Efficient single-layer electroluminescent device based on a bipolar emitting boron-containing material†

Hongyu Zhang, Cheng Huo, Jingying Zhang, Peng Zhang, Wenjing Tian and Yue Wang*

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A novel multifunctional 1,6-bis(2-hydroxyphenyl)pyridine boron bis(4-*n*-butyl-phenyl)phenyleneamine compound in which the hole-transporting (HT), electron-transporting (ET), and emitting (EM) components are integrated into a single molecule was synthesized and used as an emitting material to fabricate an efficient single-layer electroluminescent device.

The development of organic electroactive and photoactive materials has been greatly progressed due to their potential applications in optoelectronic devices, such as electroluminescent (EL) devices, photovoltaic devices, thin film transistors, and solid-state lasers.[1–17] Development of high-performance organic EL devices requires various materials that perform different roles, including hole-transporting and electron-transporting materials, as well as light-emitting materials, and typically devices commonly contain three layers of organic materials. However, fabrication of multilayer devices is often tedious, difficult and more expensive than single-layer devices. In view of this, one of the key challenges on the path of developing the next generation of high-performance OLEDs is the design and synthesis of molecules that are capable of functioning as efficient emitters as well as charge-transport materials. Therefore, materials for use in the emitting layer should meet the requirements of energy levels matching the injection and transport of both holes and electrons, and hence should desirably possess bipolar character to permit the formation of both stable cation and anion radicals. To endow a single organic material with multifunctions, which generally have to be realized by at least two kinds of molecules, is very difficult.[18–24] Stable multifunctional materials remain to be the most challenging and most sought-after materials in OLEDs.

In our previous work, we have reported white light emission EL devices which come from exciplex[25–26] by introducing mixed phenol–pyridine functional groups to tetrahedral coordinated boron compounds that exhibited electron mobility and emitting properties. To improve the performance of the boron compounds, we modified the boron molecule by attaching the triphenylamine group to the boron center by a B–C bond to produce a novel molecule. The triphenylamine group is known to have a superior hole mobility,[27–28] therefore, the proposed molecule may have bipolar transport character and thus offer good recombination sites for hole and electron charge carriers. In this paper, we focus on the structure and properties of 1,6-bis(2-hydroxyphenol)pyridinel boron bis(4-*n*-butyl-phenyl)phenyleneamine ((dppy)BTPA) by incorporating a light-emitting center, hole-transporting and electron-transporting fragments into one molecule. This new compound is stable with respect to sublimation and thus is suitable for vacuum deposition in OLEDs.

The pyridine–phenol ligand H_2dppy was synthesized according to the literature procedure[26] and the boron compound was prepared following the synthetic route shown in Scheme S1(see ESI†).‡ The X-ray diffraction study shows that compound (dppy)BTPA in the solid state has a tetrahedral structure,§ typical of boron compounds (Fig. 1). The conformation of the dppy moiety is slightly distorted from planarity with inter-ring torsion angles of 10.5 and 16.7° between the pyridyl ring and the phenolate rings, while the triphenylamine moiety is greatly distorted from planarity with dihedral angles 68.1, 68.9 and 76.37° between the three phenyl rings. Therefore, the introduction of the bulky triphenylamine group decreases the symmetry of the compound and the resultant compound (dppy)BTPA has a non-planar molecular structure, which can easily form uniform thin films. The crystal packing diagram given in Fig. 2 shows that in the crystal (dppy)BTPA molecules display a molecular chain arrangement. Moreover, the compound is observed to self-assemble into a supramolecular zig-zag motif by intermolecular hydrogen-bonding interaction. The distance of C–H···O hydrogen bond is 2.568 Å with an angle of 157.4°. The special 1-dimensional feature of the (dppy)BTPA molecules in solid state may enhance the charge-transport ability.

