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Novel Bipolar Bathophenanthroline Containing Hosts for Highly Efficient Phosphorescent OLEDs

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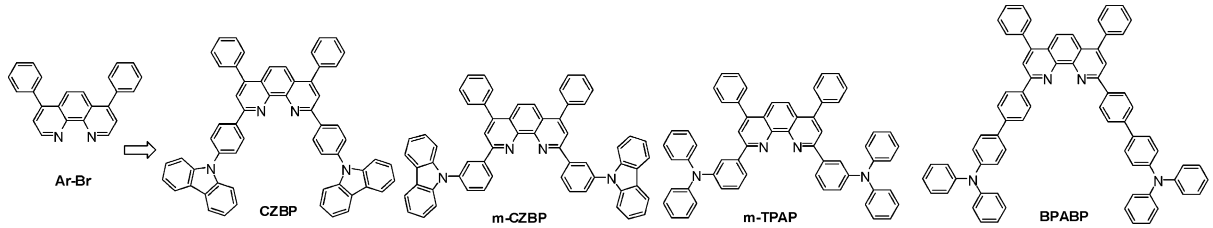
ABSTRACT



The electronic structures of eight bathophenanthroline derivatives were elucidated by DFT calculations, and four representatives of which CZBP, *m*-CZBP, *m*-TPAP, and BPABP were synthesized and employed as the hosts to afford highly efficient phosphorescent OLEDs. The calculated molecular orbital energies agree well with the experimental results, which further demonstrates that the localization of HOMO and LUMO at the respective hole- and electron-transporting moieties is desirable in bipolar molecular designs.

Since the seminal work by Baldo et al.,[1] considerable progress has been achieved on phosphorescent organic light-emitting diodes (PHOLEDs) in the past decade. This arises from the fact that the guest materials of transition metal complexes such as *fac*-tris(2-phenylpyridine)iridium (Ir(ppy)$_3$) possess both singlet and triplet excitons to realize a fast and efficient phosphorescent decay, leading to high external quantum efficiencies.[2] To achieve maximum efficiency for the host materials used in PHOLEDs, they should possess a higher triplet energy gap, ΔE (T_1-S_0), than that of phosphorescent guest molecules to prevent the reverse energy transfer of triplet excitons from the guest back to the host. On the other hand, bipolar molecules[3] containing both guest and host moieties have attracted much interest in OLEDs since a balanced density of charge and high efficiency could be attained by simultaneously supplying the electron and hole to electroluminescent (EL) materials sandwiched between two electrodes.

Recently, from our endeavors to develop new strategies for molecular design in OLEDs, we have demonstrated that disrupting molecular π-conjugation favors localization of the HOMO and LUMO at their respective hole- and electron-transporting moieties and increases the triplet energy gaps in bipolar molecules. For further investigation of this concept, we designed novel bipolar host molecules, simultaneously combining the charge separation and the suitable triplet energy gaps with the aid of density functional theory (DFT) calculations. Avilov et al.[4] reported a strategy based on DFT investigations to design hosts with carbazole and 9,9′-

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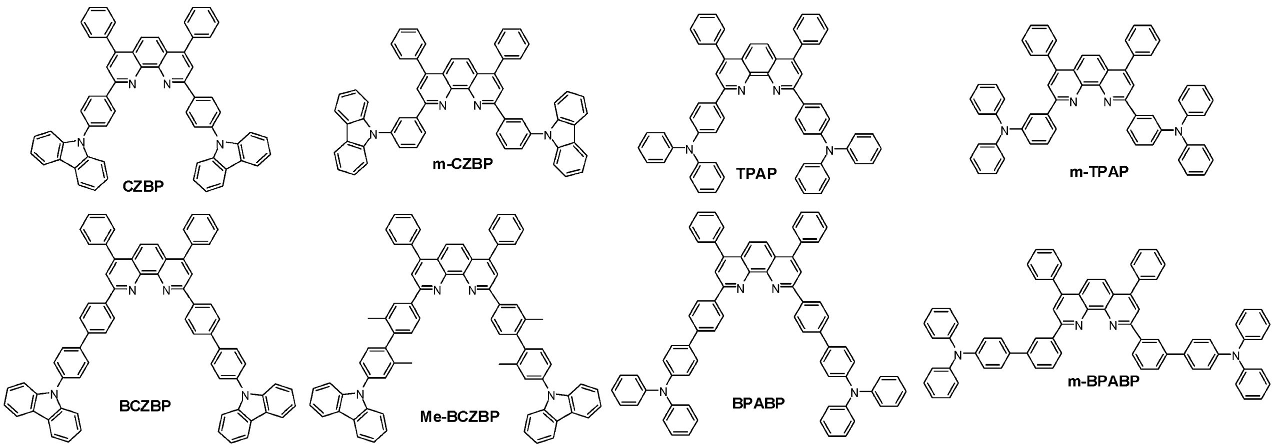

Figure 1. Molecular models of bathophenanthroline derivatives for DFT calculation.

spirobifluorene repeat units for PHOLEDs. However, they only presented the experimental energy levels with respect to the theoretical calculations without further investigating the device performance. To date, there is still a lack of comprehensive studies detailing the structure−performance correlation in PHOLEDs.

