Novel Starburst Molecule as a Hole Injecting and Transporting Material for Organic Light-Emitting Devices

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We report the synthesis of a novel starburst molecule, 4,4′,4′′-tris(*N*-3-methylphenyl-*N*-(9-ethylcarbazyl-3)amino) triphenylamine (PCATA), and its application in organic light-emitting devices (OLEDs). The introduction of PCATA into the standard NPB/Alq_3 OLED as the hole injecting and transporting layer dramatically enhanced the device efficiency to 5.7 cd/A and 2.2 lm/W, which are a factor of 2 higher than those of the standard OLED without the PCATA layer. The performance enhancement is attributed to a better balance of hole and electron injection in the PCATA-added OLED.

Introduction

Organic light-emitting devices (OLEDs) have the potential to achieve low-cost, full-color flat panel displays due to their merits of high brightness, easy fabrication, and the availability of a wide range of emission colors.[1,2] The past decade has seen great progress in both device fabrication techniques and materials development.[3] However, further improvement in both the efficiency and durability of OLEDs is still necessary. In the prototypical NPB/Alq_3 double-layer OLED, in which NPB stands for 4,4′-bis(1-naphthylphenylamino)-biphenyl and Alq_3 stands for tris(8-hydroxyquinolinato)-aluminum, it has been found that the cationic Alq_3 species are responsible for the low efficiency and long-term intrinsic degradation of the device.[4] The cationic Alq_3 is primarily formed at the NPB/Alq_3 interface because the hole drift mobility in the NPB layer is orders of magnitude faster than the electron transport mobility in Alq_3. Therefore, it is essential to balance the hole and electron injected into the emitting layer of the OLEDs to improve the electroluminescence (EL) efficiency and durability and to reduce intrinsic degradation. Besides improving the electron injection by inserting an electron injecting layer such as LiF[5−6] at the cathode−electron transporting layer interface and increasing the electron transporting mobility by developing novel electron-transporting materials such as $DAlq_3$,[7] there are at present two general approaches in terms of hole injection and transport to balance the charges injected into emitting layer in OLEDs. One is to reduce the hole drift mobility in the hole transporting layer (HTL) by doping the HTL with hole-trapping material,[8] which inevitably complicates the device fabrication techniques. Another is to hold back the hole injection at the ITO/HTL interface by inserting a buffer layer at the hole-injecting contact.[9] However, due to the insulating nature of most buffer layers, the usage of hole buffer layers usually increases the operating voltage of the device and correspondingly leads to low power efficiency.[10] Since electron transporting materials with higher electron transport mobility are not available at present to match the existing hole transporting materials, development of novel hole transporting materials with moderate hole drift mobility to match the present electron transporting materials and with a low enough ionization potential (I_p) to guarantee efficient hole injection at the ITO/HTL interface should be a good alternative to balance the hole and electron, and thus reduce the intrinsic degradation and improve the EL efficiency of OLEDs.

Meanwhile, it is generally accepted that a morphologically stable amorphous organic layer, especially HTL, will lead to a longer lasting OLED. Crystallization or melting of amorphous organic materials caused by Joule heat or a short-circuit current due to pinholes in thin films are considered common causes of device degradation.[11] In principle, all the organic layers forming the EL devices should have glass transition temperatures (T_g) as high as possible. The individual layer that has the lowest T_g is likely to limit the thermal stability of the OLED. Furthermore, all the organic materials, especially the charge transporting materials, of OLEDs should have high transparency to visible light emitted from the device to ensure a high light collecting efficiency.[12] Therefore, a morphologically stable amorphous HTL having

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(1) Tang, C. W.; Vanslyke, S. A. *Appl. Phys. Lett*. **1987**, *51*, 913.
(2) Shen, Z.; Burrows, P. E.; Bulović, V.; Forrest, S. R.; Thompson, M. E. *Science*, **1997**, *276*, 2009.
(3) Chen, C. H.; Shi, J.; Tang, C. W. *Macromol. Symp*. **1997**, *125*, 1.
(4) Aziz, H.; Popovic, Z. D.; Hu, N.-X.; Hor, A.-M.; Xu, G. *Science* **1999**, *283*, 1900.
(5) Hung, L. S.; Tang, C. W.; Mason, M. G. *Appl. Phys. Lett.* **1997**, *70*, 152.
(6) Kido, J.; Iizumi, Y. *Appl. Phys. Lett.* **1998**, *73*, 2721.
(7) Ma, D. G.; Wang, G.; Hu, Y. F.; Zhang, Y. G.; Wang, L. X.; Jing, X. B.; Wang, F. S.; Lee, C. S.; Lee, S. T. *Appl. Phys. Lett.* **2003**, *82*, 1296.
(8) Aziz, H.; Popovic, Z. *Appl. Phys. Lett*. **2002**, *80*, 2180.
(9) Vanslyke, S. A.; Chen, C. H.; Tang, C. W. *Appl. Phys. Lett*. **1996**, *69*, 2160.
(10) Popovic, Z. D.; Aziz, H. *IEEE J. Sel. Top. Quantum Electron*. **2002**, *8*, 362.
(11) Kuwabara, Y.; Ogawa, H.; Inada, H.; Nona, N.; Shirota, Y. *Adv. Mater*. **1994**, *6*, 667.

