

OLEDs with enhanced high temperature operational stability

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ABSTRACT

Temperature dependence of electroluminescence degradation is studied in organic light emitting devices containing an emitting layer composed of a mixture of different hole transport molecules and tris(8-hydroxyquinoline)aluminum (AlQ₃) electron transport and emitter molecule. The emitting layer is sandwiched between hole and electron transport layers. Devices containing the hole transport molecule *N,N'*-di(naphthalene-1-yl)-*N,N'*-diphenyl-benzidine (NPB), doped with quinacridone (DMQ) green emitter showed remarkable temperature stability. For these devices, a half-life of about 78,500 hours, 18,700 hours, and 8,600 hours can be projected for operating temperatures of 22°C, 70°C and 100°C, respectively, at an initial device luminance of 100 cd/m². Activation energies for device degradation were determined for devices with different hole transport molecules and it was found that devices with higher activation energy show better high temperature stability. These results are consistent with the recently proposed degradation mechanism based on the unstable cationic AlQ₃ species.

1. INTRODUCTION

Recent advances in the development of organic light emitting devices (OLEDs) have led to the realization of devices with high operational stability, reflected in a device half-life (time elapsed before efficiency decreases to 50% of its initial value) amounting to many thousands of hours.¹⁻² The high operational stability, however, has so far been essentially demonstrated in devices operated at room temperature. In order to meet durability requirements for a wide variety of potential technological applications, OLEDs must also demonstrate sufficient stability when operated at elevated temperatures (~ 70-90°C). Since OLED degradation is accelerated by temperature, achieving a satisfactory operational stability at these temperatures has been particularly challenging.³

Studies focusing on the temperature-dependence of OLED degradation have been few, and hence our understanding of thermally-induced degradation behavior of OLEDs is still limited. In addition, most of these studies have been limited to establishing the role of the glass transition temperature of the organic materials on device shelf-life (non-operational stability),^{4,5} or on increasing the critical temperature above which catastrophic failure of the OLED would occur.⁶⁻⁹ One systematic study on temperature-dependence of OLED operational stability has been presented by Choong *et al.* on single-layer devices utilizing *N,N'*-di(naphthalene-1-yl)-*N,N'*-diphenyl-benzidine (NPB) and tris(8-hydroxyquinoline)aluminum (AlQ₃) "organic alloy" layer, that further contained methyl quinacridone as a fluorescent dopant.¹⁰ The devices were studied at temperatures ranging from room temperature to 65°C. When operated at 65°C, these "organic alloy" devices demonstrated a half-life, $t_{1/2}$, of about 320 hours for an initial luminance, L_o , of 1486 cd/m², which can be projected to a $t_{1/2}$ of 4,800 hours at L_o of 100 cd/m². The projected half-life value is derived from accelerated aging tests, assuming coulombic degradation scaling law,¹

$$(L_o)(t_{1/2}) = \text{constant.} \quad (1)$$

Recently, Ishii and Taga¹¹ studied the influence of temperature and drive current in OLEDs with a high Tg hole transport molecule and CuPc buffer layer on ITO. They found that the shape of the electroluminescence decay curve did not change with temperature and that proper scaling of the time axis made all the curves to overlap. The universal decay curve was well represented with a stretched exponential. They also studied the validity of scaling law given by Eq. (1) and concluded that it is generally valid. The observed deviations were attributed to sample self-heating, which lead to a larger decrease of observed device life at high operating currents than predicted by Eq. (1). This also means that if this

scaling law is used to predict device life at lower luminances from measurements at higher luminances, any error will lead to an underestimate of device life at lower light levels.

In this paper, we first review results on high temperature performance of a new device structure utilizing a mixed emitting layer consisting of a hole transport material, an electron transport material, which can also contain an emitting dopant, sandwiched between hole and electron transport layers.¹² Although the emitting layer in our device is similar to the “organic alloy” layer of Choong *et al.*¹⁰, the different overall device architecture proposed in this work leads to a significant improvement in device performance, which will be discussed later. We also present new results which explore the influence of different hole transport molecules in the mixed emitter layer on device life.

