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https://doi.org/10.1007/s11426-018-9413-5

Simultaneous enhancement of efficiency and stability of OLEDs with thermally activated delayed fluorescence materials by modifying carbazoles with peripheral groups

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Received October 26, 2018; accepted January 10, 2019; published online January 30, 2019

Albeit their high efficiencies, the operational stability of the organic light emitting diodes (OLEDs) based on thermally activated delayed fluorescence (TADF) emitters is still far from satisfaction, and few strategies have been proposed to improve their stability. Here, we show that by modifying the carbazole unit, one of the most commonly used donors in TADF emitters, with peripheral groups, both the device efficiency and operational stability can be greatly improved. A well-known TADF molecule— 4,5-di(9*H*-carbazol-9-yl)phthalonitrile (2CzPN) was chosen as the prototype and modified by introducing peripheral *tert*-butyl and phenyl groups to the 3,6-positions of the carbazole (named 2*t*BuCzPN and 2PhCzPN, respectively). The introduced groups not only improve the compounds' electrochemical stabilities referred to the cyclic voltammetry multi-sweep results, but also promote their photoluminescence quantum yields. Furthermore, reduced singlet-triplet energy gaps are observed, leading to the shortened exciton lifetimes which are benefit to suppress the exciton annihilations. Besides, the steric hindrance of introduced phenyl groups can partly restrain the concentration quenching of the TADF emitter. Consequently, OLEDs based on 2*t*BuCzPN and 2PhCzPN achieved improved maximum external quantum efficiencies (EQEs) of 17.0% and 14.0%, respectively (compared to 8.5% for 2CzPN). Meanwhile, 2PhCzPN based OLED showed reduced roll-off characteristics and a longer lifetime of 7.8 times higher than that of 2CzPN, testifying the effectiveness of subtle modification of the unstable moieties in simultaneous enhancement of efficiency and stability of OLEDs based on TADF emitters.

TADF, OLED, stability, carbazole, peripheral group

Citation: Zhang Y, Zhang D, Tsuboi T, Qiu Y, Duan L. Simultaneous enhancement of efficiency and stability of OLEDs with thermally activated delayed fluorescence materials by modifying carbazoles with peripheral groups. Sci China Chem, 2019, 62, https://doi.org/10.1007/s11426-018-9413-5

1 Introduction

Featuring unique properties, purely organic materials with thermally activated delayed fluorescence (TADF) have attracted tremendous attention as the next-generation emitters in organic light-emitting didoes (OLEDs) [1–8]. Technically, TADF materials possess a very small energy gap ($\Delta E_{\rm ST}$) between the lowest excited singlet state (S₁) and the lowest

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excited triplet state (T_1), in which case their triplet excitons can be up-converted into the emissive S_1 ones, leading to 100% internal electroluminescence (EL) quantum efficiency (IQE) theoretically. To date, enormous efforts have been endeavored to develop highly efficient full color TADF emitters [6–22], and the external quantum efficiencies (EQEs) of the OLEDs based on blue and green TADF emitters have been boosted to about 30% [19–22], which is comparable to the state-of-the-art phosphorescent OLEDs [23,24].

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However, the operational stability of the OLEDs based on TADF emitters (TADF-OLEDs) is still far from satisfaction, which impedes their prospective commercialization [13– 15,25,26]. Thus, methods to increase the operational stability of TADF-OLEDs have attracted increasing attention in the last several years [27–31]. Although the intrinsic cause for the instability of OLEDs is complex, it is generally accepted that the electrochemical deterioration and the severe triplettriplet annihilation (TTA), triplet-polaron annihilation (TPA), and singlet-triplet annihilation (STA) of the molecules in the vicinity of the recombination zone are intrinsically associated with the operational stability of the device [32–38]. By utilizing a stable dicarbazolylbenzene donor and a stable triazine acceptor. Lee et al. [28] designed and synthesized two stable blue TADF emitters, DCzTrz and DDCzTrz, and accomplished a long T_{80} lifetime (time to 80%) of initial luminance) of 52 h at an initial luminance of 500 cd/m². Adachi and co-workers [29] have developed four donor-acceptor (D-A) type TADF emitters consisting of a xanthone (XT) acceptor unit coupled with different donor units, and it is observed that adopting the donor units with non-planar peripheral substitutions can drastically restrain the concentration quenching behavior of TADF molecules by increasing their intermolecular distance in thin films to inhibit the electron-exchange interactions of triplet excitons. In 2016, our group [30] proposed a molecular structure with the luminance cores of TADF molecules sterically shielded by the tert-butyl units to simultaneously improve the efficiency and the operational stability of TADF-OLEDs, achieving a 5TCzBN based OLED with a maximum EQE as high as 21.2% and a record long T_{50} of 770 h at an initial luminance of 500 cd/m². Albeit these considerable efforts that have been made, to date only a few TADF emitters can realize good operational stability in OLEDs. Therefore, further design strategies for highly efficient and stable TADF emitters are still highly desired.

