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Solid-State Lighting Program: Emitter Materials for Diffuse Lighting R&D Meeting

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DOE Solid-State Lighting Program, "Emitter Materials for Diffuse Lighting R&D Meeting", October 2021.

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Comments

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1 Introduction

On October 12, 2021, experts in inorganic light-emitting diodes (LED), organic light-emitting diodes (OLED) and quantum dot light electroluminescence (QDEL) gathered at the invitation of the Department of Energy (DOE) Solid-State Lighting Program to help identify critical R&D topic areas in the fields of panel structures and manufacturing of diffuse light sources. The meeting was held virtually due to travel difficulties and concerns related to the ongoing COVID-19 pandemic. There are many challenges associated with design and deposition of the layers in which OLED molecules and quantum dots convert energy from electrical current into light. The purpose of this roundtable was to identify gaps in existing knowledge and suggest new R&D to advance understanding, foster collaboration, and share progress on research in the field. Issues associated with light extraction, supporting materials structures, and manufacturing were addressed in a separate meeting held on October 14, 2021. (See *Solid-State Lighting Program: Diffuse Panel Structures and Manufacturing.)*

The meeting commenced with "soapbox" presentations where each participant was invited to give a short presentation describing the state of understanding of the materials that are needed for stable and efficient organic light emitting diode (OLED) devices. The attendee presentations were followed by a general discussion of the R&D challenges and barriers to implementation. Finally, the participants were asked to contribute ideas regarding program content for the upcoming R&D Workshop to be held from January 31st to February 3rd, 2022. The meeting format provided an opportunity for experts in the field to exchange ideas and explore collaborative research concepts. Participants included scientists and engineers drawn from academia and industry, with outstanding graduate students as well as more seasoned researchers.

This report summarizes the outcome of the discussions on critical technology challenges and identifies corresponding R&D tasks within the existing task structure. Outlines of the participants' soapbox presentations and related remarks are included in Appendix A of the report.

1.1 Key Conclusions

The meeting format encouraged each of the attendees to participate and present their perspectives on critical R&D challenges. The discussions that followed the presentations offered a variety of valuable insights about the latest understanding of diffuse emitter materials. However, there were some recurring themes that arose during these discussions regarding research areas that could advance the development of source materials, especially for blue emitter systems. These themes are as follows and are outlined in more detail in Section 2:

- Stable and Efficient Blue Emitter Materials –including blue phosphorescence, thermally assisted delayed fluorescence (TADF), hyper-fluorescence (TADF-assisted fluorescence), metal-assisted delayed fluorescence (MADF) and quantum dot electroluminescence (QDEL)
- System Solutions and Partnerships – the value of developing all materials in the emitter system congruently and the important role of collaborations in this development
- Alternative Approaches – new ways of solving current OLED materials shortcomings, such as dilution of organic semiconductors to alter layer properties, simplified structures, high entropy hosts, novel device architectures

2 Critical R&D Topic Areas

2.1 Stable and Efficient Blue Emitter Materials

Stable and efficient blue emitters are needed to create high performance OLED based diffuse lighting. There are many materials approaches to overcome this decades-long challenge. TADF, phosphorescence, hyper-fluorescence, and metal complex based delayed fluorescence are all being investigated as potential solutions. These approaches all have promise, but none have simultaneously achieved the efficiency and stability needed for the blue component of diffuse OLED or QDEL lighting. Many white OLED (WOLED) lighting devices currently use a hybrid approach comprising of red and green (or yellow) phosphorescent emitters with a fluorescent blue emitter because the stability of blue phosphorescent materials is unsatisfactory. However, fluorescent materials fundamentally have insufficient harvesting of triplet excitons, thus resulting in poor efficiency. Current external quantum efficiency (EQE) is only around 10% EQE for fluorescent blue. Alternatives are desperately needed.

