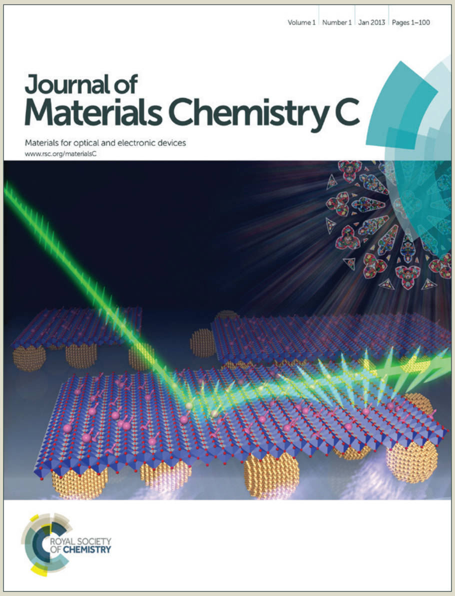
# Journal of Materials Chemistry C

Accepted Manuscript



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Cite this: DOI: 10.1039/x0xx00000x

# A simple carbazole-N-benzimidazole bipolar host material for highly efficient blue and single layer white phosphorescent organic light-emitting diodes†

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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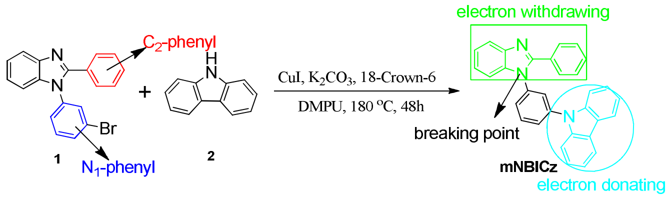
**A new simple carbazole-N-benzimidazole bipolar luminogens mNBICz was constructed and utilized as host for FIrpic-doped blue device, and exhibited high efficiencies with $\eta_{EQE,max}$ of 26.2%, $\eta_{C\ max}$ of 54.5 cd $A^{-1}$ and $\eta_{P,max}$ of 52.2 lm $W^{-1}$. Furthermore, a two-color, all-phosphor single layer white device displayed a $\eta_{EQE,max}$ of 22.9 %, $\eta_{C\ max}$ of 62.5 cd $A^{-1}$ and $\eta_{P,max}$ of 60.4 lm $W^{-1}$.**

In the past decades, organic light-emitting diodes (OLED) have been considered to be the next generation technology of full-color flat-panel displays and solid-state lighting sources.[1-4] However, blue PhOLEDs with high performance remains a challenge mainly due to the lack of appropriate host materials.[5] For efficient blue PhOLEDs host materials, there are some basic principles such as: appropriate HOMO/LUMO levels; higher triplet energy level than blue dopant (for FIrpic, $E_T \geq 2.7$ eV); bipolar carrier transporting properties and high thermal and morphological stability. [6] Additionally, simple structure and easy to prepare was an underlying request for industrial manufacture. So it will be fascinating to develop a highly efficient bipoalr host material with simple structure.

To achieve this goal, various hole and electron transporting moieties have been developed to obtain bipolar host materials with structural topology tuning of the connecting manner.[7-12]Among them, carbazole-based materials possessing high triplet energy (> 2.9 eV) and excellent hole transporting (HT) properties were widely used as blue hosts.[13-18] Benzimidazole groups were also used as functional units that facilitating electron injection and transport.[15, 19] From this point of view, many bipolar host materials incorporating these two groups have been reported.[20-22]

Our group have reported a simple benzimidazole-carbazole-based bipolar host mBICP, in which the carbazole unit is linked to the benzimidazole segment via the *meta* position of the $C_2$-phenyl, for high efficiency blue and white electrophosphorescent applications.[23] Recently, Hung et al. reported an N-connected benzimidazole compounds possessed a remarkable advantage compared with the C-connected analogues.[24] To our knowledge, the $sp^3$ hybridization of $N_1$ and *meta* position linking mode could provide much more separation of spatial distribution of electron density to increase bipolar property and improve the triplet energy level.[25] In this communication, we demonstrate a new carbazole-N-benzimidazole bipolar host material in which the carbazole unit is linked to the benzimidazole segment via the *meta* position of the $N_1$-phenyl. The synthetic procedure of **mNBICz** was illustrated in Scheme 1. 1-(3-bromophenyl)-2-phenyl-1H-benzo[d]imidazole (1) was synthesized according to the literature.[22] All of the compounds were characterized by $^1$H NMR, $^{13}$C NMR, elemental analysis, and mass data. Detailed synthetic procedures and characterization data were described in ESI†.



