FINAL SCIETIFIC/TECHNICAL REPORT

High efficiency and stable white OLED using a single emitter

Submitted in Response to DOE/NETL
Technology Focus:Solid State Lighting Core Technologies
Area of Interest:Novel Materials and Structures
(Program No. EE0005075)

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Reporting Period End Date: 9/30/2015
Report Term or Frequency: Final

This report contains the patentable data.

1. Executive Summary:

The ultimate objective of this project was to demonstrate an efficient and stable white OLED using a single emitter on a planar glass substrate. The focus of the project is on the development of efficient and stable square planar phosphorescent emitters and evaluation of such class of materials in the device settings. Key challenges included improving the emission efficiency of molecular dopants and excimers, controlling emission color of emitters and their excimers, and improving optical and electrical stability of emissive dopants. At the end of this research program, the PI has made enough progress to demonstrate the potential of excimer-based white OLED as a cost-effective solution for WOLED panel in the solid state lighting applications.

2. Project Accomplishments:

Since the proposed research focuses on the development of phosphorescent emitters and host materials for efficient and stable single-doped white OLEDs, the particular metrics like voltage, EQE without extraction and operational lifetime are used to quantify the progress of the proposed research. During this project, we are expected to improve the EQE of blue and white OLEDs using halogenated and non-halogenated Pt complexes, reduce the operational voltage of devices and increase operational lifetime of OLEDs. This is how the PI proposes to achieve the milestones at the end of each year until we demonstrate single-doped white OLED with a luminous efficiency of at least 50 lm/W and an operational lifetime over 10000 hrs @ 1000 cd/m^2 in the end of program. The specific milestones are listed as below:

1st Year goal (Planned Date: September 30, 2012)
MILESTONE A - Title: Blue Phosphorescent OLED #1
Success Criteria: blue device using Pt-based emitters with an EQE of over 15%
MILESTONE B - Title: White OLED #1
Success Criteria: reducing the driving voltage of FPt device to 4.5 V @ 1000 cd/m^2
MILESTONE C - Title: White OLED #2
Success Criteria: demonstrating a single-doped white device (CRI>80) with a PE of 25 lm/W @ 1000 cd/m^2

2nd Year goal (Planned Date: September 30, 2013)
MILESTONE D - Title: Blue OLED #2
Success Criteria: blue device using Pt-based emitters with an EQE of over 20%
MILESTONE E - Title: Blue OLED #3
Success Criteria: blue device using halogen-free Pt-based emitters with an EQE of over 10%
MILESTONE F - Title: White OLED #3
Success Criteria: demonstrating a single-doped white device (CRI> 80) with a PE of 40 lm/W @ 1000 cd/m^2 and an operational lifetime over 100 hrs @ 1000 cd/m^2

3rd Year goal (Planned Date: September 30, 2014)
MILESTONE G - Title: Blue OLED #4
Success Criteria: blue device using halogen-free Pt-based emitters with an EQE of over 15%
MILESTONE H - Title: White OLED #4
Success Criteria: demonstrating a single-doped white device (CRI> 80) with a PE of 50 lm/W @ 1000 cd/m^2 and an operational lifetime over 10000 hrs @ 1000 cd/m^2

At the end of project, we have delivered Milestones A, D, E and G based on our progress in developing blue phosphorescent OLEDs (i.e. PtON7-based OLEDs). And we realized the set goals in Milestones B

and C. We have reduced the driving voltage of FPt devices to 4.3 V at brightness of 1000 cd/m^2(shown in Figure 7) and Pt-16 devices showed a power efficiency of 28 lm/W at 1000 cd/m^2 with a CIE (.33, .32) and a CRI of 80. The progress of Pt7O7 based OLEDs also helps us to realize the partial set goal in Milestone D by achieving a better device operational lifetime and desirable power efficiency at the two different device settings. The progress demonstrated by Pd3O3 based devices has helped us to achieve 60% of Milestone F and 25% of Milestone H.

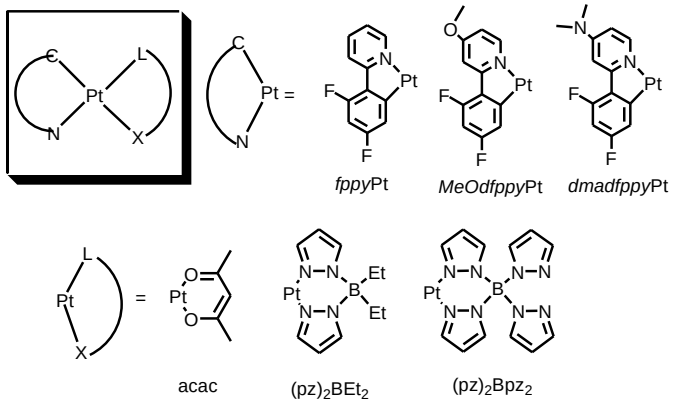
3. Project Summary:

The research project activities are outlined as below:

Task 1 Development of square planar blue phosphorescent emitters

In addition to evaluate the derivatives of platinum(II) [2-(4',6'-difluorophenyl) pyridinato-N, C$^{2'}$)](2,4-pentanedionato) (FPt), several classes of square planar phosphorescent emitters will be synthesized and studied systematically. The proposed emissive materials will be characterized in the device settings in terms of device efficacy and operational stability.

