

# Soluble Host Materials with Ortho-phenylene Group for Blue Phosphorescent Devices

Hui Jae Choi<sup>1</sup>, Ohyoung Kim<sup>1</sup>, Chil Won Lee<sup>2</sup>, Byung Doo Chin<sup>1</sup>

<sup>1</sup>Department of Polymer Science and Engineering, Dankook University  
152 Jukjeon-ro, Suji-gu, Yongin-city, Gyeonggi 16890, Korea

<sup>2</sup>Department of Chemistry, Dankook University  
119 Dandae-ro, Dongnam-gu, Cheonan-city, Chungnam 31116, Korea

Keywords: Blue Phosphorescence, Soluble Host, Ortho-phenyl-mCP, Morphology, Efficiency

## ABSTRACT

*Blue phosphorescent organic light-emitting diodes (OLED) were prepared with the host materials designed for solution process. 1,3-bis(carbazole-9-yl)benzene as the core structure with various ortho-phenyl groups between the carbazole moieties were prepared for the purpose of reducing symmetry and planarity of the molecules, hereby improving the solubility and device efficiency.*

## 1 INTRODUCTION

A solution process such as inkjet printing, or nozzle printing instead of vacuum thermal evaporation is considered as an alternative technique of a large area RGB color patterning for organic light emitting diode (OLED) [1]. The fabrication of solution-based OLED devices can be generally divided into a type in which the entire process proceeds by a solution process (so-called all-solution process) and a type in which the process from the hole injection layer (HIL) to the emitting layer (EML) proceeds to a solution process (so-called hybrid-solution process). That is, the hybrid solution process is a method in which HIL, hole transport layer (HTL) and EML are fabricated on an ITO substrate by a solution process and then the electron transport layer, the electron injection layer, and the cathode are fabricated to a vacuum thermal evaporation process. This is because it is technically very difficult to fabricate entire layer-by-layer structure by solution process. Therefore, for a fabrication of stable multilayer structure of OLED by a solution processing, a cross-linked HTL is desirable. However, there has been almost no report of cross-linking hole transporting layer materials showing characteristics comparable to conventional HTL materials [2]. When the state-of-the-art conventional HTL materials are used for solution devices, the EML layer should be soluble for various solvents to enable layer-by-layer structure formation by orthogonal process.

1,3-bis(carbazole-9-yl)benzene (mCP) or 3,5-di(9H-carbazol-9-yl)tetraphenylsilane (SimCP2) are the example of blue phosphorescent host materials previously developed, which showed high triplet energies and exhibits excellent external quantum efficiency (EQE) characteristics, even in a soluble device [3]. However,

these materials are limited in terms of solubility at general solvents because of the strong intermolecular interactions due to the planarity of the molecular structure, and are hardly soluble in solvents such as alcohol, making them difficult to apply to from a multilayer stack by solution processes. To overcome those problems, introducing an alkyl or alkoxy chains can be considered because those chains improve the solubility of such molecules by increasing the free volumes of molecules and decreasing the intermolecular interaction [4]. However, this method causes a problem of thermal stability by lowering the T<sub>g</sub> of the host material. Therefore, it is necessary to develop a material having high triplet energy and high solubility while maintaining or enhancing thermal stability as a host material for a blue phosphorescent device for solution process. In this work, we designed a host material with improved solubility by introducing ortho-phenylene group. A moiety in which two or more phenyl groups are bound to the ortho-position may increase the solubility of the host molecule by reducing the symmetry and planarity of the molecule. The ortho-phenylene moieties minimize the intermolecular interactions, thereby preventing the closely binding between the molecules and enhancing the solubility by facilitating the penetration of the solvent.

