

Multifunctional bipolar triphenylamine/oxadiazole derivatives: highly efficient blue fluorescence, red phosphorescence host and two-color based white OLEDs†

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Two simple triphenylamine/oxadiazole derivatives were synthesized and fully characterized; their multifunctionality as highly efficient non-doped blue fluorescence, excellent red phosphorescent host and single-doped two-color based white OLEDs has been demonstrated.

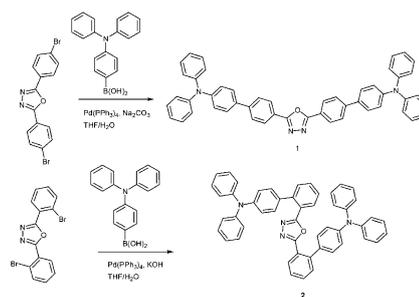
Phosphorescent organic light-emitting diodes (PHOLEDs) continue to attract intensive interest because they can approach 100% internal quantum efficiency theoretically. Highly efficient PHOLEDs with emission covering the whole visible region have been reported over the past decade.^{1–4} However great success has just been achieved in green-light phosphorescence.^{2,5} Efficient blue PHOLEDs with Commission Internationale de Eclairage (CIE) y values below 0.2 are very scarce,^{1a,b} and thus there is still a need to develop blue-emitting fluorescent materials with sufficient luminous efficiency and proper chromaticity. On the other hand, the red phosphorescent materials investigated were mostly doped into a 4,4'-bis(*N*-carbazolyl)biphenyl (CBP) host matrix, which is prone to crystallization when the dopant concentration is too low.^{4a,6} Furthermore, the driving voltages of red PHOLEDs with the CBP host are usually high because of insufficient and/or unbalanced injection of holes and electrons.⁷

Recently, bipolar hosts have aroused considerable interest in OLEDs, because they can balance the charge recombination and simplify device structures.⁸ However, there is a dilemma between the bipolar transporting properties and the band gap of the material, because the electron-donating and electron-withdrawing moieties integrated on bipolar molecules unavoidably lower the band gap of the material due to the intramolecular charge-transfer; while the low triplet energy of the host can cause reverse energy transfer from the guest back to the host, consequently leading to the decreased efficiency of the PHOLEDs. To address this issue, most recently, molecular design focuses on the interruption of π -conjugation between electron-donating and

electron-withdrawing moieties by incorporation of steric groups⁹ and/or *meta*-linkage¹⁰ of the two moieties. In our previous work,¹¹ we firstly reported an *ortho*-linked carbazole/oxadiazole hybrid molecule as a phosphorescent host, which achieved a maximum current efficiency of 77.9 cd/A for green and 13.6 cd/A for red light.

In this communication, we report a simple combination of commonly used hole-transporter triphenylamine and electron-transporter oxadiazole.¹² By introducing the triphenylamine moiety on the *o*-position relative to the oxadiazole ring of 2,5-diphenyl-1,3,4-oxadiazole, a twisted molecule TPA-*o*-OXD was acquired, which shows blue-shifted emission, less intramolecular charge-transfer and higher triplet energy levels in comparison with its *para*-structured analogue TPA-*p*-OXD. Both compounds show promising bipolar transport properties and highly efficient blue fluorescence. Furthermore, they are proven to be excellent host materials for red electrophosphorescence. Finally, a two-color based white OLED (WOLED) was constructed in a rather simple way by utilization of their dual roles as blue-emitter and host for red phosphorescence. The single-doped and single emissive layer device structure is much simple than the widely reported stacked,¹³ multi-emissive-layer¹⁴ or triple doped¹⁵ WOLEDs.

The two compounds TPA-*p*-OXD (**1**) and TPA-*o*-OXD (**2**) were readily prepared by a Pd(0)-catalyzed Suzuki cross-coupling reaction of 4-(diphenylamino)phenylboronic acid with 2,5-bis-(4'-bromophenyl)-1,3,4-oxadiazole or 2,5-bis(2'-bromophenyl)-1,3,4-oxadiazole (Scheme 1). Noticeably, for the steric torsional **2**, a high yield of 85% was obtained by using KOH as the base; this is in contrast to a low yield (below 20%) when using Na₂CO₃ as a base as in the normal Suzuki reaction. The good thermal stability of **1** and **2** is indicated by the high decomposition temperatures (T_d , corresponding to 5% weight loss) of 435 °C (**1**) and 432 °C (**2**) in the thermogravimetric analysis. The



Scheme 1 Synthesis of **1** and **2**.

