R-Display & Lighting LLC

FY 2019 Phase I – Final Technical Report (DOE-RDL-2020)
Award: DE-SC0020000
(07/06/2020)

Novel Blue Phosphorescent Emitter Materials for OLED Lighting

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Executive Summary

Research carried out under the DOE SBIR Phase I project has resulted in the identification of novel blue emitter materials that have application for OLED lighting. The materials demonstrate the capability to produce blue light when incorporated in thin-films which are useful for OLED lighting. The technology offers the potential to combine high efficiency, operational stability suitable for commercial application and lower manufacturing cost. The materials are also considered scalable for manufacturing/commercialization operations. Discovery of efficient and operationally stable blue emitters that are scalable represent a long-standing challenge for the advancement of OLED lighting.

Problem Statement

Organic Light Emitting Diode (OLED) panels manufactured for solid state lighting (SSL) currently use red and green phosphorescent emitter materials to achieve high light producing efficiency. However, less efficient blue fluorescent emitter materials are still used to achieve suitable stability for commercial applications. The department of energy SSL program has identified highly efficient and stable blue emitter materials as a major opportunity to advance the performance and subsequently commercial applications for OLED SSL panels.[1] To address the blue emitter technology gap and product market opportunities, R-Display & Lighting (RDL) has developed a new class of highly efficient phosphorescent emitters with inherent properties for improved device operational stability.

Anticipated Public Benefits

Leading OLED manufacturers are seeking more options for phosphorescent materials to drive future product development and are specifically asking for a solution to blue phosphorescent materials which are currently too unstable for commercial applications.[2] Implementation of a highly efficient blue emitter with stability suitable for commercial application would have the direct benefit of advancing energy efficient OLED panels for SSL applications.[3] Both commercial and government agencies would benefit from the energy savings. In addition, better performing OLED 2SSL panels would help expand the commercial market for OLED lighting and broaden access to key differentiating features inherent in OLED lighting such as; glare reduction, conformability, transparency, and thin and lightweight designs.[4] Additional benefits to be realized include uniform white color quality and flexible substrate applications for creative OLED lighting designs.

There is great opportunity for energy consumption reductions and improved performance. According to UBI Research, ‘the OLED lighting market (panel sales) will reach $1.9B by 2021 and will continue its fast growth to reach $5.8 billion by 2025. That represents a CAGR of 85% from 2017 to 2025.[5]

Broader Societal Impact

R-Display & Lighting new blue emitter technology could have a broader societal impact through advancing the energy efficiency of OLED lighting for building use. Specifically, contributing to the reduction in the greenhouse gas footprint would have both economic and health benefits for society. The economic impact of reducing greenhouse gases has been well studied implicating cost savings from tens of billions of dollars to trillions of dollars.[6] Health benefits from reduction in general air pollution has also been well studied and documented by government and academic institutions.

Technical Background and Project Objectives

Phosphorescence OLED Technology

of organic thin-films between electrodes (anode and cathode).[7,8,9] The basic structure of an OLED device is shown in Figure 1. Injection of holes and elections from the anode and cathode result in light emission through recombination of the holes and electrons in the emissive layer of the organic Phosphoescent ermitter technology has enabled the advancement of highly efficient Organic Light Emitting Diode (OLED) devices. OLED devices are fabricated through the strategic placement stack. Organic thin films are typically less than 50 nm in thickness resulting in low voltage operations for low power consuming devices.

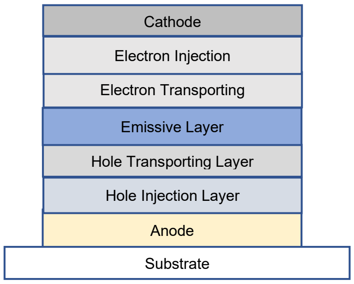


Figure 1. Basic OLED Device Structure

The excited states generated from the hole and electron injection processes establishes two pathways for light emission. Singlet and triplet exciton decay yield fluorescent and phosphorescent light respectively. The ratio of singlet to triplet exciton formation is 1:3.[10] Therefore, emissive layers comprised of fluorescent emitters and host materials which harvest singlet excitons have a theoretical limit of 25% for converting excitons into light. *However, phosphorescent systems can theoretically convert 100% of the excitons generated into light by harvesting singlet excitons (after intersystem conversion) and triplet exitons*s.[11] The exciton harvesting capability illustrates the value of phosphorescent emitters to the advancement of highly efficient OLED technology.

