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## Introduction

Due to their advantages of low driving voltage, high luminous efficiency, fast response, flexibility, being ultra-thin and so on, organic light-emitting diodes (OLEDs) are thought to be the next-generation technology for flat panel displays and solid-state light-ing sources.<sup>1–3</sup> Depending on the light-emitting mechanism, organic light-emitting materials can be classified into fluorescent and phosphorescent materials.<sup>4–8</sup> Pure organic molecules with thermally activated delayed fluorescence (TADF) properties are considered the third-generation materials for OLEDs, because of their ability to effectively harvest both singlet and triplet excitons for radiative transitions.<sup>9,10</sup> With the vigorous developments of all kinds of ways of light emission, efficient red and green materials have been quite mature, but the molecular design of

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# Synthesis and structure-property correlation of blue fluorescence isomer emitters based on rigid pyrazine-bridged carbazole frameworks<sup>†</sup>

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Three novel blue fluorescence isomer emitters, namely 2,5-bis(6,9-bis(4-(tert-butyl)phenyl)-9H-carbazol-3-yl)pyrazine (TCz-3PA-TCz), 9-(5-(6,9-bis(4-(tert-butyl)phenyl)-9H-carbazol-3-yl)pyrazin-2-yl)-3,6bis(4-(tert-butyl)phenyl)-9H-carbazole (TCz-3,9PA-TCz) and 2,5-bis(3,6-bis(4-(tert-butyl)phenyl)-9Hcarbazol-9-yl)pyrazine (TCz-9PA-TCz), with a donor-acceptor-donor structure were synthesized and characterized. TCz-3,9PA-TCz in the thin solid powder state showed much higher thermal stability than TCz-3PA-TCz and TCz-9PA-TCz. The maximum photoluminescent emission wavelengths of TCz-3PA-TCz, TCz-3,9PA-TCz and TCz-9PA-TCz in toluene solution were 423, 435 and 454 nm, which were aggregationinduced guenching active. The absolute photoluminescent guantum yields of doped films for TCz-3PA-TCz, TCz-3,9PA-TCz and TCz-9PA-TCz were 10.75%, 4.46% and 16.70%, which were considerably improved relative to those of the pure film. The driving voltage, maximum external quantum efficiency, current efficiency, power efficiency and luminance of doped OLEDs based on TCz-9PA-TCz fabricated by spin coating were 4.0 V, 2.67%, 4.12 cd  $A^{-1}$ , 2.46 lm  $w^{-1}$  and 8052 cd  $m^{-2}$ . Furthermore, the doped OLEDs with TCz-3,9PA-TCz as a dopant fabricated by thermal deposition in vacuum showed a driving voltage of 3.5 V, maximum luminance of 6369.67 cd m<sup>2</sup> and maximum external quantum efficiency of 3.85% at a brightness of 100 cd m<sup>-2</sup>. The linking model analogous to TCz-3,9PA-TCz was validated to be a more feasible way to combine pyrazine with carbazole moieties to produce highly efficient and stable electroluminescent blue light materials.

> high-efficiency organic blue materials is greatly limited by their inherent wide band gap, carrier charge transporting imbalance and low efficiency in the solid state.<sup>11,12</sup> Therefore, the synthesis of highly efficient and stable organic blue light materials is still one of the focuses of OLEDs.

> To obtain efficient and stable organic blue light materials for high performance OLEDs, researchers have presented a synthesis methodology of organic donor-acceptor (D-A) conjugated molecules to finely adjust the emission wavelength, efficiency and lifetime of the obtained emitters.<sup>13</sup> Through the asymmetric D-A molecular design, it can make the electron injection and transporting capability of the emitting layer fully match with the energy levels of electrodes and interfacial layers. The D-A molecular framework can form a carrier transporting channel inside a single molecule, which can promote intramolecular charge transfer (ICT) to some degree, thereby improving the carrier transporting capacity of the molecule as a whole.<sup>14-16</sup> On the other hand, the D-A molecular framework exhibits the properties of electron acceptors when attached to strong electron donors, and exhibits the properties of electron donors when attached to strong electron acceptors. The strength of pushingpulling electrons can be balanced by changing electron donors



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and acceptors, which makes the fine control of molecular energy levels easy and straightforward. Huang et al.17-19 proposed a strategy to control the molecular energy levels of polymers through a p-n diblock structure by using an alkoxy group as an electron-donating group and a cyano group as an electronwithdrawing group to push and pull the electron cloud in the main chain of poly(1-methyl-4-vinylbenzene), which made the lowest unoccupied molecular orbital (LUMO) energy levels -3.58 to -2.7 eV and the highest occupied molecular orbital (HOMO) energy levels -5.5 to -4.8 eV. Furthermore, as a typical feature of organic TADF materials, ICT characteristics can reduce the electronic exchange energy and achieve a small singlet-triplet splitting energy.<sup>20,21</sup> In 2017, Adachi et al.<sup>22</sup> reported TADF OLEDs based on triazine and carbazole units, in which the electronic interaction was very important for the TADF mechanism between triazine and carbazole. The deep blue light device achieved high external quantum efficiencies over 19.2% and Commission International de L'Eclairage (CIE) coordinates of (0.15, 0.10). However, the ICT characteristic sometimes also causes the emitting wavelength of the materials to red shift and the full width at half-maximum becomes wider, resulting in unexpected poor color purity. Our group has long committed to exploring new organic electroluminescent blue light materials for high-tech applications.<sup>23-25</sup> Carbazole and its derivatives, owing to their aromatic biphenyl structures with a wide energy gap in the backbones and highly efficient electroluminescence coupled with a high hole mobility and good processability, have emerged as an attractive class of conjugated materials for organic blue light-emitting materials, hole-transporting materials and hosts for phosphorescent and TADF OLEDs.<sup>26</sup> Similarly, diazine compounds contain a benzene ring in which two of the C-H fragments have been replaced by isolobal nitrogen, producing three electron-deficient isomers of pyridazine, pyrimidine and pyrazine. The availability of specific and highly region-selective coupling reactions of carbazole and diazine moieties is expected to provide a rich variety of tailored materials to finely tune the general optoelectronic properties in a wide range.27 To the best of our knowledge, there are few examples about the structure-property correlation of blue fluorescence isomer emitters based on rigid pyrazine-bridged carbazole frameworks with an ICT characteristic. In this report, three novel blue fluorescent isomer emitters TCz-3PA-TCz, TCz-3,9PA-TCz and TCz-9PA-TCz with ICT characteristics were synthesized and characterized. The results illustrated that the thermal stability, photophysical properties, energy levels and OLED performance were strongly correlated with the chemical structure of the isomer emitters.

