Improved Performance of Organic Light-emitting Diodes with a New Hole-transporting Material

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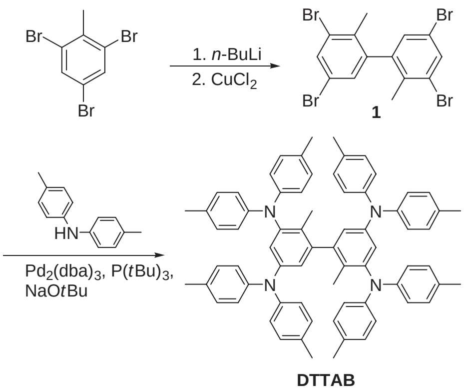
A new compound, 2,2′-dimethyl-3,3′,5,5′-tetrakis(*p*-tolyldiamino)biphenyl (DTTAB), was synthesized and investigated as a hole-transporting material for organic light-emitting diodes. The luminous efficiency of electroluminescent device was improved by using DTTAB instead of NPB at lower driving voltage, suggesting that the DTTAB layer can efficiently accept holes from the hole-injecting layer and transport holes into an adjacent emitting layer.

Since the first report of multilayered organic light-emitting diodes (OLEDs), many studies focused on improving device efficiency and enhancing the durability of OLEDs.[1] Particularly hole-transporting material is one of the significant factors of the device performance. For the hole-transporting layer, high thermal stability, especially high T_g of above 100 °C, good hole-transport ability, excellent film formability are essentially needed. A number of hole-transporting materials based on aromatic amine structure have been reported so far. Because of their good solid film-forming capabilities, various triarylamine derivatives have been utilized as hole-transporting materials.[2–4] Recently, considerable efforts have been devoted to the development of new amorphous triarylamines possessing high morphologic stability.[5–10] Certain tetraaminobiphenyl derivatives are known to have photoconductive properties. They have been used for electrophotographic applications.[11] Despite the relatively good charge-transporting properties of tetraaminobiphenyls now known, no hole-transporting properties for OLEDs have yet been reported. In this study, we synthesized a novel amorphous compound, 2,2′-dimethyl-3,3′,5,5′-tetrakis(*p*-tolyldiamino)biphenyl (DTTAB) as a hole-transporting materials with higher glass-transition temperature. We report here the preparation and properties of DTTAB and the application for the EL device.



Scheme 1. Molecular structure and synthetic procedure of DTTAB.

According to the literature, tetraaminobiphenyls can be obtained from tetrahydroxybiphenyl, primary arylamine, and aryl halide.[11] In this case, the coupling reaction of the arylhydroxybiphenyl and arylamines was not so convenient. We have found the more efficient amination reaction by using palladium catalyst. The general synthetic routes to tetraaminobiphenyls are outlined in Scheme 1. For the amination reaction, 2,2′-dimethyl-3,3′,5,5′-tetrabromobiphenyl (**1**) was synthesized by the lithiation of 2,4,6-tribromotoluene following oxidative coupling.[12] DTTAB was successfully prepared from **1** and di-*p*-tolylamine in toluene in the presence of $Pd_2(dba)_3/P(t\text{-}Bu)_3/NaOt\text{-}Bu$ at 110 °C.[13] The palladium catalyst is very effective, giving the corresponding tetraaminobiphenyl product in good yield with only a low amount of the palladium catalyst. The thermal stability data of 2,2′-dimethyl-3,3′5,5′-tetraaminobiphenyl (DTTAB) was investigated by differential scanning calorimetry and thermogravimetric analysis: The results were summarized in Table 1 with the most well-known hole-transporting materials TPD and NPB for comparison.

Table 1. Physical properties of 2,2′-dimethyl-3,3′,5,5′-tetraaminobiphenyl derivative DTTAB and common hole-transporting materials

	HOMO[a] /eV	LUMO[b] /eV	$\lambda_{\max}$[c] /nm	T_d[d] /°C	T_g[e] /°C	T_m[e] /°C
DTTAB	5.35	2.11	228, 302	364	114	272
NPB	5.40	2.30	271, 342	479	100	265
TPD	5.40	2.30	311, 353	382	60	175

[a] Determined by ultraviolet photoelectron spectroscopy (UPS). [b] Calculated based on the HOMO level and the lowest-energy absorption edge of the UV spectrum. [c] Measured in CH_2Cl_2 solution. [d] Obtained from TGA measurement. [e] Obtained from DSC measurement.

As shown in Table 1, DTTAB has higher value of T_g relative to its biphenyl analogues, TPD and NPB, proofing the high morphologic stability of the amorphous phase in a deposited film, which is a prerequisite for the application in organic light-emitting diodes. The HOMO and LUMO levels of DTTAB are also listed in Table 1. The HOMO was determined using a photoelectron spectrometer, while LUMO was calculated based on the HOMO energy level and the lowest-energy absorption edge of the UV absorption spectrum.[14] The HOMO and LUMO levels of DTTAB were measured at 5.35 and 2.11 eV. This value is comparable to that of NPB.

