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# **Graphical Abstract**



The new two *t*-APE-type derivatives are applied to OLEDs devices showing that *t*-APE-type derivatives have the excellent properties for the emitting materials of OLEDs.

# Two *trans*-1-(9-anthryl)-2-phenylethene derivatives as blue-green emitting materials for highly bright organic light-emitting diodes application

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ABSTRACT: 1-(9-Anthryl)-2-phenylethene (t-APE) is a blue-green material with high fluorescence quantum yield ( $\Phi_f$  0.44). However, it is easily crystallized. Herein, Two asymmetric blue-green emitting t-APE, materials based on (E)-9-(4-(2-(anthracen-9-yl)vinyl)phenyl)-10-(naphthalen-1-yl)anthracene (6) and (E)-9-(4-(2-(anthracen-9-yl)vinyl)phenyl)-10-(naphthalen-2-yl)anthracene (7)were firstly designed and synthesized. The two compounds possess high thermal stability, morphological durability, and bipolar characteristics. The non-doped blue-green organic light-emitting diodes (OLEDs) using 6 and 7 as emitting layers showed emission at 495 nm, full width at half maximum of 80 nm, maximum brightness of 13814, 10579 cd m<sup>-2</sup>, maximum current efficiency of 3.62, 7.16 cd A<sup>-1</sup>, and Commission Internationale de L'Eclairage (CIE) coordinate of (0.20, 0.43), respectively. Furthermore, when employing 6 and 7 as blue-green emitting layers and rubrene doped in tris-(8-hydroxyquinolinato)aluminum (Alq3) as the orange emitting layers to fabricate white OLEDs (WOLEDs), the WOLEDs exhibit a maximum brightness of 10984, 14652 cd m<sup>-2</sup>, maximum current efficiency of 2.04, 2.70 cd A<sup>-1</sup>, and CIE coordinate of (0.30, 0.40), (0.37, 0.47), Color Rendering Index (CRI) of 65, 60, stable EL spectra, respectively. This study demonstrates that the *t*-APE-type derivatives have the excellent properties for the emitting materials of OLEDs. KEWORDS: blue-green, asymmetric, bipolar, organic light-emitting diodes, white

#### 1. Introduction

Blue-green emitter instead of standard blue emitter is an effective method to improve the color rendering index (CRI) of white organic light-emitting diodes (WOLEDs) with two-element colors because its wavelength can complement the gap in wavelength between blue and orange emitters. However, there are still rare of reports on the high efficiency blue-green emitting materials [1]. In 2008, Moorthy et al. employed a blue emitting material of anthracene-anchored-bimesityls and fabricated non-doped blue-green OLEDs with CIE coordinate of (0.19, 0.38), maximum brightness of 3199 cd m<sup>-2</sup> and maximum current efficiency (CE) of 0.64 cd A<sup>-1</sup> [2]. In 2010, Qiu's group recorded the CE of 10.6 cd  $A^{-1}$  and CIE coordinate of (0.18, 0.45) by doping the TBCPF: OXD-7 host with a blue-green phosphor [3]. In 2013, Turksoy's group reported a blue-green OLEDs with CIE coordinate of (0.23, 0.42), maximum brightness of 335 cd m<sup>-2</sup> and maximum CE of 1.1 cd A<sup>-1</sup> by employing anthracene-pyridine derivatives [4]. Dumur's group proposed TCTA host materials and fabricated phosphorescent blue-green OLEDs with the power efficiency (PE) of 0.98 lm W<sup>-1</sup> and CIE coordinate of (0.21, 0.41) [5]. In 2014, Chen and colleagues synthesized a new DPA derivative and fabricated the non-doped blue-green OLEDs with CIE coordinate of (0.22, 0.37), maximum brightness of 7891 cd m<sup>-2</sup> and maximum CE of 2.5 cd A<sup>-1</sup> [6]. In 2015, Huang and his coworkers reported non-doped blue-green OLEDs and obtained CIE coordinate of (0.17, 0.39), maximum brightness of 4490 cd m<sup>-2</sup> and maximum CE of 1.43 cd A<sup>-1</sup> by employing a newly synthesized ADN derivative [7]. Park's group synthesized a new hexaphenyl benzene derivative and fabricated the non-doped blue-green OLEDs with CIE coordinate of (0.23, 0.45), and maximum CE of 2.48 cd A<sup>-1</sup> [8]. Zhang and colleagues reported extremely high-performance blue-green OLEDs with CIE coordinate of (0.19, 0.49), establishing a new world record PE of

11.8 lm W<sup>-1</sup> and 5.3% by doping the CBP host with a blue-green phosphor [9]. In 2016, Kim's group utilizing DPA derivative fabricated the non-doped blue-green OLEDs with CIE coordinate of (0.19, 0.45), maximum brightness of 1377 cd  $m^{-2}$  and maximum CE of 1.75 cd  $A^{-1}$  [10]. Although achievements have been made, there are still several problems in developing blue-green OLEDs. Firstly, in some blue-green devices using anthrance derivatives as emitting materials, the blue-green emission spectra are originated from the excimer of materials which found at the molecular interactions [2, 4, 6, 7, 10]. Secondly, the turn-on voltage (defined as the operation voltage at brightness of 1 cd m<sup>-2</sup>) of some blue-green OLEDs is higher than 7 V without explanation [4, 8]. Especially, there are a few reports on utilizing blue-green emitting materials to fabricate WOLEDs [3]. Thus, synthesis of blue-green emission (originating from excited monomer rather than excimer) and suitable energy level materials applying to WOLEDs is becoming increasingly important. In general, the HOMO levels of anthracene derivatives are near 5.5-5.6 eV [11-14]. And the excimer emission can be restrained effectively by the bulky or asymmetric substituents which inhibit intermolecular interactions [15, 16]. In line with the above-mentioned consideration and facts, the issue can be solved by constructing blue-green anthracene derivatives with bulky or asymmetric substituents.

As we know, 1-(9-anthryl)-2-phenylethene (t-APE, Scheme 1) is a blue-green material with high fluorescence quantum yield ( $\Phi_f 0.44$ ) [17]. There is no report about using t-APE to construct OLEDs because it is easily crystallized (see ESI Fig. S2b). Herein, we firstly introduced the naphthanthracene group into the t-APE molecule to improve the thermal properties while keeping their advantageous electronic and optical characteristics. The asymmetric molecule structure would suppress the aggregation of t-APE segments in the solid state which results in stable

blue-green EL emission. For this purpose, two asymmetric blue-green material of (E)-9-(4-(2-(anthracen-9-yl)vinyl)phenyl)-10-(naphthalen-1-yl)anthracene (6) and (E)-9-(4-(2-(anthracen-9-yl)vinyl)phenyl)-10-(naphthalen-2-yl)anthracene (7)firstly were designed and synthesized. The thermal and electrochemical properties, the bipolar characteristics, and the device performance of the two materials were investigated. The non-doped OLEDs using classical and simple structure based on 6 and 7 show blue-green emission (The EL spectra of these device emissions centered at 495 nm with full width at half maximum of 80 nm.), which originates from excited monomer. Since the HOMO levels of 6 and 7 are near 5.5 eV, using these two materials as blue-green emitter and rubrene doped in Alq3 as the orange emitter to fabricate WOLEDs exhibit a maximum brightness of 10984, 14652 cd m<sup>-2</sup>, CRI of 65, 60, respectively. The EL spectra of these WOLEDs are stable under high voltage without any interlayer. We believe the performance of WOLEDs could be improved by optimizing the structure of device and employing other orange materials.