### **Experimental section**

#### Materials and measurements

**Materials.** 3,6-Dibromocarbazole, 1-*tert*-butyl-4-phenylboronic acid, tetrakis(triphenylphosphine)palladium ( $Pd(PPh_3)_4$ ), 9*H*-carbazole, 1-*tert*-butyl-4-iodobenzene, *N*-bromosuccinimide, tetrabutylammonium bromide (TBAB), boranoic acid pinacol ester

and 2,5-dibromo-pyrazine purchased from Shanghai Energy Chemical were used directly in the experiment without further purification, and the solvents used in the experiments were purified by standard methods. Anhydrous tetrahydrofuran and toluene were distilled over sodium and benzophenone under a nitrogen atmosphere.

General information. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were measured on a Varian Mercury Plus 400 NMR spectrometer with tetramethyl silane as a reference. In the NMR tests, CDCl<sub>3</sub> (chemical shift set to 7.26 ppm) was used to dissolve the samples. The molecular weights of the samples were acquired using a Bruker Daltonics Flex matrix-assisted laser desorption time-of-flight mass (MALDI-TOF-MS) analysis spectrometer. Ultraviolet (UV) visible absorption spectra were measured by using a UV-3600 SHIMADZU UV-vis-NIR spectrophotometer. Photoluminescent (PL) spectra were measured by using a LS 55 fluorescence luminescence spectrophotometer. The absolute photoluminescent quantum yields (PLQYs) were determined by using a \*/FLS920 steady state transient fluorescence system. The concentration of the solution for the tests is  $10^{-5}$  mol L<sup>-1</sup>, and the thin solid film used was obtained by spin coating the dichloromethane solution  $(10^{-3} \text{ mol } L^{-1})$  of the emitters on quartz plates. The glass transition temperatures  $(T_g)$  of the samples were characterized by using a PerkinElmer Diamond differential scanning calorimeter (DSC) at a heating rate of 10 °C min<sup>-1</sup> in a scanning range of 25–200 °C under a nitrogen atmosphere. Thermal 5% weight loss analysis was performed on a SEIKO EXSTAR 6000TG/DTA 6200 at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere. Cyclic voltammetry (CV) experiments were performed by using a three-electrode structure of a glassy carbon electrode, a platinum wire electrode and a silver reference electrode. Oxidation and reduction potentials were measured in dichloromethane and tetrahydrofuran with tetrabutylammonium hexafluorophosphate (0.1 mol  $L^{-1}$ ) as the supporting electrolyte and ferrocene as the internal standard at a scan rate of 100 mV s<sup>-1</sup>.

Device fabrication and measurements. The OLED structure fabricated by spin coating is ITO/PEDOT:PSS (30 nm)/CBP:TCznPA-TCz (55 nm)/TPBi (35 nm)/Ca:Ag, where 4,4'-bis(9carbazolyl)-1,1'-biphenyl (CBP) was used as a host with doping TCz-nPA-TCz at a concentration of 5% by weight (devices A1, A2 and A3); poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and 2,2',2"-(1,3,5-benzinetriyl)-tris(1-phenyl-1-Hbenzimidazole) (TPBi) were used as hole transporting and electron transporting layers. The OLED structure fabricated by thermal deposition in vacuum is ITO/MoO<sub>3</sub> (1 nm)/TAPC (20 nm)/mCP (10 nm)/DPEPO:TCz-3,9PA-TCz/TmPyPB (40 nm)/ LiF (0.7 nm)/Al (120 nm), where TCz-3,9PA-TCz is doped in a high triplet energy host of bis[2-(diphenylphosphino)phenyl]ether oxide (DPEPO) at a concentration of 45% by weight. A hole transporting layer of 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC) and an electron transporting layer of 1,3,5-tris(3pyridyl-3-phenyl)benzene (TmPyPB) were introduced into the device to achieve efficient exciton recombination, and N,N'dicarbazolyl-3,5-benzene (mCP) layers were inserted between the TAPC layer and emitting material layer to block the excitons.

The current density-brightness-voltage of the device was recorded on a system consisting of a Keithley source measurement unit (Keithley 2400 and Keithley 2000) and a calibrated silicon photodiode. The electroluminescent spectra and CIE coordinates were measured using a PR-655 spectral scanning spectrometer. All measurements were conducted at ambient temperature.