Figure 1 - The chemical structures for the proposed Pt(C^N)(LX) complexes.



Task 1.1 FPt and its analogues

A series of (*C^N*)Pt(LX) complexes (Figure 2) will be synthesized and characterized in the device settings. The cyclometalating ligands will be modified to have a higher triplet energy gap, resulting in a blue-shifted emission spectrum. And the high energy ancillary ligands like anionic bis(pyrazolyl) borate will be used to enhance the emission efficiency of FPt analogues.

Task 1.2 Tridentate Platinum (II) complexes

A series of (*N^C^N*)PtL complexes (Table 1) will be synthesized and characterized. The cyclometalating ligands are di-pyridyl-bezene ligand and its derivatives, and the ancillary ligands could be monodentate and anionic ligands like halide and phenoxide. The emission energies of Pt(*N^C^N*)L can be blue-shifted from green emitting Pt-1 by 1) adding electron-withdrawing groups (like F-) on the phenyl ring, 2) replacing pyridyl rings with higher energy electron accepting ligands like methyl imidazole and pyrazole, 3) using higher triplet energy ligands like pyridoxyl-phenylpyridine. The use of ancillary ligands with different geometries will be explored to control the excimeric energies of (*N^C^N*)PtL complexes in order to achieve saturated white light by combining monomeric and excimeric emissions from the proposed Pt complexes.

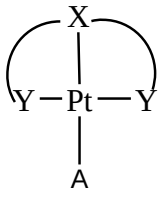
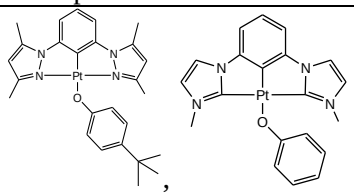
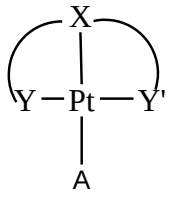
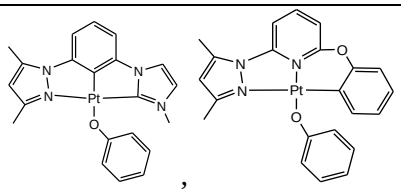
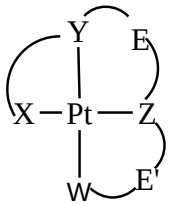
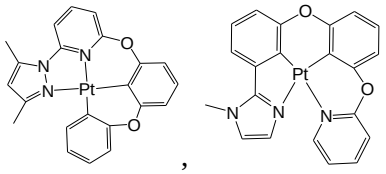
Task 1.3 Asymmetric tridentate Platinum (II) complexes

A series of (*Y^X^Y'*)PtA complexes (*Class II*, Table 1) will be synthesized and characterized, where X, Y and Y' are coordinating ligands consisting of –C or –N, A is a monoanionic ligand, and the Pt complexes are asymmetric since Y and Y' are not identical.

Task 1.4 Platinum (II) complexes with four coordinated ligands

A series of Pt complexes with four coordinated ligands, i.e. (*X^Y^Z^W*)Pt complexes (*Class III*, Table 1) will be synthesized and characterized, where X, Y, Z and W are coordinating ligands consisting of –C or –N, E and E' are linkage groups like –O- and its derivatives. High triplet energy ligands will be chosen to ensure the blue emission of Pt complexes.

Table 1.Chemical structure for proposed Pt complexes (*Class I-III*).

General forms	Description	Examples
 *Class I.*	X and Y are coordinating ligands consisting of –C or –N, A is a monoanionic ligand, and the Pt complexes have planar symmetry since two Y ligands are identical	 Pt-I-a , Pt-I-b
 *Class II.*	X, Y and Y' are coordinating ligands consisting of –C or –N, A is a monoanionic ligand, and the Pt complexes are asymmetric since Y and Y' are not identical	 Pt-II-a , Pt-II-b
 *Class III.*	X, Y, Z and W are coordinating ligands consisting of –C or –N, E and E' are linkage groups like –O- and its derivatives	 Pt-III-a , Pt-III-b

Task 2 Development of ambipolar host materials

In addition to evaluate the developed emitters in the ambipolarcabazole-based host materials, a series of metal complexes with high energy four coordinated ligands, i.e. (*X^Y^Z^W*)M complexes (M=Pt^{2+}, Pd^{2+}, etc), will be synthesized and studied systematically. The proposed host materials will be characterized in the device settings in terms of device efficacy and operational stability.

