

High-performance blue electroluminescent devices based on 2-(4-biphenyl)-5-(4-carbazole-9-yl)phenyl-1,3,4-oxadiazole

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An electron transporting moiety (1,3,4-oxadiazole) and a hole transporting moiety (carbazole) were combined to create 2-(4-biphenyl)-5-(4-carbazole-9-yl)phenyl-1,3,4-oxadiazole (CzOxa), a three layer device with a configuration of ITO/TPD(50 nm)/CzOxa(40 nm)/AlQ(40 nm)/Mg_{0.9}Ag_{0.1}(200 nm)/Ag(80 nm) which exhibited a blue emission peak at ~470 nm ($x = 0.14$, $y = 0.19$) with a maximum luminance of 26200 cd m⁻² at a drive voltage of 15 V and a maximum luminous efficiency of 2.25 lm W⁻¹.

Organic light-emitting diodes (OLEDs) have been widely investigated for their potential application in new generation display technology. Research into high efficiency and stable emitting blue materials for full color displays is one of the most active areas in this field. Recently high-performance blue emitting organic EL devices based on organic emitters and metal complex emitters have been explored with maximum brightness in the range of 6000–19000 cd m⁻².^{1–6} However, only a very few materials with a maximum brightness beyond 20000 cd m⁻² have been reported.^{7,8} With an aim of combining the electron and hole transporting moieties into one molecule we now report on the synthesis, the photoluminescence (PL) and electroluminescence (EL) of a new compound, 2-(4-biphenyl)-5-(4-carbazole-9-yl)phenyl-1,3,4-oxadiazole (CzOxa).[†] It is a white powder, which shows a high thermal stability with a decomposition temperature of 406 °C measured by thermogravimetric analysis (TGA). The synthetic route is shown in Scheme 1.

Fig. 1A shows the UV-Vis absorption spectra of CzOxa in CHCl₃ solution (a) and its vacuum deposition thin film (b). A dilute CHCl₃ solution of CzOxa (10⁻⁵ mol L⁻¹) absorbs at 259, 293, 306 and 342 nm with a tail extending to about 378 nm originating from the π - π^* transitions of the conjugated π -electron system, while the two absorptions at 293 and 342 nm show a slight red shift to 296 and 346 nm for the solid film on quartz, respectively [Fig. 1A(b)]. The absorption at 293 nm is ascribed to the carbazole moiety, and the other three absorptions at 259, 306 and 342 nm arise from the substituted oxadiazole group.

In order to have a better understanding of the relationship of the energy level of materials used in the devices, HOMO and LUMO energy levels of CzOxa were determined. The highest occupied molecular orbital energy level (HOMO) was measured by cyclic voltammetry to be 6.22 eV, and the lowest unoccupied molecular orbital energy level (LUMO), 3.13 eV, can be estimated by referring to the optical band gap energy of the absorption spectrum edge (402 nm, corresponding to 3.09

eV). The HOMO and LUMO energy levels of TPD and AlQ are cited from the literature,^{9,10} and thus the energy level diagram of device 2 can be obtained (Fig. 2).

To study the electroluminescent properties of CzOxa, two electroluminescent devices were fabricated by high vacuum (8×10^{-4} Pa) thermal evaporation techniques onto a pre-cleaned indium-tin oxide glass substrate with a sheet resistance of 15 Ω per square which was supplied by China Southern Glass Holding Co., Ltd. A shadow mask with 5 mm diameter openings was used to define the cathode of a 200 nm thick layer of Mg_{0.9}Ag_{0.1} alloy, with an 80 nm thick Ag cap. *N,N'*-Diphenyl-*N,N'*-bis(3-methylphenyl)(1,1'-biphenyl)-4,4'-diamine (TPD) and tris(8-hydroxyquinolino)aluminium (AlQ) were used as the hole transporting and electron transporting materials, respectively. The configurations of the two devices as follows:

Device 1: ITO/TPD(50 nm)/CzOxa(50 nm)/Mg_{0.9}Ag_{0.1}(200 nm)/Ag(80 nm)

Device 2: ITO/TPD(50 nm)/CzOxa(40 nm)/AlQ(40 nm)/Mg_{0.9}Ag_{0.1}(200 nm)/Ag(80 nm)

Device 1 exhibited an onset voltage of 4 V for the luminance. The peak luminous efficiency was 1.35 lm W⁻¹ at a luminance of 524 cd m⁻² and its maximum luminance was 9200 cd m⁻² at

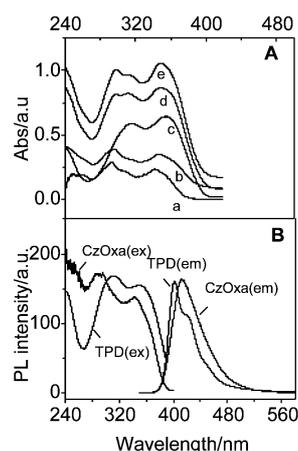
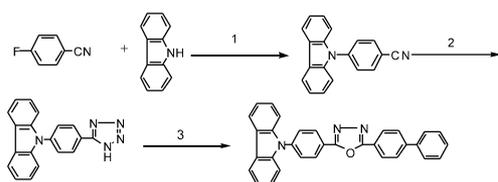


Fig. 1 A: UV-Vis absorption spectra: CzOxa in CHCl₃ solution (a) and its solid film on quartz (b); TPD on quartz (c); a mixture of TPD and CzOxa (1 : 1) on quartz (d). The sum of the absorption spectra of TPD and CzOxa (1 : 1) (e); B: The excitation (ex) and emission (em) spectra of CzOxa and TPD solid films on quartz.



