Degradation Behaviors of NPB Molecules upon Prolonged Exposure to Various Thermal Stresses under High Vacuum below 10^{-4} Pa

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ABSTRACT: Understanding of the long-term thermal stabilities of organic light-emitting diode (OLED) materials during film deposition is important to accurately identifying their processing windows. The thermal stresses imposed on OLED materials in the evaporation source during the deposition process may cause phase transition and/or degradation of the source materials, which results in variations in their purity and thermal properties, such as the vapor pressure and, ultimately, the device degradation. In this work, we designed a simple and efficient apparatus to determine the long-term thermal stability of OLED materials, which allows prolonged heating of a minimal amount of the sample (~2 g) for 50 h even under high vacuum below 10^{-4} Pa where the organic powder samples easily and rapidly vaporized because of exposure to temperature above their deposition temperature. We used this apparatus to evaluate the thermal degradation behaviors of N,N'-bis(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB), which is a widely used hole-transporting material in OLEDs, upon prolonged exposure to various thermal stresses. After prolonged heating at 330 °C (380 °C) for 25 h (50 h), the change in purity, mass, vapor pressure, and phase of the heated NPB were analyzed by high-performance liquid chromatography, liquid chromatography–mass spectrometry, thermogravimetric analysis, and X-ray diffraction. The lifetime of OLEDs using the heated NPB was measured to study how the thermally induced material degradation affects the device characteristics. The results showed that the NPB degradation caused by prolonged exposure to 330 °C accelerated over time. In addition, it was confirmed that the degradation products with high molecular weight that form due to exposure to 380 °C was the main cause of device degradation.

INTRODUCTION

Organic light-emitting diode (OLED) materials in the evaporation source are heated to a temperature at which a sufficient evaporation rate can be obtained until one complete cycle of the deposition process for a certain duration (approximately several tens to several hundreds of hours). The thermal stress may cause isomerization, polymerization, and/or decomposition of the materials. The phase transition and purity change of the material to be evaporated can change their thermal properties, such as the melting point and vapor pressure; therefore, they can affect the morphological stability of the deposited film and successive changes in electrical and optical characteristics of the device. Little attention has been paid to the changes in purity and physical properties of deposition source materials during OLED fabrication, that is, the long-term thermal stability of OLED materials.

Gilge et al. used a quartz ampoule test method to evaluate the long-term thermal stability of OLED materials in 10 days at 318 and 368 °C. However, the result may be different from that of a deposition source material in the evaporation source that was continuously effused into the high-vacuum chamber because the material degradation can be accelerated by the impurities in the process of material synthesis, purification, and sample loading and/or the impurities generated by the decomposition and polymerization of the material during the heat treatment. Therefore, it is essential to develop a long-term thermal stability evaluation method that is close in real evaporation condition, can reduce the consumption of the expensive materials, and can more quickly and accurately screen the process window of newly developed materials before the deposition process.

In this paper, we have developed a simple and efficient apparatus to evaluate the long-term thermal stability of OLED materials in high vacuum to understand the effects of the changes in purity of the deposition source material, which occur during the OLED deposition process, on the fabricated thin film and OLED. The changes in purity and vapor pressure...
of \(N,N'-\text{bis}(1\text{-naphthyl})-N,N'\text{-diphenyl-(1,1'-biphenyl)}-4,4'\)-diamine (NPB) heated under various thermal stress conditions (temperature and duration) were measured. By confirming the characteristics of devices obtained from these materials, the long-term thermal stabilities of NPB in high vacuum were tested.

\section*{RESULTS AND DISCUSSION}

Variations in purity and the concomitant modification of the physical properties of the deposition source materials during OLED fabrication have been largely overlooked. In the thermal evaporation source, OLED materials are heated to obtain a sufficient evaporation rate and held at the given temperature for a single deposition cycle, which may last from several tens to several hundreds of hours. Sivasubramaniam et al.\textsuperscript{7} suggested that the thermal stresses in the deposition source material may cause isomerization, polymerization, and/or decomposition of the materials. Variations in material purity can also result from variations in the thermal properties, such as the melting point and vapor pressure, which can affect the deposition rate and subsequent modifications of the electrical and/or optical characteristics of the device.