In this study, we present an integrated investigation encompassing the DFT molecular modeling, material synthesis, and device characterization based on a series of bipolar hosts containing electron-transporting bathophenanthroline and hole-transporting carbazole/triphenylamine units. We choose bathophenanthroline and carbazole/triphenylamine as the building blocks since the electron-deficient bathophenanthroline derivatives, such as 2,9-dimethyl-4,7-diphenyl-1,-10-phenanthroline (BCP), are well-known as electron-transporting and hole-blocking materials, while the electron-rich carbazole[5] and triphenylamine[6] derivatives have been used extensively as hole-transporting materials for their high hole-transporting mobility. In addition, bipolar molecules based on bathophenanthroline have not been reported to date.

Thus, eight bathophenanthroline derivatives were newly designed (Figure 1), and the HOMO and LUMO energy levels as well as the triplet energy gaps were calculated using DFT. The calculated triplet energy gaps, ΔE (T_1-S_0), range from 2.62 to 2.77 eV for this series of compounds (Table S-1). It should be noted that the triplet energy gap of *m*-CZBP is higher than that of CZBP by 0.09 eV, which is associated with the decrease of π-conjugation caused by the twisted conformation arising from the meta-configuration. The same tendency can be found by comparing other paired compounds for similar structures with decreased conjugation, for example, BCZBP and Me-BCZBP, TPAP and *m*-TPAP, and BPABP and *m*-BPABP, respectively. The results clearly indicate that disrupting the molecular conjugation is an effective way to increase the triplet energy gaps. However, the substitution of different carbazole or triphenylamine moieties into bathophenanthroline exhibits little effect on the triplet energy gap, indicating that their electronic structures are dominated by the bathophenanthroline moiety.

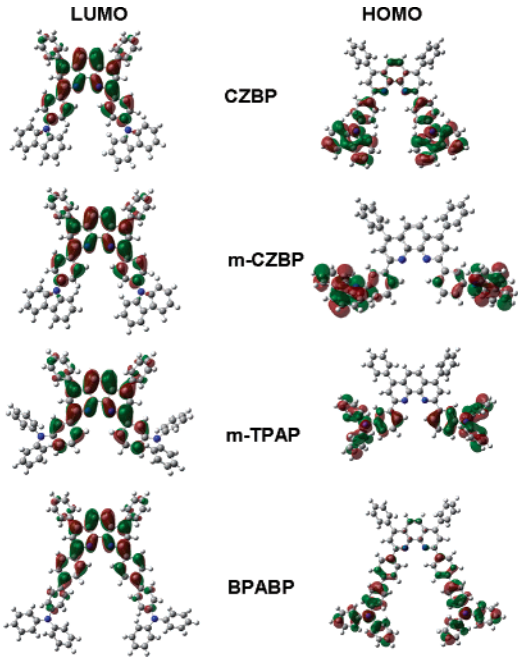

Figure 2. Three-dimensional structures of CZBP, *m*-CZBP, *m*-TPAP, and BPABP.

Figure 2 illustrates the calculated spatial distributions of HOMO and LUMO for CZBP, *m*-CZBP, *m*-TPAP, and BPABP. It is interesting to note that *m*-CZBP and *m*-TPAP show significant separation in the spatial distributions between HOMO and LUMO at their respective hole- and electron-transporting moieties, while CZBP and BPABP

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exhibit less localization. Figure S-1 shows that Me-BCZBP and *m*-BPABP with more twisted structures exhibit complete charge separation. This implies that the one-electron HOMO → LUMO transition became a typical charge transfer (CT), which is preferable for efficient hole and electron transfer and the prevention of back energy transfer.

