

# Synthesis of Benzodifurans Derivatives and Their Application to Organic Semiconducting Devices

ベンゾジフラン誘導体の合成と有機半導体デバイスへの応用

三津井 親彦

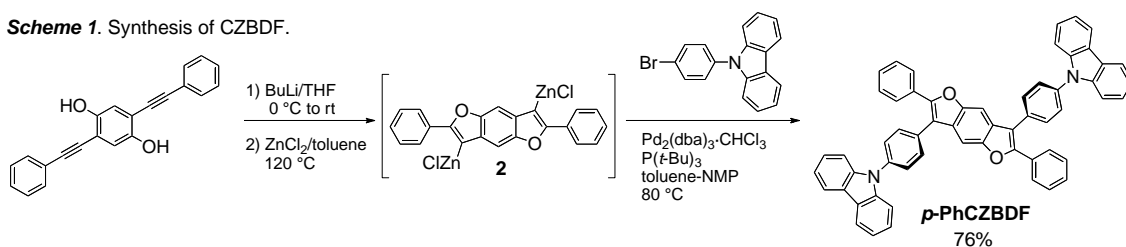
## Introduction

Development of novel aromatic compounds have been continuously desired for their application to organic semiconducting devices, such as OLED, OPV, and OFET. Organic semiconductors are classified in *p*-type, *n*-type, and ambipolar materials. Among them, ambipolar semiconductivity is a distinctive character and such materials possess potential utility in a wide range of organic electronics. In organic light-emitting diodes (OLEDs), they are used as host materials, which function as conducting matrix of emitting dopants in emission layer. However, due to the paucity of synthetic accessibility to a new class of ambipolar materials, the current repertoire is quite limited. Designing wide gap ambipolar material is a challenging work, because increasing the band gap of the material to possess high singlet and triplet excited energies often adversely affects the charge transporting properties. Thus, during my Ph.D. course study, I demonstrated potential application of new ambipolar materials based on benzodifuran (BDF) skeleton for OLED devices and shed light on the structure-property relationship among synthesized BDF derivatives.

## High mobility ambipolar material for full-color OLED devices

In my master course study, I developed a new and versatile synthetic method to construct a series of BDF derivatives. The robust BDF skeleton afforded the compounds with high thermal stability as well as excellent hole-transporting property. Being aware that steric congestion twists the 3- and the 7-aryl groups out of the BDF plane, I considered that installation of the electron transporting groups at 3- and 7-positions would make the molecule ambipolar and secure wide-gap character, which is requisite for full-color emission by various color dopants.

**Scheme 1.** Synthesis of CZBDF.



For this purpose, I chose carbazolyl group, and synthesized according to the zinc-mediated double cyclization protocol as shown in Scheme 1. Using thus synthesized *p*-PhCZBDF, I first verified its ambipolar and wide-gap character. Time-of-flight (TOF) mobility measurements using amorphous films of *p*-PhCZBDF indicated the generation of hole and electron photocurrent, and the carrier mobilities are  $3.7 \times 10^{-3}$  and  $4.4 \times 10^{-3}$  cm<sup>2</sup>/Vs for hole and electron, respectively. Differential pulse voltammetry determined the oxidation and reduction potentials to be 0.72 V (in CH<sub>2</sub>Cl<sub>2</sub>) and -2.60 V (in THF), respectively (vs Fc/Fc<sup>+</sup>), which corresponds to HOMO and LUMO energy levels are -5.52 eV and -2.20 eV, respectively. These data indicate the feasible formation of both radical cation and anion as well as wide HOMO-LUMO gap character (3.32 eV), which is efficient for confinement of excitations within various color dopants.

Encouraged by these property measurements, OLED devices were fabricated and evaluated with heterojunction architecture (ITO/PEDOT:PSS/ $\alpha$ -NPD/EML (emitting layer)/Alq<sub>3</sub>/Liq/Al, where *p*-PhCZBDF was used in the EML either as an emitting material by itself (undoped) or as a host material for various dopants), and found that *p*-PhCZBDF functions as both a blue-emitting dye by itself and a host material for various dopants. Figure 1 shows *p*-PhCZBDF serves as an effective emission host material for various dopants over the full range of visible region. From the viewpoint of device performances (Table 1), CZBDF-based device F showed superior performance and much longer device lifetime compared to the conventional host material, such as CBP (device G). In addition, taking advantage of the well-balanced high charge mobility of *p*-PhCZBDF, homojunction devices, which simply composed of a single organic matrix (*p*-PhCZBDF) doped with inorganic dopants and an emissive dye, were also developed.

