



Journal of Nanoscience and Nanotechnology Vol. 19, 4799–4802, 2019 www.aspbs.com/jnn

# Synthesis and Electroluminescence Property of Green Fluorescent Dopant Including Anthracene and Diphenylamine Moiety

Hyocheol Jung, Jaemin Ryu, Seokwoo Kang, Hayoon Lee, and Jongwook Park\*

Department of Chemical Engineering, Kyung Hee University, Yongin-si, Gyeonggi-do, 17104, Republic of Korea

We have synthesized green fluorescent emitters of  $N^9, N^9, N^{10}, N^{10}$ -tetraphenylanthracene-9,10-diamine (TAD) and  $N^9, N^9, N^{10}, N^{10}$ -tetra-o-tolylanthracene-9,10-diamine (*o*Me-TAD) including anthracene and diphenylamine moiety and evaluated properties of compounds. The methyl groups were introduced to the diphenylamine to prevent molecular aggregation of the dopant and reduce self-quenching through steric hindrance of molecular structure. In solution state, photoluminescence (PL) maximum wavelength is 508 nm for TAD and 519 nm for *o*Me-TAD. In film state, PL maximum wavelength is 518 nm for TAD and 527 nm for *o*Me-TAD. In electroluminescence (EL) spectra, EL maximum wavelength of TAD is 508 nm and EL maximum wavelength of *o*Me-TAD is 522 nm. The doped device using TAD as green fluorescent dopant exhibited CE of 17.7 cd/A, PE of 7.74 lm/W, and EQE of 6.11%. The doped device using *o*Me-TAD as dopant exhibited CE of 19.8 cd/A, PE of 7.23 lm/W, and EQE of 5.97%.

Keywords: Organic Light-Emitting Diode, by Green & Fluorescent Dopant, Anthracene, Diphenylamine.

## **1. INTRODUCTION**

Organic light-emitting diodes (OLEDs), first reported by Tang and VanSlyke, have received much attention in academic and industrial fields until recently.<sup>1</sup> In particular, OLEDs have received attention to full-color display and lighting applications. For application in full-color display and lightings fields, development of red, green, and blue emitters with high photoluminescence (PL) and electroluminescence (EL) efficiency is essential.

To design emitters with high PL and EL efficiency, a core-side concept has been used. Chromophores with high photoluminescence quantum yield (PLQY) such as anthracene, pyrene, and chrysene are selected as core groups. In the case of side groups, bulky side groups such as *m*-terphenyl (TP) or triphenylbenzene (TPB) can effectively prevent intermolecular packing. Also, electrondonating group such as diphenylamine (DPA) or triphenylamine (TPA) as side groups can improve the EL efficiency of emitters.<sup>2-7</sup>

\*Author to whom correspondence should be addressed.

Recently, many studies have been reported on the introduction of methyl groups into chromophores such as anthracene and chrysene to form highly twisted molecular structures.<sup>8-9</sup> Highly twisted molecular structure can effectively prevent intermolecular packing, thus reducing the concentration quenching effect of emitters. In addition, substituting functional group at *ortho* position can help control not only the absorption and emission wavelength of material, but also energy levels such as highest occupied molecular orbital (HOMO) level and lowest unoccupied molecular orbital (LUMO) level of the material. Because it can affect the conjugation and electronic effects of the molecule.<sup>8-9</sup>

In this study,  $N^9, N^9, N^{10}, N^{10}$ -tetraphenylanthracene-9,10-diamine (TAD) and  $N^9, N^9, N^{10}, N^{10}$ -tetra-*o*-tolylanthracene-9,10-diamine (*o*Me-TAD) based on anthracene core and diphenylamine side groups were designed and synthesized (Scheme 1). In particular, in the molecular structure of *o*Me-TAD, the reason for introducing methyl groups at the *ortho* position is that it can make a more highly twisted molecular structure relative to the *meta* and *para* positions.<sup>9</sup>

J. Nanosci. Nanotechnol. 2019, Vol. 19, No. 8



Scheme 1. Synthetic routes of synthesized compounds.

