

New Host Containing Bipolar Carrier Transport Moiety for High-Efficiency Electrophosphorescence at Low Voltages

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Organic light-emitting diodes (OLEDs) are very attractive for next-generation flat-panel displays and lighting technology, because of their self-emission properties, fast response times, wide-viewing angles, high contrast, and light weights. After two decades of intensive research and development, since their discovery in 1987,^[1] the focus of OLED research is now mainly on the improvement of device stability and power efficiency. To achieve low power consumption in OLEDs, two key issues—improving the current efficiency, and reducing the device driving voltage—have been largely addressed in the past few years.^[2–4] With the introduction of triplet emitters in OLEDs, an internal quantum efficiency of 100% can theoretically be achieved, overcoming the limitation of 25% efficiency in conventional fluorescent OLEDs.^[5] As singlet and triplet excitons form under electrical excitation in the ratio approximately 1:3, emission from triplet excitons via phosphorescent materials would be more efficient than that from conventional fluorescent materials.

Hence, tremendous efforts have recently been made in the development of highly efficient phosphorescent organic light-emitting devices (PHOLEDs).^[6–9] In PHOLEDs, phosphorescent materials are often doped into a host matrix as guest emitters, in order to reduce aggregation quenching and triplet-triplet annihilation. To achieve efficient electrophosphorescence, the choice of host material is of extreme importance. Generally, the HOMO–LUMO (HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital) energy gap (E_g) and the triplet energy level of the host material must be higher than those of the dopants, to ensure exothermic energy transfer and confinement of triplet excitons on the dopant. However, if the E_g of the host material is too large, it would induce deep and strong charge traps on the dopant emitter, resulting in a high driving voltage of the device.^[6,10] The large difference in HOMO level and/or LUMO level between the carrier-transporting and the emitting layer would also cause energetically unfavorable charge injection, leading to a high driving voltage.^[11] Furthermore, poor carrier mobility and unbalanced charges in the emitting layer have been shown to be detrimental to the power efficiency of OLEDs.^[4] To improve carrier drift mobility and achieve good charge balance, electron-transporting and/or hole-transporting molecules blended with a polymer to form a composite host have been shown to be useful in polymer PHOLEDs.^[12,13] But physical blending increases the risk of phase separation at high loads. The approach of using host polymers bearing both hole-transporting and electron-transporting units has also shown to improve charge transport and charge balance in polymer PHOLEDs.^[14]

Carbazole derivatives,^[15–17] which possess sufficiently large triplet energies and hole-transporting properties, are widely used as host materials in PHOLEDs. The most commonly used carbazole-based material, 4,4'-bis(*N*-carbazolyl)-1,1'-biphenyl (CBP), with which PHOLEDs exhibit good current efficiency and high quantum efficiency, has been shown useful for green- and red-light-emitting PHOLEDs.^[18–24] However, high driving voltages are often observed in these devices, and this is attributed to the low drift mobility of the carrier^[25,26] and the wide energy gap^[27] of CBP, as well as the large difference in the HOMO level between the hole-transporting layer and CBP.^[11] Thus, it is highly desirable to develop a host material that has a higher triplet energy than that of the phosphorescent guest emitter, a relatively narrow E_g with an appropriate HOMO level, and good carrier-transporting properties; by doing so, highly efficient,

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low-driving-voltage PHOLEDs could be realized. Up to now, research directed toward the design and synthesis of such a host material has been rather limited.^[11]

In this communication, a new host material for use in high-efficiency low-voltage PHOLEDs, 4,7-dicarbazol-9-yl-[1,10]-phenanthroline (BUPH1), is introduced. BUPH1 possesses high triplet energy, a relatively narrow energy gap with an appropriate HOMO level, and good carrier mobility. BUPH1 is composed of an electron-transporting phenanthroline core^[28] and two peripheral hole-transporting carbazole substituents; its charge-carrier mobility is therefore anticipated to be superior to that of CBP. The dipolar nature of BUPH1 can also promote the strong π - π intermolecular stacking of molecules in the solid state, which can facilitate high charge transport. Moreover, the electron-donating carbazole moieties are conjugated to the electron-accepting phenanthroline core; the donor-acceptor intramolecular interaction tends to decrease the energy gap. It has been demonstrated that PHOLEDs with BUPH1 as the host material and *fac*-tris(2-phenylpyridine)iridium ($\text{Ir}(\text{ppy})_3$)^[6] as the green-phosphorescent dopant exhibit low driving voltages of 2.6, 3.5, and 5.3 V for current densities of 1, 10, and 100 mA cm^{-2} , respectively. These driving voltages are significantly lower than those of conventional CBP-based PHOLEDs, which require 3.8, 4.9, and 7.2 V, respectively, to reach the corresponding current densities. With such low driving voltages, the power efficiency of the BUPH1-based device is dramatically enhanced to 33 and 20 lm W^{-1} at 100 and 1000 cd m^{-2} , respectively.