To realize a small ΔE_{ST} , most TADF emitters possess spatially separated electron-donors and acceptors. As aforementioned, to prepare stable TADF emitters, the adopted electron donor and acceptor moieties should possess excellent stability [28]. As one of the most commonly used electron-donors in TADF molecules, the carbazole unit features relatively good stability because it is made up of only aromatic moieties with high bond dissociation energies. However, the hydrogen atoms in the 3,6-positions of the carbazole are comparatively electrochemically active, leading to the dimerization [39,40], which hinders the long-term stability of the corresponding TADF emitters.

In the present study, we show that by simply modifying the carbazole units with peripheral groups, simultaneous enhancement of the efficiency and the operational stability of OLEDs can be realized. The *tert*-butyl and phenyl groups were attached to the 3,6-positions of carbazole units as

peripheral groups in two TADF emitters with a stable o-phthalodinitrile (PN) as the acceptor (named 2tBuCzPN and 2PhCzPN, respectively). The photo-physical and electrochemical properties of those emitters were systematically studied. Compared with their analogue 2CzPN that employs carbazole as the electron donor, the electrochemical stability of 2tBuCzPN and 2PhCzPN was dramatically improved, and the shortened exciton lifetimes were observed derived from the reduced $\Delta E_{\rm ST}$ s. Furthermore, the steric hindrance of the peripheral phenyl group can effectively restrain the intermolecular interaction. The OLEDs based on 2tBuCzPN and 2PhCzPN achieved improved maximum EQEs of 17.0% and 14.0%, respectively (8.5% for 2CzPN), and enhanced lifetimes with T_{50} of 7.6 and 13.4 h at 500 cd/m², respectively (1.7 h for 2CzPN), as well as reduced roll-off characteristic for the 2PhCzPN based OLED. These results have proved the rationality of carbazole modification with peripheral groups and potential advantages of TADF materials in OLEDs.

2 Experimental

2.1 Syntheses of 2CzPN, 2tBuCzPN and 2PhCzPN

The syntheses of the three TADF emitters: 4,5-di(9H-carbazol-9-yl)phthalonitrile (2CzPN), 4,5-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)phthalonitrile (2tBuCzPN), and 4,5-bis (3,6-diphenyl-9H-carbazol-9-yl)phthalonitrile (2PhCzPN), were easily achieved in a nitrogen atmosphere through aromatic nucleophilic substitution reactions by using carbazolyl units as nitrogen nucleophiles and the phthalonitrile unit as the electrophile, as outlined in Scheme 1. The syntheses were performed according to the synthetic methods reported previously [7,41]. The reagents and all the solvents were used as received without any further purification. 9H-carbazole (2.04 g, 12.2 mmol), 3,6-di-tert-butyl-9H-carbazole (3.41 g, 3.6-di-phenyl-9*H*-carbazole 12.2 mmol), or (3.89 g. 12.2 mmol) was dissolved in dry N,N-dimethylformamide (DMF) (20 mL) and then added dropwise to a stirred solution of potassium tert-butoxide (1.36 g, 12.2 mmol) in dry DMF (10 mL) under a nitrogen atmosphere at room temperature. After stirring at 40 °C for 30 min, 4,5-difluorophthalonitrile (1.0 g, 6.1 mmol) dissolved in dry DMF (10 mL) was added dropwise. The reaction mixture was stirred at 80 °C for 12 h. After it was cooled to room temperature, the reaction mixture was quenched with saturated potassium carbonate aqueous solution (100 mL), and the resulting precipitate was collected by filtration. The residue was dried in a vacuum drying oven at 100 °C for 5 h, and then purified by the column chromatography on the silica gel (petroleum ether:dichloromethane, 5:1, v/v). The three compounds were further purified by vacuum sublimation, yielding green or yellowish green powder. 2CzPN (1.95 g, 70%), ¹H NMR (400 MHz,