Blue Emitter Problem and Competitive Approaches

The OLED industry has largely converted from use of less efficient red and green fluorescent emitters to more efficient phosphorescent systems. However, blue fluorescent emitters remain the only commercial option due to stability problems associated blue phosphorescent emitters.[12] Phosphorescent cyclometalated Iridium complexes commercialized by Universal Display Corporation are the current industry standard for red and green emitters.[13] Attempts to develop blue phosphorescent cyclometalated emitters from this platform have been largely unsuccessful. The problem is linked to the photophysics of high energy exitons generated during the production of blue phosphorescent light. The energy levels are comparable to the energy required to rupture molecular bonds. Theoretical studies indicate the weak link in cyclometaled Iridium complexes is the Ir-N donor-acceptor (or dative) bond which is predicted to rupture during excited state interactions.[14] The extended lifetime of phosphorescent emitters also increases the probability of high energy interactions initiating the rupture of molecular bonds, and specifically the relatively weak Ir-N donor-acceptor bond. Shorter excited state lifetimes of fluorescent singlet exitons (nanoseconds versus microseconds) is the principle reason why blue florescent emitters provide more stability.[15]

Over the last 8 years, thermally activated delayed fluorescence (TADF) and hyperfluorescence (TADF + fluorescence emitter) technology have received considerable attention and funding across the OLED industry as alternative high efficiency emitter materials.[16] Interest has been based on the potential to combine high efficiency with a lower cost approach. TADF and hyperfluorescence eliminates the high cost of precious metals used for current cyclometalated phosphorescent emitter materials. However, device stability issues associated with TADF technology have been difficult to overcome. The problem can be ascribed to the photophysics involving additional steps in the excited state. Starting with the initially populated T1 state, the next step is reverse intersystem crossing to the S1 state for TADF and an additional energy transfer to a second S1 state for hyperfluorescence). It is reasonable to assume the extra steps increases the potential for decomposition pathways to become more competitive. In contrast, phosphorescence occurs through direct relaxation from the initially populated T1 state.

Innovation and market Solution

Based on a several significant discoveries from the DOE Phase I project, RDL is in position to potentially deliver new breakthrough blue emitter technology that combines the lower-cost benefits of TADF emitters, with desirable photophysics of phosphorescence without the weak link associated with cyclometalated emitters. Highly efficient, blue emitting “pure organic” room temperature phosphorescent (RTP) compounds were discovered as part of the Phase I emitter development work. Pure organic RTP emitters are rare.[16] The materials that have been discovered are likely the first examples of highly efficient, blue emitting, pure organic RTP emitters

Original goals from the Phase I project centered around new Pt metal based phosphorescent emitters with enhance metal-ligand bond stability based on Density Functional Theory calculations. The target emitter materials have been successfully synthesized characterized and evaluated. The first discovery originated from attempts to sublime the high molecular weight complexes. The sublimation process involved placement of the material into a horizontal sublimation system for final purification. Upon heating, the materials melted before product vaporization. The evaporated material was collected from the walls of the sublimation tube. The product was characterized by using mass spectral techniques and elemental analysis. Two pure organic compounds were identified as the dominant vaporized product(s). The products are apparently produced through a novel reductive elimination process.

