

Impact of Chemical Degradation at HTL/EML Interface on Device Performance of Blue OLEDs

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Abstract

We examined the impact of chemical degradations at the HTL/EML interface on blue OLED performance. Our study showed that photo-induced C-N dissociation of HTL materials has little effect on the blue OLED lifetime while photochemical reactions with water/oxygen on the HTL surface can severely degrade the device efficiency and lifetime.

Author Keywords

Blue OLED; chemical degradation; device lifetime; LDI-TOF imaging.

1. Introduction

The relatively short lifetime of blue OLEDs compared to the red and green OLEDs remains a critical issue for commercial OLED displays. Blue OLEDs typically use an amine-based fluorescent dopant with a hydrocarbon host as the emitting layer (EML). Previous studies on archetypical OLEDs have indicated that C-N bond dissociation of amine-based materials is a major cause for operational instability.^[1,2] It has also been reported that the chamber condition during fabrication, such as the residual water, can affect OLED lifetime to a great degree.^[3,4] However, the significance of these factors in blue OLEDs are still unclear. Furthermore, it is not well understood what role the HTL/EML interface plays in initiating chemical reactions and producing charge traps and luminescent quenchers.

In this study of blue OLED degradation, we deliberately induced chemical reactions such as C-N dissociation and oxidation/hydroxylation at the HTL/EML interface with UV irradiation. By subjecting the HTL to UV under various conditions prior to the deposition of the EML, we seek to introduce latent reactants associated with oxygen and water at the HTL surface, which can cause additional chemical reactions or lifetime degradation in a completed OLED device under operation. Specifically we will use laser desorption ionization – time of flight (LDI-TOF) imaging, for the identification of possible chemical byproducts and reaction pathways.^[5]

2. Experiments

Blue OLED devices were fabricated by vacuum thermal evaporation in a vacuum chamber at 10^{-6} Torr. Figure 1 shows the molecular structures of the materials used for fabricating devices of the following layer structure: ITO/HATCN (10 nm)/HTL1 (40 nm)/ BD:BH 8.5% (20 nm)/LG201 (30 nm)/Liq (2 nm)/Al. After HTL1 was deposited, the substrate was subjected to UV irradiation (365 nm, 10 mW/cm²) under vacuum in the same vacuum chamber or in a glovebox ($H_2O/O_2 < 0.1$ ppm) connected to the vacuum chamber for 10 h prior to completing the deposition of the remaining layers. For comparison, reference devices were fabricated and kept under identical conditions, except that the HTL1 layer was not subjected to UV irradiation. To evaluate the photochemical degradation of HTL1 alone under similar conditions, a 16 mm diameter, 50 nm thin film was subjected to

UV irradiation in vacuum or in glovebox with half of the film shielded as reference. The chemical composition changes in the degraded films were characterized in-situ by LDI-TOF imaging with a raster width of 1 mm using a MALDI-TOF mass spectrometer.

3. Results

Blue OLED devices fabricated for this study in our laboratory have an external quantum efficiency (EQE) of about 3.5% and a T_{90} lifetime around 20 h with an initial brightness of 2300 cd/m². It has been determined that at current densities higher than 10 mA/cm², the recombination was largely confined to the HTL1/BD:BH interface.^[6] Since HTL1 has a S_1 of 2.95 eV, which is higher than those of BH (2.82 eV) and BD (2.72 eV),^[7] it is likely that HTL1 has a greater propensity for photochemical degradation at the HTL1/EML interface.

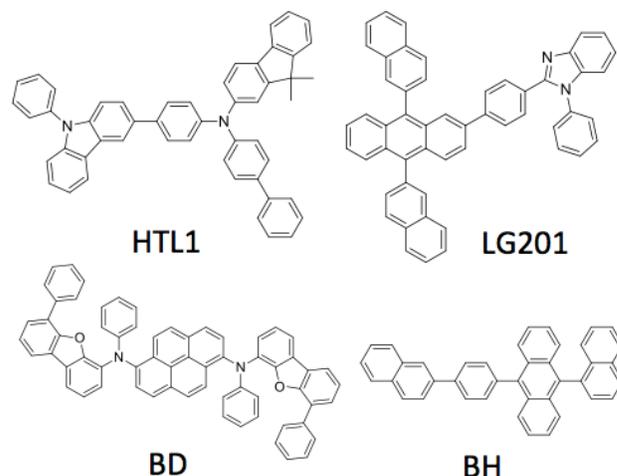


Figure 1. Materials used in blue OLED devices.