#### 2. Experiment section

#### 2.1. Materials

All materials were received from Tianjin Heowns Biochemical Technology Co., Ltd. and used without further purification unless otherwise stated. All solvents were purchased from Tianjin Rianlon Corporation. 1,4-Dioxane was carefully dried and distilled from a sodium benzophenone mixture under argon (Ar) atmosphere before use.

## 2.2 General procedures

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a Bruker ACF400 (400 MHz) spectrometer in chloroform-d (CDCl<sub>3</sub>) with tetramethylsilane as reference. Mass spectra were carried out on an

Agilent MALDI-TOF. UV-Vis absorption and photoluminescence spectra of THF solution and film were collected with Thermo Evolution 300 UV-Vis spectrophotometer and Hitachi F-4500 fluorescence spectrophotometer, respectively. Fluorescence lifetime measurements were recorded on the HORIBA Jobin-Yvon, NanoLog using time-correlated single photon counting (TCSPC). Absolute photoluminescence quantum efficiency at room temperature was measured using an absolute photoluminescence quantum yield measurement system (Edinburg FLS-980 fluorescence spectrometer) with a calibrated integrating sphere. Differential scanning calorimeter (DSC) was undertaken using a TA Q20 instrument under nitrogen atmosphere at a heating rate of 10 °C min<sup>-1</sup>. Thermo gravimetric analysis (TGA) was carried out on a TA Q500 thermo gravimetric analyzer under nitrogen atmosphere at a heating rate of 10 °C min<sup>-1</sup>. Atomic force microscopes (AFM) were measured using NTEGRA Spectra. Cyclic voltammetry (CV) was taken on a CHI-600C electrochemical analyzer. The measurements were determined using a conventional three-electrode configuration consisting of a glassy carbon working electrode, a platinum-disk auxiliary electrode and an Hg/KCl reference electrode. And the scan rate was 10 mV s<sup>-1</sup>. DFT calculations were performed to characterize the 3D geometries and the frontier molecular orbital energy levels of 6 and 7 at the B3LYP/6-31G(d) level by using the Gaussian 03 program. All measurements were conducted at room temperature.

#### 2.3. Device fabrication and measurement

The EL devices were fabricated by vacuum thermal evaporation technology. Before the deposition of an organic layer, the indium tin oxide (ITO) substrates were rinsed in an ultrasonic bath by the following sequences: in acetone, methyl alcohol, distilled water and kept in isopropyl alcohol for 48 h and dried by  $N_2$  gas gun. The clear substrates treated by oxygen plasma with the

conditions of  $10^{-2}$  Pa at 80 W for 3 min. The deposition rate of organic compounds was 0.7-1.4 Å S<sup>-1</sup>. Finally, a cathode composed of LiF (1 nm) and aluminum (100 nm) were sequentially deposited onto the substrate in the vacuum of  $5 \times 10^{-4}$  Pa. All of properties of the EL devices such as *J-V-B* curves, current efficiency (CE), and CIE chromaticity coordinates of devices were measured with a Keithley 2400 Source meter and Chroma meter CS-2000. All measurements were carried out at room temperature under ambient conditions.

#### 2.4. Synthesis

The designed compounds were synthesized as outlined in Scheme 1.



Scheme 1. Synthetic routes and molecular structures of 6 and 7

### 2.4.1. Diethyl benzylphosphonate (1)

Diethyl benzylphosphonate as the basis compound for the synthesis of the *t*-APE isomers was prepared according to literature [18, 19]. Benzyl bromide (1.50 g, 8.8 mmol) was suspended in 5 mL of toluene, containing triethylphosphite (6.00 g, 35 mmol). The mixture was refluxed at 140 °C for 2 h. Excess triethylphosphite and toluene were removed by distillation to give the required product as a yellow oil (1.80 g, 89.9%). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  7.53 – 7.25 (m,

5H),3.96 – 3.91 (m, 4H), 3.15 (d, *J* = 21.6 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 6H).

#### 2.4.2 Diethyl-4-Bromobenzylphosphonate (2)

Compound **2** was synthesized according to the method described in synthesis of compound **1** with yield of 92.5%. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  7.51 (dd, J = 8.4, 0.9 Hz, 2H), 7.25 (dd, J = 8.4, 2.5 Hz, 2H), 3.96 – 3.91 (m, 4H), 3.25 (d, J = 21.6 Hz, 2H), 1.19 (t, J = 7.1 Hz, 6H).

## 2.4.3 (*E*)-9-styrylanthracene (**3**, *t*-**APE**)

Diethyl benzylphosphonate (1.10 g, 4.8 mmol) and 9-anthraldehyde (1.00 g, 4.8 mmol) were added into a 100 mL round-bottom flask with the protection of N<sub>2</sub>. *N*,*N*-Dimethylformamide (30 mL) was added to above flask, then cooled to 0 °C. The *N*,*N*-Dimethylformamide solution of *t*-BuOK (0.54 g, 4.8 mmol) was added dropwise to above flask, stirred for 30 min at 0 °C, followed with stirring at room temperature until the 9-anthraldehyde was consumed completely (monitored by thin-layer chromatography). The reaction was terminated with ice water, and the product was extracted with ethyl acetate 100 mL. After the solvent was evaporated, the crude product was purified by chromatography on a silica gel column (petroleum ether: ethyl acetate = 4:1 as eluent) to give the title compound as a pure (*E*)-9-styrylanthracene (1.3 g, 86.9%): Mp:132 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.36 (dd, *J* = 12.3, 6.3 Hz, 3H), 8.06 – 7.96 (m, 2H), 7.90 (d, *J* = 16.5 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.59 – 7.40 (m, 6H), 7.35 (t, *J* = 6.9 Hz, 1H), 6.94 (d, *J* = 16.5 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  137.35, 132.81, 131.55, 129.78, 128.87, 128.73, 128.05, 126.64, 126.50, 126.07, 125.50, 125.21, 124.93.

#### 2.4.4. 6 (*E*)-9-(4-bromostyryl)anthracene (4)

Compound **4** was synthesized according to the method described in synthesis of compound **3** with yield of 59.7%: Mp:167 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.44 (s, 1H), 8.37 – 8.28 (m, 2H),

8.05 (dd, *J* = 5.7, 3.9 Hz, 2H), 7.92 (d, *J* = 16.5 Hz, 1H), 7.65 – 7.46 (m, 8H), 6.91 (d, *J* = 16.5 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.24, 136.08, 132.29, 131.96, 131.51, 129.69, 128.78, 128.10, 126.73, 125.85, 125.72, 125.64, 125.25.