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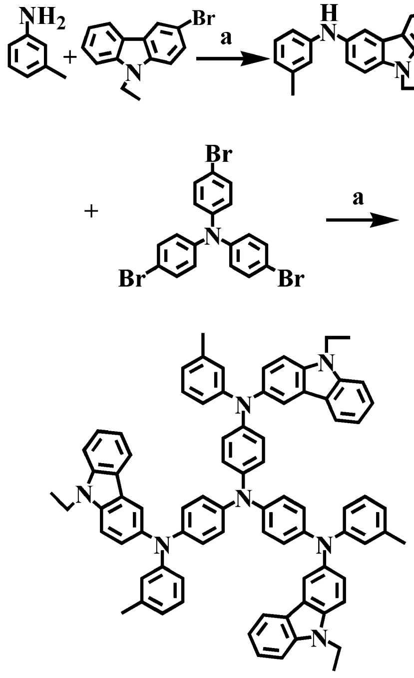
a moderate hole drift mobility to match the present electron transport material, a properly low I_p to ensure efficient hole injection, and high transparency to visible light and good film property is desirable for realizing highly efficient and stable OLEDs. In this paper, we report a novel starburst amorphous molecule, 4,4′,4″-tris(*N*-3-methylphenyl-*N*-(9-ethylcarbazyl-3)amino) triphenylamine (PCATA), and its application as an excellent hole injecting and transporting material in an Alq$_3$-emitting OLED. The PCATA device exhibited much enhanced brightness and efficiency over a similar device without the PCATA layer. The mechanism for the enhancement in brightness is discussed.

Scheme 1. Molecular structure and synthetic procedure of PCATA



PCATA

a : Pd(AcO)$_2$, DPPF, t-BuONa, toluene, 100 ^{0}C

Experimental Section

Materials and Instruments. All the reagents and solvents used for the synthesis of PCATA were purchased from Aldrich and Acros companies and used without further purification. Alq$_3$ and NPB used for EL devices fabrication were synthesized in our laboratory and purified by train sublimation.

^{1}H NMR spectra were recorded on a Bruker DPX-400 spectrometer (400 MHz). The infrared (IR) spectra were measured as KBr pellets on a BIO-RAD FTS-165 FT-IR spectrometer. Elemental analyses (EA) were performed by a Flash EA 1112 method. The photoluminescence and absorption spectra of PCATA in solution and in films were recorded with a Perkin-Elmer LS50 fluorescence spectrometer and a Perkin-Elmer Lambda 2S UV−Visible spectraphotometer, respectively. The differential scanning calorimeter (DSC) measurement and thermogravimetric analysis (TGA) were performed on Perkin-Elmer DSC 7 and Dupont Instruments 983 Dynamic Mechanical Analyzer, respectively.

Preparation of PCATA. The molecular structure and the synthetic procedure of PCATA are shown in Scheme 1. It can be prepared by two-step palladium-catalyzed N-arylation reactions along with the procedure in the scheme.

N-(9-Ethylcarbazyl-3)-2-methylaniline. A three-necked flask was charged with 9-ethyl-3-bromocarbazole (3.3 g, 12 mmol), *m*-toluidine (1.54 g, 14.4 mmol), Pd(AcO)2 (53.76 mg, 0.24 mmol), DPPF (159 mg, 0.288 mmol), *t*-BuONa (1.728 g, 18 mmol), and dry toluene (45 mL) and heated to 100 °C under nitrogen current for 10 h. The solvent was evaporated under vacuum and the dark residue was isolated by column chromatography on silica gel using a hexane/ethyl acetate mixture (15:1) as eluent to yield 3.3 g (92%) of the title compound as a colorless crystal. MS: *m*/*z* 300 ([M]$^+$). Anal. Calcd. for $C_{21}H_{20}N_2$: C, 84; H, 6.67; N, 9.33%. Found: C, 83.96; H, 6.70; N, 9.31%.

