Cyclic arylamines functioning as advanced hole-transporting and emitting materials

Li Long [a], Minyan Zhang [a], Shihua Xu [b], Xuehua Zhou [b], Xicun Gao [b,*], Yuzhu Shang [a], Bin Wei [a,*]

[a] Key Laboratory of Advanced Display and System Application, Ministry of Education, Shanghai University, 149 Yanchang Road, Shanghai 200072, PR China
[b] Department of Chemistry, School of Science, Nanchang University, 999 Xue-Fu Road, Hong-Gu-Tan New District, Nanchang 330031, PR China

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ABSTRACT

We have developed two kinds of cyclic arylamines functioning as hole-transporting and light-emitting materials of organic light emitting diodes (OLEDs), respectively. The hole-transporting cyclic arylamine (C1)-based device exhibited an improved maximum luminance efficiency of 4.21 cd/A, utilizing a single light-emitting layer of tris(8-hydroxyquinolinato) aluminum. While the maximum luminance efficiencies for N,N′-bis-(naphthyl)-N,N′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB) and 4,4′,4′′-tris-N-naphthyl-N-phenylamino-triphenylamine/NPB-based devices were 2.28 and 3.02 cd/A, respectively. In addition, a non-doped deep-blue (448 nm) light-emitting device was obtained, employing cyclic arylamine (C2) as emission layer. And the exciplex formation occurred at C1/C2 interface or in the emission layer of C2 doped C1, which leaded to a wide EL emission. Furthermore, we have developed a very simple bluish-white OLED using C2 (5 wt.%) doped C1, which showed particularly wide full width at half maximum of 135 nm.

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1. Introduction

Organic light-emitting diodes (OLEDs) have attracted much attention due to various advantages such as excellent image quality, light weight, easy manufacturability, low cost, and large-area extendibility [1–4]. The future potential application for OLEDs will be focused on the larger size displays, flexible displays and lighting [5,6]. However, some of the critical factors such as stability, production cost and deep-blue-emitting materials/devices have not been fully resolved yet, hindering the large-scale OLEDs' marketing.

The morphological instability of the hole-transporting layer (HTL) affects the stability of devices, especially at higher temperatures. The joule heat generated in the HTL may accelerate the crystallization and lead to reduce of the device's lifetime. From the synthetic organic chemistry point of view, this problem can be solved perfectly using hole-transporting materials (HTMs) with high glass-transition temperature (T_g) or inserting a hole-injection layer (HIL) between indium-tin-oxide (ITO) anode and HTL. Typical small-molecule HTMs such as N,N′-bis-(naphthyl)-N,N′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB), 4,4′,4′′-tris-N-naphthyl-N-phenylamino-triphenylamine (2T-NATA) have appreciable hole-transporting properties because

of their relatively shallow highest-occupied-molecular-orbital (HOMO) levels. But they have some disadvantages such as low T_g and low hole-mobility which are responsible for lifetime and efficiency of devices. For example, the T_g and the hole-mobility for widely used hole-transporting material, NPB are 98 °C and 5.1×10^{-4} cm^2 V^{-1} s^{-1}, respectively [7]. The hole-transporting materials with high T_g are highly desirable for devices operated at high current densities with high luminance.

Organic materials, especially primary RGB emitting-materials, are also crucial to development of white OLEDs [8,9]. To date, a growing number of OLED materials emitting colorful light have been synthesized. However, blue OLEDs have not exhibited desirable performance when compared to the green or red counterparts because the intrinsically wide band gap (E_g) makes it hard for charges to inject into blue-emitting materials. Besides, efficient and long-lifetime pure-blue or deep-blue OLEDs with desirable Commission Internationale de L'Eclairage (CIE) are relatively rare. Furthermore, the deep-blue OLEDs can improve the color rending index or color saturation when applied to the lighting, full-color display and color conversion technologies.

