

White Organic Light Emitting Diodes for Solid State Lighting –

A Path

Towards High Efficiency and Device Stability

by

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ABSTRACT

White organic light emitting diodes (WOLEDs) are currently being developed as the next generation of solid state lighting sources. Although, there has been considerable improvements in device efficiency from the early days up until now, there are still major drawbacks for the implementation of WOLEDs to commercial markets. These drawbacks include short lifetimes associated with highly efficient and easier to fabricate device structures. Platinum (II) complexes are being explored as emitters for single emissive layer WOLEDs, due to their higher efficiencies and stability in device configurations. These properties have been attributed to their square planar nature. Tetradentate platinum (II) complexes in particular have been shown to be more rigid and thus more stable than their other multidentate counterparts. This thesis aims to explore the different pathways via molecular design of tetradentate platinum II complexes and in particular the percipient engineering of a highly efficient and stable device structure. Previous works have been able to obtain either highly efficient devices or stable devices in different device configurations. In this work, we demonstrate a device structure employing Pt2O2 as the emitter using mCBP as a host with EQE of above 20% and lifetime values (LT_{80}) exceeding 6000hours at practical luminance of 100cd/m^2 . These results open up the pathway towards the commercialization of white organic light emitting diodes as a solid state lighting source.

DEDICATION

To Oluwadamilola Abiodun Oloye, who will never grow up to achieve his dreams.

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LIST OF ABBREVIATIONS

26mCPy - 2,6-bis(N-carbazolyl)pyridine

Al - Aluminum

Alq₃ – tris-(8-hydroxyquinoline) aluminum

BmPyPB - 1,3-bis[3, 5-di(pyridin-3-yl)phenyl]benzene

CBP - 4-4'-bis(carbazol-9-yl)biphenyl

CCT- Color Correlated Temperature

CFL – Compact Fluorescent Lamps

CH₂Cl₂ - Dichloromethane

CIE – Commission d'Internationale Eclairge

CO₂ - Carbon dioxide

COT – Cyclo-Octatetraene

CRI – Color Rendering Index

DOE – Department of Energy

DPPS - diphenyl-bis[4-(pyridin-3-yl)phenyl]silane

EBL – Electron Blocking Layer

EIL – Electron Injection Layer

EL – Electroluminescence

EL – Emissive Layer

EQE- External Quantum Efficiency

ETL – Electron Transport Layer

FPt - platinum (II) [2-(4',6' – difluorophenyl)pyridinato-N,C^{2'}](2,4-pentane-dinato)

HATCN - 1,4,5,8,9,11-hexaazatriphenylene-hexacarbonitrile

HBL – Hole Blocking Layer

HIL – Hole Injection Layer

HOMO – Highest Unoccupied Molecular Orbital

HTL – Hole Transport Layer

ILCT – Intra Ligand Charge Transfer

IQE – Internal Quantum Efficiency

Ir(FI₃Py)₃. - fluorenepyridine ligands

ISC – Intersystem Crossing

ITO – Indium Tin Oxide

I-V-L – Current-Voltage-Luminance

LED – Light Emitting Diodes

LiF – Lithium Fluoride

LT - Lifetime

LUMO – Lowest Unoccupied Molecular Orbital

MC – Metal Centered

mCBP - 4, 4-bis(carbazol-9-yl)-2,2-biphenyl

mCBT - 9, 9' - (2,8-dibenzothiophenediyl) bis-9H-carbazole

mCP - 1,3-bis(9-carbazolyl)benzene

M-L – Metal-Ligand

MLCT – Metal –to- Ligand Charge Transfer

NHC – N-heterocyclic carbene

NPD - N,N'- diphenyl-N,N'-bis (1-naphthyl)-1,1'-biphenyl-4,4''-diamine

OLED – Organic Light emitting Diodes

OVJP - Organic Vapor Jet Printing

PF2/6am4 - poly [9, 9-bis (2-ethylhexyl) fluorene-2, 7-diyl]

PL - Photoluminescence

PVK - poly (N-vinylcarbazol)

PVK- poly (N-vinylcarbazol)

RGB – Red Green Blue

RISC – Reverse Intersystem Crossing

RZ – Recombination Zone

SOC – Spin Orbit Coupling

TAPC - di-[4-(N, N-ditolyl-amino)-phenyl] cyclohexane

WOLED – White Organic Light Emitting Diodes

1. INTRODUCTION

Through the evolution of humanity over the ages, one of the constant needs aside from food, clothing and shelter has been lighting. Lighting of our indoor and outdoor spaces have evolved over the ages from when our Homo erectus forebears used naked fires as a source of lighting. The quest for a controlled, safe and cheap source of lighting has seen humankind go from those early days of naked fires made from grease and oils, to modern day forms, which include lighting from incandescent bulbs, compact fluorescent lamps, gas discharge lamps and so on. The issues with these light sources are they are either efficient, but harmful to humans and the environment or, they are inefficient and expensive.

Incandescent bulbs have held steady as the most common source of indoor lighting for decades. While they are cheap to manufacture and produce useable illumination, there has been an active move to cease production, with some countries even passing legislation for its phasing out. (2014 in the United States^{1,2}, 2009 in Australia³). The major reason for this push is the gross inefficiency of the incandescent light bulb.⁴ The majority of the energy is converted to heat, with only about 5% converted to visible light.⁵ This has accounted for massive energy wastages in the amount of terawatts annually, which also correlates to massive amounts of CO₂ emissions into the atmosphere.⁶

While, there are definitely more efficient alternatives like the Compact Fluorescent Lamps (CFL), which use one-fifth to one-third the amount of energy required to light an incandescent light source and has a longer lifetime, it is a more expensive light

source.⁷ Another downside to the use of CFLs is its mercury content.⁸ Mercury has been proven highly toxic to humans.

In a quest to overcome these deficiencies, scientists have turned their attention to Solid State Lighting.⁹ SSL refers to light generated from electroluminescence in Light Emitting Diodes (LEDs), Organic Light Emitting Diodes (OLEDs) and Polymer Light Emitting Diodes (PLEDs). LED lamps are more efficient than CFLs and contain no harmful elements, but are also more expensive, which restricts their penetration into the mainstream. Aside from their cost, LED lamps have been shown to be sensitive to excessive heat and electrical surges, although these issues can be combated with integration of heat sinks and surge protection devices, which ultimately add up to the final cost of the LED lamps.¹⁰

An organic light emitting diode (OLED) uses electric current to emit light from an organic electroluminescent material. OLEDs have already seen applications in digital displays for televisions, mobile phones, laptops, tablets and the likes.^{11, 12} White Organic light emitting diodes (WOLEDs) have been gaining momentum as an alternative lighting solution, due to the steady and gradual increase in its efficiency values (lumen/Watts) when compared to conventional incandescent bulbs, fluorescent lighting, and conventional LEDs.¹³ WOLEDs are being developed as the next generation of solid-state lighting, although the initial markets are envisioned to be niche markets such as the automobile and aviation industries. The major attraction of WOLEDs as a solid-state light source is that the light generated and emitted can be scaled from square millimeters in the laboratory to potentially square meters in future applications. What this means is

that WOLEDs are intrinsically glare-free and can provide homogeneous lighting as opposed to the point source illumination of light emitting diodes.¹⁴

At the forefront of the push for commercialization of white organic light emitting diodes as a source of indoor lighting is the research into cyclometalated platinum complexes as the emitting layer material, due to the lack of complexity these materials introduce into WOLED devices.¹⁵ Platinum complexes are being studied extensively for their excimer emission properties, which in addition to the emission from their primary monomer state can provide a spectral coverage of the visible spectrum, which is analogous to white light and is deemed suitable for indoor lighting.¹⁶

At present, devices fabricated have exceeded 20% EQE due to the possibility of emission from triplet excitons via phosphorescence.¹⁷ While this is groundbreaking, in terms of prospects of WOLEDs for solid-state lighting, there is still the issue of lifetime and device stability, which is one of the frontiers left before these devices can be offered as an alternative to present lighting devices.

This work will hopefully serve as a study to the pathway to stable and longer lasting white organic light emitting diodes based on square planar platinum (II) complexes. We will start with a general introduction as to how organic LEDs operate, the evolution of indoor lighting, the different device architectures that have been explored on this road to a potentially cheap and uncomplicated solid-state lighting device.

Subsequent chapters will delve into the particulars of excimer based WOLEDs, and in this study, full attention will be placed on excimer emissions from square planar platinum (II) complexes, the evolution from bidentate and tridentate to tetradentate

complexes, and the ways in which the design of tetradentate complexes can improve the lifetime of WOLEDs.

2 WHITE ORGANIC LIGHT EMITTING DIODES FOR SOLID STATE LIGHTING

2.1 ELECTROLUMINESCENCE IN ORGANIC MATERIALS

Electroluminescence was first observed in organic compounds in the early 50's by Professor Bernanose, in the University of Nancy, in France.¹⁸ Professor Bernanose conducted trials with acridine derivatives and carbazole. Adsorbates of these materials were prepared on cellulose films and showed phosphorescence. This discovery heralded research into organic fluorescent compounds and their luminescent characteristics.

But, it was not until the late 80's that this branch of organic electronics picked up with the fabrication of the modern day OLED device structure by Ching W. Tang and Steve Van Slyke at the Eastman Kodak Laboratories in 1987. They reported a novel bilayer structure, which had separate layers for hole and electron injection functions.¹⁹ This novel structure used Indium Tin Oxide (ITO) as the anode and a Mg:Ag alloy as the cathode. The device showed an improvement over previous structures in terms of EQE, luminous efficacy, and most importantly required a driving voltage below 10V.²⁰⁻²²

This bilayer device opened up the possibility of using organic materials with electroluminescent properties in optoelectronic devices. The device had ITO as its anode, diamine served as a hole transport layer, while the Alq₃ was the emitting material. Light emission, visible only in forward bias, was measured from around 2.5V direct current input. With its comparably lower drive current, and higher efficiency, (~0.46%), this device became the prototype for modern day OLEDs.¹⁹

The contemporary organic light emitting diodes are thin-film multilayer devices in which active charge transport and light emitting materials are sandwiched between two thin film electrodes. At least one of the two electrodes must be transparent to light, so that the light emitted can pass through. Traditionally, a high work function, low sheet resistant and optically transparent material such as indium tin oxide (ITO) is used as an anode, while the cathode is a low work function metal.²³⁻²⁶ When an electric field is applied across the electrodes, electrons and holes are injected into states of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO), respectively and transported through the organic layer. Inside the semiconductor electrons and holes recombine to form excited state of the molecule.¹²

Light emission from the organic material occurs when the molecule relaxes from the excited state to the ground state. Highly efficient WOLEDs which are being developed at present, contain many layers with different functionality like hole injection layer(HIL), hole transport layer (HTL),electron blocking layer(EBL), emissive layer(EL), hole blocking layer(HBL), electron transport layer(ETL) and electron injection layer(EIL).^{27, 28} A schematic diagram of a multilayer WOLED structure is shown in Figure 1.