Phosphorescent approaches have been researched using a heavy metal-based emitter for high luminescence efficiency. Phosphorescent materials have almost 100% internal quantum efficiency (IQE). Their spectrum can be tuned by ligand design and they offer a wider spectrum than fluorescent emitters. However, they tend to require higher voltage and have poor lifetime. TADF has been vigorously investigated in the past 5-10 years as a potential alternative to phosphorescent emitters due to their similar, near unity IQE, wide spectrum, and potential for cost reduction over phosphorescent materials. However, TADF shares the same lifetime shortcomings as phosphorescence and attendees suggested that this approach appears to be unsatisfactory for blue. Hyper-fluorescence uses the ~ 100% exciton harvesting of TADF dopants to generate excitons. The excited energy then transfers to a fluorescent molecule. Four times more light is emitted by the fluorescent in the TADF-assisted approach as compared to conventional fluorescence with the same input energy. Multiple attendees indicated that hyper-fluorescence seems the most promising approach, as a deep blue color, a high color purity, and high efficiency can be achieved at potentially reduced cost. The downsides of this approach are not only lifetime, but also a more complex system which requires a host, TADF assistant dopant, and fluorescent emitter to be developed in concert.

QDEL approaches also struggle with the blue stability and lifetime, but tremendous improvements have been recently achieved. Quantum dots are attractive materials for diffuse emitters because they have high IQE, high luminance at low voltage, they emit an easily tailorable narrow spectrum, and they are solution processable for low cost. EQE of blue is currently around 14% and lifetime LT50 (the time it takes until emitted light reaches 50% of the initial output) at@ 1,00 cd/m2 is now around 2000 hours. This technology has great promise, but much work is needed to improve the performance of quantum dot emitters and integrate them into white device structures.

2.2 System Solutions & Partnerships

Participants stressed the need for solving materials issues with complete system solutions. For optimal light generation and stability, hosts and dopants must work harmoniously. Device efficiency and stability reflect the quality of the individual components and the system as a whole. Investigations solely focusing on one component of a blue light system have limited value until the work is done to integrate them into a complete system with hosts, emitters, assistant-dopants, charge generation, and transport layers that may include blocking layers.

Strategic partnerships are key to achieve co-development of all molecules for a blue emitter system. Collaborations between small companies or universities with materials or panel manufacturers can enable access to state-of-the-art materials and device optimization needed to demonstrate the longevity relevant to lighting applications. With the cumbersome work of device optimization in the hands of those with the materials, processes, and know-how to achieve best results, a material’s potential can be satisfactorily assessed. There was resounding agreement amongst attendees that more partnership work would be beneficial and that complete materials solutions are essential.

2.3 Alternative Approaches

While there was agreement that there is a need for deeper understanding of materials properties and performance relationships as well as continued development work, some attendees promoted thinking outside the box to find solutions. Simultaneously stable and efficient blue emitters have been elusive for materials developers despite decades of work in the field. Though not proposing to abandon standard materials approaches, they suggested other possible ways of addressing the lifetime and efficiency shortcomings of blue emitters.

In particular, device architecture modifications can be used to enhance blue performance. For example, the device stack can be tailored to broaden the recombination zone, which can lead to reduced excited state annihilation events. Molecular glasses could also be used to keep excited states apart and minimize roll-off. Another approach to longer lifetime is to simplify the device stack. By reducing the number of materials in a device or using materials that relax manufacturing requirements (e.g., neat films, single material hosts, low complexity emitter systems, reduced number of transport/injection layers), more devices can be stacked in a tandem architecture without compromising manufacturability and cost. Such architectures allow much greater device lifetimes due to the lowered current density needed to achieve a desired luminance. One approach to stack simplification is to reduce the number of charge transport and injection layers, possibly through Fermi-level engineering to enable ohmic contacts and improved charge generation layers for multijunction devices. Besides simplifying the stack, attendees suggested consideration of novel structures, such as quantum confinement for bandgap tuning and carrier confinement. Hybrid architectures were also proposed, such as using blue LEDs in conjunction with OLEDs to achieve the desired performance in diffuse light sources.

Novel thinking about ways to discover and approach materials was also proposed. For instance, using dilution molecules to alter properties of the organic semiconductors is a novel approach. This could be used to change the index of refraction of the OLED stack, which could lead to significant light outcoupling improvements. For rapid materials discovery and design, the use of artificial intelligence (AI) tools and computational chemistry was proposed as a way of understanding the effects of aggregation.

2.4 Quantum Dots Electroluminescence (QDEL)

It has been known for several decades that QDs can produce light with a narrow peak in wavelength across the whole visible spectrum. The position of the peak can be adjusted by varying the size of the dots, enabling more flexibility in spectral tuning of light fixtures. QDEL devices can be produced by low-cost printing processes and so may lead to substantial cost reductions. However, this may be difficult for devices with many active layers, due to problems with solvent compatibility. The requirements on encapsulation may be less severe than for OLEDs, but this needs to be confirmed.

