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Pure white OLED based on an organic small molecule: 2,6-Di(1H-benzo[d]imidazol-2-yl)pyridine



SPECTROCHIMICA ACTA

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HIGHLIGHTS

- 2,6-Di(1H-benzo[d]imidazol-2yl)pyridine (DBIP) was synthesized.
- The single-crystal structure of DBIP was obtained.
- The pure white OLED based on DBIP was demonstrated.
- The thermal stability, UV-vis and photoluminescent spectra of DBIP were investigated.

G R A P H I C A L A B S T R A C T

A pure white emission from DBIP-based OLED was achieved. The chemical structure of DBIP and the electroluminescent spectrum at 14 V (left), the CIE color coordinate and its corresponding emissive color (right).



A R T I C L E I N F O

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Introduction

White light is the most common and practical light due to widely used in the fields of backlighting display and illumination. There are some white-light sources, such as incandescent light, light-emitting diode (LED), fluorescent lamp, etc. However, they are imperfect in some ways, for example, high-energy consumption, and high-made cost and so on. White OLEDs have potential

ABSTRACT

2,6-Di(1H-benzo[d]imidazol-2-yl)pyridine (DBIP) was synthesized. The single-crystal structure of DBIP was resolved. DBIP-based OLED was fabricated. The electroluminescence for the device corresponds to a pure white emission. In addition, thermal stability, UV-vis, photoluminescence and electrochemical behaviors of DBIP were investigated as well.

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applications for backlighting display and general illumination because of their cost-effective fabrication [1-4], high light-emitting efficiency [5-8] and low-energy consumption [9-12]. Therefore, over the past decades, extensive studies have been performed on the development of white OLED [13-16]. It is not easy to fabricate a pure white OLED because of required appropriate multiemission and emissive intensity, so, there is much work for the preparations of pure white OLEDs. The previous reported white OLEDs were based on phosphors, such as iridium or platinum complexes. Although the phosphor-based OLED had high light-emitting efficiencies, they showed impure emissions. For example, Williams

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et al. reported an excimer-based white phosphorescent OLED with 81% of white rendering index ^[17]. Piao et al. demonstrated an efficient white OLED with the Commission Internationale de L'Eclairage (CIE) coordinates of (0.163, 0.325) by combining the phosphorescent and fluorescent emissions [18]. Hung et al. [16] obtained a white OLED by using a novel iridium complex as dopant, the electroluminescent spectrum gave a $CIE_{(x,y)} = (0.530,$ 0.467). However, rare pure white OLEDs based on organic small molecules were reported [19]. Organic compounds used as white emissive materials in OLED possess their advantage: purified easily via thermal sublimated [20], and very stable properties in the atmosphere. Here, we obtained a pure white OLED based on an organic small molecule DBIP due to combining the emissions of DBIP and the low-lying singlet excitons, as was leaded to only a tri-laver structure's device being structurally simpler than the white OLEDs achieved by combining the emissions of red. green. and blue [21–23].

Experimental details

Synthesis of DBIP

All solvents and chemicals (analytical grade) are commercially available, and used without further purification. 5.00 g (0.046 mol) of benzene-1,2-diamine and 3.35 g (0.02 mol) of pyridine-2,6-dicarboxylic acid were added to a 50 mL of porcelain mortar, mixed and ground for 15 min. The mixed material was transferred into a 25 mL of three-neck round-bottom flask; 10 mL of 85% (wt) phosphoric acid was added into the flask. The reaction was conducted under magnetic stirring and 190 °C for 10 h. Then, the content of the flask was allowed to cool to room temperature, and then poured into 300 mL of purified water. The resulting mixture was filtered, washed with a 30% (w/w) aqueous sodium hydroxide and distilled water until the filtrate became neutral one. The crude product was dried at 80 °C for 12 h, and purified by using thermal sublimation. A light yellow powder was obtained, vield: 65% (w/w). ¹H NMR (500 MHz, DMSO- d_6) ppm 13.01 (s, 2H), 8.36 (dd, J = 7.8, 1.9 Hz, 2H), 8.20 (td, J = 8.1, 2.1 Hz, 1H), 7.78 (s, 4H), 7.34 (s, 4H). m/z: 312.11 ([M+1]⁺), elemental analysis (EA) data for DBIP (C19H13N5) was found (calculated) % C = 73.26 (73.30), H = 4.30 (4.21), N = 22..42 (22.49).

Culture of single crystal and determination of structure

A single crystal of DBIP was obtained by slowly evaporation from methanol under ambient temperature. The single crystal with suitable dimension was chosen for X-ray diffraction testing performed on a BRUCKER SMART APEX-CCD diffractometer equipped with a graphite-monochromatic MoKa radiation ($\lambda = 0.71073$ Å) at 293(2) K. A total of 36,357 reflections were collected in the range of 1.79 < θ < 26.00° by using a ψ - ω scan mode with 3820 independent ones (Rint = 0.0244). The data was corrected by SADABS program. The parameters of the unit cell were obtained with the least-squares refinements. The structure was solved by direct methods with SHELXS-97 and refined by full-matrix least-squares method on F^2 with SHELXL-97. The final refinement gave R = 0.0514, wR = 0.1360. The crystal structure drawing and the packing diagram were acquired by diamond 3 software.