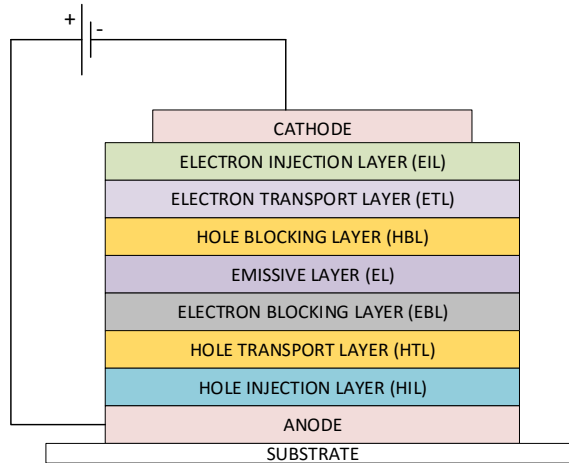


Figure 1 – Typical Structure of an Organic Light Emitting Diode (adapted).²⁹

The HIL and HTL are used to increase the injected hole numbers from the anode, and ensure that the maximum possible number of holes reach the EL for recombination. These two layers can be replaced by one layer possessing both hole injection and transporting abilities. Similarly, the EIL and ETL serve the same purpose, albeit for electrons from the cathode, and can be replaced by one layer with both electron injection and transporting abilities. The EML is the location for hole and electron carrier recombination and can be one or several layers that recombine carriers with different band gaps (different colors). The HBL and EBL are beneficial because that they confine most of the carriers to the EML and enhance the luminous efficiency of the OLED.³⁰

The mode of operation of an organic LED is dissimilar to the mode of operation of a conventional inorganic LED. Charge transport in an OLED occurs by hopping between localized states, as opposed to coherent motion within extended bands in conventional LEDs.^{29, 31, 32}

The operation of OLEDs involves the following: charge injection at the electrodes, transport of charge carriers, recombination of the charge carriers to generate electrically excited states, also known as excitons, and then deactivation of the exciton by emission by fluorescence or phosphorescence.^{12,33} Under zero bias, the Fermi levels of the two metal electrodes align, causing a built-in voltage, which is equal to the difference between the work functions of the metal electrodes, to appear across the organic layers. The flat band position, which is when the threshold of the device is attained, occurs when the applied voltage exceeds the difference in the work function. The application of a forward bias causes charge carriers to be injected into the material.

On the anode side, holes will be injected from the ITO to the HOMO level of the HIL or HTL. The role of the HIL is to lower the energy barrier to facilitate hole injection from the anode. The HTL should have a higher ionization potential than the HIL and should have a high hole drift mobility and facilitate movement of holes towards the emissive layer. The HTL material should be able to undergo reversible anodic oxidation to form stable cation radicals. The HTL sometimes also functions as an EBL, in the absence of a particular material serving this role. On the cathode side, electrons are injected into the EIL, and then transported via the ETL to the emissive layer. There could either be a separate material as a HBL or the ETL can serve dual roles as an electron transporting and hole blocking layer. The role of the HBL is to ensure that holes do not escape from the emissive layer. The ETL material should be able to undergo reversible cathodic reaction to form stable anion radicals and have high electron drift mobility.

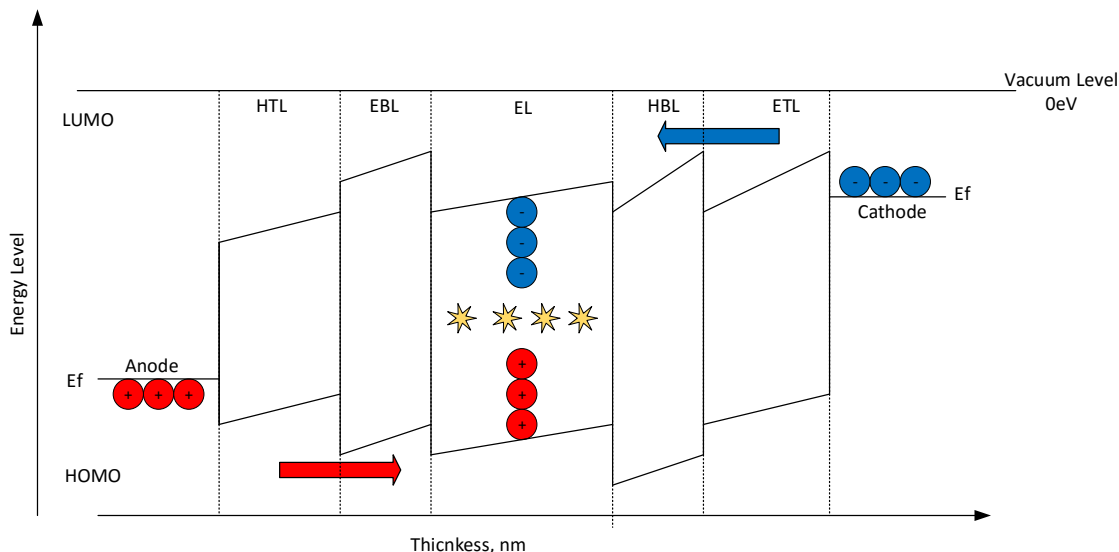


Figure 2 - Energy Diagram of a Typical OLED (adapted).¹²

Carrier transport and injection properties in OLEDs are determined by intersite hopping of charge carriers and between localized states as well as hopping from delocalized states in the metal to localized states in the organic layer.³⁴

Recombination of the charge carriers occurs at the recombination zone (RZ) of the emissive layer. Recombination involves the formation of the excitons, which are electron-hole pairs. Excitons in organic materials spatially limited to one excited molecule, are Frenkel excitons. In molecular materials, excitons can be in either a singlet or triplet state with 25% and 75% probabilities respectively.³⁵ Excitons should combine at an organic-organic interface, where the carriers are expected to have been blocked, to increase the probability of recombination. Excitons can relax either by radiative or non-radiative decay.³⁶ Radiative decay can occur via fluorescence, phosphorescence, thermally assisted delayed fluorescence^{37, 38} metal-assisted delayed fluorescence³⁹ or a combination of one or the other as shown in Figure 3.

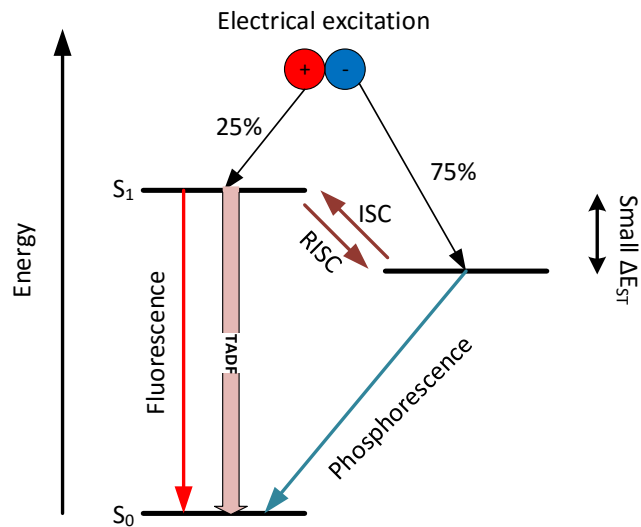


Figure 3 – Light Emission in OLEDs (adapted).²⁹

2.2 CHARACTERIZATION PARAMETERS

In terms of color rendering, white light can be characterized by three major parameters: CIE coordinates, CCT, and CRI

CIE Coordinates

The emission color of white light, perceived by the human eye can be described by a pair of (CIE) Commission International d’Eclairage (x, y) coordinates. The human eye contains photoreceptors for color vision, with three sensitivity peaks. These sensitivity peaks are short (S at 420 – 440nm), middle (M at 530 – 540nm) and long (L at 560 -580nm) wavelengths.⁴⁰ These three parameters are used to describe a color sensation. The (x, y) coordinates can be plotted on a color chart as shown in the figure below.