To investigate hole-transporting ability of DTTAB, two types of hole-transproting layer were examined (Figure 1). We fabricated device II with DTTAB as a hole-transporting layer for green device with tris(8-quinolinolato)aluminum (Alq_3) doped with 1% of Coumarin 545T as green emitting layer. A ref-

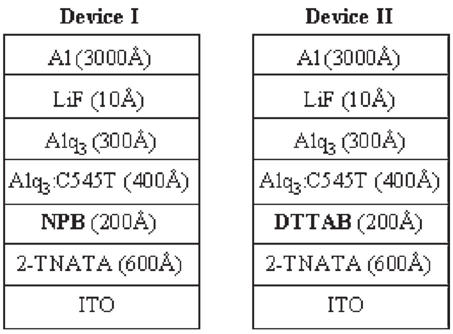


Figure 1. Structures of EL devices used in this study.

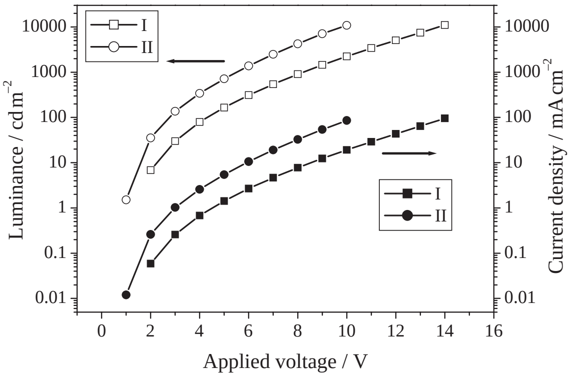


Figure 2. The EL characteristics of the two devices; current density vs. voltage of the device I (■), current density vs. voltage of the device II (●), luminance vs. voltage of the device I (□), luminance vs. voltage of the device II (○).

erence device I composed of NPB as a hole-transporting material with the same thickness was also constructed for comparison.

Figure 2 shows the luminance and the current density characteristics in the two devices. The device I turns on at a voltage of 3 V. On the other hand, the device II has a lower threshold voltage of 2.5 V. The device II with DTTAB as a hole-transporting material showed remarkable luminance and current density performance compared to the reference device I. The luminance and the current density of the device II are about four times higher than those of the device I. The luminance and the current density of the device II, 4247 cd/m^2 and 32.77 mA/cm^2 at 6 V, were much higher than those of the device I, 906 cd/m^2 and 7.77 mA/cm^2 at the same voltage. The external quantum efficiency (EQE) values of devices I and II were 3.31 and 3.88% at 50 mA/cm^2, respectively. The luminance of the device II was higher than that of the device I at lower voltage. Thus, the DTTAB hole-transporting layer on the OLED enhances the intensity of luminance. Figure 2 shows that the device I needs higher electric power than the device II. In other words, it is thought that the hole-transporting ability of DTTAB is superior to that of NPB. As we mentioned before, this high performance of the device II with DTTAB can be attributed to the higher T_g of DTTAB compared to that of NPB and the stable morphology of the deposited film.

Figure 3 shows the power efficiency–current density characteristics of the DTTAB device II and the NPB standard device I. The power efficiency for the device II is higher than that of the standard device I within the measured current density, indicating more effective recombination at the emitting layer of device II. DTTAB is expected to be more thermally stable on the basis of its higher T_g value. Further investigation of the device stabilities of the device I and device II are in progress.

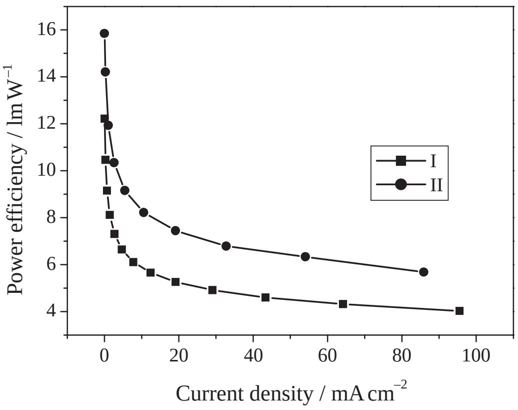


Figure 3. The Power efficiency–current density characteristics of the two devices; device I (■), device II (●).

In summary, we designed and prepared 2,2′-dimethyl-3,3′,5,5′-tetrakis(*p*-tolyldiamino)biphenyl (DTTAB) as a hole-transporting material. The device of fluorescent C-545T-doped green OLED by using DTTAB as the hole-transporting layer has much better overall EL performance than the standard device with NPB layer. DTTAB was found to be good candidate for highly efficient OLEDs as a hole-transporting material.

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