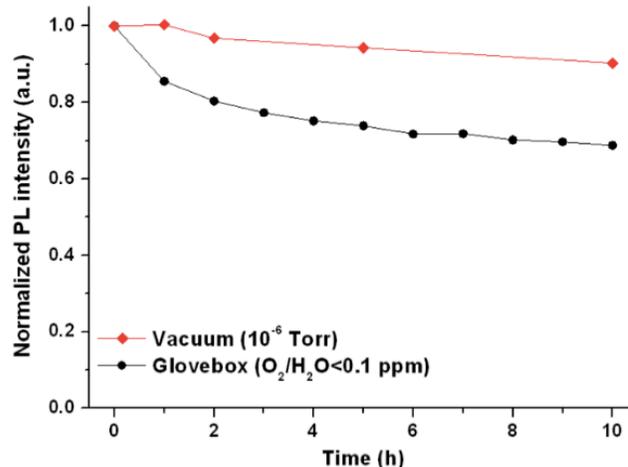


Figure 2. PL decay of UV (365 nm) irradiated HTL1 films.

HTL1 thin films were found to undergo photochemical degradation under UV irradiation. Figure 2 shows the photoluminescence (PL) decay of HTL1 films subjected to 10 h of UV irradiation 1) under 1×10^{-6} Torr vacuum and 2) in glovebox ($\text{H}_2\text{O}/\text{O}_2 < 0.1$ ppm). The PL intensity is decreased to 90% and 69%, respectively. The HTL1 film degraded in vacuum exhibits an almost linear PL decay whereas the HTL1 film degraded in glovebox shows a faster initial decay. The partial pressure of H_2O and O_2 in the 1×10^{-6} Torr vacuum chamber were roughly 5×10^{-7} Torr and 5×10^{-9} Torr, respectively, as measured by a residual gas analyzer (RGA). These values are two to four orders of magnitudes lower than the partial pressure of H_2O and O_2 in glovebox, assuming the H_2O and O_2 were at 0.1 ppm.

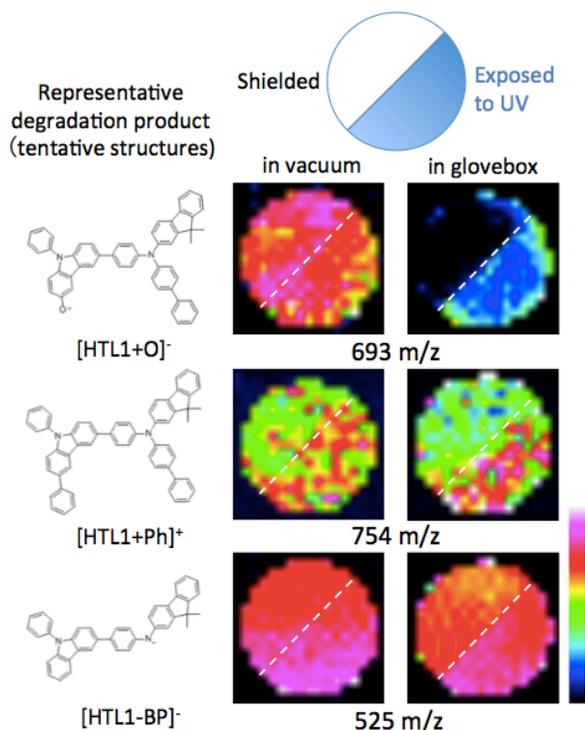


Figure 3. LDI-TOF imaging intensity maps of representative degradation products identified in HTL1 films irradiated with 365 nm, $10 \text{ mW}/\text{cm}^2$ UV light under vacuum and glovebox conditions. The dashed lines indicate the UV irradiation boundary.