The identified products were well separated on the LC column from the LCMS analysis. Product 1A, is apparently produced through cleavage of the isoquinoline N-Pt bond and the tertiary amine-pyridyl N-C bond of the chelating ligand. Whereas product 1B is interpreted to be produced through the oxidation of product 1A resulting in a novel cyclized product. The reduction product is platinum metal. A similar process is observed for the analogous quinoline complex

The qualitative mass spectral technique, atmospheric solids analysis probe mass spectrometry (ASAP-MS) provided a stronger mass/z signal for the cyclized product in the above scheme. However, the quantitative LCMS analysis indicated a 1A:1B product ratio of approximately 2:1.

Photoluminescence studies of the isolated product mixture show the novel products are unique phosphorescent emitters. It was assumed initially the sublimed product consisted of the target Pt metal complex. As a standard practice, simple oxygen quenching experiments were conducted to determine if solutions of the product demonstrated emissive properties consistent with phosphorescence.

Phosphorescence emission is typically quenched in the presence of oxygen due to the extended excited state lifetime which is normally on the microsecond timescale.[17] On the other hand, oxygen quenching is typically not observed for fluorescence as the excited state lifetime occurs on the nanosecond timescale. For the quenching experiments, solutions of the sublimed product were prepared in air using polar solvents then exposed to UV light to qualitatively observe any luminance. Subsequently, the solutions were purged with nitrogen while being exposed to the UV light. A significant increase in luminance was observed during this process along with a bathochromic shift the in emission. These observations are consistent with phosphorescent emission. An example of the observed increase in luminance is provided in the following images (Figure 3).

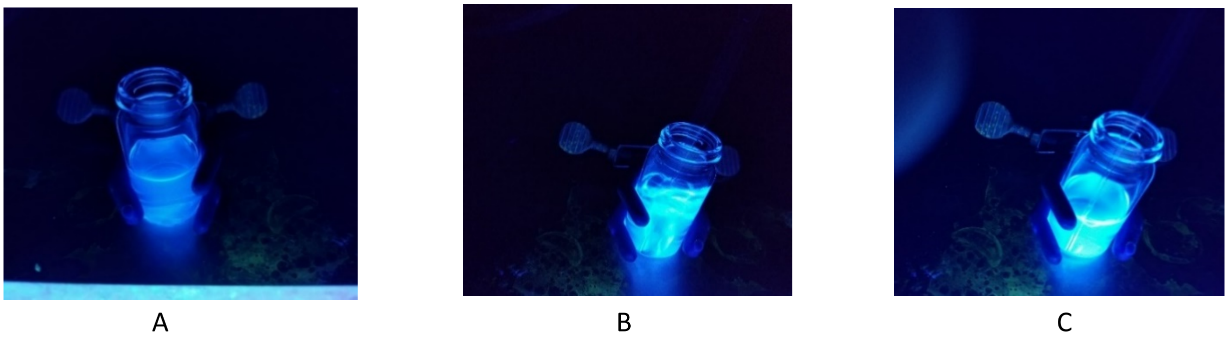


Figure 3. (a) blue emitter solution prepared in air, (b) solution purged with nitrogen and (c) solution after purging process.

Supporting data for phosphorescence emission was provided from direct photoluminescence (PL) measurements and the calculated Stokes shift. The energy difference between the absorption or excitation band maxima and the emission band maxima is called the Stokes shift.[18] The Stokes shift provides a reliable metric for distinguishing between fluorescence and phosphorescence emission. Phosphorescence occurs from energy released from the T1 excited state which is the lowest energy level of the triplet exciton manifold. The T1 state is always at a lower energy position relative to the S1 state from which fluorescence light is generated. In both cases the absorption/excitation energy promotes the S0 → S1 transition as the first step. The energy gap between the excitation energy and fluorescence is typically small resulting in a Stokes shift that is usually < 30 nm. Population of the T1 state occurs through intersystem crossing from the higher energy S1 state. As a result, there is a larger energy gap between the excitation energy and phosphorescence emission. The observed Stokes shift for phosphorescence emission is typically > 70 nm. The calculated Stokes shift for the novel elimination product(s) 1A/1B was 74 nm providing strong evidence for phosphorescence emission. The emission spectrum of the product(s) is represented in Figure 4.

