INVESTIGATIONS OF OPERATIONAL LIFETIME AND
MODES OF FAILURE OF ORGANIC LIGHT EMITTING
DEVICES

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AFRL-HE-WP-TR-2003-0154

This report has been reviewed by the Office of Public Affairs (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public.

This technical report has been reviewed and is approved for publication.

FOR THE COMMANDER

//Signed//

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Reliability limitations of organic light emitting devices (OLEDs) were explored in a joint effort project lead by Princeton University, with subcontracting efforts by the University of Southern California, the University of Texas and Universal Display Corporation. Methodologies and protocols for screening of device structures and materials were developed. Extended lifetimes of red, green and blue phosphorescent OLEDs were achieved. For example, lifetimes of over 50,000 hours were obtained for both red and green devices. Blue device lifetimes observed were still less than 1000 hours. This difference in blue lifetime was studied using both photo- and electro-luminescence methods, and was determined to be due, in part, to the high energies needed to excite the blue lumophores, which results in charge imbalance in the emission layers of the OLEDs. Contact degradation was also studied at the microscopic scale using near-field scanning optical microscopy (NSOM) in concert with our transparent OLED structure (TOLED). It was found that defects introduced during processing are largely responsible for the formation and growth of dark spots.
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FOREWORD

This grant MDA 972-01-1-0032 was selected under Air Force Office of Scientific Research (AFOSR) Broad Agency Announcements BAA 2001-01. Proposal number 01-NL-113 entitled "Investigation of the Operational Lifetime and Modes of Failure of Organic Light Emitting Devices" was reviewed by an interagency panel of experts from the Air Force Research Laboratory Human Effectiveness Directorate (AFRL/HE), the Defense Advanced Research Projects Agency (DARPA), the Army Research Laboratory Sensors and Electron Devices Directorate (ARL/SEDD), and the Natick Soldier Center (NSC) led by Dr. Charles Y-C Lee of AFOSR/NL and found to be scientifically sound and acceptable for award consideration. Because of DARPA's interest in this area, AFOSR recommended the proposal to DARPA for funding consideration. The grant was issued from DARPA to the Princeton University and required the DARPA to provide 100% of the total project funding of $700,000 via ARPA Order No. H731/14. Dr. Hopper at AFRL was the DARPA Agent and was designated by DARPA as the government Contracting Officer's Technical Representative (COTR).

In addition to the body of the report, the results of this two-year project are documented in one patent listed in Appendix A and in 10 publications listed in Appendix B. Personnel involved and graduate degrees awarded with funding under this effort are listed in Appendices C and D. An extensive pictorial presentation of the results are available in the form of the 11 June 2003 final review presentation charts in Appendix E.

This project built on the foundation of a previous $5,438,957 DARPA-funded AFRL-managed grant F33615-94-1-1414 led by Princeton University from 13 June 1994 through 30 April 2002. Accomplishments on this earlier grant, funded under the DARPA High Definition Systems Program, have been published in two earlier technical reports, which are available from the National Technical Information Service:

Stephen R. Forrest, Mark E. Thompson, and Juan Lam,
"Novel, Full Color Flat Panel Display Technology Employing High Performance Crystalline Organic Semiconductor Light Emitting Diodes"

Stephen R. Forrest,
"Vacuum Deposited Organic Light Emitting Devices on Flexible Substrates"

This report AFRL-HE-WL-TR-2003-0154 has been formatted in accordance with a commercial standard, with tailoring from the AFRL Scientific Technical Information Office. This standard is as follows: "Scientific and Technical Reports—Elements, Organization, and Design,” American National Standard ANSI/NISO Z39.18-1995 (NISO Press, Bethesda MD, 1995), which is available electronically via the following website address:

The technical review of this document was accomplished by Dr. Darrel G. Hopper of AFRL.
PREFACE

The objective of this applied research program was to determine the physics, chemistry, and device engineering causes for the short lifetime of organic light emitting diode devices and to determine methods to overcome these failure mechanisms.

Princeton University in Princeton NJ assembled a team comprising the University of Southern California (USC), the University of Texas at Austin (UTA), and the Universal Display Corporation. Princeton University provided program management and concentrated on device fabrication issues. The University of Southern California concentrated on materials issues. The University of Texas at Austin concentrated on special analytical techniques. The Universal Display Corporation concentrated on lifetime issues. All participants contributed to all issues, accomplished various tests, and collaborated in the analysis of one-another’s results. The degree of integration of effort is illustrated by the creation of materials at USC, fabrication of devices at PU, and near-field scanning optical microscopy (NSOM) work at UTA.

Technology transition between Princeton University and the University of Southern California to Universal Display Corp. has been continuous throughout the course of the project. Specifically, tools and methods to monitor photophysical degradation, as well as numerous compounds for use in blue PHOLEDs have been transitioned during the project.

ACKNOWLEDGEMENTS

We gratefully acknowledge the financial support received from DARPA under grant number MDA 972-01-1-0032. We thank Dr. Robert W. Tulis of DARPA and Dr. Darrel G. Hopper of AFRL for their support throughout the project. Furthermore, the authors thank PPG Industries for their work on new materials, Vitex Systems and DoE Pacific Northwest National Laboratory for their work on barrier coated plastics, and Prof. C. Adachi of Chitose Institute of Science and Technology for helpful discussions.
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1. SUMMARY

The reliability limitations of organic light emitting diode (OLED) displays was explored in a joint effort lead by Princeton University, with subcontracting efforts by the University of Southern California (USC), the University of Texas at Austin (UTA), and Universal Display Corporation (UDC).

Methodologies and protocols for screening of device structures and materials were developed using each of three types of OLED structure shown in Figure 1(a-c).

Extended lifetimes of red, green and blue phosphorescent OLEDs were achieved. Lifetimes of >50,000 hours for both red and green OLED devices were obtained, with blue device lifetimes still less than 1000 hours observed. This difference in blue lifetime was studied through phot- and electro-luminescence methods, and was found to be due in part to the high energies needed to excite the blue lumophores, resulting in charge imbalance in the emission layers of the OLEDs.

Contact degradation was also studied at the microscopic scale using simultaneous near-field scanning optical microscopy (NSOM) and optical microscopy in experiments enabled by our transparent OLED (TOLED) structure. A key result from all of the experiments is that defects introduced during processing are largely responsible for the formation and growth of dark spots in OLEDs.

![Types of OLEDs](image)

(a) Conventional OLED with ITO/glass anode and reflective cathode
(b) Transparent OLED with ITO/glass anode and thin metal/ITO compound cathode
(c) Top-emitting OLED with reflective anode and thin metal/ITO compound cathode.

Figure 1 (a-c): Types of OLED display devices.
2. INTRODUCTION

The focus of this research was to understand failure modes in OLED display devices, develop protocols for the quantification of reliability, and improve the operational lifetime of these devices. Our technology platform is based on phosphorescent OLEDs (PHOLEDs) which have proven to be the highest efficiency emissive source yet developed for displays. In Figure 1(d) we show a typical test structure—the conventional PHOLED consisting of an indium tin oxide (ITO) anode, hole injection layer (HIL), hole transport layer (HTL), phosphor-doped emission layer (EML), hole and exciton blocking layer (HBL), electron transport layer (ETL), and metal cathode.

![Schematic diagram of a simple, conventional OLED display device.](image)

Figure 1(d): Schematic diagram of a simple, conventional OLED display device.

The complexity of the device provides some insight into the difficulties encountered in determining failure mechanisms in OLEDs. All adjacent layers, interfaces and dopants can chemically interact, and individually they can all lead to degradation of device performance over time. Hence, it is important to develop methodologies that can isolate separate modes effects arising from each of the layers and their interactions.

The specific research objectives were as follows: (a) establish protocols for accelerated aging of transparent, conventional and flexible organic light emitting device (FOLED) displays; (b) using NSOM and other analytical techniques, investigate the growth of dark spots on the above-noted displays, including the acceleration of this effect after flexing; (c) investigate effects of material grading of the organic/organic heterojunction and determine the dependence of long term stability on this factor; (d) investigate different encapsulation methods for both flexible and rigid display substrates; (e) develop models to understand results of long term aging studies; (f) continue studies and gathering data on contact, transport layer, doping, packaging, and flexing experiments; (g) accomplish detailed pre- and post-aging measurements of the energetics and operational characteristics (including photoelectron spectroscopy measurements of aged and aging interfaces) of the molecular devices grown by both organic vapor phase deposition (OVPD) and vacuum thermal deposition.
3. RESULTS AND DISCUSSION

3.1 Phosphorescent Blue Reliability

High-efficiency PHOLEDs have now been demonstrated in the red, green and blue portions of the visible spectrum. The single greatest obstacle remaining in the path to a full-color, long-lifetime OLED display is material and device reliability. Device lifetimes in the green and red portions of the spectrum are reaching the levels required for conventional display applications while lifetimes in the blue portion of the spectrum remain below the threshold for usability.

The question of blue reliability is not one that can be addressed in a single series of experiments, the solution to this problem needs to be attacked on a variety of fronts, by examining the materials themselves on both chemical and physical levels as well as considering the lifetime of given device structures and the susceptibility of such structures to certain conditions. These conditions include environmental (e.g. testing atmosphere) and operational (e.g. more sensitivity to one charge carrier—positive or negative—than another). Understanding the results of such experiments will prove critical to understanding the physical mechanism behind device degradation as well as the means to engineer materials and device structures which lend to greater overall operational stability.

The most successful (in terms of both quantum efficiency and operational stability) PHOLEDs demonstrated to date have employed either bis- or tris-cyclometallated Ir(III) compounds as the emissive material. Not surprisingly, the material under investigation for this particular study of phosphorescent blue reliability is iridium(III)bis[(4,6-di-fluorophenyl)-pyridinato-N,C\(^2\)]\(\text{Ir}\), which goes by the acronym “FIrpic.” Since the operational stability of a device can often be the net result of a series of competing effects, it is typically instructive to try and reduce the number of variables under consideration for a given experiment. For an OLED, this can be accomplished by removing layers from the device structure to see the effect their omission has on the lifetime of the device. As a further simplification, one can go so far as to remove the “device” altogether and examine only the photostability of the host-guest emissive layer or further, the photostability of a neat film of the guest material. The path selected for this study of FIrpic involved examining first the operational lifetime of a completed device structure (to obtain a calibration point), and then continuing the study by examining the photostability of FIrpic in neat film. Then we examined the blue PHOLED material and the HBL.
3.1.1 Photophysical Degradation

Photophysical degradation of emissive phosphors was instituted as a primary screening method for determining the stability of dopants, as well as the stability of dopant/host systems. The principle of measuring photophysical degradation is that by observing the decrease in luminance of a film consisting of the dopant and host due to steady state excitation by a pump laser, one can infer the importance of excitons in the materials degradation process. That is, only neutral excited states are produced on optical excitation. Hence, if there is a loss of luminance over time incurred simply by optical pumping, we can eliminate, or at least ignore to first order, the role that charge plays in reducing system stability. This method, developed at Princeton University and then transferred during the program to Universal Display Corporation, was applied primarily to the study of blue phosphors such as Flrpic which are known to result in blue emitting PHOLEDs with only modest stabilities (100-1000 hours). An example decay curve for the luminescence of Flrpic due to optical pumping is shown in Figure 2.

![Photophysical decay of Flrpic](image)

**Figure 2:** Photophysical decay of Flrpic
One generally observes that the operational lifetime of an OLED depends on the level of excitation (whether optical or electrical) to which the device is subjected. For the purposes of this study, the lifetime is defined as the point at which the initial device (or film) luminescence drops to one-half of its starting value. The structure used to examine the device operating lifetime under electrical excitation consisted of a 10-nm-thick copper phthalocyanine (CuPc) hole injection layer, a 30-nm-thick 4-4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (α-NPD) HTL, a 30-nm-thick emissive layer consisting of 6% Flrpic (by weight) codeposited with either mCP (N,N'-dicarbazolyl-3,5-benzene), tCP (1,3,5-tri-(N-carbazolyl)benzene) or CBP (N,N'-dicarbazolyl-4-4'-biphenyl), followed finally by a 40-nm-thick ETL consisting of 4-biphenyloxolato aluminum(III)bis(2-methyl-8-quinolinato)4-phenylphenolate (BA1q). These devices were packaged with desiccant using a ultraviolet (UV)-curable epoxy, and then excited with a current density sufficient to generate a lumincance of 100 cd/m² in the forward viewing direction. The lifetime does not vary significantly between all three devices (mCP:[123±12 hours], tCP:[190±12 hours]), CBP:[122±12 hours]), suggesting that the choice of host (at least between mCP, tCP and CBP) does not significantly affect overall device lifetime. This came as a sort of surprise as the authors expected the devices employing mCP and tCP as hosts to exhibit improved lifetimes as a result of improved energy transfer between mCP or tCP and Flrpic. As has been previously reported, transfer between the CBP and Flrpic triplet energy levels is strongly endothermic in nature, leaving the transfer mechanism very susceptible to trap states caused by defects or impurities introduced into the device during growth and processing. In comparison, devices based on mCP and tCP are exothermic, meaning the energy transfer from the host triplet energy level to the Flrpic triplet energy level is very favorable and efficient, presumably leading to a reduced sensitivity to trap states, allowing one to speculate that such devices should have improved lifetimes. The fact that this is not the case suggests that the poor reliability of devices based on Flrpic is not rooted in the efficiency of host-guest energy transfer and could instead be intrinsic to the chosen device structures or, to Flrpic itself.

Since investigations into device lifetime under electrical excitation suggested that Flrpic itself could be the source of poor overall device reliability, the next phase of this study was to focus on the photophysical stability of Flrpic in neat film. Films of Flrpic were grown on quartz and excited using a filtered mercury lamp (with wavelength about 366 nm). Characteristic photoluminescence (PL) from the film was collected with a Si-photodetector while spectra were collected using a fiber-coupled spectrometer. All experiments were performed with unpackaged films, enclosed in a vacuum tube pumped to a base pressure of about 10⁻⁷ Torr. The results of two of these experiments, for an initial lumincance of 200 cd/m² and 400 cd/m² are depicted in Figure 2. A clear dependence on initial luminescence is observed, with the film excited at 200 cd/m² (20 hours) having a lifetime 5-6 times greater than the film excited at 400 cd/m² (110 hours). Interesting to note is the fact that the lifetime under optical excitation (200 cd/m² photoluminescence) is on the same order as the lifetime under electrical excitation (100 cd/m² electroluminescence), which suggests that the stability of the film is increased under optical excitation. These results indicate that there may be intrinsic stability problems associated with the device structure previously discussed and possibly as well with the excitation of the molecule electrically versus optically.
In an attempt to better understand the results of the photodegradation experiments performed on Flrpic, the absorption and photoluminescence spectra of the tested sample were examined before and after testing. One would in general expect that if chemical bond breaking (for instance) was the source of film degradation, the accompanying absorption spectrum should change significantly (likely a decrease in absorption or, a shift in absorption to a different portion of the spectrum). In Figure 3, one notes that no such change in absorption (or photoluminescence shape for that matter) is observed. This result is very interesting as it suggests that molecules of Flrpic may not be destroyed during the photodegradation study. This data also suggests that the study may simply be introducing non-radiative, exciton quenching sites into the film which serve to reduce the overall photoluminescence efficiency of the film. We propose that such non-radiative quenching centers could actually be formed by the presence of oxygen in the film, either incorporated during growth, or leaked into the system during testing.