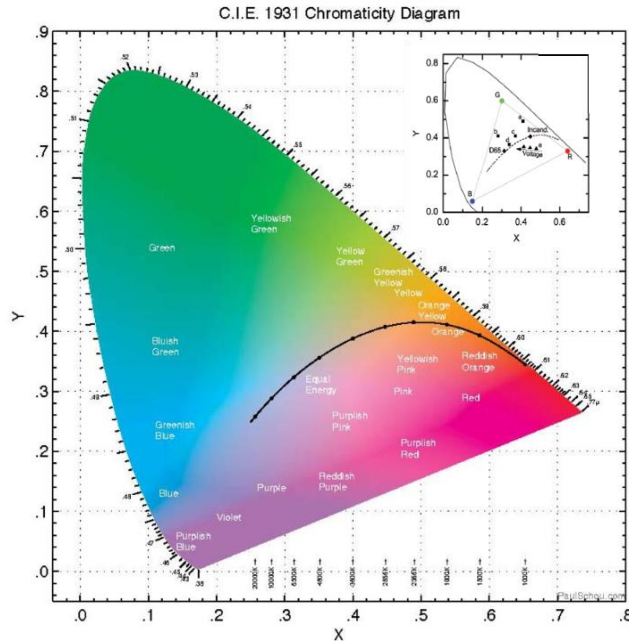


Figure 4 – The CIE 1931 Color Chromaticity Diagram. (Inset shows the color chart with CIE values of different light sources).^{14, 41}

In the figure above, the horseshoe shape is referred to as the monochromatic locus. This monochromatic locus corresponds to monochromatic light of different wavelengths across the visible spectrum from about 450 nm at the lower left of the diagram to about 630 nm at the right end of the line. The black solid line represents the Planckian locus which is the plot of radiation from a blackbody source as its temperature is gradually increased from about 1100 K (at the right end) to 20 000 K (left end). The inset shows CIE coordinates for red (R), green (G), and blue (B) primary colors that are used as standards for color displays, CIE values of the standard for incandescent light bulbs (Incand.) and the standardized daylight spectrum (illuminant D65). The other symbols correspond to CIE coordinates of OLED emission spectra of different WOLED

structures and emissive materials.¹⁴ For general illumination, a light source should typically have CIE coordinates close to that of the equal white energy of (0.33, 0.33).⁴²

Color Rendering Index (CRI)

Color Rendering Index is a dimensionless index ranging from 0 to 100, introduced by the Commission Internationale de l'Eclairage in 1965. CRI serves as a measure of how well a light source can reveal or interpret the color of an object, when said light source is compared to a natural source of light. The reference light source is either a Planckian radiator or daylight spectrum. A CRI value of greater than 80 is required for indoor lighting applications.^{43, 44}

Correlated Color Temperature (CCT)

The correlated color temperature of a light source is defined as the temperature of a blackbody radiator that has a color that most closely matches the emission from the non-blackbody light source. CCT is typically used as a metric when the CIE (x, y) coordinates of a light source do not sit on the Planckian locus. CCT values for high quality white light should be between 2500K and 6500K.⁴⁵ For example, the CCT of sunlight is 5800K, while that of the incandescent bulb is from 2000 to 3000K.⁴⁶

Table 1 – color rendering parameters for some common sources of white light

(adapted).⁴⁷

LIGHT SOURCE	CIE coordinates	CCT (K)	CRI
Incandescent Bulb	(0.448, 0.408)	2854	100
Tungsten Halogen Lamp (CIE Standard Illuminant A)	(0.448, 0.407)	2856	100
Daylight (CIE Standard Illuminant D ₆₅)	(0.313, 0.329)	6500	90
Xenon Lamp	(0.324, 0.324)	5920	94
High Pressure Sodium Lamp	(0.519, 0.417)	2100	24
Fluorescent (cool white)	(0.375, 0.367)	4080	89
Fluorescent (warm white)	(0.440, 0.403)	2940	72
White LED ^{48,1}	----	2700 - 5700	70,80

Quantum electroluminescence (EL) efficiency is the ratio of photon emitted per injected charge carrier in an electroluminescent device, and is given by equation 1.⁴⁹

$$\varphi_{EL} = \frac{e\Phi_{EL}}{j} = \frac{eU}{hv}\eta \quad (1)$$

Where, e – electron charge

Φ_{EL} – electroluminescent quantal ($h\nu$) flux per unit area (A)

¹ White LED used as reference is the LUMILED LUXEON FlipChip White 10

$j = \frac{di}{dA}$ is the current density

U – applied voltage

$\eta = \frac{\Phi_R}{U_i}$ is the energy conversion efficiency

Photoluminescence quantum efficiency also known as the PL quantum yield for molecular and polymeric materials, such as those used in organic light emitting diodes, is measured using an integrating sphere. An integrating sphere is a hollow sphere, which has its inner surface coated with a diffusely reflecting material. PLQY can be defined by equation 2.⁵⁰

$$\eta_{PL} = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}} \quad (2)$$

The Internal Quantum Efficiency of an OLED device is the total number of photons generated inside the device per electron-hole pair injected into the device.

The current efficiency is obtained from the luminance L_0 , obtained in the forward direction, and the current density passing through the device and is given by equation 3.⁴⁹

$$\eta_{CE} = \frac{L_0}{j_{meas}} \left[\frac{cd}{A} \right] \quad (3)$$

The luminous efficacy, sometimes referred to as the power efficiency is a measure of the ratio of the power of the emitted light as perceived by the human eye, to the

electrical power input¹⁷. Simply put, it is the measure of luminous flux per input of electrical power. It is given by equation 4.⁴⁹

$$\eta_{LE} = \eta_{CE} \frac{f_D \pi}{V(J_{meas})} \left[\frac{lumens}{Watt} \right] \quad (4)$$

where, $V(J_{meas})$ – *voltage at the point of measurement*

$$f_D = \frac{1}{\pi I_0} \int_0^{\pi/2} \int_{-\pi}^{+\pi} I(\theta, \phi) \sin\theta d\phi d\theta$$

where f_D is the angular distribution of the emitted light intensity $I(\theta, \phi)$ in the forward hemisphere which is a function of two angles, azimuth and polar. An integrating sphere or a goniometer is used to determine the value of f_D , which is the angular distribution of emitted light intensity.

External quantum efficiency (EQE) is the total number of photons emitted from the device per electron-hole pair injected into the device. Radiometric external quantum efficiency, which accounts for the efficiency of organic light emitting diodes in relation to how it is viewed by the human eye can be calculated by equation 5.⁴⁹

$$\eta_{EQE} = \eta_{CE} \frac{f_D \pi e}{K_r E_{ph}} [\%] \quad (5)$$

where, E_{ph} – *the average photon energy of the emitted device spectrum*

K_r – *luminous efficacy of radiation*

The luminous efficacy of radiation is used to quantify the amount of lumens a particular spectrum can produce per watt of electric energy. K_r helps to transition

between radiometric and photometric quantities. Photometric quantities measure electromagnetic radiation, which is light for the purpose of this work, in relation to its distribution in space.

With regards to the particular type of OLEDs with which this work pays particular attention, EQE can be calculated as shown in equation 6 below.¹⁷

$$\eta_{EQE} = \chi \cdot \eta_r \cdot \eta_t \cdot \eta_{out} \cdot \Phi_{PL} \quad (6)$$

where, χ – *fractions of excitons which can contribute to emission**

η_r – *efficiency of exciton formation from injected charges*

η_t –

efficiency of the energetic transfer from host to dopant molecules

η_{out} – *efficiency of outcoupling of emitted light to air*

Φ_{PL} – *the photoluminescent quantum yield of the emitter*

The fraction of excitons that contribute to emissions is 0.25 for fluorescent emitters and unity for phosphorescent emitters.

2.3 EMISSIVE LAYER ARCHITECTURE IN WOLEDs

Over time, there have been different attempts at the generation of white light from OLEDs, with the aim of improving efficiency, and lowering manufacturing costs. Methods for WOLED fabrication vary in terms of method of processing (solution processing, thermal deposition, chemical vapor deposition and even hybrid of any two of these methods); number of emissive layers, architecture of device and so on.⁵¹⁻⁵⁴ This

section covers the classification of white organic light emitting diodes, based on their emissive layer architecture.

A perfect emissive layer material would be one that has a high luminance, balanced charge injection, high IQE and EQE. Unfortunately, these different requirements are hard to achieve in one single material, and has led to the development of multiple layers made from different emissive materials, each of which is selected for a particular functionality.^{29, 49}

There are generally two broad classifications of WOLEDs based on emissive layer structure. A WOLED can have a single emissive layer sandwiched between the charge transporting layers, or multiple emissive layers in various configurations.^{49, 55-59} The basic principle of multiple emissive layers is the combination of complimentary or fundamental colors, which emit simultaneously as white light. However, one of the challenges inherent with multiple emissive-layered WOLEDs is the need for a level of detailed control of the relative amount and interaction of the various color components on both the molecular and device level.

Another challenge with the designing of multiple layered WOLEDs is in ensuring that the emission from the different layers emitting from different parts of the spectrum is balanced.⁴⁹ This can be achieved by either inserting thin HBL and EBLs between the emissive layers or, by ensuring that there is an offset between the HOMO and LUMO of the different emissive layers.¹⁴

Stacked or tandem WOLEDs can be achieved by arranging a complementary color set (example blue and orange) or the set of primary colored (red, green and blue)

OLEDs, connected electrically in series, to emit simultaneously via electroluminescence. The individual subdevices are vertically stacked and connected by the transparent charge generating layers.^{60, 61} The resulting emitting spectrum more or less covers the entire visible spectrum, which can be approximated as a white light spectrum.

An advantage of stacked WOLEDs is that the thickness or dopant concentration of each color layer can be optimized independently to improve the overall emission spectrum. The objective of the stacking approach is to increase current efficiency, which is possible because multiple photons are emitted per unit charge. The tradeoff of this is an increase in operating voltage, and as such, the power efficiency of such a device is technically the same as that of a conventional device.¹⁴ Furthermore, stacked OLEDs have been shown to be less vulnerable to brightness dependent color shifts observed in conventional devices. This can be attributed to having an equal amount of current density in the independent devices. This means that the emission color remains stable with an increase in device brightness. Although, this holds true only up to a certain voltage, because as voltage increases, the issue of efficiency roll-off sets in. If the separate color stacks have different efficiency roll-off points, then the problem of differential color aging sets in.⁴⁹

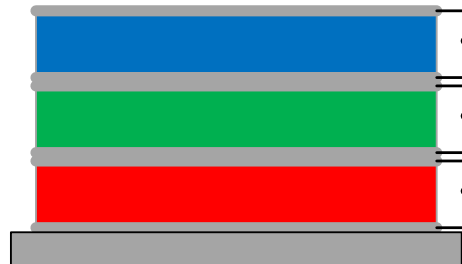


Figure 5 – Schematic of a Stacked OLED⁶²

The biggest advantage in stacked OLEDs for white light is the relationship between its applied current and brightness. As the lifetime of an OLED device depends strongly on its current density, the possibility of reducing the current by at least a factor of two or three ultimately increases the useful lifetime of the device by a factor of four to nine.¹²