4,4′,4″-Tris(N-3-methylphenyl-N-(9-ethylcarbazyl-3)amino) Triphenylamine (PCATA). The synthetic method is similar to that for the above intermediate, except that the molecular ratio of 4,4′,4″-tribromophenyamine to the above intermediate is 1:3.3 and the mixed reactants were heated for 24 h to guarantee the complete reaction of the three active sites in the molecule of 4,4′,4″-tribromophenyamine. The product was isolated from the concentrated residue by column chromatography on silica gel using a hexane/ethyl acetate mixture (5:1) as eluent. The product is readily dissolvable in common organic solvents such as acetone and ethyl acetate. Recrystallization in mixed hexane and ethyl acetate (1:1) yields highly pure desired product (over 90%) as pale yellow powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm]: 1.4 (t, 9H), 2.2 (s, 9H), 4.45 (q, 6H), 6.65−6.9 (m, 12H), 6.95 (s, 9H), 7.1 (t, 6H), 7.25 (s, 3H), 7.4 (t, 3H), 7.5 (d, 6H), 7.9 (s, 3H), 8.0 (d, 3H). IR (KBr): 3032, 2966, 2919, 2873, 1598, 1490, 1306, 1260, 1229, 1142, 779 and 743 cm^{-1}. MS: *m*/*z* 1139 ([M]$^+$). Anal. Calcd. for $C_{81}H_{69}N_7$: C, 85.34; H, 6.06; N, 8.60%. Found: C, 84.749; H, 6.3973; N, 8.93%.

Fabrication and Testing of OLEDs. A three-layer OLED was fabricated by vacuum deposition with a configuration of ITO(30 Ω/□)/PCATA(60 nm)/NPB(10 nm)/Alq$_3$(70 nm)/Mg:Ag/Ag, in which PCATA was used as a hole injecting and transporting layer, NPB acts as a second HTL, and Alq$_3$ acts as electron transporting emitter layer. Before loading into a deposition chamber, the ITO substrate was cleaned with detergents and deionized water, dried in an oven at 120 °C for about 2 h, and treated with UV-ozone for 25 min. The device was fabricated by evaporating organic layers at a rate of 0.1−0.3 nm/s onto the ITO substrate sequentially at a pressure below 5×10^{-6} mbar. Onto the Alq$_3$ layer a 200-nm-thick Mg/Ag (mass ratio of 9:1) alloy was deposited at a rate of 0.6 nm/s as the cathode. Finally, a 50-nm-thick layer of Ag was deposited to protect the alloy cathode from oxidation in air. For comparison, a standard double-layer NPB(70 nm)/Alq$_3$(70 nm) device was also prepared and tested under identical conditions. The EL spectra and current−voltage−luminance characteristics were measured with a Spectrascan PR 650 photometer and a computer-controlled DC power supply under ambient conditions. The emission area of the devices was 0.1 cm^2 as determined by the overlap area of the anode and the cathode.

Results and Discussion

Design and Synthesis of PCATA. PCATA is a π-electron starburst derivative of triphenylamine. Carbazole was introduced as an important component into the core structure of PCATA molecule because of its chemical stability, easy structure-modification at 3-, 6-, and 9-positions, and potential to raise T_g of the product molecules based on its rigid

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(12) Vanslyke, S. A.; Chen, C. H.; Tang, C. W. *Appl. Phys. Lett*. **1996**, *69*, 2160.

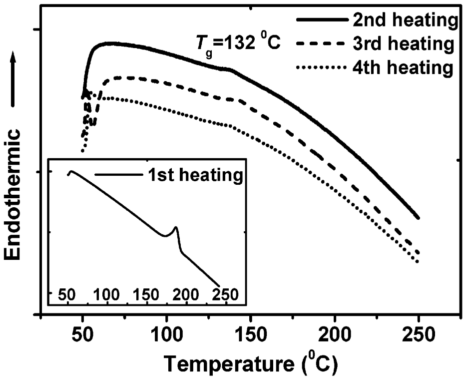

Figure 1. DSC thermograms of PCATA at a heating rate of 20 °C/min.

skeleton.[13] PCATA was synthesized through a two-step palladium-catalyzed N-arylation procedure as shown in Scheme 1. Such N-arylations of arylamines can be successfully achieved with the use of Pd(AcO)$_2$/DPPF as catalyst combination, which was initially developed by Hartwig and co-workers,[14] in the presence of *t*-BuONa as the alkali. Tao, Lin, and co-workers expanded the use of the palladium catalysts in the preparation of a wide series of arylamine derivatives functioning as emitting and transporting materials in OLEDs.[15,16] The palladium-catalyzed reactions are usually characterized by high yields of products. The isolation yield for each step reaction in the synthesis of PCATA is high up to 90%.