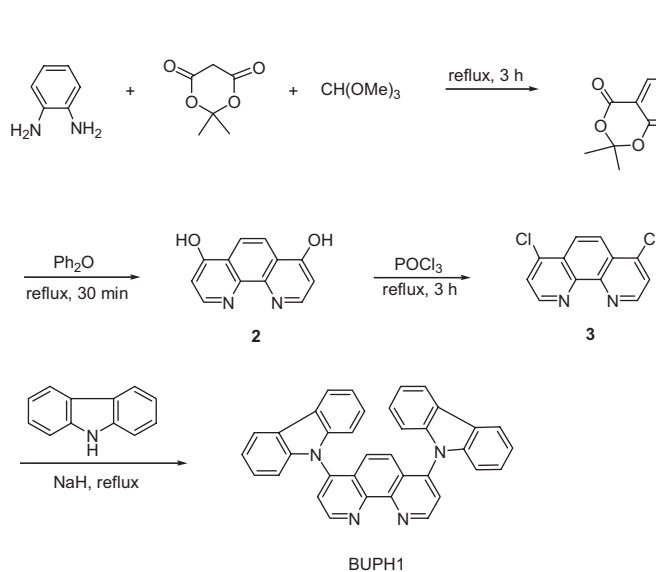
BUPH1 was synthesized by the reactions outlined in Scheme 1. Literature procedures were adapted to synthesize 4,7-dichloro-1,10-phenanthroline (**3**).^[29] Reaction of *o*-phenylenediamine with in-situ-generated 5-methoxymethylene Meldrum's acid in trimethylorthoformate at reflux produced the bis-adduct, **1**. Thermal decarboxylation/cyclization of **1** in refluxing diphenyl ether produced 4,7-dihydroxyl-1,10-phenanthroline, **2**. Treatment of **2** with phosphoryl chloride generated 4,7-dichloro-1,10-phenanthroline, **3**. Nucleophilic aromatic substitution of **3** with carbazole

in the presence of NaH furnished the desired product BUPH1. Results from ^1H NMR and ^{13}C NMR elemental analyses and high-resolution mass spectroscopy (HRMS) were consistent with the proposed structure. BUPH1 shows excellent thermal properties with a glass-transition temperature (T_g) of 155 $^\circ\text{C}$, a melting point of 322 $^\circ\text{C}$ (both determined by differential scanning calorimetry (DSC)), and a decomposition temperature (T_d) of 449 $^\circ\text{C}$ (determined by thermal gravimetric analysis (TGA)). Such a high T_g is highly desirable for host materials in OLEDs, in order to prevent morphological changes and to suppress the formation of aggregation upon exposure to the heat that is produced when the device is operated. The fluorescence quantum yield Φ of BUPH1 in CHCl_3 is 0.1, as was estimated by a relative method using quinine in 1 M H_2SO_4 ($\Phi_{334 \text{ nm}} = 0.56$) as standard.

Figure 1a shows the absorption spectra of thin films of BUPH1 and CBP. The long-wavelength absorption peaks of BUPH1 are at 280, 335, and 364 nm, respectively. It is obvious that the optical band gap of BUPH1, with a cutoff wavelength, λ_{cutoff} , at 390 nm (3.1 eV), is about 0.3 eV less than that of CBP, with λ_{cutoff} at 365 nm (3.4 eV), which is close to the value reported in the literature.^[27] The photoluminance (PL) spectra of BUPH1 measured at room temperature (RT) and 77 K are shown in Figure 1b. The triplet energy of BUPH1, estimated from low-temperature PL, is about 2.4 eV, which is very close to the triplet energy of CBP (2.55–2.6 eV).^[30,31] Thus, BUPH1 could be a good host material for green- and red-phosphorescent guest emitters. The HOMO energy (or first ionization potential) of BUPH1 was determined by UV photoemission spectroscopy to be 5.9 eV. By subtracting the optical band gap from the HOMO energy, the LUMO level was estimated to be 2.8 eV.