The LDI-TOF imaging result, as shown in Figure 3, clearly illustrates the different photochemistry of the two HTL1 films. In the film degraded in glovebox, oxidized and hydroxylated HTL1 are identified as the dominating byproducts accompanied by species related to C-N bond dissociation. For example, the intensity map of the mass peak at 693 m/z, which corresponds to $[\text{HTL1}+\text{O}]^-$, shows significantly higher peak intensities in the UV-degraded part of the film and a clear demarcation between the irradiated region and the shielded region. Mass peaks of higher-order oxidation byproducts were also identified with increased intensities in the UV-irradiated area. Similarly, species from C-N bond dissociation, such as the adduct $[\text{HTL1}+\text{Ph}]^+$ at 754 m/z and the fragment $[\text{HTL1}-\text{BP}]^-$ at 525 m/z, exhibited intensity maps that match with the UV irradiation pattern. On the other hand, LDI-TOF imaging on the film degraded in vacuum only revealed minute byproducts from C-N bond dissociation as the degradation product. The intensity map of $[\text{HTL1}+\text{Ph}]^+$ shows sporadic hot spots in the degraded film area. Neither $[\text{HTL1}-\text{BP}]^-$ nor

$[\text{HTL1}+\text{O}]^-$ exhibits an intensity contour that matches with the UV pattern. The LDI-TOF imaging results indicate that HTL1 degrades almost exclusively through C-N dissociation in high vacuum condition. In contrast, it mainly undergoes oxidation and hydroxylation with C-N dissociation as a minor degradation pathway in glovebox atmosphere where $\text{H}_2\text{O}/\text{O}_2$ content is much higher.

For device degradation studies, UV irradiation under conditions similar to that performed on the standalone HTL1 films were carried out at the HTL/EML interface (see Experimental Section). Thus reaction products corresponding to HTL1 degradation due to irradiation in various environments can be created predominantly at HTL1/EML interface where charge recombination takes place.

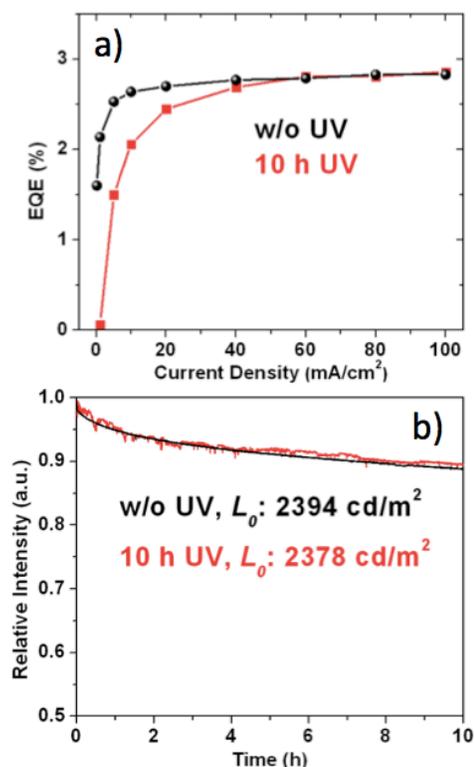


Figure 4. a) EQE and b) lifetime of devices exposed to vacuum for 10 h with and without 365 nm UV irradiation. Devices were driven at $60 \text{ mA}/\text{cm}^2$ in the lifetime test.

Figure 4 shows the initial EQE and EL degradation for a blue OLED where the HTL1 has been degraded by UV irradiation in vacuum. It can be seen that under a good vacuum condition, the device performance is largely unaffected. At $60 \text{ mA}/\text{cm}^2$, the EQE is about the same at 2.7%, with or without irradiation of the HTL1 layer. The EL decay curves are essentially identical. These results strongly indicate that the majority of the byproducts produced by the degradation of HTL1 (10% loss in PL) do not function as effective quenchers at the EML/HTL1 interface in the OLED device. This may seem contradictory to previous findings that C-N bond dissociation in amines like NPB produces deep charge traps that function as quenchers.^[1] However, the chemical degradation in our experiments is induced exclusively by photo-excitation, which unlike electrical excitation does not involve any free charges. The radical reactions initiated by C-N cleavage will be eventually terminated via radical annihilation or disproportionation reactions, resulting in stable, neutral byproducts, such as $[\text{HTL1}+\text{Ph}]^+$ identified in LDI-TOF imaging.