Scheme 1 The synthesis routes for TADF emitters

DMSO- d_6), δ (ppm): 7.05 (m, 8H), 7.27 (d, 4H), 7.88 (d, 4H), 7.66 (t, 8H), 8.80 (s, 2H); HRMS (ESI) m/z: [M]⁺ calculated for C₃₂H₁₈N₄, 458.1526, found, 458.2921. 2*t*BuCzPN (2.08 g, 50%), ¹H NMR (400 MHz, CDCl₃), δ (ppm): 1.33 (s, 36H), 6.78 (d, 4H), 6.93–6.96 (m, 4H), 7.26 (s, 4H), 7.63 (d, 4H), 8.26 (s, 2H); HRMS (ESI) m/z: [M]⁺ calculated for C₄₈H₅₀N₄, 682.4030, found, 682.5565. 2PhCzPN (1.86 g, 40%), ¹H NMR (400 MHz, DMSO- d_6), δ (ppm): 7.25–7.29 (m, 4H), 7.38 (t, 8H), 7.47 (s, 8H), 7.66 (t, 8H), 8.42 (d, 4H), 8.89 (d, 2H); HRMS (ESI) m/z: [M+Na]⁺ calculated for C₅₆H₃₄N₄Na, 785.2676, found, 785.2676 (Figure S1).

2.2 Material characteristics

The molecular structures of the products were determined with ¹H NMR, mass spectroscopy, and elemental analysis. The ¹H NMR spectra were measured by a JEOLAL-400 MHz spectrometer (Japan) at ambient temperature with tetramethylsilane as the internal standard. The high-resolution mass spectra were recorded on ESI IT-TOF MS, LCMS-IT/ TOF (Shimadzu, Japan). The thermal stabilities were investigated with thermal gravimetric analysis (TGA) under nitrogen atmosphere at a heating rate of 10 °C/min using a STA 409PC (Netzsch, Germany). The UV absorption spectra in toluene solutions at room temperature were obtained by an UV-Vis spectrophotometer (Agilent 8453, USA), and photoluminescence spectra (PL) spectra were recorded with a fluorospectrophotometer (Jobin Yvon, FluoroMax-3). The electrochemical properties of the three emitters were investigated by the cyclic voltammetry (CV) measurements on a Princeton Applied Research potentiostat/galvanostat Model 283 voltammetric analyzer. CV measurements were conducted in 2.0 mM concentrations of the three emitters in super dry dichloromethane at a scan rate of 150 mV/s at room temperature. The electrochemical cell comprised of disk platinum as a working electrode, an Ag wire electrode as a reference electrode standardized against ferrocene/ferrocenium (Fc/Fc^{+}), a platinum coil as an auxiliary electrode, and 0.1 M ⁿBu₄NClO₄ as a supporting electrolyte. The highest occupied molecular orbital (HOMO) energy level was calculated from the onset of the oxidation curve of the first sweep. The absolute potential of Fc/Fc^+ in nonaqueous electrolytes is 4.8 eV. This leads to the following equation: $E_{\text{HOMO}} = -4.8 - (E_{\text{ox}} - E_{1/2 \text{ (Fc/Fc}^+)}) \text{ eV.}$ The measured $E_{1/2 \text{ (Fc/Fc}^+)}$ has a little difference for the three emitters: 0.748, 0.745 and 0.720 V for 2CzPN, 2tBuCzPN and 2PhCzPN, respectively. The energy band gap (E_{g}) between HOMO and lowest unoccupied molecular orbital (LUMO) is calculated from the absorption edge (λ_{abs}). And the LUMO energy level is calculated from the formula E_g =LUMO-HOMO. Absolute photoluminescence quantum yields (PLQYs) of solutions and thin films were obtained using a Quantaurus-QY measurement system (C11347-11, Hamamatsu Photonics, Japan). Decay profiles of emission intensity were measured by an Edinburgh FLS 980 spectrometer (UK).