To verify the results of DFT calculations and explore the structure–performance relations, four representatives, CZBP, *m*-CZBP, *m*-TPAP, and BPABP, were synthesized by the coupling of bathophenanthroline with arylbromide and utilized to fabricate OLEDs. Figure 3 outlines the general synthetic route for CZBP, *m*-CZBP, *m*-TPAP, and BPABP. In a typical synthetic procedure, such as that of CZBP, the arylbromide **1** (2.4 equiv) was converted to a lithio-substituted carbazole in Et_2O, to which a suspension of bathophenanthroline (1 equiv) in dried toluene was added. The mixture was heated at reflux for 24 h, then hydrolyzed with water and extracted with dichloromethane. The organic phase was stirred with MnO_2 for 6 h, filtered, and purified by column chromatography to afford CZBP in a 52% yield. *m*-CZBP, *m*-TPAP, and BPABP were prepared by the similar procedure as CZBP starting from **2**, **3**, and **4**, respectively.[7]

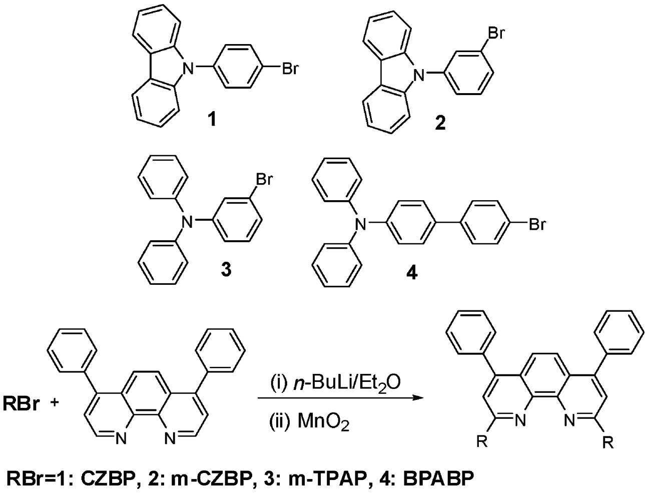

Figure 3. Synthesis of bathophenanthroline derivatives.

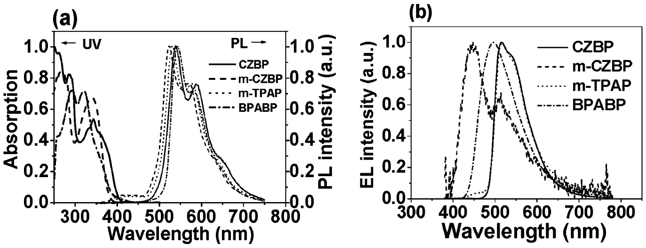

Figure 4. (a) UV and PL spectra of bathophenanthroline derivatives in THF. (b) EL spectra of the devices.

The photophysical properties of the bathophenanthroline derivatives were measured by UV absorption and photoluminescence spectra (PL) as shown in Figure 4a and Table 1. In UV spectra, the absorption at 282 nm for CZBP and 300 nm for *m*-CZBP are attributed to the carbazole-centered n–π* transition, while those at 278 nm for *m*-TPAP and 296 nm for BPABP are due to the n–π* transition at the triphenylamine moiety. On the other hand, the longer wavelength absorption observed at 301–375 nm for all compounds originates from the π–π* transitions from the electron-donating carbazole or triphenylamine moiety to the electron-accepting bathophenanthroline moiety. In the PL spectra, all of the compounds exhibit a maximum around 520 nm with identical spectral shapes owing to their similar molecular structures. It was found that the meta-structured *m*-CZBP and *m*-TPAP exhibit slight blue shifts of 10 nm as compared CZBP with *m*-CZBP and BPABP with *m*-TPAP, respectively, which is attributed to the twisted structure disrupting the π-conjugation between triphenylamine/carbazole and bathophenanthroline units.

Table 1. Physical Properties of the Compounds and Devices

compound	$\lambda_{abs}{}^{a}$/nm	$\lambda_{em}{}^{b}$/nm	PL/nm	$T_m{}^{c}/T_g{}^{d}/T_d{}^{e}$/°C
CZBP	282, 341	516	531, 572	219/NA/541
m-CZBP	300, 346	447	518, 556	240/133/487
m-TPAP	278, 301	517	524, 562	360/171/498
BPABP	296, 375	498	534, 564	300/174/540

[a] Absorption maximum (measured in THF). [b] Emission maximum of devices. [c] Melting point. [d] Glass transition temperature. [e] Decomposition temperature.

The HOMO levels were measured with a Riken AC-2 photoemission spectrometer (PES), and the LUMO (S_1) and T_1 levels were estimated from the UV and phosphorescent spectra, respectively. As shown in Figure 5a, the experimental triplet energy gaps ranged from 2.41 to 2.61 eV, which is in good agreement with the calculated values (2.62–2.77 eV). The triplet energy level of CZBP (2.41 eV) was

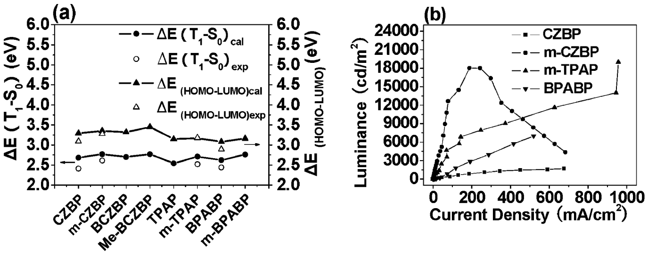

Figure 5. (a) Calculated and experimental triplet energy gaps and HOMO–LUMO energy gaps. (b) Luminance versus current density characteristics for the devices.

