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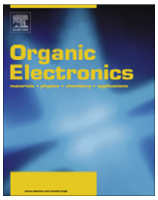

Simply structured, deep-blue phosphorescent organic light-emitting diode with bipolar host material

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ABSTRACT

We developed an efficient, deep-blue phosphorescent organic light-emitting diode (POLED) with a simplified device structure using a new host material. There are only three organic layers in the deep-blue POLED, namely, a hole-transporting layer, an emitting layer and an electron-transporting layer. The new host material exhibits bipolar carrier transportability and high triplet energy. The POLED utilizes a phosphorescent guest material, iridium(III) bis(4′,6′,-difluorophenylpyridinato)tetrakis(1-pyrazolyl)borate, that exhibits an external quantum efficiency of about 13% and a power efficiency of about 15 lm/W at a current density of 0.1 mA/cm^2. The efficiencies of the POLED are comparable to those of conventional POLEDs consisting of at least four organic layers. The bipolar host material will be useful for simplifying the device structure of deep-blue POLEDs.

1. Introduction

There have been many reports on phosphorescent organic light-emitting diodes (POLEDs) because their emission efficiencies are higher than those of conventional fluorescent OLEDs [1–3]. Red, green, and blue emissions in OLEDs are important for full-color flat-panel display and lighting applications. Red and green POLEDs with higher efficiencies as a result of using phosphorescent dyes have already been reported [4–7]. On the other hand, until recently, highly efficient blue POLEDs had been difficult to realize because of the lack of a suitable host/carrier-transporting material. A host/carrier-transporting material that exhibits a high carrier mobility and a high triplet energy (E_T) is essential for high-efficiency blue POLEDs. The external quantum efficiency (η_{EQE}) of blue POLEDs, which consist of iridium(III) bis[(4,6-difluorophenyl)-pyridinato-N,C 2′]picolinate (FIrpic) and/or iridium(III) bis(4′,6′-difluorophenylpyridinato)tetrakis(1-pyrazolyl)borate (FIr6), has been improved by synthesizing suitable materials [8–18]. Despite this improvement, many deep-blue POLEDs require at least four organic layers to attain a high efficiency [13–18]. The four organic layers are a hole-transporting layer, emitting layer, electron-transporting layer, and either a carrier/exciton-blocking layer or another emitting layer. This fourth layer is necessary for blocking carriers/excitons or distributing the recombination region due to the unipolar carrier transportability of the hosts, and a high efficiency is obtained particularly in double-emitting-layer (DEL)-structured devices [13–18]. As a consequence, the device structure of the deep-blue POLEDs becomes more complex than that of green or red POLEDs [6,7].

Recently, highly efficient blue OLEDs have been reported using bipolar host materials [19–23]. Emitters bluer than FIr6, such as FCNIr and Ir(dbfmi), are also used in these highly efficient blue OLEDs. It is proposed that the development of a bipolar host is critical to the high quan-

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tum efficiency due to charge balance in the emitting layer. The highly efficient deep-blue OLEDs can surely be realized by using bipolar host materials without employing a DEL structure, and thus, one of the key methods of simplifying the device structure of deep-blue POLEDs is the development of a suitable host material. It has been difficult to synthesize a bipolar host material with high E_T to confine the triplets of deep-blue dopant in the guest. The only molecular architecture that combines high E_T and bipolar carrier transport properties has been realized by combining a hole-transporting carbazole substituent and an electron-transporting phosphine oxide (phosphine sulfide) substituent [19–23]. The novel molecular architecture should be proposed to discuss more about the effect of such a bipolar host material on the efficiency of simplified deep-blue POLEDs.

In this paper, we report on a new bipolar host material for use in simply structured, deep-blue POLEDs, 2-[(4-carbazolyl-9-yl)phenyl]-2-[(4-pyridoindolyl-9-yl)phenyl]adamantane (Ad-CzPd). The simplified POLED consists of only three layers, namely, a hole-transporting layer, an emitting layer, and an electron-transporting layer, yet the η_{EQE} of the FIr6-based POLED is 13% at a current density (J) of 0.1 mA/cm^2. This efficiency is three times higher than the previously reported value for the same device structure [14]. The new host has both a hole-transporting carbazole substituent [16] and an electron-transporting pyridoindole substituent [18]. By combining these two substituents, an ideal host for a blue POLED, which exhibits both high E_T and bipolar transportability, can be realized. We have found that this novel molecular architecture is useful for simplifying and fabricating highly efficient, deep-blue POLED devices, since it distributes the carrier recombination region within the emitting layer.