The sensitivity of the photoluminescence efficiency of cyclometallated Ir(III) complexes to oxygen, specifically triplet oxygen is well documented in solution. We carried out similar crude experiments involving the degassing of thin films of Flrpic with dry nitrogen and observed increases in film photoluminescence efficiency of more than 25% (depending on degassing pressure), presumably resulting from the displacement of oxygen from the film by the dry nitrogen, reducing any quenching effect the presence of oxygen may have on the luminescent properties of the film. This observed effect is reversible, meaning if the film is again permitted to sit undisturbed in room air, the photoluminescence from the sample is reduced, and then under flow of dry nitrogen, the photoluminescence again increases. It is conceivable that a similar effect could be present in our studies of the photodegradation of Flrpic, suggesting that the degradation in Flrpic may be partially reversible.

In summary, the primary focus of this study was an attempt to isolate the various causes of degradation in the cyclometallated Ir(III) complex Flrpic. It was determined that the overall device lifetime is the net result of intrinsic instabilities in the chosen device structure as well as intrinsic instabilities in Flrpic itself. Specifically, we investigated these instabilities in Flrpic by examining the photodegradation of Flrpic under intense illumination. Based on our preliminary findings, we suspect that the presence of oxygen is a likely culprit for the short lifetime of Flrpic under optical excitation. We further postulate that oxygen is likely playing a significant role in the degradation of devices which employ Flrpic as an emissive material. Experiments examining the photoluminescent lifetime as a function of the oxygen partial pressure in the testing atmosphere should help to clarify and confirm this theory.
Figure 3: Flrpic spectra taken both prior to and following aging studies.
3.1.2 Lifetime

Long operational stability of blue OLEDs presents a particularly difficult problem to solve. In both fluorescent and phosphorescent OLEDs, blue emitters have dramatically shorter lifetimes than red and green devices. The problem is most severe in both triplet emitting devices and in polymers. We addressed this problem during the course of the program from a fundamental as well as “new chemistry” viewpoint. Specifically, blue triplet emitters have the problem of requiring energy transfer from a fluorescent host. Hence, an excess 0.7 to 1 eV exchange of energy is required to excite the host. At the already high energies of blue emission, this additional charge can result in accelerated degradation of the host. Hence, in our work, we have developed a new approach to blue emission: that of embedding the dopant directly in a “passive” ultrawide-energy gap host (UGH) series of compounds. Here, the blue phosphor (Flr6, etc) is directly excited by charge injection from the HBL and the HTL sides of the structure. Furthermore, the phosphor is responsible for charge conduction. The only purpose of the host is to “hold the dopant molecules in place,” separated from each other such that concentration quenching is avoided. Using this method, 12% external quantum efficiencies are obtained for deep blue emitting devices. We have described this work in more detail in R. J. Holmes, et al. Appl. Phys. Lett., 83, 3818 (2003).

In conventional energy transfer systems there also are problems in the energetics of blue emission that impact device lifetime. That is, it is difficult to effect energy transfer from host to guest due to the very high triplet and singlet energies of the phosphor. Hence, in the first demonstrations of blue electrophosphorescence, the host-guest transfer process occurred by endothermic energy transfer, whereby the host energy was slightly less than the guest triplet energy. Impurities present in the host matrix thereby present a robust mechanism for energy loss and potentially lower device operational stability. Hence, during this program we developed large energy gap hosts, such as mCP, demonstrating to our knowledge the first exothermic energy transfer to occur in a blue emitting phosphor OLED. The guest in this case was Flpic, and the efficiency of the blue device was significantly improved from that of the endothermic pair employing 4,4’-bis(N-carbazolyl)biphenyl (CBP) as a host. We have fully described this work in R. J. Holmes, et al., Appl. Phys. Lett., 82, 2422 (2003).

Finally, by continued improvement in the fabrication processes and purity of the source materials, during this program we were successful in vastly improving the reliability of red, green and blue PHOLEDs. Currently the blue lifetime stands at 1000 hours, green at 50,000 hours, and red at 50,000 hours when normalized to an initial display luminance of 100 cd/m². Indeed, the red and green PHOLED lifetimes are completely compatible with the most stringent demands of display lifetime, while the blue remains inadequate, with improvements of a factor of 10 still required. We continue, after the close of the program, to investigate the fundamental energetic limitations to blue PHOLED lifetime, and continue to expand our class of compounds that may lead to longer lived blue electrophosphorescent devices. We have provided a snap shot of PHOLED reliability at the end of this program in R. C. Kwong, et al. Appl. Phys. Lett., 81, 162 (2002).
3.1.3 Hole Blocking Layer (HBL)
We also investigated the operational lifetime limitations presented by the HBL. We found that the morphological instabilities of bathocuproine (BCP) were one of the predominant mechanisms leading to a reduction in operating lifetime of high efficiency PHOLEDs. Systematic studies indicated that doping of the HBL with a higher glass transition impurity could lead to improved morphological stability. This was an important finding, as it allowed us to employ an HBL that could provide high efficiency, and at the same time high PHOLED stability. In our case, we doped BCP with BAlq, an alternative hole blocker that gives high stability at reduced efficiency. This work has resulted in a patent disclosure, listed in Appendix A, and full details of our results are presented in B. W. D’Andrade, et al., *Appl. Phys. Lett.*, 83, 3858 (2003).
3.2 Extrinsic Degradation of OLEDs

Extrinsic degradation of OLEDs is typically manifested in the growth of dark spots. The growth of these dark spots is tied to the environment that the devices are run in. Atmospheric exposure accelerates the growth of dark spots significantly.

We initially used atomic force microscopy (AFM) and optical microscopy to study the growth of dark spots in OLEDs in a collaborative effort between the groups at USC, U. Texas, and Princeton U (see Section 3.3). In order to be used in these studies the OLEDs needed to be transparent to obtain good registry between the AFM and optical images. The devices used for this study had Mg-Ag/ITO cathodes. From these devices we were able to draw a number of conclusions. We found that electroluminescent (EL) dark spots in OLEDs originate as non-conductive areas at the metal/organic interface, and rapidly grow as a result of atmospheric exposure. The dark spots are attributed to regions of poor electron injection formed by local oxidation. Continuous diffusion of oxygen and water into the device leads to growth of the oxidized region of the cathode, radially from the central defect. Significant structural changes in the cathodes occur well after initial formation and growth of the EL dark spots takes place. In contrast to the growth of dark spots, bubble formation was found to be enhanced at high current densities.

The next step of this study, conducted at USC, was to ascertain what factors are most important in determining the rate of growth of dark spots. If one can retard the growth of dark spots, the packaging requirements would be far less than for standard devices. For this work we needed an efficient method to evaluate the distribution of dark spots and their growth rate as a function of the environment, materials, device architecture, et cetera. The system shown in Figure 4 was built for this study. The environmental chamber was built of plexiglass. The OLED was placed inside the chamber and run. The digital camera sat outside the chamber and recorded the image of the degrading device as the dark spots grew. From the digital camera images, we determined the growth rate of the dark spots. The chamber was fitted with a humidity controller that controlled the relative humidity between 7 and 100% with an accuracy of ±2%. Using mass flow controllers the oxygen level was to be varied between 0 and 100%. This allowed us to independently vary the oxygen and water levels in the atmosphere and study their effects on dark spot growth independently. One may think that the lowest level of water and oxygen in the atmosphere would have been desirable for these studies, but this was not the case. If we had held the water and oxygen levels at very low levels we would have packaged devices and would not have been able to study dark spot growth easily. Our goal was to be able to monitor dark spot growth and collect all of the data that needed in a few hours. That way we could readily monitor a wide range of devices under a wide range of different conditions. We, thus, determined the effect of water and oxygen on the growth rate, and the best conditions for accelerating dark spot growth to a rate readily measured in a few hours of device operation.

The images shown in Figure 5 were taken of a standard OLED with a thin-layer structure as follows: [ITO/NPD(400Å)/Alq3(500Å)/LiF(10Å)/Al(1000Å)]. The device was operated at 80% relative humidity, under nitrogen. The device was run at a constant current, and the images shown are for t = 0 and t = 160 min. Images were taken at 20 minute intervals. The line scans of
one of the dark spots are shown to the right of the images. By plotting the width of the dark spot versus time we can get the rate of dark spot growth. This plot is shown in Figure 6 for this device, as well as for other devices. The linearity of these plots is quite good leading an accurate estimation of the dark spot growth rate. Both lithium fluoride/aluminum (LiF/Al) and magnesium-silver (Mg-Ag) cathode give the same rate of dark spot growth (0.28 μm/min) at 80% relative humidity and a lower rate (0.16 and 0.11 μm/min for LiF/Al and Mg-Ag cathodes respectively) as the humidity is decreased to 30%. This is consistent with the picture that water significantly accelerates dark spot growth. It is interesting that the rate of dark spot growth appears to be independent of the cathode material. These measurements have only been made for a few dark spots for each device at this point. We need to extend out analysis to a statistically significant number of dark spots. In addition, we need to analyze the dark spot density as a function of the humidity and oxygen levels.

Our original hypothesis for what caused dark spot growth in vacuum deposited OLEDs was oxidation of the ETL/cathode interface. If that were the case, one would expect the dark spot growth rate to be affected by the identity of the ETL material. In order to determine if ETL composition affected dark spot growth we prepared four different devices, with different materials at the ETL/cathode interface. The general device structure was ITO/NPD (400 Å)/Alq3 (400 Å)/EIL (100 Å)/Mg-Ag, where EIL = electron injecting layer, which was varied amongst Alq3 (reference), C60, BCP (bathocuprine), and Flrpic (phosphorescent dopant). The growth rate of the dark spots is shown in Figure 7. The graph to the left shows the total number of dark pixels in the digital image and the right shows the normalized total dark area.

Power Supply

Environmental Chamber

Humidity Controller

Digital Camera

OLED

Optical Microscope

Figure 4: Controlled environment chamber
Figure 5: Initial and final images of a device during degradation. The line scans are shown at 20 min. intervals.

Figure 6: Dark spot growth rates.
Figure 7: Growth rates of dark pixels (left) and dark area (right).

These data were compiled from 150 digital images. The EIL clearly affects the rate of growth of the dark spots in these devices. Flrpic is a well known blue emissive dopant in phosphorescent OLEDs. It has also been used as an electron transporting and injecting layer in OLEDs. While the use of Flrpic leads to efficient OLEDs, it significantly enhances the growth rate of dark spots. Both BCP and C_{60} interface layers apparently give markedly slower dark spot growth than the reference device, however, the BCP data is misleading. The BCP devices have darks spots grow by forming halos first and then expanding. Halo growth does not occur for the C_{60} based devices. The use of C_{60} as an EIL has not been reported previously. C_{60} is an efficient EIL for both retarding dark spot growth and efficiently injecting electrons from the Mg-Ag cathode and Alq3. We have examined the C_{60} thickness dependence for dark spot growth in these devices, Figure 8. The most efficient device for retarding dark spots has a 100 Å C_{60} layer. The most important conclusion to take away from this data is that the organic/cathode interface is very important in controlling dark spot growth. This supports our original hypothesis that oxidation at this interface is the principal cause of dark spot growth.
Figure 8: C₆₀ thickness dependence for dark spot growth in devices.

3.3 Singlet Oxygen Generation by Phosphor Dopants

The chemistry of cyclometallated Ir(III) complexes has received a great deal of attention recently. These complexes have proven to be very efficient emissive dopants in molecular and polymeric light emitting diodes. While studying the photophysical properties of these complexes, it was noticed that the quantum efficiencies, φ, and triplet lifetimes, τ, are severely reduced by oxygen, only giving high values (φ > 0.5 and τ > 2 μs) for rigorously degassed samples. This observation prompted us to investigate these complexes as potential singlet oxygen (¹O₂) sensitizers, as singlet oxygen formation is a likely quenching process. We now report that a variety of bis-cyclometalated Ir(III) complexes are indeed useful photosensitizers for the production of ¹O₂, with generally high quantum efficiencies and small concomitant physical quenching of singlet oxygen.


The Ir(III) complexes employed in this $^1$O$_2$ generation study are depicted in Figure 9. These complexes were prepared by literature procedures.$^3$ The lowest energy ( emissive) excited state of these complexes is a mixture of metal-ligand charge transfer (MLCT) and $^3(\pi-\pi^*)$ states,$^{1(a)}$ composed principally of C$^\wedge$N ligand orbitals, with the \( \beta \)-diketone ligand (Figure 6, L$^\wedge$X = D) acting as an ancillary ligand. Stern-Volmer analysis shows that phosphorescence from these complexes is efficiently quenched by triplet oxygen, at near diffusion controlled rates (Table 1).

![Diagram of complexes](image)

**Figure 9:** Structures of phosphor dopants used in $^1$O$_2$ generation study.

Oxygen quenching of the photoexcited Ir complexes does involve the formation of $^1$O$_2$, as all of the Ir complexes studied here proved to be excellent singlet oxygen sensitizers. The quantum yields for $^1$O$_2$ production ($\Phi_A$) were obtained by measuring the intensity of the $^1$O$_2$ luminescence signal ($\lambda_{max} = 1268$ nm) and are listed in Table 1. Measurements were taken with 355 and 532 nm excitation, in air-saturated solutions. Triplet-triplet (T-T) annihilation was negligible at these concentrations, as evidenced by the fact that the $^1$O$_2$ intensity does not decrease as the sensitizer concentration is increased (see Figure 10), as it would if T-T annihilation were depleting the excited sensitizer. The $^1$O$_2$ quantum yields are very large and near unity for all of the \( \beta \)-diketone complexes examined here. The $\Phi_A$ values are high for both ligand based excitation (355 nm) and direct excitation of the lowest energy excited state (MLCT+$^3$LC) at 532 nm.

Table 1: Quantum yields for singlet oxygen generation ($\Phi_a$) with 355 or 532 nm excitation ($\lambda$), rate constants for oxygen quenching of the phosphor excited state, determined by Stern-Volmer analysis ($k_{sv}$), and rate constants for singlet oxygen quenching by the Ir complex sensitizer ($k_q(\text{O}_2)$).