The single crystal of 2PhCzPN was grown from very slow evaporation of petroleum ether/dichloromethane (5:1, v/v) solutions at room temperature. The single-crystal X-ray experiment was performed on a RIGAKU SATURN 724 + CCD diffractometer equipped with graphite monochromatized Mo K α radiation. The structure (Figure S2, Supporting Information online) was solved by direct methods and refined with a full-matrix least-squares technique based on F2 with the SHELXL-97 crystallographic software package.

2.3 OLED devices fabrication and characterization

The patterned indium-tin-oxide (ITO) glass substrates with sheet resistance of 15 Ω /square were cleaned using chemical methods (see Supporting Information online), and then dried for 2 h under an infrared lamp. After a 10 min UV-ozone treatment, ITO substrates were immediately transferred into a deposition chamber. During the deposition process, the pressure of the chamber maintained at less than 10^{-5} Torr. The organic materials were sequentially deposited onto the cleaned ITO glass substrates through thermal evaporation at a rate of 0.5–1.0 Å/s. The layer thicknesses of the deposited materials were monitored in situ by the oscillating-quartz thickness monitors. Then a LiF buffer layer and an Al cathode were sequentially deposited onto the organic layers at a deposition rate of 0.1-0.2 Å/s and 2.0-6.0 Å/s, respectively. The devices were encapsulated in a glove box under nitrogen atmosphere. Then the current-voltage (J-V) characteristics of the devices were recorded with a Keithley 2400 sourcemeter (USA), and the EL spectra and Commission Internationale de L'Eclairage (CIE) color coordinates were measured with a Spectrascan PR-650 photometer (Photo Research, USA). All the measurements were carried out at room temperature under air atmosphere.

4

3 Results and discussions

3.1 Theoretical calculations

For insight into the effects of the substituent groups of the carbazole on the geometrical and electronic structures of the TADF emitters, density functional theory (DFT) and timedependent DFT (TDDFT) calculations were performed on 2CzPN, 2*t*BuCzPN, and 2PhCzPN at the B3LYP/6-31G(d) level with the Gaussian 09 package.

As shown in Figure 1, highly twisted structures with dihedral angles between the carbazolyl units and the PN acceptor in the range of 50-52 °C were observed from the optimized molecular structures of their S₀ states, leading to spatially separated frontier orbital distributions. The LUMOs of the three molecules are mostly distributed on the PN acceptors and only partially on the adjacent N atoms of the carbazolyl units, while the HOMOs are mainly localized on the donors and slightly on the PN acceptor. Therefore the overlaps between the HOMOs and the LUMOs of the three molecules are small, indicating that the HOMO-to-LUMO transition has a strong charge transfer character, thus small electron exchange energies can be expected.

Specifically, the HOMO of 2*t*BuCzPN scarcely disperses over the *tert*-butyl groups owing to the sp³-hybridized carbon atom, while that of 2PhCzPN delocalizes over the phenyl groups due to their conjugation nature, expanding the delocalization degree of the HOMO, so the overlap between the HOMO and LUMO of 2PhCzPN will be further decreased, leading to a smaller ΔE_{ST} . According to the results estimated from TDDFT calculation, the ΔE_{ST} of 2CzPN, 2*t*BuCzPN and 2PhCzPN are 0.34, 0.32 and 0.25 eV, respectively, which are small enough for efficient reverse intersystem crossing (RISC) (Table 1).

In the case of the spin density distributions (SDD) of the T_1 states, compared to that of 2CzPN distributing over the entire molecule, the introduced peripheral *tert*-butyl groups and phenyl groups partly cover the 2CzPN core like a shield, reducing the exposure degrees of the T_1 states of 2*t*BuCzPN and 2PhCzPN, respectively, which may suppress the triplet related annihilation, such as TTA, TPA and TSA, via restraining the intermolecular electron-exchange interactions of the triplet excitons.

3.2 Photo-physical characteristics

Figure 2(a, c, e) shows the absorption and PL spectra of



Figure 1 Calculated spatial distributions of HOMO and LUMO of TADF emitters in their S_0 states, and the spin density distribution (SDD) of their T_1 states, optimized at the DFT/B3LYP/6-31G(d) level (color online).