## 2 EXPERIMENT

The synthesis of the materials was carried out using a general Suzuki coupling reaction and the boronic acid compound was synthesized by an electrophilic borylation including an organic lithium (scheme in Fig 1). The ortho-biphenyl and ortho-terphenyl substituted d-Ph-mCP and t-Ph-mCP, respectively, were found to be effectively high T<sub>g</sub> behavior compared to the mCP and soluble at many common solvents. In addition, 3,5-di(9H-carbazol-9-yl)-1,1'-biphenyl (Ph-mCP) having one phenyl group introduced into mCP was synthesized, and its optical and electrochemical characteristics were investigated.

## 3 RESULTS and DISCUSSION

Fig.2 shows the UV-Vis absorption and photoluminescence (PL) spectra for Ph-mCP, d-Ph-mCP,

and t-Ph-mCP. The optical band gaps determined from the band edges of UV-vis absorption spectra were measured at 3.49 eV, 3.52 and 3.53 for Ph-mCP, d-Ph-mCP, and t-Ph-mCP, respectively. The UV-vis absorption spectra in the 300-350 nm region showed a similar pattern despite the additional introduction of the phenyl group, which was due to the  $\pi-\pi^*$  transition and the  $n-\pi^*$  transition of the mCP core. The maximum PL emission wavelengths of Ph-mCP, d-Ph-mCP, and t-Ph-mCP in the PL spectra measured at room temperature were located at 360, 360, and 348nm, respectively. Ph-mCP and d-Ph-mCP showed broad and featureless emission spectra, but two peaks were observed at 348 and 361nm for t-Ph-mCP, indicating the mCP unit and ortho-terphenyl group emission. These properties can be explained by the geometric structure of the reference material and the new host molecule shown in Fig 3 (results of Gaussian simulation).

Both for vacuum- and solution-processed OLED devices, hosts prepared in this study (mCP, Ph-mCP, d-Ph-mCP, and t-Ph-mCP) with 10% sky-blue dopant (Bis[2-(4,6-difluorophenyl) pyridinato-C2,N](picolinato) iridium (III); FIrpic) were employed as emitting layer. Structure of evaporated devices was ITO /PEDOT:PSS /TAPC /Host: FIrpic (10%, 25nm) /TSPO1 /LiF /Al, while in case of solution-devices, TAPC was replaced with PVK. As seen in Fig 4. characteristics of the evaporated devices with various mCP-series-host materials were acceptable, ranging from 10 to 17% EQE depending on the structure of attached phenyl groups. Device with t-Ph-mCP showed highest EQE (19.3% max) and low driving voltage behavior at evaporated device. The performance as a host of solution processed device exhibited rather limited improvement, showing that 5-6% EQE of mCP-based devices were improved to 8-9% for Ph-mCP and d-Ph-mCP, while t-Ph-mCP exhibited a decrease in peak EQE. This might be explained by the charge transport behavior of t-Ph-mCP with longer ortho-phenyl chain.

However, t-Ph-mCP were superior in terms of good solubility for various solvents and high triplet energy value (3.00eV of  $T_1$ , compared with 2.74 and 2.82 for Ph-mCP and d-Ph-mCP, respectively). Table 1 shows the results of t-Ph-mCP-based blue devices with various soluble EML/HTL stack condition. Devices 1, 2 and 3 (with HTL of poly-TPD thickness of 10, 15, and 20nm, respectively) were fabricated from the solution coating of t-Ph-mCP:Firpic dissolved in IPA/cyclohexane (3:7) solution, which still maintains acceptable film quality. The device 4 was prepared by dissolving t-Ph-mCP and FIrpic in toluene solution. Device 2 with the poly-TPD thickness of 15 nm showed the best characteristics, with maximum external quantum efficiency of 5.8% and maximum current efficiency of 9.5 cd/A. As seen in a poor efficiency of Device 4, poly-TPD was removed or intermixed when forming the EML on top of poly-TPD with the toluene solution. Atomic force microscopy (AFM) analysis of the

spin-coated t-Ph-mCP:Firpic film (Fig. 5) revealed that the root-mean-square surface roughness was 0.40nm, and a very smooth thin film was obtained.