Nevertheless, the multiplicity of layers adds complexity to the manufacturing of stacked multiple layered WOLED structures, and in the case of solution processing, the successive deposition of each layer is unfavorable to the surface morphology of the preceding emissive layer.⁴⁹

Taking a cue from inorganic LED fabrication, the striped WOLED has been attempted, albeit with a few adaptations. The basic structure of a striped WOLED is to have red, blue and green emitting devices positioned side by side. The RGB pattern is repeated in such a way that white emission from the device has to give the impression of spatial homogeneity. Color tuning is used to adjust the ratio of the red, blue or green emission from the device. The major advantage of striped RGB OLEDs is that it maximizes output for a given energy consumption.⁶² The biggest drawback of striped WOLEDs is the need for additional driving electronics to adjust the current density in the individual primary color emitting devices.¹⁴

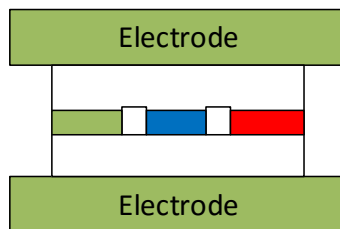


Figure 6 – Schematic of a Striped RGB OLED (adapted).⁶²

White organic light emitting devices using a single layer as the emissive layer can operate in a number of ways. These can be by blending polymers with two complementary or three primary emission color, by doping a wide energy gap material (host) with small percentages of lower energy emitters (guest);⁶³ or by using a single molecular entity, which simultaneously emits from individual excited states and excited aggregate states(excimers and exciplexes). Using a single emitting layer allows for an easier device fabrication process and the possibility of low cost large area devices. However, a careful control of morphology and composition of the emissive layer is crucial to the energy transfer processes involved in the emission of white light.

The first reported WOLED with a reasonable amount of brightness was obtained by blending the emissive layer materials for red, blue and green emission.⁶⁴ It reportedly had an efficiency of 0.83 lm /W and was fabricated by doping the hole conductor poly (N-vinylcarbazol) (PVK) with orange, green, and blue emitting laser dyes.⁵⁶ Another example is the use of a blend of fluorescent polymer poly [9, 9-bis (2-ethylhexyl) fluorene-2, 7-diyl] (PF2/6am4) and phosphorescent Iridium complex with extended fluorenepyridine ligands (Ir(FI₃Py)₃).⁶⁵

The Iridium complex serves as the dopant, and emits in the orange-yellow region of the spectrum, while the PF2/6am4 serves as the host and emits in the blue region of the spectrum. Doping the emissive layer material in this manner poses a risk of phase separation in the blend over time, which will result in film inhomogeneity, color shift, and a local increase in current density.¹⁴ It is harder to control the differential aging of blended emitters with precise molar ratio. Blending approaches are generally considered

to offer simpler device fabrication than most other methods. If all components required to generate white light are mixed into one material, one can fabricate a WOLED with a single active layer that is sandwiched between two electrodes. This reduces the number of processing steps for device fabrication and allows straightforward deposition of the active layer using conventional solution-based processes.¹²

In white organic light emitting diodes based on a single emitting layer of a host-dopant system, the host is accountable for charge transport, and in some cases, for blue emission while the dopants emit light by charge trapping or energy transfer from the host.⁶³ The host needs to be ambipolar, to be able to transport both holes and electrons effectively and be able to transfer energy efficiently to the dopant.⁶⁶ To ensure that all emission emanates from a single layer, several dopants mixed up into a single host are required to produce white light. One of the inherent challenges in a single layer host-dopant system is the difficulty in controlling energy transfer between the different emitters. Polymer fluorescent and phosphorescent white organic light emitting diodes with three emissive dopants as well as doubly doped emissive layers from small molecules have been reported.⁴⁵

A promising approach to reducing the number of dopants and structural inhomogeneities found in multiple emissive layer architecture is the use of a luminophore that emits from its excited individual and aggregate states.⁶⁷ This approach also helps to address the issue of differential aging of individual luminophores combined to produce white light.⁴⁵ These WOLEDs are based on a single emissive material which forms a broadly emitting state whose wavefunction or spectrum overlaps a neighboring dissimilar

molecule (in the case of an exciplex)^{68, 69} or a similar molecule (excimer)⁶⁷, in its excited state.

Excimers typically have a broad emission spectrum, spanning wavelengths from 450nm to 800 nm.²⁹ Thus, emission in the entire spectrum is usually covered using just one or two dopants. One of the most significant advances in the use of excimers has been the use of cyclometalated Platinum (II) complexes (bi-, tri-, and tetra-dentate complexes), due to their square planar coordination geometry and high emission efficiency.⁷⁰⁻⁷³

3 DEVELOPMENT OF SQUARE PLANAR PLATINUM (II) COMPLEXES FOR EXCIMER BASED WOLEDs

3.1 PHYSICS OF EXCIMER EMISSIONS

Excimer-based WOLEDs are considered a viable route to stable, efficient and simple to manufacture solid-state lighting. They have been proven to overcome the challenge of differential aging of stacked, striped and tandem WOLEDs.^{17, 67, 74} Excimer-based WOLEDs are characterized by a broad featureless emission band that is red-shifted from the emission of the monomer, and can be observed in both solutions and solids.¹⁷

An excimer is a short-lived dimeric (comprising of two monomers) molecule, at least one of which has a completely filled valence shell. It is associative in its excited electronic state, and dissociative in its ground state, hence it can be said that an excimer has no ground state.⁴⁵ An excimer is most often diatomic, and comprises of molecules, that would not ordinarily bind, if both were in the ground state.⁷⁵ The energy of an excimer is always lower than the energy of an excited monomer, as seen in Figure 7.⁷⁶

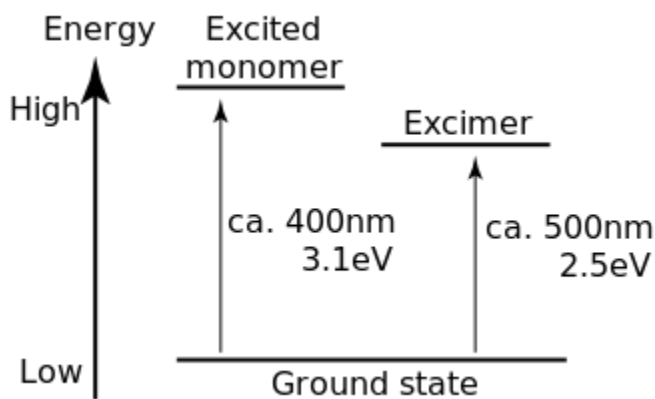


Figure 7 – Energy Diagram of an Excited Monomer and Excimer

Excimer emissions in organic materials are typically associated with a combination of ligand centered π - π^* interactions and bimetallic interactions of heavy metal atoms like platinum, iridium, palladium, generally the platinum group metals. The presence of these heavy metal atoms in an organic complex leads to a rapid intersystem crossing of an excitation from a singlet to a triplet ligand state.^{36, 67, 70, 77}

Square planar platinum complexes are at the forefront of single emitting layer WOLEDs due to their excimer emission properties. The square planar geometry is a result of the shape formed by the constituent atoms surrounding the central atom and is prevalent for transition metal complexes with d^8 configuration.⁷⁸

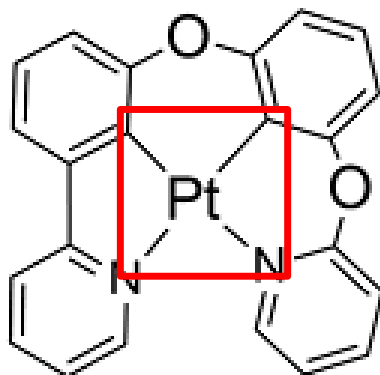


Figure 8 – The Square Planar Shape Formed by the Constituent Atoms Surrounding the Pt Atom (adapted).¹⁷

Square planar platinum metal complexes have a geometry with open axial coordination sites, which allows for structural distortion, inner sphere substrate binding, and intermolecular interactions, all of which can significantly alter the ground and excited state properties.^{15, 79, 80} Also platinum being a third-row transition element has the

second largest spin-orbit coupling (SOC) constant, which is responsible for the fast intersystem crossing (ISC), and forbidden triplet radiative decay.^{77, 81}

State of the art phosphorescent white organic light emitting diodes based on Pt(II) emitters have exhibited high external quantum efficiencies exceeding 20%^{71, 82}. Two main approaches have been taken to improve the EQE of WOLED devices based on Pt(II) complexes. These are the minimization of the excited state structural distortion, and the alteration of the coordination environment to destabilize the metal centered (MC) ligand-field excited states.⁷¹

The vacant axial sites associated with square planar coordination geometries allows for the flexibility of structural reorganization, which increases the possibility of non-radiative decay. Also, the emissions of Pt(II) complexes typically have a ³MLCT (metal to ligand charge transfer) state mixed with a significant ligand state, for example, from intra-ligand charge transfer (³ILCT) and ligand-centered ³ π - π^* excited states.¹⁵ Therefore, one way to reduce non-radiative decay rates would be to design ligands in which the excited state structural distortion is minimal. Another path to reducing non-radiative decay rates would be to raise the MC ³d-d excited states above the emitting triplet state. A common method is to use strong σ -donor ligands, such as C-deprotonated cyclometalating ligands, N-heterocyclic carbenes (NHCs) and phenoxide ions.⁸³

In as much as the efficiencies of WOLEDs based on platinum metal complexes have increased over the years, there are however, a few hurdles left to the commercialization of these WOLED devices. One of such hurdles is the stability of the platinum emitters employed. To address the issue of device stability in these devices, triplet-emitting materials should be:

- tolerant to thermal deposition during device fabrication⁷¹
- resistant to structural rearrangement during thermal treatment⁸⁴
- stable against chemical degradation that leads to color aging.⁸³

Generally, the degradation pathways of phosphorescent transition metal complexes, platinum complexes in this scenario, is via the rupturing of the metal-ligand (M-L) bond. To effectively alienate this particular degradation pathway, there is a need for methods to reduce this M-L bond rupturing. Strengthening of the M-L bonds by introducing strong σ -donor ligands and employing multidentate ligands are two ways by which these degradation pathways can be abolished.

