ARTICLES

# Construction of deep-blue AIE luminogens with TPE and oxadiazole units

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In this paper, two AIE-active luminogens (**Oxa-***p***TPE** and **Oxa-***m***TPE**) constructed from tetraphenylethene and oxadiazole units were successfully synthesized and their thermal, optical and electronic properties were investigated. By linking TPE to the oxadiazole core through *meta*- or *para*- position, the intramolecular conjugation is effectively controlled. Thanks to the intelligent molecular design and specific AIE feature, when fabricated as emissive layers in non-doped OLEDs, they exhibit blue or deep-blue emission with CIE coordinates of (0.17, 0.23) and (0.15, 0.12), and good efficiencies with  $\eta_{C, max}$  and  $\eta_{P, max}$  up to 1.52 cd A<sup>-1</sup> and 0.84 Im W<sup>-1</sup>, shedding some light on the construction of deep-blue AIE fluorophores.

aggregation-induced emission, tetraphenylethene, deep-blue emitter, organic light-emitting diodes

# 1 Introduction

Luminescent materials, with wide technological applications such as biological probes, chemosensors and organic light-emitting diodes (OLEDs), have attracted worldwide interests due to their remarkable properties for optoelectronics and biological science [1–5]. When fabricated as thin solid films in practical applications, most fluorophores suffer from the notorious aggregation-caused quenching (ACQ) effect, which is still a big challenge for the design and utilization of novel luminophors [6, 7]. Although various chemical, physical and engineering approaches have been employed to alleviate the ACQ effect [8–10], for example, the attachment of bulky alicyclics, adopting hostguest systems and blending with transparent polymers. These methods met with limited success and might also bring side effects such as more difficult synthesis, compli-

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cated fabrication processes, or jeopardizing the electronic conjugation in the luminophores.

In 2001, Tang et al. [11] have discovered a class of nonplanar propeller-shaped luminogens with intriguing characteristic termed as aggregation-induced emission (AIE), which demonstrated dramatically enhanced emission once aggregated as nanoparticles or solid films, in contrast to their weak emission in the solution state. This is totally opposite to the ACQ phenomenon. The systematic researches have shown that the restriction of intramolecular rotation is the main cause for the AIE effect [12–16]. This unique luminescent property aroused a new research topic of AIE materials, with tetraphenylethene (TPE) as a prototype AIE molecule for its facile synthesis and outstanding AIE effect [17]. Besides the exciting results of TPE-based fluorophors as bioprobes and chemosensors, OLED devices with TPE-based fluorophors as the emissive layers, demonstrated excellent EL performance [18-35]. For example, BTPE, constructed by two simple TPE units, exhibits outstanding improvement in EL performance with the current efficiency

up to 7.3 cd  $A^{-1}$  [20], compared to TPE (0.45 cd/A) [17], and the pyrene-cored luminogen TTPEPy is also an excellent emitter with external quantum efficiency and current efficiency up to 4.95% and 12.3 cd  $A^{-1}$ , respectively [21]. However, their EL emission has red-shifted at a large extent to greenish-blue or green for the intrinsic extention of intramolecular conjugation, no longer in the deep-blue region as TPE, proving that good blue light emitting AIE materials are still very scarce on another side. Actually, the lack of highly efficient blue light emitting materials caused by their intrinsic wide-band-gap nature, is still a critical drawback to realize full color displays [36, 37]. Therefore, the development of blue OLEDs with good performance based on the AIE materials becomes particular urgent.