\textbf{High-Performance Liquid Chromatography Analysis.}

In previous studies, we confirmed that increasing impurities caused by the decomposition of NPB when NPB was exposed to thermal stress affected the OLED properties.\textsuperscript{9} Figure 1 shows the more-detailed high-performance liquid chromatography (HPLC) analysis results than previous studies for the purity change of NPB by thermal stress. Very small amounts of impurities were detected despite long-term exposure to thermal stress compared to thermogravimetric analysis (TGA) measurements, which showed a mass loss of 0.5\% at 368.6 °C.

When NPB was exposed to thermal stress in a high-vacuum environment similar to an actual evaporation environment (open system), a small amount of impurity remained and was detected, unlike the TGA measurement environment (closed system). It is expected to minimize the decomposition in the high-vacuum open system because some volatile impurities generated from NPB by thermal stress were volatilized. In the future, further research is necessary on different decomposition behaviors of organic materials because of the exposure to thermal stress in a closed system, where a volatile impurity does not volatilize, and in an open system similar to the actual evaporation process.

In this study, it was important to understand the generation and behavior of impurities in the simulation of an actual evaporation environment because a small amount of impurity can affect the stability and lifetime of OLEDs.\textsuperscript{10}

The chemical mechanisms of NPB decomposition are not exactly known, but it was widely known that C–N bonds, which are relatively weak bonds of arylamine molecules, were preferential dissociations and generated by products such as phenyl (P), naphthyl (N), and N-phenyl-2-naphthylamine (NPA). At this time, degradation products combined with naphthyl (N) or phenyl (P) are formed by the attack of free radicals of arylamines (Figure 2).\textsuperscript{6,7,11}

The HPLC full-range spectrum shows five main peaks that are considered to be impurities except for the solvent peak and NPB peak that appeared near 16.5 min (Figure 1a). In particular, NPBs heated at 330 °C for 25 and 50 h each have the same amount but different types of impurities (Figure 1b).

\textbf{Liquid Chromatography–Mass Spectrometry Analysis.}

It was important to define the degradation products related to the impurity peak of HPLC to understand the NPB decomposition mechanism because of the exposure to thermal stress. The liquid chromatography–mass spectrometry (LC–MS) analysis was done to define the impurities of NPB (Figures 3–6), and the LC spectrum shows some peculiarities as NPB was exposed to thermal stress.

Nonheated NPB has peaks with a low intensity at 0.85–0.90 min. Because of the exposure to thermal stress for 25 h at 330 and 380 °C, the intensity of the peak at 0.85–0.90 min increases. When the exposure time to thermal stress increases to 50 h, the intensity of the peak at 0.85–0.90 min decreases again (Figure 3). The MS spectrum associated with the LC spectrum at 0.85–0.90 min shows that the intensity of the 100 amu peak was large, and there was no peak with greater mass than that of NPB (588.75 amu) when the peak intensity at 0.85–0.90 min was small and close to 0.90 min. Meanwhile, the 100 amu peak had a small intensity, and there was a peak with greater mass than that of NPB when the peak intensity at 0.85–0.90 min was large and close to 0.85 min (Figure 4).

The 100 amu peak was expected to be the peak of phenylsodium (sodium; benzene) formed by combining phenyl, which was produced by the decomposition in NPB, and a sodium ion introduced during material synthesis, storage, sampling, and analysis. When NPB was exposed to thermal stress for 25 h, the mass peak of NPB–N (462.6 amu)
appeared definitely distinctive because the dissociation of naphthalene from NPB accelerated regardless of temperature, and partial NPB−N was combined with sodium ions (485.5 amu). At this time, naphthalene decomposed from NPB was volatilized in a high-vacuum environment of 10⁻⁴ Pa or less to simulate the actual process environment, so no mass peak was observed. When the thermal stress temperature was raised for 25 h, the peak intensity of NPB + P (664.8 amu) combined

Figure 3. LC−MS results of nonheated NPB and NPB exposed to thermal stress: (a) nonheated, (b) 330 °C 25 h, (c) 330 °C 50 h, (d) 380 °C 25 h, (e) 330 °C 50 h.

Figure 4. MS spectrum related to the nearby 0.85−0.90 min LC spectrum peak: (a) nonheated, (b) 330 °C 25 h, (c) 330 °C 50 h, (d) 380 °C 25 h, (e) 330 °C 50 h.
with NPB with phenyl was raised, and the NPB + N (714.9 amu) peak, which was NPB combined with naphthalene, appeared in the MS spectrum. As the thermal stress of NPB exposure increased from 330 to 380 °C, partial naphthalene was not volatilized because of increasing NPB decomposition, and the 128.2 amu peak appeared because the remaining naphthalene was combined with NPB (Figure 4).