In general, square planar platinum complexes used in single layer organic white light emitting diodes can be grouped into three main categories, which are bidentate, tridentate and tetradentate complexes. Denticity is the number of times a ligand bonds to a metal through non-contiguous sites (bi-dentate = binds through 2 sites; tri-dentate = binds through 3 sites and tetradentate binds through 4 sites).

The first set of square platinum (II) complexes that were studied for efficient excimer emission were bidentate complexes. These complexes were analogous to Iridium complexes, from which OLED devices had already been fabricated with relative success. Bidentate Platinum (II) complexes were the first set of synthesized platinum complexes that were luminescent in solution under ambient conditions.⁷³

Another example of bidentate platinum (II) complexes exhibiting excimer emissions is those containing dimesitylboryl functionalized phenyl-1,2,3-triazole C^N type cyclometalating ligands. In particular, complexes with pyridyl-1, 2, 4-triazole ancillary ligands are promising candidates for single doped white OLEDs. The presence

of methyl and t-butyl as functional groups in this complex produced a balanced white emission at moderate doping concentrations.¹⁷

Tridentate ligands with the ability to bind via three rings in a planar conformation are thought to possess a more rigid binding, which reduces the distortion associated with unstable bidentate ligands. This distortion is associated with increased non-radiative decay, which has an unfavorable effect on luminescent quantum yields.

Tridentate Pt (II) complexes with N[^]N[^]C-binding ligands, especially those with σ -alkynyl ligands in the fourth coordination site of the metal ion [Pt(N[^]N[^]C)(-C \equiv C-R)] have been studied extensively. The emission in these complexes is credited to a ³MLCT ($d_{Pt} \rightarrow \pi^*_{NNC}$) state, which is supported by the influence of the strong field cyclometalating carbon, strong field acetylide and the rigidity of the tridentate ligand (structural modifications of the N[^]N[^]C ligand and the acetylide).⁷³ These complexes were employed as the emissive layer of OLED devices prepared by vapor deposition. A high luminance of 9800cd/m² at 12V and EQE of 1.1%, was observed for a device that used [(C[^]N[^]N)PtC \equiv CC₆F₅] at a 4% doping level in CBP.⁸⁵ The low efficiency and generally inferior performance observed were ascribed to aggregate-induced quenching.

Pt(N[^]C[^]N) based complexes with tridentate ligands based on 1, 3-di (2-pyridyl)benzene (dpybH) have also been studied extensively, and studies have shown that the N[^]C[^]N coordination is effective at closing off pathways of potential thermally activated non-radiative decay, as a result of the strong ligand field.⁸⁶ They have also been shown to have high luminescence PL yields, and these attributes make them particularly attractive for fabricating single-doped emissive layer OLEDs.

Overall, while bidentate and tridentate platinum (II) complexes have opened the pathway for developing white OLEDs with a single emissive layer, the devices have typically been shown to have EQE less than 20%, with poor CRI and CIE coordinates, which make them unsuitable for solid state lighting applications. Furthermore, the inclusion of monoanionic ligands as the fourth coordinating ligand has proven to be unstable for devices.

Table 2 shows an overview of bi- and tridentate devices employed in different device architectures and their basic characteristics.

Table 2 – Overview of color parameters and device efficiencies of WOLED devices employing bidentate and tridentate platinum (II) complexes.

Emitter	Host /(% Dop.)	CIE coord.	EQE (%)	PE (lm/W)	Ref.
Pt(dpphen)(Ar ^F) ₂	CBP/6%		2.1		^{73, 87}
bppz	CBP/6%	(0.21, 0.52)	2.926	3.453	⁸⁸
	CBP/20%	(0.26,0.54)	2.174	2.861	
fppz	CBP/7%	(0.38, 0.54)	4.202	14.031	
	CBP/20%	(0.42, 0.53)	5.965	19.702	
FPt1	26mCPy/12%	(0.46,0.47)	15.9 (@500 cd/m ²)	12.6	¹⁷
Pt(m-Bptrz) (t-Bupytrz-Me)	26mCPy/10%	(0.31,0.44)	15.6	33.9	
[(C ^N)Pt(C≡C C ₆ F ₅)]	CBP/4%	(0.44,0.50)	1.1	n/a	⁸⁵
PtL ² Cl	CBP:OXA /15%	(0.41, 0.41)	12.6	n/a	⁸⁹

3.2 DEVELOPMENT OF TETRADENTATE PLATINUM (II) COMPLEXES FOR SINGLE EMISSIVE LAYER WOLEDs

While bidentate and tridentate platinum (II) complexes have opened the pathway for developing white OLEDs with a single emissive layer, the devices have typically been shown to have EQE less than 20%, with poor CRI and CIE coordinates, which make them unsuitable for solid state lighting applications. Furthermore, the inclusion of monoanionic ligands as the fourth co-ordinating ligand has proven to be unstable for devices.¹⁷

Most recently, tetradentate platinum (II) complexes with efficient monomer and excimer emissions have been designed.^{16, 90-92} These complexes have been able to eliminate the requirement for a monoanionic ligand as a fourth coordinating ligand, and subsequently eliminated a potential degradation pathway, which ultimately improves lifetime and stability.⁹²

Li and coworkers reported on the synthesis of Pt7O7, a symmetric tetradentate cyclometalated platinum complex that showed high efficiencies in both its monomer and excimer emission. When incorporated into a white device, its EQE peaked at 25.7% with CIE coordinates of (0.37, 0.43), and operational lifetime of 36 hours at LT₅₀. Pt7O7 showed a primary emission peak at 472nm which was ascribed to a low oxidation potential and small electrochemical bandgap. The device structure employed was ITO/HATCN (10nm)/NPD (30nm)/TAPC (10nm)/x% Pt7O7:mCBP(25nm)/DPSS (10nm)/BmPyPB (40nm)/LiF/Al, where HATCN is 1,4,5,8,9,11-hexaazatriphenylene-hexacarbonitrile,^{93, 94} NPD is N,N'-diphenyl-N,N'-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine, TAPC is di-[4-(N,N-ditolyl-amino)-phenyl]cyclohexane,⁹⁵

mCBP is 4, 4-bis(carbazol-9-yl)-2,2-biphenyl,⁹⁶ DPPS is diphenyl-bis[4-(pyridin-3-yl)phenyl]silane,⁹⁷ and BmPyPB is 1,3-bis[3, 5-di(pyridin-3-yl)phenyl]benzene.^{90, 98, 99} Devices of Pt7O7 showed high efficiencies across different doping concentrations with a peak EQE value of 24.5% at 14% Pt7O7 doping concentration. Improved conductivity and charge balance at higher concentrations led to lower roll-off in EQE values.⁹⁰ Figure 9 below shows the EL spectra, PE, EQE, and molecular structure of Pt7O7.

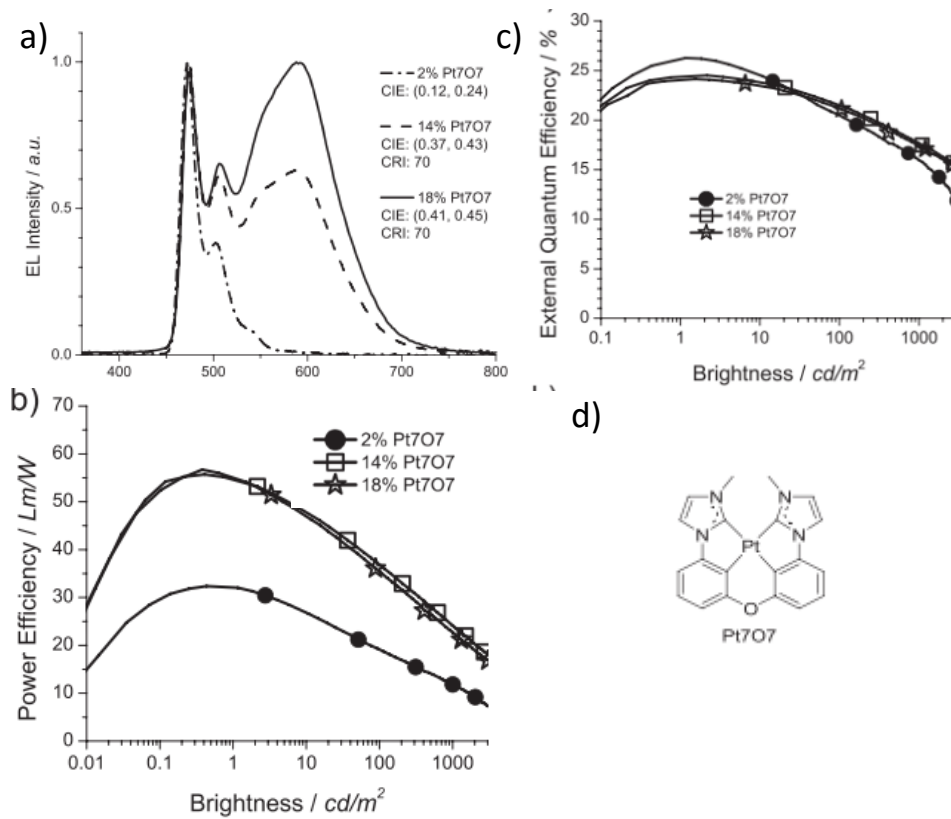


Figure 9 – Graphs of a) EL Spectra of Pt7O7 Devices; b) Graph Of EQE Against Brightness; c) Molecular Structure Of Pt7O7; d) Graph Of Power Efficiencies Against Brightness At Doping Concentrations of 2%, 14% and 18% Pt7O7 in device structure ITO/HATCN (10nm)/NPD (40nm)/TAPC (10nm)/x% Pt7O7:mCBP(25nm)/DPPS (10nm)/BmPyPB (40nm)/LiF/Al.⁹⁰

Based on the symmetric planar backbone of Pt7O7, the complex Pt1O2 was synthesized. Pt1O2 contains a phenyl pyrazole ligand.⁹²

Devices fabricated with Pt1O2 in the structure ITO/HATCN (10nm)/NPD (40nm)/TAPC (10nm)/x% emitter:26mCPy(25nm)/DPPS (10nm)/BmPyPB (40nm)/LiF/Al showed EQE values between 22.6% and 24.1% at different doping concentrations.