Previously, by properly adjusting the balance of the elongation of  $\pi$ -conjugation and the linkage of additional rotators, or the utilization of the feature of crystallization induced blue-shifted emission of AIE molecules, we have successfully developed some TPE-based blue emitters [38, 39], which demonstrated good EL efficiencies (up to 5.0 cd  $A^{-1}$ ), thanks to their AIE characteristics. In addition, we have also obtained four deep-blue AIE luminogens simply constructed from two TPE units with ortha-, meta- or para-linkage mode, which represent different conjugation degree [40]. As a result, the conjugation is effectively controlled, and all the molecules exhibit deep-blue emission ranging from 435 to 459 nm and good electroluminescence efficiencies up to 2.8 cd  $A^{-1}$ . Thus, to further realize our synthetic ideas and develop new blue or deep-blue AIE systems, in this work, we have incorporated TPE moieties to the central electron-dominated oxadiazole unit through meta- or paralinkage, and obtained two AIE luminogens Oxa-pTPE and **Oxa-mTPE**. It is hoped that the EL performance could be enhanced with the aid of the oxadiazole group while maintaining blue or deep-blue emission in comparison with



Chart 1 Chemical structures of Oxa-mTPE and Oxa-pTPE.

TPE itself. Fortunately, the device performance confirmed our ideas: when fabricated as emissive layers in OLEDs, **Oxa-pTPE** and **Oxa-mTPE** exhibit blue and deep-blue emissions with CIE coordinates of (0.17, 0.23) and (0.15, 0.12), respectively, and the maximum current efficiency is up to 1.52 cd  $A^{-1}$ , much higher than that of TPE (0.45 cd  $A^{-1}$ ). Herein, we would like to present the synthesis, thermal and photophysical properties and electroluminescence of the two emitters in detail.

# 2 Experimental

## 2.1 Charaterization

<sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Mecuryvx300 spectrometer. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a CARLOERBA-1106 microanalyzer. Mass spectra were measured on a ZAB 3F-HF mass spectrophotometer. UV-Vis absorption spectra were recorded on a Shimadzu UV-2500 recording spectrophotometer. Photoluminescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit at a heating rate of 15 °C min<sup>-1</sup> from room temperature to 300 °C under argon. The glass transition temperature  $(T_g)$  was determined from the second heating scan. Thermogravimetric analysis (TGA) was undertaken with a NETZSCH STA 449C instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 10 °C min<sup>-1</sup> from 25 to 600 °C. Cyclic voltammetry (CV) was carried out on a CHI voltammetric analyzer in a three-electrode cell with a Pt counter electrode, a Ag/AgCl reference electrode, and a glassy carbon working electrode at a scan rate of 100 mV s<sup>-1</sup> with 0.1 M tetrabutylammonium perchlorate (purchased from Alfa Aesar) as the supporting electrolyte, in anhydrous dichloromethane solution purged with nitrogen. The potential values obtained in reference to the Ag/Ag<sup>+</sup> electrode were converted to values versus the saturated calomel electrode (SCE) by means of an internal ferrocenium/ferrocene  $(Fc^{+}/Fc)$  standard.

## 2.2 Computational details

The geometrical and electronic properties were optimized at B3LYP/6-31g(d) level using Gaussian 09 program. The molecular orbitals were obtained at the same level of theory.

#### 2.3 OLED device fabrication and measurement

The hole-transporting material NPB (1,4-bis(1-naphthylphenylamino)-biphenyl), electron-transporting materials 1,3,5tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI) and tris(8hydroxyquinolinato)aluminium (Alq<sub>3</sub>) were purchased from Changzhou Mascot Import & Export Co., LTD. The EL devices were fabricated by vacuum deposition of the materials at a base pressure of  $5 \times 10^{-6}$  Torr onto glass precoated with a layer of indium tin oxide (ITO) with a sheet resistance of 25  $\Omega$  square<sup>-1</sup>. Before the deposition of an organic layer, the clear ITO substrates were treated with oxygen plasma for 3 min. The deposition rate of organic compounds was 0.9–1.1 Å s<sup>-1</sup>. Finally, a cathode composed of lithium fluoride (1 nm) and aluminium (100 nm) was sequentially deposited onto the substrate in the vacuum of  $10^{-5}$  Torr. The *L–V–J* of the devices was measured with a Keithley 2400 Source meter and PR655. The EL spectra were measured by PR655. All measurements were carried out at room temperature under ambient conditions.