Figure 5 shows the MS spectrum associated with 2.61 and near 9.05–9.16 min of LC spectra. The MS spectrum associated with the LC spectrum at 2.61 min shows that it is related to NPA (N-phenylnaphthalen-2-amine, 219.3 amu) produced by decomposition and NPB-NPA (4-naphthalen-1-ylphenyl-3-phenylaniline, 371.5 amu). (Figure 5a).

The peak near 9.05–9.16 min of the LC spectrum was related to NPB (Figure 5b). In general, all substances are partially deuterated by excess protons, which results in an isotope distribution. We can predict that NPB has three isotope distributions with different levels of deuteration, $^{58}$8.26 amu (100%), $^{59}$8.26 amu (47.6%), and $^{60}$0.26 amu (11.1%), and it was confirmed to be identical to the isotope distribution of the MS spectrum. NPB exposed to thermal stress for 50 h at 330 °C had a peak near 610–611 amu, unlike NPB exposed to the thermal stress of other conditions. This peak was expected to be due to the binding of sodium ions to NPB. In addition, in Figure 3, NPB exposed to thermal stress for 50 h at 330 °C behaved differently from the degraded NPB exposed to thermal stress under different conditions, such as the presence of 1.80 and 4.15 min peaks in the LC spectrum. The MS spectra related to the 1.80 and 4.15 min peaks of the LC spectrum show that NPB–N was present in combination with sodium ions and that NPB was an impurity bound with potassium ions (Figure 6). As previously mentioned, NPBs exposed to 330 °C thermal stress have the same impurity ratio regardless of the time exposed to thermal stress. Although the exactly factors were unknown, the dissociated impurity of NPB exposed to thermal stress for 50 h was combined with alkali ions, and they behaved differently from the NPB exposed for 25 h at the same temperature.

Based on the LC–MS analysis, it was difficult to accurately define the substance related to the HPLC impurity peak, but we can expect that peaks 1 and 5 are associated with NPB-NPA and NPA, respectively. Peak 3 may be related to the impurity of phenyl and naphthalene decomposed in NPB, and peak 2 may be related to the impurity of NPB–N to alkali metal ion.

Meanwhile, when the exposure time to thermal stress at 380 °C was extended to 50 h, although it showed a clear color change based on the decomposition temperature of NPB (368.6 °C), it had a MS spectrum very similar to that of nonheated NPB (Figures 4 and 5). In this study, the employed electro spray ionization method for LC–MS analysis should generate cations for mass analysis.13

Figure 5. MS spectrum associated with 2.61 and nearby 9.05–9.16 min of LC spectra: (a) associated with 2.61 min, (b) associated with near 9.05–9.16 min.

Figure 6. MS spectrum of NPB exposed to 330 °C for 25 h. (a) MS spectrum for 1.80 min. (b) MS spectrum for 4.15 min.
With a very similar MS spectrum to nonheated NPB, any material produced that was difficult to cationize by acetonitrile (ACN) or with high mass over the measurement range was produced, and mass detection was not possible.

**Thermogravimetric Analysis.** Figure 7 shows the vapor pressure changes of NPB degraded by thermal stress. The vapor pressure was measured by TGA for each of the three samples under identical conditions, and the average measured values were plotted on the graph. The vapor pressure of nonheated NPB was approximately $1.88 \times 10^{-20} \text{ Pa}$ in the temperature range of $300\text{–}380^\circ\text{C}$. The vapor pressures of NPB exposed to $330^\circ\text{C}$ for 25 and 50 h thermal stress are $0.680 \times 10^{-39.47}$ and $0.680 \times 10^{-39.47}$ Pa, respectively. The vapor pressure of NPB exposed to thermal stress was $0.62 \times 10^{-37.70}$ and $0.66 \times 10^{-39.22}$ Pa when it was heat treated at $380^\circ\text{C}$ for 25 and 50 h, respectively. The NPB exposed to thermal stress had at least a 50% vapor pressure drop in comparison to nonheated NPB.

In general, vapor pressure is known to decrease according to Raoult’s law when a nonvolatile impurity is present in the pure materials. According to Oja et al., mixtures of high molecular weight aromatic compounds exhibit nonideal behavior, and the vapor pressure is lower than that in the ideal Raoult’s law when there is a strong electron donor group and an electron acceptor group in the molecules. Therefore, NPB exposed to thermal stress has a lower vapor pressure than that in the ideal Raoult’s law because of the decomposition product and high-weight molecules produced during decomposition.