# 2. EXPERIMENTAL DETAILS

#### 2.1. Synthesis

# 2.1.1. N<sup>9</sup>,N<sup>9</sup>,N<sup>10</sup>,N<sup>10</sup>-Tetraphenylanthracene-9,10-Diamine (TAD)

9,10-dibromoanthracene (1.31 g, 3.91 mmol), diphenylamine (1.68 g, 9.77 mmol),  $Pd_2(dba)_3$  (0.11 g, 0.12 mmol), and sodium tert-butoxide (2.72 g, 19.5 mmol) were dissolved in toluene (100 mL) under N<sub>2</sub>. Then, tritert-butylphosphine (0.15 mL, 0.35 mmol) was added to the mixture. The mixture was stirred at 110 °C for 2 h. After evaporation of toluene in the crude material, the crude material was extracted with CHCl<sub>3</sub> and water. The organic layer was dried over anhydrous magnesium sulfate (MgSO<sub>4</sub>) and filtered. After evaporation of CHCl<sub>3</sub>, the crude material was purified by silica gel column chromatography with  $CHCl_3$ : *n*-hexane (1:3) as the eluent to obtain a yellow solid. (0.4 g, yield 21%); <sup>1</sup>HNMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.20–8.17 (q, 4H), 7.37–7.33 (q, 4H), 7.23–7.17 (t, 8H), 7.13–7.10 (d, 8H), 6.93–6.88 (t, 4H).

# 2.1.2. N<sup>9</sup>,N<sup>9</sup>,N<sup>10</sup>,N<sup>10</sup>-Tetra-o-Tolylanthracene-9,10-Diamine (oMe-TAD)

9,10-dibromoanthracene (2.00 g, 5.86 mmol), di-*o*-tolylamine (2.60 mL, 14.2 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (0.21 g, 0.34 mmol), and sodium tert-butoxide (2.82 g, 56.9 mmol) were dissolved in toluene (100 mL) under N<sub>2</sub>. Then, tritert-butylphosphine (0.20 mL, 1.02 mmol) was added to the mixture. The mixture was stirred at 110 °C for 2 h. After evaporation of toluene in the crude material, the crude material was extracted with CHCl<sub>3</sub> and water. The organic layer was dried over anhydrous MgSO<sub>4</sub> and filtered. After evaporation of CHCl<sub>3</sub>, the crude material was purified by silica gel column chromatography with CHCl<sub>3</sub>: *n*-hexane (1:3) as the eluent to obtain a yellow solid. (0.50 g, yield 15%); <sup>1</sup>H NMR (300 MHz, CDCl3,  $\delta$ ): 8.13–8.10 (*q*, 4H), 7.22–7.17 (*q*, 4H), 7.09–7.00 (*m*, 8H), 6.95–6.90 (*t*, 8H), 1.85-1.83 (*s*, 12H).

#### 2.2. Measurements

<sup>1</sup>H-NMR spectra were recorded on Brucker, Advance 300. The optical absorption spectra were obtained by HP 8453 UV-VIS-NIR spectrometer. Perkin Elmer luminescence spectrometer LS55 (Xenon flash tube) was used for PL spectroscopy. The EL performances of the fabricated doped devices were obtained by Keithley 2400 electrometer, and light intensity was obtained by Minolta CS-1000A.

### 3. RESULTS AND DISCUSSION

Figure 1(a) shows normalized UV-Visible absorption and PL spectra in solution state. TAD and *o*Me-TAD show UV-Visible absorption in the 330 nm to 500 nm range. In particular, the UV-Visible maximum peak (458 nm) of TAD and the UV-Visible maximum peak (470 nm) of *o*Me-TAD are intramolecular charge transfer (ICT) peaks that occur from the diphenylamine moiety to the anthracene moiety.<sup>2, 10, 11</sup> As can be seen in Figure 1(b), the ICT peaks were also found in the UV-Visible absorption spectra of the two materials in the film state.