Task 3 Device fabrication

Task 3.1 Device optimization

OLED devices incorporating p- and n-doped transporting layers will be fabricated. The emissive layer will consist of Pt-based emitters (FPt and developed emitters) and host materials (mCP and its analogues). The current-voltage-light (I-V-L) characteristics of the resulting white emitting devices will be measured. The dopant concentration and profile will be optimized for device performance.

Task 3.2 Lifetime testing

In addition to testing the operational lifetime of each white OLEDs, the developed emitters from the Task 1 will be tested individually with literature-reported host materials from stable blue, green and red phosphorescent OLEDs. The light-time (L-t) characteristics of the resulting OLED will be measured at the constant driving current of 20 mA/cm^2 or higher

During the last 4 years, we have made significant progress in the Task 1.1, Task 1.2 and Task 1.4, where the research outcomes of latter two tasks are quite satisfactory and help to successfully reach several milestones proposed in the research plan in a timely fashion. A brief description of research highlights from Task 1.2 and Task 1.4 are presented as below.

Task 1.2 Tridentate Platinum (II) complexes

A series of Pt-based complexes have been successfully synthesized according to the research plan described in Task 1.2. The blue-emitting compounds including Pt-14, Pt-15, Pt-16 and Pt-17 have been synthesized (Figure 2). And the white OLEDs,based on platinum(II) bis(N-methyl-imidazolyl)benzene chloride (Pt-16), have be fully characterized (Figure 3). A single-doped white OLED with a CIE (.33, .32) and a CRI of 80 was demonstrated with a maxim power efficiency of 51 lm/W at low brightness and a power efficiency of 28 lm/W at 1000 cd/m^2.

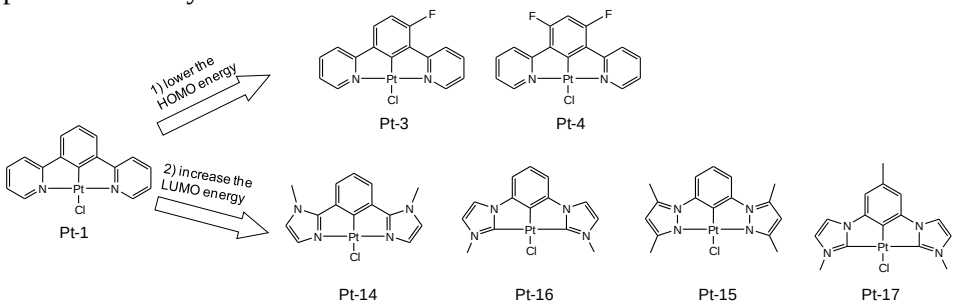
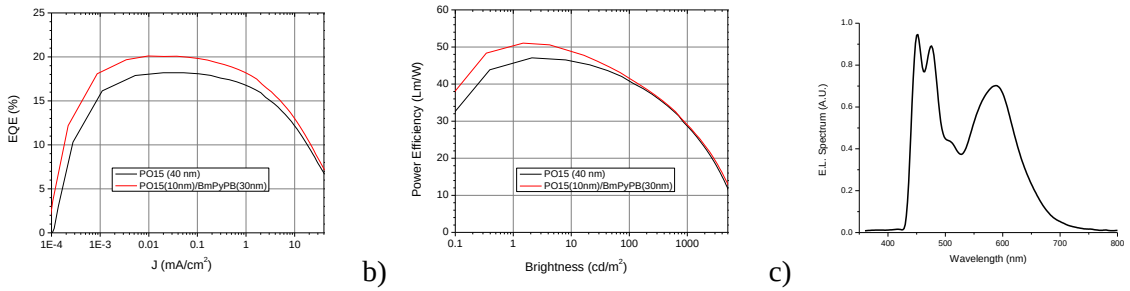


Figure 2**.**Materials design and chemical structures of tridentate platinum-based blue phosphorescent emitters discussed in this report.



a) b) c)

Figure 3**.** Performance characteristics of Pt-16 based WOLEDs using TAPC:PO15 as co-host materials. a) Forward viewing external quantum efficiency versus luminance, b) power efficiency versus luminance and c) electroluminescent spectrum of the WOLED. The device structures areITO/PEDOT/NPD(30nm)/TAPC(10nm)/10%Pt-16:TAPC:PO15(25nm)/ETL/LiF/Al, where ETLs are PO15(40nm) or PO15(10nm)/BmPyPB(30nm).