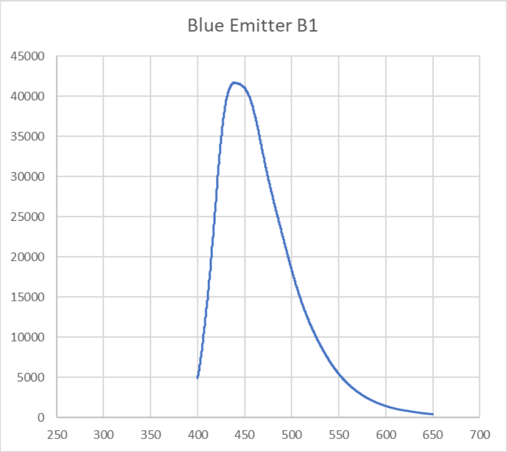


Figure 5. Photoluminescence spectrum of novel reductive elimination product(s).

The measurement indicated very high efficiency for the novel blue emitter materials with 42,000 intensity units observed. To gauge the relative efficiency, the well-known blue-green phosphorescent emitter bis[2-(4,6-difluorophenyl)pyridinato-C^2,*N*](picolinato)iridium) or FIrpic was used as a reference. The quantum yield for FIrpic has been reported above 80%.[19] Solutions of the product and the reference emitter were prepared under nitrogen. The excitation wavelengths were selected by scanning with the detector positioned at 460 nm as a common emission wavelength. To our surprise, the emission intensity of the product was several orders of magnitude greater than the reference FIrpic. Since the excitation wavelength was selected based on 460 nm emission as opposed to 470 nm (reported maximum wavelength for FIrpic) a falloff in efficiency is not unexpected. The magnitude of the efficiency gap however could not be predicted.

To probe the unexpected efficiency gap, the PL spectrum of FIrpic produced on the same instrument as part of a separate experiment was reviewed. In this case, the excitation wavelength was optimized at an emission wavelength of 470 nm (near emission maximum). The concentration of the two FIrpic solutions was estimated to be within a factor of two based on best practices. In comparing the emission spectra, a very weak emission signal (~20 intensity units) was recorded for the 460 nm optimized spectrum versus an emission signal of ~18,000 intensity units recorded for the 470 nm optimized spectrum. For the later, the emission intensity is on the same scale as the 42,000 intensity units recorded for the novel product(s).

Two key points from the study; 1) efficiency at the desired blue wavelength of 460 nm is extremely high for the new product compared to the reference FIrpic, 2) based on the raw intensity data, a quantum yield that exceeds 100% cannot be ruled out for the novel emitters without further studies. Solution PL quantum yields as high as 200% have been previously recorded for pure organic emitter materials.[20] This occurs through an excited state process called Singlet fission. This involves the photophysical process of the excited S1 state combing with the S0 ground state and splitting into two triplet T1 states thereby doubling the efficiency.[21]

As previously suggested, several discovers of pure organic RTP emitter materials have been made. The new compounds Product 2 and Product 3 were initially detected as side products, from synthesis of the quinoline and isoquinoline tetradentate ligands. Subsequently, the amine compounds were directly synthesized to evaluate as potential ligands for phosphorescent metal complexes. Using the same solution measurements previously discussed, phosphorescent properties of the new compounds were confirmed.

A Stokes shift of 70 nm consistent with phosphorescence was calculated for Product 2. The recorded emission intensity was 48,000 intensity units at the same concentration used for product(s) 1A/1B. The emission intensity compares favorably to the intensities observed for the reductive elimination product(s) (42,000 intensity units) and the reference FIrpic (18,000 intensity units). The PL spectrum of Product 2 is shown in Figure 6. There is a common molecular framework between the reductive elimination product(s) and the directly synthesized phosphorescent amine emitters that could explain the comparable emissive properties.

