This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Efficient blue fluorescent organic light-emitting diodes based on novel 9,10-diphenyl-anthracene derivatives

Five 9,10-di(naphthalen-2-yl)anthracene (ADN) derivatives with fluorenamine or indenocarbazole moiety have been successfully developed for blue emitters of OLEDs. All materials showed good chemical and thermal stability, moreover the OCADN based device exhibited highly efficient sky-blue emission with current efficiency of 2.25 cd/A, power efficiency of 1.13 lm/W and CIE(x,y) coordinate of (0.16, 0.30) at 8 V.
Efficient blue fluorescent organic light-emitting diodes based on novel 9,10-diphenyl-anthracene derivatives

Hongwei Chen,*a Wenqing Liang,*b Yi Chen,a Guojian Tian,a Qingchen Dong,*b Jinhai Huang,*a and Jianhua Su*a

A series of novel 9,10-di(naphthalen-2-yl)anthracene (ADN) derivatives were designed and synthesized as blue fluorescent emissive materials by inducing diverse aromatic groups to CN2 position of ADN. UV-Vis absorption, fluorescence emission spectroscopy and cyclic voltammetry (CV) were carried out to generally investigate the relationships between the physical properties and molecular structures. Moreover, four non-doped OLED devices adopting OCADN, FA3PADN, FA4PADN and OC4PADN as emitting materials were fabricated to study their electroluminescence (EL) performances. Among them, device based on OCADN exhibited highly efficient sky-blue emission with current efficiency of 2.25 cd/A, power efficiency of 1.13 lm/W and CIE (x,y) coordinate of (0.16, 0.30) at 8 V. In addition, the device of OC4PADN showed efficient blue emission with CIE(x,y) coordinate of (0.16, 0.14) at 8 V.

Introduction

Organic light-emitting diodes (OLEDs) have attracted enormous attentions owing to their excellent performances such as rapid response, high brightness, flexibility, low driving voltage and full-color emission, etc.1-5 Because of its high technological potential for high-quality flat-panel displays and solid state lighting, OLEDs have made great process and successfully applied in mobile phones and digital cameras since Tang and his co-workers firstly introduced an efficient OLEDs.6-9 To achieve full-color displays, the red, green and blue emission of relatively equal stability, efficiency and color purity were required. Although a great number of red and green emitters have been developed to satisfy the requirements of OLEDs in the practical usage, efficient and stable organic blue emitting materials are still rare.10-14 Thus, the development of blue-emitting materials with high performance still remains to be challenge.

To date, many small-molecule emitters, including anthracene10-18, carbazole19-22, fluorine23-25, triarylamine26-28, and pyrene29-31 derivatives, have been reported for application in blue OLEDs. As known to all, anthracene was widely used as an attractive building block and starting material for fluorescent blue emitting in OLEDs, due to its high fluorescence quantum yield, wide energy band-gap and easy modification.1,10-18 However, the anthracene with large π-conjugation is easy to aggregate in condensed phase, leading to fluorescence quenching and emission wavelength red-shift. Thus, many endeavours have been made to avoid the planar configuration by introducing different functionalized blocks to the 9,10-positions of anthracene.1,12-38 For example, Shi and Tang firstly reported a 9,10-substituted anthracene derivatives, the di(2-naphthyl)anthracene (ADN), as blue emitter host in 2002.39 But the incorporation of two perpendicularly naphthyl can not completely overcome the red-shifting and fluorescence quenching problems. Therefore, some further work has been processed about introducing different bulky groups at 2,3,6,7-positions of ADN, and their devices showed good morphologic stability and performance, indicating that the molecule...
aggression can be remarkably suppressed by disrupting the symmetry of ADN.

Fluorene derivatives were also widely used in OLEDs as blue emitters due to several advantages including their capability of emitting in the blue region spectrum, chemical and morphologic stability, and thermal durability under operation. Arylamine group is well-known for its ability to transport charge carriers, and incorporated it into other molecules can improve hole injection and carrier transport properties and increase bulky volumes and thermal stability, as well as improve device stability due to the amorphous structure, charge balance and reduce energy consumption. The materials with fluorenamine or indenocarbazole group have shown excellent hole-injection and transporting capability.