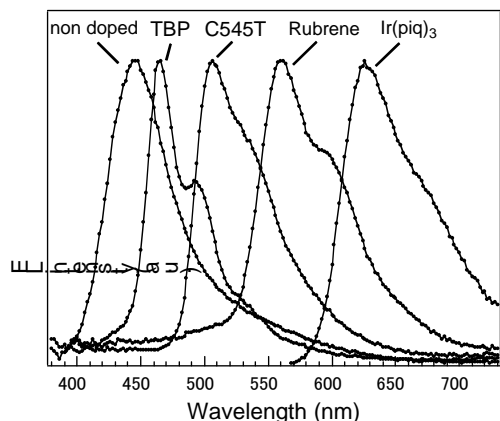


Figure 1. EL spectra from CZBDF-based devices.

Table 1. Summary of OLED performances.<sup>a</sup>

Device	Host	Dopant	$V_{1000}^b$ [V]	$\eta_{1000}^c$ [lm/W]	$EQE^d$ [%]
A	<i>p</i> -PhCZBDF	non doped	8.3	0.5	1.0
B	<i>p</i> -PhCZBDF	TBP	7.2	1.0	1.5
C	<i>p</i> -PhCZBDF	C545T	6.7	3.1	2.4
D	<i>p</i> -PhCZBDF	rubrene	6.8	2.5	2.1
E	<i>p</i> -PhCZBDF	TBP&rubrene	8.4	1.1	1.5
F	<i>p</i> -PhCZBDF	Ir(piq) <sub>3</sub>	7.6	1.8	8.0
G	CBP	Ir(piq) <sub>3</sub>	10.0	1.8	7.1

<sup>a</sup> OLED performance data collected at a luminance of 1000 cd/m<sup>2</sup>.

<sup>b</sup> Driving voltage. <sup>c</sup> Luminous efficiency. <sup>d</sup> External quantum efficiency.

## Modulation of excited triplet energy level for phosphorescent emission

For high emission efficiency to reach over 5% external quantum efficiency (EQE) in OLED devices, phosphorescent emission is requisite. Although, host material employed must possess higher excited triplet energy level ( $E_T$ ) than those of phosphorescent dopants, the  $E_T$  of **CZBDF** is not sufficient for blue and green phosphorescent emission. Thus, I designed a new host materials with high triplet energy level based on benzodifuran in terms of disrupting  $\pi$ -conjugation between BDF core and the substituents as well as tuning the furan fusion manner to construct **MeCZBDF** derivatives (Figure 2).

The phosphorescence spectra, taken in a frozen 2-methyl tetrahydrofuran matrix at 77 K, afforded the  $E_T$  values: 2.64 and 2.77 eV for *p*-**MeCZBDF** and *o*-**MeCZBDF**, respectively, which are high enough to emit green and blue phosphorescent dyes, respectively. The origin of the higher  $E_T$  value of *o*-**MeCZBDF** than that of *p*-**MeCZBDF** is attributed to the different ring fusion manner. This trend is quite similar to the

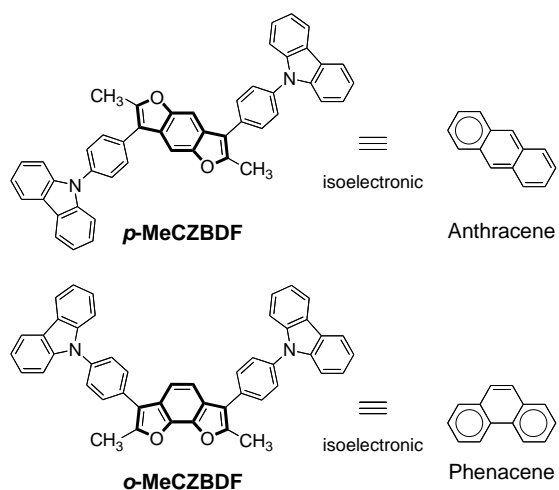


Figure 2. Structures of phosphorescent host materials.

relationship between phenanthrene and anthracene, a set of structural isomers of the carbon analogue. That is, *p*-BDF skeleton corresponds to anthracene-like acene system, whereas *o*-BDF to phenanthrene-like phenacene system, supported by X-ray single crystal analysis. TOF mobility measurements suggested that both *p*-**MeCZBDF** and

***o*-MeCZBDF** possess high charge carrier mobility for hole and electron over  $10^{-3}$   $\text{cm}^2/\text{Vs}$ . Utilizing ***o*-MeCZBDF** and ***p*-MeCZBDF** as hosts with phosphorescent dopants, phosphorescent blue and green OLED devices were realized, respectively, at over 5% EQE value.

## **Conclusion**

I have developed the wide-gap ambipolar materials via zinc-mediated cyclization reaction. ***p*-PhCZBDF** possesses well-balanced hole and electron mobilities as high as greater than  $10^{-3}$   $\text{cm}^2/\text{Vs}$ . ***p*-PhCZBDF** serves as an effective emission host material for various dopants over the full range of visible region. Furthermore, to increase emission efficiency, higher  $E_T$  **MeCZBDF** derivatives were also developed. Using these materials, phosphorescent blue and green emissions were also achieved.