# 2.4 Preparation of compounds

All other chemicals and reagents were obtained from commercial sources and used as received without further purification. Solvents for chemical synthesis were purified according to the standard procedures. 3-Bromobenzophenone [41], p-TPE-Br, compound **2** and **3** were synthesized according to the literatures [42].

## Synthesis of mTPE-Br

A 2.3 M solution of *n*-butyllithium in hexane (4.09 mmol, 1.78 mL) was added to a solution of diphenylmethane (0.86 g, 5.12 mmol) in anhydrous tetrahydrofuran (40 mL) at 0 °C under an argon atmosphere. After stirring for 1 h at this temperature, 3-bromobenzophenone (0.89 g, 3.41 mmol) was added. After 2 h, the mixture was slowly warmed to room temperature. Then, the reaction was quenched with an aqueous solution of ammonium chloride and the mixture was extracted with dichloromethane. The organic layer was evaporated after drying with anhydrous sodium sulfate and the resultant crude product was dissolved in toluene (25 mL). The p-toluenesulfonic acid (0.12 g, 0.68 mmol) was added, and the mixture was refluxed overnight and cooled to room temperature. The mixture was evaporated and the crude product was purified by silica gel column chromatography using petroleum ether as eluent to yield a white powder in the yield of 50% (0.70 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.20–7.11 (m, 11H), 7.02–7.01 (m, 5H), 6.96– 6.95 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ): 146.0, 143.4, 143.3, 143.1, 142.2, 139.5, 134.2, 131.3, 130.1, 129.6, 129.3, 128.0, 127.8, 126.9, 126.8, 121.9; MS (EI), m/z: 412.13 ( $[M^+]$ , calcd for C<sub>26</sub>H<sub>19</sub>Br, 411.33).

# Synthesis of compound 1

A 2.3 M solution of *n*-butyllithium in hexane (15.0 mmol, 6.5mL) was added to a solution of *m*-TPE-Br (4.12 g, 10.0 mmol) in anhydrous tetrahydrofuran (60 mL) at -78 °C under an argon atmosphere. After stirring for 4 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.1

mL) was added. After 2 h, the mixture was slowly warmed to room temperature. After stirring overnight, the reaction was terminated by the added brine. The mixture was extracted with dichloromethane, the organic layer was combined, and dried over anhydrous sodium sulfate. After filtration and solvent evaporation, the crude product was purified by silica gel column chromatography using petroleum ether/dichloromethane (v/v = 5/1) as eluent. White powder of **1** was obtained in the yield of 60% (2.30 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.53–7.48 (m, 2H), 7.09–7.02 (m, 17H), 1.28 (s, 12H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ ): 143.6, 143.3, 142.9, 141.1, 140.8, 137.5, 134.2, 132.7, 131.3, 131.2, 127.5, 127.0, 126.3, 126.2, 83.6, 24.7; MS (EI), *m/z*: 458.35 ([M<sup>+</sup>], calcd for C<sub>32</sub>H<sub>31</sub>BO<sub>2</sub>, 458.40).