**X-ray Diffraction Analysis.** Figure 8 shows the X-ray diffraction (XRD) spectra of NPB powder before or after receiving thermal stress. Leung et al. argued in their study that NPB powder with crystallization becomes a dominantly amorphous film after deposition and that crystallization of NPB was induced by small crystalline domains that react with humidity because of the exposure to thermal stress. The nonheated NPB shows an XRD spectrum similar to the result of Leung et al. Meanwhile, NPB exposed to thermal stress shows two major changes. The peak marked with the red arrow disappeared after the exposure to thermal stress. Another peak marked with the blue arrow disappeared after the exposure to thermal stress at $330^\circ\text{C}$ for 25 h; when the exposure time to thermal stress was extended to 50 h, a peak split occurred. NPB exposed to $380^\circ\text{C}$ thermal stress disappeared regardless of the exposure time. It was not possible to accurately define the peaks that change and their associated phase, but degradation products produced by the thermally induced dissociation of NPB also affect the phase characteristics of NPB.

To predict the decomposition mechanism of NPB by thermal stress by integrating the results of HPLC, LC–MS, vapor pressure, and XRD measurements, degradation products with low-molecular weight were produced because the NPB decomposition accelerated when NPB was exposed to...
temperatures below the decomposition temperature (330 °C). Given prolonged exposure to thermal stress (50 h), the decomposition products and NPB react with alkali ions, and very small amounts of degradation products with high molecular weight are produced when the reaction time among the impurities increases. Meanwhile, it was assumed that degradation products with high molecular weight that were bound with very small amounts of phenyl and naphthalene was increased when NPBs were exposed to temperatures above the decomposition temperature (380 °C) because of the increasing degradation products with low-molecular weight, which were caused by the attack of radicals generated by the C−N bond dissociation. Subsequent exposure to thermal stress (50 h) led to complex reactions among degradation products with high molecular weight, degradation products with low-molecular weight, NPB, and decomposition products, which produced giant molecules that are difficult to detect in LC−MS (Figure 9).

**OLED Characteristic.** Eventually, impurities generated from NPBs exposed to thermal stresses affect the characteristics and lifetime of OLEDs. Figure 10a shows the luminous efficacy−current density characteristics of the OLEDs using nonheated NPB and NPB exposed to thermal stress. The luminous efficacy of OLEDs using NPB exposed to thermal stress is decreased. The luminous efficacy of OLEDs using nonheated NPB was 1.42 lm/W at approximately 25 mA/cm². The luminous efficacy at approximately 25 mA/cm² of the OLED with NPB heated for 50 h at 330 and 380 °C is clearly lower (1.31 and 1.27 lm/W, respectively). Figure 10b shows the driving voltage at which the initial OLED luminance of ~1000 cd/m² was reduced to 80% luminance ($L_{80}$). OLEDs using nonheated NPB take approximately 300 h to reach $L_{80}$.
However, it takes approximately 213 and 180 h to reach $L_{80}$ when it is exposed to thermal stress for 25 and 50 h at 330 °C. It takes approximately 115 and 34 h to reach $L_{80}$ when it is exposed to thermal stress for 25 and 50 h at 380 °C. In addition, the driving voltage must be 8.22 V because the OLED emits the initial luminance (∼1000 cd/m²) when using nonheated NPB but requires 7.80 and 8.56 V when using NPB exposed to thermal stress for 25 and 50 h at 330 °C, the driving voltage of 8.65 and 10.40 V is required, respectively. Especially, OLEDs using NPB exposed to thermal stress at 380 °C for 50 h show a very high initial driving voltage and very short lifetime, perhaps because of the degradation products with high molecular weight effect produced by exposure to thermal stress. As expected in Figure 9, the degradation products with high molecular weight produced because of exposure to thermal stress at 380 °C for 50 h degrade the hole-transport characteristic of the NPB; therefore, high driving voltages are required for the same OLED initial luminance (∼1000 cd/m²). More heat was also generated in the OLED by the high resistance of the degradation products with high molecular weight, which accelerates the lifetime degradation of the OLED.

Meanwhile, OLEDs using NPB exposed to thermal stress at 330 °C for 25 h had lower driving voltage than OLEDs using nonheated NPB, but their lifetime was shortened.