The charge-carrier transport properties of thin films of CBP and BUPH1 were investigated and characterized in electron-only and hole-only devices. The electron-only device had the structure ITO/BCP (8 nm)/CBP or BUPH1 (60 nm)/BPhen (8 nm)/LiF (1 nm)/Al (60 nm), while the hole-only device had the structure ITO/NPB (8 nm)/CBP or BUPH1 (60 nm)/NPB (8 nm)/Al (60 nm) (ITO: indium tin oxide; BCP: 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline; BPhen: 4,7-diphenyl-1,10-phenanthroline; NPB: *N,N'*-bis-(1-naphthyl)-*N,N'*-diphenyl,1,1'-biphenyl-4,4'-diamine). The current-density-voltage characteristics of these single-carrier devices are shown in Figure 2. It is evident that both BUPH1-based devices show higher current densities than the CBP-based devices at the same electric field, indicating superior charge-carrier mobility of BUPH1 and, thus, the potential of BUPH1 for use as a host material in low-driving-voltage PHOLEDs.

PHOLEDs were fabricated using a three-layer device configuration of ITO/NPB (60 nm)/8% $\text{Ir}(\text{ppy})_3$ in BUPH1 or CBP (40 nm)/BPhen (20 nm)/LiF (1 nm)/Al (60 nm), where $\text{Ir}(\text{ppy})_3$ functioned as the green-phosphorescent dopant emitter and BUPH1 or CBP functioned as the host material. BPhen is used as an electron-transporting layer.^[28] Figure 3a shows the electroluminescence (EL) spectra of the devices driven at 100 mA cm^{-2} . In contrast to the EL



Scheme 1. Synthesis of BUPH1.

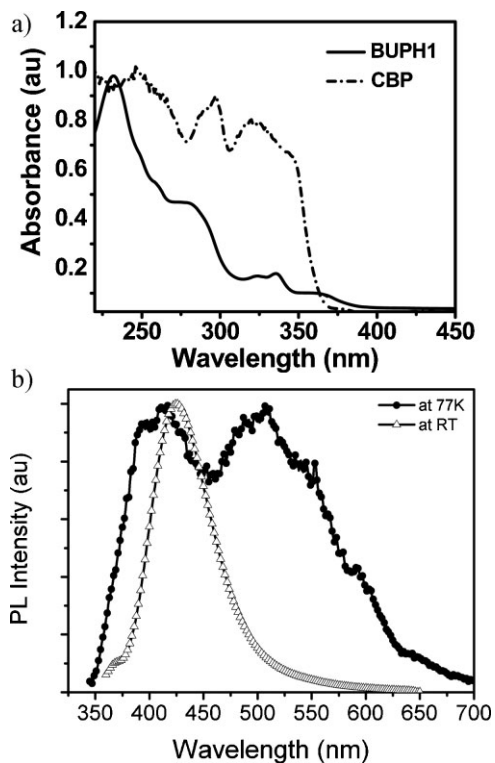


Figure 1. a) UV-vis absorption spectra of thin films of BUPH1 and CBP. b) PL spectra of BUPH1 at RT and 77 K in tetrahydrofuran (THF).

spectrum of the CBP-based device, the EL spectrum of the BUPH1-based device does not show any residue emission from the host and/or adjacent layer, even at high current densities, indicating complete energy and/or charge transfer from the host exciton to the triplet dopant emitter upon electrical excitation, and excellent confinement of charge carriers and excitons in the emitting layer. The current-density–driving-voltage–luminance characteristics of the BUPH1-based and CBP-based devices are shown in Figure 3b. The turn-on voltage, defined as the bias required to attain a brightness of 1 cd m^{-2} , is 2.2 and 3.2 V for the BUPH1-based and CBP-based devices, respectively. The BUPH1-based device required low driving voltages of 2.6, 3.5, and 5.3 V

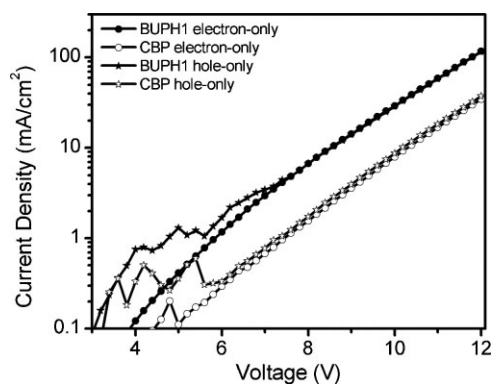


Figure 2. Current-density–voltage characteristics of the electron-only and hole-only devices based on BUPH1 and CBP.