#### Synthesis of the target compounds

9-(4-(tert-Butyl)phenyl)-9H-carbazole<sup>28,29</sup>. A mixture of 9H-carbazole (4.0 g, 23.9 mmol), 1-tert-butyl-4-iodobenzene (7.0 g, 26.9 mmol), Cu (0.5 g, 7.5 mmol), potassium carbonate solid (10.2 g, 60 mmol) and 60 mL nitrobenzene was added to a 150 mL flask. The mixtures were refluxed at 180 °C for 24 h under a nitrogen atmosphere. After nitrobenzene was distilled off under reduced pressure, the residue was extracted with H<sub>2</sub>O and dichloromethane three times. The solvent in the organic layer was evaporated under reduced pressure. The crude product was purified by column chromatography (petroleum ether/dichloromethane by volume = 20:1) to give 4.6 g 9-(4-(tert-butyl)phenyl)-9H-carbazole as a white solid in a yield of 64%. <sup>1</sup>H-NMR of compound 9-(4-(tert-butyl)phenyl)-9Hcarbazole (400 MHz,  $CDCl_3$ ):  $\delta$  = 8.16–8.14 (d, J = 8.0 Hz, 2H), 7.62-7.60 (d, J = 8.0 Hz, 2H), 7.50-7.48 (d, 2H), 7.44-7.40 (dd, J<sub>1</sub> = 8.0 Hz, J<sub>2</sub> = 16.0 Hz, 4H), 7.29–7.28 (d, J = 4.0 Hz, 2H), 1.44 (m, 9H).

3,6-Bis(4-(tert-butyl)phenyl)-9H-carbazole<sup>30</sup>. A mixture of 3,6-dibromocarbazole (3.0 g, 9.25 mmol), 1-tert-butyl-4-phenylboronic acid (4.0 g, 22.4 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.9 g, 0.78 mmol), TBAB (2 mg, 0.005 mmol), potassium carbonate aqueous solution (30 mL, 2 mol  $L^{-1}$ , 60 mmol), and 80 mL deoxygenated toluene was added to a 200 mL flask. The mixture was heated to 90 °C and refluxed under a nitrogen atmosphere for 24 h. After evaporation of the solvent, the residue was diluted with H<sub>2</sub>O and extracted with dichloromethane. The solvent in the organic layer was evaporated under reduced pressure. The crude product was purified by column chromatography (petroleum ether: ethyl acetate by volume = 10:1). 2.4 g pale yellow powder was obtained in a yield of 60%. <sup>1</sup>H-NMR of compound 3,6-bis(4-(tert-butyl)phenyl)-9*H*-carbazole (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.32–8.31 (d, J = 4.0 Hz, 2H), 8.16 (s, 1H), 7.66 (m, 6H), 7.50 (m, 6H), 1.45-1.39 (m, 18H). MALDI-TOF, m/z: theoretical value: 431.26, experimental value: 431.35.

**3,6-Dibromo-9-(4-(***tert***-butyl)phenyl)-9***H***-carbazole<sup>29</sup>. 9-(4-***tert***-Butyl-benzene)-9***H***-carbazole (4.0 g, 13.4 mmol),** *N***-bromosuccinimide (7.0 g, 40.0 mmol) and 45 mL** *N***,***N***-dimethylformamide were added to a 100 mL flask. The mixture was stirred at room temperature for 12 h. The reaction solution was dissolved in ethyl acetate and further washed with H<sub>2</sub>O several times. The solvent in the organic layer was evaporated under reduced pressure. The crude product was purified by column chromatography (petroleum ether : ethyl acetate by volume = 20 : 1). A pale yellow powder of 4.8 g was obtained in a yield of 80%. <sup>1</sup>H-NMR of compound 3,6-dibromo-9-(4-(***tert***-butyl)phenyl)-9***H***-carbazole (400 MHz, CDCl<sub>3</sub>): \delta = 8.19 (d,** *J* **= 2.0 Hz, 2H), 7.62–7.60 (d,** *J* **= 8.0 Hz, 2H), 7.50–7.48 (d,** *J* **= 8.0 Hz, 2H), 7.42–7.40 (d,** *J* **= 8.0 Hz, 2H), 7.50–7.48 (d,** *J* **= 8.0 Hz, 2H), 7.42–7.40 (d,** *J* **= 8.0 Hz, 2H), 7.50–7.48 (d,** *J* **= 8.0 Hz, 2H), 7.42–7.40 (d,** *J* **= 8.0 Hz, 2H), 7.50–7.48 (d,** *J* **= 8.0 Hz, 2H), 7.42–7.40 (d,** *J* **= 8.0 Hz, 2H), 7.50–7.48 (d,** *J* **= 8.0 Hz, 2H), 7.50–7.40 (d,** *J* **= 8.0 Hz, 2H), 7.50–7.50 (d,** *J* **= 8.0 Hz, 2H), 7.50–** 

2H), 7.28–7.26 (d, *J* = 8.0 Hz, 2H), 1.44 (m, 9H); MALDI-TOF, *m*/*z*: theoretical value: 461.01, experimental value: 461.28.

**3-Bromo-6,9-bis(4-(***tert***-butyl)phenyl)-9***H***-carbazole<sup>30</sup>. 3-Bromo-6,9-bis(4-(***tert***-butyl)phenyl)-9***H***-carbazole was synthesized following the same synthetic procedure for 3,6-bis(4-(***tert***-butyl)phenyl)-9***H***-carbazole. 9-(4-***tert***-Butyl-benzene)-3,6-dibromo-9***H***-carbazole (6.0 g, 13.14 mmol), 1-***tert***-butyl-4-phenylboronic acid (2.34 g, 13.14 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.9 g, 0.78 mmol), TBAB (2 mg, 0.005 mmol), potassium carbonate aqueous solution (30 mL, 2 mol L<sup>-1</sup>, 60 mmol), 80 mL deoxygenated toluene. 2.5 g white powder was obtained in a yield of 38%. <sup>1</sup>H-NMR of compound 3-bromo-6,9-bis(4-(***tert***-butyl)phenyl)-9***H***-carbazole (400 MHz, CDCl<sub>3</sub>): \delta = 8.29 (t, 2H), 7.67–7.60 (m, 5H), 7.53–7.43 (m, 6H), 7.31 (s, 1H), 1.46–1.42 (m, 9H), 1.41–1.37 (m, 9H), MALDI-TOF,** *m/z***: theoretical value: 510.21, experimental value: 510.63.** 