2CzPN, 2*t*BuCzPN, and 2PhCzPN in toluene solutions. The three molecules show very similar spectra. The strong absorption at around 290 nm could be ascribed to the π - π * transitions, while the weak absorption band at around 350–450 nm is attributed to the intra-molecular charge transfer (ICT) transition from the donor to the acceptor. At room temperature, all the three compounds exhibit broad and structureless emission bands. Besides, as the polarity of the solvent increases (Figure 2(b, d, f)), their emission peaks are red-shifted and the intensities of their emissions are reduced, which further manifests the ICT nature of the electronic transitions in these molecules.

The introduction of *tert*-butyl and phenyl groups to the carbazole units enhances their electron donating abilities, resulting in stronger ICT interactions. Thus the absorption edges shift to longer wavelengths in the order of 2CzPN (417 nm), 2tBuCzPN (438 nm), and 2PhCzPN (440 nm). Also, the energy levels of their S₁ states are considerably reduced in the order of 2CzPN (2.96 eV), 2tBuCzPN (2.82 eV), and 2PhCzPN (2.78 eV). On the other hand, the introduction of tert-butyl and phenyl groups slightly reduces the energy levels of their T₁ states, thus leading to a decrease in the $\Delta E_{\rm ST}$. From the energy difference between the onset of the emission spectrum at room temperature in toluene (S_1 energy level) and the highest peak of the emission spectrum at 77 K with 5 ms delay in toluene (T_1 energy level), the $\Delta E_{\rm ST}$ of 0.31, 0.24 and 0.19 eV are extracted for 2CzPN, 2tBuCzPN, and 2PhCzPN, respectively, which are in accord with the theoretical computational results. The PLQYs of

Table 1 Computed energy levels, exchange energies, and oscillator strengths of 2CzPN, 2tBuCzPN, and 2PhCzPN

	<u> </u>		e	,	· · · · · · · · · · · · · · · · · · ·			
	HOMO (eV)	LUMO (eV)	$E_{\rm g}~({\rm eV})$	$S_1 (eV)$	$T_1 (eV)$	$\Delta E_{\rm ST}$ (eV)	$f(S_0 \rightarrow S_1)$	
2CzPN	-5.90	-2.52	3.38	2.84	2.50	0.34	0.0898	
2tBuCzPN	-5.64	-2.39	3.25	2.73	2.41	0.32	0.1107	
2PhCzPN	-5.65	-2.55	3.10	2.61	2.36	0.25	0.1288	



Figure 2 (a, c, e) UV-Vis absorption and PL spectra of the TADF emitters measured in toluene solutions; (b, d, f) the emission spectra of the TADF emitters measured in *n*-hexane, toluene, and dichloromethane solutions at room temperature (color online).

2CzPN, 2*t*BuCzPN, and 2PhCzPN in aerated and de-aerated toluene solution are 22.5%/37.7%, 27.2%/50.7%, and 24.8%/69.1%, respectively. The photo-physical properties are summarized in Table 2.

3.3 Electrochemical properties and thermal stability

To investigate the effect of the substituent groups of the carbazole on the electrochemical properties of the TADF emitters, cyclic voltammetry multi-sweep was performed in super dry CH_2Cl_2 solutions. As shown in Figure 3, all the three compounds showed steady reversible reduction behavior during continuous 5 times cathodic scan, which can be attributed to the excellent electron-withdrawing and electron-transporting ability of the stable PN moiety. Although

the oxidation processes of the three compounds are all irreversible, the sweep curves of 2tBuCzPN and 2PhCzPNshowed little change during the multiple anodic scan, whereas that of 2CzPN was gradually changed with the current decreasing and a shoulder peak emerging, indicating that the introduction of peripheral groups to the 3,6-positions of carbazole units can dramatically enhance the electrochemical stability of the TADF emitters, which is of benefit to the operational stability of the corresponding OLED devices. Compared with the HOMO energy level of 2CzPN (-5.78 eV), shallower HOMOs are obtained for 2tBuCzPNand 2PhCzPN (-5.68 eV), which is consistent with the better hole-injection abilities of the tBuCz and PhCz donors.

