 eV, 0.12 eV and 0.03 eV for **BN-AC**, **BN-PXZ** and **BN-PZ**, respectively. Such a tiny  $\Delta E_{ST}$  can benefit efficient recycling of the triplet excitons *via* the rapid RISC process. The PL spectra of **BN-AC**

and **BN-PXZ** in dilute toluene are almost identical, resulting from the similar emissions in solution originating from their LE states, but the curve of **BN-PXZ** in the region over 510 nm is relatively higher than that of **BN-AC**, which is consistent with the stronger CT state of **BN-PXZ** (Fig. 4b). The solvent polarity-dependent emission behaviors of emitters were studied using the Lippert–Mataga model, in which the  $X$ -axis stands for the solvent polarity factor  $f$ , and the  $Y$ -axis represents Stokes' shift (Fig. S14 and Table S2, ESI<sup>†</sup>). The UV-vis absorption spectrum of **BN-AC** and **BN-PXZ** showed a slight change within a scope of 5 nm as the solvent polarity increased, indicating a negligible dipolar change in the  $S_0$  state with the change in solvent polarity. The dipole moment of  $S_1$  excitons can be estimated from the fitted line of experimental points. Their two-section lines corresponded to the two different exciton states with two distinguishable small and large dipole moments in low-polarity

Table 1 Physical properties of **BNCz**, **BN-TC**, **BN-AC**, **BN-PXZ** and **BN-PZ**

Compounds	$\lambda_{\text{abs}}^a$ (nm)	$\lambda_{\text{em}}^a$ (nm)	FWHM <sup>a</sup> (nm)	Stokes shift <sup>a</sup> (nm)	$E_{S_1}/E_{T_1}/\Delta E_{ST}^c$ (eV)	HOMO/LUMO <sup>d</sup> (eV)	$T_d^e$ (°C)
<b>BNCz</b> <sup>f</sup>	467	481	44	14	2.66/2.53/0.13	−5.40/−2.85	—
<b>BN-TC</b>	460	464	22	4	2.64/2.50/0.14	−5.46/−2.85	—
<b>BN-AC</b>	464	479 (484) <sup>b</sup>	26	14	2.59/2.45/0.14	−5.33/−2.74	447
<b>BN-PXZ</b>	464	480 (486) <sup>b</sup>	28	14	2.57/2.45/0.12	−5.14/−2.55	458
<b>BN-PZ</b>	464	634 (610) <sup>b</sup>	82	70	2.34/2.31/0.03	−4.58/−1.99	466

<sup>a</sup> In toluene,  $1.0 \times 10^{-5}$  M. <sup>b</sup>  $\lambda_{\text{em}}$  measured in the 15%-doped film in mCBP host. <sup>c</sup>  $E_{S_1}$  and  $E_{T_1}$  were determined from the onsets of LTFL and LTPh, respectively;  $\Delta E_{ST} = E_{S_1} - E_{T_1}$ . <sup>d</sup> HOMO levels were determined from the onset of the oxidation curves, and LUMO levels were calculated by using the HOMO levels and  $E_g$ . <sup>e</sup> Measured from thermal gravimetric analysis (TGA). <sup>f</sup> Literature.<sup>19,28,29</sup>

and high-polarity solvents, respectively. In the case of low-polarity solvents, the  $S_1$  excitons of **BN-AC** and **BN-PXZ** behaved as LE states with small dipole moments of 4.47 D and 7.54 D, respectively, while their  $S_1$  excitons exhibited large dipole moments of 14.23 D and 14.02 D, respectively, in high-polarity solvents, which clearly illustrated a considerable contribution of ICT character in the excited state. Compared with the other emitters, **BN-PZ** exhibits only CT-dominant emission in both low- and high-polarity solvents, demonstrating the ICT characteristic expected from molecular design. In addition, **BN-PZ** exhibits a wider photoluminescence (PL) spectrum than the others, resulting from dominance of the CT state rather than the LE state, which is consistent with the theory of spontaneous emission that the full width at half maximum (FWHM) is proportional to the square of the emission peak wavelength.<sup>29</sup> When doped in a 3,3'-bis(carbazol-9-yl)biphenyl (mCBP) host, all three materials display slightly broadened spectra due to  $\pi$ - $\pi$  interactions (Fig. 4c). It is noted that, due to the host-guest interaction, the CT state also participates in the emission in the doped film, in which **BN-PXZ** exhibits a red-shifted shoulder peak in the region over 510 nm. Moreover, the  $\Phi_{\text{PL}}$  values in mCBP doped films are measured to be 94%, 97% and 98% for **BN-AC**, **BN-PXZ** and **BN-PZ**, exhibiting PL emission at 484 nm, 486 nm and 610 nm, respectively.