3,9-Bis(4-(tert-butyl)phenyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole<sup>31</sup>. A mixture of 3-bromo-6,9-bis(4-tertbutyl-benzene)-9H-carbazole (2.0 g, 7.33 mmol), boranoic acid pinacol ester (1.85 g, 7.33 mmol), [1,1-bis(diphenylphosphino)ferrocene]palladium dichloride (0.1 g, 0.73 mmol), potassium acetate solid (1.0 g, 10 mmol) and 40 mL 1,4-dioxane was added to a 100 mL flask. The mixture was refluxed at 80 °C for 24 h under a nitrogen atmosphere. After completion of the reaction, the residue was extracted with H<sub>2</sub>O and dichloromethane three times. The solvent in the organic layer was evaporated under reduced pressure. The crude product was purified by column chromatography (petroleum ether: ethyl acetate by volume = 10:1). A white powder of 2.4 g was obtained in a yield of 59%. <sup>1</sup>H-NMR of compound 3,9-bis(4-(*tert*-butyl)phenyl)-6-(4,4,5,5tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.68 (s, 1H), 8.40 (s, 1H), 7.84 (s, 1H), 7.69-7.57 (m, 5H), 7.53-7.33$ (m, 6H), 1.41-1.37 (m, 30H), MALDI-TOF, *m/z*: theoretical value: 557.35, experimental value: 556.77.

TCz-3PA-TCz. TCz-3PA-TCz was synthesized following the same synthetic procedure for 3,6-bis(4-(tert-butyl)phenyl)-9Hcarbazole.<sup>30</sup> 3,9-Bis(4-(tert-butyl)phenyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (1.00 g, 1.8 mmol), 2,5-dibromo-pyrazine (0.214 g, 0.9 mmol), potassium carbonate aqueous solution (30 mL, 2 mol  $L^{-1}$ , 60 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.1 g, 0.1 mmol), TBAB (2 mg, 0.005 mmol) and 10 mL deoxygenated toluene. 0.3 g yellow powder was obtained in a yield of 25%. <sup>1</sup>H-NMR of compound TCz-3PA-TCz (400 MHz,  $CDCl_3$ ):  $\delta$  = 9.29–9.27 (d, J = 8.0 Hz, 2H), 8.97–8.96 (d, J = 4.0 Hz, 2H), 8.54-8.52 (d, J = 8.0 Hz, 2H), 8.20-8.18 (d, J = 8.0 Hz, 2H), 7.82-7.50 (m, 22H), 1.54-1.42 (m, 36H). <sup>13</sup>C-NMR of compound **TCz-3PA-TCz** (100 MHz, CDCl<sub>3</sub>);  $\delta$  = 29.74, 31.47, 34.56, 34.88, 110.42, 110.59, 118.91, 123.92, 124.21, 125.82, 126.48, 126.89, 126.99, 134.60, 133.75 138.97, 140.99, 142.27, 149.64, 150.50, 150.81. MALDI-TOF, m/z: theoretical value: 938.53, experimental value: 938.74. Elemental analysis: calcd (%) for C<sub>68</sub>H<sub>66</sub>N<sub>4</sub>: C 86.95, H 7.08, N 5.96; found: C 86.79, H 7.22, N 5.81.

**L1. L1** was synthesized following the same synthetic procedure for **TCz-3PA-TCz**.<sup>30</sup> 3,9-Bis(4-tetra-*tert*-butyl-benzene)-6-(4,4, 5,5-tetramethyl-[1,3,2]dioxapentyl boron alkyl)-9*H*-carbazole (0.668 g, 1.2 mmol), 2,5-dibromo-pyrazine (0.714 g, 3 mmol), potassium carbonate aqueous solution (30 mL, 2 mol L<sup>-1</sup>, 60 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.1 g, 0.1 mmol), TBAB (2 mg, 0.005 mmol) and 10 mL deoxygenated toluene. 0.42 g white powder was obtained in a yield of 58%. <sup>1</sup>H-NMR of compound L1 (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.92 (s, 1H), 8.85 (s, 1H), 8.75 (s, 1H), 8.45 (s, 1H), 8.04 (s, 1H), 7.72–7.68 (m, 4H), 7.56–7.48 (m, 6H), 7.05 (s, 1H), 1.48–1.44 (m, 18H). MALDI-TOF, *m*/*z*: theoretical value: 587.19, experimental value: 588.14.