In addition, all the three molecules show good thermal stability (Figure 4), with high decomposition temperatures of

 Table 2
 Photo-physical properties of 2CzPN, 2tBuCzPN, and 2PhCzPN

	Absorption ^{a)} (nm)	Emission ^{a)} (nm)	${{ m S_1}^{b)}}$ (eV)	$T_1^{c)}$ (eV)	$\Delta E_{\rm ST}$ (eV)	$E_{\rm HOMO}^{\rm d)}$ (eV)	$E_{\rm LUMO}^{e)}$ (eV)	PLQY ^{f)} (prompt/total)	$k_{\mathrm{RISC}} \overset{\mathrm{g})}{(\mathrm{s}^{-1})}$
2CzPN	289/330/376	470	2.96	2.65	0.31	-5.78	-2.81	(22.5%/37.7%)	1.74×10 ⁵
2tBuCzPN	296/338/387	491	2.82	2.58	0.24	-5.68	-2.85	(27.2%/50.7%)	5.93×10 ⁵
2PhCzPN	287/346/395	500	2.78	2.59	0.19	-5.68	-2.86	(24.8%/69.1%)	1.58×10^{6}

a) All data were measured in toluene solutions at a concentration of 10^{-5} M for 2CzPN, 2*t*BuCzPN, and 2PhCzPN; b) S₁ is calculated from the onset of the emission spectrum in toluene at r.t. (Figure S3); c) T₁ is calculated from the highest peak of the emission spectrum in toluene at 77 K with 5 ms delay; d) E_{HOMO} is calculated from the onset of oxidation curve of cyclic-voltammetry (Figure 3); e) E_{LUMO} is calculated from E_{HOMO} plus the energy of λ_{abs} ; f) ϕ_{PL} (prompt) was measured in toluene solution without degassing oxygen, and ϕ_{PL} (total) was measured after the toluene solution was degassed by N₂ bubbling for 10 min; g) the calculation method of k_{RISC} is clarified in the supporting information.



Figure 3 Repeated cyclic voltammograms for 2CzPN, 2*t*BuCzPN, and 2PhCzPN in CH₂Cl₂ solutions (color online).

322, 333, and 447 °C for 2CzPN, 2*t*BuCzPN, and 2PhCzPN, respectively. Moreover, the glass transition temperature (T_g) of 2PhCzPN is as high as 187 °C (Figure S4), which is beneficial to the stability of its amorphous films and thus device operational stability.



Figure 4 The TGA curves of TADF emitters (color online).

3.4 PL characteristics and morphology of solid films

To further compare the photo-physical properties of the three emitters in solid films, both pure films and films of the emitters doped in bis[2-(diphenylphosphino)phenyl] ether oxide (DPEPO) with a concentration of 20 wt% were fabricated by vacuum evaporation. DPEPO was chosen as the host material because of its high T_1 state, which suppresses back energy transfer from the guest to the host and confines the triplet excitons within the guest molecules. The pure films were fabricated in order to see if the peripheral groups could inhibit the aggregation induced quenching at high exciton density.

Compared with the PL spectra of the toluene solutions, the emission peaks of the doped films are red-shifted to 494, 508 and 531 nm for 2CzPN, 2*t*BuCzPN, and 2PhCzPN, respectively (Figure 5(b)), owing to the highly doped concentration. The PLQYs of the doped films are 82.4% for 2CzPN, 88.1% for 2*t*BuCzPN, and 89.2% for 2PhCzPN (Table 3), which increase in the same order as the PLQYs of toluene solutions. The higher PLQYs of the doped films are due to the fact that some molecular rotations and violations are restrained in the rigid films. The pure films' emission peaks are further red-shifted (Figure 5(d)), and the PLQYs of all the pure films are lower than those of the doped films because of the severe aggregation induced quenching. Specifically, the



Figure 5 The PL transient decay spectra of the doped films (a) and the pure films (c); the PL spectra at room temperature of the doped films (b) and the pure films (d) (color online).

 Table 3
 Photo-physical properties of doped films and pure TADF emitter films ^{a)}

		DPEPO	Pure emitter			
	$\tau_{\rm p}~({\rm ns})$	$\tau_{\rm d}~(\mu { m s})$	λ_{\max} (nm)	$\phi_{ m PL}$	λ_{\max} (nm)	$\phi_{ m PL}$
2CzPN	22.0	5.0	494	82.4%	512	65.2%
2 <i>t</i> BuCzPN	24.0	2.0	508	88.1%	515	52.8%
2PhCzPN	27.5	1.5	531	89.2%	545	77.8%

a) The data were measured with an excitation wavelength of 360 nm.