It is only logical that these neutral species, which are various substituted equivalents of HTL1, do not serve as effective quenchers. It indirectly proves the necessity of charged species in the degradation of amine-based materials in OLED devices.

OLED devices with the HTL1 layer degraded in glovebox, on the other hand, showed drastically decreased efficiency and lifetime. As shown in Figure 5, 10 h UV irradiation on the HTL1 left the device with less than half of the EQE and only one tenth of the T_{90} lifetime as compared to the control device. Based on the results of LDI-TOF imaging, the oxidized or hydroxylated HTL1 is evidently the culprit of this performance loss. These byproducts not only function as quenchers that incur immediate damage to the HTL1/EML interface but also are more vulnerable to electrical excitations during device operation, further comprising the lifetime. From energy consideration, the hydroxylated species [HTL1+OH] is expected to have a higher HOMO level than HTL1 and consequently a higher probability of direct recombination on itself. Upon electrical excitation, its O-H bond or Ph-O bond may dissociate into highly reactive radical pairs. Alternatively, the radical cation [HTL1+OH]⁺, when excited via exciton-polaron annihilation, may generate phenol radical [HTL1+O][•] and free hydrogen cation, which will further degrade the device. Our experiments clearly demonstrated that photochemical reactions with minute amount of H₂O and O₂ could significantly deteriorate OLED device performance. Amine-based materials with large bandgaps, such as HTL1, are particularly vulnerable to such reactions. Even the control device with HTL1 exposed in glovebox without UV irradiation exhibited slightly shorten lifetime with respect to a device fabricated without any interruption. However, it should also be noted that any reaction of HTL1 with trace H₂O and O₂ present in 10⁻⁶ Torr vacuum typical for device fabrication may not necessarily affect the device lifetime as indicated in Figure 4.

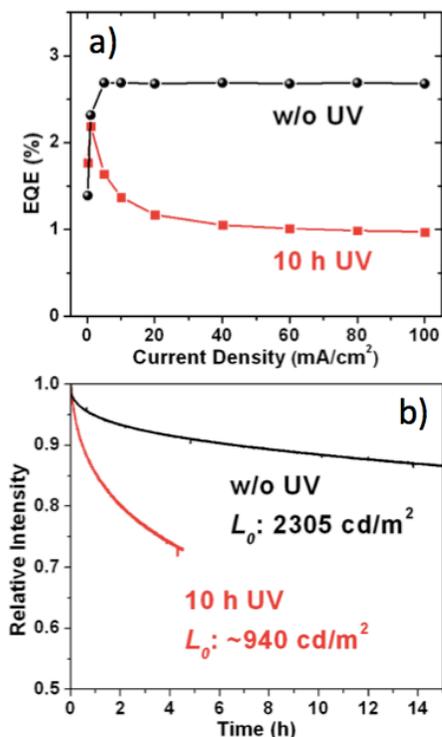


Figure 5. a) EQE and b) lifetime of devices exposed to glovebox for 10 h with and without 365 nm UV irradiation. Devices were driven at 60 mA/cm² in the lifetime test.