With respect to all mentioned above, in this work, five asymmetric blue light emitting materials of the ADN derivatives, N-(9,9-diethyl-9H-fluoren-2-yl)-9,10-di(naphthalen-2-yl)-N-phenyl-anthracen-2-amine (FAADN), 5-(9,10-di(naphthalen-2-yl)anthracen-2-yl)-7,7-dimethyl-5,7-dihydroindencarbazole (OCADN), N-(3-(9,10-di(naphthalen-2-yl)anthracen-2-yl)phenyl)-9,9-diethyl-N-phenyl-9H-fluoren-2-amine (FA3PADN), 9,9-diethyl-N-phenyl-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-fluoren-2-amine (FA4PADN) and 7,7-dimethyl-5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-5,7-dihydroindencarbazole (OC4PADN) were designed and synthesized. The fluorenamine and indenocarbazole moiety which were introduced to the 2-position of di(2-naphthyl)anthracene were to prevent the emission red-shifting and fluorescence quenching in solid, as well as to increase the hole transporting capability, thermal stability and morphologic stability. The incorporation of a phenyl bridge between ADN core and modified moiety is aimed to increase the molecule twisty degree of the molecule and reduce the π-electron conjugation between the two moieties. In order to explore the influence of these substituents of ADN, we fully investigated the thermal and photophysical properties and measured the HOMO and LUMO values. Moreover, to estimate the practical utilities of these ADN derivatives, four non-doped devices with a multilayer structure of ITO/PEDOT: PSS (50 nm)/NPB (60 nm)/ADNs (40 nm)/TPBI (20 nm)/LiF/Al were fabricated. The OCADN based device showed a reasonable good performance among these four studied blue devices, with maximum brightness of 5839 cd/m², current efficiency of 2.25 cd/A, power efficiency of 1.13 lm/W and a sky-blue color purity of CIE (0.16, 0.30).

Results and discussion

Synthesis and characterization

The synthetic routes of the intermediates and target compounds were shown in Scheme 1 and 2. The starting materials 1-2 and 9,10-di-n(2-bromo-2-naphthalenyl)anthracene were obtained from Shanghai Taoe chemical technology Co., Ltd. Other intermediates 3-6 were synthesized according to literature with

\[
\begin{align*}
\text{AcOK, Pd(dppf)Cl}_2, & \quad \text{1} \rightarrow \text{2} \\
\text{KOH, CuI, Orthophenanthroline} & \quad \text{3} \rightarrow \text{4}
\end{align*}
\]

Scheme 1 Synthetic routes of intermediates 3-8.

Fig. 1 (a) UV-Vis absorption spectra of all ADN derivatives in toluene. (b) PL spectra of all ADN derivatives in toluene and (c) PL spectra of these compounds in thin film.
Scheme. 2 Synthetic routes of ADN derivatives.

high yields.\textsuperscript{46-48} The target products were prepared by Buchwald-Hartwig and Suzuki coupling reaction between the 2-bromo-9,10-di(naphthalen-2-yl)anthracene and the corresponding aryl amine or aryl boronic acid, then purified by flash column chromatograph and recrystallization with yields of 32-62.5%. Repeated temperature-gradient vacuum sublimation was required for further purification of these ADN derivatives when used in OLEDs. The molecule structures of these compounds were characterized by \textsuperscript{1}H NMR, \textsuperscript{13}C NMR spectroscopy, and high-resolution mass spectrometry (HRMS).

Photophysical properties

The absorption and emission spectra of ADN derivatives were studied in toluene and solid thin films, which were dissolved in dichloromethane solution with PMMA and spin-coating on quartz plates. As shown from spectra, the UV-Vis absorption spectrum of ADN derivatives exhibits characteristic peaks in the range from 350 to 460 nm, which is attributed to the \( \pi-\pi^* \) transition of the characteristic vibrational structures of anthracene groups. FA4P ADN and FAADN showed broadening and red-shifting of the absorption spectra compared with other three compounds due to the stronger electron donating ability of fluorenamine moiety and their larger \( \pi \)-electron conjugation of molecule.