**TCz-3,9PA-TCz. TCz-3,9PA-TCz** was synthesized following the same synthetic procedure for 9-(4-(*tert*-butyl)phenyl)-9*H*carbazole.<sup>28,29</sup> 3,6-Bis(4-*tert*-butyl-benzene)-9*H*-carbazole (1.2 g, 2.7 mmol), **L1** (0.42 g, 0.7 mmol), Cu (0.5 g, 7.5 mmol), potassium carbonate solid (10.2 g, 60 mmol) and 15 mL nitrobenzene. 0.4 g yellow powder was obtained in a yield of 67%. <sup>1</sup>H-NMR of compound **TCz-3,9PA-TCz** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.35–9.30 (s, 1H), 9.20 (s, 1H), 9.00 (s, 1H), 8.60 (s, 1H), 8.41–8.40 (d, *J* = 4.0 Hz, 2H), 8.06–8.04 (d, *J* = 8.0 Hz, 2H), 7.80–7.70 (m, 11H), 7.60–7.45 (m, 11H), 1.45–1.40 (m, 36H). <sup>13</sup>C-NMR of compound **TCz-3,9PA-TCz** (100 MHz, CDCl<sub>3</sub>);  $\delta$  = 31.48, 34.58, 34.90, 110.53, 110.72, 111.60, 118.66, 125.37, 125.84, 126.03, 126.50, 126.94, 126.99, 133.85, 134.54, 134.95, 138.70, 138.90, 138.99, 139.32, 140.23, 141.04, 146.17, 149.72, 149.87. MALDI-TOF, m/z: theoretical value: 938.53, experimental value: 938.75. Elemental analysis: calcd (%) for C<sub>68</sub>H<sub>66</sub>N<sub>4</sub>: C 86.95, H 7.08, N 5.96; found: C 86.83, H 7.25, N 5.91.

TCz-9PA-TCz. TCz-9PA-TCz was synthesized following the same synthetic procedure for 9-(4-(tert-butyl)phenyl)-9H-carbazole.28,29 3,6-Bis(4-tert-butyl-benzene)-9H-carbazole (0.38 g, 0.88 mmol), 2,5-dibromo-pyrazine (0.11 g, 0.5 mmol), Cu (0.5 g, 7.5 mmol), potassium carbonate solid (10.2 g, 60 mmol) and 6 mL nitrobenzene. 0.31 g yellow powder was obtained in a yield of 73%. <sup>1</sup>H-NMR of compound **TCz-9PA-TCz** (400 MHz, CDCl<sub>3</sub>):  $\delta = 1.00$ (s, 1H), 8.42 (s, 2H), 8.10 (d, J = 8.0 Hz, 2H), 7.82-7.80 (d, J = 8.0 Hz, 2H), 7.75-7.73 (d, J = 8.0 Hz, 4H), 7.55 (m, 7H), 6.45 (m, 4H), 6.15 (m, 4H), 5.90 (m, 4H), 1.50-1.40 (m, 36H). <sup>13</sup>C-NMR of compound **TCz-9PA-TCz** (100 MHz, CDCl<sub>3</sub>);  $\delta = 29.72, 31.27, 31.46, 31.53, 110.02, 110.37, 118.28, 118.93,$ 120.88, 123.86, 124.21, 125.61, 125.80, 126.42, 126.50, 126.87, 126.90, 133.70, 138.94, 143.22, 149.58, 150.79, 157.27. MALDI-TOF, m/z: theoretical value: 938.53, experimental value: 938.62. Elemental analysis: calcd (%) for C<sub>68</sub>H<sub>66</sub>N<sub>4</sub>: C 86.95, H 7.08, N 5.96; found: C 86.76, H 7.14, N 5.83.



Scheme 1 Synthetic route and chemical structures of the target emitters.

### **Results and discussion**

#### Synthesis and thermal properties

As depicted in Scheme 1, Suzuki and Ullmann reactions were used to synthesize blue fluorescence isomer emitters TCz-3PA-TCz, TCz-3,9PA-TCz and TCz-9PA-TCz, and their chemical structures were fully characterized by using <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and MALDI-TOF-MS spectra (Fig. S1-S18, ESI<sup>†</sup>). The thermal stability of TCz-3PA-TCz, TCz-3,9PA-TCz and TCz-9PA-TCz in the thin solid powder states was measured by DSC and thermogravimetric analysis (TGA) measurements (Fig. 1). The  $T_{\alpha}$  values of TCz-3PA-TCz, TCz-3,9PA-TCz and TCz-9PA-TCz thin solid powders were 99, 101 and 100 °C, and their 5% weight loss temperatures were 200, 393 and 171 °C for TCz-3PA-TCz, TCz-3,9PA-TCz and TCz-9PA-TCz. These results indicate that the TCz-3,9PA-TCz thin solid powder shows much higher thermal stability than those of TCz-3PA-TCz and TCz-9PA-TCz, and OLEDs based on TCz-3,9PA-TCz can be prepared both by spin-coating and thermal deposition in vacuum.

#### Photophysical properties

To gain insight into the photophysical properties of emitters **TCz-3PA-TCz**, **TCz-3,9PA-TCz** and **TCz-9PA-TCz**, we tested their UV absorption and PL emission spectra in different solvents at



Fig. 1 TGA (a) and DSC (b) curves for compounds TCz-3PA-TCz, TCz-3,9PA-TCz and TCz-9PA-TCz in the thin solid powder state.

a fixed concentration of  $10^{-5}$  mol L<sup>-1</sup> (Fig. 2). Detailed properties are summarized in Table 1. The strong absorption peaks appearing at 290–350 nm can be ascribed to the  $\pi$ - $\pi$ \* transition of the carbazole framework. The weak absorption peaks at 350-450 nm can be classified as ICT transitions from carbazole units to the central nitrogen heterocyclic pyrazine ring.<sup>32,33</sup> Based on the UV absorption spectra of the three compounds in toluene solution, the optical energy band gaps of compounds TCz-3PA-TCz, TCz-3,9PA-TCz and TCz-9PA-TCz were calculated to be 2.94, 2.90 and 2.74 eV, respectively. In the thin solid film state, the ICT absorption of the three compounds gradually weakens or even disappears compared to the solution state. The PL emission spectra of the neat films are red shifted about 40-50 nm relative to those of the solution state, which may be due to the  $\pi$ - $\pi$  stacking of the solid film.<sup>34</sup> After the three emitters are doped into CBP at a weight ratio of 5%, the full width at half-maximum of the PL spectra of TCz-3PA-TCz, TCz-3,9PA-TCz and TCz-9PA-TCz in the film state is narrowed and blue shifted. The absolute PLQYs of TCz-3PA-TCz, TCz-3,9PA-TCz and TCz-9PA-TCz solid powder were 3.78%, 1.55% and 6.18%, and the PLQYs of the three emitters doped into CBP at a weight ratio of 5% were 10.75% for TCz-3PA-TCz, 4.46% for TCz-3,9PA-TCz and 16.7% for TCz-9PA-TCz. The PLQY of TCz-9PA-TCz was the highest among the three emitters due to the reduced intermolecular interaction caused by stronger steric hindrance.