# Synthesis of Oxa-mTPE

A mixture of compound 3 (380 mg, 1 mmol), compound 1 (940 mg, 2.05 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.10 g, 4% mmol) and potassium hydroxide (560 mg, 10 mmol) in 15 mL of THF and 3 mL of distilled water in a 50 ml Schlenk tube was refluxed for 2 days under argon. The mixture was extracted with dichloromethane. The combined organic extracts were dried over anhydrous sodium sulfate and concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel using dichloromethane/petroleum ether (v/v = 1/1) as eluent to afford the product as a white powder in the yield of 63.2% (758 mg). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 7.55–7.52 (m, 2H), 7.42– 7.33 (m, 4H), 7.09–7.02 (m, 35H), 6.91–6.90 (m, 5H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ): 164.5, 143.8, 143.7, 143.6, 143.3, 142.1, 141.4, 140.6, 139.9, 132.0, 131.5, 131.4, 131.3, 131.2, 130.9, 130.4, 129.7, 127.8, 127.7, 127.4, 127.1, 126.5, 122.6; MS (EI), m/z: 882.28 ([M+], calcd for C<sub>66</sub>H<sub>46</sub>N<sub>2</sub>O, 883.08); Anal. Calcd for C<sub>66</sub>H<sub>46</sub>N<sub>2</sub>O: C, 89.77; H, 5.25; N, 3.17. Found: C, 89.55; H, 4.94; N, 3.44.

# Synthesis of Oxa-pTPE

The synthetic procedure was similar to that of **Oxa-mTPE**, with compound **2** and **1** as the starting materials. White solid. Yield: 68%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.78–7.76 (m, 2H), 7.59–7.40 (m, 6H), 7.08–6.97 (m, 26H), 6.93–6.88 (m, 12H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ ): 165.3, 144.0, 143.8, 143.7, 143.1, 142.3, 141.5, 140.5, 138.5, 131.6, 131.4, 131.3, 130.5, 128.3, 127.9, 127.8, 127.7, 126.8, 126.6, 123.0; MS (EI), *m/z*: 882.94 ([M+], calcd for C<sub>66</sub>H<sub>46</sub>N<sub>2</sub>O, 883.08); Anal. Calcd for C<sub>66</sub>H<sub>46</sub>N<sub>2</sub>O: C, 89.77; H, 5.25; N, 3.17. Found: C, 89.62; H, 5.23; N, 3.44.

# 3 Results and discussion

## 3.1 Synthesis

Scheme 1 illustrates the synthetic route to **Oxa-***p***TPE** and **Oxa-***m***TPE**. The detailed procedures for the synthesis of

the intermediates and target molecules are presented in the Experimental Section. Briefly, TPE boronic ester 1 or 2 was obtained from diphenylmethane and 3-bromobenzophenone or 4-bromobenzophenone in three steps. Compound 3 was prepared according to the literatures. Suzuki coupling reactions of 3 with 1 or 2 were catalyzed by  $Pd(PPh_3)_4$  with good yields. The final products were carefully purified by column chromatography on silica gel using petroleum ether-dichloromethane as eluent and fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR, mass spectrometry, and elemental analysis, which well confirmed their molecular structures. Single crystal of Oxa-mTPE was isolated from its dichloromethane/methanol solution and was crystallographically characterized. The target molecules were soluble in common solvents, such as dichloromethane, chloroform and tetrahydrofuran, but insoluble in water.

investigated by thermal gravimetric analyses (TGA) and differential scanning calorimetry (DSC). As shown in Figure 1, their thermal-decomposition temperatures ( $T_d$ , corresponding to 5% weight loss) were determined to be about 414 and 400 °C (Table 1), respectively. **Oxa-pTPE** possessed better thermal stability and exhibited higher glass transition temperatures ( $T_g$ ) of 113 °C, than that of **Oxa-mTPE** (103 °C). This should be ascribed to the more planar and rigid conformation of **Oxa-pTPE**, which was constructed from TPE moiety and oxadiazole unit through *para*-linkage, in another word, it is more conjugated. Thus, their good thermal stability with high  $T_d$  and  $T_g$  values would contribute to the preparation of the homogeneous and stable amorphous emissive layer in OLED device.