Fig. 3 shows the cyclic voltammograms of (dppy)BTPA. The compound showed reversible redox properties, exhibiting one

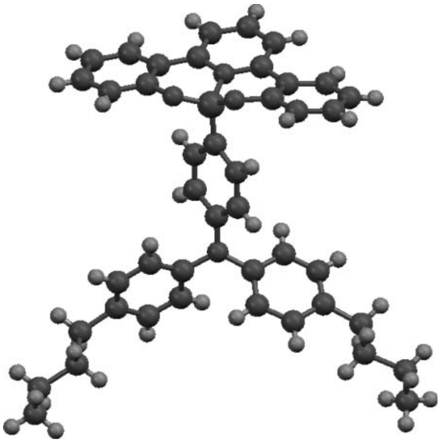

Fig. 1 The molecular structure of (dppy)BTPA.

Key Laboratory for Supramolecular Structure and Materials of Ministry of Education, College of Chemistry, Jilin University, Changchun, 130012, P. R. China. E-mail: yuewang@jlu.edu.cn;
Fax: 86-431-5193421; Tel: 86-431-5168484

† Electronic supplementary information (ESI) available: details of synthesis and Scheme S1. See DOI: 10.1039/b513918j

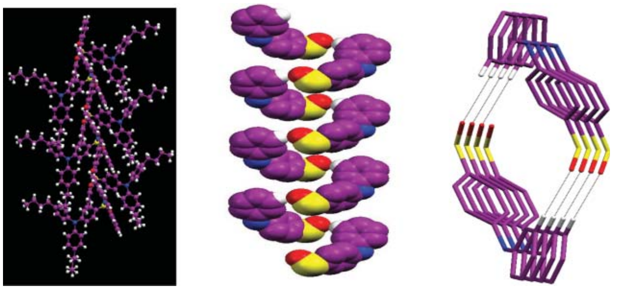

Fig. 2 Molecular chain (left); zig-zag motif of (dppy)BTPA along side (middle) and axis (right) directions. Purple, C; yellow, B; red, O; blue, N; white, H; H-bond contacts, broken black lines. For middle and right: most of the atoms are omitted for clarity, and the only H atoms are those for H-bond contacts.

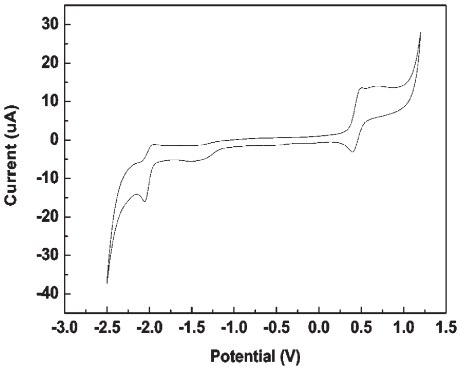

Fig. 3 Cyclic voltammogram of (dppy)BTPA in DMF at a scan rate of 100 mV s^{-1}.

anodic and cathodic wave on oxidation and reduction, respectively. Based on the electrochemical measurement the HOMO and LUMO energy levels of (dppy)BTPA were calculated to be -5.3 eV and -2.9 eV, respectively. The LUMO level of (dppy)BTPA is comparable to that of tri(8-hydroxyquinolino)-aluminium (Alq_3 -3.0 eV),[29] that was demonstrated to be a good electron injection and transport material. Simultaneously, the HOMO level of (dppy)BTPA is close to that of *N*,*N*′-diphenyl-*N*,*N*′-bis(1-naphthyl)-(1,1′-biphenyl)-4,4-diamine (NPB, -5.4 eV),[29] which was often used as a hole injection and transport material. A compound that can stabilize the formation of both cation and anion radicals is probably promising bipolar (electron-transport (*n*-type) and hole-transport (*p*-type)) material and suggested to be beneficial to OLEDs.[30–31] Therefore, we anticipated that (dppy)BTPA may be able to transport holes and electrons in OLEDs. The energy levels of electrodes and organic material are shown in Fig. 4.