Thermal Properties of PCATA. The thermal properties of PCATA were determined by DSC and TGA measurements. Figure 1 illustrates the DSC thermograms of PCATA at a heating rate of 20 °C/min. When a polycrystalline sample of PCATA obtained from organic solvent was heated for the first cycle, an endothermic peak due to melting was observed at 187 °C as shown in the inset of the figure. When the isotropic liquid was quickly cooled by swirling water, an amorphous glass of PCATA was spontaneously formed via a supercooled liquid. When the amorphous glass was heated for the second time, a glass-transition phenomenon was observed at 132 °C, which is defined as the glass transition temperature (T_g) of PCATA. As illustrated in Figure 1, the glass-transition phenomenon can be repeated when the melted sample is cooled and the amorphous glass is reheated more times at the same heating rate. It should be noted that the endothermic melting peak at 187 °C did not appear in the second and further reheating cycles. This may be caused by the fast heating rate, which should be further confirmed. The sample after four heating cycles in the DSC measurement was analyzed to be the same chemical component as the initial sample by thin-layer chromatography and spectral data including ^{1}H NMR and mass spectra, which excludes the possibility of decomposition and further confirms the glass transition at 132 °C. The T_g of PCATA is significantly higher than those of the most widely used hole transporting material NPB (96 °C) and the hole injecting and transporting material *m*-MTDATA (75 °C),[17] indicating a higher morphological and thermal stability of PCATA. The thermal stability of PCATA was further confirmed by TGA measurement. A weight-loss transition corresponding to the endothermic evaporation was detected at 526 °C. Before and during evaporation no decomposition was observed, indicating a good thermal stability of PCATA.

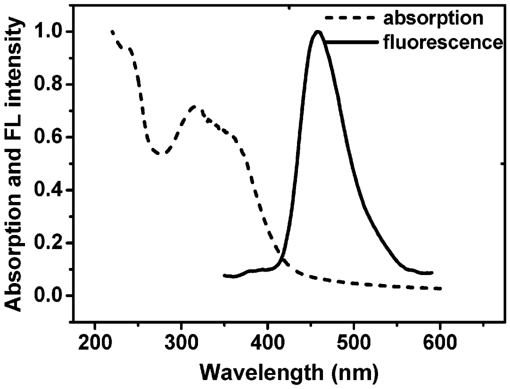

Figure 2. Absorption and fluorescence spectra of PCATA film on quartz substrate.

Optical Properties of PCATA. Figure 2 shows the absorption and fluorescence spectra of the thermal-evaporated film of PCATA on quartz. The absorption spectrum of PCATA simply covers the near-ultraviolet region (200−400 nm) and mainly displays the double-peak characteristic of the carbazole moiety at 320 and 360 nm. PCATA hardly absorbs light at wavelengths longer than 400 nm, implying its high transparency to visible light. This merit of PCATA is expected to contribute efficient light collection and avoid unnecessary absorption of the visible light emitted from the OLEDs which usually occurs in CuPc-containing devices.[12] PCATA is moderately fluorescent with emission peaking at 460 nm in film. The luminescence spectrum is relatively narrow with a full width at half-maximum of 60 nm. The fluorescence quantum yield of PCATA in dilute dichloromethane solution was measured to be 0.45 using quinine sulfate as a standard.

The highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO/LUMO) energy gap for PCATA was estimated as ca. 2.93 eV from the absorption edge of the optical absorption spectrum of PCATA film on quartz substrate. The HOMO energy level of PCATA was determined to be 4.73 eV by ultraviolet photoelectron spectroscopy. The LUMO level of PCATA was calculated to be 1.80 eV by subtracting the HOMO/LUMO band gap from the HOMO level. The high HOMO level of PCATA is almost identical to the work function of ITO at 4.7 eV, indicating that the hole injection barrier from ITO anode to PCATA layer is small and PCATA can act as a hole injecting material in OLEDs. The energy levels of PCATA and other organic and electrode materials used to fabricate OLEDs in the present study are shown in Figure 3.