In general, phosphorescence-based OLEDs (PHOLEDs) are more favorable than fluorescence-based OLEDs (FLOLEDs) for having a three times higher limit of theoretical electroluminescence (EL) efficiency. However, blue fluorescent materials will revive because some problems have been found in phosphorescent materials for white lighting, such as short operational lifetimes, high material cost and so on. More critically, true blue PHOLEDs always have low external quantum efficiency (η_{EXT}) and exhibit serious
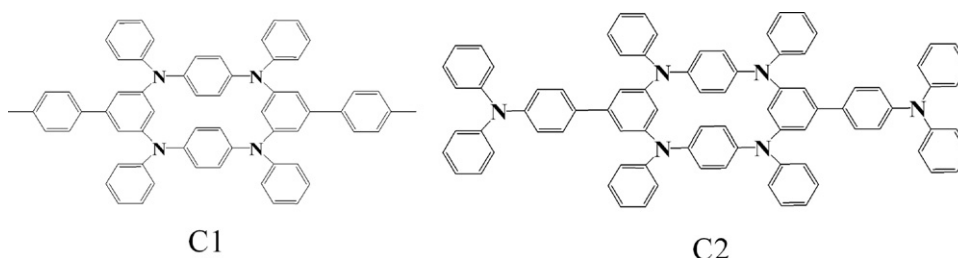

Fig. 1. The molecular structure of cyclic arylamines.

efficiency roll-off at high elevated driving current density due to triplet–triplet annihilation. Based on the above summary, blue FLOLEDs have more advantages over PHOLEDs [10–15].

In this paper, we reported the EL properties of two novel cyclic arylamines. One of them is C1 with high T_g (395 °C), which not only can function as hole-transporting material, but also as a host material. The other is cyclic arylamine (C2) functioning as a guest for deep-blue light-emitting material.

2. Experimental details

The synthesis of cyclic arylamines, C1 and C2, were performed through palladium catalyzed reaction of the doubly brominated benzene derivative and N,N′-diphenyl-p-phenylenediamine [16–20], and their molecular structures are shown in Fig. 1. For C1, yellow solid, m.p. 416 °C. ^{1}H NMR (CDCl3, 400 MHz), 6.80–7.31 (m, 42H); 2.33 (s, 6H). Anal. Calc. for $C_{62}H_{48}N_4$ (%): C, 87.70; H, 5.70; N, 6.60. Found: C, 87.63; H, 5.56; N, 6.75. ESI-MS: *m/z* 848.29 [M]+. For C2, yellow solid, m.p. 425–427 °C. ^{1}H NMR (CDCl3, 400 MHz), 6.80–7.26 (m, 62H). Anal. Calc. for $C_{84}H_{62}N_6$ (%): C, 87.32; H, 5.41; N, 7.27. Found: C, 86.92; H, 5.57; N, 7.13. ESI-MS: *m/z* 1155.51 [M+H]+.

Cyclic voltammograms were recorded by an Autolab Potentiostat 30 with a glass-carbon electrode in CH_2Cl_2 solutions containing ~0.0005 M of the compound and 0.10 M (n-Bu)4NBF4 against Ag/AgCl with ferrocene (Fc) as the internal standard. The oxidation potentials for C1 and C2 are 0.68 eV and 0.70 eV, respectively, and their calculated HOMO levels are 5.40 eV and 5.42 eV, respectively.

The excitation (E_{xc}) and photoluminescence (PL) spectra of C1 and C2 were recorded using a Hitachi F-4500 fluorescence spectrophotometer. The devices were fabricated by conventional vacuum deposition of the organic layers and cathode onto an ITO (15 Ω/sheet, 150 nm) coated glass substrate under a base pressure lower than 2×10^{-4} Torr. The substrates were successively cleaned in detergent, de-ionized water, acetone, and isopropanol. Immediately prior to loading into a custom-made high vacuum thermal evaporation chamber (with a base pressure of ~10^{-4} Torr), the substrates were exposed to a UV-ozone environment for 15 min. The typical deposition rates were 0.6 Å/s, 0.1 Å/s and 5.0 Å/s for organic materials, lithium fluoride (LiF), aluminum (Al) and aurum (Au), respectively.