2. Experimental

2.1. Preparation of Ad-CzPd

Ad-CzPd was synthesized by the reactions outlined in Scheme 1. 2,2-Bis(4-aminophenyl)damantane **1** was synthesized by adapting the dehydration method [24]. The reaction of 2-adamantanone with aniline and aniline hydrogen chloride in refluxing produced bis-aminophenyl product 1. Bis-iodophenyl product 2 was synthesized by the Sandmeyer reaction, in which aromatic amino compounds were converted into halogeno benzene derivatives. The nucleophilic aromatic substitution of 2 with 5H-pyrido[4,3-b]indole in the presence of Cu furnished mono-iodophenyl intermediate 3. Furthermore, nucleophilic aromatic substitution of 3 with carbazole in the presence of Cu furnished the desired product Ad-CzPd.

The structure of Ad-CzPd was identified using NMR. The following 37 hydrogen signals were detected by ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.4 (1H, s), 8.5 (1H, d, J = 5.5 Hz), 8.2 (1H, d, J = 7.6 Hz), 8.1 (2H, d, J = 7.6 Hz), 7.7 (4H, dd, J = 19.2, 7.8 Hz), 7.5–7.4 (6H, m), 7.4–7.3 (4H, m), 7.3 (4H, dd, J = 19.2, 7.8 Hz), 3.4 (2H, s), 2.2 (4H, t, J = 13.7 Hz), 2.0 (2H, s), 1.9 (4H, d, J = 12.4 Hz), 1.8 (2H, d).

Ad-CzPd showed excellent thermal properties with a glass transition temperature (T_g) of 165 °C and a melting point of 345 °C, both of which are determined by differential scanning calorimetry. The purity of Ad-CzPd confirmed to be over 99% from high performance liquid chromatography.

2.2. Device fabrication

To clarify the carrier transportability of Ad-CzPd, we compared the hole and electron transport properties of Ad-CzPd, Ad-Cz and Ad-Pd thin films in the hole-only and electron-only devices, as shown in Fig. 1a and b. Furthermore, we compared the carrier transport properties of Ad-CzPd and 4,4′-bis(*N*-carbazolyl)-1,1′-biphenyl (CBP), which is a well-known bipolar host material [19]. The structure of the hole-only device is ITO/PEDOT:PSS (35 nm)/α-NPD (8 nm)/Ad-CzPd or Ad-Cz or Ad-Pd or CBP (60 nm)/α-NPD (8 nm)/Al (100 nm) (ITO: indium-tin oxide; PEDOT:PSS: poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonic acid); α-NPD: 4,4′-bis[*N*-(1-naphthyl)-*N*-phenyl-amino]biphenyl). The structure of the electron-only device is ITO/PEDOT:PSS (35 nm)/UGH2 (10 nm)/Ad-CzPd or Ad-Cz or Ad-Pd or CBP (40 nm)/TmPyPB (20 nm)/LiF (1 nm)/Al (100 nm) (UGH2: *p*-bis(triphenylsilyly)benzene; TmPyPB: 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene) [11,13]. Then, we developed three types of FIr6-based OLEDs as shown in Fig. 1c. The device structure is ITO/PEDOT:PSS (35 nm)/TAPC (40 nm)/3 wt.% FIr6 in Ad-Cz or Ad-Pd or Ad-CzPd (35 nm)/TmPyPB (40 nm)/LiF (1 nm)/Al (100 nm) (TAPC: 1,1-bis[(di-4-tolylamino)phenyl] cyclohexane). Since TmPyPB has a relatively high E_T in a commercially available electron-transporting material, we selected it as the electron-transporting/hole-blocking layer [11]. The hole-only and electron-only devices, and POLEDs were developed on a glass substrate coated with a 150-nm-thick indium-tin oxide (ITO) layer. Prior to the fabrication of the organic layers, the substrate was cleaned with ultra-purified water and organic solvents, and treated with a UV-ozone ambient. To reduce the possibility of electrical shorts within the device, PEDOT:PSS, diluted in water, was spun onto the substrate to form a 35-nm-thick PEDOT:PSS layer after being baked for 1 h at 180 °C. The other organic layers were sequentially deposited onto the substrate without breaking the vacuum at a pressure of about 10^{-5} Pa. After cathode formation, the devices were encapsulated using a UV-epoxy resin and a glass cover within a nitrogen atmosphere. The electroluminescent (EL) spectra and luminance were measured with a spectroradiometer (Minolta CS-1000). A digital source meter (Keithley 2400) and a desktop computer used to operate the devices were connected. We assumed that the emission from the OLED device was isotropic, such that the luminance was Lambertian, and calculated the η_{EQE} from the luminance (L), J, and EL spectra.

3. Results and discussion

Fig. 2 shows the molecular structure and absorption spectrum of Ad-CzPd. The optical band gap (E_g) of Ad-CzPd was estimated to be 3.5 eV from the cutoff wavelength of the absorption peak (354 nm). The ionization potential (IP) of Ad-CzPd was estimated to be 5.9 eV (close to that