Instrumentations and measurements

¹H NMR was recorded on a Bruker DRX 500 spectrometer operating at 500 MHz, in deuterated dimethylsulfoxide solution with tetramethylsilane as reference. Mass spectrometer (MS) was obtained by the mass spectrometer of SDAPCI-MS (surface desorption atmospheric pressure chemical ionization mass spectrometry), elemental analysis (EA) was carried out on a Perkin Elmer 2400 elemental analyzer. Thermogravimetric analysis (TGA) was conducted under atmospheric conditions using a Shimadzu DT-40 system at a heating rate of 10 °C min⁻¹ from 30 to 500 °C. Absorption spectrum was obtained by using a Perkin Elmer Lambda-35 UV-vis spectrometer. Fluorescence spectra were recorded by using an FLsp920 fluorescence spectrophotometer (Xenon lamp) with 2.5 nm of slit for the measurements of excitation and emission. The cyclic voltammetry was performed by using CHI760 electrochemical workstation under nitrogen. Pt plate was used as working electrode, Pt wire as auxiliary electrode, standard calomel electrode as reference electrode and $(n-C_4H_9)_4NPF_6$ as a supporting electrolyte. Prior to the measurement, nitrogen was purged into the solution for 5 min. The cyclic voltammogram was recorded at a scan rate of 50 mV s^{-1} .

Fabrication and testing of device

The light-emitting diode was fabricated by the following procedure: ITO glass substrate was carefully pre-cleaned and treated with oxygen plasma for 5 min. Then, all the materials were successively deposited on the ITO glass substrate by thermal evaporation under a high vacuum of 1×10^{-4} Pa. The active device area was 0.15 cm². Resistance of the sheet ITO substrate was 10Ω sq⁻¹ The current density–voltage–brightness data of the electroluminescent device were obtained with a Keithley 2400 Source meter and a Keithley 2000 Source multimeter equipped with a calibrated silicon photodiode. The electroluminescent (EL) spectrum was measured with a JY SPEX CCD3000 spectrometer. All measurements were carried out under ambient temperature.

Results and discussion

Crystal structure

Fig. 1(a) is a perspective view with atomic labeling scheme. Fig. 1(b) is the crystal packing drawing. As shown in Fig. 1(a), the structure of DBIP adopts an anti-anti-configuration, *i.e.* two N–H groups and one nitrogen atom are in the same side. There is a hydrogen bond between H₂O and N–H. In addition, some hydrogen bonds between H₂O and H₂O or CH₃OH are outside of DBIP plane. The dihedral angles of plane 1 (C27,C28,C29,C30,C31,N1) and plane 2 (C20,C21,C22,C23,C24,C25), plane 1 and plane 3 (C34,C35,C36,C37,C38,C39), plane 2 and plane 3 are 8.937°, 6.628° and 2.322°, respectively. From Fig. 1(b), it can be seen that all planes of DBIP are parallel to each other, and they constitute a one-dimensional linear chain linked by the hydrogen bonds among H₂O, CH₃OH and DBIP. Interestingly, the CH₃OH acting as a bridging role converts the direction of DBIP once for each two DBIP.

Thermal stability of DBIP

As shown in the TGA figure of DBIP (see Fig. 2), the compound sublimated before reaching the decomposition temperature. The initial sublimation occurred at 320 °C, and the fastest sublimation rate appeared at 420 °C.

Photophysical and electrochemical properties

The UV-vis absorption and photoluminescent (PL) spectra of DBIP in CH₂Cl₂ at 3×10^{-6} mol L⁻¹ and in solid films were illustrated in Fig. 3. The absorption spectra of DBIP in CH₂Cl₂ show a highly structured peak at 330 nm and a weak shoulder peak at 310 nm, respectively. Both of them are attributed to π - π *



Fig. 1. Molecular structure (a) and crystal packing diagram (b) of DBIP.

transition. The optical bandgap is 3.48 eV [24] determined by the absorption edge at 356 nm in CH₂Cl₂. For the PL spectra of DBIP in CH₂Cl₂ excited at 353 nm, only one emission band can be observed with one peak at 376 nm; the PL spectra of DBIP in solid film excited at 362 nm show two emissive peaks at 384 and 474 nm, which are attributed to the exciton transitions for the single- and aggregated-molecular DBIP, respectively.

Fig. 4 gives the cyclic voltammogram (CV) curve of DBIP in CH_2Cl_2 at 1×10^{-6} mol L^{-1} , LUMO and HOMO levels of the



Fig. 2. Thermogravimetric analytical (TGA) and differential thermogravimetric (DTG) curves of DBIP.

materials [5,25] and their chemical structures. For the CV curve, in the process of anodic sweep, an oxidation peak exhibits at 1.25 V, its onset potential is 0.75 V determined by the intersection of the rising oxidative and background current's tangents. The highest occupied molecular orbital (HOMO) level is -5.60 eV based on the oxidative onset potential. According to its optical bandgap (3.48 eV), so, the lowest unoccupied molecular orbital (LUMO) level is -2.7 eV. In the process of cathodic sweep, a weak reduction peak revealed at -0.60 V.