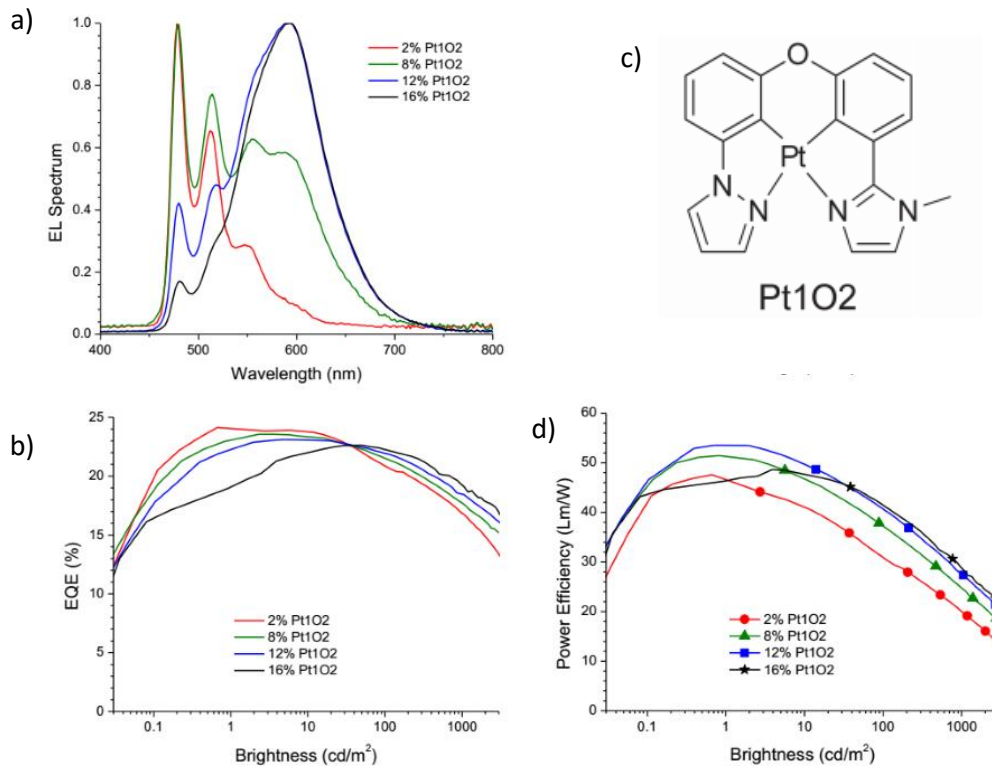


Figure 10 – Graphs of a) EL Spectra of Pt1O2 Devices; b) Graph Of EQE Against Brightness; c) Molecular Structure Of Pt1O2; d) Graph Of Power Efficiencies Against Brightness At Doping Concentrations of 2%, 8%, 12% and 16% Pt1O2me₂ in device structure ITO/HATCN (10nm)/NPD (40nm)/TAPC (10nm)/x% Pt1O2:26mCPy(25nm)/DPPS (10nm)/BmPyPB (40nm)/LiF/Al.⁹²

Another Pt(II) complex, Pt1O2me₂, was also synthesized on the basis of Pt7O7 and similar to Pt1O2. Pt1O2me₂ contains a phenyl dimethyl pyrazole ligand as opposed to the phenyl pyrazole ligand in Pt1O2. Pt1O2me₂ has a PL peak at 472nm and showed a relatively blue-shifted monomer emission. Devices fabricated from Pt1O2me₂ had EQE values between 24.2% and 26.5% with varying doping concentrations, as shown in Figure 11.⁹²

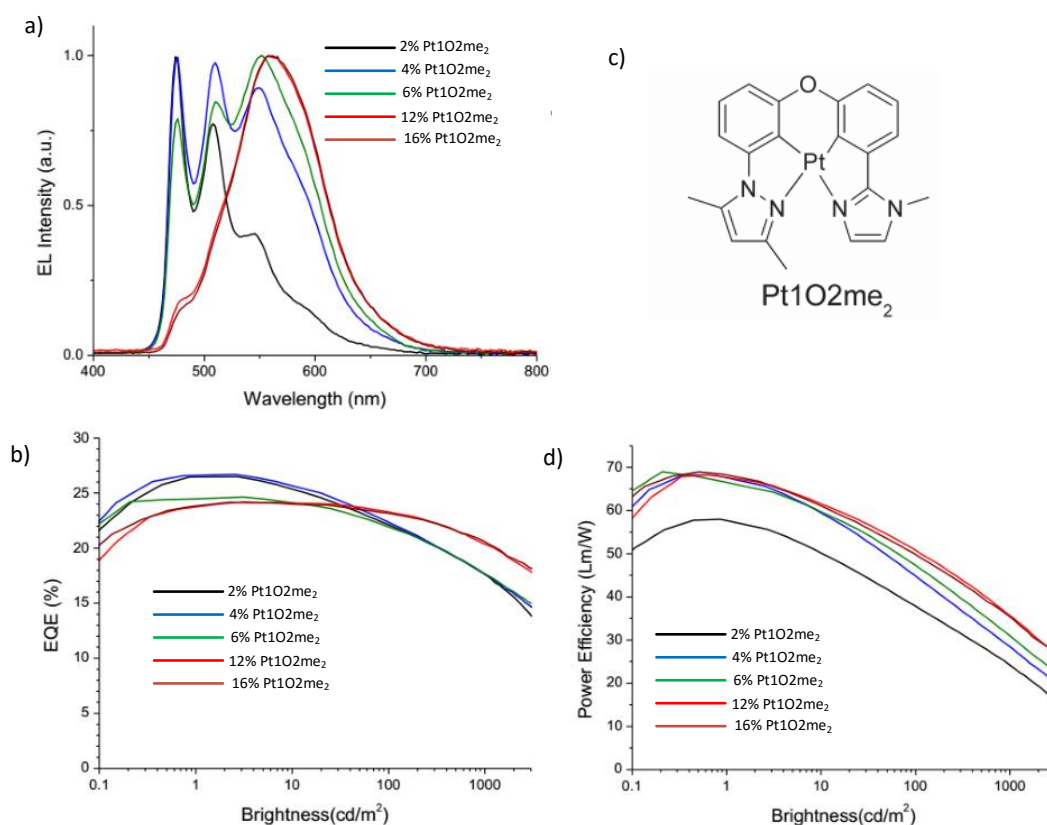


Figure 11 – Graphs of a) EL Spectra of Pt1O2me₂ Devices; b) Graph Of EQE Against Brightness; c) Molecular Structure Of Pt1O2me₂; d) Graph Of Power Efficiencies Against Brightness At Doping Concentrations of 2%, 4%, 6%, 12% and 16% Pt1O2me₂ in device structure ITO/HATCN (10nm)/NPD (40nm)/TAPC (10nm)/x% Pt1O2me₂:26mCPy(25nm)/DPPS (10nm)/BmPyPB (40nm)/LiF/Al.⁹²

Despite the high efficiencies reported for these set of devices employing the aforementioned tetradentate platinum complexes, there still exists the challenge of lifetime and stability that needs to be overcome before these complexes can be employed in commercial solid-state lighting applications. The device structure employed for its efficiency tests was deemed unsuitable for lifetime and stability tests due to the unstable nature of TAPC and DPPS employed as charge blocking materials.^{91, 100}

Thus, a stable but relatively inefficient structure using structure ITO/HATCN (10nm)/NPD (40nm)/x% emitter:CBP(25nm)/BAIq (10nm)/Alq (30nm)/LiF/Al was employed for Pt102 and Pt1O2me₂.⁹² With this new device structure, the EQE values for Pt102 and Pt1O2me₂ reduced by about 50%, however lifetime values showed considerable improvements when compared to the previous device structure containing DPPS and TAPC.

For the Pt7O7 complex, complex the device structure of ITO/HATCN (10nm)/NPD (40nm)/x% Pt7O7:mCBP(25nm)/BAIq (10nm)/Alq (30nm)/LiF/Al was employed for lifetime tests and its EQE also decreased by around 67% of its previous value from devices containing DPPS and TAPC. Lifetime tests for all the devices were carried out at a constant driving current of 20mA/cm², which equals an initial luminance of 2775cd/m² for the Pt7O7 device and 3060cd/m² for Pt1O2me₂. The lifetimes for the devices were extrapolated with equation 7 below.^{17, 101}

$$LT(L_1) = LT(L_0) * \left(\frac{L_0}{L_1}\right)^{1.7} \text{ [hrs]} \quad (7)$$

where, L_1 – *calculated lifetime*

L_0 – *measured lifetime*

Figure 12 below shows operational lifetime graphs for the device.