The energy level alignments of (dppy)BTPA enlighten us to fabricate a single-layer device with structure of [ITO/(dppy)BTPA(100 nm)/LiF(1 nm)/Al(200 nm)] (device **1**).¶ This single-layer device reached a maximum efficiency of 5.2 cd A^{-1} (3.6 lm W^{-1}) and a maximum brightness of 2654 cd m^{-2}. To our knowledge, the efficiency is the highest value for small molecule single-layer EL devices that have been achieved until now. The single active layer device reported previously displayed a maximum efficiency of 1.2 cd A^{-1} and a maximum brightness of 1065 cd m^{-2}.[32] The EL emission of device **1** is identical to the photoluminescent (PL) spectrum of (dppy)BTPA thin film (Fig. 5). The quite low turn-on voltage of 3.8 V (defined as the voltage required to give a luminance of 1 cd m^{-2}) and low operation voltages suggest that (dppy)BTPA function well for charge transport. The results demonstrate that (dppy)BTPA is capable of functioning as a hole-transporting layer (HTL), an electron-transporting layer (ETL) and an emitting layer (EML) in EL device, consistent to the results of the cyclic voltammogram. The yellow light emission from the single-layer device is stable and its EL spectra are insensitive to driving voltage. The typical current–light–voltage (*I–L–V*) characteristics of device **1** is inset in Fig. 5. We have not yet studied the lifetime of the device, but the unencapsulated device was stable, and the emission color and the *I–L–V* did not change during the measurement of EL data in air.

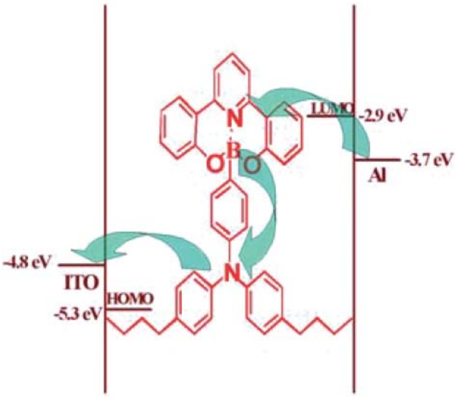

Fig. 4 Diagram showing the energy level of (dppy)BTPA in the single-layer device.

In order to compare, two double-layer devices and one three-layer device were fabricated. The device structures are [ITO/NPB(50 nm)/(dppy)BTPA(50 nm)/LiF(1 nm)/Al(200 nm)] (device **2**), [ITO/(dppy)BTPA(50 nm)/Alq_3(50 nm)/LiF(1 nm)/Al(200 nm)] (device **3**), and [ITO/NPB(50 nm)/(dppy)BTPA(40 nm)/Alq_3(10 nm)/LiF(1 nm)/Al(200 nm)] (device **4**). Device **2** with NPB as HTL and (dppy)BTPA as EML and ETL exhibits the maximum luminescence of 800 cd m^{-2} at 13.5 V, and the maximum efficiency of 1.5 cd A^{-1} (at 7 V). Device **3** with Alq_3 as ETL produces a green EL emission with a spectrum typical of

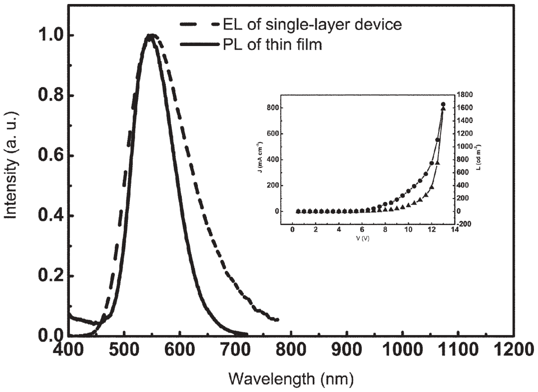

Fig. 5 EL and PL spectra for [ITO/(dppy)BTPA/LiF/Al] and (dppy)BTPA thin films, respectively; the inset shows the *I–V* (●) and *L–V* (■) characteristics for the device.