Moreover, a deep blue OLED with a maximum EQE of 15.7% and CIE coordinates of (0.16, 0.13) was fabricated based on Pt-16, as shown in Figure 4 and Table 2.

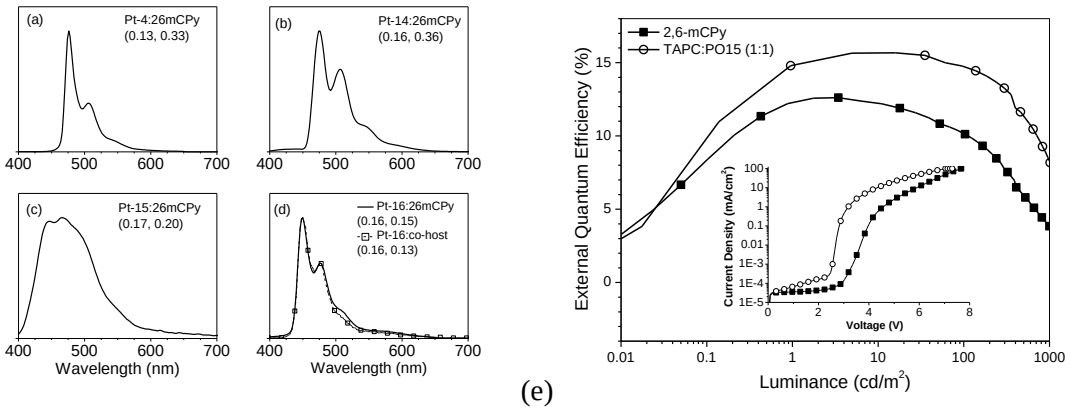


Figure 4**:** Normalized electroluminescent spectra, accompanied by CIE values of (a) Pt-4, (b) Pt-14, (c) Pt-15 and (d) Pt-16 devices at 1mA/cm^2. The general device structure is ITO/PEDOT:PSS/NPD(30 nm)/TAPC(10 nm)/2% emitter: host(25 nm)/PO15(40 nm)/LiF/Al. The host materials could be ether 26mCPy or co-host of TAPA:PO15 (1:1). (e) External quantum efficiency-luminance and current density-voltage (inset) characteristics for the Pt-16 devices with different host materials: 26mCPy and co-host of TAPC:PO15 (1:1). The general device structure is ITO/PEDOT:PSS/NPD(30 nm)/TAPC(10 nm)/2% Pt-16:host(25 nm)/PO15(40 nm)/LiF/Al.

Table 2. A summary of device characteristics for the structure: ITO/NPD(30 nm)/TAPC(10 nm)/EML(25 nm)/PO15(40 nm)/LiF/Al. Each device is listed by its emissive layer at a luminance of 100 cd/m^2. Parameters listed are driving voltage (bias), current density, forward viewing external quantum efficiency (EQE), CIE coordinates and power efficiency (P.E.).

Emissive Layer	Bias [V]	Current Density [mA/cm^2]	EQE [%]	CIEx	CIEy	P.E. [Lm/W]
2% Pt-4:26mCPy	5.1	0.35	15.9	0.13	0.33	17.4
2% Pt-14:26mCPy	5.2	0.24	18.1	0.16	0.36	23.3
2% Pt-15:26mCPy	7.8	25.7	0.68	0.17	0.20	0.16
2% Pt-16:26mCPy	4.5	0.81	10.1	0.16	0.15	8.96
2% Pt-16:co-host	3.0	0.51	14.8	0.16	0.13	19.3

Task 1.4 Platinum (II) complexes with four coordinated ligands

A series of Pt-based complexes have been successfully synthesized according to the research plan described in Task 1.4. The blue-emitting compounds including PtOO1, PtON1, PtOO7 and PtON7 have been synthesized and characterized in the device settings (Figure 5). Our developed blue PhOLED, i.e. Pt-ON7 based devices, have achieved a maximum EQE of over 22% with CIE coordinates of (0.14, 0.15), as illustrated in Figure 6.