#### 3.3 Optical properties

## 3.2 Thermal properties

The thermal properties of Oxa-pTPE and Oxa-mTPE were

The absorption spectra of Oxa-pTPE and Oxa-mTPE are shown in Figure 2(a). Their absorption maximums are about 320 and 302 nm, respectively, indicating that the former is

<b>Table 1</b> The thermal, electrochemical and photophysical data of <b>Oxa</b> - <i>p</i> <b>TPE</b> and <b>Ox</b>
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	$T_{\rm d}^{\rm a)}$ (°C)	$T_{g}(^{\circ}C)$	$E_{\rm g}^{\rm b)}({\rm eV})$	$E_{\rm HOMO}^{\rm c)} ({\rm eV})$	$E_{\rm LUMO}^{\rm d)} ({\rm eV})$	$\lambda_{abs}^{e)}(nm)$	PL $\lambda_{max} (aggr)^{f}$ (nm)	PL $\lambda_{max}$ (film) (nm)
Oxa-pTPE	414	113	3.30	5.55	2.25	320	479	480
Oxa-mTPE	400	103	3.39	5.57	2.18	302	465	464

a) 5% Weight loss temperature measured by TGA under N<sub>2</sub>; b) band gap estimated from optical absorption band edge of the solution; c) calculated from the onset oxidation potentials of the polymers; d) estimated using empirical equations  $E_{LUMO} = E_{HOMO} + E_g$ ; e) observed from absorption spectra in dilute THF solution; f) determined in THF:H<sub>2</sub>O = 1:99 solution.



Scheme 1 Synthetic route to Oxa-mTPE and Oxa-pTPE.



Figure 1 TGA (a) and DSC (second heating cycle) thermograms (b) of **Oxa-***m***TPE** and **Oxa-***p***TPE** recorded under  $N_2$  at a heating rate of 10 and 15 °C min<sup>-1</sup>.

more conjugated than the latter, as a result of the different of *meta*- or *para*-linkage mode of TPE and oxadiazole unit. In addition, compared to that of TPE (299 nm), the maximum absorption wavelength of **Oxa**-*p***TPE** has red-shifted about 20 nm, while that of **Oxa**-*m***TPE** almost remained the same, further demonstrating our synthetic ideas of utilizing the different conjugation degree of different linking positions. Thus, **Oxa**-*p***TPE** possesses more planar and rigid conformation than **Oxa**-*m***TPE**. Actually, the different linkage is also a method to subtly adjust the electronic properties of the resultant molecules.

To investigate the possible AIE characteristic of these



**Figure 2** (a) UV spectra in THF solution. Concentration ( $\mu$ M): 12.1 and 10.7 for **Oxa-mTPE** and **Oxa-pTPE**, respectively; (b) the PL spectra of the films of **Oxa-mTPE** and **Oxa-pTPE**. The thin films were spin-coated onto ITO glass from dilute THF solution with concentrations of 1 mg mL<sup>-1</sup>.

two dyes, their fluorescent behaviors were studied. Considering the good and poor solvents should be well miscible, tetrahydrofuran and water were chosen as the solvent pair. Both of Oxa-pTPE and Oxa-mTPE are nonemissive when molecularly dissolved in organic solvents, but show strong emission in the aggregate state. Figure 3 demonstrates the PL change and fluorescent image of Oxa-pTPE in THF and THF/water mixtures. It is easily seen that in dilute THF solution, the PL curve is practically flat lines parallel to the abscissa, confirming that it is nearly nonemissive in the solution state. However, when a large amount of water is added, intense emission is observed. As shown in Figure 3, when the water fraction is over 80%, the PL intensity increases swiftly, indicating the formation of the aggregates. At a  $f_w$  value of 99%, the PL spectrum peak is at 479 nm for Oxa-pTPE, and the PL intensity is 120-fold higher than that in pure THF. Similar behavior was observed for Oxa-mTPE (Figure 4). However, unlike Oxa-pTPE, when the water fraction increases from 80 to 99%, the emission maximum of the PL spectra of Oxa-mTPE in THF/water mixtures is blue shifted from 490 to 465 nm, possibly due to the morphological change of the aggregates from amorphous to crystalline state, that is, crystallization will blue-shift the emission. Thus, it seems easier to crystallize for Oxa-mTPE than Oxa-pTPE, owing to its more twisted conformation caused by the meta-linkage of TPE and oxadiazole unit.