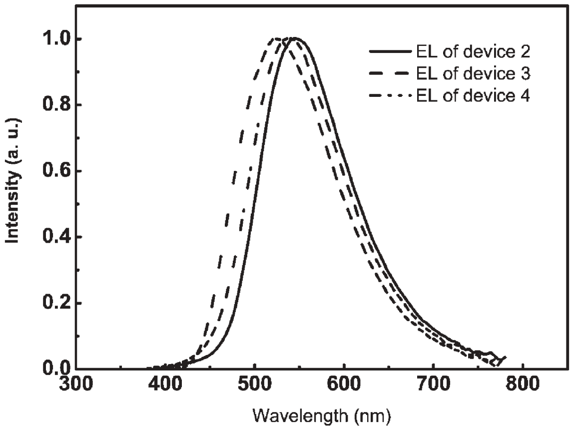

Fig. 6 EL spectra of devices **2–4**.

Alq_3. This indicates that the emission takes place in the Alq_3 layer. For device **3**, the maximum luminescence is 730 cd m^{-2} at 13.0 V, and the maximum efficiency is 1.1 cd A^{-1} (at 8.0 V) with turn-on voltage 5.0 V. Device **4** is a typical three-layer device which exhibits a green-yellow EL light emission, suggesting that there is a contribution from the Alq_3 emission in device **4**. The EL spectra of devices **2–4** are shown in Fig. 6. Device **4** shows the maximum brightness of 2773 cd m^{-2} at 12.0 V and the maximum efficiency of 6.8 cd A^{-1} (4.3 lm W^{-1}). The single-layer device **1** displays higher efficiency and brightness than the double-layer devices **2–3**. The EL performance of device **1** is similar to the three-layer device **4**. Above results demonstrated that (dppy)BTPA really has multifunctional characteristics.

In conclusion, a novel boron compound (dppy)BTPA combining a light-emitting center, hole- and electron-transporting groups in one molecule, was synthesized and demonstrated to be a promising yellow-light emitting material in an EL device. The incorporation of electron-rich TPA and electron-deficient phenol–pyridine–boron groups leads to the formation of bipolar material. Efficient single-layer and non-doping EL device based on (dppy)BTPA is constructed. Although the EL performance of the single layer device is lower than that of multilayer devices, the device structure fabrication processes are dramatically simplified.[33]

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Notes and references

‡ Mass, ^1H NMR spectroscopic and elemental analysis: (dppy)BTPA: EIMS: *m/z* 628. $\delta_H(CDCl_3$, 500 MHz) 8.371 (t, J = 8.0 Hz, 1H), 8.317 (d, J = 7.0Hz, 2H), 8.040 (d, J = 6.5 Hz, 4H), 7.398 (m, 4H), 7.203–7.143 (m, 4H), 7.035–6.992 (m, 4H), 6.961–6.929 (m, 4H), 2.454 (m, J = 7.0 Hz, 4H), 1.478 (m, J = 4.0 Hz, 4H), 0.867 (t, J = 7.5 Hz, 6H). Anal. Calcd. for $C_{43}H_{41}BN_2O_2$: C, 82.16; H, 6.57; N, 4.46. Found: C, 82.05; H, 6.85; N, 4.29%.

§ *Crystal data:* (dppy)BTPA: $C_{43}H_{41}BN_2O_2$, Mr = 629, monoclinic, space group $P2_1/c$, a = 16.815(3), b = 10.182(2), c = 20.772(4) Å, β = 99.93(3)°, V = 3503.3(2) $Å^3$, Z = 4, Dc = 1.192 g cm^{-3}, $F(000)$ = 1336. 8315 reflections measured, 7814 unique (R_{int} = 0.089). Structure diffraction intensities were collected on a Rigaku RAXIS-PRID diffractometer using the ω-scan technique with graphite-monochromated MoKα (γ = 0.071073 Å) ratio. The structure was solved with direct methods and refined with a full-matrix least-squares technique, using the SHELXIL programs. Hydrogen atoms were assigned isotropic displacement coefficients. CCDC 285222. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b513918j

¶ The device of [ITO/(dppy)BTPA/LiF/Al] was prepared in vacuum at a pressure of 5×10^{-6} Torr, and the organic materials were deposited onto an indium–tin–oxide at a deposition rate of 1–2 Å s^{-1}. Aluminium electrode was thermally evaporated onto the organic surface resulting in active areas of $\sim$5 mm^2. The thickness of the organic material and the cathode layers were controlled using a quartz crystal thickness monitor.

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