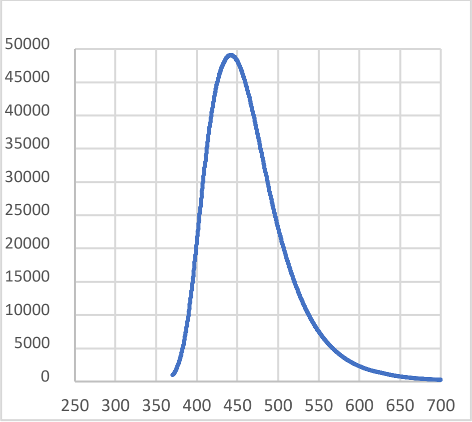


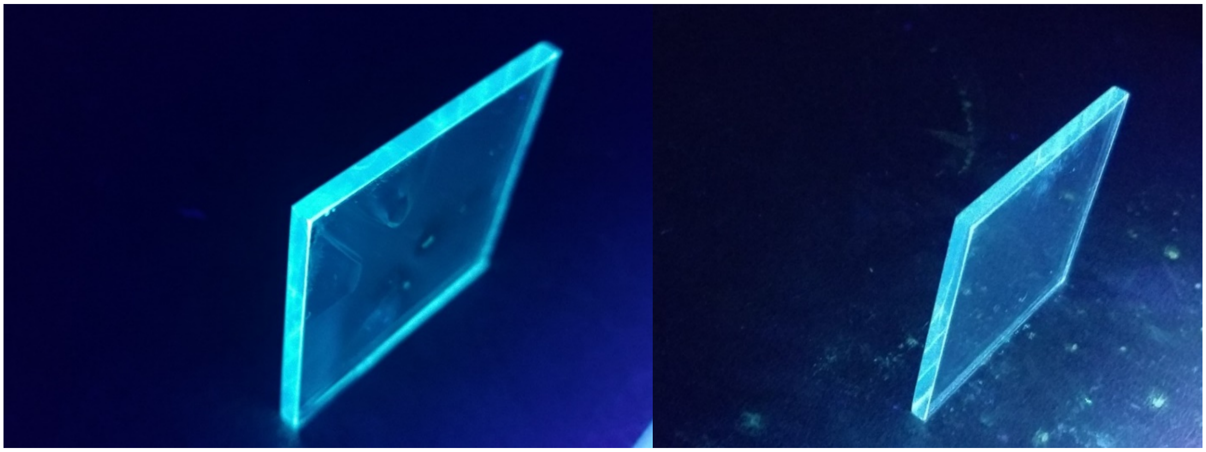
Figure 6. Emission spectrum of Product 2

Product 2 was used as a ligand to prepare a main-group gallium complex. The complex was isolated by reacting the organometallic compound dimethyl-gallium(cyclopentadienyl) (Me_2GaCp) with the amine ligand in Toluene.

Unlike most platinum metal complexes that have been prepared, the gallium complex can be readily sublimed as part of the final purification process**. Through qualitative photoluminescence experiments, it was observed that the phosphorescent gallium complex uniquely shows high efficiency in the bulk solid state and in diluted states. There are favorable device stability implications based on the ability to use high emitter or dopant concentrations in an OLED emissive layer**

Another important property exhibited by the gallium complex as well as the other blue emitter materials, is lower sensitivity to phosphorescence quenching from ambient oxygen. This could indicate a relatively shorter excited state lifetime which is desirable for both device stability and efficiency roll-off problems often experienced with phosphorescent emitters. Excited state lifetime measurements will be conducted as part of the Phase II project work.

Due to the work stoppage in NYS as result of COVID-19, opportunities to evaluate the emitter materials in OLED devices were not available. Timing of the work shutdown also removed the opportunity for additional PL measurements including measurements for the gallium complex. However, to demonstrate potential application for thin-film OLED devices, thin-film coatings of the blue emitting gallium complex were deposited on glass plates using standard spin-coating techniques. Solutions were prepared by combining high Triplet energy host materials with the emitter in organic solvents such as Toluene or dichloromethane. After thin-film deposition was completed, the coatings were exposed to a standard UV lamp to determine qualitatively the light producing efficiency. Images of exposed coatings prepared from PMMA and a PNNL acquired Si based host are shown in Figures 7. In both cases, **bright** light-blue or turquoise-blue light was observed emitting from the glass. Significant light was directed out from the sides of the glass through light piping.