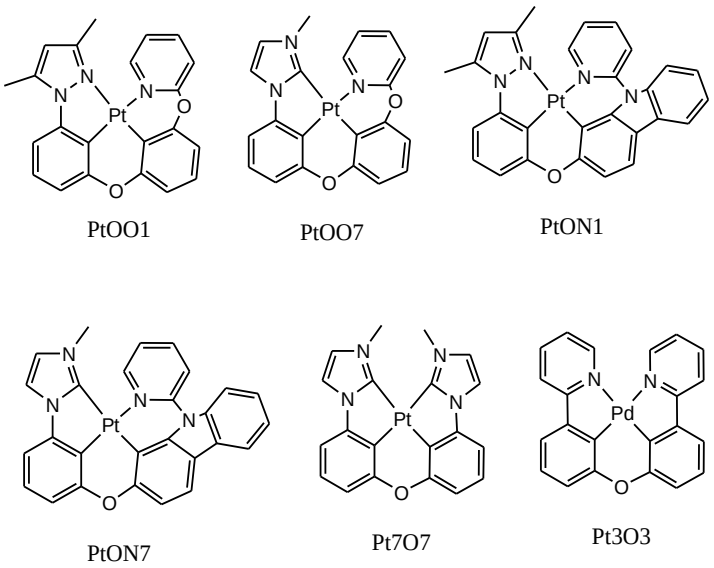


Figure 5**.**Materials design and chemical structures of tetradentate platinum-based and palladium-based blue phosphorescent emitters discussed in this report.

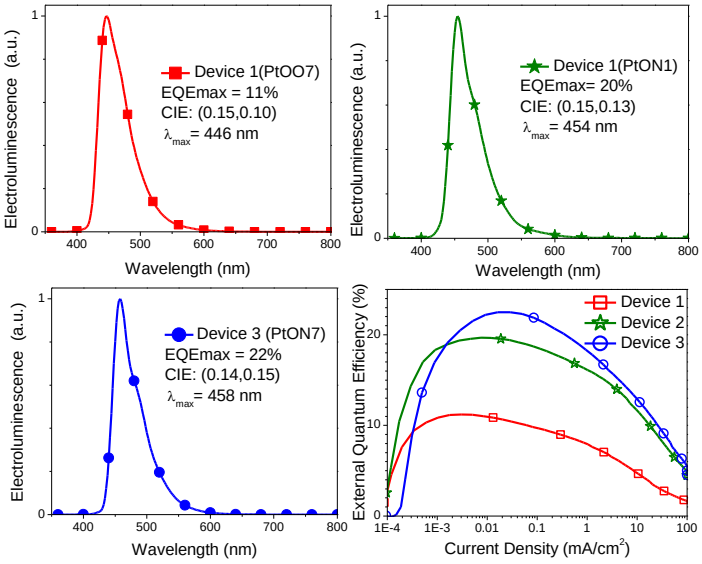
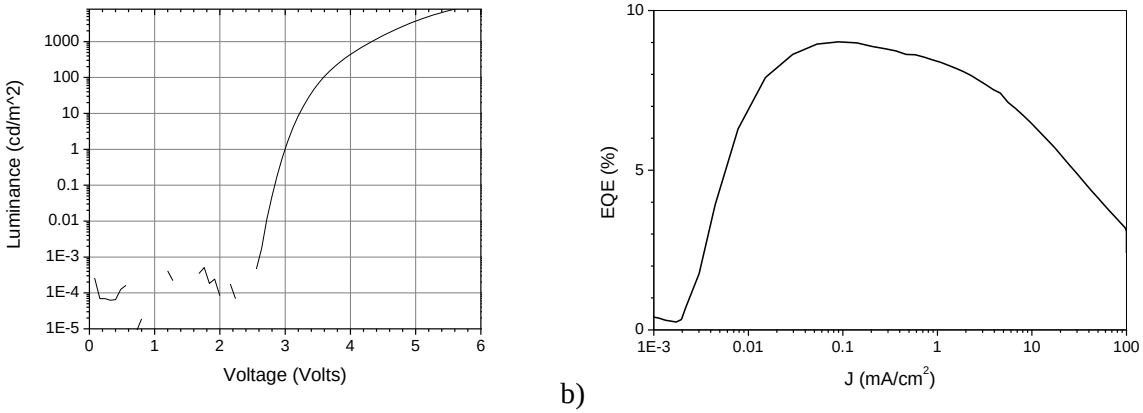


Figure 6. Electroluminescent emission and external quantum efficiency Pt complex device properties with a general device structure of ITO/PEDOT:PSS(40nm)/TAPC(20nm)/8% emitter:26mCPy (25nm)/PO15(10 nm)/BmPyPB(30nm)/LiF/Al.



a) b)

Figure 7.Plots of a)brightness versus driving voltage and b) forward viewing external quantum efficiency versus current density, of FPt-based WOLED. The device structure isITO/PEDOT:PSS/TAPC(10nm)/22%FPt:26mCPy(15nm)/PO15(10nm)/BmPyPB(20nm)/LiF/Al.