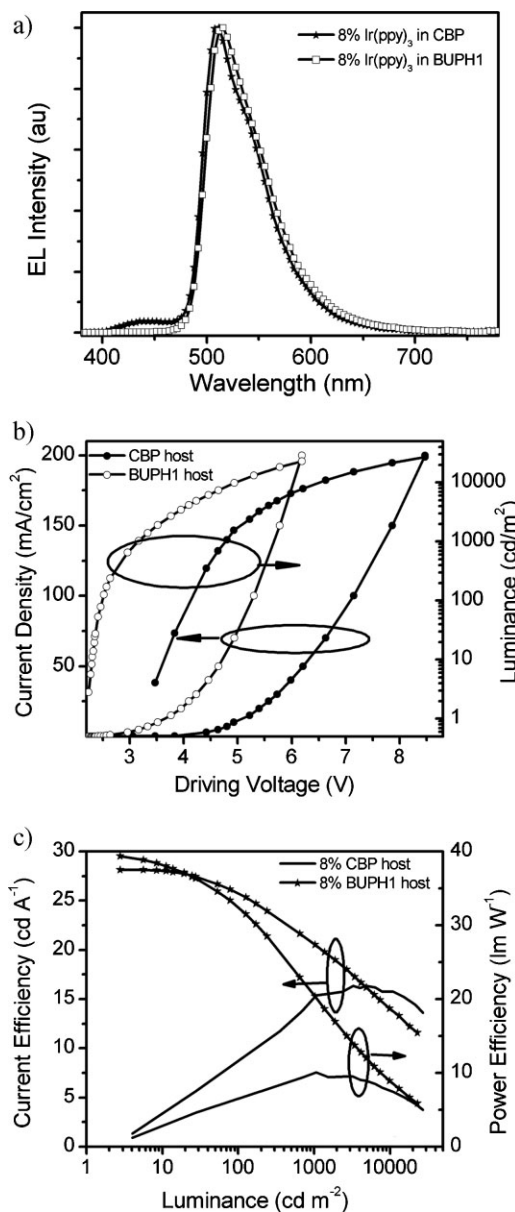


Figure 3. a) EL spectra of 8% Ir(ppy)₃ in BUPH1-based and CBP-based devices driven at 100 mA cm^{-2} . b) Current-efficiency–voltage–luminance characteristics of BUPH1-based and CBP-based devices. c) Current-efficiency–luminance–power-efficiency characteristics of BUPH1-based and CBP-based devices.

for current densities of 1, 10, and 100 mA cm^{-2} , respectively, compared to voltages of 3.8, 4.9, and 7.2 V for the same current densities for the CBP-based device. Remarkably, the driving voltages required for brightnesses of 10, 1000, and 10000 cd m^{-2} were 2.5, 3.2, and 5.0 V, respectively, which are comparable to those previously reported for OLEDs with p–i–n structures.^[32,33] With such low driving voltages, the power efficiency of the BUPH1-based PHOLED is dramatically enhanced, with values of 33 and 20 lm W^{-1} at 100 and 1000 cd m^{-2} , respectively (Fig. 3c).^[34] We are convinced that the low driving voltage and the high efficiency of BUPH1-based devices is a result of the narrow

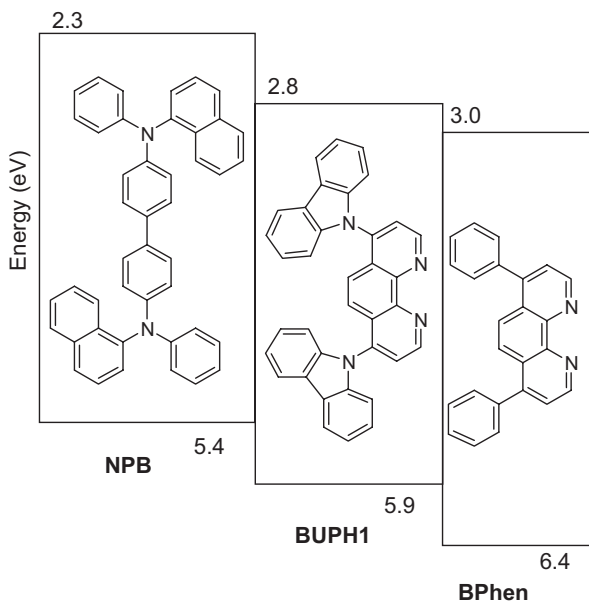


Figure 4. The energy diagram of a BUPH1-based PHOLED device.

energy gap with appropriate HOMO level, the high triplet energy, and the relatively high charge-carrier drift mobility of BUPH1, which cause the charges to be trapped on the Ir triplet emitters, effectively reducing the hole-injection barrier between the hole-transporting and emitting layers.