<table>
<thead>
<tr>
<th>Sensitizer *</th>
<th>$\lambda$ (nm)</th>
<th>$\Phi_a$</th>
<th>$k_{sv}$ ($10^9$ M$^{-1}$ s$^{-1}$)</th>
<th>$k_q(\text{O}_2)$ ($10^4$ M$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSN</td>
<td>355</td>
<td>0.59±0.07</td>
<td></td>
<td>6.3 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>532</td>
<td>0.89±0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BSN*</td>
<td>355</td>
<td>0.60±0.06</td>
<td>2.9 ± 0.1</td>
<td>4.0 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>532</td>
<td>0.77±0.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PQ</td>
<td>355</td>
<td>0.62±0.05</td>
<td>7.2 ± 0.3</td>
<td>1.0 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>532</td>
<td>0.89±0.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BT</td>
<td>355</td>
<td>0.86±0.07</td>
<td>5.9 ± 0.6</td>
<td>0.5 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>532</td>
<td>1.00±0.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BSN-G</td>
<td>355</td>
<td>0.54±0.02</td>
<td></td>
<td>1.7 = 0.5</td>
</tr>
<tr>
<td></td>
<td>532</td>
<td>0.81±0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BT-G</td>
<td>355</td>
<td>0.72±0.08</td>
<td>3.5±0.2</td>
<td>2.6 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>532</td>
<td>0.77±0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BT-py</td>
<td>355</td>
<td>0.95±0.09</td>
<td>None detected</td>
<td></td>
</tr>
<tr>
<td></td>
<td>532</td>
<td>0.97±0.14</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\* a: Measurements were made in C$_6$H$_5$ solvent. b: The references for quantum yield measurements were C$_{60}$ (0.76), TPP (0.62) and Perinaphthenone (0.95), at 355 nm and TPP (0.62) at 532 nm.

Other Ir complexes are known to form $^1\text{O}_2$ upon optical excitation (e.g. [Ir(bpy)$_3$]$^{3+}$ and [Ir(phen)$_3$]$^{3+}$), however, they are also very efficiently $^1\text{O}_2$ quenchers. Large $^1\text{O}_2$ quenching rates would severely limit potential applications of the bis-cyclometallated Ir complexes as photosensitizers. We therefore determined $^1\text{O}_2$ quenching rates for all of the Ir complexes reported here. These quenching rate constants [$k_q(\text{O}_2)$] are given in Table 1. The quenching rates for all of the complexes with $\beta$-diketonate ancillary ligand were found to be small, ranging from $(10 \pm 2) \times 10^5$ M$^{-1}$sec$^{-1}$ for PQ to $(6 \pm 0.2) \times 10^6$ M$^{-1}$sec$^{-1}$ for Iridium (III) bis(2-(1-naphthyl)benzothiazolato-N,C$^2$) acetylacetonate (BSN). These $^1\text{O}_2$ quenching rates are roughly three orders of magnitude slower than the phosphorescence quenching rates ($k_{sv}$), consistent with the high $\Phi_a$ values observed here. For the Iridium (III) bis(2-phenyl benzothiazolato-N,C$^2$) acetylacetonate (BT) complex the singlet oxygen quenching rate is in fact smaller than those of many standard singlet oxygen sensitizers such as 5,10,15,20-tetraphenylporphyrin (TPP) [$k_q = (6\pm2) \times 10^7$ M$^{-1}$s$^{-1}$], while the quantum yield is near unity. Even though the three

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cyclometalling ligands used here (A, B and C in Figure 6) give rise to very different absorption and emission energies,\(^1\) their efficiencies for singlet oxygen production are very similar. Based on spectroscopic measurements for these four complexes,\(^1\) the orbital make-up for the triplet excited states are similar, and largely ligand based (i.e. \(\pi-\pi^*\)). Hence, it is not too surprising that they have similar efficiencies for \(^1\)O\(_2\) generation. The slight decrease of \(\Phi_\Delta\) of BSN at 532 nm relative to BSN\(^*\) at 532 nm appears to be out of the error range and may be due to a steric blocking effect.

All of the phosphors are photostable under aerobic conditions, as we have not detected significant decomposition for irradiation times of up to 60 minutes. Thus, we expect that \(^1\)O\(_2\) sensitization may only marginally affect the lifetimes of light emitting diodes doped with these Ir based emitters. Moreover, OLEDs must be packaged under anaerobic conditions to maintain long lifetime and prevent dark spot growth, which will prevent oxygen from reaching the sensitizer.

**Figure 10:** \(^1\)O\(_2\) luminescence intensity (arbitrary units) vs. optical density at 355 nm for BT, BT-py and TPP.
3.4 Overcoating OLEDs to Retard Dark Spot Growth

Many, if not all, of the dark spots are the result of pinholes and particle related defects in the cathode. These cathode defects allow the ambient water and oxygen to access the cathode/organic interface, leading to dark spot growth. Changing the organic materials in contact with the cathode can affect the rate of dark spot growth, as discussed above, but we chose to investigate an alternate approach. If the cathode defects could be filled, the rate of water and air diffusion into the device could be reduced markedly. We have examined several coating materials to see if a simple overcoating affects the dark spot growth rate. A simple device was chosen for this study (ITO/Cupc/NPD/Alq3/LiF-Al). Each device was coated with a different material and the growth of dark spots examined. Some of the overcoating materials we examined actually increased the rate of dark spot growth. The coatings included metal eutectic mixtures (InGa and InGaSn) and silicone. Other materials lead to marked decreases in dark spot growth rates. The relative dark spot growth rates are shown in Figure 11. The best results were obtained for carbon paste, which consisted of a mixture of silicone bath oil and carbon black.

![Graph showing dark spot growth rates for various OLED overcoatings.](image_url)

**Figure 11:** Relative dark spot growth rates for various OLED overcoatings.
3.5 NSOM Studies of OLED Failure

Near Field Scanning Optical Microscopy (NSOM) studies were used to investigate TOLED device failure in phosphorescence based OLEDs. The focus of this work is the investigation of dark spot formation and other aspects of device failure under a variety of conditions involving aging with or without current passing through the device and in the presence and/or absence of exposure to an ambient atmosphere. The results have clearly shown that ambient exposure is a major causative factor in dark spots. In addition, the results demonstrate that dark spots can be induced by physical damage of the electrode surface by indentation with a scanning probe microscopy tip. Most importantly, the results show, more than any other study, that initially formed dark spots are predominantly due to electrode damage rather than damage of the underlying organic emitting layer, which are surprisingly undamaged even at the interface with the electrode. These investigations have also explored physical damage to the TOLED structure that occurs late in the dark spot formation process, as the resistive heating of the device causes melting and eventually gas formation. The work on this project was completed by late 2002.

The model TOLED device structure that was investigated is shown in Figure 12. The NSOM tip was scanned over the ITO cathode. The initial morphology of the device was extremely smooth with less than 1 nm of root-mean-square (RMS) roughness. The NSOM induced phosphorescence was highly uniform on the 100 nm scale of the NSOM technique, and the phosphorescent spectrum was identical to that observed in the far field. A topographic image of the TOLED device is shown in Figure 13. Figure 14 shows an NSOM experiment on a dark spot formed by damage of the electrode induced by an electronic near-field scanning optical microscope (ENSOM) tip. Note that the dark OLED spot appears as a bright spot in the NSOM image. This is apparently due to less quenching of the phosphorescence by the cathode in the region of a dark spot. This is an interesting observation that will be explored in greater detail in future experiments since it opens the door to improved OLED efficiency. Figure 15 reveals the extreme device damage that occurs when darks spots continue to develop. This damage is probably due to resistive heating of the device. Under these conditions, the organic is heated beyond its sublimation point, allowing for organics to boil out of pin holes in the top of the electrode. This process causes volcano-like specks on the top electrode and a rippling of the entire OLED surface.

Another interesting observation in this work has been the discovery that the top electrode protects the organic layer from photo-oxidation when the device is exposed to intense radiation in an ambient atmosphere. This is probably a key factor in favoring electrode structure over organic layer destruction during the dark spot formation process.

Work is under way to prepare publications on the NSOM studies of device failure and on the use of electrically biased ENSOM tips to investigate TOLED device operation.
TOLED: Transparent Organic LED

Figure 12: TOLED structure.

Figure 13: Topographic image of the TOLED device.
Figure 14: NSOM experiment on dark spot formed by damage of electrode induced by an NSOM tip.

Figure 15: Extreme device damage that occurs when dark spots continue to develop.
3.6 Electrophosphorescent Device Stability

Universal Display Corporation accomplished an operational device stability study of electrophosphorescent display devices as a part of the presently reported effort. A full review of this device stability work is available elsewhere (see Kwong et al. paper listed in Appendix B).

All devices were fabricated by high vacuum (<10^{-7} Torr) thermal evaporation and are illustrated schematically in Figure 1(d). For the PHOLEDs described here that emit from the substrate surface (referred to as bottom emission), the anode electrode is ~1200 Å of ITO. For the top emission devices, the anode is comprised of a reflective stack of 160 Å ITO on silver (Ag) with a glass substrate. The organic stack is comprised of 100-200 Å thick of copper CuPc as HIL, 300-500 Å of α-NPD as the HTL, 300 Å of CBP doped with 4-12 wt% of the phosphorescent emitter as the EML, 100-150 Å of BAlq as the EML-ETL interface layer, and 300-500 Å of Alq3 as the ETL. The cathode consisted of 10 Å of LiF followed by 1,000 Å of Al for bottom-emission devices. The cathode for the top-emitting PHOLEDs consisted of 200 Å Ca deposited by vacuum thermal evaporation, followed by 800 Å ITO by sputter deposition. For the transparent PHOLEDs, a compound cathode of 100 Å of MgAg (10:1 weight ratio of Mg to Ag) followed by 800 Å of sputtered ITO was used. The active area of all the devices was 5 mm^2. All devices, unless otherwise noted, were encapsulated with a glass lid sealed with an epoxy resin in a nitrogen glove box (<1 ppm of H_2O and O_2) immediately after fabrication, and a moisture getter was incorporated inside the package.

The reflectivities and transmissivities of various anodes and cathodes were measured with a Varian Cary 100 UV-Vis spectrophotometer. The electroluminescence was measured with a Photo Research PR705 spectrophotometer, and the current-voltage-luminance (J-V-L) characteristics were measured with a Keithley 236 source measure unit and a calibrated Si photodiode. Device operational stabilities, measured on several identically fabricated devices, were determined to be within ±5%. All lifetests were conducted in continuous direct current (DC) drive at room temperature without any initial burn-in periods. Half-life, T_{1/2}, is defined as the time for the luminance to decay to 50% of the initial luminance (i.e., 0.5L_0).

3.6.1 Bottom-Emission PHOLEDs on Glass Substrates

Green PHOLED based on fac-tris(2-phenylpyridine)iridium [Ir(ppy)_3] as the phosphorescent dopant give a T_{1/2} of 10,000 hours at L_0=500 cd/m^2. In our recent effort to optimize the device, the stability of the Ir(ppy)_3 devices projects to T_{1/2}>10,000 hours at L_0=600 cd/m^2 (Figure 16). The initial luminous efficiency (LE) was 23.0 cd/A, corresponding to an external quantum efficiency (η_{ext}) of 6.5%. The drive current density of this device was 2.62 mA/cm^2 at an initial voltage of 7.6 V. After 1,000 and 5,000 hours of operation, the device luminance dropped to 88.2% and 67.4% of the initial value respectively. The Commission Internationale de l'Eclairage (CIE) coordinate of the device was (0.30, 0.63) and was essentially unchanged during lifetest. Extrapolating the lifetime at L_0=600 cd/m^2, this Ir(ppy)_3 PHOLED has T_{1/2}>10,000 hours.
In the more recent work on improving the efficiency and stability for green PHOLEDs, we have developed a new material system with essentially the same spectral characteristics of Ir(ppy)3. This new system, Dopant Green 2, has brought further improvement in both efficiency and lifetime in the green PHOLED family. At 600 cd/m², the initial efficiency of this green PHOLED device was 29.3 cd/A ($\eta_{\text{ext}} = 7.8\%$). The CIE coordinate was (0.31, 0.64), indistinguishable from the Ir(ppy)3 device by the human eye. At the same initial luminance as the Ir(ppy)3 device, i.e., $L_0 = 600$ cd/m², it can be seen that the Green 2 device is more stable (Figure 16). The drive current was 2.05 mA/cm² at an initial voltage of 8.0 V. After 1,000 hours of operation, the luminance dropped to 93.5% of its initial value, compared to 88.2% of the Ir(ppy)3 device. We expect its $T_{1/2}$ to be $\sim$15,000 hours.
Due to the low photopic response of the human eye to red, and the relatively large contribution of the red in brightness for a balanced white color, the red component constitutes a large portion of the total power consumption for a full color display. It is therefore critical to develop highly efficient red devices with high stabilities. We previously reported a 17.6 cd/A orange-red PHOLED based on iridium(III) bis(2-phenylquinolyl-N,C\textsuperscript{2})acetylacetonate [PQ\textsubscript{2}Ir(acac)] as the phosphorescent emitter to have a T\textsubscript{1/2}>5,000 hours at L\textsubscript{0}=300 cd/m\textsuperscript{2}.

We report here more recent results on red PHOLEDs using dopants we refer to as Red 1, Red 2 and Red 3. The efficiencies of these red PHOLEDs are very high. The CIE coordinates, independent of current density, are (0.61, 0.38), (0.61, 0.39), and (0.65, 0.35), respectively. Obviously, Red 1 and Red 2 are orange-red, and Red 3 is red emitting. The luminous efficiency for devices fabricated using these three red PHOLEDs is plotted against the luminance in Figure 17. The efficiencies do not suffer from significant roll-off as observed in some platinum porphyrin red devices. One explanation is the shorter triplet exciton lifetime of the new red phosphorescent dopants (typically <5 μs), leading to reduced T-T exciton annihilation, compared to platinum porphyrins (typically >30 μs). But more importantly, the overall device composition such as the type and thickness of the charge transporting materials, electrode materials, emitter doping concentrations, etc., critically affects the efficiency roll-off, not just the exciton lifetime alone. This hypothesis is well supported by the fact that certain fluorescent small molecule and polymer OLEDs, with very short-lived singlet exciton (typically <10 ns), show the same degree of, or even higher, efficiency roll-off compared to phosphorescent OLEDs. The maximum efficiencies of the Red 1, Red 2 and Red 3 device are 23.9 cd/A at 410 cd/m\textsuperscript{2}, 18.1 cd/A at 66 cd/m\textsuperscript{2}, and 12.8 cd/A at 175 cd/m\textsuperscript{2}, respectively. At 300 cd/m\textsuperscript{2}, a typical display luminance for the red component in full color displays, the efficiencies are 23.9 cd/A, 17.0 cd/A, and 12.7 cd/A, respectively. Even at 10,000 cd/m\textsuperscript{2}, high efficiencies of 18.6 cd/A, 9.3 cd/A, and 8.0 cd/A are retained. The performance of these new red materials is summarized in Table 2. The external quantum efficiencies are greater than 10%. The relatively lower luminous efficiency of the Red 3 device is only due to the deeper red color compared to the orange-red color of the Red 1 and Red 2 devices. The outstanding performance at both low and high current drives enables their use in both active and passive modes in displays.