In solution state, the UV maximum wavelength  $(UV_{max})$  of *o*Me-TAD was 12 nm red-shifted compared to UV<sub>max</sub> of TAD and 9 nm red-shifted in film state. In *o*Me-TAD, the methyl group was substituted for the *ortho* position of the diphenylamine group, and the *ortho* position of the phenyl ring could affect the conjugation. The methyl groups were substituted at the *ortho* position to increase the conjugation



Figure 1. Normalized UV-visible absorption and PL spectra of synthesized compounds (a) solution state, toluene,  $1 \times 10^{-5}$  M (b) film state, thickness: 50 nm.

J. Nanosci. Nanotechnol. 19, 4799-4802, 2019

Jung et al.

Synthesis and EL Property of Green Fluorescent Dopant Including Anthracene and Diphenylamine Moiety

Table I. Op	Table II.	EL				
	Solution state <sup>a</sup>		Film state <sup>b</sup>			1
Compounds	UV <sub>max</sub> (nm)	PL <sub>max</sub> (nm)	UV <sub>max</sub> (nm)	PL <sub>max</sub> (nm)	Dopant	(
TAD øMe-TAD	458 470	508 518	468 477	518 528	TAD <i>o</i> Me-TAD	
	470	510	+//	520		

Notes: <sup>a</sup>:  $1 \times 10^{-5}$  M in toluene, <sup>b</sup>: Film on glass, thermal evaporated film (thickness: 50 nm).

length of *o*Me-TAD, and thus the  $UV_{max}$  values of *o*Me-TAD were red-shifted compared to  $UV_{max}$  of TAD.

This phenomenon is also seen in PL spectra. As shown in Table I, in the solution state, the TAD shows a PL maximum wavelength ( $PL_{max}$ ) of 508 nm and the *o*Me-TAD shows a  $PL_{max}$  of 518 nm. Meanwhile, in the film state, TAD represents  $PL_{max}$  of 518 nm and *o*Me-TAD represents  $PL_{max}$  of 528 nm. In solution and film state, *o*Me-TAD showed 10 nm red-shifted  $PL_{max}$  compared to TAD.

Comparing the results between solution state and film state, in case of TAD, the  $UV_{max}$  of the film state was 10 nm red-shifted compared to  $UV_{max}$  of the solution



**Figure 2.** (a) PL spectrum of host and absorption spectra of the synthesized dopants and (b) current efficiencies of EL devices using synthesized materials as dopant.

J. Nanosci. Nanotechnol. 19, 4799-4802, 2019

Table II.	EL performances of doped OLED devices at 10 mA/cm <sup>2</sup> .						
Dopant	Volt (V)	CE <sup>a</sup> (cd/A)	PE <sup>b</sup> (lm/W)	$EQE^{c}$ (%)	$CIE^d (x, y)$	EL <sub>max</sub> (nm)	
TAD <i>o</i> Me-TAD	7.98 9.52	17.71 19.78	7.74 7.23	6.11 5.97	(0.23, 0.60) (0.29, 0.63)	508 522	

*Notes*: <sup>*a*</sup>: Current efficiency, <sup>*b*</sup>: Power efficiency, <sup>*c*</sup>: External quantum efficiency, <sup>*d*</sup>: Commission Internationale de l'Eclairage.

state, and oMe-TAD was 7 nm red-shifted. oMe-TAD showed a smaller red-shifted value than TAD because oMe-TAD effectively prevented intermolecular packing in film state compared to TAD. This may be because the methyl groups contained in the side groups of oMe-TAD made intramolecular steric hindrance, and oMe-TAD had a more twisted molecular structure relative to TAD.