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glass-transition temperature (T_g) of 116 °C (**1**) and 94 °C (**2**) determined through differential scanning calorimetry (DSC) are much higher than that of CBP (62 °C)¹⁶ and comparable to NPB (1,4-bis[(1-naphthylphenyl)amino]biphenyl) (95 °C),¹⁷ which is essential for the morphological stability of thin films.¹⁸

Fig. 1 shows the electronic absorption and fluorescence spectra of **1** and **2**. The absorption around 300 nm for both **1** and **2** originates from the triphenylamine-centered $n-\pi^*$ transition.^{9b} The absorption at 375 nm for **1** can be attributed to $\pi-\pi^*$ transition from the electron-donating triphenylamine moiety to the electron-accepting oxadiazole moiety. Notably, the $\pi-\pi^*$ absorption transition is blue-shifted by 40 nm and remarkably reduced in intensity as only a shoulder for **2**, which implies the inhibition of intramolecular charge-transfer. The PL spectrum of the *ortho*-structured **2** also exhibits a hypsochromic shift of 13 nm with respect to **1** in the solid state. The above phenomena can be attributed to the large space torsion disrupting the π -conjugation between triphenylamine and oxadiazole moieties for **2**. The two compounds are blue-emitting with an extraordinarily high quantum yield of 93% for **1** and 74% for **2** in CH_2Cl_2 solution (Table 1).

To evaluate the performance of **1** and **2** as blue-emitters, device **A** with the structure ITO/MoO₃ (10 nm)/1,4-bis-[(1-naphthylphenyl)amino]biphenyl (NPB, 80 nm)/**1** or **2** (20 nm)/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP, 10 nm)/Alq₃ (30 nm)/LiF (1 nm)/Al (100 nm) was fabricated. NPB and Alq₃ were used as the hole- and the electron-transporting materials, respectively, and BCP was used as the hole and exciton blocking layer, while MoO₃ and LiF served as the hole- and electron-injecting layers, respectively. All devices are blue-emitting, and representative EL spectra are shown in Fig. 1. Voltage-luminance-current density and current efficiency-current density characteristics for representative devices are shown in Fig. S1 and S2, respectively (ESI†). The device

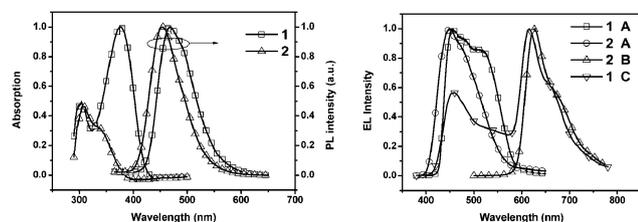


Fig. 1 Normalized absorption (in CH_2Cl_2 solution) and PL (film) spectra of **1** and **2** (left) and electroluminescence spectra of the devices (right).

Table 1 Physical data of **1** and **2**

	1	2
$T_m/T_g/T_d$ (°C) ^a	320/116/435	270/94/432
λ_{abs} (nm) ^b	304, 375	309, 335 (sh)
$\lambda_{\text{em, max}}$ (nm) ^c	467	454
Φ^f (%) ^d	93	74
HOMO/LUMO (eV) ^e	5.28/2.60	5.25/2.41

^a T_m : melting point. T_g : glass-transition temperature. T_d : thermal decomposition temperature. ^b Absorption maximum, measured in CH_2Cl_2 . ^c Emission maximum, measured in film. ^d Measured in CH_2Cl_2 with an integrating sphere. ^e Determined from the onset oxidation/reduction potentials of cyclic voltammetry curve in DMF.

performances are summarized in Table 2. We note that the device derived from **1** emits blue light with a maximum emission of 459 nm and a low energy shoulder at 520 nm; whereas the EL spectrum based on **2** shows an emission peak at 453 nm and no shoulder emission. The suppression of shoulder emission may be contributed to the twisted molecular configuration of **2**. This may provide a new strategy to avoid charge-transfer or excimer emission in non-doped blue light-emitting devices. A maximum brightness of 7364 cd/m^2 at 13.3 V and a maximum current efficiency of 3.9 cd/A at 3.26 mA/cm^2 for **1**, and 9441 cd/m^2 at 12.9 V and 3.1 cd/A at 0.7 mA/cm^2 for **2** were achieved. In addition, all devices display low turn-on voltages in the range 2.7–3.1 V. These performances are comparable with those of non-doped blue-emitting devices reported in literature.^{9a,17,19}