The operational stability of the red devices is very high. The initial luminance for stability testing was selected to be 300 cd/m\textsuperscript{2} for all three devices. In Figure 18, the normalized luminance is plotted against the operational time. The drive current was 1.26, 1.80, and 2.36 mA/cm\textsuperscript{2} at initial voltages of 8.8, 8.5, and 7.9 V for the Red 1, Red 2 and Red 3 devices, respectively. After 1,000 hours of continuous operation, the luminance was retained respectively at 92.5%, 99.4% and 93.3%. Again, the exact projection of the half-life at this point is difficult; however, in our experience, based on these lifetime trends, T\textsubscript{1/2}>15,000 hours.
Figure 17: Luminous efficiency vs luminance of the Red 1, Red 2, and Red 3 PHOLEDs.

Table 2: Performance summary of Red 1, Red 2, and Red 3 PHOLEDs; efficiency and lifetime are recorded at $L_0 = 300 \text{ cd/m}^2$.

<table>
<thead>
<tr>
<th>PHOLED</th>
<th>CIE</th>
<th>$\eta_{\text{ext}}$ (%)</th>
<th>LE (cd/A)</th>
<th>% retained at 1000 hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red 1</td>
<td>0.61, 0.38</td>
<td>13.6</td>
<td>23.9</td>
<td>94.6 at 470 hrs</td>
</tr>
<tr>
<td>Red 2</td>
<td>0.61, 0.39</td>
<td>10.6</td>
<td>16.7</td>
<td>94.5</td>
</tr>
<tr>
<td>Red 3</td>
<td>0.65, 0.35</td>
<td>11.3</td>
<td>12.7</td>
<td>93.5</td>
</tr>
</tbody>
</table>
Figure 18: Lifetime of the Red 1 and Red 2, and Red 3 PHOLEDS at $L_0=300$ cd/m$^2$ (CIE coordinates of each device are in parentheses).
3.6.2 Transparent Top-Emitting PHOLEDs on Glass Substrates

Conventional OLEDs employ a bottom-emitting structure where the cathode is a reflective metal, the anode is a transparent ITO anode, and light is emitted through the anode and the glass substrate as illustrated in Figure 1(a). While this represents the most mature OLED technology, alternative electrode configurations are possible. Top-emitting OLEDs, with an opaque/reflective bottom anode and a transparent top cathode, as illustrated in Figure 1(c), have been demonstrated by Bulovic et al. in 1997. Top-emitting OLEDs are well suited in high-resolution active-matrix OLED displays where they are deposited over a planarized back-plane, thus increasing the aperture ratio over displays employing bottom-emitting OLEDs. Recently, our group has demonstrated that top-emitting OLEDs can be more efficient than corresponding bottom-emitting OLEDs due to favorable microcavity effects. Another possibility is to use a transparent cathode in conjunction with an ITO anode to make a fully transparent device as illustrated in Figure 4(c) with obvious applications in see-through displays, etc. In this section, we will review recent progress in top-emitting and transparent OLEDs which are enabled by the same transparent cathode technology.

All devices in this section used the Ir(ppy)$_3$ PHOLEO standard structure. The emission intensity of top-emitting OLEDs depends strongly on the top ITO layer thickness due to microcavity effects. Both experimental data and modeling indicate that 800Å is the optimal ITO thickness for these green phosphorescent top-emitting OLEDs. The current-voltage-luminance (J-V-L) characteristics of the top and bottom emitting OLEDs are plotted in Figure 19. The J-V curves of the top and bottom emission OLEDs are identical within measurement uncertainties, while the top emission OLED has a slightly higher luminous efficiency. At 10 mA/cm$^2$ the luminance efficiency is 20.3 cd/A for the bottom emission and 23.1 cd/A for the top emission OLED (through the cover glass), i.e., 15% higher. The transmissivity of glass/Ca (200 Å)/ITO (800 Å) is 62.8% at $\lambda = 515$ nm [the peak of Ir(ppy)$_3$ emission], much less than the transmissivity of 89.9% for the ITO coated glass. The reflectivity of the Ag/ITO anodes is 85.5% at $\lambda = 515$ nm, again less than that of the aluminum (Al) cathodes at 88.5%. Overall, the electrodes of the bottom emission OLEDs are more reflective/transmissive than those of the top emission ones. Therefore, the enhanced luminance in top emission OLEDs can only be attributed to the more favorable microcavity structure.

The J-V-L curve of the transparent OLED is also shown in Figure 19. The current density at a given bias voltage is lower than that of the top and bottom emission OLED because of the slightly thicker organic layer used and the lower electron injection from the MgAg/ITO cathode. At 10 mA/cm$^2$, the luminance efficiency is 16.4 cd/A which is based on the sum of the emission from both sides. Approximately 75% of the light is emitted through the ITO anode. The luminance efficiency is lower due to the low transmission of the MgAg/ITO cathode (55% at 515 nm).
Figure 19: Comparison of J-V-L curves of top-emitting, transparent, and bottom-emitting OLEDs (luminance measured through the cover glass).

The far-field photon radiation from these devices was measured directly with a PhotoResearch PR705 spectrophotometer. Due to the relative size of the devices and the focal spot of the spectrophotometer this measurement could be carried out reliably only up to a far-field angle of 60° from normal. Figure 20 shows the angular dependence of photon radiation for the top-emitting OLED (through the cover glass), the same top-emitting OLED corrected for the cover glass, and the corresponding bottom-emitting OLED. In accordance with our predictions, photon radiation is higher in these top-emitting OLEDs even uncorrected for the cover glass. There is only a weak angular dependence which indicates that the emission is approximately Lambertian in this angular range. Estimating the integrated photon flux by the formula $\Sigma I(\theta) \sin(\theta) \Delta \theta$, where $I(\theta)$ is the photon radiation at angle $\theta$, the uncorrected and corrected top emission devices were found to emit 4.2% and 20.8% more photons than the bottom emission OLED in the forward 120° cone, respectively.
Figure 20: Photon radiation vs far-field angle; all data was taken at $J = 10 \text{ mA/cm}^2$.

Figure 21 shows DC life-testing results of a typical long-lived bottom-emitting OLED and a transparent OLED with a MgAg/ITO based compound cathode. The initial luminance is 600 cd/m$^2$ for both devices. For the transparent OLED, it is the sum of the emission from both sides. The current density through the transparent OLED is slightly higher due to the lower external efficiency because of the absorption in the MgAg layer. The bottom-emitting OLED has a half-life of $\sim$10,000 hours, and the transparent OLED is projected to reach over 6,000 hours. The luminance degradation is observed to be Coulombic, i.e., solely dependant upon the aggregate charge flowing through the device ($J_{\text{OLED}} T_{\frac{1}{2}, \text{OLED}} \equiv J_{\text{TOLED}} T_{\frac{1}{2}, \text{TOLED}} \equiv \text{constant}$). This has been reported by other groups and indicates the absence of extrinsic decay mechanisms such as dark-spot formation.
2.6.3 Bottom Emission PHOLEDs on Flexible Plastic Substrates
Glass substrates do not allow exploitation of the flexibility of both polymeric and small molecule OLEDs to enable new light weight, rugged, flexible displays produced by roll to roll manufacturing. Plastic substrates, however, do allow for such displays. Examples of PHOLEDs grown on flexible substrates are shown in a previous Air Force Research Laboratory report. Although flexible FOLED displays on a plastic substrate have been demonstrated, conventional

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encapsulation techniques are ineffective due to moisture permeation through the substrate and long lifetimes had not been shown until recently. To enable a device lifetime of 10,000 hours, the maximum permeability of a substrate to the ingress of water can be estimated within an order of magnitude to be $5 \times 10^{-6}$ g/m$^2$/day. This is an estimated upper limit on the requirement for the substrate and does not take into account any degradation processes at the anode/organic interface or within the organic materials themselves that may be catalyzed by water. Typically, plastic materials have a water vapor permeation rate of $10^{-1}$ to $10^{-1}$ g/m$^2$/day at 25°C and are therefore inadequate for OLEDs. Furthermore, a leak rate below $10^{-2}$ g/m$^2$/day is difficult to achieve using inorganic barrier layers deposited at or near room temperature, due to pinholes and defects. The high surface roughness of commercially available plastic substrates exacerbates these problems.

Here we present PHOLEDs with extended operating lifetimes using a hybrid organic-inorganic multi-layer barrier coating on 175 μm thick heat stabilized polyethylene terephthalate (PET), demonstrating that suitably processed plastic substrates can be used to fabricate long-lived OLEDs. The composite barrier consists of alternating layers of polyacrylate films and an inorganic oxide. By repeating the alternating films, the polymer layers ‘decouple’ any defects in the oxide layers. This prevents the propagation of defects through the multilayer structure. The optical and barrier properties of the composite substrate can be tailored by varying the total number and thickness of the polymer and inorganic layers in the thin-film coating, yielding an engineered flexible substrate. The barrier-coated PET substrates exhibit moisture barrier performance below the limit of MOCON, Inc. detection instruments (5x10^{-3} g/m$^2$/day). More detailed measurements of permeation rate based on the corrosion of Ca are published elsewhere and indicate a permeation rate through the substrate and barriers estimated to be 4x10^{-6} g/m$^2$/day.

PHOLEDs were fabricated on the barrier coated flexible substrates to test the viability of using them to make long lived flexible displays. Onto the barrier were grown sequentially deposited layers of patterned ITO [160 nm] as the anode contact. All materials and fabrication steps were identical to the Ir(ppy)$_3$ based PHOLED described in the previous section.

The FOLED had a peak luminous efficiency of 17.5 cd/A ($\eta_{\text{ext}}=4.8\%$) at 600 cd/m$^2$. This is slightly lower than the same device on glass, primarily because of the lower transparency and light outcoupling efficiency due to the thicker ITO and the multilayer barrier coating on the plastic substrate. (Note: more recently, the barrier coated substrates have been further optimized to enable better light outcoupling from the substrate, and plastic substrate devices have shown efficiency comparable to that of glass substrate devices). The lifetime was measured at an initial luminance of 425 cd/m$^2$ at a current density of 2.5 mA/cm$^2$. Figure 22 shows a typical plot of normalized luminance versus time for this device. A device fabricated on glass with the same organic and metal layers as the FOLED and encapsulated using the same procedures (i.e., with glass lid) is also shown for comparison. It was driven at 2.6 mA/cm$^2$ ($L_0=600$ cd/m$^2$). After a brief initial rise in luminance during the first 24 hours of testing, the FOLED decays to 50% of its initial luminance in 3,800 hours, as compared to 10,000 hours for equivalent devices made on glass. At 3,800 hours the PHOLED on glass is at 69% of its initial luminance. Assuming lifetime is inversely proportional to drive current, these results correspond to a lifetime of 16,000 hours at

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*MOCON, Inc, 7500 Boone Ave. N., Minneapolis, MN 55428, (763) 493-6370, mocon@mocon.com.*
100 cd/m² for the encapsulated plastic device. The shorter lifetime for the devices on the barrier-coated plastic substrate may be partly due to the superior barrier properties of the glass substrates. However, we note that the epoxy exhibited poorer adhesion to the barrier-coated plastic than to the glass; indeed, after ~3,000 hours a high failure rate of the plastic package due to delamination of the lid was observed. Faster diffusion of moisture through the edge seal of the flexible plastic versus glass substrate could therefore contribute to the lifetime enhancement of the glass based pixels.

The same type of multilayer barrier structure used on the PET substrate can also be applied over the PHOLED as a hermetic encapsulant. In this truly flexible (substrate and encapsulation) configuration, the PHOLED is protected on all sides from moisture ingress. Furthermore, no edge seal or glass/metal lid is required, reducing package volume and materials cost. Preliminary results indicate that the lifetime of FOLEDs encapsulated using a multilayer barrier structure approaches that of similarly encapsulated PHOLEDs on glass.

![Graph showing lifetime comparison]

**Figure 22:** Lifetimes of Ir(ppy)_3 PHOLEDs on barrier coated PET (driven at 2.5 mA/cm²) and ITO coated glass (driven at 2.6 mA/cm²).
4. DISCUSSION AND CONCLUSIONS

This program has resulted in the establishment of new protocols in the understanding and improvement of OLED device reliability. During the course of this project, vast improvements in PHOLED reliability were demonstrated, with electrophosphorescent green and blue devices now meeting virtually all the demands of modern flat panel display applications. However, much further improvement is required to meet these demands for blue phosphors and fluorophores. Nevertheless, considerable fundamental progress in understanding degradation mechanisms in blue PHOLEDs, with their unique energetic properties, have been made. Finally, new direct observation methods have been developed for observing the evolution of dark spots in OLED cathodes. This work is based on the use of our proprietary transparent cathode technology in conjunction with near field scanning optical microscopy tools.

Inspection of transparent contacts employed the novel combination of NSOM and optical microscopy in conjunction with a TOLED. By microscopic observation of the development and growth of dark spots as a function of time under TOLED operation, we found that all dark spots are present upon device manufacture, and that these dark spots grow with time during operation. The dark spots are associated with dust particles on the substrate that disrupt the metal/organic interface, and leave fractures in the metal surface that permit the ingress of contaminants upon exposure to atmosphere. We have described this work in detail in an article by D. Kosolov, et al., J. Appl. Phys., 90, 3242 (2001).

Efficient and stable bottom/top emission and flexible PHOLEDs have been demonstrated. Enabled by new phosphorescent materials, bottom emission, long-lived green PHOLEDs showed efficiencies of $>$29 cd/A. Two orange-red and one red devices showed efficiencies of 23.9 cd/A, 17.0 cd/A, and 12.7 cd/A respectively. All these devices have lifetimes predicted to be $>$15,000 hours at display brightness. Even at higher brightness, these devices retain very high efficiencies, thus suitting not only active matrix but also passive matrix display operations.

We demonstrated that top-emitting OLEDs employing identical organic layers can be more efficient than conventional bottom-emitting devices due to favorable microcavity effects. Top-emitting OLEDs based on Ag/ITO anodes and Ca/ITO transparent compound cathodes emit 20.8% more photons in the forward 120° cone than corresponding bottom-emitting OLEDs. We also fabricated long-lived transparent OLEDs with MgAg/ITO cathodes which proved that the lifetime is not limited by the sputter deposition of ITO. We expect both types of OLEDs to enable a new generation of displays.

Operational stabilities of high-efficiency green and red electrophosphorescent bottom-emission devices with various emitting dopants were been studied. Operational lifetimes of 10,000 hours or more, operated at an initial brightness of 600 cd/m² and 300 cd/m² for green and red, respectively, are reported. Operational stabilities of top-emission electrophosphorescent devices and electrophosphorescent devices built on barrier coated plastic substrates have also been studied and show lifetimes $>$5,000 hours and $>$2,000 hours, respectively, under display level luminance conditions.
For devices on plastic substrates, in order to realize the barrier properties necessary to prevent degradation of FOLEDs, a novel non-conformal multilayered film was used that reduces the permeation rate of water vapor through a flexible substrate to less than $2 \times 10^{-6}$ g/m$^2$/day. Based on measurements of an epoxy sealed PHOLED package with a barrier coated PET substrate and glass lid, a $T_{1/2}$ of 3,800 hours from an initial luminance of 425 cd/m$^2$ was observed.

