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# Synthesis and Electro-Optical Properties of Adamantane-Based Host and Hole-Transporting Material for Thermal Stable Blue Phosphorescent OLEDs

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New host/hole-transporting material, namely  $9,9'-\{5-[(3r,5r,7r)-adamantan-1-yl]-1,3-phenylene\}$ bis(9*H*-carbazole) (ad-mCP) and  $N^4$ -(3-((3r,5r,7r)-adamantan-1-yl)phenyl)- $N^4'$ -(3-((2R,5S,6as)-hexahydro-2,5-methanopentalen-3a(1*H*)-yl)phenyl)- $N^4$ ,  $N^{4'}$ -diphenyl-[1,1'-biphenyl]-4,4'-diamine (ad-TPD), were designed and synthesized by introducing rigid adamantane unit into 1,3-Bis(*N*-carbazolyl) benzene and  $N^4$ ,  $N^4$ ,  $N^{4'}$ ,  $N^{4'}$ ,  $N^{4'}$ -tetraphenyl-[1,1'-biphenyl]-4,4'-diamine via a Suzuki coupling reaction. Thermal, photophysical, and electrochemical properties of ad-mCP and ad-TPD were investigated. Using adamantane unit leads to enhance thermal stability. Phosphorescent organic light-emitting diodes constructed using ad-mCP emitting layer and ad-TPD hole transporting layer produce bright blue emissions with a high maximum current efficiency of 7.0 cd/A.

Keywords: PhOLED, Host Material, Hole Transporting Material, Thermostability, Adamantane.

## **1. INTRODUCTION**

Organic light-emitting diodes (OLEDs) has attracted the attention and efforts of a substantial number of researchers, due to their superior properties such as high efficiency, low driving voltage, lightweight, and large area light source.<sup>1-4</sup> Recently, application of OLEDs in the field of an automotive display is rapidly increased. But in order to be actually used in the electronics such as an automotive display, the thermal stability and the operating lifetime of OLEDs are crucial factors. If OLED devices are heated above the glass transition temperature of one of the organic materials in the device, the expansion of the materials is observed at its  $T_{e}$ , leading to significant disruption of the multilayer structure.5-7 Previous research indicates that OLEDs based on a high glass transition temperature amorphous thin film are less vulnerable to heat damage, and hence, are more stable in use.<sup>8</sup> Therefore, studies on the design and synthesis of OLED materials have been continually focused on finding materials with high thermal and thin film morphological stabilities. To realize high thermostability of OLEDs, various efforts have been proposed, including the use of starburst amorphous molecular glass, spiro linkage, isoindole derivatives, etc.<sup>9–11</sup> In particular, adamantane has the rigid alicyclic structure composed of three cyclohexane rings in chair conformation, which enhances thermal stability and increases the glass transition temperature.<sup>12, 13</sup> Therefore, adamantane is the candidate for incorporation into OLED materials without sacrificing their electrical and optical properties. In many OLED materials, mCP (1,3-Bis(*N*-carbazolyl)benzene) and TPD (*N*,*N'*-Bis(3-methylphenyl)-*N*,*N'*-diphenylbenzidine) is a very good host and hole transporting material with excellent EL efficiencies and low turn-on voltages but has rather low glass transition temperature (*T<sub>g</sub>*) of 60 °C (mCP) and 65 °C (TPD). Therefore, there are needs for improving the thermal stability of mCP and TPD for forming amorphous glass film and stable operating of devices.

In this paper, we introduce adamantane unit into mCP and TPD structure because it is bulky and rigid, and thus expected to improve the thermal stability of OLED materials. The synthesis and thermal and optical properties of mCP and TPD with adamantane unit are investigated. Finally, the EL device was fabricated using ad-mCP and ad-TPD as an EML and HTL material. The relationship between molecular structure and the electroluminescence properties of OLED device was systematically investigated herein.

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### 2. EXPERIMENTAL DETAILS

## 2.1. Materials and Synthesis

For the synthesis for ad-mCP and ad-TPD, all reagents and chemicals were purchased from commercial sources (Aldrich, TCI) and used without further purification unless stated otherwise.

# 2.1.1. 9,9'-[5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-1,3-phenylene]bis(9H-carbazole) (1)

1,3,5-tribromobenzene (5 g, 16 mmol), carbazole (8.8 g, 52 mmol), cuprous iodide (0.3 g, 1.6 mmol), potassium phosphate (13.8 g, 65 mmol) and 1,4-dioxane (50 mL) were combined in a 250 mL round bottom flask. The trans-1,2-cyclohexane diamine (1.9 mL, 16 mmol) was added to the reaction mixture. The resultant solution was refluxed under the atmosphere of nitrogen gas for 19 hr. The reacted solution was cooled the room temperature. Methylene chloride and water were added to the solution and the organic layer was separated. The organic layer washed with water and dried with anhydrous sodium sulfate. After the organic solvent was removed by distillation under reduced pressure until the amount of the organic solvent decreased to about one fifth of the original amount, the formed crystals were separated by filtration and washed with ethyl acetate. The obtained residue was purified with column chromatography. The purified 9,9'-(5-bromo-1,3phenylene)bis(9H-carbazole) (1.6 g) was obtained.