2. EXPERIMENTAL

The device structure is shown schematically in Figure 1. In addition to NPB we also used other two hole transport molecules (HTMs) in the mixed layer, N,N'-diphenyl-N,N'-bis(3-methylphenyl)(1,1'-biphenyl)-4,4'-diamine (TPD), and 1,1'-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC). The OLEDs studied had the following structure: indium-tin-oxide (ITO) anode/ NPB hole transport layer (~200Å thick) / HTM(~50%)+AlQ₃(~50%)+(optional dopant, ~0.4%) mixed emitting layer (~800Å thick) / AlQ₃ electron transport layer (~200Å thick)/ Mg:Ag cathode. The devices were fabricated by the deposition of the organic materials and the cathode metals using thermal evaporation at vacuum base pressure of about 5×10^{-6} torr on UV ozone cleaned ITO-coated glass substrates. The mixed emitting layer was formed by co-deposition of HTM, AlQ₃ and optional dopant at a rate of ~4Å/s, 4Å/s, and 0.03Å/s, respectively. Mg:Ag cathode (~1200Å thick) was formed by co-deposition of Mg and Ag at a rate of 4Å/s and 0.4Å/s, respectively. Deposition rates were individually controlled using quartz crystal monitors. OLED operational stability measurements were carried out using 1 KHz, 50% duty cycle AC driving conditions at an average constant current density of 31.25 mA/cm² in the forward bias direction and -15 V reverse bias. AC as opposed to DC driving was used as it is known to reduce the possibility of device shorting.¹ For testing at elevated temperatures, flexible electric heating tape was wound around the OLED test box, and controlled using *Omega CN9000* temperature controller. The OLED temperature was monitored using a thermocouple in contact with the OLED substrate. The OLEDs were kept in a dry nitrogen atmosphere throughout the experiment.

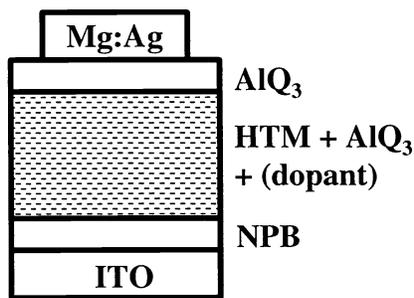


Figure 1. Schematic diagram of OLED structures described in this work. Dopant in the mixed emitter layer is optional.

3. RESULTS AND DISCUSSION

The use of different hole transport molecules in the mixed emitter layer lead to significant difference in device life. We will first discuss performance of devices with NPB hole transport molecule, which showed by far the best performance. Later we will discuss TPD and TAPC containing devices and propose an explanation for the observed differences in device behavior.

3.1 NPB in mixed emitter layer

Results from device operational stability tests, represented in the form of normalized luminance [Luminance (L)/ Initial Luminance (L_0)] vs. time of operation for two OLEDs of structure as shown in Figure 1, driven at 31.25 mA/cm^2 , and operated at 22°C and 70°C , are shown on Figure 2, curves A and B, respectively. L_0 , measured at the respective device testing temperature, was 1724 and 1800 cd/m^2 , for the two devices, respectively. Under these conditions, $t_{1/2}$ was 4560 and 1040 hours, for operation at 22°C and 70°C , respectively. We were also successful to achieve stable OLED operation for temperatures exceeding 70°C by introducing further device modifications, without changing the mixed emitting layer. Curve C on Figure 2 shows results from the modified device when operated at 100°C . Under the same driving conditions described previously, L_0 of this device was 1710 cd/m^2 . At this temperature, $t_{1/2}$ was 505 hours. Assuming coulombic degradation (Eq. 1),¹ for operation at L_0 of 100 cd/m^2 , $t_{1/2}$ is projected to be $78,500$ hours, $18,700$ hours and $8,600$ hours, for operation at 22°C , 70°C , and 100°C , respectively. Compared to results reported for single-layer “organic alloy” OLEDs when operated at 65°C ($t_{1/2} \sim 320$ hours for L_0 of 1486 cd/m^2 , which can be projected to $t_{1/2} \sim 4800$ hours for L_0 of 100 cd/m^2),¹⁰ $t_{1/2}$ of our devices is about 4 times longer at a somewhat higher temperature (70°C).