To further investigate the photophysical properties of these emitters, the transient PL spectra of the doped films in mCBP host matrix were recorded. As depicted in Fig. 4d, **BN-AC**, **BN-PXZ** and **BN-PZ** exhibited a significantly delayed fluorescence behavior owing to the small  $\Delta E_{\text{ST}}$  values, showing prompt

fluorescence lifetimes ( $\tau_{\text{p}}$ )/delayed fluorescence lifetimes ( $\tau_{\text{d}}$ ) of 3.8 ns/9.7  $\mu\text{s}$ , 8.9 ns/1.7  $\mu\text{s}$  and 39.4 ns/1.2  $\mu\text{s}$ , respectively. Thereinto, the **BN-AC**-based doped film displayed shorter  $\tau_{\text{p}}$  compared to the tens of nanoseconds for **BN-PZ**, which is consistent with the gradual decreasing proportion of the prompt fluorescence component from **BN-AC** to **BN-PZ** (Table S3, ESI<sup>†</sup>). Moreover, the short  $\tau_{\text{d}}$  value of about 1  $\mu\text{s}$  of the **BN-PZ** is conducive to the rapid RISC process. Furthermore, by incorporating the large rate constants of singlet radiative decay, the concentration quenching of triplet excitons and efficiency roll-off in electroluminescent devices can be effectively alleviated at high brightness.<sup>27,30</sup> The temperature dependence of transient decay in the doped films clearly shows that the delayed fluorescence (DF) component increased progressively along with rising temperature, indicating the TADF process in the molecules (Fig. S15, ESI<sup>†</sup>).

To understand the  $S_1$  and  $T_1$  exciton dynamic processes of these TADF emitters in doped films, the rate constants, such as singlet radiative decay rate constants ( $k_{\text{r}}$ ), nonradiative decay rate constants ( $k_{\text{nr}}$ ), internal conversion rate constants ( $k_{\text{IC}}$ ), intersystem crossing rate constants ( $k_{\text{ISC}}$ ), and reverse intersystem crossing rate constants ( $k_{\text{RISC}}$ ) are estimated according to the formulas provided in the literature and summarized in the Table S3 (ESI<sup>†</sup>).<sup>31–33</sup> Resulting from the highly rigid planar parent core **BNCz** unit, the  $k_{\text{r}}$  values of these emitters are over  $10^7 \text{ s}^{-1}$ . Benefiting from the increasing ICT character and small  $\Delta E_{\text{ST}}$ , the  $k_{\text{RISC}}$  value of **BN-PZ** is in the range of  $10^6 \text{ s}^{-1}$ , which is much higher than those of most of the reported **BNCz**-based