2.4.5. (*E*)-2-(4-(2-(anthracen-9-yl)vinyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5)

A mixture of (E)-9-(4-bromostyryl)anthracene (0.72 g, 2 mmol), bis(pinacolato)-diboron (0.65 g,

2.5 mmol), [1,1'-bis(diphenylphophino)ferrocene]-dichloro-palladium(II) (0.05 g, 0.06 mmol), potassium acetate (0.65 g, 6 mmol), and anhydrous 1,4-dioxane (20 mL) was added into a 50 mL round-bottom flask with the protection of Ar. The reaction system was refluxed for 24 h under stirring. After cooling, the mixture was evaporated under reduced pressure, treated with saturated sodium chloride solution, extracted with ethyl acetate, and the organic layer was dried over anhydrous MgSO<sub>4</sub>. After removal of the solvent, the residue was purified by column chromatography on silica gel using ethyl acetate/petroleum at 1:10 by volume as the eluent to give a yellow powder (0.70 g, 86.0%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.44 (s, 1H), 8.40 – 8.33 (m, 2H), 8.03 (dd, *J* = 13.4, 9.0 Hz, 3H), 7.93 (d, *J* = 7.9 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.62 – 7.39 (m, 4H), 7.00 (d, *J* = 16.6 Hz, 1H), 1.42 (s, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  139.97, 137.33, 135.33, 132.62, 131.51, 129.73, 128.70, 126.59, 125.99, 125.88, 125.55, 125.21, 83.87, 24.91. 2.4.6. (*E*)-9-(4-(2-(anthracen-9-yl))vinyl)phenyl)-10-(naphthalen-1-yl)anthracene (**6**)

A mixture of 9-bromo-10-(naphthalen-1-yl)anthracene (0.42 g, 1.1 mmol), (*E*)-9-(4-(2-(anthracen-9-yl)vinyl)phenyl)-10-(naphthalen-1-yl)anthracene (0.49 g, 1.2 mmol), tetrakis(triphenylphosphine)palladium(0) (0.03 g, 0.03 mmol), and 1 M sodium carbonate (2.7 mL) in 40 mL of 1,4-dioxane was stirred at 100 °C for 48 h under nitrogen atmosphere, cooled down to room temperature. The title compound was obtained by simple filtration from the reaction mixture. Yellow solid (0.40 g, 66.4%). MALDITOF-TOF-MS (m/z): [M + H]<sup>+</sup> calcd for C<sub>46</sub>H<sub>30</sub>, 582.23; found, 582.3. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.49 (dd, J = 13.6, 6.5 Hz, 3H), 8.23 – 7.81 (m, 9H), 7.77 – 7.33 (m, 13H), 7.33 – 7.20 (m, 4H), 7.16 (d, J = 16.7 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  137.09, 136.78, 136.59, 135.21, 133.70, 133.59, 131.92, 131.60, 130.71, 129.97, 129.85, 129.24, 128.78, 128.26, 128.16, 127.16, 127.01, 126.67, 126.57, 126.31, 126.12, 126.01, 125.64, 125.60, 125.27, 125.25, 125.23.

2.4.7. (E)-9-(4-(2-(anthracen-9-yl)vinyl)phenyl)-10-(naphthalen-2-yl)anthracene (7)

Compound **7** was synthesized according to the method described in synthesis of compound **6** with yellow solid (0.45 g, 74.7%). MALDITOF-TOF-MS (m/z):  $[M + H]^+$  calcd for C<sub>46</sub>H<sub>30</sub>, 582.23; found, 582.4. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.49 (dd, J = 13.6, 6.5 Hz, 3H), 8.23 – 7.81 (m, 9H), 7.77 – 7.33 (m, 13H), 7.33 – 7.20 (m, 4H), 7.16 (d, J = 16.7 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  137.09, 136.78, 136.59, 135.21, 133.70, 133.59, 131.92, 131.60, 130.71, 129.97, 129.85, 129.24, 128.78, 128.26, 128.16, 127.16, 127.01, 126.67, 126.57, 126.31, 126.12, 126.01, 125.64, 125.60, 125.27, 125.25, 125.23.

## 3. Result and discussion

3.1. Synthesis, thermal and Morphology properties of 6 and 7

The synthesis of **6** and **7** is outlined in Scheme 1, involving a series of Suzuki reactions (see Experiment section). The thermal properties of **6** and **7** were investigated by TGA and DSC under nitrogen atmosphere. And the related data are listed in **Table 1**. As displayed in **Fig. 1**, the decomposition temperature ( $T_d$ , 5% weight loss) values of the compound **6** and **7** were determined to be 427 °C and 425 °C, respectively, which are higher than the 223 °C determined for *t*-APE (See ESI **Fig. S1**). Such high  $T_d$  values suggest that these compounds are stable and have the

potential to be fabricated into device by vacuum thermal evaporation technique, which is a prerequisite for high performance OLED applications [20]. As shown in **Fig. 1** (insert), DSC analysis reveals that the glass transition temperatures  $(T_g)$  of both compounds amount to 105 °C. The similarly thermal data may be attributed to their similar structures. Moreover, no distinct crystallization was observed in this series upon heating at a temperature beyond  $T_g$ . The high  $T_g$  values implies that it is possible to get stable glasses from these materials and means good stability of the amorphous film during fabrication and operation of OLEDs [21, 22].



Fig. 1. TGA and DSC thermograms (insert) of 6 (a) and 7 (b).

To confirm the thermal stability and morphological durability against thermal stress, the surface morphologies of vacuum-deposited thin films was studied by atomic force microscopy (AFM). The vacuum-deposited of the two new compounds on a silicon wafer substrate were about 40 nm thickness to match that used in the actual electroluminescent device. As illustrated in Fig. 2, the thin films of **6** and **7** exhibited a uniform surface morphology having a root-mean-square (RMS)

surface roughness of 0.236 nm and 0.239 nm, respectively. These films did not undergo any significant morphological change after annealing at 60 °C and 90 °C for 24 h suggesting their excellent thermal and amorphous stability, which indicates that the asymmetric molecules with number of conformers increased the energy needed for crystallization and favors the stability of amorphous films [23-25].



**Fig. 2.** Atomic force microscope (AFM) topographic images of **6** and **7** with thermal treated samples (a) 25 °C 24 h, (b) 60 °C 24 h, and (c) 90 °C 24 h).

#### 3.2. Optical properties and energy levels

The normalized UV-Vis absorption and photoluminescence (PL) spectra of **6** and **7** in THF solution  $(1 \times 10^{-5} \text{ M})$  andvacuum-deposited thin films (quartz plate) are shown in **Fig. 3**, relevant data are summarized in **Table 1**. For a direct comparison, the UV-Vis absorption and PL spectra of *t*-APE in THF solution and in films was collected (See ESI **Fig. S2**). In the THF solution, there are three peaks located at around 350-406 nm in the UV-Vis absorption spectra of *t*-APE, **6** and **7** indicating that the characteristic absorption peaks are caused by  $\pi$ - $\pi$ \* transition of the *t*-APE moiety [26]. Compare the UV-Vis absorption spectra of THF solution with that of thin films, the shape and peak position of **6** and **7** are similar. No obvious red-shift of absorption peaks manifests that no significant aggregation or crystallization occurs in the films [27]. However, the UV-Vis absorption and peak position in the films. As shown in Fig. **S2b**, the crystallization of *t*-APE in THF solution and thin films due to crystallization in the films. As shown in Fig. **S2b**, the crystallization of *t*-APE in 12



the films probably attributed to the thermal delay [28].