As shown in Fig. 1, all the compounds exhibited the maximum emission wavelength at around 438-497 nm in toluene and 453-505 nm in the solid thin film. The slight red shifted in the emission spectrum of the thin film from the solution could be attributed to the intermolecular \( \pi-\pi \) stacking of these ADN derivatives. All of these derivatives exhibited blue fluorescent color both in toluene and in solid state. It indicated that the co-planarity and \( \pi \) conjugation of molecule have been disrupted to some extent by the twist between functionalized moieties and anthracene core. OCADN and OC4PADN, which modified by indenocarbazole, showed blue-

<table>
<thead>
<tr>
<th>ADN derivatives</th>
<th>( \lambda_{ab} ) (nm)</th>
<th>( \lambda_{set;on} ) (nm)</th>
<th>( \lambda_{em} ) (nm)</th>
<th>( \Phi_\text{f} ) (%)</th>
<th>( \lambda_{em} ) (nm)</th>
<th>HOMO\textsuperscript{2} (eV)</th>
<th>LUMO\textsuperscript{2} (eV)</th>
<th>( E_g ) (eV)</th>
<th>( T_d ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA3P ADN</td>
<td>410</td>
<td>431</td>
<td>459</td>
<td>38</td>
<td>460</td>
<td>-5.17</td>
<td>-2.29</td>
<td>2.88</td>
<td>423</td>
</tr>
<tr>
<td>FA4P ADN</td>
<td>426</td>
<td>453</td>
<td>468</td>
<td>62</td>
<td>483</td>
<td>-5.10</td>
<td>-2.36</td>
<td>2.73</td>
<td>495</td>
</tr>
<tr>
<td>OCADN</td>
<td>423</td>
<td>445</td>
<td>454</td>
<td>46</td>
<td>458</td>
<td>-5.34</td>
<td>-2.55</td>
<td>2.79</td>
<td>408</td>
</tr>
<tr>
<td>FAADN</td>
<td>458</td>
<td>489</td>
<td>497</td>
<td>64</td>
<td>505</td>
<td>-5.02</td>
<td>-2.48</td>
<td>2.53</td>
<td>407</td>
</tr>
<tr>
<td>OC4PADN</td>
<td>412</td>
<td>431</td>
<td>438</td>
<td>46</td>
<td>453</td>
<td>-5.35</td>
<td>-2.47</td>
<td>2.88</td>
<td>492</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Measured in toluene. \textsuperscript{b}Measured in thin film on quartz substrate. \textsuperscript{c}Measured versus ferrocene, The HOMO and LUMO energy levels were determined using the following equations: \( E_{\text{HOMO}} = [E_{\text{ox}} - E_{\text{1/2}} (\text{ferrocene}) + 4.8] \), \( E_{\text{LUMO}} = E_{\text{HOMO}} - E_g \). \textsuperscript{d}Obtained from onset of the absorption spectra by extrapolation (\( E_g = 1240/\lambda_{\text{set\;on}} \)). \textsuperscript{e}Measured by TGA at a heating rate of 10 °C min\textsuperscript{-1}. 

---

This journal is © The Royal Society of Chemistry 2012
The conjugation between the substituted unit and ADN core. However, the compounds with the same substituted group (FAADN and FA4PADN or OCADN and OC4PADN) exhibited totally different maximum emission peak in the similar order (FA4PADN < FAADN or OC4PADN < OCADN). It showed that the incorporation of phenyl ring significantly increased the molecule twist and reduced the π conjugation. In addition, the maximum emission of the para-disposition linkage compound (FA4PADN) was observed at long wavelength with respect to that of the meta-disposition isomer (FA3PADN), it would be attributed to the para-disposition linkage could partially enlarge the π conjugation between ADN core and fluoronamene group.

As shown in Table 1, the fluorescence quantum yields of OCADN, OC4PADN, FAADN, FA3PADN and FA4PADN were measured from 33% to 64% in solution. The ϕ_l data were consistent with the PL emission, the ϕ_l of FAADN and FA4PADN were higher than OCADN and OC4PADN in toluene, which indicated that the fluoronamene unit enhanced the electron donating ability of the molecule.