A B

Figure 7. UV exposed coatings of gallium metal-complex emitter in; (A) PMMA host and (B) PNNL Si based Host

As a follow-up, thin-film coatings of the reduction elimination product(s) and Product 2 were deposited on glass plates. Images of the coating are shown in Figures 8 and 9 along with the respective solution PL spectra for comparison.

Coatings with the reduction elimination product(s) were prepared using the PNNL high Triplet energy host and PMMA was used as the host for Product 2. A more pure-blue color was observed from the reduction elimination product(s) coating when exposed to UV light. The luminance observed from Product 2 coating was close in color and brightness to the gallium complex coatings. A glass blank was also used as shown in Figure 9 for the experiment.

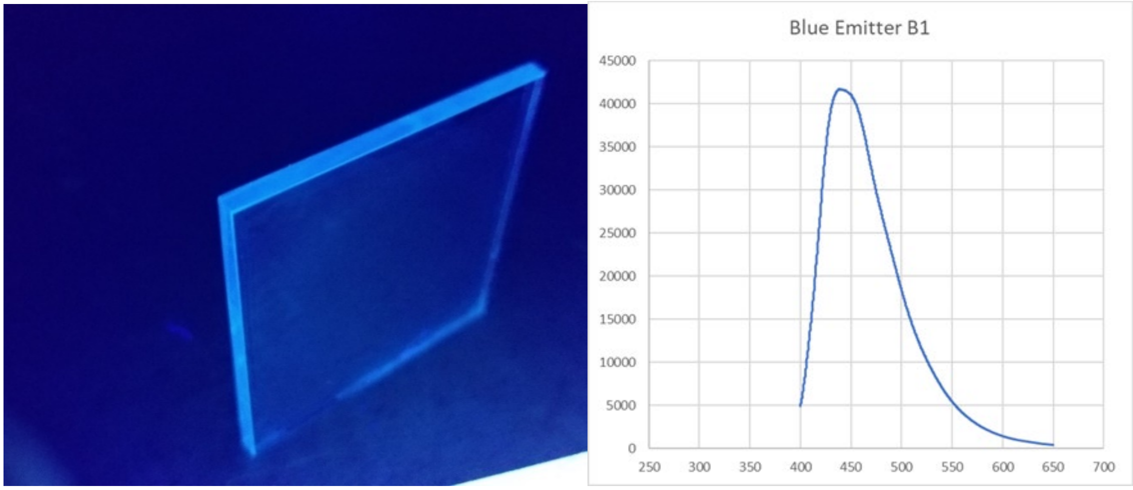


Figure 8. UV exposed coating of the reductive elimination product(s) in PNNL host and the solution PL spectrum of the emitter.