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(7) See Supporting Information for experimental details.

lower than that of Ir(ppy)$_3$ (2.42 eV),[8] implying CZBP was not suitable as a host material for Ir(ppy)$_3$.

The thermal properties of the bathophenanthroline derivatives were investigated by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). As shown in Table 1, the compounds possess high T_g of 133−174 °C and high melting point ($T_m = 219-360$ °C). TGA measurements show the compounds are thermally stable up to 480 °C with the decomposition temperatures (T_d) in the range of 487−541 °C in nitrogen. The excellent thermal stability enables preparation of homogeneous and stable amorphous thin films by vacuum deposition.

OLED devices based on CZBP, *m*-CZBP, *m*-TPAP, and BPABP were fabricated by multilayer vacuum deposition with the structure of indium tin oxide (ITO)/ PEDOT (20 nm)/host + 6 mol % of Ir(ppy)$_3$ (70 nm)/TPBI (30 nm)/Cs: BCP (1:1) (20 nm)/Al (100 nm). Poly(3,4-ethylenedioxythiophene) (PEDOT)[9] is employed to promote the hole injection, and 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI) serves as the hole and exciton blocker. Cs-doped BCP acts as electron injection layer. Bathophenanthroline derivatives doped with 6 mol % of Ir(ppy)$_3$ are used as the emitting layer.

In the EL spectra (Figure 4b), the devices based on CZBP and *m*-TPAP exhibit green luminescence around 510 nm from Ir(ppy)$_3$. It is surprising to note that the luminescence from the *m*-CZBP and BPABP device was blue-shifted by 60 and 20 nm, respectively, compared to the typical green emission (510 nm), which might be attributed to the phase separation or aggregation of the dopants.

The current−luminance ($I-L$) characteristics of the devices are outlined in Figure 5b. The EL performance of device *m*-CZBP (maximum luminance = 18 000 cd m^{-2}; current efficiency = 16.20 cd A^{-1}) is much better than that for CZBP (1149 cd m^{-2}; 0.15 cd A^{-1}), which can be attributed to the combined effects of enhancement in charge localization and the increase of triplet energy gap of the host material. The DFT calculation results indicate that *m*-CZBP has more significant localization of the HOMO and LUMO than CZBP, which is desirable for charge separation and prevention of back excitation transfer. Furthermore, the triplet energy gap of *m*-CZBP is higher than the guest Ir(ppy)$_3$ by 2.61 to 2.44 eV, whereas that of CZBP is lower than Ir(ppy)$_3$ by 2.41−2.44 eV, which allows back energy transfer from the guest to the host. Although phase separation or aggregation of dopants was observed from the EL spectra of *m*-CZBP, the charge localization may play a more important role in giving rise to the improved device performance. Consequently, *m*-TPAP with both obvious charge localization and a high triplet energy gap also exhibits excellent device performance with the maximum luminance and current efficiency of 19 000 cd m^{-2} and 10.69 cd A^{-1}, respectively. BPABP device indicates a relatively low performance (7000 cd m^{-2} and 1.34 cd A^{-1}) attributed to the incomplete localization of HOMO and LUMO and low triplet energy gap (2.44 eV). Clearly, the experimental results validate our theoretical modeling that the localization of HOMO and LUMO at their respective hole- and electron-transporting moieties and modification of triplet energy gap are two important factors that should be considered when designing bipolar molecules for PHOLEDs.

In summary, we have modeled a series of novel bipolar compounds containing bathophenanthroline and carbazole/ triphenylamine and investigated their energy levels by DFT calculations. Four representative compounds were successfully synthesized and employed as host materials to afford highly efficient OLEDs with the luminance and current efficiency in the range of 1149−19 000 cd m^{-2} and 0.15−16.20 cd A^{-1}, respectively. The theoretical and experimental results demonstrate that the effective disruption of π-conjugation is an efficient way to obtain desirable localization of HOMO and LUMO and increase the triplet energy gap in bipolar hosts, which provides a promising avenue in molecular design for PHOLEDs.

Supporting Information Available: Calculation details and results, measurements, experimental, and ^{1}H and ^{13}C NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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