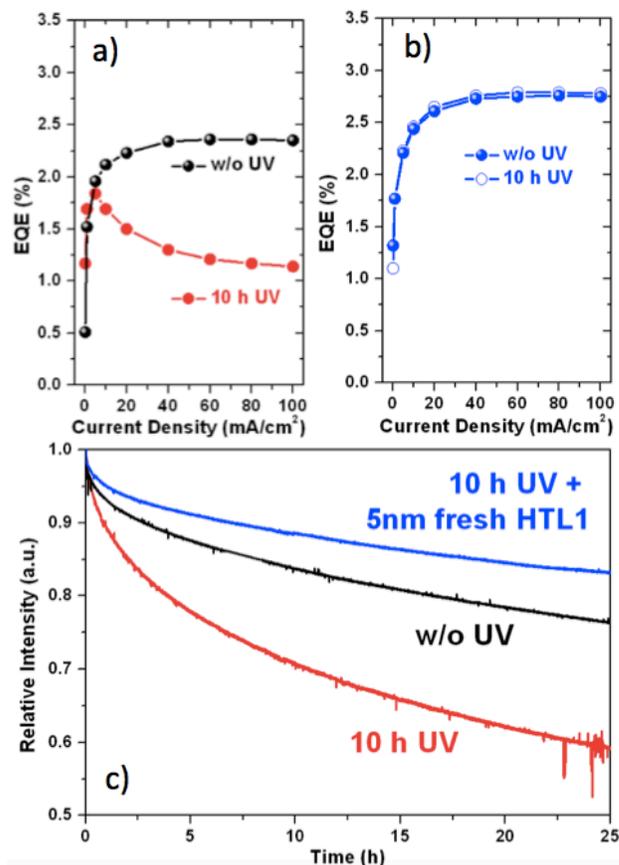


Figure 6. a) EQE of blue devices exposed to glovebox with and without UV for 10 h; b) EQE of devices with a 5 nm fresh HTL1 deposited on top of the HTL1 layer exposed in glovebox with and without UV for 10 h; c) device lifetime tested at 60 mA/cm².

In another experiment, we fabricated a blue OLED with a layer of fresh HTL1 (5 nm) deposited on top the HTL1 layer that was previously exposed to UV irradiation in glovebox. As shown in Figure 6, the efficiency and lifetime of the UV-degraded device are recovered with a thin overlayer of fresh HTL1. This result ascertains that the chemical degradation in the HTL1/EML interface is primarily responsible for the loss of device performance.

4. Conclusion

Our study of UV irradiation of HTL/EML interfaces and chemical analysis with LDI-TOF imaging show that photo-induced C-N dissociation of the amine-based HTL materials has little effect on the blue OLED lifetime, whereas electrical charges are necessary for the production of permanent charge traps and luminescent quenchers at the HTL/EML interface. We have also demonstrated that photochemical reactions of the HTL with H₂O and O₂ at the HTL/EML interface can cause marked device degradation. Away from this interface, chemical degradation of bulk HTL has little effect on device performance.

5. Impact

This work provides a better understanding of the effect of chemical degradation of the HTL/EML interface, specifically the photochemical reactions of amine-based HTL with H₂O and O₂, on the performance of blue OLED devices.

6. References

- [1] D. Y. Kondakov, "Role of chemical reactions of arylamine hole transport materials in operational degradation of organic light-emitting diodes," *Journal of Applied Physics* **2008**, *104* (8), 9.
- [2] D. Y. Kondakov, W. C. Lenhart, W. F. Nichols, "Operational degradation of organic light-emitting diodes: Mechanism and identification of chemical products," *Journal of Applied Physics* **2007**, *101* (2), 7.
- [3] H. Yamamoto, J. Brooks, M. S. Weaver, J. J. Brown, T. Murakami, H. Murata, "Improved initial drop in operational lifetime of blue phosphorescent organic light emitting device fabricated under ultra high vacuum condition," *Appl. Phys. Lett.* **2011**, *99*, 033301.
- [4] D. C. Le, S. Oyama, H. Sakai, T. Porcelli, F. Siviero, E. Maccallini, M. Urbano, H. Murata, "Fivefold enhancement in stability of organic light-emitting diodes with addition of non-evaporable getter pumps," *Appl. Phys. Express* **2017**, *10*, 071601.
- [5] S. C. Dong, C. W. Tang, "Photo-Degradation of Hole Transport Materials Studied by LDI-TOF Imaging," *IDW'17 Digest*, **2017**.
- [6] By inserting a thin rubrene layer at different positions in the EML as the sensing layer, the recombination zone of this device was determined to be at the BD:BH/LG201 interface at low current densities and quickly shifted to HTL1/BD:BH interface as the current density increased.
- [7] Y. Mizuki, H. Ito, "Aromatic amine derivative, material for organic electroluminescent element, and organic electroluminescent element," U.S. Patent 10,056,558 B2.