Scheme 1 Synthetic route to CzOxa. Reagents and conditions: 1, DMSO/K₂CO₃, 12 h, 60%; 2, NaN₃/NH₄Cl/DMF, 100 °C, 24 h, 75%; 3, 3,4-Biphenylcarbonyl chloride/pyridine, refluxing 2 h, 90%.

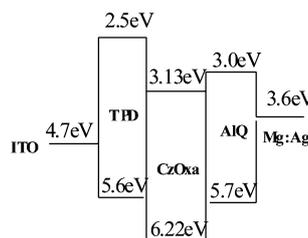


Fig. 2 Energy level diagram for device 2.

a drive voltage of 15 V. Device **2** in which electron transporting material AIQ was added showed a dramatic improvement in EL performance compared with device **1**, the merit of device **2** is its blue color purity ($x = 0.14$, $y = 0.19$) on a CIE (Commission International de l'Éclairage) 1931 chromaticity diagram in addition to the maximum luminous efficiency of 2.25 lm W^{-1} at a luminance of 2170 cd m^{-2} and the maximum luminance as high as 26200 cd m^{-2} at a drive voltage of 15 V. The current–voltage and voltage–luminance characteristics for device **2** are presented in Fig. 3.

It is worthwhile to note that the EL spectra of devices **1** and **2** (see Fig. 4) are similar and the maximum peak is centred at 470 nm with a shoulder at 404 nm. In Fig. 1B, CzOxa shows blue photoluminescence at $\sim 412 \text{ nm}$, and TPD exhibits its emission at 400 and 412 nm, which indicates that the exciplex is responsible for the EL emission. Usually an exciplex forms in the interface when the excited state of a very polarizable species participates in charge transfer interaction with polarizable species in the ground state. As a result, the metastable species, termed as exciplex, gives a broad structureless band at the red side of emission of the monomer. In order to identify the emission origin from devices **1** and **2**, the mixture of TPD and CzOxa (molar ratio 1 : 1) was spin-coated onto a quartz

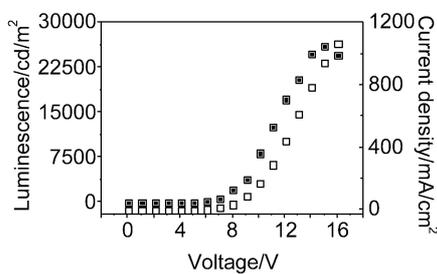


Fig. 3 The voltage–current density (\square) and voltage–luminance (\blacksquare) characteristics of device **2**.

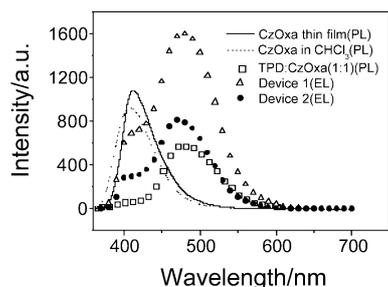


Fig. 4 The PL spectra of CzOxa in CHCl_3 and on the quartz (60 nm), and TPD : CzOxa (1 : 1) on the quartz, and the EL spectra of devices **1** and **2**.

substrate using a dichloroethane solution. Two emission bands at 400 and 470 nm can be found in the PL spectrum and the photoluminescence excited at 292 and 343 nm is the same except that the emission intensity is different. The disappearance of emissions from CzOxa (at 412 nm) and the appearance of the new emission (at 470 nm) imply that a new species is generated. Fig. 1A shows the absorption spectra of TPD, CzOxa and the mixture of TPD : CzOxa (ratio 1 : 1). The absorption of the mixture of TPD : CzOxa (ratio 1 : 1) is the sum of the TPD layer and the CzOxa layer absorptions. The lack of any new absorption band from the 1 : 1 mixture of TPD and CzOxa implies that the new emitting species is not from a ground state complex, such as a charge transfer complex, which supports the assignment of the existence of the exciplex.

In conclusion, a new thermally stable compound CzOxa with high efficiency and blue EL properties was designed and synthesized. The triple layer device exhibited a maximum luminance of 26200 cd m^{-2} at 15 V and an emission centred at 470 nm. This is mainly ascribed to the increased formation of the exciplexes at the interface of the TPD and CzOxa layers. Incorporation of the electron-transporting moiety with the hole-transporting moiety into one molecule is expected to increase the number of the two opposite carriers injected into the layers, which would offer a greater chance to form exciplexes at the interface between the two layers, and thus, the highest brightness of blue emission was obtained when compared with other corresponding compounds.

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Notes and references

† $^1\text{H-NMR}$ (400 MHz, CDCl_3): CzOxa, δ : 8.39–8.42 (d, 2H); 8.24–8.27 (d, 2H); 8.15–8.17 (d, 2H); 7.78–7.81 (d, 4H); 7.67–7.69 (d, 2H); 7.47–7.52 (m, 4H); 7.43–7.45 (m, 3H); 7.31–7.35 (m, 2H). m.p. 215–217 °C.

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