Figure 4 shows the energy diagram of a BUPH1-based PHOLED device. The HOMO and LUMO levels of NPB, CBP, and BPhen were taken from the literature.^[24,28] Obviously, because of the high hole mobility in NPB, the recombination zone in the BUPH1-based device is anticipated to be confined within the BUPH1 layer, as there is a ca. 0.5 eV barrier for electron injection from the LUMO of BUPH1 to the LUMO of NPB, and a 0.5 eV barrier for hole injection from the HOMO of BUPH1 to the HOMO of BPhen. The barrier for hole injection from the HOMO of NPB to the HOMO of BUPH1 is 0.5 eV, which is significantly smaller than the barrier for hole injection from the HOMO of NPB to the HOMO of CBP (6.1 eV) in the CBP-based device (0.7 eV). In addition, there is a small barrier for electron injection from the LUMO of BPhen to the LUMO of BUPH1. Thus, the carrier charges will easily transport into the BUPH1 layer and recombine within this layer. As a result, a high-efficiency, low-voltage PHOLED can be realized, because of the high carrier mobility together with the low injection barriers for both electron and hole in the BUPH1-based device.

In summary, the synthesis and characterization of a new host material, BUPH1, which possesses superior charge mobility and a narrower energy gap than CPB, has been reported for use as a phosphorescent guest emitter. Its application in a high-efficiency, low-voltage PHOLED has been demonstrated. The charge traps on the emitters and the hole-injection barrier between the hole-transporting layer and the emitting layer are effectively reduced, because of the narrower energy gap and the desirable HOMO level of BUPH1. The results show that BUPH1 is a promising host material to replace the commonly used CBP, both

in terms of power efficiency and thermal stability. Despite the absence of a p-i-n device structure, the PHOLED produced using Ir(ppy)₃ as dopant emitter exhibited low driving voltages of 2.6, 3.5, and 5.3 V for current densities of 1, 10, and 100 mA cm⁻², respectively, and exhibited power efficiencies of 33 and 20 lm W⁻¹ at luminances of 100 and 1000 cd m⁻², respectively. The important concept of integrating both hole-transporting and electron-transporting moieties into a host molecule has proven to be successful in PHOLED devices. These findings could provide a useful strategy in the design of new host materials to satisfy the special criteria required for PHOLEDs.

Experimental

Spectroscopic Data: ¹H NMR (400 MHz, CDCl₃) δ = 9.52 (d, J = 4.4 Hz, 2H), 8.15 (d, J = 6.8 Hz, 4H), 7.91 (d, J = 4.8 Hz, 2H), 7.40 (s, 2H), 7.29–7.37 (m, 8H), 7.07 (d, J = 7.6 Hz, 4 H); ¹³C NMR (100 MHz, CDCl₃) δ = 151.3, 147.9, 143.7, 141.0, 126.40, 126.4, 123.9, 122.9, 121.0, 120.6, 109.9; HRMS (matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF), m/z) [M⁺] calcd for C₃₆H₂₂N₄: 511.1917; found: 511.1922. Anal. calcd for C₃₆H₂₂N₄: C 84.68, H 4.34, N 10.97; found: C 84.40, H 4.28, N 10.76.

OLED, Hole- and Electron-Only Device Fabrication, and Measurements: The OLEDs were fabricated using a vacuum thermal evaporation chamber with a base pressure of 1.33 × 10⁻⁴ Pa. Two shadow masks were used to define the deposition areas for the organic and metal cathodes. Current-density–voltage–luminance characteristics and EL spectra of the device were measured using a computer-controlled dc power supply and a Spectrascan PR650 photometer at room temperature. The emission area of the devices was determined to be 0.1 cm², based on the overlapping area of the anode and the cathode. The ionization potential (or HOMO) of the BUPH1 thin film was measured by UV photoemission spectroscopy using a Surface Analyzer model AC-2.

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- [34] As BPhen has a HOMO level of 6.4 eV, it does not block the holes efficiently from CBP layer (HOMO = 6.1 eV). As a result, there is an initial increase in the efficiency of the Ir(ppy)₃ doped CBP-based device at low current density, reaching a maximum value and then a decrease with increasing current density.