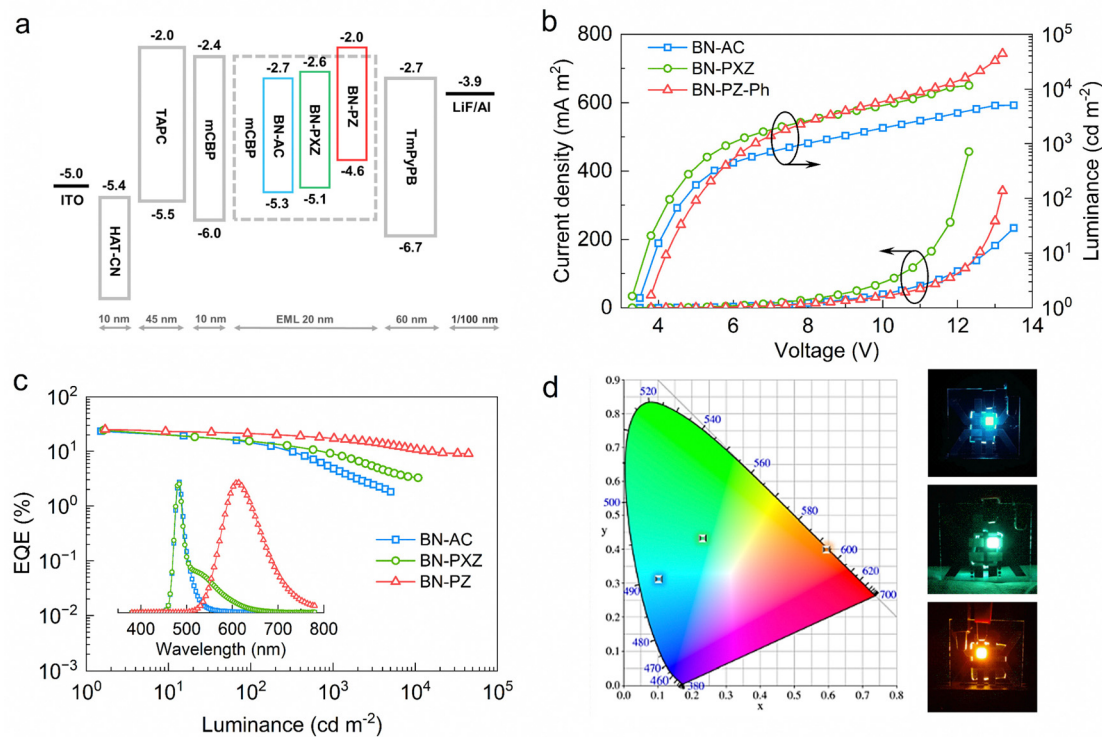


Fig. 5 (a) Device structure and energy level diagram of the materials used. (b) Current density and luminance versus voltage ( $J-V-L$ ). (c) External quantum efficiency versus luminance (EQE-L) curves of the devices (inset: EL spectra of the devices). (d) The color coordinates of the devices on the CIE 1931 color space and the photographs showing the emission color of the 15 wt%-doping devices.

Table 2 The device performances of **BNCz**, **BN-TC**, **BN-AC**, **BN-PXZ** and **BN-PZ**

Compounds	$V_{ON}^a$ (V)	$\lambda_{EL}^b$ (nm)	FWHM <sup>c</sup> (nm)	$L_{max}^d$ (cd m <sup>-2</sup> )	CE <sub>max</sub> <sup>e</sup> (cd A <sup>-1</sup> )	PE <sub>max</sub> <sup>f</sup> (lm W <sup>-1</sup> )	EQE <sup>g</sup> (%)	CIE <sup>h</sup> (x, y)
<b>BNCz</b>	3.8	490	32	5017	34.3	29.0	21.1/13.0/5.9	(0.13, 0.41)
<b>BN-TC</b>	4.1	474	37	4448	28.2	21.6	21.2/8.7/4.2	(0.13, 0.20)
<b>BN-AC</b>	3.5	484	27	5089	35.1	31.5	23.4/15.9/5.5	(0.10, 0.31)
<b>BN-PXZ</b>	3.3	482	25	11710	51.2	48.7	24.4/15.5/8.2	(0.23, 0.43)
<b>BN-PZ</b>	3.8	612	104	44210	34.9	29.2	25.0/21.2/17.6	(0.60, 0.40)

<sup>a</sup> Turn-on voltage at 1 cd m<sup>-2</sup>. <sup>b</sup> EL maximum wavelength. <sup>c</sup> Full width at half maximum. <sup>d</sup> Maximum luminance. <sup>e</sup> Maximum current efficiency. <sup>f</sup> Maximum power efficiency. <sup>g</sup> Maximum external quantum efficiency and values at 100 and 1000 cd m<sup>-2</sup>. <sup>h</sup> Value at 100 cd m<sup>-2</sup>.

TADF emitters, which suggests an efficient T<sub>1</sub> → S<sub>1</sub> exciton up-conversion and high utilization of excitons.