We also investigated the operational lifetime limitations presented by the HBL. We found that the morphological instabilities of bathocuproine (BCP) were one of the predominant mechanisms leading to a reduction in operating lifetime of high efficiency PHOLEDs. We doped BCP with BAlq, an alternative hole blocker that gives high stability at reduced efficiency. This work has resulted in a patent disclosure, listed in Appendix A, and full details of our results are presented in B. W. D’Andrade, et al., *Appl. Phys. Lett.*, 83, 3858 (2003).
5. RECOMMENDATIONS

The novel technique of studying OLED devices with a simultaneous combination of NSOM and optical microscopy in conjunction with a TOLED should become a routine technique and should be further improved to increase the pace of OLED research.

Much further improvement in blue phosphors and fluorophores is needed to meet product requirements for the blue phosphorescent material.

Top-emitting structures are more efficient than the traditional bottom-emitting structures due to a quantum cavity effect. This effect should be further developed to decrease the power and increase the reliability of OLEDs in applications.

Our results represent a critical first step in the realization of plastic-based OLEDs for flexible displays. Combined with a conformal encapsulation or lamination technology, which could be based on the same hybrid multilayer stack as used in the present reliability research, flexible and rollable display technology development has been enabled.

Further work should be done on the role of various layers of the OLED structure on the operational lifetime. This study focused primarily on the electrode interfaces and the HBL. These and other layers shown in Figures 1(a) and 1(b) need to be systematically investigated—both in terms of materials and structure.
6. SYMBOLS, ABBREVIATIONS, AND ACRONYMS

AFRL  Air Force Research Laboratory (in Dayton OH)
Al    Aluminum
Alq3  Tris(8-hydroxyquinolinate) aluminum, aka aluminum trisquinolate
       (electron transporting layer material; also, the emissive layer in original OLEDs)
AFM  Atomic force microscopy
AM    Active matrix (active element holds desired electrical signal for full frame time),
       (backplane substrate TFT array used to address AMOLED), (see passive matrix)
AMOLED  Active matrix organic light emitting display
Backplane  Electrical circuitry built on back substrate of a flat panel display to apply
           electrical representation of an image in a manner (driver-conditioned signals) that
           modulates/controls photonic emission from each picture element.
BAIrq  4-biphenyloxalato aluminum(III)bis(2-methyl-8-quinolinato)4-phenylphenolate,
       (hole blocking layer material)
Barrier Coating  Multiple alternating layers of polyacrylate films and an inorganic oxide
BCP   2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (hole blocking layer material),
       aka "bathocuproine"
Brightness  Psychological dimension in which visual stimuli are ordered continuously from
            light to dark which is correlated with light intensity
BSN   Iridium (III) bis(2-(1-naphthyl)benzothiazolato-N,C2') acetylacetonate
BSN*  Iridium (III) bis(2-(1-naphthyl)benzothiazolato-N,C2') 2,2,6,6-tetramethyl-3,5-
       heptane-dionate
BT    Iridium (III) bis(2-phenyl benzothiazolato-N,C2') acetylacetonate
btIr  A red phosphor based on Iridium
btPtIr  A red phosphor based on Iridium
ca. Calculated
CBP   N,N'-dicarbazolyl-4,4'-biphenyl (host material for emissive layer of device)
       4,4'-bis(N-carbazolyl)biphenyl (alternate chemical name)
Candella  Luminous intensity of a source emitting 540 GHz radiation at an intensity
          of 683\(^1\) w sr\(^{-1}\) in a given direction.
Cd    Candella
cd/m\(^2\)  Candella per square meter (standard unit of luminous intensity per unit area)
cd/A   Candella per Ampere (unit for measuring of luminance efficiency)
       (unit of energy conversion efficiency in current driven device)
CIE   Commission Internationale de l'Eclairage (standard color space coordinates)
cm\(^2\)/V-s  Unit of charge mobility (in semiconductor materials subjected to electric field)
CMOS  Complementary metal oxide semiconductor (power-conserving circuit design)
COTR  Contracting Officer’s Technical Representative
Cp\(^{5\times}\)  1,2,3,4,5-pentaphenylcyclopentadienyl radical
CRE   Color rendering index
CuPc  Copper phthalocyanine (hole injection layer material)
C\(^{3\times}\)N   mono-anionic cyclometallating ligand
DARPA Defense Advanced Research Projects Agency
DCM2  Red dye (a fluorescent material)
EBL  Electron blocking layer
EIL  Electron injection layer
EL  Electroluminescent

Electroluminescence
Luminescence resulting from application of electrical energy to a material

Electrophosphorescence
Luminescence caused by application of electrical power (current) via energy excited states similar to, or identical with, those involved in phosphorescence

EP  Electrophosphorescent (material)
EPR  Electron paramagnetic resonance.
ET  Electron transporter (layer within a device structure)
EML  Emissive layer
ETL  Electron transport layer
ETM  Electron transporter material

Firpic  Iridium(III)bis[(4,6-di-fluorophenyl)-pyridinato-\(N,C^2\)]

Fluorescence
Radiation emitted (usu. visible) resulting from and occurring only during the absorption of radiation (e.g. ultraviolet or two-photon infrared) from some other source. The absorbed radiation (e.g. UV) is often the result of an electrical discharge, with two energy conversions occur (from electrical to UV to visible).

Fluorescent  Glowing as a result of fluorescence
FOLED  Flexible OLED
HBL  Hole blocking layer
HDS  High Definition Systems (applied research program for displays at DARPA)
HOMO  Highest occupied molecular orbital
HIL  Hole injection layer
HRL  Hughes Research Lab (in Malibu CA)
HT  Hole transporter (layer within a device structure)
HTL  Hole transport layer
HTM  Hole transporter material
IJP  Ink jet printing

Inverted OLED  Device with cathode “down” and the anode “up” (opposite to the normal sense of an OLED structure). The direction for observation of emitted light is often through the top (anode) surface.

IP  Intellectual property
Ir  Iridium (atomic element)
Ir complexes  Heavy metal complex dopant, or phosphor, based on Ir
Irppy  Iridium tris-(phenyl-pyridine). (Also sometimes written Irppy)
fac-tris(2-phenylpyridine)iridium (alternative chemical name)

ISB  bis-iminostilbene-biphenyl
ISF  N,N’-iminostilbene-4,4’-fluorene
ITO  Indium tin oxide (material for fabrication of transparent, thin-film electrodes)

J-V-L  Current-voltage-luminance (characteristics)
KOH  Potassium hydroxide (etching solution used in thin-film electronics fabrication)
L₀  Initial luminance (value at t = 0 for a newly made display device)
LE  Luminous efficiency (in cd/A)
<table>
<thead>
<tr>
<th>Term</th>
<th>Definition/Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>Lithium</td>
</tr>
<tr>
<td>lm</td>
<td>Lumen</td>
</tr>
<tr>
<td>lm/W</td>
<td>Lumen per Watt (power conversion efficiency unit for electro-optical device)</td>
</tr>
<tr>
<td>Lumen</td>
<td>Unit of luminous flux equal to the light emitted in a unit solid angle by a uniform point source of one candella intensity.</td>
</tr>
<tr>
<td>luminance</td>
<td>Luminous intensity of a surface in a given direction per unit of projected area</td>
</tr>
<tr>
<td>luminescence</td>
<td>Quality or state of emitting or reflecting usu. steady, suffused, or glowing light</td>
</tr>
<tr>
<td>lumophore</td>
<td>Luminous molecule</td>
</tr>
<tr>
<td>LX</td>
<td>Ancillary bidentate (ligand)</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>mCP</td>
<td>N,N'-dicarbazolyl-3,5-benzene (a material doped to create a luminescent layer)</td>
</tr>
<tr>
<td>MLCT</td>
<td>Metal-ligand charge transfer</td>
</tr>
<tr>
<td>MF-TOLED</td>
<td>Metal-free TOLED</td>
</tr>
<tr>
<td>MOCON</td>
<td>Name of a company, MOCON, Inc.</td>
</tr>
<tr>
<td>MOCVD</td>
<td>Metal oxide chemical vapor deposition</td>
</tr>
<tr>
<td>niBr</td>
<td>N-2,6 dibromophenyl-1,8-naphthalimide (electron transporter film material)</td>
</tr>
<tr>
<td>α-NPD</td>
<td>4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (an HTL material)</td>
</tr>
<tr>
<td>NPD</td>
<td>N,N’-diphenyl-N,N’-diphenyldimethylene (hole transporting material)</td>
</tr>
<tr>
<td>NSOM</td>
<td>Near-field scanning optical microscopy</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic light emitting diode (device, display)</td>
</tr>
<tr>
<td>OVPD</td>
<td>Organic vapor phase deposition</td>
</tr>
<tr>
<td>O^O</td>
<td>Diketonate ligand</td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene terephthalate (a plastic flexible substrate material)</td>
</tr>
<tr>
<td>PHOLED</td>
<td>Phosphorescent OLED (material structured to have 100% quantum efficiency)</td>
</tr>
<tr>
<td>Phosphorescence</td>
<td>Luminance that is caused by the absorption of radiations and continues for a noticeable time after these radiations have stopped; an enduring luminescence without sensible heat. Emission is from an excited state with forbidden direct transition to ground state (i.e. low probability direct optical transitions), (e.g. triplet excited state emissions in most materials).</td>
</tr>
<tr>
<td>Phosphorescent</td>
<td>Light emitted involving non-optically allowed transitions</td>
</tr>
<tr>
<td>Pixel</td>
<td>Picture element, smallest portion of a display device capably of producing the full range of colors, graylevels, and angular distribution function of the full display</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>PLED</td>
<td>Polymer light emitting diode</td>
</tr>
<tr>
<td>PM</td>
<td>Passive matrix (multiplexed electrical addressing scheme involving the sequential application of signals to each pixel of the display device; no active element exists in the display screen to retain the image control signals during frame time), (perception of a complete image relies on the relatively slow chemistry in the retina of the human eye to create an illusion that the entire image is present), (OLED light emission occurs only at moment control signal is applied to pixel).</td>
</tr>
<tr>
<td>PMOS</td>
<td>Positively-doped-channel metal oxide semiconductor</td>
</tr>
<tr>
<td>POEM</td>
<td>Center for Photonics and Optoelectronic Materials (at Princeton University)</td>
</tr>
<tr>
<td>PQ</td>
<td>Iridium (III) bis(2-phenylquinolyl-N,C2') acetylacetonate</td>
</tr>
<tr>
<td>PQ2Ir(acac)</td>
<td>Iridium(III) bis(2-phenylquinolyl-N,C2')acetylacetonate (orange-red PH dopant)</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>ppy</td>
<td>Phenyl pyradine (a ligand molecule used in forming dopants, aka phosphors)</td>
</tr>
<tr>
<td>Pt</td>
<td>Platinum (atomic element)</td>
</tr>
<tr>
<td>Pt complex</td>
<td>Heavy metal complex dopant, or phosphor, based on cyclometalated Pt</td>
</tr>
<tr>
<td>PU</td>
<td>Princeton University (in Princeton NJ)</td>
</tr>
<tr>
<td>RMS</td>
<td>Root-mean-square</td>
</tr>
<tr>
<td>Sheet Resistance</td>
<td>Ratio of material resistivity to sheet thickness (in Ω/□)</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon (atomic element)</td>
</tr>
<tr>
<td>SOI</td>
<td>Silicon on insulator</td>
</tr>
<tr>
<td>SOLED</td>
<td>Stacked OLED</td>
</tr>
<tr>
<td>T₁/₂</td>
<td>Half-life (in hours)</td>
</tr>
<tr>
<td>T₉</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>TiN</td>
<td>Titanium nitride</td>
</tr>
<tr>
<td>TiW</td>
<td>Titanium tungsten</td>
</tr>
<tr>
<td>TFT</td>
<td>Thin film transistor</td>
</tr>
<tr>
<td>TOLED</td>
<td>Transparent OLED</td>
</tr>
<tr>
<td>Torr</td>
<td>Unit of pressure</td>
</tr>
<tr>
<td>TCE</td>
<td>Trichloroethylene</td>
</tr>
<tr>
<td>tCP</td>
<td>1,3,5-tri-(N-carbazolyl)benzene</td>
</tr>
<tr>
<td>TPD</td>
<td>N,N-di-(3-methylphenyl)-N,N diphenyl-4,4-diaminobiphenyl</td>
</tr>
<tr>
<td>TPP</td>
<td>5,10,15,20-tetraphenylporphyrin</td>
</tr>
<tr>
<td>T-T</td>
<td>Triplet-triplet (annihilation)</td>
</tr>
<tr>
<td>TT</td>
<td>Technology Transfer (to industry), Technology Transition (to defense) application</td>
</tr>
<tr>
<td>UTA</td>
<td>University of Texas at Austin (in Austin TX)</td>
</tr>
<tr>
<td>UDC</td>
<td>Universal Display Corporation (in Ewing NJ)</td>
</tr>
<tr>
<td>UGH</td>
<td>Ultrawide-energy gap host</td>
</tr>
<tr>
<td>USC</td>
<td>University of Southern California (in Los Angeles CA)</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>WOLED</td>
<td>White OLED</td>
</tr>
<tr>
<td>α-NPD</td>
<td>4,4'-bis[N-(1-naphthyl)-N-phenylamino)biphenyl (an HTL material)</td>
</tr>
<tr>
<td>φ</td>
<td>C₆H₅ (phenyl unit)</td>
</tr>
<tr>
<td>ηext</td>
<td>External quantum efficiency</td>
</tr>
<tr>
<td>λmax</td>
<td>Wavelength at which maximum light emission is observed</td>
</tr>
<tr>
<td>Ω</td>
<td>Ohm, standard unit of electrical resistance</td>
</tr>
<tr>
<td>□</td>
<td>Ratio L/W of the length, L, to the width, W, of a thin-film conductor</td>
</tr>
<tr>
<td>Ω/□</td>
<td>Unit of sheet resistance: ratio of material resistivity to thin-film thickness</td>
</tr>
<tr>
<td>'O₂</td>
<td>Singlet oxygen (molecule)</td>
</tr>
</tbody>
</table>
APPENDIX A.
LIST OF PATENTS RESULTING FROM THIS DARPA-SPONSORED GRANT

1. 03-1990-1, Princeton University Invention Disclosure, “Doping to Extend Reliability”
   Inventors: Anna Chwang, Brian D'Andrade, Stephen Forrest
   Assignee: Princeton University
   Application No. Serial No. 10/680,065 filed 10/6/2003
APPENDIX B.
LIST OF TECHNICAL JOURNAL PUBLICATIONS RESULTING FROM THIS
DARPA-SPONSORED GRANT
(cumulative, chronological, including papers in press or planned)

1. "Direct observation of structural changes in organic light emitting devices during
   degradation,” D. Kolosov, D. S. English, V. Bulovic, P. F. Barbara, S. R. Forrest and M. E.