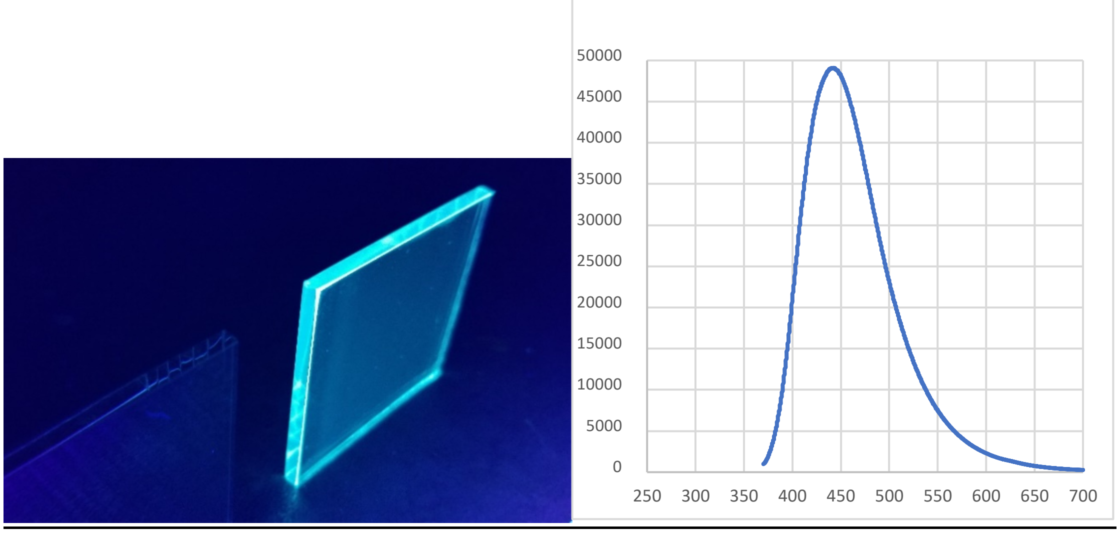


Figure 9. UV exposed coating of Product 2 emitter in PMMA host and the solution PL spectrum

To better assess the potential for use as dopants in OLED devices, the electronic structures of the emitters were probed using electrochemical measurements to estimate HOMO/LUMO levels. As a reference, measurements were also conducted for mCBP, a commonly used host for blue phosphorescent devices. The following Table shows results from the measurements. It should be noted that a single electrochemical wave was observed for the elimination product(s). No indication of more than one compound. The HOMO level is calculated from the direct electrochemical measurements, whereas the LUMO level was estimated after UV absorption energy gap measurements. The data shows the HOMO/LUMO levels of the emitting materials fall within the levels measured for the mCBP host material. Based on these measurements, efficient charge transfer from the host material to the emitter materials would be expected in an operating OLED device.

Material	Calculated HOMO (eV)	Calculated LUMO (eV)	∆E (eV)
Product 1A/1B	-5.48	-2.75	2.73
Product 2	-5.39	-2.63	2.76
mCBP	-5.70	-2.10	3.56

Project Summary

Original goals for the Phase I project centered around new Pt metal based phosphorescent emitters with enhance metal-ligand bond stability based on Density Functional Theory calculations. The target emitter materials were successfully synthesized characterized and evaluated. However, several unique material discoveries were also made as part of the Phase I development work. Discovery of highly efficient, blue emitting, pure organic RTP emitters were made that establish building blocks for a breakthrough in OLED emitter technology. Pure organic phosphorescent emitter materials are rare, especially blue emitters. To our knowledge, the discovery from the Phase I project represents the first example of highly efficient, blue emitting, pure organic RTP emitters. The following is an excerpt from a recent review publication on pure organic RTP emitters (Front Chem. 2019; 7: 305.): "*Different from TADF materials, which have been demonstrated great success in OLEDs, the application of pure organic RTP nmaterials in OLEDs is still in its initial stage, because high efficiency and short-lived RTP molecules suitable for OLEDs are rare. Nevertheless, RTP materials will provide more possibilities for high performance OLEDs and deserve to be explored further.* "

Absent the capability to fabricate OLED devices for evaluation, thin-film coating experiments of three blue phosphorescent emitters were carried out to demonstrate application for thin-film OLED devices. The experiments qualitatively demonstrated the ability to produce bright blue light from the thin film coatings. There is also the potential advantage of using very-high concentrations of a main-group phosphorescent complex to produce bright blue light. This is an approach that could significantly improve device lifetime. Currently used phosphorescent emitters experience is a tradeoff of efficiency for stability at higher dopant concentrations due to self-quenching effects. The new discovery of blue emitting pure organic phosphorescent emitters should be explored as an alternative technology for combining high efficiency with potential device stability suitable for commercial applications.

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