We studied the PL emission spectra of the three compounds in a mixture of tetrahydrofuran and water with different water volume fractions at a fixed concentration of  $10^{-5}$  mol L<sup>-1</sup> and the PL emission spectra are shown in Fig. S19 (ESI†). It illustrated that their PL emission intensities in the mixture showed a decreasing trend with the increase of the water volume fraction. Their blue light emission was aggregation-induced quenching active, and no expected aggregation-induced emission was observed among three emitters.<sup>35</sup> As for the emission behavior, we also obtained the PL emission spectra of the three compounds in solvents with different polarities. The emission spectra of the three compounds showed red shifts to some degree with the increase of the solvent polarity, and we constructed the Lippert–Magada curve to further characterize this phenomenon<sup>36–38</sup> (Fig. 3):

$$hc(\nu_{\rm abs} - \nu_{\rm fluo}) = \frac{1}{4\pi\varepsilon_0} \frac{2\Delta\mu_{\rm gc}^2}{a^3} \Delta f + C \tag{1}$$

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \tag{2}$$

$$a = \left(\frac{3M}{4N\pi d}\right)^{1/3} \tag{3}$$

where *h* is the Planck constant,  $\nu_{abs}$  and  $\nu_{fluo}$  are the absorption and photoluminescence of the three compounds in wavenumbers,  $\varepsilon_0$  is the vacuum permittivity, and *a* is the Onsagar cavity radius (7.19 Å) calculated from the Avogadro constant *N*, the speed of light (*c*), a constant (*C*) and the density of the compound ( $d = 1.0 \text{ g cm}^{-3}$ ). The detailed data are listed in Table S1 (ESI†). The dipole moment  $\mu_{ge}$  between S<sub>0</sub> and S<sub>1</sub> can be calculated to be 1.02 D for **TCz-3PA-TCz**, 0.8 D for **TCz-3,9PA-TCz** 



Fig. 2 UV-vis absorption and PL emission spectra of compounds TCz-3PA-TCz (a), TCz-3,9PA-TCz (b) and TCz-9PA-TCz (c) in different solvents and PL emission spectra in film of TCz-nPA-TCz doped into BCP on quartz at a weight ratio of 5% (d).

Fable 1	The key thermal,	optical and elect	rochemical proper	ties of <b>TCz-3PA</b>	-TCz, TCz-3,9	PA-TCz and TCz	-9PA-TCz
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Emitters	$Abs_m^a$ (nm)	$\operatorname{Abs_m}^b(\operatorname{nm})$	$PL_{m}^{a}(nm)$	${\rm PL_m}^b  ({\rm nm})$	$E_{g}^{c}$ (eV)	$T_{\rm d}/T_{\rm g}$ (°C)	LUMO/HOMO <sup><math>d</math></sup> (eV)	$E_{g}^{e}$ (eV)	$S_1^{f}(eV)$	$PLQY^{g,h}$ (%)
TCz-3PA-TCz	292/370/390	291/408	423	474/545	2.94	200/99	-3.19/-6.11	2.92	3.13	3.78/10.75
TCz-3,9PA-TCz	290/391	288/404	435	475/558	2.90	393/101	-3.36/-6.10	2.74	3.10	1.55/4.46
TCz-9PA-TCz	298/394	289/404	454	472/552	2.74	171/100	-3.21/-5.81	2.60	3.02	6.18/16.7

<sup>*a*</sup> Measured in toluene solution ( $10^{-5}$  mol L<sup>-1</sup>). <sup>*b*</sup> Measured in a spin-coated film state. <sup>*c*</sup> The optical energy band gaps calculated from the UV-vis onset absorption in toluene solvent. <sup>*d*</sup> According to the CV curve. <sup>*e*</sup> Calculated according to  $E_g = E_{HOMO} - E_{LUMO}$  in d. <sup>*f*</sup> Single energy levels calculated from the PL emission in toluene solvent. <sup>*g*</sup> PLQYs of solid powder measured using an integrating sphere with an excitation wavelength of 400 nm. <sup>*h*</sup> PLQYs of films (**TCz-nPA-TCz** doped in CBP at a weight ratio of 5%) measured using an integrating sphere with an excitation wavelength of 400 nm.

and 0.85 D for **TCz-9PA-TCz**. The relatively slight change in the dipole moment  $\mu_{ge}$  of **TCz-3,9PA-TCz** and **TCz-9PA-TCz** suggested a weak ICT characteristic existing between the carbazole and pyrazine units in the two emitters,<sup>39,40</sup> which was beneficial to suppress dipole–dipole interaction induced quenching in OLED applications.<sup>41</sup>