2. “Extremely efficient red electrophosphorescent devices,” Raymond C. Kwong, Matthew
   Nugent, Tan Ngo, Kamala Rajan, Lech Michalski, Yeh-Jiun Tung, Julie J. Brown, Proceedings
   of the 21st International Display Research Conference in conjunction with the 8th
International Display Workshops (2001), 1774.

3. “Bis-Cyclometallated Ir(III) Complexes as Efficient Singlet Oxygen Sensitizers,” Ruomei
   Gao, David G. Ho, Billy Hernandez, Matthias Selke, Drew Murphy, Peter I. Djurovich, Mark E.
   Thompson, Journal of the American Chemical Society, 2002, 124(50), 14828-14829

4. “1,8-Napthalimides in Phosphorescent Organic LED’s: The Interplay Between Dopant,
   Exciplex, and Host Emission,” Dmitry Kolosov, Vadim Adamovich, Peter Djurovich, Mark E.
   Thompson, and Chihaya Adachi, Journal of the American Chemical Society, 2002, 124(33),
   9945-9954.

5. “High operational stability of electrophosphorescent devices,” R. C. Kwong, M. R. Nugent,

6. “Blue organic electrophosphorescence using exothermic host-guest energy transfer,” R. J.
   Holmes, S. R. Forrest, Y.-J. Tung, R. C. Kwong, J. J. Brown, S. Garon and M. E. Thompson,

7. “Efficient deep blue organic electrophosphorescence by guest charge trapping,” R. J. Holmes,
   (2003).

8. “Operational stability of electrophosphorescent devices containing p and n doped transport

   Weaver, M.-H. Michael Lu, Yeh-Jiun Tung, Anna B. Chwang, Theodore X. Zhou, Michael

10. A. B. Chwang, M. A. Rothman, S. Mao, R. Hewitt, M. S. Weaver, J. A. Silvernail, K. Rajan,
APPENDIX C.
LIST OF PROFESSIONAL PERSONNEL ASSOCIATED WITH THIS EFFORT

Persons who contributed to technical work on this effort are listed by institution below.

Princeton University
Steve Forrest, Department of Electrical Engineering, Principal Investigator
Russel Holmes, Department of Electrical Engineering, Research Assistant
Brian D’Andrade, Department of Electrical Engineering, Research Assistant
Jiangeng Xue, Department of Electrical Engineering, Research Assistant
Shashank Agashe, Department of Electrical Engineering, Research Assistant
Marc Baldo, Department of Electrical Engineering, Research Associate

University of Southern California
Mark Thompson, Department of Chemistry, Subcontractor Principal Investigator
Peter Djurovich, Department of Chemistry, Research Associate
Steve Cordero, Department of Chemistry, Research Associate
Dmitry Kolosov, Department of Chemistry, Research Assistant
Azad Hassan, Department of Chemistry, Research Assistant
Vadim Adamovich, Department of Chemistry, Research Assistant
Simona Garon, Department of Chemistry, Research Assistant
Xiaofan Ren, Department of Chemistry, Research Assistant
Drew Murphy, Department of Chemistry, Research Assistant

University of Texas at Austin
Paul Barbara, Department of Chemistry and Biochemistry, Subcontractor Principal Investigator
Doo Young Kim, Department of Chemistry and Biochemistry, Research Assistant
Jason McNeill, Department of Chemistry and Biochemistry

Universal Display Corporation
Julie Brown, Chief Technology Officer, Subcontractor Principal Investigator
Yeh Tung, Research Engineer
Ray Kwong, Research Engineer
Anna Chwang, Research Engineer
APPENDIX D.
LIST OF ADVANCED DEGREES AWARDED
FOR RESEARCH ACCOMPLISHED UNDER THIS GRANT

Advanced degrees awarded in association with research sponsored under this grant are listed below by institution in the following format: (date, recipient, type of degree, thesis title).

Princeton University:
none.

University of Southern California:

2001, Dmitry Kolosov, "1,8-Napthalimides as Novel Materials for Phosphorescent Organic Light Emitting Devices and Degradation Studies of Transparent Light Emitting Devices."


University of Texas at Austin:
none.
APPENDIX E.
JUNE 11, 2003 FINAL REVIEW MATERIALS
Investigations of the Operational Lifetime and Modes of Failure of Organic Light Emitting Devices

Final Program Review
June 11, 2003

Princeton University/USC/Universal Display Corp./UT

Objectives

- To develop methods for the determination of long term failure modes of OLEDs
- To determine the primary sources of OLED failure
- To eliminate or reduce failure mechanisms active in OLEDs

Programmatic Details

- Start date: April 1, 2001
- End Date: June 1, 2003
- Program Total: $700,000
- Contract No.: MDA972-01-1-0032
  (UDC contract expired January 1, 2003)

Team

- Princeton University: Steve Forrest (PI)
  - Russell Holmes
  - Brian D'Andrade
  - Jiandong Xue
  - Steven Agapie
  - Marc Barco (posi-doc)
- USC: Mark Thompson
  - Peter Djurovich
  - Dmitry Kolosov
- Universal Display Corp.: Julie Brown
  - Yeh Tung
  - Ray Kwong
- Anna Chawla
- University of Texas: Paul Barbara
  - Doo Young Kim
  - Jason McNeil

Methods for Investigating OLED Failure

- Lifetime: $[\tau_{50}]_{LT}$
- Failure Modes:
  1. Mechanical: cathode delamination
  2. Thermal: device heating, molecular bond breaking
  3. Electrical: current leading to heating, charge imbalance (OLEDs)
  4. Chemical: unstable excited species, reaction with air
Methods

- Choose model system (blue PHOLEDS, conductivity doped PHOLEDS)
- Standardize OLED fab. processes
- Measure photophysical degradation
- Measure electrically induced degradation
  - Hole only and electron only devices
- Change chemical compositions in systematic fashion to solve problems
  - Dopants, blockers, hosts
- Use NSOM for examination of cathode and other physical defects and effects on lifetime using TOLED platform

The blue difference

- Endothermic vs. exothermic energy transfer
- Non-blocking structures
- New chemistry

Energy transfer rates and directions

<table>
<thead>
<tr>
<th>Forward (exothermic) transfer</th>
<th>Reverse (endothermic) transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="URI" alt="Diagram" /></td>
<td><img src="URI" alt="Diagram" /></td>
</tr>
</tbody>
</table>

> Donor energy > Acceptor energy
> $k_D > k_A > k_{X_D}$
> Radiative rate determined by $k_D$
> Route for red and green emission

> Acceptor energy = Donor energy
> $k_A = k_D = k_{X_A}$
> Radiative rate determined by $k_A$, $k_D$
> Route for red and blue emission

Exothermic energy transfer: Reduced Temperature Dependence

Princeton Accomplishments

- Developed methods to observe photophysical degradation in new dopants and structures.
  - Transferred to UDC
- Developed use of TOLEDs for visualizing dark spot evolution (USC, UT)
- Developed blocker doping to improve stability (UDC)
- Investigated new blocker/dopant combinations to achieve charge balance in blues (USC)
- Developed high power efficiency conductivity doped PHOLEDs and investigated operational lifetime for first time.
- Worked closely with all partners to integrate results and conclusions
**p-i-n devices**

- Low voltage devices with high power efficiency
- Low voltage inverted structures
- Ultra-thin emissive layers (30 Å)
- p and n doped organic layers
  - low contact resistance
  - high conductivity

**PIN device characteristics**

- EQE vs. L
- PE vs. J

**P-i-n devices**

Stability issues with p-i-n device

- BPhen phase change
  Note: BPhen/Li0.5 is the best combination for n-doped organic
- Li diffusion
- Confinement of excitons and charge in thin EML

**BPhen Crystallization**

Si substrate / BPhen

- 1 mm
  - After 1 day
- 1 mm
  - After 3 days
  - After 2 weeks, substrates completely covered

Si substrate / BPhen/Li / BPhen

- 1 mm
  - After 1 day
- 1 mm
  - After 3 days
  - After 2 weeks, substrates completely covered
**The glass transition temperature**

- $T_g$ of a thin film can be modified by mixing
  \[
  T_g = \frac{w_1 T_{g1} + w_2 T_{g2}}{w_1 + w_2}
  \]

  **BPhen** ($T_g = 62^\circ$C) + **BAlg** ($T_g = 62^\circ$C)

- Modification of molecular structure of material
  Incorporate bulky constituents on parent structure

**Mixed HBL, BPhen:BAlg**

- Normalized Luminance
  - $Z = \text{BAlg}$
  - $Z = \text{BAlg}_{25}$ w.t% BPhen
  - $Z = \text{BAlg}_{50}$ w.t% BPhen

- Increasing $T_g$ of HBL
  - Time (hours)

**Mixed HBL, BPhen:BAlg**

- Luminous Efficiency
  - Increasing blocking efficiency
  - HOMO energies
    - BPhen, BCP, CBP

**No change in J-V with mixed HBL**

- Current Density (mA/cm²)

**Structures of derivatives of 4.7-diphenyl-1.10-phenanthroline**

**Tg of derivatives of 4.7-diphenyl-1.10-phenanthroline**

<table>
<thead>
<tr>
<th>Compound name</th>
<th>BCP</th>
<th>t-BBC</th>
<th>s-BBC</th>
<th>PBC</th>
<th>Mono-PBC</th>
<th>mono-tol-BC</th>
<th>mono-XYBC</th>
<th>mono-tol-BC</th>
<th>P/HBC</th>
<th>P/BTC</th>
<th>mono-tol-BC</th>
<th>p-TBC</th>
<th>mono-tol-BC</th>
<th>Mono-XYBC</th>
<th>BTBC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_g(^\circ)$</td>
<td>71.90</td>
<td>79.34</td>
<td>80.36</td>
<td>80.36</td>
<td>82.21</td>
<td>82.21</td>
<td>82.21</td>
<td>82.21</td>
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</tbody>
</table>
Li diffusion

- Previously, SIMS was used to measure Li diffusion into BPhen
- Here, model diffusion using ellipsometry
- Li:BPhen reaction makes it possible to distinguish between BPhen and BPhen:Li layers.

Properties of BPhen: Li thin films

Grew this structure

- Graphical representation of Li diffusion into BPhen thin films
- Ellipsometry model of structure

Charge Balance in thin emissive region

- Graphical representation of EL intensity vs. wavelength
- Table of energy barriers for electrons and holes
**Electron Blocking Layer**

- Electron/exciton blocker
- LIF:Al (40 nm) BCP
- (X nm) mCP: 7% FP1
- (10 nm) Irppy2
- (40 nm) NPD
- PEDOT/PSS
- Glass

**Theory**

\[ J(x) = \frac{kT}{q} \mu \left( \frac{dn}{dx} \right) ^2 \]

\[ \eta(x) = \eta_0 \exp(-x/L_e) + \eta_s \exp(x/L_s) \]

Boundary Conditions:

\[ J(x=0) = -\eta \mu n(0) T \left( \frac{dn}{dx} \right) \]

\[ -\eta \mu n(x) T \left( \frac{dn}{dx} \right) \]

Solve for \( n(x) \):

**Electron Density within EML**

- Electron pile-up
- EBL/EML Interface
- HBL/EML Interface

**Voltage versus EML thickness**

- \( J = 10 \text{ mA/cm}^2 \)

**EQE versus EML thickness**

- Lines are fits to theory
- Optimal conc. of dopant
- Confinement of charge and excitons <100%

**p-i-n Device Stability**

- Normalized luminance
- Time (hours)

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Fluorescence emission is quenched by oxygen

Fluorescence emission in CCl4COCl at 256 nm excitation FT at the same intensity after heating the gas for 1 hour and at the same intensity after heating the gas for 2 hours.

Fluorescence emission in CCl4COCl at 300 nm excitation FT at the same intensity after heating the water to the same.

Fluorescence emission in CCl4COCl at 300 nm excitation FT at the same intensity after heating the water to the same.

Fluorescence emission in CCl4COCl at 300 nm excitation FT at the same intensity after heating the water to the same.

Water does not affect the emission.

Fluorescence is bleached by oxygen + UV light

Current Package

Disadvantages
- No O₂ getter
- 3 mm thickness

Current Package

Glasses

Intensity %

Air 19.4
O₂ 40.2
N₂ 8.0
H₂O 54.5
CO₂ 100.0
H₂O 26.3

In Vacuo Packaging/Lamination

Aluminum layer > 1 μm
Thin film / Device
A-Electrical Insulator
Glass

View through glass next slide

View through the glass substrate

Glass

Aluminum or other metal

A-Electrical Insulator

Thin film/device
High Efficiency, Deep Blue OLEDs – Guest Charge Trapping for Improved Charge Balance

R.J. Holmes and Prof. S.R. Forrest
Department of Electrical Engineering, Princeton University
X. Ren, J. Li and M.E. Thompson
Department of Chemistry, University of Southern California
June 11, 2003

Outline
-Host-guest energy transfer vs. guest charge trapping in OLEDs
-Progress to date in achieving efficient blue electrophosphorescence
-What is charge balance in OLEDs?
-Deep blue, hole-trapping emitters and wide energy gap hosts
-Device performance of deep blue OLEDs
-Evidence of guest charge trapping vs. host-guest energy transfer
-Conclusions

Routes to Efficient Phosphorescence

Host-Guest Energy Transfer:
Injected carriers form excitons at host molecular sites
Excitation is transferred nonradiatively to guest molecules, where radiative recombination takes place

Guest Charge Trapping:
Injected charge is trapped by guest molecules, allowing for carriers to form excitons on guest molecules
Radiative recombination takes place on guest molecules

Blue Organic Electrophosphorescence

-Efficient blue electrophosphorescence based on exothermic host-guest energy transfer has been previously demonstrated during this study (Holmes et al. Appl. Phys. Lett. 82, 2422, 2003)
-External quantum efficiency >75%, CIE co-ords (0.16, 0.37)
-Problems: Emission is not blue enough, devices are unreliable
-Device instability is partially the result of the buildup of charge in the emissive layer of the device, poor charge balance
-Current study examines blue electrophosphorescence by means of direct charge trapping on guest molecules
-High efficiencies are still reachable, alleviate some of the charge buildup in the emissive layer
-Direct trapping allows control over charge balance in the emissive layer of the device by varying the doping concentration

What is Charge Balance in Phosphorescent OLEDs?

-Overall carrier injection is balanced, one electron is injected for every hole into the device as a whole
-Injection into the emissive layer may still be unbalanced, as a result of the different potential barriers, mobilities or traps that each carrier experiences
-Results in a buildup of charge at interfaces, leading to poorer overall device operation (i.e. quantum efficiency) and also to less reliable devices
-Above, holes reach the emissive layer at a faster rate than electrons, leading to a surplus of holes and a charge imbalance

Deep Blue Electrophosphorescence by Charge Trapping

Overall carrier injection is balanced, one electron is injected for every hole into the device as a whole
-Injection into the emissive layer may still be unbalanced, as a result of the different potential barriers, mobilities or traps that each carrier experiences
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-Above, holes reach the emissive layer at a faster rate than electrons, leading to a surplus of holes and a charge imbalance

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Blue Electrophosphorescence by Charge Trapping

Host UGH1 and dopant FIr6 (10%) yield a high device efficiency of almost 9% at an operating current of 0.03 mA/cm², a luminance of 3000 cd/m² and a voltage of 5.7 V.