To investigate the electroluminescence (EL) properties of the two materials, an EL devices were fabricated. Also, to minimize intermolecular packing, both materials were applied as dopants. The device structure is ITO/2TNATA (60 nm)/NPB (15 nm)/ $\alpha$ , $\beta$ -ADN + 4% dopant (35 nm)/Alq3 (20 nm)/LiF (1 nm)/Al (200 nm). Figure 2(a) shows the overlap graph between the PL of host and the absorption spectra of dopants. The PL spectra of host and the absorption spectra of dopants were wellmatched and it could confirm that Foster energy transfer from host to dopant effectively occur. Figure 2(b) shows the current efficiency (CE) of the two materials, and the EL performances of the fabricated doped devices are summarized in Table II. TAD and oMe-TAD showed an EL maximum wavelength (EL<sub>max</sub>) of 508 nm and 522 nm, respectively, which is similar to the  $PL_{max}$  of the solution state. The CIE (x, y) of TAD and oMe-TAD are (0.23, (0.60) and (0.29, 0.63), respectively, corresponding to the green emission. Looking at the CE of the two materials, TAD was 17.71 cd/A and oMe-TAD was 19.78 cd/A. The relatively high CE of oMe-TAD compared to TAD is due to the effective prevention of intermolecular packing due to the twisted molecular structure. Also, the methyl groups in oMe-TAD, which is weak electron donating group can improve EL efficiency of materials. Therefore, oMe-TAD showed relatively higher CE value than TAD not containing methyl group. And two doped OLED devices showed similar external quantum efficiency (EQE) values. In power efficiency (PE) values, oMe-TAD showed slightly lower PE value than the PE value of TAD. This is because the voltage of oMe-TAD showed higher value than the voltage of TAD.

#### 4. CONCLUSION

TAD and *o*Me-TAD were successfully synthesized through Buchwald-Hartwig amination. UV-Visible absorption spectra of TAD and *o*Me-TAD appeared in the range of about 458 nm to 477 nm. Also, PL spectra of two

materials appeared in the range of 508 nm to 528 nm corresponding to green color. In doped device, TAD and oMe-TAD applied as dopant of doped device were CE of 17.71 and 19.78 cd/A, respectively. *o*Me-TAD containing methyl groups at ortho position showed higher CE than CE of TAD.

**Acknowledgment:** This work was supported by a grant from Kyung Hee University in 2018 (KHU-20180318).

## **References and Notes**

- 1. C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.* 51, 913 (1987).
- 2. H. Lee, M. Jo, G. Yang, H. Jung, S. Kang, and J. Park, *Dyes Pigments* 146, 27 (2017).

- **3.** H. Lee, H. Jung, S. Kang, J. H. Heo, S. H. Im, and J. Park, *J. Org. Chem.* 83, 2640 (**2018**).
- 4. H. Shin, H. Jung, B. Kim, J. Lee, J. Moon, J. Kim, and J. Park, J. Mater. Chem. C 4, 3833 (2016).
- 5. H. Shin, B. Kim, H. Jung, J. Lee, H. Lee, S. Kang, J. Moon, J. Kim, and J. Park, *RSC Adv.* 7, 55582 (2017).
- J. Lee, H. Jung, H. Shin, J. Kim, D. Yokoyama, H. Nishimura, A. Wakamiya, and J. Park, J. Mater. Chem. C 4, 2784 (2016).
- M. Jung, J. Lee, H. Jung, S. Kang, A. Wakamiya, and J. Park, *Dyes Pigments* 158, 42 (2018).
- 8. Y.-H. Yu, C.-H. Huang, J.-M. Yeh, and P.-T. Huang, *Org. Electron.* 12, 694 (2011).
- S. Kang, H. Lee, H. Jung, M. Jo, M. Jung, and J. Park, *Dyes Pigments* 156, 299 (2018).
- X. Wei, L. Bu, X. Li, H. Agren, and Y. Xie, *Dyes Pigments* 136, 480 (2017).
- S. Sasaki, K. Hattori, K. Igawa, and G.-I. Konishi, J. Phys. Chem. A 119, 4898 (2015).

Received: 30 May 2018. Accepted: 31 October 2018.

P: 5.62.154.61 On: Mon, 06 May 2019 11:10:14 Copyright: American Scientific Publishers Delivered by Ingenta