9,9'-(5-bromo-1,3-phenylene)bis(9*H*-carbazole) (6 g, 12.3 mmol), Bis(pinacolato)diboron (4.7 g, 18.4 mmol), potassium acetate (3.6 g, 37 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.4 g, 0.3 mmol) were dissolved in distilled 1,4-dioxane. The reaction mixture was refluxed for 12 hours under nitrogen and then allowed to cool to room temperature. After the mixture washed with ethyl acetate, the solvent was removed under vacuum. The crude material was purified by column chromatograph on silica gel (ethyl acetate:hexane = 1:3 as eluent) to give the title compound 1 (yield: 70%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 8.20 (*d*, 6H), 7.60–7.40 (*m*, 9H), 7.35–7.26 (*m*, 4H), 1.30–1.45 (*m*, 12H).

## 2.1.2. 9,9'-{5-[(3r,5r,7r)-adamantan-1-yl]-1,3-Phenylene} bis(9H-carbazole) (ad-mCP)

Reactant 1 (1.5 g, 2.8 mmol), 1-bromoadamantane (1.1 g, 4.2 mmol), and palladium (0.16 g, 0.14 mmol) were dissolved in distilled THF. The reaction mixture was then stirred for 1 hour at room temperature. Potassium carbonate was added to the reaction mixture. The reaction mixture was refluxed for 12 hours under nitrogen and then allowed to cool to room temperature. After the reaction was finished, the mixture was washed three times with distilled water and extracted with ethyl acetate. The organic layer was separated, dried over anhydrous magnesium sulfate, and the solvent was removed under vacuum. The crude material was purified by column chromatography on silica gel (ethyl acetate:hexane = 1:3 as eluent) to give the ad-mCP as a white power product (yield: 60%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 8.26 (*d*, 4H), 8.20 (*S*, 2H), 8.0 (*s*, 1H), 7.71 (*d*, 4H), 7.60 (*t*, 4H), 7.40 (*t*, 4H), 1.30–1.50 (*m*, 9H), 1.0–1.10 (*m*, 6H).

# 2.1.3. N<sup>4</sup>,N<sup>4</sup>'-diphenyl-N<sup>4</sup>,N<sup>4</sup>'-bis[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-[1,1'-biphenyl]-4,4'-diamine (2)

The same procedure for compound 1 was applied to give powder (60%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 7.60 (*t*, 4H), 7.32–7.50 (*m*, 12H), 7.25–7.40 (*m*, 10H), 1.6 (*s*, 24H).

# 2.1.4. N<sup>4</sup>-(3-((3r,5r,7r)-adamantan-1-yl)phenyl)-N<sup>4</sup>-(3-((2R,5S,6as)-hexahydro-2,5-methanopentalen-3a(1H)-yl)phenyl)-N<sup>4</sup>, N<sup>4'</sup>-diphenyl-[1,1'biphenyl]-4,4'-diamine(ad-TPD)

The same procedure for compound ad-mCP was applied to give white powder (55 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 8.5 (*d*, 4H), 7.7 (*d*, 6H), 7.43–7.6 (*m*, 6H), 7.3–7.38 (*m*, 8H), 1.3–1.53 (*m*, 22H), 1.25–1.1 (*m*, 8H).

### 2.2. Measurement

The <sup>1</sup>H NMR spectra were recorded on a Bruker 300 MHz spectrometer. UV/Vis and fluorescence spectra were collected on a Shimadzu UV/Vis spectrometer and a PerkinElmer spectro-fluorometer, respectively. Decomposition temperature  $(T_d)$  and glass transition temperature  $(T_g)$  of the synthesized compounds were determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) on a NETZSCH thermogravimetric analyzer and PerkinElmer Differential Scanning Calorimeter. Cyclic Voltammetry (CV) was carried out on a RersaSTAT3 electrochemistry workstation. Film thickness was measured using a TENCOR surface profiler.