The quantitative enhancement of emission was evaluated by the PL quantum yield ( $\Phi_{\rm F}$ ), using 9,10-diphenylanthracene as the standard. From pure solution in THF to aggregate states in 95% or 99% aqueous mixtures, the  $\Phi_{\rm F}$  values of **Oxa-***p***TPE** and **Oxa-***m***TPE** increase from 0.0052 and 0.0044 to 0.27 and 0.346. Evidently, these two dyes are AIE-active.

Closer inspection of the PL spectra of **Oxa-***p***TPE** and **Oxa-***m***TPE** in the solid state were carried out, because they are often fabricated as thin solid films in practical applications. As shown in Figure 2(b), the film of **Oxa-***p***TPE** exhibits sky-blue emission peaked at 479 nm, which is almost



**Figure 3** (a) PL spectra of **Oxa**-*p***TPE** in THF/H<sub>2</sub>O mixtures with different water fractions ( $f_w$ ). Concentration ( $\mu$ M): 10.7; excitation wavelength (nm): 320; (b) plots of fluorescence quantum yields determined in THF/H<sub>2</sub>O solutions using 9,10-diphenylanthracene ( $\Phi = 90\%$  in cyclohexane) as standard versus water fractions. Inset in (b): photos of **Oxa**-*p***TPE** in THF/water mixtures ( $f_w = 0$  and 99%) taken under the illumination of a 365 nm UV lamp.



**Figure 4** (a) PL spectra of **Oxa-mTPE** in THF/H<sub>2</sub>O mixtures with different water fractions ( $f_w$ ). Concentration ( $\mu$ M): 10.7; excitation wavelength (nm): 320; (b) plots of fluorescence quantum yields determined in THF/H<sub>2</sub>O solutions using 9,10-diphenylanthracene ( $\Phi = 90\%$  in cyclohexane) as standard versus water fractions. Inset in (b): photos of **Oxa-mTPE** in THF/water mixtures ( $f_w = 0$  and 99%) taken under the illumination of a 365 nm UV lamp.

the same as the values obtained from the corresponding PL spectra of the aggregates with 99% water fraction, suggesting that the aggregates with  $f_w$  of 99% are in the amorphous state. However, the film of Oxa-mTPE shows deep-blue emission peaked at 456 nm, similar to the aggregates with 99% water fraction, but about 34 nm blue-shifted than the aggregates with 80% water fraction, indicating that the film is in the crystalline state, and the aggregates with 80% water fraction are in the amorphous state. This could be attributed to the twisted conformation of Oxa-mTPE with metalinkage between TPE and oxadiazole group, which makes the molecules more easily crystallized. In addition, the results have also shown that **Oxa-pTPE** is more conjugated than Oxa-mTPE, confirming that the intramolecular conjugation could be tuned through different linking positions. This is in consistent with our design idea.

# 3.4 Theoretical calculations

To further understand the photophysical properties at the

molecular level, Density Functional Theory (DFT) calculations (B3LYP/6-31g\*) were carried out to obtain orbital distributions of HOMO and LUMO energy levels ofOxa-pTPE and Oxa-mTPE. The dihedral angle between the adjacent phenyl blades of TPE and oxadiazole unit is ~54° for **Oxa-***p***TPE**, higher than that of **Oxa-***m***TPE** (~72°). Thus, Oxa-pTPE is more planar and conjugated, in good accordance with the UV data. As shown in Figure 5(a), the LUMOs of both molecules are located on the electronaccepting oxadiazole unit, and the HOMO orbitals are mainly distributed on the TPE moiety, showing the almost separation of HOMO and LUMO orbitals. Fortunately, we have obtained the single crystal of Oxa-mTPE from a dichloromethane-methanol solution. From the ORTEP drawing (Figure 5(b)), Oxa-mTPE has a twisted conformation and nearly no intermolecular interactions are found in the packing arrangement, which would be beneficial to prevent the formation of species detrimental to emission.