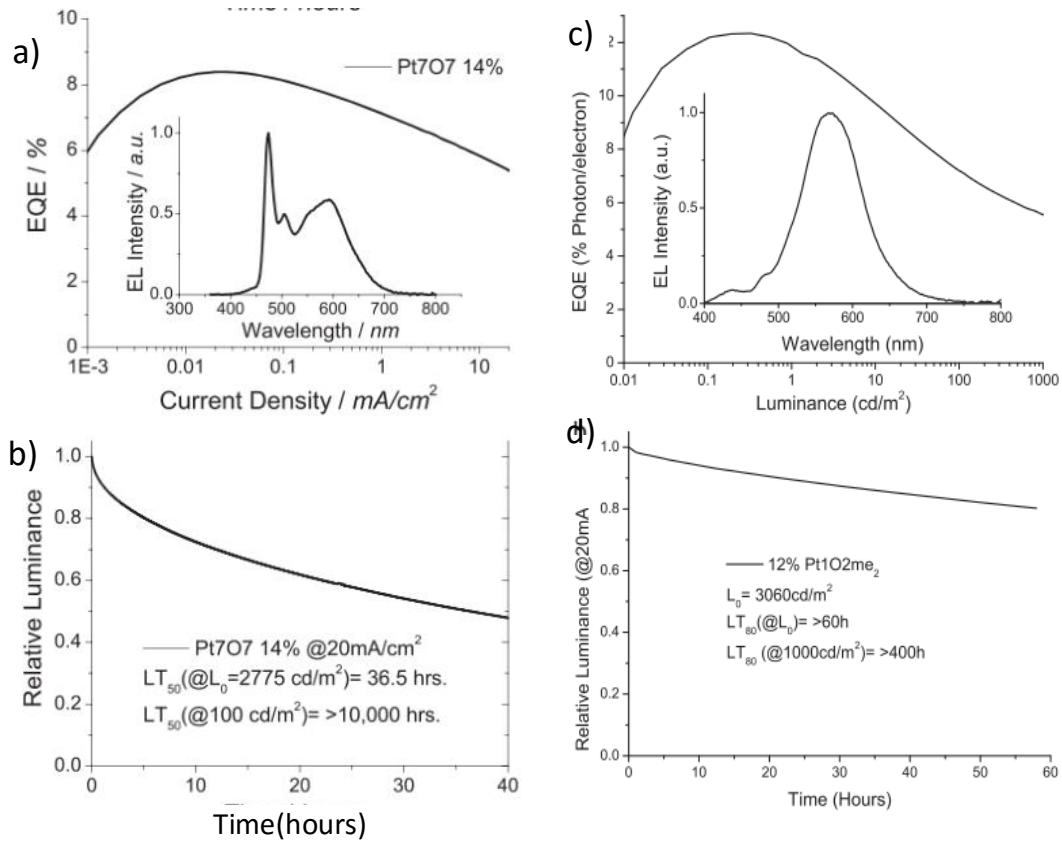


Figure 12 – Graphs of a) EQE versus Current Density of Pt7O7 and Inset is EL Spectra; b) Relative Luminance versus Time @ Constant Current Density of $20\text{mA}/\text{cm}^2$ for Pt7O7; c) EQE versus Current Density of Pt1O2me2 and Inset is EL Spectra; d) Relative Luminance versus Time @ Constant Current Density of $20\text{mA}/\text{cm}^2$ for Pt1O2me2 in a Stable but Inefficient ITO/HATCN (10nm)/NPD (40nm)/12% Pt1O2me2:CBP(25nm)/BAIq (10nm)/Alq (30nm)/LiF/Al and ITO/HATCN (10nm)/NPD (40nm)/14% Pt7O7:Mcbp(25nm)/BAIq (10nm)/Alq (30nm)/LiF/Al Device Structure.⁹⁰

While WOLEDs based on Pt7O7 and Pt1O2(me₂) have shown tremendous improvements in terms of stability through the optimization of the device structure, the problem of reduced EQE values with the stable device structure needs to be addressed.

3.3 A STABLE AND EFFICIENT WOLED DEVICE EMPLOYING Pt2O2 AS EMITTER

Building on the high efficiencies recorded with Pt7O7 as an excimer emitter in WOLED devices, a novel complex based on the same symmetric planar backbone, but with a phenyl methyl-imidazole cyclometalating ligand called Pt2O2 was synthesized.⁹² In Figure 13 the PL spectrum of Pt2O2 showed the efficiency from both its monomer and excimer emissions as well as its primary emission peak at 490nm.⁹²

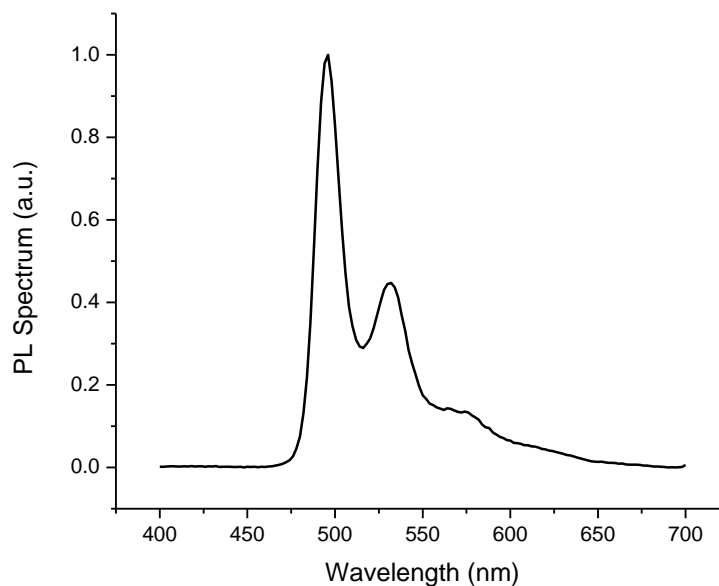


Figure 13 – PL spectrum of Pt2O2 at room temperature in CH₂Cl₂

Devices were fabricated with Pt2O2 with the structure ITO/HATCN (10nm)/NPD (40nm)/TAPC (10nm)/x% Pt2O2:26mCPy(25nm)/DPPS (10nm)/BmPyPB (40nm)/LiF/Al. As the doping concentration of Pt2O2 was varied from 2% to 16%, the excimer emission increased with the formation of a red-shifted peak. At 2% dopant concentration, there was no excimer formation with a green emission and CIE coordinates of (0.231, 0.565). At 16% doping concentration, an orange white emission is observed with CIE coordinates (0.48, 0.48) and a CRI of 72. The CIE coordinates and CRI values obtained at 16% doping concentration can be attributed to a lack of monomer emission in the blue range of the spectrum, which makes for an unbalanced coverage of the visible spectrum.⁹² Notwithstanding, the monomer and excimer emissions can be said to be efficient, as shown in Figure 14. Also, a peak EQE value of 26.5% at 12% doping concentration of Pt2O2 was recorded.

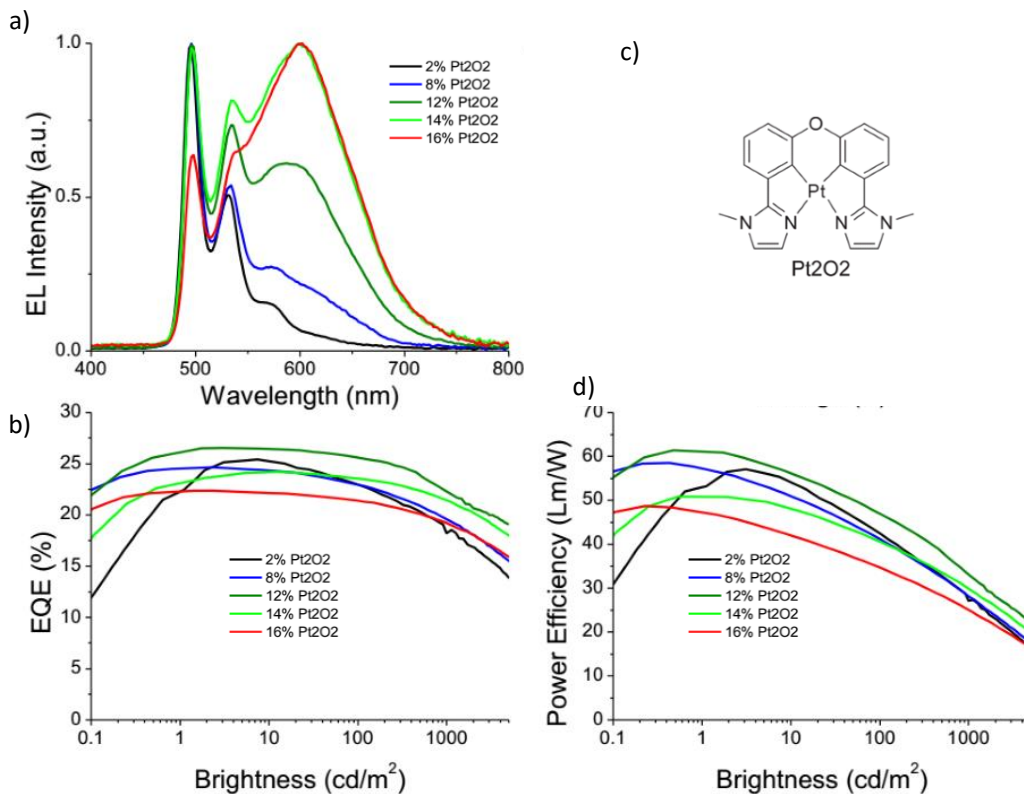


Figure 14 – Graphs of a) EL Spectra of Pt2O2 Devices; b) Graph Of EQE Against Brightness; c) Molecular Structure of Pt2O2; d) Graph Of Power Efficiencies Against Brightness At Doping Concentrations of 2%, 8%, 12%, 14% and 16% Pt2O2 in device structure ITO/HATCN (10nm)/NPD (40nm)/TAPC (10nm)/x% Pt2O2:26mCPy(25nm)/DPPS (10nm)/BmPyPB (40nm)/LiF/Al.⁹²

While devices with Pt2O2 have been proven to have high EQE values of above 20% in an efficient structure, the problem of stability is still a major challenge towards commercialization. Stability issues typically arise from electrochemical degradation of the charge blocking materials like DPPS and TAPC utilized in the previously tested device structures. For the purpose of further analysis, device **1** will be regarded as

structure ITO/HATCN (10nm)/NPD (40nm)/TAPC (10nm)/12%
Pt2O2:26mCPy(25nm)/DPPS (10nm)/BmPyPB (40nm)/LiF/Al.