PLQY of the pure 2*t*BuCzPN film decreased significantly to 52.8%, which could infer that the introduction of *tert*-butyl groups altered the molecular stacking structure in which way the aggregation induced quenching could not be effectively suppressed [42]. While the PLQY of the pure 2PhCzPN film only decreased to 77.8%, which was probably because the steric hindrance of phenyl groups increased the intermolecular distance and restrained the bimolecular interaction, indicating that the introduction of phenyl groups to the carbazole can partly inhibit the concentration quenching of the TADF emitter.

Similar to the previously reported TADF emitter—2CzPN [7,32], both 2*t*BuCzPN and 2PhCzPN exhibited two exponential PL decay components (Figure 5(a)), which consisted of prompt fluorescence with a lifetime (τ_p) of 24–27.5 ns, followed by delayed fluorescence with shorter lifetimes (τ_d) of 1.5–2.0 µs than that of 2CzPN (5.0 µs) due to their smaller ΔE_{ST} and hence faster RISC process (see k_{RISC}

in Table 2 and Table S1, Supporting Information online). Besides, the proportion of the delayed component in the total emission increases with the introduction of *tert*-butyl and phenyl groups (ϕ_{TADF} =15.2%, 23.5%, and 44.3% for 2CzPN, 2*t*BuCzPN and 2PhCzPN, respectively), which agree with the decrease of their ΔE_{ST} . For the pure films, 2PhCzPN showed the largest proportion of the delayed component (Figure 5(c)), which means less aggregation induced quenching occurred.

As the *tert*-butyl substitution has been proved to be of benefit to the solubility of the TADF emitter and thus the morphology of its solution-processed film [12], we examined whether the introduction of *tert*-butyl and phenyl groups affects the morphology of the guest-host co-evaporated films. Atomic force microscopy (AFM) analysis of the DPEPO:20 wt% TADF emitter co-evaporated films revealed that the introduction of the peripheral groups has little effect on the surface roughness of the co-evaporated films, as the root-mean-square values of the three films were similar and less than 1 nm (Figure S5), implying uniform dispersion of the TADF emitters in the host material.

3.5 OLEDs' performances

Using these doped films as emitting layers (EML), multilayer OLEDs were fabricated. The structures and energy levels of the molecules used in the devices were shown in Figure 6. The OLEDs' structures were: ITO/HATCN (5 nm)/ NPB (30 nm)/TCTA (10 nm)/mCP (10 nm)/DPEPO:x% emitter (30 nm)/DPEPO (10 nm)/Bphen (30 nm)/LiF (0.5 nm)/Al(150 nm), where 1,4,5,8,9,11-hexaazatriphenylene hexacarbonitrile (HATCN) was used as the hole-injection layer (HIL), 4,4'-N,N'-bis[N-(1-naphthyl)-Nphenylamino] biphenyl (NPB) and tris(4-(9H-carbazol-9yl)-phenyl)amine (TCTA) as the hole transporting layer (HTL), 1,3-bis(carbazol-9-vl)benzene (mCP) and DPEPO as the exciton-barrier layers, bathophenanthroline (Bphen) as the electron-transporting layer (ETL), LiF as the electroninjection layer (EIL). The doping concentrations of the emitters were optimized to be 20 wt% for 2CzPN, 30 wt% for 2tBuCzPN and 2PhCzPN. The electroluminescence (EL) characteristics of the OLEDs are shown in Figure 7, and their electrical performance data are summarized in Table 4 (Figure S6 shows the EQE-Brightness characteristics and EL spectra of the doped devices at different concentrations).



Figure 6 The energy level diagram and structures of the materials used in OLEDs (color online).

The OLED containing 2CzPN gave bluish green EL centered at 494 nm with color coordinates of CIE (0.23, 0.42), and showed a turn on voltage of 5.5 V, a peak power effi-



Figure 7 The electrical characteristics and EL spectra of the OLEDs (color online).