#### 3.5 Electrochemical properties

Cyclic voltammetry (CV) was carried out to investigate the electrochemical behaviors of these materials. The highest occupied molecular orbital (HOMO) energy levels were estimated from the onset oxidation potentials according to the equation:  $E_{\rm HOMO} = -(4.8 + E_{\rm ox})$  (eV). Therefore, the HOMO energy levels of **Oxa-pTPE** and **Oxa-mTPE** were calculated to be -5.55 and -5.57 eV, respectively, suggesting the two molecules possessed similar hole-transporting ability. And the lowest unoccupied molecular orbital (LUMO) energy levels could be obtained from optical bandgap energies (estimated from the onset wavelengths of the UV absorptions) and HOMO values, which gave LUMO values as



**Figure 5** (a) Calculated molecular orbital amplitude plots of HOMO and LUMO levels and optimized molecular structures of **Oxa-***p***TPE** and **Oxa-***m***TPE**; (b) ORTEP drawing of **Oxa-***m***TPE**.

<b>TADIC 2</b> LE DETIDITIANCES OF $OAa^{-}D$ <b>I L</b> and $OAa^{-}n$ <b>I I</b>	Table 2	EL performances	of Oxa-pTPE	and Oxa-mTPE <sup>a</sup>
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-2.25 and -2.18 eV for **Oxa-***p***TPE** and **Oxa-***m***TPE**, respectively.

## 3.6 Electroluminescence

The efficient solid-state emission, good thermal and morphological stability of **Oxa-***p***TPE** and **Oxa-***m***TPE** prompted us to investigate their electroluminescence properties. We have fabricated non-doped multilayer organic lightemitting diodes (OLEDs) with configurations of ITO/NPB (60 nm)/EML(40nm)/TPBi(10 nm)/Alq<sub>3</sub>(20 nm)/Al(100 nm) by vacuum deposition. In the devices, NPB, TPBi and Alq<sub>3</sub> act as the hole-transporting layer, hole-blocking layer and electron-transporting layer, respectively, while **Oxa-***p***TPE** and **Oxa-***m***TPE** served as emitters.

As listed in Table 2, device based on Oxa-pTPE possesses lower turn-on voltage (5.1 eV) than that of Oxa-mTPE (6.25 eV), showing its smaller injection barrier from transporting layers. However, from the current density-voltageluminance curves (Figure 6(a)), we can see that the current density of Oxa-mTPE increases more quickly than that of Oxa-pTPE, accompanying by the increasement of the operating voltage. In addition, the luminance of the device based on Oxa-*m*TPE (750 cd  $m^{-2}$ ) is higher than that of Oxa*p***TPE**, suggesting the more efficient exciton combination in the emissive layer for Oxa-mTPE. Altogether, device based on Oxa-pTPE shows much higher EL efficiencies than that of Oxa-mTPE. In detail, device of Oxa-mTPE exhibits maximum current efficiency ( $\eta_{C, max}$ ) and maximum power efficiency ( $\eta_{P, max}$ ) of 0.72 cd A<sup>-1</sup> and 0.49 Im W<sup>-1</sup>, respectively. Much better EL performance is observed for OxapTPE with  $\eta_{C, max}$  and  $\eta_{P, max}$  of 1.52 cd A<sup>-1</sup> and 0.84 Im  $W^{-1}$ . It is worthy to note: although the chemical structures of the two luminogens are nearly the same, that is, the minor different para- or meta- linkage mode of TPE and oxadiazole core, their device performance is with big difference. It is reasonable. The conformation of Oxa-pTPE is more planar than that of **Oxa-mTPE**, in another word, it is more conjugated, which is good for the carrier transporting when served as emissive layers. For Oxa-pTPE, the corresponding OLED device exhibits sky-blue emission with EL peak at 470 nm and the CIE coordinate of (0.17, 0.23). However, much bluer emission is observed for Oxa-mTPE, with EL peak at 452 nm and CIE coordinates of (0.15, 0.12), because the meta-linkage of TPE and oxadiazole is less contributable to the elongation of intramolecular conjugation