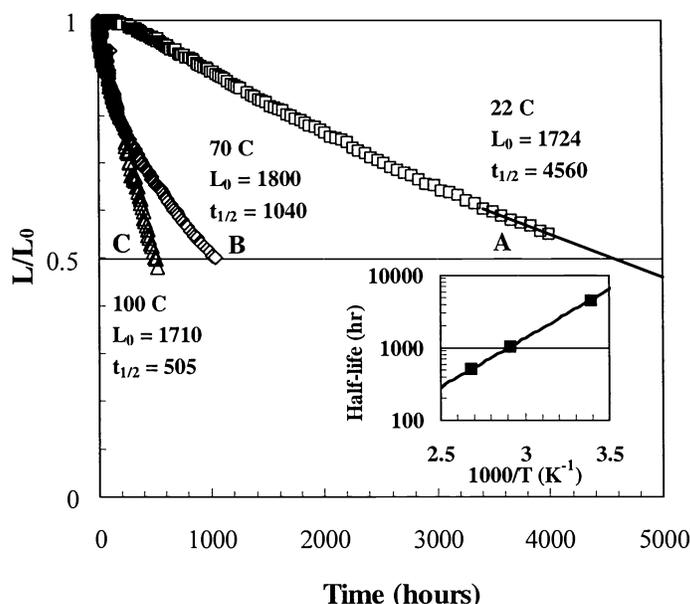
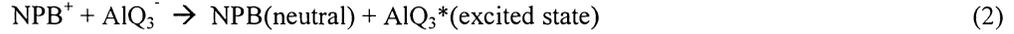


Figure 2. Normalized luminance [Luminance (L)/Initial Luminance (L_0)] versus time for NPB containing OLED operated at different temperatures, using AC driving at an average constant current density of 31.25 mA/cm^2 . The straight line around 4000 hours represents extrapolation of the data in order to determine half-life of the device operated at room temperature. L_0 values are in cd/m^2 , and the half-life values, $t_{1/2}$, are in hours. The insert shows OLED half-life versus reciprocal temperature in semi-logarithmic plot. Best straight line fit to the data gives activation energy of 0.27 eV .

The insert in Figure 2 shows a linear-log plot of the half-life vs. OLED reciprocal operating temperature for average driving current of 31.25 mA/cm^2 . The straight-line fit of the data gives an activation energy of 0.27 eV for the electroluminescence degradation process. In order to correlate this number with material parameters, we will assume that the degradation mechanism in OLEDs with the mixed emitting layer is primarily governed by the model based on instability of cationic AIQ_3 species.^{13,14} The model has been successful in explaining a wide range of experimental observations, including stability of OLEDs with mixed emitting layer,¹³ and single-layer “organic alloy” OLEDs.^{10,15} In order to understand the relationship between the activation energy for device degradation and material parameters, in particular ionization potentials, an energy diagram of the OLEDs studied is presented in Figure 3. During device operation, in the mixed layer, holes will be transported by hopping between NPB molecules, and electrons by hopping between AIQ_3 molecules. The light emission is accomplished by direct recombination of holes and electrons to generate an AIQ_3 excited state, which can then transfer energy to the dopant. This process, described by the following equation,



does not involve the generation of the unstable cationic AlQ_3^+ intermediate, and hence enhances device stability.¹³⁻¹⁵ Alternatively, the dopant may act as a recombination center, where the creation of the excited state is generated on the dopant directly after capturing both an electron and a hole. In this case, as well, no AlQ_3^+ intermediate is needed to generate the excited state. However, Boltzman distribution requires that some AlQ_3^+ species will still be formed in the mixed emitting layer as a result of thermal excitation. The activation energy, ΔE , for promoting a hole from NPB molecule to an AlQ_3 molecule is approximately equal to the difference of the ionization potentials, I_p , of the two materials,

$$\Delta E = I_p(\text{AlQ}_3) - I_p(\text{NPB}) \quad (3)$$

and therefore, the concentration of AlQ_3^+ cations, $\langle \text{AlQ}_3^+ \rangle$, will be proportional to $\exp(-\Delta E/kT)$. As a result, the device half-life is expected to be inversely proportional to the concentration of the AlQ_3^+ species, and will, therefore, be given by

$$t_{1/2} \sim 1/\langle \text{AlQ}_3^+ \rangle \sim \exp(\Delta E/kT) \quad (4)$$

This leads to the conclusion that activation energy for device degradation should be equal to the difference in the ionization potentials of the electron and hole transport materials. From UV photoemission studies, the ionization potential for NPB and AlQ_3 is estimated to be $\approx 5.2\text{--}5.4$ eV,^{16,17} and $5.6\text{--}5.7$ eV,^{16,18} respectively. Accordingly, a value for ΔE of about 0.35 ± 0.15 eV can be calculated, which is in good agreement with a measured activation energy of 0.27 eV for device degradation (insert, Fig. 2). As our mixed emitting layer is also doped, it could be argued that the presence of an additional energy level (that of the dopant) can change the AlQ_3^+ population statistics. However, simple calculations based on Boltzman statistics show that for small dopant concentrations ($< 2\%$), and for a dopant with an ionization potential between those of NPB and AlQ_3 , the change in activation energy is negligible. Even when the ionization potential of the dopant is smaller than that of NPB by ~ 0.1 eV, variation in activation energy will be less than 10%. Similar experiments on OLEDs, which did not contain a dopant in the mixed emitting layer showed essentially the same lifetimes when operated at the same current density and the same activation energy, and hence support this argument.