**Scheme 1.** The route of synthesis **mNBICz**

The three-dimensional geometries and the frontier molecular orbital energy levels of **mNBICz** were calculated using density functional theory (Fig. 1). The spatial distribution of electron density of HOMO is mainly localized on the carbazole unit and the LUMO orbital is dispersed in the benzimidazole moiety. The completely separation of HOMO and LUMO can be rationalized by the broken conjugation at $N_1$ position of benzimidazole. The separated FMOs (Frontier Molecular Orbitals) indicates their potential ambipolar characteristics. The calculated HOMO/LUMO energy levels of **mNBICz** were estimated to be -5.48 and -2.55 eV, respectively.

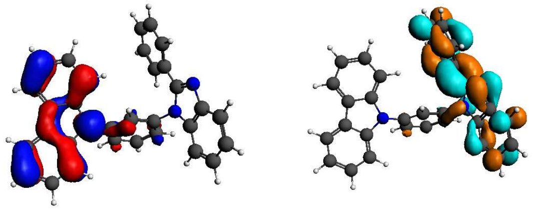


**Fig.1** HOMO and LUMO distributions of **mNBICz**

The thermal properties have been investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). **mNBICz** exhibits good thermal stability with decomposition temperature ($T_d$, 5% weight loss) at 349.3 □ and glass transition temperature ($T_g$) at 86 □ (see Fig. S1 and S2). The electrochemical properties were determined by the cyclic voltammetry (CV). The HOMO /LUMO energy level of **mNBICz** were measured to be -5.82/-2.25 eV, respectively. The HOMO level was calculated from its oxidative onset potential by comparing with ferrocene (Fc) (HOMO = − ($E_{ox}$ + 4.68) eV). The LUMO energy level was calculated from the obtained HOMO level and optical bandgap (Fig. S3 in the ESI†).

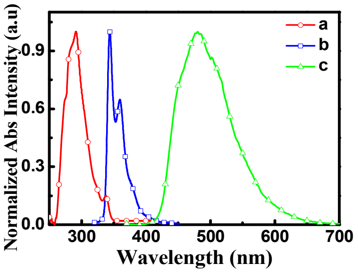


**Fig.2** (a) UV-Vis absorption spectrum of **mNBICz** in toluene; (b) photoluminescence （PL） spectrum of **mNBICz** in toluene at 298 K; (c) PL spectrum of **mNBICz** in 2-methyl tetrahydrofuran at 77 K.

The UV absorption, photoluminescence (PL), and low-temperature PL emission spectra of mNBICz are shown in Fig. 2. The maximum absorption peak at 292 nm can be assigned to the carbazole-centered n–π* transition. The optical bandgap calculated from the absorption edge of the absorption spectrum of mNBICz is 3.57 eV. PL emission of **mNBICz** in toluene at 298 K was observed at 343 and 360 nm, which corresponds to the singlet emission. And the triplet energy（$E_T$）of **mNBICz** is 2.78 eV, obtained from the first phosphorescent emission peak (λ = 446 nm) of the low-temperature PL spectrum measured at 77 K. Detailed data are summarized in Table S1.

In order to confirm the bipolar transporting properties of **mNBICz**, we used time-of-flight (TOF) techniques to measure their carrier mobility based on the device configuration of [ITO/ Host (um)/Al]. Fig.3 shows typical TOF transients of hole/electron for **mNBICz** under different applied electrical field. The hole mobility of **mNBICz** lay in the range of $3.34\times10^{-5}$ and $5.72\times10^{-5}$ cm$^2$ V$^{-1}$s$^{-1}$ for fields varying from $4.2\times10^5$ to $6.0\times10^5$ V cm$^{-1}$, which were colse to the electron mobility between $4.2\times10^{-5}$ and $7.0\times10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$ for fields varying from $3.36\times10^5$ to $5.57\times10^5$ V cm$^{-1}$. Here, we also compare the hole/electron mobility under same applied electrical field (Fig. S4 in ESI†). Under a certain electron field of $5.0\times10^5$ V cm$^{-1}$, the electron mobility was measured to be $6.12\times10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$, which was close to the value of the hole, $4.32\times10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$. All of these results showed that mobilities of hole and electron are close to each other, indicated the bipolar transporting properties of **mNBICz.**

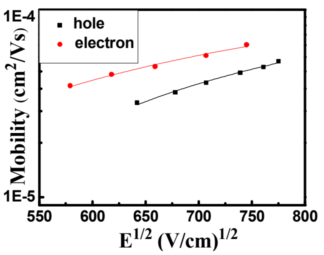


**Fig.3** Electron mobilities plotted with respect to $E^{1/2}$ of **mNBICz.**

Encouraged by its bipolar charge transport properties and proper energy levels for charge injection, **mNBICz** was evaluated as the host materials for blue PHOLEDs. Phosphorescent OLEDs using FIrpic as dopants were fabricated as follows: ITO/$MoO_3$ (10 nm)/ TAPC (60 nm) / TCTA (5 nm)/ **mNBICz**: FIrpic (7 %, 20 nm)/ TmPyPB (35 nm)/ LiF(1 nm)/ Al(device A) (Fig. S5). Device B with mCP as host material was applied as a comparision. TAPC and TmPyPB were applied as the hole- and electron-transporting layers, respectively; TCTA was chosen as the exciton blocker to prevent the diffusion of excitons to the hole-transporting layer. Meanwhile, TCTA also can reduce the hole injection barrier from TAPC to host; $MoO_3$ and LiF served as hole- and electron- injecting layer, respectively. Fig. 4 shows device performance of blue PHOLEDs A and B.