Fig. 3. UV-Vis absorption and PL spectra of 6 (a) and 7 (b) dilute solution  $(1 \times 10^{-5} \text{ M})$  in THF and neat thin films.

In the THF solution, *t*-APE, **6** and **7** exhibit similar trends with similar maximum PL ( $PL_{max}$ ) values at blue-green wavelengths of 470 nm, 475 nm and 475 nm and full width at half maximum (FWHM) values 76 nm, 80 nm and 80 nm respectively. Compared to *t*-APE, the  $PL_{max}$  values of **6** and **7** are red-shifted by 5 nm and the FWHM values of **6** and **7** are increased by 4 nm. This implies that the conjugation lengths of these anthracene derivatives are enhanced by introducing a naphthanthracene to *t*-APE group. There were no differences in PL spectra of *t*-APE between solution and thin film which might be originated from crystallization-induced emission (See ESI **Fig. S2a**) [29-31]. Nevertheless, the maximum emission peak in PL spectra of **6** and **7** in thin film state showed slight red-shift about 20 nm without change of FWHM, comparing with their PL spectra in THF solution. The red-shift of the emission observed in the film state is probably due to the difference in relative permittivity or dielectric constant of the environment [32]. And this 13

red-shift emission also can suggest that the presence of weak intermolecular interactions or aggregation in film states due to the twisted asymmetrically bound aryl groups. Nonetheless, the presence of molecular aggregates will also support the enhancement of charge transport properties due to specific restrictions on intramolecular rotations [33]. In degassed THF solutions, the photoluminescence quantum yields (PLQYs, 0.47 for **6** and 0.46 for **7**) are very similar with that of *t*-APE. The excited-state lifetime ( $\tau$ ) is 2.0 ns for both **6** and **7**, which is equal to those of previously reported anthracene derivatives [34]. However, the lifetime of **6** and **7** is much short than *t*-APE (3.3 ns, see **Fig. S3**) indicating that the  $k_f$  values of **6** and **7** increased [35].



Fig. 4. Molecular structures (a) and electron density distributions of the HOMO (b)/LUMO (c)

#### calculated with B3LYB/6-31G(d).

To obtain a better understanding on the optical and thermal properties in the molecular level, density functional theory (DFT) calculations (B3LYP/6-31G(d)) were carried out by using Gaussian 03 software [36]. The optimized geometry and the electron distribution of compounds **6** and **7** are shown in **Fig. 4**. The calculation results indicate that both **6** and **7** have non-coplanar molecular structures. The dihedral angles of two compounds between anthrancene and 1-naphthyl, and 2-naphthyl were calculated 89°, 103°, respectively, and dihedral angles between anthrancene and phenyl of *t*-APE-moiety were calculated 103°, 102°, respectively, and dihedral angles between anthrancene anthrancene and double bond were calculated 49°, 50°, respectively. The non-coplanar structures would prevent the intermolecular interaction and self-aggregation from forming molecular 14

recrystallization, which improves the morphological stability [37]. The shapes of the HOMO and LUMO orbitals of **6** and **7** are almost the same. The LUMO is located on the *t*-APE moiety. The HOMO is dominated by the orbitals from the *t*-APE-antrancene core. Thus it is suggest that **6** and **7** show more red-shifted emission in comparison to *t*-APE.

	6	7
$T_{\rm d}^{\rm a}$ (°C)	427	425
<i>T</i> <sup>b</sup> <sub>g</sub> (°C)	105	105
$\lambda_{abs}^{c}$ (nm)	362,380,398/364,384,406 <sup>l</sup>	363,381,398/366,386,406 <sup>1</sup>
PL <sup>d</sup> (nm)	475/495 <sup>1</sup>	475/495 <sup>1</sup>
$\Phi_{\rm f}[\tau  {\rm [ns]]}^{\rm e}$	0.47[2.0]	0.46[2.0]
$E_{g}^{f}(eV)$	2.85	2.85
HOMO <sup>g</sup> (eV)	-5.48	-5.51
$LUMO^{h}(eV)$	-2.63	-2.66

Table 1. The optical, thermal properties and energy levels of the as-synthesized compound

<sup>a</sup> Measured by TGA at a heating rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere. <sup>b</sup> Measured by DSC according to the heat-cool-heat procedure. <sup>c</sup> Absorption spectra were recorded in the 1.0 x 10<sup>-5</sup> mol L<sup>-1</sup> THF solution. <sup>d</sup> PL spectra were recorded in the (1.0 x 10<sup>-5</sup> mol L<sup>-1</sup>) THF solution. <sup>e</sup> In degassed THF solutions. <sup>f</sup> Optical energy gaps calculated from the absorption thresholds from UV-Vis absorption spectra of THF solution. <sup>g</sup> Measured with CV. <sup>h</sup> | LUMO | = | HOMO |  $-E_g$ . <sup>1</sup> Absorption or PL peaks of thin films.

In order to measure the HOMO values of the compounds 6 and 7, cyclic voltammetry (CV) measurements using a three-electrode cell were conducted (See ESI Fig. S4). The edge of the UV-Vis spectra was used to calculate the band gap ( $E_g$ ) of 6 and 7. The band gaps and the HOMO

and LUMO levels are summarized in **Table 1**. The HOMO levels of **6** and **7** are -5.48 eV and -5.51 eV which in agreement with the results of previous studies [11-14, 34]. The slight difference of HOMO levels between **6** and **7** may be caused by the different dihedral angles of two compounds between anthrancene and naphthyl [38, 39]. This result implies that **6** is easier to inject holes than **7** in the OLEDs.

#### **3.3. Electroluminescent properties**

#### 3.3.1. Non-doped blue-green OLEDs

To check the potential application of the compound **6** and **7** as emitters, non-doped OLEDs with the optimized structures of ITO/TPD (25 nm)/**6** or **7** (40 nm)/Alq3 (15 nm)/LiF (1 nm)/Al (100 nm) were firstly fabricated. In these devices, N,N'-Diphenyl-N,N'-di(m-tolyl)benzidine (TPD), **6** or **7**, and Alq3 were utilized as the hole-transport layer (HTL), emitting layer (EML) electron-transport layer (ETL), respectively. LiF was employed as the electron-injecting layer (EIL) and Al metal served as the cathode. The device structures and the energy level diagrams of used materials are shown in **Fig. 5**.



Fig. 5. The device energy-level diagram (a), configuration (b) and molecular structures of the

materials used in this study (c).