We have first fabricated the C1-based hole-only device for studying hole-transporting ability of the cyclic arylamines. The hole-only devices were fabricated by depositing single organic material as hole-transporting layer and Au/Al as the cathode. Furthermore, we have fabricated three devices with a single emission layer of tris(8-hydroxyquinolinato) aluminum (Alq3) and different hole-transporting materials. Their structures were ITO/HTL (50 nm)/Alq3 (40 nm)/LiF (0.3 nm)/Al (100 nm). The HTL were NPB, 2T-NATA (30 nm)/NPB (20 nm), and C1, which were represented as Devices, A-1, A-2, A-3, respectively.

To investigate light-emitting properties of another cyclic arylamine material (C2), we fabricated a non-doped OLED (Device

B-1) whose structure was ITO/C1 (40 nm)/C2 (20 nm)/1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBi) (30 nm)/LiF (0.3 nm)/Al (100 nm), where C1, C2 and TPBi were hole-transporting layer, light-emitting layer and electron-transporting layer, respectively. However, to avoid concentration quenching and enhance energy harvesting, fluorescent materials are often doped or solved in host materials. Thus, a doped OLED (Device B-2) with a structure ITO/C1 (40 nm)/C2 (5 wt.%) doped in C1(20 nm)/TPBi (30 nm)/LiF (0.3 nm)/Al (100 nm) was fabricated.

Finally, two-peaks white OLEDs, Devices C-1 and C-2, were fabricated using rubrene doped C2 as EML, in which doping concentration were 3.0 wt.% for Device C-1 and 0.5 wt.% for Device C-2, respectively. Their structures were ITO/C1 (40 nm)/EML (20 nm)/TPBi (30 nm)/LiF (0.3 nm)/Al (100 nm).

The active area of the devices defined by the overlap between the electrodes was 4 mm² in all cases. Current density–voltage–luminance (*J–V–L*) characteristics of the OLEDs were measured using a Hewlett-Packard 4140B source measure unit and a PR-650 luminance color meter. The luminance was calibrated using a Minolta LS-100 luminance meter.

3. Results and discussion

3.1. Photophysical properties of host and guest materials

The appropriate host and guest materials are very important for realizing efficient energy transfer between the host and guest and for facilitating the carrier transport inside OLEDs [21]. The excitation and PL spectra of C1 and C2 thin films (60 nm) are shown in Fig. 2. The PL peak wavelengths of the C1 and the C2 films are 438 nm and 442 nm, respectively. The spectra overlap between the PL band of the C1 film and the excitation band of the C2 film was small, resulting in the insufficient energy transfer between C1 and C2. In addition, there exists a large spectra overlap between the PL band of the C2 film and the excitation band of the rubrene, indicating that C2 can be energetically transferred to rubrene by Forster energy transfer (Coulomb interaction) [22–25]. Therefore, an efficient white emission can be produced from OLED with rubrene doped C2 being as an emission layer.

3.2. Hole-transporting property

As shown in the inset of Fig. 3, the hole-only devices of ITO/NPB or C1 (60 nm)/Au/Al were fabricated for the evaluation of the hole-injection capability [26] in terms of current density of NPB and C1. Fig. 3 shows that C1 exhibits significantly higher current density than NPB. In general, current density of hole-only devices is determined by several factors, such as the hole-injection barrier between the electrode and organic layer, the difference of the HOMO energy levels between the adjacent organic layers and hole-mobility of each organic layer [10]. The HOMO energy level of C1 (5.40 eV) is shallower than that of NPB (5.60 eV), therefore, the hole injection from ITO into C1 was relatively smoother than that into NPB.