Thermal property

The device lifetime of OLEDs is directly related to the thermal stability of the light-emitting layer. Thus, high thermal decomposition temperature (Tₙd) is desirable for light-emitting material to be utilized in OLEDs. The thermal properties of ADN derivatives were investigated by thermogravimetry (TGA) measurement, the relative data are listed in Table 1 and are shown in Fig. 2. OCADN, OC4PADN, FAADN, FA3PADN and FA4PADN, which were C-2 modified ADN derivatives, exhibited high Tₙd (corresponding to 5% weight loss) of 408, 492, 407, 423, 495 °C, respectively. The values of Tₙd of OC4PADN, FA3PADN and FA4PADN are much higher than that of OCADN and FAADN, which is attributed to the presence of more aromatic rings in the molecule of OC4PADN, FA3PADN and FA4PADN. Due to the large-volume substituents at the C-2 position of ADN, all these five compounds revealed high thermal stability and were capable of enduring the vacuum thermal deposition process in OLED fabrication, which suggested that the emitting layer composed with these ADN derivates has stable morphological properties and was desirable for OLEDs with high stability and efficiency.⁴⁰,⁴⁹

Electrochemical properties

The electrochemical behavior of ADN derivatives was investigated by cyclic voltammery using a standard three-electrode electrochemical cell in an electrolyte solution (0.1 M TBAPF₆/DCM), and ferrocene as external reference. The highest occupied molecular orbital (HOMO) estimated from the onset potentials of oxidation peak, were calculate to be -5.02 to -5.35 eV, while the lowest unoccupied molecular orbital (LUMO) of these derivatives measured by HOMO and band gap energy (E_g), were calculated to be -2.29 to -2.55 eV. The data of HOMO, LUMO energy levels and E_g was summarized in Table 1. The HOMO levels of OCADN and OC4PADN were lower than that of the other three compounds, which indicated that their greater steric hindrance between the ADN core and indenocarbazole moiety would dilute the electron density. In addition, the HOMO energy of these ADN derivatives were higher than those of ADN (-5.8 eV), due to the electron-donating functionalized moieties on C-2 position of ADN. It would certainly decrease the energy barrier between hole-transporting layer and light-emitting layer, and then further improve device performance.

Electroluminescence

In order to investigate the electroluminescence (EL) performance of these new blue emitting materials (excluding FAADN, which were spectroscopically unsatisfactory), four non-doped devices were fabricated by vacuum thermal deposition with the configuration of ITO/ PEDOT: PSS (50 nm)/ NPB (60 nm)/ ADNs (40 nm)/ TPBI (20 nm)/ LiF/ Al. Here, TIO was used as an anode electrode and the LiF/Al layers were employed as a composite cathode. Poly(3,4-ethylenedioxythiophene)/ poly(styrenesulfonate) (PEDOT: PSS) was used as the hole-injection layer, 4,4'-bis[N-(1-naphthyl)-N-phenyl-1-amino]-biphenyl (NPB) as the hole-transporting layer,
and 2,2',2''-(1,3,5-benzenetriyl)-tris(1-phenyl-1H-benzimidazole) (TPBI) as the electron-transporting layer and the hole-blocking layer. The structures and the energy levels of the materials used in these devices are demonstrated in Fig. 3 and the key performance data were summarized in Table 2.

The current density-voltage (J-V) curve of these four devices is displayed in Fig. 4 (a). As we can see, the turn-on voltages were range from 4.1 to 5.6 eV. The primary reason for the low turn-on voltage is that the HOMO and LUMO energy level of ADN derivatives are matched with the NPB and TPBI, which reduced the energy barrier between hole/electron transporting layer and emitting layer, and then profited the hole and electron transporting and recombination in emitting layer.

Fig. 4 (a) Current density-voltage characteristics and (b) Luminance-voltage characteristics of the four devices.

Fig. 5 (a) Current efficiency and (b) Power efficiency of the four device.

### Table 2 Characteristics of OLEDs^a^

<table>
<thead>
<tr>
<th>ADN derivatives</th>
<th>Turn-on Voltage^b^ (V)</th>
<th>Max. luminance^c^ (cd/m^2^)</th>
<th>Max. efficiency^c^ (cd/A, lm/W)</th>
<th>λ_{EL}, FWHM^d^ (nm)</th>
<th>CIE(x,y)^e^</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA3PADN</td>
<td>4.5</td>
<td>4369</td>
<td>1.14, 0.65</td>
<td>487, 76</td>
<td>(0.18, 0.33)</td>
</tr>
<tr>
<td>FA4PADN</td>
<td>4.1</td>
<td>4490</td>
<td>1.43, 0.85</td>
<td>486, 65</td>
<td>(0.17, 0.39)</td>
</tr>
<tr>
<td>OCADN</td>
<td>5.1</td>
<td>5839</td>
<td>2.25, 1.13</td>
<td>477, 62</td>
<td>(0.16, 0.30)</td>
</tr>
<tr>
<td>OC4PADN</td>
<td>5.6</td>
<td>3146</td>
<td>0.99, 0.48</td>
<td>451, 53</td>
<td>(0.16, 0.14)</td>
</tr>
</tbody>
</table>