#### 2.4. Electroluminescent device performance

The EL properties of these TADF emitters were further investigated with the device structures of indium tin oxide (ITO)/1,4,5,8,9,11-hexaazatriphenylenehexacarbonitrile (HATCN, 10 nm)/di-[4(*N,N*-ditolyl-amino)-phenyl] cyclohexane (TAPC, 60 nm)/3,3'-di(carbazol-9-yl)biphenyl (mCBP, 10 nm)/mCBP:*x* wt% emitters (20 nm)/1,3,5-tri(*m*-pyrid-3-ylphenyl)benzene (TmPyPB, 45 nm)/LiF (1 nm)/Al (100 nm). Herein, ITO and Al were used as the anode and cathode, respectively; HATCN and LiF served as the hole- and electron-injecting layers, respectively; TAPC and TmPyPB played the role of hole- and electron-transporting layers, respectively; mCBP acted as an electron blocking layer (EBL) and the host to form an emitting layer (EML). The corresponding energy level diagrams of each layer are illustrated in Fig. 5a. For the emitting layer, the optimized dopant concentration is 5 wt% for both **BNCz** and **BN-TC**, and 15 wt% for the other three TADF emitters (Fig. S16, ESI<sup>†</sup>). The current density–voltage–luminance (*J*–*V*–*L*) characteristics of these devices are shown in Fig. 5b and the key data of the devices are summarized in Table 2. The OLEDs based on **BN-AC** and **BN-PXZ** display attractively narrow EL emissions, with emission peaks at 484 nm and 482 nm, FWHM values of 27 nm and 25 nm, high maximum EQE values of 23.4% and 24.4%, and CIE coordinates of (0.10, 0.31) and (0.23, 0.43), respectively (Fig. 5c and 5d). Expectedly, the presence of a shoulder peak in the EL spectrum of **BN-PXZ** catches our attention. One explanation attributes this type of shoulder peak to dimer emission;<sup>18,31</sup> however, there is no shoulder peak in the EL spectrum of **BN-AC** with a similar conformation and dihedral angle. Hence, we propose a more plausible explanation: both LE state emission and relatively weak CT state emission exist in the emission of **BN-PXZ**, so a shoulder peak appears. And this is consistent with the NTO simulation results and PL spectra. Besides, the EL spectra of **BN-AC**, **BN-PXZ** and **BN-PZ** are highly stable under different operating voltages without emission shifting, and the device performances of **BNCz** and **BN-TC** are essentially the same as those reported in the literature. (Fig. S17 and S18, ESI<sup>†</sup>).<sup>26,27</sup> More importantly, the **BN-PZ**-based OLEDs exhibit prominent EL performances with a high maximum luminance ( $L_{max}$ ) of 44210 cd m<sup>-2</sup> and orange-red emission with a peak at 612 nm, which is in agreement with the PL spectra in doped films. Without using TADF-sensitizing fluorescence (TSF) technology, this device achieves a maximum EQE (EQE<sub>max</sub>) as high as 25.0%. Furthermore, the **BN-PZ**-based device displays significantly alleviated efficiency

roll-off of 15.2% and 29.6% with EQE values of 21.2% and 17.6% in 100 and 1000 cd m<sup>-2</sup> (Fig. 5c and Table 2), respectively. In comparison with most sensitizer-free TADF OLEDs in the emission region over 610 nm, the **BN-PZ**-based device exhibits state-of-the-art EQE in 1000 cd m<sup>-2</sup> and a lower efficiency roll-off, which can be attributed to the suppressed TTA and TPA in EML at high brightness due to its higher  $k_{RISC}$  (Fig. S19 and Table S4, ESI<sup>†</sup>).<sup>4,14,16,34–59</sup> Although the orange-red device displays high EQE and low efficiency roll-off, we expect to find a suitable TADF sensitizer that will be employed to further improve device efficiency and stability.

### 3. Conclusions

In conclusion, we propose a novel strategy of introducing a shallow HOMO-energy donor unit at the *para*-carbon position in the core of B,N-PAHs, effectively enabling red-shifted emission. Benefiting from a novel strategy of modulating the HOMO level and predominance of the LE/CT state, these TADF materials exhibit full-color emission and  $\Phi_{PL}$  values of nearly 100%. The OLEDs based on these dopants achieve high EQEs of over 20%. Owing to the strong ICT character and faster RISC ( $k_{RISC} > 10^6$  s<sup>-1</sup>), the orange-red device utilizing **BN-PZ** as an emitter shows a maximum EQE of 25% with an emission peak at 612 nm, and attains a high maximum  $L_{max}$  of 44210 cd m<sup>-2</sup> and low efficiency roll-off with a remarkable EQE of 17.6% in 1000 cd m<sup>-2</sup>, which is the highest value reported for sensitizer-free TADF OLEDs with EL peaks over 610 nm so far. This work has provided a facile and effective strategy to modulate the LE/CT state of B,N-containing PAHs for efficient and stable red TADF-OLEDs.

### 4. Experimental section

#### Synthesis

Detailed synthetic procedure and general analysis of the materials are described in the ESI<sup>†</sup>.

#### Device fabrication and measurements

Devices were fabricated at a vacuum level lower than  $1 \times 10^{-4}$  Pa for both organic and metal layers. ITO coated glasses with a sheet resistance of 15  $\Omega$  square<sup>-1</sup> were used as the substrate and cleaned with ultra-purified water and organic solvents, and then irradiated in UV-ozone for 15 min. Organic materials were evaporated to ITO at a rate of about 1  $\text{\AA}$  s<sup>-1</sup>, while LiF and Al were evaporated at rates of around 0.1 and 5  $\text{\AA}$  s<sup>-1</sup>,

respectively. The intersection of ITO and the metal electrodes gave a 10 mm<sup>2</sup> active device area.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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