#### **Electrochemical properties**

The electrochemical properties of the three emitters were examined by cyclic voltammetry, and the results are shown in Fig. 4. The oxidation onsets of compounds **TCz-3PA-TCz**, **TCz-3,9PA-TCz** and **TCz-9PA-TCz** were observed at 1.36, 1.35 and 1.06 V. According to the oxidation potentials and the equation:  $E_{\text{HOMO}} = -4.75 - E_{\text{ox}}$  (eV), the HOMO energy levels

of TCz-3PA-TCz, TCz-3,9PA-TCz and TCz-9PA-TCz were calculated to be -6.10, -6.09 and -5.81 eV.<sup>42-47</sup> Similarly, according to the reduction potentials and the equation:  $E_{LUMO} = -4.75 - E_{red}$  (eV), the reduction potentials were calculated to be -1.33, -1.52 and -1.30 V for TCz-3PA-TCz, TCz-3,9PA-TCz and TCz-9PA-TCz. Subsequently, the LUMO energy levels of TCz-3PA-TCz, TCz-3,9PA-TCz and TCz-9PA-TCz were calculated to be -3.19, -3.36 and -3.21 eV. The N-linked model in TCz-9PA-TCz can elevate the HOMO energy level to some degree, while the 3,9-linked model in TCz-3,9PA-TCz can make the LUMO energy level deeper when compared with that of TCz-3PA-TCz. The energy band gaps can be calculated to be 2.92, 2.74 and 2.60 eV for TCz-3PA-TCz, TCz-3,9PA-TCz and TCz-9PA-TCz, which is consistent with the optical band gaps



Fig. 3 Lippert–Magada plots for compounds TCz-3PA-TCz, TCz-3,9PA-TCz and TCz-9PA-TCz. The *y* and *x* values in the fitted equation represent the Stokes shift and solvent orientation.



Fig. 4 The oxidation curves in dry dichloromethane (right) and reduction curves in dry tetrahydrofuran (left) of compounds TCz-3PA-TCz, TCz-3,9PA-TCz and TCz-9PA-TCz.

obtained from the UV absorption spectra of the three compounds in toluene solution.

#### OLED devices fabricated by the solution spin coating method

In order to explore the electroluminescence performance of compounds **TCz-3PA-TCz**, **TCz-3,9PA-TCz** and **TCz-9PA-TCz**, we have fabricated blue OLED devices consisting of ITO/PED-OT:PSS (30 nm)/CBP:**TCz-nPA-TCz** (55 nm)/TPBi (35 nm)/Ca:Ag (**TCz-3PA-TCz** for A1, **TCz-3,9PA-TCz** for A2 and **TCz-9PA-TCz** for A3) by solution spin coating. The electroluminescence spectra, current density-voltage-luminance characteristics, current efficiency-current density characteristics and external quantum efficiency-current density characteristics of the blue devices are shown in Fig. 5. The device performance is summarized in Table 2. All devices show blue emission with peaks at 448, 444 and 464 nm, whose CIE values are (0.163, 0.121) for A1, (0.157, 0.103) for A2 and (0.163, 0.205) for A3. As shown in Fig. 5(b), the maximum luminance of devices A1, A2 and A3 is 3252 cd m<sup>-2</sup>, 4404 cd m<sup>-2</sup> and 8052 cd m<sup>-2</sup>, and the maximum current

efficiency of devices A1, A2 and A3 is 1.86 cd  $A^{-1}$ , 2.39 cd  $A^{-1}$ and 4.12 cd  $A^{-1}$ . The external quantum efficiency of devices A1, A2 and A3 is 2.19%, 2.30% and 2.64% at a luminance of 100 cd  $m^{-2}$ . The general performance of the TCz-9PA-TCz doped device is much better than that of TCz-3PA-TCz and TCz-3,9PA-TCz, which illustrates that the low  $\mu_{ge}$  does not play a unique role in suppressing the dipole-dipole interaction induced quenching in the doped emitting layer, and the external quantum efficiency of the devices is roughly consistent with the absolute PLQYs of emitters TCz-3PA-TCz, TCz-3,9PA-TCz and TCz-9PA-TCz in the undoped and doped solid powder states. The PLQY of TCz-3PA-TCz is higher than that of TCz-3,9PA-TCz in both the solid state and the doped film, respectively. The EQE of device A2 is higher than that of device A3, which may be caused by the reduced quenching of the emission layers.

#### OLED devices by thermal deposition in vacuum

The thermal stability results indicated that TCz-3,9PA-TCz had obviously higher thermal stability. We then prepared four sets of OLED devices with optimized structures consisting of ITO/MoO<sub>3</sub> (1 nm)/TAPC (20 nm)/mCP (10 nm)/DPEPO:TCz-3,9PA-TCz (15 nm for B1, 20 nm for B2, 25 nm for B3 and 30 nm for B4)/ TmPvPB (40 nm)/LiF (0.7 nm)/Al (120 nm) by thermal deposition in vacuum, in which we doped TCz-3,9PA-TCz in a high triplet energy host of DPEPO with a concentration of 45% by weight. All devices B1-B4 show blue emission with electroluminescent peaks at around 452 nm, whose CIE values are (0.161, 0.152) for B1, (0.164, 0.160) for B2, (0.168, 0.168) for B3 and (0.169, 0.169) for B4. As shown in Fig. 6(b), the current efficiency of devices B1, B2, B3 and B4 at a luminance of 100 cd  $m^{-2}$  is 4.16 cd  $A^{-1}$ , 4.72 cd  $A^{-1}$ , 5.06 cd  $A^{-1}$  and 5.13 cd  $A^{-1}$ . Due to the blue emission, the external quantum efficiency of devices B1, B2, B3 and B4 at a luminance of 100 cd  $m^{-2}$  is 3.49%, 3.74%, 3.79% and 3.85%. Device B4 with a film thickness of 30 nm shows a driving voltage of 3.5 V, maximum luminance of 6369.67 cd  $m^{-2}$ and external quantum efficiency of 3.85% at a luminance of 100 cd m<sup>-2</sup>. As shown in Fig. S24 and S25 of the ESI,† a constituting fragment of isomer emitters, namely 3,6-bis-(4-tertbutyl-phenyl)-9-phenyl-9H-carbazole, has been synthesized, whose melting point and 5% weight loss temperature are 252 and 355 °C. The device performance illustrates that the maximum electroluminescence peak of the device based on 3,6-bis-(4-tert-butylphenyl)-9-phenyl-9H-carbazole is obviously blue shifted and the general efficiency is inferior to the device based on the isomer emitters synthesized in this research.