^a^ITO/ PEDOT: PSS (50 nm)/ NPB (60 nm)/ ADNs (40 nm)/ TPBI (20 nm)/ LiF/ Al. ^b^Turn-on voltage at 1 cd/m^2^. ^c^Maximum values. ^d^Maximum EL emission peak and full-width-at-half-maximum were recorded at 8.0 V. ^e^Commission Internationale d’ Éclairage (CIE) at 6.0 V.
the current efficiency (IE) and luminous efficiency (LE) of the fabricated devices. Among the four devices, the OCADN-based device exhibited the most efficient performance with current efficiency of 2.25 cd/A and power efficiency of 1.13 lm/W, mainly attributed to its lowest LUMO energy level and the smallest energy barrier between OCADN and TPBI among these four compounds, which was helpful for electron transporting. Meanwhile, its relative lower HOMO energy level was also reduced the barrier between hole-transporting layer and emitting layer and beneficial for hole transporting. The devices with these four materials, especially the OCADN, showed high maximum brightness, maximum current and power efficiency. It indicated that the incorporation of fluorenamine or indenocarbazole moiety was helpful for improving the device performance. And it was worthwhile to note that all four devices showed a near flat current efficiency versus current density response, which indicated that the hole transporting nature of indenocarbazole and fluorenamine unit could reduce the efficiency roll-off and enhance the EL performance of device.

From the EL spectra shown in Fig. 6, we can know that all of these devices exhibited blue emissions with maximum emission peaks at 486, 487, 477, 451 nm and the corresponding CIE coordinates of devices were (0.18, 0.33), (0.17, 0.39), (0.16, 0.30) and (0.16, 0.14) at 8.0 V, respectively. The devices with our four materials maintained good EL emission in the blue region spectrum, which suggested that the red shifting were effectively suppressed when these materials used as emitter to devices. In accordance with the solid state PL emission, the device of OC4PADN and OCADN exhibited deeper blue EL compared with FA3PADN and FA4PADN. It could be attributed to the larger steric hindrance between the rigid and co-planar indenocarbazole unit and the ADN core, which reduced the coplanarity and π conjugation between the two moieties. Moreover, the device using OC4PADN as emitter showed the most deep-blue emission with the CIE (x,y) of (0.16, 0.14) at 8.0 V, due to the more twisty configuration of OC4PADN which incorporation a phenyl ring between the donor and the anthracene core. Furthermore, it was worth to note that there is almost no EL color shift vary different driving voltages for all devices, it demonstrated that the hole-electron pairs for recombination were well confined in the blue emitter layer. The EL spectra of these four devices under different driving voltages were shown in the (ESI†).

**Experimental**

**Materials**

All starting materials were purchased from J & K Chemical Co., Aladdin Chemical Co. and Shanghai Taoe chemical technology Co., Ltd. without further purification. Solutions were carefully dried and distilled from appropriate drying agents prior to use. All reactions and manipulations were carried out under N₂ atmosphere. Silica gel (300-400 mesh) column chromatography was used as the stationary phase in the column.

The ¹H NMR and ¹³C NMR spectra were measured using a Bruker AM 400 spectrometer. The mass spectra were obtained on a Waters LCT Premier XE spectrometer. The ultraviolet-visible (UV-Vis) absorption spectra of the samples were characterized using a Varian Cary 500 spectrophotometer. Photoluminescence (PL) measurements were conducted by a Varian-Cary fluorescence spectrophotometer at room temperature. The cyclic voltammetry experiments were performed by a Versastat II electrochemical workstation (Princeton applied research) using a conventional three-electrode configuration with a glassy carbon working electrode, a Pt wire counter electrode, and a regular calomel reference electrode in saturated KCl solution, 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in dichloromethane solution as the supporting electrolyte with a scan rate of 100 mV/s. The E₁/₂ values were determined by (Eₚ + Eₚₐ)/2 using Ferrocene as an external standard, where Eₚ and Eₚₐ were the anodic and cathodic peak potentials, respectively. Thermo gravimetric analysis was carried out using a TGA instrument under a nitrogen atmosphere with a heating scan rate of 10 °C/min.