Following a similar material engineering method, we have demonstrated that a square planar blue-emitting Pt7O7 can have both efficient monomer and excimer emission. As illustrated in Figure 8 a-b, all of Pt7O7 based devices have peak EQEs in the range of 24-26% with the variation in their dopant concentrations. Moreover, 14% doped Pt7O7 device have demonstrated a reasonable device operational lifetime with LT_{50} over 35 hrs at constant current of 20 mA/cm^2 with initial luminance of around 3000 cd/m^2, which can be translated to a LT_{50} over 300 hrs at initial luminance of 1000 cd/m^2. Although the device efficiency drops significantly with the incorporation of stable device architecture, these are very encouraging results for us to further optimize the device architecture to achieve the desirable device efficiency and operational lifetime.

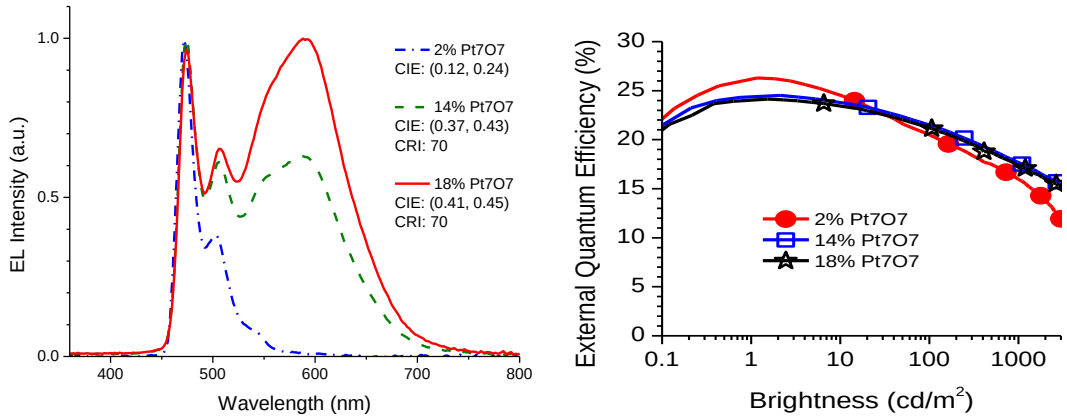


Figure 8. Plots of (a) the EL spectrum and (b) external quantum efficiency vs. brightness for devices: ITO/HATCN(10 nm)/NPD(40 nm)/TAPC(10 nm)/x% Pt7O7:mCBP(25 nm)/DPPS(10 nm)/BmPyPB(40 nm)/LiF/Al, where x ranges from 2-18.

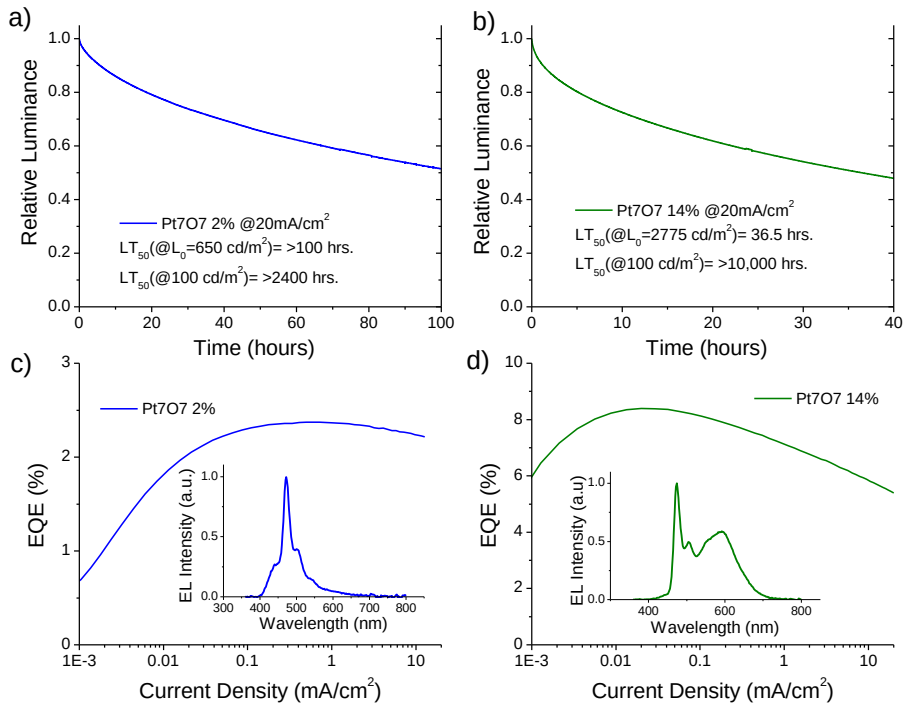


Figure 9. The operational lifetime for (a) 2% Pt7O7 and (b) 14% Pt7O7 devices run at a constant current of 20mA/cm^2 and the EQE versus current density for (c) 2% Pt7O7 and (d) 14% Pt7O7 devices with El spectra at a current of 1mA/cm^2 inset. Devices are in the general structure: ITO/HATCN(10 nm)/NPD(40 nm)/x% Pt7O7:mCBP(25 nm)/BAlq(10 nm)/Alq(30 nm)/LiF/Al.