### 2.3. Fabrication of OLED Device

To investigate electroluminescent properties, we fabricated two types of devices, with the device configurations: device I: ITO/PEDOT:PSS (30 nm)/NPB (30 nm)/ mCP:FIr6 (9 wt%, 30 nm)/TPBi (10 nm)/Alg<sub>3</sub> (30 nm)/ LiF (1 nm)/Al; device II: ITO/PEDOT:PSS (30 nm)/NPB (30 nm)/ad-mCP:FIr6 (9 wt%, 30 nm)/TPBi (10 nm)/Alq<sub>3</sub> (30 nm)/LiF (1 nm)/Al; device III: ITO/PEDOT:PSS (30 nm)/ad-TPD (30 nm)/mCP:FIr6 (9 wt%, 30 nm)/TPBi (10 nm)/Alq<sub>3</sub> (30 nm)/LiF (1 nm)/Al; device IV: ITO/ PEDOT:PSS (30 nm)/ad-TPD (30 nm)/ad-mCP:FIr6 (9 wt%, 30 nm)/TPBi (10 nm)/Alq<sub>3</sub> (30 nm)/LiF (1 nm)/ Al. Bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine (NPB) was used as the hole transporting material. 2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole (TPBi) and tris(8-hydroxyquinoline)aluminum (Alq<sub>3</sub>) used as the hole blocking material and the electron transporting Bis(2,4-difluorophenylpyridinato)-tetrakis(1material. pyrazolyl) borate iridium(III) (FIr6) as a blue dopant. The ITO-coated glass substrates were cleaned by ultrasonic

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Scheme 1. Synthetic procedure for (a) ad-mCP and (b) ad-NPD.

(b) ad-TPD

treatment in deionized water and acetone. PEDOT:PSS layer, acting as a hole injection layer, was spin-coated onto the ITO glass and dried at 120 °C for 20 min. The organic layers were thermally deposited at a base pressure of  $10^{-7}$  torr and then lithium fluoride (LiF) and Aluminum (Al) were deposited successively.

The current–voltage (I-V) and current density– luminance (J-L) data of OLEDs were collected by Keithley 236 source measurement unit. The area for measurement of OLED emission was 4 mm<sup>2</sup> for all the samples studied in this work. Electroluminescence (EL) spectra and CIE coordinate were measured by using a PR-650 SpectraScan Spectrophotometer.

#### 3. RESULTS AND DISCUSSION

Scheme 1 illustrated the synthetic route for ad-mCP and ad-TPD. The Suzuki cross-coupling reaction of



Figure 1. DSC and TGA curve of ad-mCP.

9,9'-[5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3phenylene]bis(9*H*-carbazole) (1) and 1-bromoadamantane with palladium catalyst led to ad-mCP. The same procedure for  $N^4, N^{4'}$ -diphenyl- $N^4, N^{4'}$ -bis[3-(4,4,5,5tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-[1,1'-biphenyl]-4,4'-diamine (2) was applied to give ad-TPD. The chemical structure was confirmed by <sup>1</sup>H NMR.

The thermal properties of the adamantane-linked materials were investigated by DSC and TGA. Figures 1 and 2 show DSC and TGA curves of ad-mCP and ad-TPD, respectively. As shown in Figures 1 and 2, no obvious crystallization peak is observed during the scanning from room temperature to 300 °C, implying that ad-mCP and ad-TPD show the prominent stability of these materials, which can be attributed to the presence of the adamantane unit. TGA curves show that ad-mCP and ad-TPD have high thermostability with 5 wt% loss temperature of 420 °C. These results indicate that the thermal stabilities of the ad-mCP and ad-TPD are high enough for them to be used in OLEDs.<sup>14, 15</sup>

Figure 3 shows the absorption and photoluminescence spectrum of ad-mCP and ad-TPD in chloroform solution. The two absorption peaks of ad-mCP at 310 nm and 330 nm, respectively, appeared similar to that of mCP. The PL spectrum of ad-mCP solution shows a blue emission peak at 355 nm. We can see that the

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Figure 2. DSC and TGA curve of ad-TPD.

PL spectrum of ad-mCP is overlapped with the absorption of FIr6 in a range of  $350 \sim 400$  nm. Therefore, the efficient energy transfer from ad-mCP to FIr6 can be expected. The HOMO-LUMO band gap of ad-mCP was determined from the absorption spectrum of ad-mCP film to be 3.65 eV. HOMO level of ad-mCP was measured from cyclic voltammetry (CV). The HOMO energy level of ad-mCP was estimated from the oxidation onset potential was -6.15 eV. The LUMO energy level was calculated to be



Figure 3. UV/vis absorption and photoluminescence spectrum of admCP and ad-TPD in solution.

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Figure 4. Energy level diagram and schematic structure of the blue OLED.

2.5 eV by subtraction of the optical band gap from the HOMO energy level. In the same way, absorption onset of UV/Vis spectrum and HOMO energy level of ad-TPD was 3.1 eV and 5.4 eV, respectively. The energy diagram for the devices is shown in Figure 4.