Comment is as follows: The host UGH1 has a large energy gap on which it is likely difficult to form excitons.

What is the dominant means of electron formation and light emission in this device?

Based on the energetics of FIr6 and UGH1, suspect that charge trapping on FIr6 is responsible for the high efficiencies.

Neat FIr6 Devices

- FIr6 is extremely efficient in neat film devices with an efficiency of 5.1% at 0.06 mA/cm² and 5.5 V.
- FIr6 is a conductor and can efficiently transport charge and form excitons on its own.

Operating Voltage vs. FIr6 Concentration

- Devices relying on energy transfer between host and guest should have driving voltages that are independent of dopant concentration.
- A dependence of driving voltage on dopant concentration suggests that the dopant is playing a role in charge transport.
- Current for neat UGH1 device is made up of both a recombination current from NPD as well as an electron current transported by UGH1 across the device.

Emission Spectrum vs. FIr6 Concentration

- In addition to the observed decrease in operating voltage with increasing FIr6 concentration, NPD emission is observed for very low concentrations of FIr6 in UGH1.
- Both results support the theory that FIr6 behaves as a low resistance pathway for holes into the emissive layer, consistent with a charge trapping view of device operation.

Neat UGH1 Devices

- Doping neat UGH1 device exhibits very poor device characteristics, no pure emission from the host is observed.
- Without FIr6, UGH1 behaves as a hole blocker, forcing exciton formation to occur in the NPD transport layer instead of in the wide energy gap UGH1.
- UGH1 is a good electron conductor but is a very poor hole conductor, making exciton formation on UGH1 difficult.
Step Layers and Charge Balance – Remove Step Layer

- Devices missing the step layer are very poor, resulting in significant NPD emission
- Poor behavior suggests need for mCP deep layer to aid hole injection into the emissive layer and help confine excitons in the emissive layer
- By increasing hole injection into the emissive layer, charge balance is also expected to increase

Controlling Charge Balance

- The shape change observed for a plot of quantum efficiency vs current density as a function of concentration suggests that charge balance in the emissive layer can be optimized by varying the dopant concentration
- This is only the case because the system in question relies on guest charge trapping and not energy transfer from host to guest
- Here, optimum charge balance occurs for a concentration between 5 and 10% F85

Conclusions

- Demonstrated efficient, deep blue electrophosphorescence based on charge trapping and excitation formation directly on the guest molecules of F85 in a system of U8H1 and F85
- Optimized the device for maximum charge balance by adjusting dopant (F85) concentration and hence, the state with which electrons and holes can enter and transport through the emissive layer of the device
- Suggest that by using a dopant that traps charge, and that by regulating charge flow into the emissive region with the help of step layers and varying dopant concentrations, charge buildups can be reduced or eliminated in the emissive region
- The elimination of such charge buildups should ultimately lead to more reliable devices since regimes of charge buildups seem to generally compromise device stability by exploiting any instabilities to excess charge present at the molecular scale in the emissive species
Failure Modes in Organic Light Emitting Devices

Mark Thompson – University of Southern California
Steve Forrest – Princeton University
Paul Barbara – University of Texas
Julie Brown – Universal Display Corporation

Extrinsic Degradation studies of OLEDs (dark spot growth)

- Unpackaged devices degrade very rapidly
  - hours to days for complete failure
- Devices die by formation and growth of dark spots
- Degradation has been correlated with the environment and operating parameters
  - e.g. device power, humidity and oxygen levels
- An understanding of dark spot growth will enhance stability toward environmental contaminants
  - Devices with greater environmental resistance require less stringent packaging for long-life operation
- Unpackaged devices (e.g. TOLEDs) allow the use of surface techniques to probe devices during degradation in situ studies

Experimental Setup for TOLED Study

Correlated AFM and EL at Early Stages of Degradation

Changes in Devices After Extended Time Periods

92 h in ambient, run at 1.5 mA for 58 h

92 h in ambient, no applied bias

[Diagrams and images related to OLED failure modes and experimental setups]
Questions to be resolved in Dark Spot Formation/Growth

- What other factors or materials choices affect the rate of dark spot growth?
- Is it possible to prevent or retard diffusion of water and oxygen into the OLED without using epoxy sealed or hermetic packages?

We need an efficient method to evaluate the distribution of dark spots and their growth rate as a function of the environment, materials, device architecture, etc.

Environmental control of dark spot formation and growth

- Independent control of O₂ and H₂O is important to determine the role each plays in dark spot growth
  - System allows the control of relative humidity 0% - 100% (± 3%)
  - oxygen 0 - 100% (± 0.5%)

- Devices will be run in a controlled environment and monitored as a function of humidity and oxygen levels
  - number vs. time gives nucleation rate
  - size vs. time gives the rate of growth

- High humidity is needed to accelerate dark spot growth

Controlled environment OLED testing box

- OLED structure: NPD(100A)/Alq3(50A)/LiF(1A)/Al(100A)
- Conditions: Ambient Humidity 90%
  - T=23°C
  - Current density 20mA/cm²
  - Area shown: 600 x 450 μm²

Nucleation rate: within 1 hour all dark spots are visible. No new dark spots form. Dark spots are the result of defects built into the device.

Dark spot density and growth rate

- Data analysis - growth rate
- Can collect data for many spots

Dark spot growth rate as a function of cathode material and humidity

- OLED structure: ITO NPD(400A)/Alq3(50A)
  - Cathode (LiF/N or MgAg)
- Conditions: Ambient Humidity 90% and 80% T=23°C
  - Current density 20mA/cm²
**Does the nature of the cathode/ETL interface affect dark spot growth?**

How interface-layers can affect the dark spot growth. Do spots grow from the inside?

ITO/NPD/Alq3/IF (100 Å)/LiF-Al: IF = BCP, LjX, ORG,

- Environmental conditions are all the same:
  - Nitrogen, 80% rel. humidity, 22°C

---

**Do dark spots grow faster on working or non-working devices?**

- OLED was on at 5 mA for 256 min
- OLED was off for 256 min

Total dark spot areas of the driven and undriven devices are very similar.

---

**Do the different organic interface layers affect the growth rate of the dark spots? (ITO/NPD/Alq3/IF (100 Å)/LiF-Al: IF = BCP, LjX, ORG)**

- Organic layers clearly give very high dark spot growth rates
- Multiple spots have to do with the increase in current density as the device area is decreasing
- BCP looks slower than it really is
- Halo region is largely counted as bright

---

**Total area plot: ORG, Flp and BCP interface**

---

**ORG, EIL affects OLED performance**

- ORG used as EIL enhances the QE and the brightness

For the device with 60 Å of ORG, up to 20 000 CD/m²

---

**Thicknesses of EIL affects the rate of Dark Spot Growth**

- All the devices were run at 5 V during degradation studies
Why does ORG help prevent Dark Spots Growth?

- When operating the device at constant voltage (V0), the dark spot growth follows a linear law: D(t) = 0.069
- Due to high field under the operating conditions used, water reduction occurs:
  2 H2O → 2 e- + H2 + 2 OH- (Equation: -0.82V)
- ORG used as barrier for water penetration prevents the reduction of ORG since the reduction of ORG occurs easily:
  ORG + e → ORG
- ORG is stable to water
- Alternatively, Alq reacts rapidly with H2O, hydriding the ligands, forming AlqO. ORG is stable to water.

Devices with ORG did not show any bubble formation during the environmental life-test study, no H2O formation.

Effect of Hole Injectors on the Degradation of OLEDs

- Devices run at a constant current, initial brightness = 700 Cd/m²
- Some dark spots grow at irregular rate. Often linked to the merging of dark spots. Merging rate grows faster.
- Tracking often occurs prior to merging.

At Constant Current
- Hole injectors can either stabilize or destabilize OLEDs.
- Growth Rate
- C6P: 0.85 %/Area/min
- SS: 0.17 %/Area/min
- Std: 0.92 %/Area/min
- TPD: 0.30 %/Area/min

Removable package for OLEDs

- The device must be tested and run under an inert environment prior to degradation testing.
- Package needs to be removed while the device is in the desired environment.
- We must be able to remove the trap form outside the
- Solution: a vacuum chuck

Vacuum Trap

Removable package for OLEDs

- DC Power Supply
- Optical Camera
- Optical Microscope
- Humidity Controller
- Temperature Controller
- X-Y-Z Positioning Stage

Effect of Hole Injectors On The Degradation Of OLED’s

- The Standard Device has the Longest Lifetime.
- The Presence of Hole Injectors Destabilizes The Devices.
- Total Growth Rate:
  - SS: 1.16 %/Area/min
  - Std: 0.51 %/Area/min
  - TPD: 0.49 %/Area/min
UDC prepared and packaged OLEDs

- Dark spots can be seen as soon as the seal is taken off of an encapsulated device.

Effect of Hole Injectors on the Degradation of OLEDs

- Individual area with more dark spots degrade at a faster rate.
- Standard device prepared in the clean room is less stable than the device with CuPc and has a shorter life span.

Sources of dark spots

- Water Molecules
- Dust Particle
- Cathode
- Surface Defects

Dual particle based defect
Should not be prevalent in cleanroom prepared devices

Galveno defect
May be a particle or grain boundary. Expected in all devices.

Devices Made in UDC Clean room

- Graphs showing degradation over time with dark spot area.

Devices Made In The Lab

- Graphs showing degradation over time with dark spot area.

5 pixels = 4 µm, 20 pixel area = 5 mm diameter
Can Liquid Metals (Eutectics) Be Used To Stop The Growth Of Dark Spots?

Cathode Surfaces Of Undegraded Device Before And After Applying The Ga-In-Sn Eutectic

- The Ga-In-Sn eutectic does adhere to the cathode surface
- The device becomes non-reactive in treated areas.

Effect of Silicone on the Degradation of OLEDs

- Silicone grease fail to slow down the rate of dark spot growth

Effect of Paraffin Wax and Paraffin Oil on the Degradation of OLEDs

- Paraffin wax increases the life expectancy of a badly degraded device
- The dark area does not grow for 3.5 hours
- After the induction period of 3.5 hours the rate rapidly increases with a half life of 4.17 hours.

Effect of Silicone Bath oil on the Degradation of OLEDs

- Silicone bath oil slows down the growth rate of dark spots
- Silicone oil is more effective than paraffin oil

Effect of Carbon Paste on the Degradation of OLEDs

- Carbon paste decreases the rate of dark spot growth
Summary

- Dark spots are the result of atmospheric exposure
  - The growth rate is not affected by device driving conditions
  - Metal over coating (Ag) does not affect the growth rate of dark spots
- Growth rate is accelerated by spot merger
- The identity of the compound in contact with the electrodes affects the growth rate of dark spots:
  - LiF/K decreases the rate of growth, OOG increases it
  - Cupc retards dark spot growth – planarizes the substrate, cuts down particulates
- Dark spot growth rate appears constant for differing spot sizes
- Over-coating with organic materials can significantly decrease the growth rate
  - Need to look at affect of coating on long-term lifetime

Is the hole transporter stable?

- NPD solution was oxidized to give NPD
- Solution is stable for hours under aerobic conditions
- Addition of water leads to rapid bleaching of the NPD' signal
  - Solution was stable for 2.5 minutes after addition of water
  - Similar reaction is observed for most thiophenes
- Can we come up with other hole transporters that are stable in water in both their neutral and cationic forms? Metal complexes

Characterization of fac-Co(pza)3 complex

- UPS data: E_HOMO = 5.3 eV
- Co(pza)_3 is colorless and has reversible electrochemistry
- Metal complex is stable, T > 150°C
- HOMO energy is lower than NPD

Device structure: ITO/HTL(50Å)/Alq(300Å)/LIF/AI

- A 0.7 eV energy offset between the HOMOs of fac-Co(pza)3 and Alq
- Such large energy offsets are expected to lead to an increased barrier for migration of holes from the HTL to Alq
- Poor carrier recombination is a likely loss mechanism in fac-Co(pza)3 devices.
* A 0.7 eV energy offset between the HOMO of fac-Co(ppy)$_3$ and Alq$_3$.
* Such large energy offsets are expected to lead to an increased barrier for migration of holes from the HTL to Alq$_3$.
* Poor carrier recombination is a likely loss mechanism in fac-Co(ppy)$_3$ devices.
* Inserting an NPD layer lowers the hole barrier and increases the electron barrier.

**Stability study: ITO/Co(ppy)$_3$/NPD/Alq$_3$/LiF/Al**

- Co(ppy)$_3$ degrades very rapidly, leading to high voltage operation.
- Co(ppy)$_3$ gives a stable device.

**Chemical oxidation of fac-Co(ppy)$_3$**

Oxidation agent: (H$_2$Re$_3$O$_3$)$\cdot$H$_2$O$_2$ (512/2 H$_2$O$_2$ vs. Fd/Asc)

Product is not Co(ppy)$_3$III.

In the device the complex will stop at the cationic state, trapping charge permanently.

**Singlet Oxygen production by Phosphorescent Materials**

\[ ^3\text{M} + ^3\text{O}_2 \rightarrow ^1\text{M} + ^1\text{O}_2 \]

- Triplet excited states can be quenched by oxygen to form singlet oxygen
- Process analogous to T-T annihilation
- Singlet oxygen reacts spontaneously and vigorously with organic materials
- Could be the source of device degradation

Questions:
- Do the phosphors react with $^3\text{O}_2$ in their excited states?
- Do the excited phosphors form $^3\text{O}_2$?
- Does this contribute to dark spot formation?
Oxygen Quenching of Phosphorescence

- Four compounds were chosen that have appreciable absorbance at 355 and 532 nm.
- These are the laser wavelengths used for measurements.
- All show substantial quenching of phosphorescence in air.
- Stern-Volmer Analysis allows us to determine the quenching rate constants.

\[ \frac{I_0}{I} = 1 + \frac{k_{q}}{k_{p}} [Q] \]

where \( k_{q} \) is second-order rate constant for \( \text{O}_2 \), and \( k_{p} \) is phosphorescence rate constant.

Singlet Oxygen Production

\[ ^{1}M \rightarrow ^{1}M^* + \text{O}_2 \rightarrow ^{1}M + \text{O} \]

- We have demonstrated quenching, but does the system make \( ^{1}	ext{O}_2 \)?
- Quenching could involve other processes.
- Quenching via electron transfer and exciplex has been demonstrated for phosphors and fluophorons.
- Oxygen has ample quenching strength to explore the excited phosphor.