The electroluminescence (EL) spectra, current density-voltage-brightness (J-V-B) characteristics,

CE, and PE of the devices 1 and 2 using compounds 6 and 7 as the emitting materials are shown in Fig. 6, respectively. Devices 1 and 2 show a main peak centered at the 495 nm with FWHM 80 nm. The corresponding CIE coordinates of the blue-green electroluminescence are (0.20, 0.43). The tendency of the EL spectra of device 1 and 2 is similar to the film PL spectra of compounds 6 and 7. This implies that the emission of device 1 and 2 originates mainly from the excited monomer of compounds 6 and 7. In some blue-green devices using anthrance derivatives as emitting materials the blue-green emission spectra are originated from the excimer of materials which found at molecular interactions [2, 4, 6, 7, 10]. In considering these results, the absence of emission at longer wavelength from the excimer in the EL spectra of 1 and 2 should be attributed to the suitable energy level and the non-coplanar molecular structures of 6 and 7. As can be seen in Fig. 6a and Fig. 6b, The devices 1 and 2 exhibit a maximum brightness of 13814, 10579 cd m<sup>-2</sup>, turn-on voltages (defined as the operation voltage at brightness of 1 cd m<sup>-2</sup>) of 4.2, 4.6V, maximum current efficiency of 2.34, 2.22 cd A<sup>-1</sup>, maximum power efficiency of 0.82, 0.53 lm W<sup>-1</sup>, respectively. What is more, when their current density is increased to 500 mA cm<sup>-2</sup>, the CE value is still remained at high levels (2.18 cd  $A^{-1}$  for **6** and 2.22 cd  $A^{-1}$  for **7**), indicating a much slower CE efficiency roll-off than most previous reports [2, 4, 10]. A comparison between these results and performance data of recently reported blue-green OLEDs is list in Table 2. The HOMO energy level of compound 7 (-5.51 eV) in device 2 is lower than that of compound 6 (-5.48 eV) in device 1 indicating that the hole-injections into the emitting layer of device 1 is more effective than device 2. The device performance of 1 is superior in turn-on voltage and efficiency supporting the effective hole-injection properties of compound 6.



Fig. 6. (a) Electroluminescence spectra of devices. (b) current density-voltage-brightness (*J-V-B*) characteristics. (c) current efficiencies and power efficiencies *versus* current density. (d) current density *versus* voltage characteristics of hole-only and electron-only devices for 6 and 7.

To best understand the different device performance, the hole and electron injection/transport properties of the two emitting materials are identified by single-carrier devices with the structures of ITO/TPD (15 nm)/6 or 7 (30 nm)/TPD (15 nm)/Al (100 nm) for hole only devices and ITO/TPBI (15 nm)/6 or 7 (30 nm)/TPBI (15 nm)/LiF (1 nm)/Al (100 nm) for electron-only devices. TPD and 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBI) layer are used to prevent electron and hole injection from the cathode and anode, respectively [9, 20, 40-42]. The current density *versus* voltage (*J-V*) curves of the four single-carrier devices are shown in Fig. 6d. The *J-V* characteristics of single-carrier devices indicate that 6 and 7 are capable of transporting both electron and hole carriers, suggesting their bipolar transporting nature. The current density of 6 in electron-only curve is lower than that in the hole-only curve while it is opposite for 7. This indicates a better hole transporting characteristic than hole transporting for 7. Moreover, the current density of 6 is lower than that for 7 at same voltage level suggesting 6 is easier transporting carrier in 18

comparison with 7. It is noteworthy that 6 and 7 have similar molecular structure, but show different transporting behaviors. A possible explanation for this behavior is that a twist angle (dihedral angles between anthrancene and naphthyl) greater than 100 for 7 can suppress the conjugation and therefore affects the carrier transport [43-45]. As described above, the device performance differences of 6 and 7 was attributed to the imparity energy level and disparity carrier balance.

Compound	$V_{ m on}$	EL <sub>max</sub> <sup>a</sup>	Brightness	CE <sup>b</sup>	PE <sup>c</sup>	EQE <sup>d</sup>	FWHM	CIE <sup>d</sup>	D.C
	(V)	(nm)	$(cd/m^2)$	(cd/A)	(lm/W)	(%)	(nm)	( <i>x</i> , <i>y</i> )	Ket
6	4.2	495	13814	2.34	0.82		80	0.20,0.43	This work <sup>e</sup>
			(3133) <sup>f</sup>	(3.62) <sup>f</sup>	(1.33) <sup>f</sup>				I IIIS WOFK
7 4.6	4.6	105	10579	2.22	0.53	_	80	0.20,0.43	This work <sup>e</sup>
	4.0	475	$(2868)^{\mathrm{f}}$	(7.16) <sup>f</sup>	(2.65) <sup>f</sup>				
FA4PADN	4.1	486	4490	1.43	0.85	-	65	0.17,0.39	[7] <sup>e</sup>
2	3.5	498	3199	0.64	0.31	0.28	82	0.19 , 0.38	[2] <sup>e</sup>
5c	7.7	505	335	1.1	0.33	0.43	-	0.23,0.42	[4] <sup>e</sup>
5P-2An	7.37	496		2.48	1.16	1.06	-	0.23,0.45	[46] <sup>e</sup>
2	-	484	1377	1.75	1.27	0.79	-	0.19,0.45	[10] <sup>e</sup>
PPODPA	4.0	496	7891	2.5	1.1	0.7	96	0.22,0.37	[6] <sup>e</sup>

Table 2. Key performance parameters of reported blue-green OLEDs

"**This work**" is defined as the devices reported in this article. <sup>a</sup> Maximum electroluminescence wavelength. <sup>b</sup> Maximum current efficiency. <sup>c</sup> Maximum power efficiency. <sup>d</sup> Maximum external quantum efficiency. <sup>e</sup> Non-doped devices. <sup>f</sup> Optimized device

In order to further improve the performance of blue-green devices, the HTL (TPD) was replaced with NPB and ETL (Alq3) was replaced with TPBi using the structures of ITO/NPB (25 nm)/6 (device **A**) or **7** (device **B**) (40 nm)/TPBi (15 nm)/LiF (1 nm)/Al (100 nm). As shown in **Fig. S5** and **Table 2**, the devices **A** and **B** exhibit maximum CE of 3.62, 7.16 cd  $A^{-1}$ , maximum PE of 1.33, 2.65 lm W<sup>-1</sup>, respectively. The performances of the blue-green devices were significantly enhanced because of the hole-blocking properties of TPBi [47]. However, the devices **A** and **B** exhibit a maximum brightness of 3133, 2868 cd m<sup>-2</sup> due to the low current density comparing with devices **1** and **2**. But overall, the brightness of devices **A** and **B** reach 700, 1400 cd m<sup>-2</sup> at a current density of 20 mA cm<sup>-2</sup>, respectively, indicating the *t*-APE-type derivatives have the excellent properties for the emitting materials of OLEDs.