#### 4 CONCLUSIONS

The blue phosphorescent host structure introducing the ortho-phenylene groups for mCP-based structure is unique and advantageous for an increase in the solubility of the host by reducing the symmetry and planarity of the molecule. The design concept of a materials was capable of a significant increase in the solubility while excluding the introduction of alkyl groups commonly used for solubility enhancement, and have led to excellent thermal stability, and triple energy suitable for blue phosphorescent OLEDs. Fabrication of multilayered solution-processed device could be successfully formed.

#### REFERENCES

- [1] Y. J. Kang, R. Bail, C. W. Lee, and B. D. Chin, "Inkjet Printing of Mixed-Host Emitting Layer for Electrophosphorescent Organic Light-Emitting Diodes", *ACS Appl. Mater. Interfaces*, Vol. 11, pp 21784-21794 (2019)
- [2] K. S. Yook and J. Y. Lee, "Small molecule host materials for solution processed phosphorescent organic light-emitting diodes.", *Adv. Mater.*, Vol. 26, pp 4218-4233 (2014).
- [3] J. H. Jou, W. B. Wang, S. Z. Chen, J. J. Shyue, M. F. Hsu, C. W. Lin, S. M. Shen, C. J. Wang C. P. Liu, C. T. Chen, M. F. Wu and S. W. Liu, "High-efficiency blue organic light-emitting diodes using a 3,5-di(9H-carbazol-9-yl) tetraphenylsilane host via a solution-process", *J. Mater. Chem.*, Vol. 20, pp 8411-8416 (2010)
- [4] M. C. Suh, S. R. Park, Y. R. Cho, D. H. Shin, P. G. Kang, D. A. Ahn, H. S. Kim and C. B. Kim, "Synthesis of Soluble Host Materials for Highly Efficient Red Phosphorescent Organic Light-Emitting Diodes", *ACS Appl. Mater. Interfaces*, Vol. 8, pp 18256-18265 (2016).

#### ACKNOWLEDGMENTS

This study was supported by Gyeonggi Regional Research Center Program (GRRRC Dankook 2016-B01). Support from the MOTIE (Ministry of Trade, Industry & Energy, 10067821) with development of core-technology and components in organic electronics for ICT convergence support program for the development of the future display device is also acknowledged

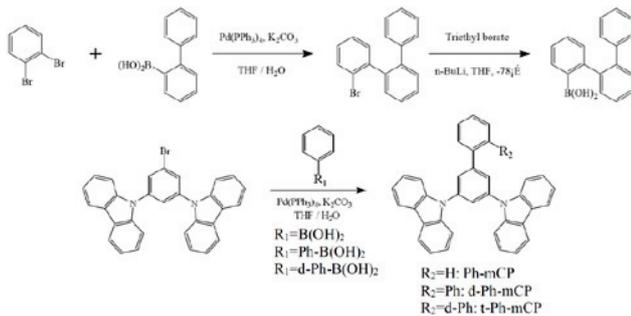


Fig. 1 The synthesis of the materials of mCP-derived compounds

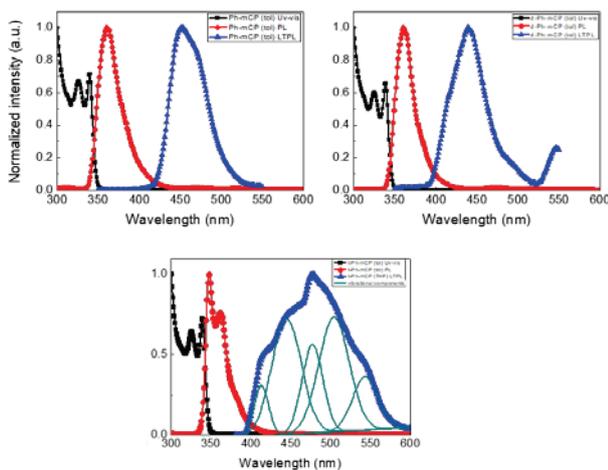


Fig. 2 UV-Vis absorption (black line), PL (red line) and phosphorescent spectra (blue line) of the mCP derived compounds