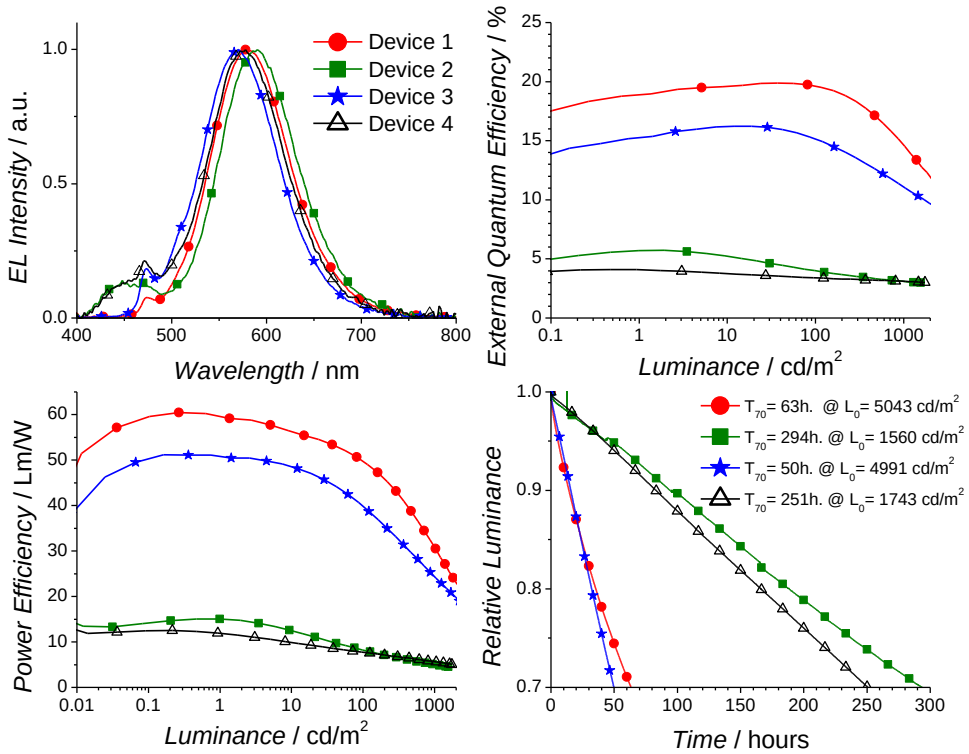


Figure 10 a)Electroluminescent spectra, b)external quantum efficiency versus luminance, c) power efficiency versus luminance and d) operational lifetime for Pd3O3 in Device 1 (circles), Device 2 (squares), Device 3 (stars), and Device 4 (triangles), Device 1: ITO/HATCN/ NPD/TrisPCz /10% Pd3O3:mCBP/BAlq/BPyTP/LiF/Al, Device 2: ITO/HATCN/NPD/10% Pd3O3:mCBP/BAlq/ BPyTP/LiF/Al, Device 3: ITO/HATCN/NPD/TrisPCz /10% Pd3O3:26mCPy/BAlq/BPyTP/LiF/Al, Device 4: ITO/HATCN/NPD/10% Pd3O3:26mCBP/BAlq/BPyTP/LiF/Al. The device operational lifetime was measured at a constant drive current of 20mA/cm^2.

Additionally, we developed a planar deep blue emitting palladium complex, Pd3O3, for potential use in excimer based white devices. After thoroughly optimizing the device performance of Pd3O3 in the past several months, we have demonstrated that phosphorescent excimers will indeed have the potential to be useful for organic solid state lighting applications. As illustrated in Figure 10, the device 1 with Pd3O3 was very efficient reaching peak EQEs and power efficiencies of 19.9% and 60.5 lm/W. The roll-off for these devices were also less significant than most reported excimer-based WOLEDs with EQE values of 14.6% at 1000cd/m^2. The device operational lifetimes of all 4 stable devices were measured at accelerated conditions by driving the devices at a constant current of 20mA/cm^2. Device 1 also demonstrated a very good operational lifetime to 70% of initial luminance (LT_{70}) of 63h at the brightness of 5043cd/m^2. Furthermore, extrapolating these accelerated testing results to practical luminance of 1000cd/m^2 yields lifetimes of 986 h for devices. These high lifetimes (LT_{70} ~ 1000 hrs) and high power efficiency (> 30 lm/W) at practical luminance of 1000 cd/m^2 represent a substantial improvement upon previous reports of excimer emitting Pt complexes.