## 3.3.2. White OLEDs

To realize the application of the blue-green fluorescent emitter in white OLEDs (WOLEDs), device **4** and **5** with the optimized configuration of ITO/TPD (25 nm)/**6** or **7** (20 nm)/[Alq3:4 Wt% rubrene] (20 nm)/Alq3 (15 nm)/LiF (1 nm)/Al (100 nm) were fabricated. The compound **6** and **7** were used as the blue-green emitter, rubrene doping in Alq3 (ETL) was used as the orange emitter, respectively. All the devices data are listed in **Table 3**. The orange device **3** with the configuration of ITO/TPD (25 nm)/[Alq3:4 Wt% rubrene] (40 nm)/Alq3 (15 nm)/LiF (1 nm)/Al (100 nm) was constructed for comparison (See ESI **Fig. S6, Table S1**). **Fig. 7** schematically shows an energy level diagram and the structure of the WOLEDs.



**Fig. 7.** (a)The energy-level diagram of the WOLEDs. (b) structure of the WOLEDs. (c) molecular structures of the materials used in this study.

Fig. 8 reveals the EL spectra of the devices at 7, 9, 11V. As can be seen, the spectra almost cover the whole visible light region from 400 nm to 750 nm and shows two main peaks centered at 495 nm and 565 nm which match with the emission peaks in monochromatic OLEDs using 6, 7 and rubrene. There is no other emission except for the two characteristic emissions, which indicates that there is no exciplex formation at the interface between charge transporting layer and light emitting layer, and the energy transfer from the Alq3 to orange dopant can be efficient. The CRI and the CIE coordinates of the device 4 and 5 are 65, 60, (0.30, 0.40) and (0.37, 0.47), respectively. It is well known that the spectral stability of WOLEDs is very significant for the application in either displays or solid state lighting. In the two WOLEDs, the blue-green and orange emissions are enhanced simultaneously with the driving voltage increase meaning that CIE coordinates of the two WOLEDs do not change with the driving voltage increase. In other words, the EL spectra of device 4 and 5 are stable under high voltage. In the EL process, there exists charge trapping effect due to the energy level of the rubrene [48]. However, the high concentration of rubrene (4 Wt%) can accelerate the electron transporting of Alq3 [49]. In addition, both 6 and 7 process bipolar characteristics, which result in charge carrier transmission is balanced in the

region of EML and finally carrier confined in the EML under the high voltage [50]. This is possible a reason for the stable EL spectra. And it is noteworthy that the device **4** exhibits cool white while device **5** is warm white.



Fig. 8. The normalized EL spectra of the device 4 (a) and 5 (b) at various voltages.

As can be seen in **Fig. 9**, the devices **4** and **5** exhibit a maximum brightness of 10984, 14652 cd  $m^{-2}$ , turn-on voltages of 3.2 V, maximum current efficiency of 2.04, 2.70 cd  $A^{-1}$ , maximum power efficiency of 0.99, 0.82 lm  $W^{-1}$ , respectively. Besides, device **5** with compound **7** is more effective than device **4** with compound **6** which is opposite to their monochromatic OLEDs though threshold curve is very alike.



Fig. 9. (a) Current density-voltage-brightness (J-V-B) characteristics. (b) current efficiencies and

power efficiencies versus current density.



Fig. 10. Schematic diagrams of the emission mechanisms of device 4 (a) and 5 (b).

To further comprehend the different performance of the two WOLEDs, the emission mechanism has been investigated. The hole injection barrier between **6**, and Alq3 is 0.32 eV while that for **7** is 0.29 eV. For the device **4**, due to the Alq3 ETL, the electron transport is relatively quick by it while holes can easily pass through TPD to reach the blue-green EML and then be blocked by Alq3. As shown in **Fig. 10a**, considering the thin blue-green EML, the main exciton generation zone is located at the blue-green EML and partially at the orange EML, resulting in low performance and cool white emission in device **4**. As can be seen in **Fig. 10b**, for the device **5**, due to the smaller holes injection barrier between **7** and Alq3 than **6**, the holes can easily pass through TPD to reach the orange EML. As a result, the main exciton generation zone is located at the blue-green EML. Then, device **5** exhibits high performance with warm white emission. As described above, the different performance and CIE coordinates of the two WOLEDs were attributed to the different energy level of **6** and **7**.

Device	$V_{ m on}$	EL <sub>max</sub> <sup>a</sup>	Brightness	CE <sup>b</sup>	PE <sup>c</sup>	CRI <sup>d</sup>	$CIE^{d}$
	(V)	(nm)	$(cd m^{-2})$	$(cd A^{-1})$	(lm W <sup>-1</sup> )		( <i>x</i> , <i>y</i> )
4	3.2	495,565	10984	2.04	0.99	65	0.30, 0.40
5	3.2	495,565	14652	2.70	0.82	60	0.37, 0.47

Table 3. Key performance parameters of the WOLEDs

<sup>a</sup> Maximum electrobrightness wavelength. <sup>b</sup> Maximum current efficiency. <sup>c</sup> Maximum power efficiency. <sup>d</sup> Recorded at 7 V.

#### 4. Conclusions

In conclusion, the new two blue-green materials, **6** and **7**, were designed and synthesized by incorporating naphthalene anthracene group into the *t*-APE molecule. The two compounds possess high thermal stability and morphological due to the asymmetric molecule structure. These two materials were employed as emitters to fabricate non-doped blue-green OLEDs that exhibit CE of 3.62, 7.16 cd A<sup>-1</sup>. When using **6** and **7** to construct the two-element WOLEDs, the WOLEDs exhibit stable EL spectra at high voltage (7 to 11 V). Further optimizing the structure of WOLEDs to improve the performance is currently in progress in our laboratory.

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#### References

[1] C.-L. Ho, W.-Y. Wong, Small-molecular blue phosphorescent dyes for organic light-emitting devices, New J. Chem., 37 (2013) 1665.

[2] J.N. Moorthy, P. Venkatakrishnan, P. Natarajan, D.F. Huang, T.J. Chow, De novo design for functional amorphous materials: synthesis and thermal and light-emitting properties of twisted anthracene-functionalized bimesitylenes, J. Am. Chem. Soc., 130 (2008) 17320-17333.

[3] L. He, L. Duan, J. Qiao, D. Zhang, L. Wang, Y. Qiu, Efficient blue-green and white organic light-emitting diodes with a small-molecule host and cationic iridium complexes as dopants, Appl. Phys. A, 100 (2010) 1035-1040.

[4] G. Haykir, E. Tekin, T. Atalar, F. Türksoy, Highly efficient non-doped blue organic light emitting devices based on anthracene–pyridine derivatives, Thin Solid Films, 548 (2013) 171-177.

[5] F. Dumur, M. Lepeltier, B. Graff, E. Contal, G. Wantz, J. Lalevée, C.R. Mayer, D. Bertin, D. Gigmes, Blue and blue–green PhOLEDs prepared with neutral heteroleptic iridium(III) complexes comprising substituted pyridine-1,2,4-triazoles as the ancillary ligands, Synth. Met., 182 (2013) 13-21.