To investigate the electroluminescence properties and the current-voltage-luminance characteristics of ad-mCP and ad-TPD, we fabricated the device using ad-mCP and ad-TPD as host and hole transporting material. The four devices all showed the typical blue emission from FIr6 but no emission from either the FIr6 or any exciplex was observed. This indicates that ad-mCP only plays the role of a host material. The voltage-current and current density-current efficiency of the devices are also shown in Figure 5. The devices using ad-mCP as host material exhibited the lowest turn-on voltage of about 4.8 V and 5.1 V (device II and IV), which is lower than that of device I and III fabricated by mCP (about 5.7 V). The devices using ad-mCP rapidly declined at same device thickness than those using mCP when the current density increased. We cannot now have a clear explanation for the low turn-on voltage and rapid decline of the current efficiency, which the reason is probably higher charge transporting property of ad-mCP. The turn-on voltage of device III using ad-TPD as the hole transporting material is similar to that of device I using NPB. It indicated that ability of hole transporting of ad-TPD was similar to that of NPB. In the current efficiency, the device IV showed the best performance with a maximum current efficiency of 7 cd/A. On the other hand, device I to III showed 5.1 cd/A, 5.5 cd/A, and 5.5 cd/A, respectively. It indicated that ad-mCP



Figure 5. (a) Voltage–current curves and (b) current density–current efficiency curves of fabricated PhOLEDs.

as emitting layer matched well with ad-TPD as hole transporting layer.

The device configuration has not been optimized in the present work and we do not have enough facilities to do stability experiments of the device, but further performance improvement may be expected by fine tuning device structure. In addition, it is generally known that OLEDs based on a high glass transition temperature amorphous thin film are less vulnerable to heat damage, and hence, are more stable in use. The present results suggest that ad-mCP and ad-TPD are a potentially good candidate for applications as host and hole transporting materials in OLEDs and related optoelectronic devices.

# 4. CONCLUSION

We have synthesized adamantane derivatives that have high thermal stability. OLEDs constructed using ad-mCP as a host material produced blue emissions. PhOLEDs made using ad-mCP and ad-TPD as host and hole transporting layer revealed the best performance with a maximum current efficiency of 7 cd/A, which are comparable to the efficiencies of the control OLED based on mCP and NPB. This approach could prove useful in future PHOLED applications in the automotive display. Further modification and optimization of the structure and device are in progress.

#### **References and Notes**

- 1. S. Nakano, T. Sekitani, T. Yokata, and T. Semeya, *Appl. Phys. Lett.* 92, 053302 (2008).
- L. Xiao, Z. Chen, B. Qu, J. Luo, S. Kong, Q. Gong, and J. Kido, *Adv. Mater.* 23, 926 (2011).
- 3. K. Hong and J.-L. Lee, Electronic Materials Letters 7, 77 (2011).
- J. H. Kim, J.-Y. Cho, J. Park, B. K. Lee, K.-H. Baek, H. Lee, and L.-M. Do, *Electronic Materials Letters* 10, 27 (2014).
- Q. Fang, B. Xu, B. Jiang, H. Fu, W. Zhu, X. Jiang, and Z. Zhang, Synth. Met. 155, 206 (2005).
- E.-M. Han, L.-M. Do, M. Fujihira, H. Inada, and Y. Shirota, J. Appl. Phys. 80, 3297 (1996).
- B. X. Mi, P. F. Wang, M. W. Liu, H. L. Kwong, N. B. Wong, C. S. Lee, and S. T. Lee, *Chem. Mater.* 15, 3148 (2003).
- J. H. Kim, Y. M. Jeon, J. G. Jang, S. Ryu, H. J. Chang, C. W. Lee, J. W. Kim, and M. S. Gong, *Bull. Korean Chem. Soc.* 30, 647 (2009).
- N. Aizawa, Y.-J. Pu, H. Sasabe, and J. Kido, Org. Electro. 14, 1614 (2013).
- C. Poriel, J. Rault-Berthelot, D. Thirion, F. Barriére, and L. Vignau, *Chem. Eur. J.* 17, 14031 (2011).
- Z. Li, Z. Wu, W. Fu, D. Wang, P. Liu, B. Jiao, X. Lei, G. Zhou, and Y. Hao, *Electronic Materials Letters* 9, 655 (2013).
- 12. C.-H. Chen, W.-J. Dhen, K. Jakka, and C.-F. Shu, Synth. Met. 143, 215 (2004).
- Y. Gu, X. Zhou, Y. Li, K. Wu, F. Wang, M. Huang, F. Guo, Y. Wang, S. Gong, D. Ma, and C. Yang, *Org. Electro.* 25, 193 (2015).
- O. G. Gardens, Trends in Optical Materials, Nova Science Publisher, New York (2007), p. 78.
- L. Duan, L. Hou, T.-W. Lee, J. Qiao, D. Zhang, G. Dong, L. Wang, and Y. Qiu, J. *Mater. Chem.* 20, 6392 (2010).

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