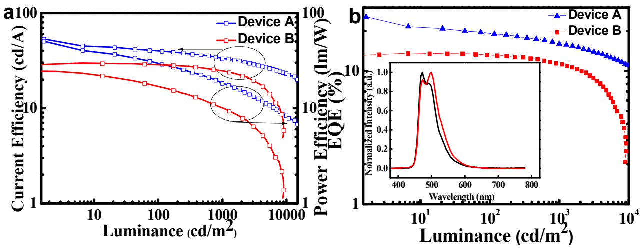


**Fig 4.** (a) Power and current efficiency–luminance and (b) quantum efficiency -luminance curves of device A and B. Inset: the EL spectra of the device A (black line) and device B (red line)

Device A shows a low turn-on voltage of 3.3 V, a high $L_{max}$ of 47995 cd m$^{-2}$ at 11.9 V and the maximum external quantum efficiency, current efficiency, and power efficiency are 26.2 %, 54.5 cd A$^{-1}$ and 52.2 lm W$^{-1}$, respectively. Device B exhibits a low turn-on voltage of 3.65 V, a high $L_{max}$ of 9093 cd m$^{-2}$ at 13.25 V and the maximum external quantum efficiency, current efficiency, and power efficiency are 13.3 %, 27.7 cd A$^{-1}$ and 24.7 lm W$^{-1}$, respectively. The efficiency of device A is ca. 50% higher than device B. The high efficiency of device A can be attributed to the bipolar feature of **mNBICz** and matched HOMO/LUMO to the adjacent layers. Meanwhile, device A remained a competitive performance of 33.2 cd A$^{-1}$ at a practical brightness of 1000 cd m$^{-2}$, and exhibited low efficiency roll-off. In general, the outstanding performance of blue PHOLEDs certified our purpose developing a highly efficient bipoalr host material with a simple structure. All of the key performance parameters of devices were summarized in Table 1.

**Table. 1** EL performance of device A-F

| Device | $V_{on}$ | $L_{max}$(cd m$^{-2}$) (V)$^a$ | $\eta_C$(cd A$^{-1}$)$^b$ | $\eta_P$ ( lm W$^{-1}$)$^c$ | $\eta_{extmax}$(%)$^d$ | CIE [x, y]$^e$ |
|---|---|---|---|---|---|---|
| **A** | 3.31 | 47995(11.9) | 54.5/33.2 | 52.2/19.6 | 26.2 | (0.14, 0.32) |
| **B** | 3.65 | 9093 (13.25) | 27.7/24.6 | 24.7/10.1 | 13.3 | (0.15, 0.14) |
| **C** | 3.32 | 48460 (13.9) | 46.9/34.0 | 44.6/17.4 | 17.2 | (0.35, 0.44) |
| **D** | 3.32 | 48380 (12.5) | 54.7/45.7 | 48.7/23.4 | 17.5 | (0.39, 0.46) |
| **E** | 3.32 | 48202 (12.5) | 62.5/49.9 | 60.4/27.4 | 22.9 | (0.39, 0.45) |
| **F** | 3.32 | 48504 (12.5) | 55.3/47.7 | 52.7/24.7 | 20.0 | (0.44, 0.47) |

$V_{on}$: turn-on voltage at 1 cd m$^{-2}$. [a] $L_{max}$: maximum luminance; V: voltage at the maximum luminance. [b] $\eta_C$: current efficiency at 1 cd m$^{-2}$ and 1000 cd m$^{-2}$. [c]$\eta_P$: power efficiency at 1 cd m$^{-2}$ and 1000 cd m$^{-2}$. [d] $\eta_{ext.max}$: the maximum EQE. **[**e**]**Measured at 8.0 V.

Inspired by the impressive results obtaining from the blue PhOLEDs, a single two-color white phosphorescent organic light-emitting diodes (WOLEDs) adopting Firpic and the orange dopant Ir(bt)$_2$(acac)[26] with the configuration of ITO/MoO$_3$ (10nm)/TAPC(60nm)/TCTA(5nm)/Host:FIrpic:Ir(bt)$_2$(acac)(7 %:n%,20 nm)/TmPyPB (35 nm)/LiF(1 nm)/Al were fabricated (C, D, E, F) corresponding to n=0.5, 1, 1.5, 2, respectively. Fig. 5 shows device performance of C-F.