Fig. 3. UV-vis and PL spectra of DBIP in CH₂Cl₂ and in solid film.



Fig. 4. CV curve of DBIP (a), energy-level diagram (b) and molecular structures (c) of the materials used in the OLED.



Fig. 5. EL spectra of device under several voltages (a), the CIE color coordinate and its corresponding white emission at 14 V (b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Performances of OLED

The structure of the device was ITO/MoO₃ (10 nm)/NPB (70 nm)/DBIP (20 nm)/TPBi (35 nm)/LiF (1 nm)/Al. ITO substrate was used as an anode, MoO₃ as a hole-injection layer, N⁴,N^{4'}-di(naphthalen-1-yl)-N⁴,N^{4'}-diphenylbiphenyl-4,4'-diamine (NPB) as a hole-transfer layer, 1,3,5-tris(1-phenyl-1H-benzo[d]imidazol-2-yl)benzene (TPBi) as an electron-transport/hole-block layer, LiF as an electron-injection layer, Al as a cathode. Based on this structure, the holes and electrons in device are capable of moving and recombining under forward voltage, then, showing the electroluminescence.

Fig. 5 displays the electroluminescent (EL) spectra under several voltages. The emissions correspond to some white ones, especially,

at 14 V to a pure white one. The Commission Internationale de L'Eclairage (CIE) color coordinate of the EL spectrum at 14 V is $CIE_{(x,y)} = (0.360, 0.319)$. The other CIE coordinates under 10, 12, 13 and 14 V are (0.470, 0.360), (0.450, 0.360), (0.420, 0.350) and (0.390, 0.330), respectively. The each EL spectrum shows two peaks locating at 492 and 644 nm, respectively. The former is attributed to the recombination transition of electrons and holes on the aggregated-molecular DBIP corresponding to the PL emission at 474 nm with a red-shift of 18 nm. The latter probably corresponds to the recombination transition of low-lying singlet excitons (electrons) on TPBi and holes transferring from the anode, as was analogously reported in the literature [1]. The low-lying singlet excitons on TPBi formed is because they were blocked by DBIP due to DBIP's higher LUMO level. However, the strong emission



Fig. 6. Plots of external quantum efficiency and current efficiency vs. current density.



Fig. 7. Current-voltage-luminance characteristics.

at 384 nm in the PL spectrum of DBIP in solid film disappeared in this EL spectrum, the reason is due to without single-molecular DBIP in the device. This pure white OLED was attributed to the appropriate emissions of DBIP and the excitons, *i.e.* appropriate emissive regions and emissive intensities. So, DBIP is an efficient pure-white-emission material for OLEDs.

Fig. 6 presents the curves of the external quantum efficiency (EQE) and luminous efficiency (LE) vs. current density. The maximum EQE and LE are 0.13% and 0.14 cd/A, respectively, obtained at a current density of 74.76 mA cm⁻². The peak power efficiency (PE) is 0.022 Im W^{-1} achieved at 47.29 mA cm⁻². Compared to the luminous efficiency of iridium or platinum complexes, that of this organic small molecular-based OLED was low because of maximally 25% of singlet excitons being harvested in the process of electroluminescence excitons [26], but we tentatively assume the light-emitting performances could further be improved by optimizing the device's structure, such as appropriately increasing the DBIP's and TPBi's thicknesses. Because of with the increase of DBIP's thickness, more low-lying singlet excitons are blocked by DBIP, resulting in the enhanced recombination of low-lying singlet excitons and holes on TPBi; while with the increase of TPBi's thickness, more electrons can transfer from TPBi to DBIP due to TPBi's electron-transfer nature, too resulting in the enhanced recombination of carriers on DBIP. The enhanced recombination can improve the two emission intensities and the light-emitting efficiency simultaneously, and the white OLED can still be achieved in a range of forward voltages.

Fig. 7 gives the characteristics of current density, luminance vs. voltage. The curve of current density vs. voltage shows a typical I–V characteristic for diodes under forward bias. The peak luminance and threshold voltage are 239 cd m⁻² and 9.3 V, respectively.

Conclusion

In summary, we obtained a pure white OLED based on organic small molecule DBIP. This white device can be demonstrated to maybe be attributed to the following three factors: (1) The electroluminescent spectrum of DPBI showed in a suitable emission zone with an appropriate intensity; (2) there exist the recombinationtransition emission of the low-lying singlet excitons due to being blocked by DPBI; (3) the low-lying singlet excitons can be formed on TPBi. So, DBIP can act an efficient pure-white-emission material for OLEDs. Although the luminous efficiency was low, it is able to being further enhanced by optimizing device structure.

Acknowledgments

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