Some NPBs decomposed by being exposed to thermal stress at 330 °C for 25 h make favorable hole transport. However, the decomposition products of NPB accelerate the decomposition reaction during the operation of the OLED, which accelerates the degradation of the OLED lifetime.

**CONCLUSIONS**

In this study, we used the newly designed long-term thermal stability apparatus for OLED materials to test the actual deposition simulation environment. The apparatus was employed to study the NPB decomposition by thermal stress and its effect on the OLED. NPB exposed to the thermal stress of 330 °C, which was lower than the decomposition temperature of NPB, decomposes into products such as NPB−P and NPB−N. The decomposition was accelerated or combined with alkali ions by longer exposure time to thermal stress. Meanwhile, NPB exposed to a thermal stress of 380 °C, which was higher than the decomposition temperature of NPB, rapidly decomposed from the early stage, and the accelerated radical attacks produced degradation products with high molecular weight. A longer exposure time to thermal stress corresponds to a higher molecular weight, which degrades the performance of NPB as a hole-transport layer and the device characteristics such as OLED lifetime and driving voltage. Therefore, OLED materials should be closely examined to improve the reliability of OLEDs. The newly designed long-term thermal stability apparatus developed in this study is expected to be employed to evaluate the reliability of newly developed OLED materials as a very useful tool.

**EXPERIMENTAL SECTION**

**New Long-Term Thermal Stability Test Apparatus.** Figure 11 shows a schematic of the newly constructed long-term thermal stability test apparatus. The apparatus was designed to obtain information about the long-term thermal stability of OLED materials. The new apparatus was constructed from a sample heating and recovery system, cylindrical vacuum buffer chamber, and vacuum pumping system.

The sample heating and recovery system for long-term thermal stability testing of the OLED materials in high vacuum includes a sample container (quartz tube), sample holder, cold trap, stripper, and furnace. The sample container was fixed by the sample holder and heated by a cylindrical electric furnace. The sample heating and recovery system for long-term thermal stability testing of the OLED materials in high vacuum was calibrated with an industrial platinum resistance thermometer temperature probe using the ASL bridge model F26. The cylindrical electric furnace was controlled by a programmable PID controller (Cerin Co., Ltd, South Korea). A stripper was placed inside a sample container made of a quartz tube to help with sample recovery.
The sample holder was surrounded with the cold trap of a double-wall structure jacket type to maintain 10 °C water cooling using a chiller (HL-20H, JeioTech, South Korea). The cold trap made a rapid temperature gradient in the vertical direction of the quartz tube and prevented the buffer chamber from being contaminated by the vaporized evaporation material in the high vacuum. The sample holder was connected to a cylindrical vacuum buffer chamber by a four-way cross fitting (type-304 stainless steel) with connections of stainless steel 304L tubing and a CF flange. The four-way cross fitting facilitated connecting the three sample holders, containers, and vacuum systems with a manually operated Y-shape inline valve (MBC-2.75-L, iSAN, South Korea). The pressure of the cylindrical vacuum buffer chamber was monitored by a convection gauge (VC120, ISVT, South Korea), absolute capacitance manometer (MKS, USA) [0.1 Torr (TYPE 627D1TBD1B), 10 Torr (TYPE 626B11TBD)], and hot cathode ion gauge (the 274003, Graville-Phillips, USA).

The vacuum system was composed of a rotary vane pump and cryopump. A rotary vane pump (DUO 20M, Pfeiffer vacuum, Germany) used the rough pumping of the buffer chamber and cryopump and was connected to the cylindrical vacuum buffer chamber by a pneumatically operated angle valve (Genius, South Korea and Neoma Inc., South Korea). A cryopump (Brooks CTI-Cryogenics, USA) was employed to make a high vacuum environment below 10⁻⁴ Pa and connected by a pneumatically operated gate valve (VCGV08-PISO, VITZRO, South Korea).

**Long-Term Thermal Stability Test Procedure.** The NPB in this study, which was a representative aromatic amine OLED hole-transport layer material, was purchased from EMINDEX (CAS number 123847-85-8, purity by HPLC 99.9%).

To improve the NPB purity, as-received NPB was prepurified to remove volatile impurities generated during the NPB synthesis, storage, and sampling by heating to 100 °C at 10⁻⁴ Pa using the new long-term thermal stability test apparatus. Next, additional in situ sublimation purification was done three or more times at 260 °C using the new long-term thermal stability test apparatus.