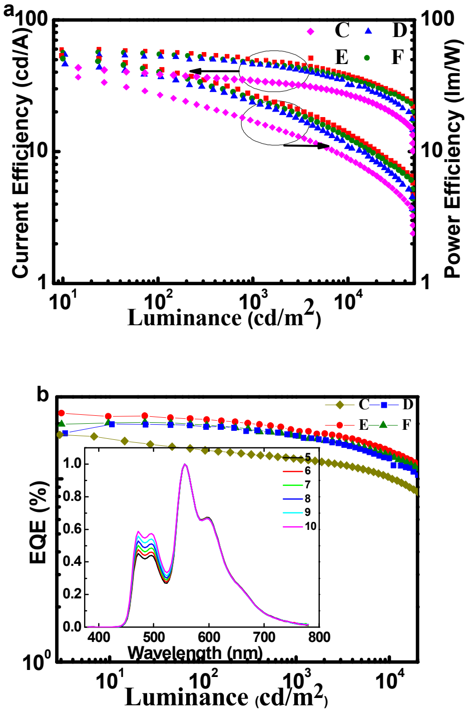


**Fig 5**. (a) The current efficiency and power efficiency versus luminance curves. (b) The external quantum efficiency (EQE)–luminance curves of white OLEDs C-F. Inset: EL spectrum of Device E under different voltages.

As shown in Fig.5 and Table. 1, with the increase of the doping concentration, the colour will gradually shift to red, but there will be an increase of luminous efficiency. When the concentration of orange dopant Ir(bt)$_2$(acac) reached to 1.5%, the best performance white device E were obtained. Device E achieves a $\eta_{c,\ max}$ of 62.5 cd A$^{-1}$, $\eta_{p,\ max}$ of 60.4 lm W$^{-1}$, and $\eta_{ext,\ max}$ of 22.9% and exhibits 3.32 V at the brightness of 1.0 cd m$^{-2}$. Moreover, a maximum luminance of 48202 cd m$^{-2}$ at 12.5 V with CIE values of (0.39, 0.46) was reached. These efficiency values are 46.9 cd A$^{-1}$, 44.6 lm W$^{-1}$, and 17.2 % for device C, 54.7 cd A$^{-1}$, 48.7 lm W$^{-1}$and 17.5% for device D, 55.3 cd A$^{-1}$, 52.7 lm W$^{-1}$ and 20 % for device F, respectively. The relative high efficiencies of these devices can be attributed to the bipolar characters of **mNBICz** which may result in balanced charge fluxes and a broad distribution of recombination region within the emitting layer. From the inset of Fig.5b, it can be observed that the blue emission become stronger with the increased biases. This is because that the FIrpic emission is mainly via host－guest energy transfer, whereas the orange emission is due to the direct charge-carrier trapping and then recombining on Ir(bt)$_2$(acac) molecules in the WOLED[27]. A decreased electric field is more favorable for the hole-trapping effect, which will lead to more orange emission with respect to blue emission. Although the emisssion of the blue changed with the biases, but the Internationale de L'Eclairage (CIE) of the devices is in warm white light area. Take device E for instance, the CIE coordinates are (0.40, 0.46) at 5 V and shift to (0.38, 0.45) at 10V, and the CRI ranging from 60.3 to 62.4. Additionally, device D-F exhibited a significantly practical application efficiency (>45 cd A$^{-1}$) even at 1000 cd m$^{-2}$, which have the potential to meet the requirements of daily life. All of these results suggested that **mNBICz** was suitable for dopanting FIrpic and Ir(bt)$_2$(acac) for white OLEDs.

## Conclusions

In conclusion, a simple new bipolar host material **mNBICz** for phosphorescent OLEDs has been designed and synthesized by attaching the carbazole unit to the benzimidazole segment via the *meta* position of the N$_1$-phenyl. By using **mNBICz** as a host material, we successfully developed high-performance blue OLEDs and single emission layer white OLEDs. To our knowledge, these performances are among the best reported values.[28-33] Our results unambiguously demonstrate that a synthetic strategy combining carbazole and benzimidazole subunits produces an effective molecular framework for the preparation of high $E_T$ bipolar host materials, with high quantum efficiencies above 25% achieved in blue PhOLEDs.

## Acknowledgements

This research work was supported by the NSFC/China (21161160442, 51203056), the National Basic Research Program of China (973 Program 2013CB922104) and the Doctoral Fund of the Ministry of Education of China (20100142120049).

## Notes and references

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† Electronic supplementary information (ESI) available: TGA and DSC images, quantum chemical calculation data, repeated CV scan plot, OLED device data and NMR spectra. See DOI:

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