	$V_{\rm on}({ m V})$	$L_{\rm max} ({\rm cd}{\rm m}^{-2})$	$\eta_{\mathrm{P,max}}(\mathrm{Im}\;\mathrm{w}^{-1})$	$\eta_{\rm C, max}  ({\rm cd}  {\rm A}^{-1})$	$\eta_{\mathrm{ext, max}}(\%)$	$\operatorname{CIE}\left(x,y\right)$
Oxa-pTPE	5.10	615	0.84	1.52	0.97	0.17, 0.23
Oxa-mTPE	6.25	750	0.49	0.72	0.82	0.15, 0.12

a) Abbreviations:  $V_{on}$  = turn-on voltage at 1 cd m<sup>-2</sup>,  $L_{max}$  = maximum luminance,  $\eta_{C, max}$ ,  $\eta_{C, max}$  and  $\eta_{ext, max}$  = maximum power, current and external efficiencies, respectively. CIE = Commission International de l'Eclairage coordinates.



**Figure 6** (a) Current density-voltage-luminance characteristics of multilayer EL devices of **Oxa-***p***TPE** and **Oxa-***m***TPE**; (b) changes in current efficiencies with the current density in multilayer EL devices; (c) EL spectra of **Oxa-***p***TPE** and **Oxa-***m***TPE**; (d) energy level diagrams and device configurations of multilayer EL devices. Abbreviations: NPB = 4,4-bis(1-naphthylphenylamino)biphenyl, TPBi = 1,3,5-tris(*N*-phenylbenz imidazol-2-yl)benzene. Device configurations: ITO/NPB(60 nm)/EML(40 nm)/ TPBi(10 nm)/Alq<sub>3</sub>(20 nm)/Al(100 nm).

compared to the *para*-linkage approach, similar to our previous researches. In comparison with TPE (0.45 cd  $A^{-1}$ ) itself, the device performance has been improved for **Oxa**-*p***TPE** and **Oxa**-*m***TPE**, while the EL emission still maintain in blue region. Especially for **Oxa**-*m***TPE**, the device exhibits deep-blue emission peaked at 452 nm, almost the same as TPE (445 nm). Thus, the device performance have partially realized our synthetic thought of tuning conjugation effect through different linking positions and generating good AIE-active emitters without sacrificing blue or deep-blue emission.

# 4 Conclusions

In this work, we have successfully synthesized two TPEbased luminogens of Oxa-pTPE and Oxa-mTPE. They all show splendid AIE characteristic and good thermal and morphological stabilities. By combining the TPE moiety and oxadiazole group together through meta- or para- linkage mode, their intramolecular conjugation could be effectively adjusted owing to the different molecular conformations. When served as emissive layers in OLEDs, Oxa-pTPE and Oxa-mTPE exhibit good EL performance with  $L_{\text{max}}$ ,  $\eta_{\text{C, max}}$ , and  $\eta_{\text{P, max}}$  up to 750 cd m<sup>-2</sup>, 1.52 cd A<sup>-1</sup> and 0.84 Im  $W^{-1}$ , and CIE coordinates of (0.17, 0.23) and (0.15, 0.12), respectively. Especially for Oxa-mTPE, the device exhibits deep-blue emission almost the same as TPE (445 nm) but with enhanced EL efficiencies. Apparently, the conjugation could be tuned through different linking positions, which is also believed to be an efficient approach to construct deep-blue AIE luminogens for OLEDs.

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