After sample pretreatment, the sample was heat treated in a high vacuum of 10⁻⁴ Pa (or less) for 25 and 50 h at 330 and 380 °C, respectively. The NPB exposed to 330 and 380 °C was recovered by the stripper every 10 and every 5 min by considering the sublimation speed of NPB. The number of stripings per cycle was set to four times, considering sample recovery and vacuum braking. After the heat treatment was completed, the gate valve between the cryopump and the buffer chamber was closed, dry N₂ was injected to suppress the evaporation of additional samples, and the samples were cooled to room temperature in the atmosphere.

HPLC was conducted using an HPLC system (1260 Infinity II, Agilent Technologies, Inc., USA) with C-18 column (Kinetex, 4.6 × 250 mm, 5 μm, Phenomenex, USA), and a mixture of ACN (HPLC grade, Sigma-Aldrich, USA) and water (90:10, v/v %) was used as the eluent. LC–MS was performed using an LC–MS system (1100 series, Agilent Technologies, Inc., USA) with C-18 Column (ACQUITY UPLC BEH, 2.1 × 100 mm, 1.7 μm, Waters Corp., USA), and a mixture of ACN (HPLC grade, Sigma-Aldrich, USA) and water (10 mM ammonium acetate) (90:10, v/v %) was used as the eluent. The vapor pressure was derived by detecting the isothermal mass loss using TGA (Setsys Evo. STA set, Setaram Instrumentation, France). Approximately 20 mg of sample was placed in a Pt crucible (diameter = 9 mm, depth = 3 mm) to conduct stepwise isothermal heating, and dry N₂ gas was injected during the measurement. The XRD pattern of NPB powder was recorded on an X-ray diffractometer (SmartLab, Rigaku Corp., Japan) with Cu Kα radiation at 200 mA and 45 kV.

**OLED Fabrication and Characterization.** The indium tin oxide (ITO)-coated glass (OTF Technology, South Korea, 24 mm × 24 mm, 10 Ω/sq) substrate was cleaned by ultrasonication for 10 min in the order of detergent, eionized water, acetone, and isopropyl alcohol (IPA), and it was further washed for 5 min in boiling IPA. After the cleaned substrate was dried with dry argon, surface treatment was performed by a UV–ozone cleaner (AC-6, AhTech LTS, South Korea) for 15 min.

OLED was deposited by a thermal evaporator (Daeki Hi-Tech Co. Ltd., South Korea) in an environment below 6.5 × 10⁻⁵ Pa. A 15 nm thick MoO₃ (hole injection layer) was deposited on the ITO at a deposition rate of 0.01 nm/s by vaporizing a molybdenum thermal boat (supplied by ITASCO, South Korea). Next, NPB (hole-transporting layer) before or after receiving thermal stress and Alq₃ (electron-transporting layer) were deposited at 50 and 60 nm, respectively, at a deposition rate of 0.1 nm/s. A 1 μm thick Liq electron injection layer was deposited at a deposition rate of 0.01 nm/s, and the Al cathode (supplied by ITASCO, South Korea) was patterned using a shadow mask to define the active area (2 mm × 2 mm).

To seal the fabricated OLED, UV resin (XNR 5570, Nagase Chemtex Corporation, Japan) was coated on the edge sides of the glass lid (supplied by ITASCO, South Korea) and cured using a UV curing system (JHCI-051B, Jueun UV Tech Co. Ltd., South Korea) in a dry N₂ atmosphere glovebox (<1 ppm H₂O and O₂).

The electrical and optical characteristics of OLEDs were measured with a source measurement unit (2635B, Keithley, USA) and spectroradiometer (PR-730, Photo Research Inc., USA). The OLED lifetime to relative luminance decrease with time (initial luminance: ∼100 cd/m²) was measured by an OLED lifetime test system (M6000PMX, McScience, Inc., South Korea) in a constant current density (approximately 30 mA/cm²) mode at room temperature. Knowledge of the thermal stability of OLED materials during deposition is critical for successful OLED fabrication because the thermal stress imposed on the materials from the heating source modifies their physical and chemical properties over time. We observed the thermally induced changes in NPB purity over time and reported how these impurities cause variations in the electrical and optical characteristics of the resulting OLEDs. Although prolonged heating causes only minimal changes in the NPB purity, it leads to a larger decrease in the OLED performance. In the early stages of material research and development, such knowledge of the long-term thermal stability of OLED materials in high vacuum will be useful to understand their thermal behaviors during OLED deposition.

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