[6] C.L. Wu, C.H. Chang, Y.T. Chang, C.T. Chen, C.T. Chen, C.J. Su, High efficiency non-dopant blue organic light-emitting diodes based on anthracene-based fluorophores with molecular design of charge transport and red-shifted emission proof, J Mater Chem C, 2 (2014) 7143-7438.

[7] H. Chen, W. Liang, Y. Chen, G. Tian, Q. Dong, J. Huang, J. Su, Efficient blue fluorescent organic light-emitting diodes based on novel 9,10-diphenyl-anthracene derivatives, RSC Adv., 5 (2015) 70211-70219.

[8] H. Shin, H. Kang, J.-H. Kim, Y.-F. Wang, S. Kim, K.-Y. Kay, J. Park, Synthesis and Electroluminescence Property of New Hexaphenyl Benzene Derivatives Including Emitting Core for OLED, J. Nanosci. Nanotechnol., 15 (2015) 8289-8294.

[9] D. Chen, L. Han, D. Liu, K. Ye, Y. Liu, J. Zhang, Y. Wang, High performance blue-green and green phosphorescent OLEDs based on iridium complexes with N^C^N-coordinated terdentate ligands, RSC Adv., 5 (2015) 18328-18334.

S.S. [10] Y.S. D.Y. S.E. Kim. Kim, Lee. Y.K. Kim, Yoon, N-(4-tert-Butylphenyl)-N-phenyl-4-(9,10-diphenylanthracen-3-yl)benzenamine for blue organic light-emitting diodes, Jpn. J. Appl. Phys., 55 (2016) 06GK06.

[11] X.B. Ding, J.G. Zheng, Y.D. Jin, P.L. Heremans, H.J. Geise, G. Borghs, Blue light emitting diodes(LED) based on alkoxy substituted biphenyl trimer as guest, Synth. Met., 137 (2003) 1003-1004.

[12] Y. Kim, S. Kwon, D. Yoo, M.F. Rubner, M.S. Wrighton, A Novel, Bright Blue Electroluminescent Polymer: A Diphenylanthracene Derivative, Chem. Mater., 9 (1997) 2699-2701.

[13] S.-W. Wen, M.-T. Lee, C.H. Chen, Recent Development of Blue Fluorescent OLED Materials and Devices, J. Display Technol., 1 (2005) 90.

[14] M.-X. Yu, J.-P. Duan, C.-H. Lin, C.-H. Cheng, Y.-T. Tao, Diaminoanthracene Derivatives as High-Performance Green Host Electroluminescent Materials, Chem. Mater., 14 (2002) 3958-3963.

[15] S. Wang, W.J. Oldham, R.A. Hudack, G.C. Bazan, Synthesis, Morphology, and Optical Properties of Tetrahedral Oligo(phenylenevinylene) Materials, J. Am. Chem. Soc., 122 (2000) 5695-5709.

[16] P.I. Shih, C.Y. Chuang, C.H. Chien, E.W.G. Diau, C.F. Shu, Highly Efficient Non-Doped Blue-Light-Emitting Diodes Based on an Anthrancene Derivative End-Capped with Tetraphenylethylene Groups, Adv. Funct. Mater., 17 (2007) 3141-3146.

[17] E. Ju Shin, R. Stackow, C.S. Foote, Excited state properties of some 1-(9-anthryl)-2-naphthylethene and 1-(9-anthryl)-2-quinolylethene derivativesDedicated to Professor Frank Wilkinson on the occasion of his retirement, Phys. Chem. Chem. Phys., 4 (2002) 5088-5095.

[18] J.J. Kiddle, Microwave Irradiation in Organophosphorus Chemistry. Iii. Moderate Scale Synthesis of Reagents for Olefin Formation, Synth. Commun., 31 (2006) 3377-3382.

[19] L. Al-Riyami, M.A. Pineda, J. Rzepecka, J.K. Huggan, A.I. Khalaf, C.J. Suckling, F.J. Scott, D.T. Rodgers, M.M. Harnett, W. Harnett, Designing anti-inflammatory drugs from parasitic worms: a synthetic small molecule analogue of the Acanthocheilonema viteae product ES-62 prevents development of collagen-induced arthritis, J. Med. Chem., 56 (2013) 9982-10002.

[20] D. Liu, M. Du, D. Chen, K. Ye, Z. Zhang, Y. Liu, Y. Wang, A novel tetraphenylsilane-phenanthroimidazole hybrid host material for highly efficient blue fluorescent, green and red phosphorescent OLEDs, J. Mater. Chem. C, 3 (2015) 4394-4401.

[21] N. Nagarajan, A. Prakash, G. Velmurugan, N. Shakti, M. Katiyar, P. Venuvanalingam, R. Renganathan, Synthesis, characterisation and electroluminescence behaviour of  $\pi$ -conjugated imidazole–isoquinoline derivatives, Dyes Pigm., 102 (2014) 180-188.

[22] S.F. Chen, Y. Tian, J. Peng, H. Zhang, X.J. Feng, H. Zhang, X. Xu, L. Li, J. Gao, Synthesis and characterization of arylamino end-capped silafluorenes for blue to deep-blue organic light-emitting diodes (OLEDs), J. Mater. Chem. C, 3 (2015) 6822-6830.

[23] M.M. Rothmann, S. Haneder, E. Da Como, C. Lennartz, C. Schildknecht, P. Strohriegl, Donor-Substituted 1,3,5-Triazines as Host Materials for Blue Phosphorescent Organic Light-Emitting Diodes, Chem. Mater., 22 (2010) 2403-2410.

[24] Z.-Y. Xia, Z.-Y. Zhang, J.-H. Su, Q. Zhang, K.-M. Fung, M.-K. Lam, K.-F. Li, W.-Y. Wong, K.-W. Cheah, H. Tian, C.H. Chen, Robust and highly efficient blue light-emitting hosts based on indene-substituted anthracene, J. Mater. Chem., 20 (2010) 3768.

[25] X. Yang, G. Zhou, W.Y. Wong, Functionalization of phosphorescent emitters and their host materials by main-group elements for phosphorescent organic light-emitting devices, Chem. Soc. Rev., 44 (2015) 8484-8575.

[26] E.J. Shin, H.-S. Jung, Photochemistry of anthrylethene derivatives containing heteroaromatic ring: Thiophene, furan, and their fused ring derivatives, J. Photochem. Photobiol. A: Chem., 173 (2005) 195-201.

[27] C.-S. Wu, S.-W. Fang, Y. Chen, Solution-processable hole-transporting material containing fluorenyl core and triple-carbazolyl terminals: synthesis and application to enhancement of electroluminescence, Phys. Chem. Chem. Phys., 15 (2013) 15121-15127.

[28] X. Ma, S. Wang, X. Li, Y. Xiao, Thermally induced crystallization behavior and film microstructure alteration of N,N,N',N'-tetraphenylbenzidine (TPB) and N,N,N',N'-tetra-p-tolyl-benzidine (TTB), Org. Electron., 15 (2014) 1876-1883.