Singlet Oxygen and Lifetime

\[ ^{1}M^* + \text{O}_2 \rightarrow ^{1}M + ^{1}	ext{O}_2 \]

- Solutions can be stabilized by < 80 nm (generating \( ^{1}	ext{O}_2 \)) with no loss in activity.
- The phosphor itself is very stable to \( ^{1}	ext{O}_2 \) quenching.
- Some phosphors show very low singlet oxygen quenching rates.
- Do green and blue emissive dopants show the same efficiencies for singlet oxygen production?
- Will be tested soon.
- Many fluorescent molecules also generate singlet oxygen, e.g., TDF, and the problem may affect all OLEDs.
- Sale of singlet oxygen at low doses, even in the absence of \( ^{1}	ext{O}_2 \) and \( ^{1}	ext{O}_2 \), shows a strong impact. Related to the lifetime of the excitation.
- Devices need to be packaged to avoid atmospheric degradation and oxygen affects devices in fabricated devices.
- At this point, the diffusion of oxygen into the film and oxygen must occur before phosphor in its excited state.
- Device behaviors of OLEDs run in air or in oxygen are similar to those under nitrogen.

Total dark area plot, for low and high current densities

- Dark spots grow slowly at low current densities.
- High current densities lead to rapid dark spot growth.
- As the device area shrinks, the current density goes up, and the dark spot growth rate goes up.

Devices held at constant currents (1-1.3 mA, 700 Cd/m²)

- NPD
- TPD
- ISB
- C doping

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Investigations of PHOLED Stability
Program Review, 6-11-03

UNIVERSAL DISPLAY CORPORATION

UDC Subcontract: 6-1-01 to 11-30-02

Program Focus Areas
- Understanding the parameters that affect OLED Device Lifetime Performance
- Extrinsic device parameters
- Understanding the parameters that affect PHOLED Device Lifetime Performance
- Intrinsic device parameters
- Improving PHOLED Performance
  - Efficiency
  - Lifetime
  - Summary

Device Stability Interacting Factors

- Intrinsic:
  1. Electrochemical (oxidation, reduction)
  2. Thermal (T_1, T_2, T_3)
  3. Interfacial (cathode delamination, etc.)
  4. Photochemical
  5. Carrier Balance
  6. Material Impurities

- Extrinsic:
  1. Encapsulation (H_2O, O_2, etc.)
  2. Fabrication environment (dust, etc.)
  3. Substrate (roughness, etc.)
  4. Operating conditions
  5. Storage conditions

PHOLED Reliability Study

- Material Purity
  - Blocking Layer
  - Host
  - Dopant
- Substrate Process
  - ITO Spec/Pre-treatment
- Edge Insulator
- Package Design
  - Mechanical
  - Materials
  - Process
- Device Structure Design
  - Blocking Layer
  - Doping Concentration
  - Layer Thickness
  - Materials

Typical OLED Display Package

- Cover: Metal Can or Glass
- Desiccant
- UV liquid Epoxy
- Substrate: Glass

OLED Panel Fabrication Cost

The display cost makes up 22% of the module cost

- Substrate Prep
- OLED
- Lid
- Epoxy and sealant
- Circular polarizer

©2002 Display Search Factory Cost Model
Green PHOLED Package Stability

Pixel shrinkage and dark spot growth observed

Importance of Package Volume

Pictures taken after 94 hours in 80 °C/85% RH chamber

Package with Adhesive Seal

Ring Seal with Desiccant

Face Seal

Adhesive

OLED

Desiccant

Adhesive

OLED

Adhesive

OLED

Adhesive Advantages

Supplied in Rolls

Pre-cut to shape

Carrier Film

Roll to Roll Manufacturing

Cures with UV Light - No heat cure

Constant thickness from .5 to 4 mils

Remains flexible after cure

Very low outgassing and shrinkage

Adehsive Material Processing

- Perimeter adhesive ring – 2 mm wide, 1.5 mils thick
- Apply adhesive to cover glass
- Remove release layer and attach cover glass to substrate
- UV cure

Ring Seal - UV Epoxy vs. Adhesive

UV Epoxy - Desiccant A

2nd seal - 1943 hrs

Adhesive - Desiccant B

No 2nd seal - 1904 hrs
Encapsulation With Adhesive and Desiccant

After 2940 hrs @ 60C/85% RH

After 5807 hrs @ 60C/85% RH

Pixel Shrinkage Solved By:

Packaging,
Process, and
Device Design

10mA/cm² constant DC drive, 1,000 hours

1st generation PHOLED
2nd generation PHOLED

Status of Packaging

► Developed a rugged package that does not limit the present PHOLED lifetime

► Significantly improved pixel shrinkage and dark spot growth

► Ongoing work
  ► Advanced packaging to reduce materials and manufacturing process cost
  ► Monolithic encapsulation to reduce the stringent requirements for inert packaging process
  ► Encapsulation design for high T operation

PHOLED Reliability Study

► Material Purity
  ► Blocking Layer
  ► Host
  ► Dope
► Substrate Process
  ► ITO Spec/Preinsertment
  ► Edge Insulator
► Package Design
  ► Mechanical
  ► Materials
  ► Process
► Device Structure Design
  ► Blocking Layer
  ► Doping Concentration
  ► Layer Thickness
  ► Materials

Green PHOLED Lifetime: Program Start

Normalized EL intensity

Operation time (hrs)

L<sub>2000 cd/m²</sub>
L<sub>500 cd/m²</sub>
L<sub>1000 cd/m²</sub>

Green PHOLED Performance

CIE: (0.30, 0.33); EOE: Ma = 6.7%
Green PHOLED Efficiency Performance

Green PHOLED Lifetime Performance at L₀=600nits (room temperature)

Green PHOLED lifetime
GD33 vs GD29 at 70°C, L₀=600nits

Green PHOLED Performance
Shelf and Driven Lifetest at t=7,300 hours

Emission Layer Design Optimization

Lifetime @ 70°C, 600 nits
Status of Green PHOLED Lifetime

➢ Lifetime-Efficiency Improved
  ➢ From 20 cd/A, 10,000 hrs at 600 nits
    ➢ 800 hours at 60 C, 600 nits
  ➢ To 30 cd/A, 30,000 hrs at 600 nits
    ➢ 3,000 hours at 60 C, 600 nits
➢ Ongoing work
  ➢ Further device optimization of Gen 2
  ➢ Building on materials development for long lifetime at RT and Elevated T, Gen 3 Under development

Red PHOLED Lifetime: Program Start

Red PHOLED™ Performance Summary

<table>
<thead>
<tr>
<th>Doping</th>
<th>CIE x</th>
<th>CIE y</th>
<th>Max EQE % (@100 cd/m²)</th>
<th>Max cd/A (@300 cd/m²)</th>
<th>Max Lm/W (@300 cd/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RD06</td>
<td>0.595</td>
<td>0.401</td>
<td>14.2 (200)</td>
<td>28 (200)</td>
<td>12 (50)</td>
</tr>
<tr>
<td>a</td>
<td>0.609</td>
<td>0.387</td>
<td>10 (400)</td>
<td>17.5 (400)</td>
<td>6.8 (70)</td>
</tr>
<tr>
<td>RD01</td>
<td>0.570</td>
<td>0.340</td>
<td>14.5 (200)</td>
<td>29 (200)</td>
<td>13 (100)</td>
</tr>
<tr>
<td>b</td>
<td>0.611</td>
<td>0.384</td>
<td>13.7 (400)</td>
<td>24.2 (400)</td>
<td>9.4 (55)</td>
</tr>
<tr>
<td>c</td>
<td>0.614</td>
<td>0.382</td>
<td>8.5 (800)</td>
<td>14 (800)</td>
<td>4.7 (70)</td>
</tr>
<tr>
<td>d</td>
<td>0.637</td>
<td>0.358</td>
<td>9.8 (80)</td>
<td>11.8 (80)</td>
<td>5.4 (12)</td>
</tr>
<tr>
<td>e</td>
<td>0.653</td>
<td>0.342</td>
<td>10.5 (600)</td>
<td>11.4 (600)</td>
<td>4.9 (10)</td>
</tr>
<tr>
<td>f</td>
<td>0.698</td>
<td>0.298</td>
<td>8.3 (10)</td>
<td>3.1 (10)</td>
<td>1.4 (2)</td>
</tr>
</tbody>
</table>

Red PHOLED Performance

RED PHOLED: Lifetime Progress By Manufacturing Scale-up of Materials
Red PHOLED Lifetime Performance at $L_0=300$ nits (room temperature)

RD07 Red PHOLED, 14 cd/A

RD07 PHOLED Performance Spectral Response Shelf and Driven Lifetest at $t=7,800$ hours

Status of Red PHOLED Lifetime
- Lifetime-Efficiency Improved
  - From 11 cd/A, 15,000 hrs at 300 nits
  - To 14 cd/A, 25,000 hrs at 300 nits
- Ongoing work
  - Further device optimization of Gen 2
  - Building on materials development for long lifetime at RT and Elevated T, Gen 3 Under development

High Efficiency Blue PHOLED
- CIE (0.14, 0.23)
- 10 cd/A @ 100 cd/m²
- 5% EQE
Summary

- Development of blue continues
  - New deep blue dopants and wide gap hosts
  - New charge injection layers for blue PHOLED
  - Improved understanding of blue reliability
- Progress in red and green
  - New dopants with higher efficiencies, long lifetimes
- New OLED packaging technologies promising
  - Ongoing investigation of alternative packaging technologies

Current Requirement for Fluorescent RGB

<table>
<thead>
<tr>
<th>Red color</th>
<th>Green color</th>
<th>Blue color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Panel brightness (cd/m²)</td>
<td>90</td>
<td>15</td>
</tr>
<tr>
<td>Original OLED brightness (cd/m²)</td>
<td>620</td>
<td>10</td>
</tr>
<tr>
<td>Current density (mA/cm²)</td>
<td>26.30</td>
<td>4.07</td>
</tr>
<tr>
<td>Current requirement (µA)</td>
<td>5.1</td>
<td>1.0</td>
</tr>
</tbody>
</table>

All calculations are based on peak brightness 300 cd/m², sub-pixel size 171×254 µm.

Red PHOLED Performance

- Much higher efficiency was obtained in the case of red PHOLED.
- Under same brightness, less current is needed for PHOLED.

a-Si AMOLED Development in AUO

<table>
<thead>
<tr>
<th>Color (3/1/1/1)</th>
<th>NBM EXPOS (3/1/3/1)</th>
<th>LC/CC/CC/C 2002/18/8/8</th>
<th>SID 2003</th>
<th>* LCD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max. brightness</td>
<td>24</td>
<td>80</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>CRI</td>
<td>(0.28, 0.37)</td>
<td>(0.27, 0.33)</td>
<td>(0.28, 0.34)</td>
<td>(0.31, 0.32)</td>
</tr>
<tr>
<td>Contrast</td>
<td>15</td>
<td>50</td>
<td>&gt;200</td>
<td>&gt;300</td>
</tr>
<tr>
<td>Power consumption</td>
<td>250 mW</td>
<td>400 mW</td>
<td>1.15 W</td>
<td>67 mW</td>
</tr>
</tbody>
</table>

Power Consumption

- Power consumption (%)
  - Fluorescence
  - Phosphorescence

Samsung SDI 2.2" Full-color Display using UDC PHOLEDs
THANKS!

➢ To our university collaborators
➢ To the entire UDC Team

➢ And of course thanks to you for your support (interest and $$)
Near Field Scanning Optical Microscopy Studies of TOLED Degradation

Paul F. Barbara
Doo Young Kim
Jason McNeill
Jiangeng Xue
Stephen R. Forrest
Mark E. Thompson

Organic Thin Films From Molecules to Materials
Structure/Properties/Function

ION TRAP FROM SHARP ELECTRODE
Contour plot of probe potential

○ = HOLE POLARON
(RADICAL CATION)

ORGANIC THIN-FILM

ITO ELECTRODE

More modulation with insulating layer

• More modulation: 70%
• Indicates more carriers
• ~100 hole polarons
• ~1 charge per polymer molecule
• Recombination at ITO is blocked
TOLED: Transparent Organic LED

- TOLED: 400 A / Mg/Ag 120.6 A
- BAQ 400 A: 210.4 A
- C8PPh2 (PL 400 A)
- C8PPh2: 100 A
- Anode (ITO, 1600 A)

Experimental Setup for TOLED Study

- Infrared lamp
- DC power supply
- 400 nm band filter
- Scanning stage
- Xs objective, N.A. = 0.7
- Spectrograph
- Mirror

Correlated AFM and EL at Early Stages of Degradation

- AFM (x700)
- EL (x700)
- AFM (x700)
- Surface mapped by AFM before running device (RMS roughness + 3 nm)
- No initial topographic features/detects exist in the dark spot area
- No topographic differences between EL, dark spot and EL active areas
- PL and TR images are featureless, no difference between EL active and inactive areas

Changes in Devices After Extended Time Periods

92 h in ambient, run at 1.5 mA for 58 h

- EL
- TR
- PL
- AFM, Z scale 90 nm

NSOM of burned-out device

- wrinkles and specks
- lower overall PHOSPHORESCENCE
- some specks are fluorescent

Thermal Breakdown

- Device temperature increases to above organic sublimation point in places due to resistive heating
- Organics boil out of pinholes in top electrode
- Leave behind volcano-like specks of organics
Topography and PHOSPHORESCENCE of Bumps

Device A, spent
- Bumps a few microns wide, 3-5 nm tall
- Same PHOSPHORESCENCE intensity over bumps (within 5%)

"Photobleaching" depends on O₂

Photobleaching increases in presence of O₂
Top electrode blocks O₂

Larger Spots
Device B, exposed to air
- Spontaneously form upon exposure to air (not all devices form spots on exposure)
- Grow out from pinhole, few nm tall
- Grow to ~100 micron wide within 24 hours
- Cover most of device within a few days
- Top electrode separated
- Bigger PHOSPHORESCENCE inside "dark spot" (more transmission)

Induced Dark Spots

- Form where NSOM probe impacted top electrode
- "Dark spot" grew from <1 micron to 30 micron in 3 hours

Light Quenched by Charge Carriers

- 3.2% quenching
- Quenching increases with excitation intensity (photodriven)
- Quenching increases with exposure time (photodriven)
- Similar, but less quenching for areas with top electrode (0.5%)

Key Concept - Hole Polaron

- Hole Polaron is a localized positive charge on the polymer
- Hole Polarons quench or thermalize singlet excitons by energy and/or electron transfer
- Hole Polarons and Singlet Excitons are funneled to low energy sites in organic materials
Tetracene doped with pentacene

- Crystalline solid

Field-modulation NSOM

- Efficient quenching by polarons
- Instrument-limited response
- Calculated response time: subpicosecond to picosecond

Vpp = 5V, quench = 27%

Tetracene Doped with Pentacene

- 100 ppm pentacene in tetracene
- Efficient energy transfer from tetracene to pentacene

Fluorescence Spectrum Changes with Voltage

- Tetracene fluorescence: small effect (~1%)
- Pentacene fluorescence: large effect (20%)

Conclusions

- Exposure to air causes the formation of "dark spots" which are regions where separation of the top electrode occurs.
- The presence of O2 and light or electrical excitation in the organic layers can also lead to destruction of the organic semiconductor material (pholbleaching).
- Dark spots were seen to grow from mechanically damaged spot
- Brighter PHOSPHORESCENCE inside "dark spot" indicates oxidation of metallic electrode