**Synthesis**

The synthesis of intermediates and ADN derivatives (FAADN, OCADN, FA3PADN, FA4PADN, OC4PADN) are presented in Schemes. 1 and 2. **Synthesis of 2-((3-bromophenyl)(phenyl)methyl)-9,9-dimethyl-9H-fluorene (3).**

A mixture of 1-bromo-3-iodobenzene(4.23 g, 0.015 mol), 9,9-dimethyl-N-phenyl-9H-fluoren-2-amine (2.85 g, 0.01 mol), potassium hydroxide (2.81 g, 0.01 mol), cuprous iodide (0.095 g, 0.5 mmol) and orthophenanthroline (0.09 g, 0.5 mmol) in 1,3,5-trimethylbenzene (80 ml) was stirred at 170 °C for 8 h under nitrogen atmosphere. After cooling to room temperature, the solution was evaporated to dryness under reduced pressure. The cold water was then added to the mixture and finally extracted with DCM. The combined organic phase was collected, filtered and dried over MgSO₄. The subjection of the crude mixture to silica gel chromatography using petroleum
ether/ dichloromethane (4:1, v/v) afforded 3 (2.43 g, yield: 55.4 %) as milky white solid. 1H NMR (400 MHz, DMSO) δ 7.77 (m, J = 10.6, 7.4 Hz, 2H), 7.52 (d, J = 6.8 Hz, 1H), 7.39-7.34 (m, 2H), 7.34-7.26 (m, 3H), 7.22 (t, J = 8.0 Hz, 1H), 7.17-7.08 (m, 4H), 7.06-6.99 (m, 2H), 6.97-6.92 (m, 1H), 1.37 (d, J = 7.2 Hz, 6H).


50 ml of anhydrous 1,4-dioxane was added to a mixture of 3 (1.09 g, 2.5 mmol), bis(pinacolato) diboron (0.95 g, 3.75 mmol), potassium acetate (0.74 g, 7.5 mmol), [1,1’-Bis(diphenylphosphino) ferrocene]palladium(II) dichloride (Pd(dpdpf)Cl2) (Catalytic amount). The reaction mixture was stirred at 100 °C for 2 h under nitrogen atmosphere. After the reaction was worked up by adding water, the organic layer was extracted with DCM and solution was evaporated. The crude product was purified by column chromatography using petroleum ether/dichloromethane (5:1 v/v) as eluent. A yellow solid was obtained (0.88 g, yield: 42.6 %).


A mixture of 9,9-dimethyl-N-phenyl-9H-fluoren-2-amine (0.3 g, 1.05 mmol), 2-bromo-9,10-di-(naphthalen-2-yl)anthracene (0.53 g, 1.05 mmol), potassium tert-butoxide (0.14 g, 1.26 mmol), palladium acetate (0.01 g, 0.05 mmol) and 2-dicyclohexyl phosphino-2’,4’,6’-trisopropylbiphenyl (Xphos, 0.036 g, 0.11 mmol) was dissolved in 1,3,5-trimethylbenzene (30 mL) and heated at 170 °C for 8 h under nitrogen. After cooling, the solution was concentrated under reduced pressure. The resulting solid was poured into the mixture and extracted with DCM. The organic layer was collected, filtered and dried over MgSO4, and the crude product was further purified by column chromatography using petroleum ether/dichloromethane (4:1, v/v). Finally afforded FAADN (0.32 g, yield: 42.6 %) as yellow solid.

Synthesis of N-(9,10-di(naphthalen-2-yl)anthracen-2-yl)-7,7-dimethyl-5,7-dihydroindeno[2,1-b]carbazole (OCADN).

Synthesis of 5-(9,10-di(naphthalen-2-yl)anthracen-2-yl)-7,7-dimethyl-5,7-dihydroindeno[2,1-b]carbazole (OCADN).

OCADN (0.17 g, yield: 54.0 %) was synthesized as a yellow solid in a similar manner of FAADN with 2 instead of 1.

Synthesis of N-(3-(9,10-di(naphthalen-2-yl)anthracen-2-yl)-phenyl)-9,9-dimethyl-N-phenyl-9H-fluoren-2-amine (FA3PAND).