	Ph-mCP	d-Ph-mCP	t-Ph-mCP
Structure	54.9°	71.1°	74.7°
Calculated $T_1$	3.38	3.18	3.18
HOMO			
Calculated HOMO	-5.45	-5.35	-5.36
LUMO			
Calculated LUMO	-1.18	-1.11	-1.16

Fig. 3 Calculated spatial distributions of the HOMO and LUMO levels of Ph-mCP, d-Ph-mCP, and t-Ph-mCP obtained by using Gaussian 09 with the B3LYP/6-31G\* basis set.

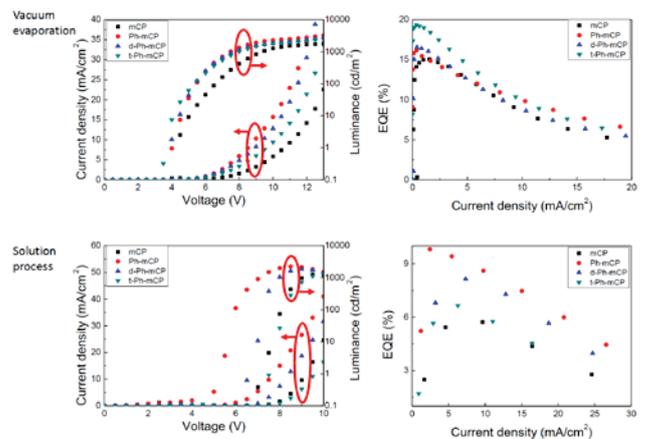


Fig. 4 Current-voltage-luminance (IVL) and EQE characteristics of vacuum-deposited and solution-processed blue OLED with various mCP-derivative host materials

Table 1. Device performance of t-Ph-mCP:Firpic emitter with various HTL (poly-TPD) stack condition by solution layer-by-layer process

Devices	Quantum Efficiency [%]		Current Efficiency [cd/A]		Color Coordinate
	max	100 cd/m <sup>2</sup>	max	100 cd/m <sup>2</sup>	
Device 1	5.1	-	9.0	-	0.16, 0.32
Device 2	5.2	2.5	9.6	4.8	0.16, 0.34
Device 3	3.9	1.6	7.5	3.2	0.17, 0.35
Device 4	0.2	-	0.1	-	-

Device 1: ITO/PEDOT:PSS (poly-TPD (10 nm)/t-Ph-mCP:Firpic (10%, 25 nm)\* /TSPO1 /TPBi/ LiF/Al.  
 Device 2: ITO/PEDOT:PSS (poly-TPD (15 nm)/t-Ph-mCP:Firpic (10%, 25 nm)\* /TSPO1 /TPBi/ LiF/Al.  
 Device 3: ITO/PEDOT:PSS (poly-TPD (20 nm)/t-Ph-mCP:Firpic (10%, 25 nm)\* /TSPO1 /TPBi/ LiF/Al.  
 Device 4: ITO/PEDOT:PSS (poly-TPD t-Ph-mCP:Firpic (10%, 25 nm)\* /TSPO1 /TPBi/ LiF/Al.  
 \*EML from IPA/cyclohexane solution; +EML from toluene solution.

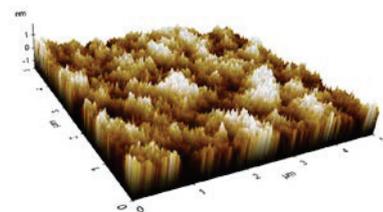


Fig. 5 AFM topographic images (5 × 5 μm<sup>2</sup>) of t-Ph-mCP:Firpic film from IPA/cyclohexane