4 Products:

a. Publications:

1) G. Li, T. Fleetham, J. Li*, "A Stable and Efficient Red-emitting Platinum Complex with Long Operational Stability", ACS Appl. Mater. & Interfaces, 7 (30), 16240-16246 (2015).

2) Z. Zhu, T. Fleetham, E. Turner, J. Li*, "Harvesting All Electro-generated Excitons through Metal Assisted Delayed Fluorescent Materials", Adv. Mater., 27(15), 2533-2537 (2015).

3) G. Li, T. Fleetham, E. Turner, X. Hang, J. Li*, "Highly Efficient and Stable Narrow-Band Phosphorescent Emitters for OLED Applications", Adv. Opt. Mater., 3(3), 390-397 (2015), top 5 downloaded article for January 2015.

4) T. Fleetham, J. Li*, "Recent Advances in White Organic Light-emitting Diodes Employing a Single-Emissive Material" (Review Article), J. Photon. Energy. 4(1), 040991 (2014).

5) T. Fleetham, G. Li, L. Wen, J. Li*, "Efficient Pure Blue OLEDs Employing Tetradentate Pt Complexes with A Narrow Spectral Bandwidth", Adv. Mater., 26 (41), 7116-7121 (2014).

6) T. Fleetham, L. Huang and J. Li*, "Tetradentate Platinum Complexes for Efficient and Stable Excimer-Based White OLEDs", Adv. Funct. Mater. 24, 6066–6073 (2014).

7) G. Li, J. Ecton and J. Li*, "Efficient and Stable Red Organic Light Emitting Devices from A Tetradentate Cyclometalated Platinum Complex", Org. Electron., 15 (8), 1862-1867 (2014).

8) B. O'Brien, G. Norby, G. Li and J. Li*, "High-efficiency White Organic Light-emitting Diodes Employing Blue and Red Platinum Emitters", J. Photon. Energy, 4 (1), 043597-043597 (2014).

9) G. Li, T.B. Fleetham and J. Li*, "Efficient and Stable White Organic Light Emitting Diodes Employing a Single Emitter", Adv. Mater., 26 (18), 2931-2936 (2014), highly cited paper (top 1% for the field and publication year) based on WEB of SCIENCE.

10) X.C. Hang, T.B. Fleetham, E. Turner, J. Brooks and J. Li*, "Highly Efficient Blue-Emitting Cyclometalated Platinum(II) Complexes by Judicious Molecular Design", Angew. Chem. Inter. Ed., 52, 6753-6756 (2013), highly cited paper (top 1% for the field and publication year) based on WEB of SCIENCE.

11) T.B. Fleetham, J. Ecton, Z. Wang, N. Bakkan, and J. Li*, "Single-Doped White Organic Light-Emitting Device with an External Quantum Efficiency Over 20%", Adv. Mater., 25, 2573-2576 (2013).

12) E. Turner, N. Bakkan and J. Li*, "Cyclometalated Platinum Complexes with Luminescent Quantum Yields Approaching 100%", Inorg. Chem., 52, 7344-7351 (2013).

b. Web site or other Internet sites that reflect the results of this project: N/A

c. Networks or collaborations fostered: N/A

d. Technologies/Techniques:

Efficient and stable single-doped white OLED as potential OLED panel for solid state lighting applications.

e. Inventions/Patent Applications:

1) J. Li, T. Fleetham, "Organic Light-Emitting Diodes with Fluorescent and Phosphorescent Emitters", Serial number: 62/040,470.

2) J. Li, L. Huang, T. Fleetham, "Non-Platinum Metal Compelexes for Excimer Based Single Dopant White OLEDs", Serial number: 62/037,802.

3) J. Li, E. Turner, "Iridium Complexes Demonstrating Broadband Emission Trough Controlled Geometric Distortion And Applications Thereof", Serial number: US 13/963,519.

4) J. Li, E. Turner, L. Huang, "Metal Compounds and Methods and Uses Thereof", Serial number: PCT/US13/56426.

We are currently in the discussion with Universal Display Corporation regarding possible licensing agreement.

f. Other products: N/A.

5 <u>Project involving computer modeling</u>: N/A