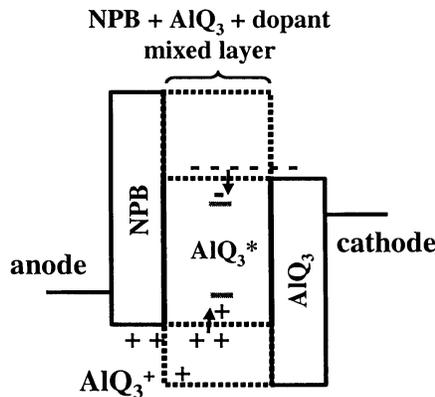


Figure 3. Qualitative schematic of the energy levels of the doped mixed emitting layer and the hole and electron transport layers. Direct recombination of NPB^+ and AlQ_3^- , without creation of the AlQ_3^+ intermediate, leads to formation of AlQ_3^* excited state (or dopant excited state, not shown). Boltzman distribution requires that some AlQ_3^+ states must still be populated.

3.2 TPD and TAPC in the mixed emitter layer

Eq. (4) leads to an interesting prediction. Smaller ionization potential difference between the AlQ_3 electron transport and emitter molecule and the hole transport molecule in the mixed emitter layer leads to a decrease of device life, but at the same time decreases temperature dependence of device life. In order to test this prediction we made devices containing TPD or TAPC in the mixed emitter layer. Typical luminances of these devices, which did not contain dopant in the mixed emitter layer, were about 700 cd/m^2 at 31.25 mA average driving current. The results for device degradation in time for temperatures between 25 C and 55 C are given in Figure 4. This temperature range was chosen to make sure that the devices are operated below glass transition temperatures, T_g , of hole transport molecules, which, for TPD and TAPC (around 65 C) are smaller than for NPB (95 C). Obviously devices containing TPD have longer lifetimes than devices containing TAPC and both have much shorter lifetimes than devices containing NPB in the mixed layer.

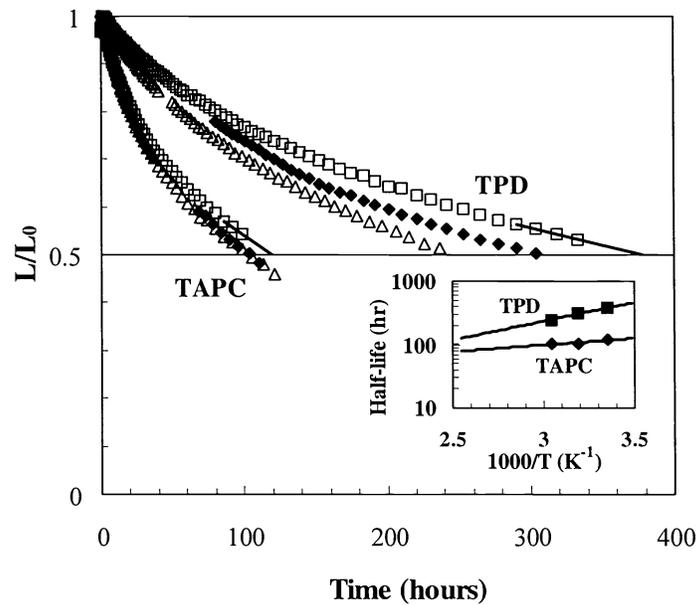


Figure 4. Normalized luminance versus time for OLEDs containing TPD and TAPC hole transport molecules in the mixed layer, using AC driving at an average constant current density of 31.25 mA/cm^2 . Measurements are done at three temperatures: 25 C (\square), 40 C (\blacklozenge), and 55 C (\triangle). activation energies for TPD and TAPC containing devices are $0.12 \pm 0.01 \text{ eV}$ and $0.04 \pm 0.02 \text{ eV}$, respectively.

The insert in Fig. 4 shows logarithms of lifetimes plotted as a function of reciprocal temperature. For TPD and TAPC containing devices the slope gives activation energies of $0.12 \pm 0.01 \text{ eV}$ and $0.04 \pm 0.02 \text{ eV}$ respectively. As predicted by Eq. (4), devices show longer life if activation energy is higher.