2-bromo-9,10-di(naphthalen-2-yl)anthracene (0.38 g, 0.75 mmol), 4 (0.25 g, 0.5 mmol), 2M aqueous potassium carbonate (10 mL) was added to the crude product (0.25 g, yield: 62.5 %) as yellow solid.

Synthesis of N-(9,9-dimethyl-9H-fluoren-2-yl)-9,10-di(naphthalen-2-yl)-N-phenylantraacen-2-amine (FAADN).
(m, 1H), 1.29 (t, J = 5.1 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 152.51, 147.37, 145.99, 141.01, 137.92, 136.33, 132.42, 131.78, 129.26, 128.47, 128.10, 127.01, 126.06, 125.90, 125.43, 125.22, 124.19, 123.37, 123.14, 122.56, 121.77, 121.43, 121.22, 120.20, 119.56, 118.42, 117.91, 45.75, 26.01. HRMS (ESI, m/z): [M+H]$^+$ calcd for C$_{38}$H$_{55}$N, 790.3474, found 790.3470.

Synthesis of 9,9-dimethyl-N-phenyl-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-fluoren-2-amine (FA4PADN). FA4PADN (0.17 g, yield: 54.0 %) was synthesized as a yellow solid in a similar manner of FA3PADN with 8 instead of 4. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.10 (m, 2H), 8.07-7.99 (m, 4H), 7.98-7.89 (m, 3H), 7.81 (d, J = 9.2 Hz, 1H), 7.77-7.70 (m, 2H), 7.69-7.64 (m, 2H), 7.60 (m, 6H), 7.55 (d, J = 8.2 Hz, 1H), 7.38 (t, J = 8.0 Hz, 3H), 7.32-7.27 (m, 3H), 7.22 (d, J = 7.4 Hz, 3H), 7.17 (d, J = 2.0 Hz, 1H), 7.11 (d, J = 7.6 Hz, 2H), 7.07 (d, J = 8.6 Hz, 2H), 7.01 (m, 2H), 1.38 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 155.10, 147.67, 147.40, 138.92, 137.12, 136.60, 134.45, 133.49, 132.83, 130.56, 130.07, 129.67, 129.27, 129.72, 127.04, 126.96, 126.28, 125.27, 124.39, 123.75, 123.48, 122.92, 122.46, 120.64, 119.46, 119.01, 46.83, 27.07. HRMS (ESI, m/z): [M+H]$^+$ calcd for C$_{38}$H$_{55}$N, 790.3474, found 790.3476.

Synthesis of 7,7-dimethyl-5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-5,7-dihydroindeno carbazole (OC4PADN). OC4PADN (0.18 g, yield: 32.0 %) was synthesized as a white solid in a similar manner of FA3PADN with 6 instead of 4.

**Conclusions**

In summary, we have synthesized and characterized a series of ADN derivatives, FAADN, OCADN, FA3PADN, FA4PADN and OC4PADN. Expect for FAADN, the other four materials exhibited satisfactory blue fluorescence emission both in toluene and solid film, which attributed to the sterically hindered substituent at C-2 position of ADN. These compounds also showed excellent thermal properties and appropriate energy levels, which can be utilized as emitting materials for OLED device. As a result, a device based on OCADN with the structure of ITO/ PEDOT: PSS/ NPB/ ADNs/ TPBI/ LiF/ Al showed efficient blue emission peaked at 477 nm and CIE chromaticity coordinates of (0.16, 0.30). The maximum current efficiency and power efficiency of the device reached 2.25 cd/A and 1.13 lm/W, respectively.

**Acknowledgements**

Q. Dong thanks the financial support from the National Natural Science Foundation of China (Grant No.: 61307030), Program for the Outstanding Innovative Teams of Higher Learning Institutions of Shanxi (OIT), Fund Program for the Scientific Activities of Selected Returned Overseas Professionals in Shanxi Province, the Natural Science Foundation for Young Scientists of Shanxi Province, China (Grant No.: 2014021019-2), the Outstanding Young Scholars Cultivating Program, Research Project Supported by Shanxi Scholarship Council of China (Grant No.: 2014-02) and the Qualified Personal Foundation of Taiyuan University of Technology (Grant No.: 2013Y003, tyut-rc201275a).

**References**