Host:DPEPO	EQE (%)	PE (lm/W)	Von	EQE (%)	$V(\mathbf{V})$	PE (lm/W)	λ_{\max}	T_{50} (h)
	max		(V)	@1000 cd/m ²			(nm)	$@500 \text{ cd/m}^2$
20% 2CzPN	8.5	10.0	5.5	4.1	11.6	2.7	494	1.7
30% 2tBuCzPN	17.0	29.0	4.2	7.7	8.6	8.3	518	7.6
30% 2PhCzPN	14.0	33.0	3.8	10	9.0	11.0	532	13.4

Table 4 The electrical performances of OLEDs

ciency of 10 lm/W, a maximum EQE of 8.9% and a EQE of 4.1% at 1000 cd/m² without any light out-coupling enhancement. The quite high turn-on voltage is owing to the broad energy gap of DPEPO, and the EL spectrum of the OLED is almost identical to the PL spectrum of the EML. Besides, the EL spectra at different driving voltages (Figure S7) are identical, indicating that the charge carriers injected and transported evenly in the EML. The OLEDs employing 2*t*BuCzPN and 2PhCzPN emitted green light peaked at 518 nm with color coordinates of CIE (0.30, 0.53) and 532 nm with color coordinates of CIE (0.37, 0.56), respectively. The maximum EQEs of the two OLEDs are higher than that of 2CzPN based OLED, 17% for 2*t*BuCzPN and 14% for 2PhCzPN, owing to the more efficient RISC process resulted from their smaller ΔE_{ST} .

Furthermore, the degrees of efficiency roll-off are compared through the ratios of EQE at 1000 cd/m^2 to EQE_{max}, which is 48%, 45%, and 71% for 2CzPN, 2tBuCzPN, and 2PhCzPN based OLEDs, respectively. The 2PhCzPN based OLED possesses improved roll-off characteristics and it can remain a high EQE up to 10% at 1000 cd/m^2 . The operation lifetimes of the OLEDs were measured under a constant current at an initial brightness of 500 cd/m², and the results are presented in Figure 7(d) and Table 4. The T_{50} of the 2CzPN, 2tBuCzPN, and 2PhCzPN based devices are 1.7, 7.6 and 13.4 h, respectively. Although the red-shift of emission spectrum is beneficial to the device lifetime, the triplet excitons related annihilation and the molecular electrochemical stability are also crucial to OLED longevity [43]. As these three emitters process similar T_1 energies, we concluded that the greatly prolonged lifetime of the 2PhCzPN based device can be attributed to the improved electrochemical stability and the shorter τ_d of 2PhCzPN as well as the steric hindrance of the phenyl groups to suppress the quenching process of the triplet excitons, indicating that the introduction of the phenyl groups to the 3,6-positions of the carbazole can be an effective method to increase the efficiency and operational stability of the TADF based OLEDs.

While Adachi's group [31] reported that operational stability enhances by introducing a second type of donor such as the phenyl unit in a D-A type emitter according to the acceleration of the RISC, we strongly believe that the remarkable improvement of device lifetime of the 2PhCzPN based OLED results from a combination of the enhanced electrochemical stability, the shorter τ_d of 2PhCzPN, and the steric hindrance of the phenyl groups.

4 Conclusions

In conclusion, we have comprehensively explored the influence of the peripheral tert-butyl and phenyl groups introduced to the 3,6-positions of the carbazole on the photophysical and electrochemical properties of the corresponding TADF materials, 2tBuCzPN and 2PhCzPN. Compared with 2CzPN whose 3,6-positions of the carbazole units are left unblocked, 2tBuCzPN and 2PhCzPN are verified to have improved electrochemical stability and shorter excited-state lifetimes due to their faster RISC processes. The EQEs of the OLEDs incorporating 2tBuCzPN and 2PhCzPN were increased to 17.0% and 14.0%, respectively, and that of 2PhCzPN based OLED remained as high as 10% even at a luminance of 1000 cd/m² for the largest k_{RISC} and the restraining function of the phenyl groups. In addition, the T_{50} of 2PhCzPN based OLED was dramatically improved to 13.4 h compared with that of 2CzPN based device (1.7 h). Thus, the introduction of phenyl groups to the electrochemically active sites of the carbazole (namely, 3,6-positions) can prepare TADF emitters with excellent stability, and will simultaneously improve the efficiency and operational stability of the corresponding OLED devices.

Acknowledgements This work was supported by the National Key Research and Development Program of China (2017YFA0204501), and the National Science Fund of China (51525304, 61890942, U1601651).

Conflict of interest The authors declare that they have no conflict of interest.

Supporting information The supporting information is available online at http://chem.scichina.com and http://link.springer.com/journal/11426. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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