It is important to note, however, that other factors must also be contributing to differences in life of devices containing different hole transport molecules in the mixed layer. If we plot the logarithm of half-life of different devices as a function of ΔE keeping the temperature constant, experimentally measured data show much smaller slope than the $\exp(\Delta E/kT)$ function. This means that pre-exponential factor of Eq. (4) must be materials dependent. This is not unreasonable, as the use of different HTMs in the mixed layer will lead to change of injection characteristics from the NPB hole transport layer to the mixed layer and the change in the distribution and density of the space charge and thus the density of AlQ_3^+ cations.

4. CONCLUSIONS

In conclusion, we demonstrated that OLEDs containing a doped mixed hole transport/electron transport emitting layer, sandwiched between hole and electron transport layers, show extraordinary stability at elevated temperatures, as high as

100°C, when NPB is used as the hole transport molecule. The activation energy of device degradation correlates well with the difference in ionization potentials of the AlQ₃ electron and NPB hole transport materials. This finding is consistent with the OLED degradation model based on instability of cationic AlQ₃ species. The degradation model based on unstable AlQ₃ ions predicts that device performance should strongly depend on the hole transport material used, with materials showing smaller activation energy leading to shorter device life. This has indeed been observed when TPD and TAPC hole transport molecules were used in the mixed emitter layer. However, the effect of activation energy changes cannot account alone for the differences in half-life of devices with different hole transport molecules in the mixed layer, indicating that other effects, like changes in injection characteristics and space charge distribution are also playing a significant role.

High temperature performance demonstrated in this work suggests that small molecule-based OLED technology can be suitable for potential harsh-environment applications, where reliable device operation at elevated temperatures for extended periods of time is required.

REFERENCES

1. S. A. Van Slyke, C. H. Chen, C. W. Tang, *Appl. Phys. Lett.* **69**, 2160 (1996).
2. J. Shi and C. W. Tang, *Appl. Phys. Lett.* **70**, 1665 (1997).
3. J.R. Sheats, H. Antoniadis, M. Hueschen, W. Leonard, J. Miller, R. Moon, D. Roitman and A. Stocking, *Science* **273**, 884 (1996).
4. H. Spreitzer, H. Schenk, J. Salbeck, F. Weissoertel, H. Riel and W. Riess, *Proceedings of the SPIE on Organic Light-Emitting Materials and Devices III*, Denver, CO, July 1999, Volume **3797**, 316 (2000).
5. H. Spreitzer, H. Vestweber, P. Stobel and H. Becker, *Proceedings of the SPIE on Organic Light-Emitting Materials and Devices IV*, San Diego, CA, July 2000, Volume **4105**, 125 (2001).
6. S. Tokito, H. Tanaka, A. Okada and Y. Taga, *Appl. Phys. Lett.* **69**, 878 (1996).
7. S. Tokito, H. Tanaka, K. Noda, A. Okada and Y. Taga, *IEEE Trans. Elec. Dev.* **44**, 1239 (1997).
8. Y. Shirota, K. Okumoto and H. Inada, *Synth. Met.* **111-112**, 387 (2000).
9. F. Steuber, J. Staudigel, M. Stossel, J. Simmerer, A. Winnacker, H. Spreitzer, F. Weissortel and J. Salbeck, *Adv. Mat.* **12**, 130 (2000).
10. V. Choong, J. Shen, J. Curless, S. Shi, J. Yang and F. So, *J. Phys. D., Appl. Phys.* **33**, 760 (2000).
11. M. Ishii and Y. Taga, *Appl. Phys. Lett.* **80**, 3430 (2002).
12. H. Aziz, Z. D. Popovic and N. X. Hu *Appl. Phys. Lett.*, to be published, July 2002.
13. H. Aziz, Z. D. Popovic, N. X. Hu, A. M. Hor and G. Xu, *Science* **283**, 1900 (1999).
14. Z. Popovic, H. Aziz, A. Ioannidis, N. Hu and P.N.M. dos Anjos, *Synth. Met.* **123**, 179 (2001).
15. J. Shen and J. Yang, *J. Appl. Phys.* **87**, 3891 (2000).
16. S. T. Lee, Y. M. Wang, X. Y. Hou, and C. W. Tang *Appl. Phys. Lett.* **74**, 670 (1999).
17. Q. T. Le, F. Nuesch, L. J. Rothberg, E. W. Forsythe, and Y. Gao *Appl. Phys. Lett.* **75**, 1357 (1999).
18. K. Sugiyama, D. Yoshimura, T. Miyamae, T. Miyazaki, H. Ishii, Y. Ouchi, and K. Seki *J. Appl. Phys.* **83**, 4928 (1998).