EL Performances of PCATA-Based Devices. In this study an EL device was fabricated using PCATA as a hole injecting and transporting layer, tris(8-hydroxyquinolinato)-

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(13) Shirota, Y. *J. Mater. Chem.* **2000**, *10*, 1.

(14) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2046.

(15) Thomas, K. R. J.; Lin, J. T.; Tao, Y.-T.; Ko, C. W. *Adv. Mater.* **2000**, *12*, 1949.

(16) Thomas, K. R. J.; Lin, J. T.; Tao, Y.-T.; Ko, C. W. *J. Am. Chem. Soc.* **2001**, *123*, 9404.

(17) Shirota, Y.; Kuwabara, Y.; Inada, H.; Wakimoto, T.; Nakada, H.; Yonemoto, Y.; Kawami, S.; Imai, K. *Appl. Phys. Lett.* **1994**, *65*, 807.

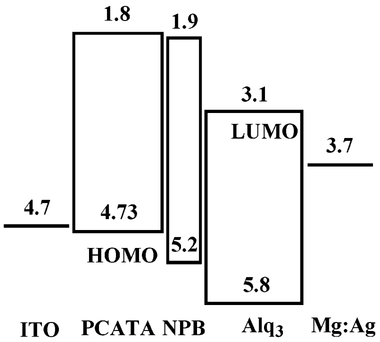

Figure 3. Energy levels of PCATA and other materials used to fabricate OLEDs in the present study.

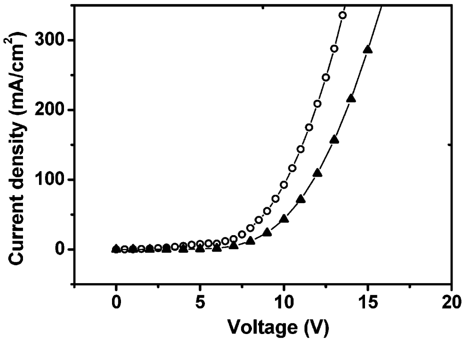

Figure 4. Current density−voltage characteristics of ITO/PCATA/NPB/Alq_3/Mg:Ag/Ag (▲) and ITO/NPB/Alq_3/Mg:Ag/Ag (○) devices.

aluminum (Alq_3) as the electron transporting emitter layer, ITO as the anode, and Mg:Ag/Ag as the cathode. To overcome the hole injection barrier from PCATA to Alq_3 layer with the HOMO level at 5.8 eV, a thin layer of NPB is inserted between them to form a three-layer OLED with a structure of ITO/PCATA(60 nm)/NPB(10 nm)/Alq_3(70 nm)/Mg:Ag. To evaluate the hole injecting and transporting ability of PCATA, a reference and standard double-layer OLED with a structure of ITO/NPB(70 nm)/Alq_3(70 nm)/Mg:Ag was simultaneously fabricated under the same vacuum cycle for comparison. Because the driving voltage of OLEDs can be affected by the thickness of the organic layers, the total thickness of the two HTLs in the three-layer device was controlled to be identical to that of the NPB layer in the double-layer reference device.

Both the PCATA-based three-layer and the double-layer reference devices showed pure green EL from Alq_3, indicating that the hole and electron recombination is located in the Alq_3 layer. Figure 4 shows the current density−voltage characteristics of the two OLEDs. At a given voltage, the current density of the three-layer device is lower than that of the double-layer device. The EL brightness−voltage characteristics of the two devices are shown in Figure 5. The PCATA-based three-layer device has a turn-on voltage of 3.9 V (at 1 cd/m^2) and a brightness of 20 000 cd/m^2 at 16 V (which is the upper measuring limit of our instrument), while the double-layer standard device has a turn-on voltage of 3.75 V and a maximum luminescence of 16 000 cd/m^2 at 15 V. The superiority in brightness of the PCATA-based three-layer device to the double-layer standard device is much more obvious at the high driving voltage region.

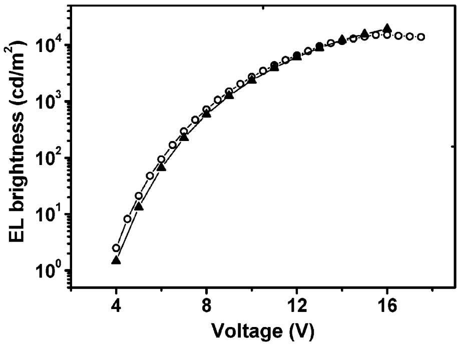

Figure 5. EL brightness−voltage characteristics of ITO/PCATA/NPB/Alq_3/Mg:Ag/Ag (▲) and ITO/NPB/Alq_3/Mg:Ag/Ag (○) devices.