[29] J. Huang, N. Sun, J. Yang, R. Tang, Q. Li, D. Ma, Z. Li, Blue Aggregation-Induced Emission Luminogens: High External Quantum Efficiencies Up to 3.99% in LED Device, and Restriction of the Conjugation Length through Rational Molecular Design, Adv. Funct. Mater., 24 (2014) 7645-7654.

[30] J. Yang, J. Huang, Q.Q. Li, Z. Li, Blue AIEgens: approaches to control the intramolecular conjugation and the optimized performance of OLED devices, J. Mater. Chem. C, 4 (2016) 2663-2684.

[31] J. Mei, N.L. Leung, R.T. Kwok, J.W. Lam, B.Z. Tang, Aggregation-Induced Emission: Together We Shine, United We Soar!, Chem. Rev., 115 (2015) 11718-11940.

[32] M.-S. Gong, H.-S. Lee, Y.-M. Jeon, Highly efficient blue OLED based on 9-anthracene-spirobenzofluorene derivatives as host materials, J. Mater. Chem., 20 (2010) 10735.

[33] Z. Zhao, S. Chen, J.W.Y. Lam, Z. Wang, P. Lu, F. Mahtab, H.H.Y. Sung, I.D. Williams, Y. Ma, H.S. Kwok, B.Z. Tang, Pyrene-substituted ethenes: aggregation-enhanced excimer emission and highly efficient electroluminescence, J. Mater. Chem., 21 (2011) 7210-7216.

[34] B.H. Thiers, Does hormone therapy improve age-related skin changes in postmenopausal women? A randomized, double-blind, double-dummy, placebo-controlled multicenter study assessing the effects of norethindrone acetate and ethinyl estradiol in the improvement of mild to moderate age-related skin changes in postmenopausal women, Yearbook of Dermatology and Dermatologic Surgery, 2009 (2009) 487-488.

[35] N. Nijegorodov, P.V. Luhanga, J.S. Nkoma, D.P. Winkoun, The influence of planarity, rigidity and internal heavy atom upon fluorescence parameters and the intersystem crossing rate constant in molecules with the biphenyl basis, Spectrochim. Acta. A. Mol. Biomol. Spectrosc., 64 (2006) 1-5.

[36] J.B. Foresman, M. Head-Gordon, J.A. Pople, M.J. Frisch, Toward a systematic molecular orbital theory for excited states, The Journal of Physical Chemistry, 96 (1992) 135-149.

[37] L. Wang, Z.-Y. Wu, W.-Y. Wong, K.-W. Cheah, H. Huang, C.H. Chen, New blue host materials based on anthracene-containing dibenzothiophene, Org. Electron., 12 (2011) 595-601.

[38] P. Raghunath, M.A. Reddy, C. Gouri, K. Bhanuprakash, V.J. Rao, Electronic properties of anthracene derivatives for blue light emitting electroluminescent layers in organic light emitting diodes: a density functional theory study, J. Phys. Chem. A, 110 (2006) 1152-1162.

[39] Z.-Y. Xia, J.-H. Su, W.-Y. Wong, L. Wang, K.-W. Cheah, H. Tian, C.H. Chen, High performance organic light-emitting diodes based on tetra(methoxy)-containing anthracene derivatives as a hole transport and electron-blocking layer, J. Mater. Chem., 20 (2010) 8382.

[40] C. Li, J. Wei, X. Song, K. Ye, H. Zhang, J. Zhang, Y. Wang, Non-doped luminescent material based organic light-emitting devices displaying high brightness under very low driving voltage, J. Mater. Chem. C, 4 (2016) 7013-7019.

[41] Y. Yuan, J.X. Chen, F. Lu, Q.X. Tong, Q.D. Yang, H.W. Mo, T.W. Ng, F.L. Wong, Z.Q. Guo, J. Ye, Z. Chen, X.H. Zhang, C.S. Lee, Bipolar Phenanthroimidazole Derivatives Containing Bulky Polyaromatic Hydrocarbons for Nondoped Blue Electroluminescence Devices with High Efficiency and Low Efficiency Roll-Off, Chem. Mater., 25 (2013) 4957-4965.

[42] S. Fan, J. You, Y. Miao, H. Wang, Q. Bai, X. Liu, X. Li, S. Wang, A bipolar emitting material for high efficient non-doped fluorescent organic light-emitting diode approaching standard deep blue, Dyes Pigm., 129 (2016) 34-42.

[43] J.-W. Cheon, C.-W. Lee, M.-S. Gong, N. Geum, Chemiluminescent properties of blue fluorophores containing naphthalene unit, Dyes Pigm., 61 (2004) 23-30.

[44] F.-C. Wu, C.-C. Lu, J. Ruan, F.-C. Tang, H.-L. Cheng, W.-Y. Chou, Enhanced and Anisotropic Charge Transport in Polymer-Based Thin-Film Transistors by Guiding Polymer Growth, Cryst. Growth Des., 17 (2016) 629-636.

[45] K. Bai, S. Wang, L. Zhao, J. Ding, L. Wang, Highly emissive carbazole-functionalized homopoly(spirobifluorene) for deep-blue polymer light-emitting diodes, Polym. Chem., 8 (2017) 2182-2188.

[46] H. Shin, H. Kang, J.H. Kim, Y.-F. Wang, S. Kim, K.-Y. Kay, J. Park, Synthesis and Electroluminescence Property of New Hexaphenyl Benzene Derivatives Including Emitting Core for OLED, J. Nanosci. Nanotechnol., 15 (2015) 8289-8294.

[47] Y.Q. Li, M.K. Fung, Z. Xie, S.T. Lee, L.S. Hung, J. Shi, An Efficient Pure Blue Organic Light-Emitting Device with Low Driving Voltages, Adv. Mater., 14 (2002) 1317-1321.

[48] Y.D. Jiang, Q. Jiang, B. Kippelen, J. Qu, J. Yu, J. Yu, S. Tao, Y. Gan, Y. Jiang, A white organic light emitting diode based on anthracene-triphenylamine derivatives, 7658 (2010) 765835.

[49] B. Mo, X. Zhang, L. Liu, H. Wang, J. Xu, H. Wang, B. Wei, Bilayer-structure white organic light-emitting diode based on [Alq3:rubrene] and the electron transporting characteristics investigation using impedance spectroscopy, Opt. Laser Technol. , 68 (2015) 202-205.

[50] J.-H. Jou, C.-J. Wang, Y.-P. Lin, Y.-C. Chung, P.-H. Chiang, M.-H. Wu, C.-P. Wang, C.-L. Lai, C. Chang, Color-stable, efficient fluorescent pure-white organic light-emitting diodes with device architecture preventing excessive exciton formation on guest, Appl. Phys. Lett., 92 (2008) 223504.

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Two asymmetric blue-green emitting materials based on *t*-APE were firstly designed and synthesized.

These two materials possess high thermal stability, morphological durability, and bipolar characteristics.

The non-doped blue-green OLEDs based on these two materials show preferable performance.

Furthermore, when applying these two materials to fabricate WOLEDs with simple structure, the WOLEDs exhibit stable EL spectra.

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