The triplet energies of **1** and **2** were determined to be 2.35 and 2.46 eV, respectively, by the highest-energy vibronic sub-band of the phosphorescence spectra at 77 K, and therefore they may act as appropriate host materials for orange/red-emitting phosphorescent emitters. The OLEDs using **1** or **2** as hosts for red phosphorescent iridium complex bis(1-phenylisoquinolino-N,C2') iridium(acetylacetonate) [(piq)₂Ir(acac)] were exploited through device **B** with configurations ITO/MoO₃ (10 nm)/NPB (80 nm)/**1** or **2**:(piq)₂Ir(acac) (6 wt%, 20 nm)/BCP (10 nm)/Alq₃ (30 nm)/LiF (1 nm)/Al (100 nm). Both devices emit red light with a CIE value of (0.68, 0.32). The EL data are summarized in Table 2. A maximum brightness of 18 333 cd/m^2 and a maximum current efficiency of 8.0 cd/A was achieved for the **1** based device. The best EL performance was obtained by using **2** as a host, with a maximum brightness of 24 416 cd/m^2 at 14.9 V, a maximum current efficiency of 11.3 cd/A (corresponding to a maximum external quantum efficiency of 14.2%) and a power efficiency of 8.2 lm/W . When the brightness reaches 1000 cd/m^2 , the current efficiency is still as high as 9.7 cd/A , which is much better than those CBP hosted devices.²⁰ To the best of our knowledge, these performance data are amongst the best pure red phosphorescent OLEDs with similar CIE coordinates reported in the literature.^{4a-c}

The better device performance achieved from **2** may be attributed to the enhancement in the localization of charges and higher triplet energy gap as demonstrated by Kakimoto and coworkers and Su *et al.*^{9b,c,10a} As shown in Fig. 2, the DFT calculated results indicated that **2** has nearly complete separation of the HOMO and LUMO at its hole- and electron-transporting moieties, respectively; whereas **1** exhibits only partial separation of the HOMO and LUMO. The optimized dihedral angles for **2** are larger than those for **1**, 55.3° to 36.5° and 23° to 0.3°. The more twisted structure of **2** leads to a significantly higher triplet energy gap for **2** (2.46 eV) than for **1** (2.35 eV).

By utilizing the dual roles of **1** and **2** as both efficient blue-emitters and excellent hosts for red phosphorescence, white OLEDs were successfully fabricated in a rather simple way with the configuration ITO/NPB (40 nm)/**1**: (piq)₂Ir(acac) (0.1 wt%, 20 nm)/BCP (10 nm)/Alq₃ (30 nm)/LiF (1 nm)/Al (100 nm) (device **C**). The EL spectrum at 10 V exhibits the blue fluorescent emission of **1** and the red phosphorescent emission of the iridium complex simultaneously (Fig. 1). A maximum current efficiency of 7.9 cd/A (corresponding to a η_{ext} of 5.2%) at 0.02 mA/m^2 and CIE value of (0.39, 0.31) were achieved. The single-doped device structure was much more simple than those stacked, multi-emissive-layer or multi-doped WOLEDs.

Table 2 EL data of the devices

Device	Compound	V_{on}^a	L_{max}^b/N	η_c^c	η_{ext}^d	η_p^e	CIE (x,y) ^f
A	1	2.8	7364, 13.3	3.9	1.7	3.6	0.18, 0.31
	2	3.3	9441, 12.9	3.1	2.0	2.6	0.17, 0.19
B	1	2.7	18 333, 12.9	8.0	9.8	7.0	0.68, 0.32
	2	3.1	24 416, 14.9	11.3	14.2	8.2	0.68, 0.32
C	1	5.3	1200, 12.5	7.9	5.2	4.7	0.39, 0.31

^a Turn-on voltage (V). ^b Maximum luminance (cd/m^2). ^c Maximum current efficiency (cd/A). ^d Maximum external quantum efficiency (%). ^e Maximum power efficiency (lm/W). ^f Commission International de l'Éclairage coordinates.

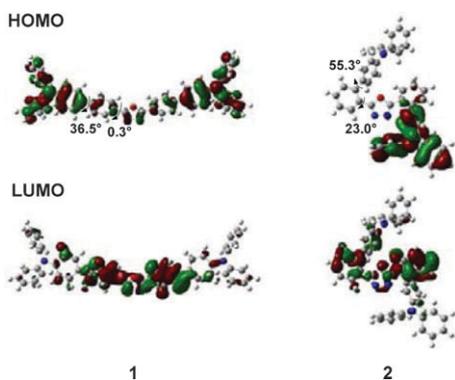


Fig. 2 DFT calculations of the spatial distributions of the HOMO and LUMO levels for **1** and **2**.

Further optimization of two-color based WOLEDs by using **1** and **2** is under way.

In summary, we have developed a simple strategy for designing bipolar molecules by the *ortho*-linkage of electron-donating triphenylamine units and the electron-accepting oxadiazole unit. The twisted molecule showed blue-shifted emission, less intramolecular charge-transfer, and a higher triplet energy level compared to its *para*-structured analogue. This may provide a new method for solving the dilemma between the bipolar transporting property and band gap of the material. The two compounds were not only used to fabricate non-doped blue-emitting devices with promising performance, but also served as host materials for red phosphorescent guests, achieving performance among the best for pure red phosphorescent OLEDs reported in the literature. Furthermore, we have demonstrated a simple single-doped way to realize two-color based WOLEDs by use of the dual roles of the compounds. We believe the EL performance of WOLEDs will be further improved by carefully optimization of device structures.

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