Figure 15 shows the results of the lifetime tests carried out using a known stable but inefficient device stack of ITO/HATCN (10nm)/NPD (40nm)/14% Pt2O2:CBP(25nm)/BAIq (10nm)/Alq (30nm)/LiF/Al (device 2). A relatively high lifetime at LT_{80} of 43 hours initial luminance of 2500cd/m^2 is recorded. This corresponds to LT_{80} of about 206 hours at a practical luminance of 1000cd/cm^2 and above 10000 hours at 100cd/cm^2 using equation 7. While the lifetime values are promising, there was a substantial reduction of about 50% in the peak EQE value of the device, which underlines the inefficiency of the employed device structure

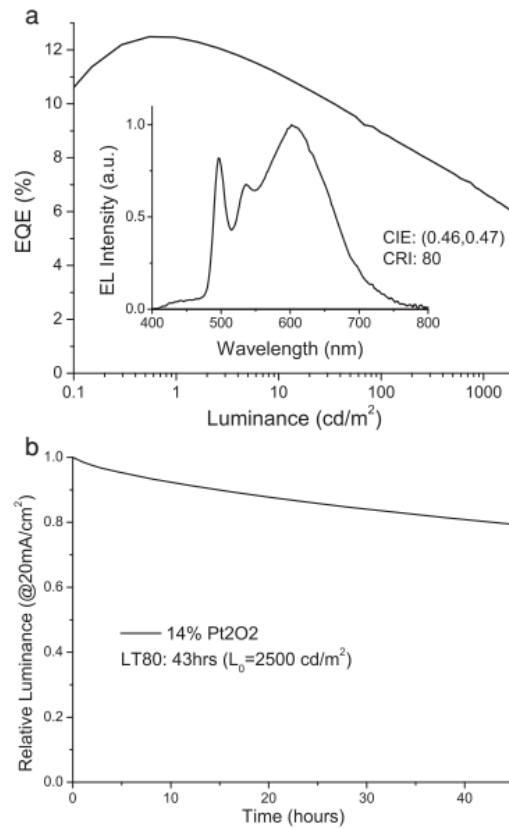


Figure 15 – Graphs of a)EQE versus Luminance with Inset of EL Spectra;
 b)Relative Luminance versus Time @ Constant Current Density of 20mA/cm² for Pt2O2
 in a Known Stable but Inefficient Device Stack Of ITO/HATCN (10nm)/NPD
 (40nm)/14% Pt2O2:CBP(25nm)/BALq (10nm)/Alq (30nm)/LiF/Al .⁹²

The challenge at present is to engineer devices, which will be both efficient and stable. This can be made possible by the careful design of emitters that have a rigid molecular structure, on which there has been great progress. Another pathway would be via the design and use of state of the art charge transporting and blocking materials.

In order to further improve the device performances, Tris-PCz as an electron blocker and mCBT as a new hole blocking layer were introduced. Tris-PCz is 9, 9'-Diphenyl-6-(9-phenyl-9H-carbazol-3-yl)-9H, 9'H-3, 3'-bicarbazole¹⁰² and mCBT is 9, 9' - (2, 8-dibenzothiophenediyl) bis-9H-carbazole. The host material CBP was replaced with mCBP, where mCBP is 3, 3-di (9H-carbazol-9-yl) biphenyl. The resulting device structure (device **3** in Figure 16) of ITO/HATCN (10nm)/NPD (40nm)/Tris-PCz (8nm)/14% Pt2O2:mCBP(25nm)/mCBT (8nm)/BPyTP (40nm)/LiF/Al had an impressive peak EQE value of above 20% similar to those obtained with the previously tested efficient device structure (Device **1**).

Device **3** demonstrated LT₈₀ value of 3.16 hours at an initial luminance of 6922cd/m². This corresponds to LT₈₀ value of 85 hours at practical luminance of 1000cd/m², and above 4000 hours at 100 cd/m².

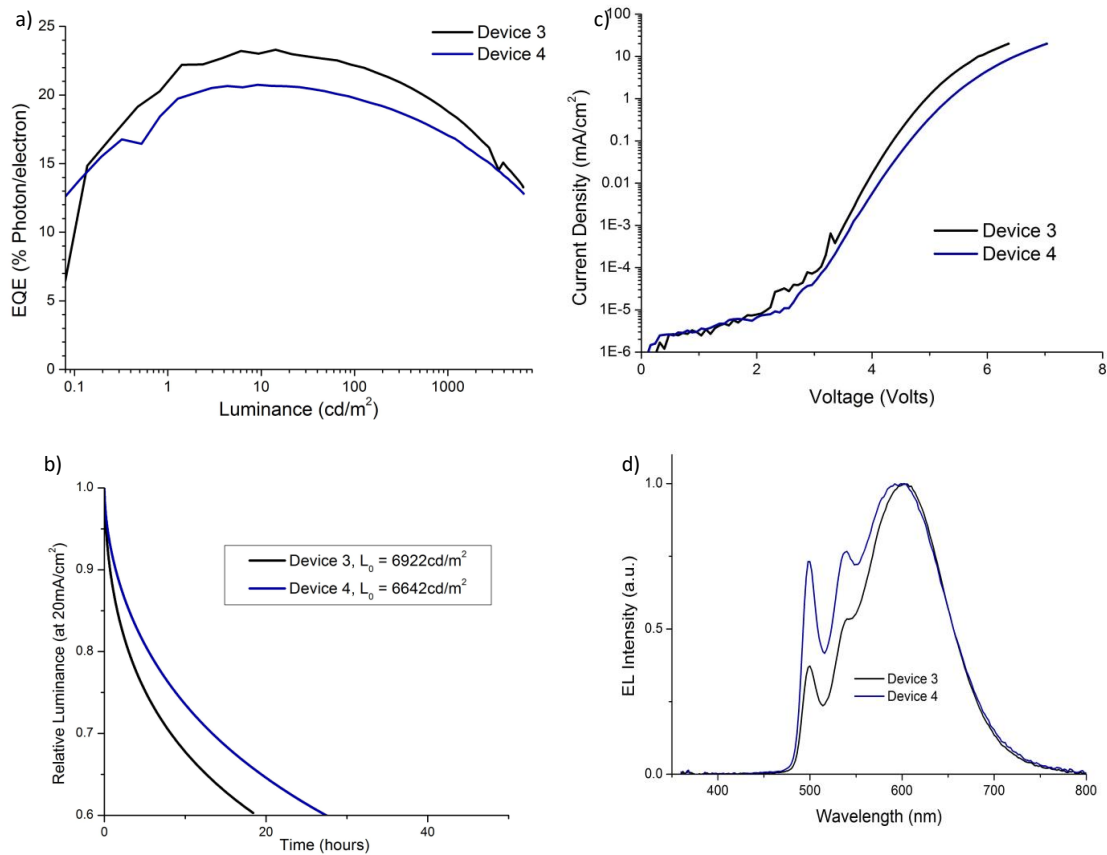


Figure 16 - Graphs of a) EQE versus Luminance; b) Relative Luminance versus Time @ Constant Current Density of 20mA/cm²; c) Current Density versus Voltage, d) EL Spectra @ Constant Current Density of 1mA/cm² of Device 3 and Device 4, where Device Structure of Device 3 is ITO/HATCN (10nm)/NPD (40nm)/Tris-PCz (8nm)/14% Pt2O2:mCBP(25nm)/mCBT (8nm)/BPyTP (40nm)/LiF/Al and Device Structure of Device 4 is ITO/HATCN (10nm)/NPD (40nm)/Tris-PCz (8nm)/14% Pt2O2:mCBP(25nm)/BAIq (10nm)/BPyTP (40nm)/LiF/Al.

Further optimization of the device structure led to the replacement of mCBT with BAIq as the hole blocking material. The resulting device structure (device 4 in figure 16) of ITO/HATCN (10nm)/NPD (40nm)/Tris-PCz (8nm)/14% Pt2O2:mCBP(25nm)/BAIq

(10nm)/BPyTP (40nm)/LiF/Al. The results were similarly impressive with a peak EQE value about 20%. Lifetime value of 5.51 hours at LT_{80} of initial luminance was recorded, where initial luminance was 6642 cd/m^2 . This corresponds to LT_{80} values of about 137 hours at 100 cd/m^2 and above 6900 hours at 100 cd/m^2 . These results show that there is some possibility after all in the quest for excimer based white organic light emitting devices with high efficiency and good stability.

Devices **3** and **4** have shown tremendous improvements over the previously tested device structures that had either good EQE values with bad lifetimes (device **1**) or good lifetimes with reduced EQE values (device **2**). The reality of engineering a device stack using a platinum-based excimer emitter with high efficiency and good lifetime figures opens up avenues for easy to fabricate and cheaper white organic light emitting devices. Table 3 shows a summary of device characteristics employing Pt₂O₂ as an emitter in different device structures.

Table 3 - Summary of device characteristics for different device structures
employing Pt2O2 as emitter

Device	%/Host	Peak EQE (%)	CIE	CRI	L ₀ (cd/m ²)	LT ₈₀ @ L ₀ (hrs)	LT ₈₀ @ 1000cd/m ² (hrs)	LT ₈₀ @ 100cd/m ² (hrs)
1	12%/26mCPy	26.5	(0.41, 0.51)	58	-	-	-	-
2	14%/CBP	12.5	(0.46, 0.47)	80	2500	43	206	10232
3	14%/mCBP	23.2	(0.41, 0.53)	48	6922	3.16	85	4247
4	14%/mCBP	20.6			6642	5.51	137	6909

SUMMARY AND FUTURE OUTLOOK

The future of white organic light emitting diodes as a solid-state lighting source is bright. At the end of the day, the goal of any new technology is affordability for the masses, efficiency, scalability in terms of production, low manufacturing cost and most importantly, it has to be safe for humans and safe for the environment.

In this work, we demonstrated white organic light emitting diodes based on tetradentate platinum (II) complexes, which covers the visible spectrum via its monomer and excimer emissions. These complexes have been proven to be efficient, having efficiencies above 20%, and was deployed in a stable device configuration as well. We got promising lifetimes (LT_{80}) of about 144 hours at 1000cd/m^2 , which is comparable to the previous stable but inefficient device stacks (device 2).

This result goes to show that the quest for a stable and highly efficient single emissive layer white organic light emitting device based on excimer emitting platinum tetradentate complex is a possibility whose realization is in the not too distant future. Although this device had obvious shortcomings in terms of poor CRI and below optimum CIE coordinates, it is believed that the shortcomings can be overcome by color tuning of the emission spectrum through careful molecular design.^{103, 104} Furthermore, with continued improvement of charge carrying and blocking materials, and innovations in design engineering of device stacks will definitely move us as close as possible to the DOE's 2020 goal of 200 lm/W for WOLEDs.¹⁰⁵

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