### Conclusions

In summary, three novel blue fluorescence isomer emitters **TCz-3PA-TCz**, **TCz-3,9PA-TCz** and **TCz-9PA-TCz** based on rigid pyrazine-bridged carbazole frameworks were synthesized and characterized. **TCz-3,9PA-TCz** in the thin solid powder state showed much higher thermal stability than that of **TCz-3PA-TCz** and **TCz-9PA-TCz**. All three isomer emitters display weak



Fig. 5 Current density-voltage-luminance characteristics (a), current efficiency-luminance characteristics (b), electroluminescent spectra (c) and external quantum efficiency-luminance (d) characteristics of the devices A1, A2 and A3.

 Table 2
 Summary of the blue OLED performance based on TCz-3PA-TCz, TCz-3,9PA-TCz and TCz-9PA-TCz by solution spin coating and thermal deposition in vacuum

					$100 \text{ cd } \text{m}^{-2}$		$1000 \text{ cd m}^{-2}$			FOF <sup>e</sup>	
OLEDs	$V_{\rm on}{}^a/{\rm V}$	$\lambda_{\rm ems}/{\rm nm}$	${\rm PE}_{\rm max}^{\ \ b}/{\rm lm} \ {\rm w}^{-1}$	${\rm CE}_{\rm max}^{\ \ c}/{\rm cd}~{\rm A}^{-1}$	$PE^b/lm w^{-1}$	CE <sup>c</sup> /cd A <sup>-1</sup>	$PE^{b}/lm w^{-1}$	CE <sup>c</sup> /cd A <sup>-1</sup>	$L_{\rm max}^{\ \ d}/{\rm cd} \ {\rm m}^{-2}$	$(100 \text{ cd } \text{m}^{-2})$	CIE(x, y)
A1	4.3	448	0.84	1.86	0.83	1.61	0.68	1.65	3252.32	2.19	(0.163, 0.121)
A2	3.9	444	1.41	2.39	1.29	2.04	1.11	2.19	4404.31	2.30	(0.157, 0.103)
A3	4.0	464	2.46	4.12	2.41	3.89	1.79	3.48	8052.0	2.64	(0.163, 0.206)
B1	3.3	452	2.33	4.16	2.33	4.16	1.13	2.96	5608.23	3.49	(0.161, 0.152)
B2	3.5	452	2.47	4.72	2.47	4.72	1.16	3.26	4283.74	3.74	(0.164, 0.160)
B3	3.5	452	2.64	5.06	2.64	5.06	1.24	3.56	4823.04	3.79	(0.168, 0.168)
B4	3.5	452	2.59	5.13	2.59	5.13	1.17	3.51	6369.67	3.85	(0.169, 0.169)
B4 <sup>a</sup> Drivii	3.5 1g volta	452 ge. <sup>b</sup> PE.	2.59 <sup>c</sup> CE. <sup>d</sup> L <sub>max</sub> . <sup>e</sup> F	5.13 COE are the ma	2.59 ximum powe	5.13 er efficiency.	1.17 current effic	3.51 ciency, brigh	6369.67 htness and ext	3.85 ernal quantum	(0.16 1 effic

solvatochromism and aggregation-induced emission quenching characteristics. The N-linked model in **TCz-9PA-TCz** can elevate the HOMO energy level to some degree, while the 3,9-linked model can make the LUMO energy level deeper when compared with that of **TCz-3PA-TCz**. The driving voltage, maximum external quantum efficiency, maximum current efficiency, maximum power efficiency and maximum luminance of doped OLEDs based on **TCz-9PA-TCz** fabricated by spin coating were 4.0 V, 2.67%, 4.12 cd A<sup>-1</sup> and 8052 cd m<sup>-2</sup>, which were much better than those based on **TCz-3PA-TCz** and **TCz-3PA-TCz**. The low  $\mu_{ge}$  does not play a unique role in suppressing dipole–dipole

interaction induced quenching in the doped emitting layer, and the external quantum efficiency of the devices is roughly consistent with the absolute PLQYs of **TCz-3PA-TCz**, **TCz-3,9PA-TCz** and **TCz-9PA-TCz** in the undoped and doped solid film states. Furthermore, the optimized OLED devices fabricated by thermal deposition in vacuum with **TCz-3,9PA-TCz** as a dopant emitter showed the highest external quantum efficiency of 3.85% at a luminance of 100 cd m<sup>-2</sup>, and the linking model analogous to **TCz-3,9PA-TCz** was validated to be a more feasible way to combine pyrazine with carbazole moieties to produce highly efficient and stable electroluminescent blue light materials.



Fig. 6 Current density-voltage-luminance characteristics (a), current efficiency-luminance characteristics (b), power efficiency-luminance characteristics (c) and external quantum efficiency-luminance characteristics (d) of devices B1-B4. Inset: The electroluminescent spectra of devices B1-B4.

# Conflicts of interest

The authors declare no competing financial interest.

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