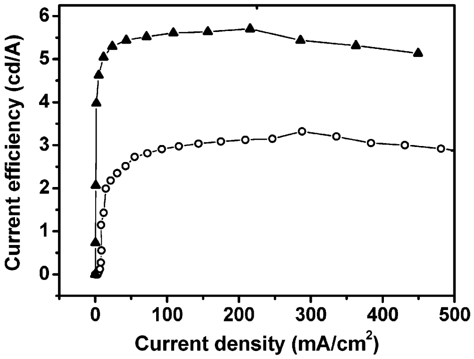

Figure 6. Current efficiency versus current density curves of ITO/PCATA/NPB/Alq_3/Mg:Ag/Ag (▲) and ITO/NPB/Alq_3/Mg:Ag/Ag (○) devices.

Figure 6 illustrates the current efficiency−current density characteristics of the two devices. The double-layer standard device, with its layer thickness optimized for device efficiency, gives a maximum current efficiency of 3.2 cd/A. The current efficiency of the PCATA-based three-layer device shows remarkable enhancement to a maximum value of 5.7 cd/A. The current efficiency of the two devices exhibits only a small decline even when the current density increases to 500 mA/cm^2. This characteristic is highly beneficial for applications that require high excitation density such as in passive dot matrix devices. Although the PCATA-based device has slightly higher turn-on and operating voltages than the standard device, its power efficiency can reach a high value of 2.2 lm/W, which is a factor of 2 higher than that (1.1 lm/W) of the standard device, and comparable to the reported value of 2.3 lm/W for the prototypical three-layer device with *m*-MTDATA as the hole injecting and transporting layer.[17]

The remarkable enhancement in brightness and efficiency of the PCATA-based device can be attributed to the better balanced charge recombination at the emitting interface. Since the cathode and the ETL in the PCATA-based device are the same as the standard device, the current decrease should result from the small hole injection barrier at interfaces and/or low hole transport through the HTL. Because the HOMO level of PCATA almost equals the work function of the ITO anode as shown in Figure 3, the hole injection barrier from the ITO anode to PCATA layer is expected to cause little voltage increase. For the same reason, the hole injection barrier from PCATA to NPB in the PCATA-based device is expected to be comparable to that from ITO to NBP in the standard device. Therefore, the hole transporting process through the PCATA layer is considered to be the main factor that affects the I−V characteristics.

The hole drift mobility in the PCATA layer is properly lower than that in the NPB layer. It has been shown that the formation of the cationic Alq_3 species in the emitting interface is the main reason responsible for the low EL efficiency and intrinsic degradation.[4] The usage of PCATA with a moderate hole drift mobility decreases the hole current and thus the amount of hole surplus at the emitting interface. As a result, the hole and electron injected into the emitting layer is better balanced compared to the standard NPB/Alq_3 device, and the brightness and efficiency are significantly enhanced. Additionally, the good film-forming property of PCATA is expected to also contribute to the efficient hole injection at the interface and to benefit the EL brightness and efficiency and device stability as well. Although the device lifetimes were not tested and compared in the present study, a high stability for the PCATA-containing device is expected due to the high morphological and thermal stability of PCATA as judged by DSC and TGA measurements.

In conclusion, a novel starburst amorphous molecule, PCATA, was synthesized for use as hole injecting and transporting material in OLEDs. The three-layer OLED using PCATA as the hole injecting and transporting layer exhibited dramatically enhanced EL brightness and efficiency compared to the standard device without PCATA layer and was comparable in performance to the *m*-MTDATA-based three-layer device. Both the current efficiency and the power efficiency were a factor of 2 higher in the PCATA-based OLED compared to the standard device. The moderate hole drift mobility in the PCATA layer balanced the hole and electron injection and recombination at the emitting interface, resulting in the brightness and efficiency enhancement. The usage of PCATA as hole injecting and transporting material is not confined to the present Alq_3-emitting devices. Based on the merits of PCATA including high T_g, good film-forming ability, high transparency to visible light, and moderate hole drift mobility, PCATA holds promise as a hole injecting and transporting material for organic photonic devices. The present study also provides a practical and efficient strategy to improve the EL efficiencies and reduce the intrinsic degradation in OLEDs by developing novel hole transporting materials with moderate hole drift mobility to match the present electron transport materials.

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