Until recently, the performance of QDELs has been poor, both with respect to efficiency and stability. Substantial progress has been reported in the past two years, but significant challenges remain. The best performance has been obtained with materials containing cadmium, which is unacceptable in many locations due to environmental concerns. Current research is therefore focused on alternatives, including indium phosphide and perovskites. Some proponents have argued that QDEL can achieve higher luminance and operate at lower voltage than OLEDs, but this has not been convincingly demonstrated. Light extraction remains a major challenge for both QDEL and OLEDs. However, the effective refractive index of the QDEL emitter stack could be lower, facilitating light extraction.

Appendix A: Participant Presentations

Mark Thompson, University of Southern California: Stable Blue Emitters

Mark Thompson, Professor at the University of Southern California, spoke on various approaches to achieve stable blue emitters. He explained that thermally assisted delayed fluorescent materials (TADF) have not solved the problem because though they can be used to lower the exciton lifetime (helping stability), fluorescence has efficiency limitations. Another approach is to decrease phosphor exciton lifetime below 1 microsecond. By increasing spin orbit coupling, higher intersystem crossing rates can be achieved, and exciton lifetime can be improved. This approach has been demonstrated across the visible spectrum using carbene metal amides for Cu-, Ag-, and Au-based phosphors. Experimenters found that exciton lifetimes in these complexes can be quite short, especially for Ag. Lifetimes are currently at < 0.5 microseconds and experimenters are seeing blue and green devices with EQE of 12-20%. Further work is needed for host development in order to achieve long-lived devices, which have not yet been realized.

Jian Li, Arizona State University: Blue Emitting Pt and Pd Complexes for Displays and Lighting Applications

Jian Li, Professor at Arizona State University, discussed the use of Pt and Pd complexes as replacements for Ir-based complexes in phosphorescent emitter systems. In particular, his team is investigating metal assisted delayed fluorescent (MADF) emitters using tetradentate complexes, which make rigid structures that are more robust and can improve photoluminescent quantum yield and lifetime. They have achieved improved amber OLED performance using Pd-based emitters. Efficiency can be maximized to close to 70% EQE by alignment of the molecules, which improves outcoupling. Prof. Li also discussed the importance of developing robust blue host and emitter systems. In theory, development of blue phosphorescent emitters with shorter radiative lifetime should improve stability. The main quenching mechanism is that n-type hosts interact with blue phosphorescent emitters. He suggests making a p-type host and decrease the n-type host to narrow emission. This approach can increase lifetime by 500% and perhaps breakthroughs can be found in coming years.

Tommie Royster, R-Display and Lighting: Novel Blue Charge-Transfer Emitter Materials for OLED Lighting

Tommie Royster, CEO and Founder of R-Display and Lighting, emphasized the industry need for stable blue emitters. He proposed an alternative approach to solve blue emitter issues using charge transfer (CT) emitter materials to get around lifetime issues associated with phosphorescence and TADF emitters. CT emitters have lifetimes less than 100 ns, but usually the CT state is not that efficient. However, good singlet-triplet mixing can be achieved if molecules are designed to get hybridized local and charge transfer states. Early data shows EQE of 6% (though 15 - 20% EQE is possible). Further work is needed to improve efficiency and to explore the influence of the host materials on these emitter systems.

Mike Molaire, Molecular Glasses: Charge-Balanced Ambipolar Hosts High-Efficiency and Low ERO WOLEDs

Mike Molaire, CEO and Founder of Molecular Glasses, spoke on the issue of efficiency roll-off of WOLEDs at high brightness. Despite the dramatic growth of WOLEDs, low roll-off efficiency in high efficiency devices still needs to be addressed. He cited causes of efficiency roll-off, including non-radiative triplet exciton quenching, triplet-triplet annihilation, and triplet-polaron annihilation in the emissive layer. To suppress triplet exciton quenching, devices can be designed to balance charge carriers to minimize polaron accumulation at the interface. Additional strategies for improvement include decreasing the local triplet exciton density, extending the exciton formation zone, and shortening triplet exciton lifetime. Molaire then presented OLEDIQ™ materials whose high entropy of mixing helps to reduce triplet-triplet annihilation, concentration quenching, and emitter aggregation since they are non-crystallizable. When combined with charge carrier balance and an extended recombination zone, very low roll-off is observed.

Marina Kondokova, OLEDWorks: Material Development for OLED Automotive and General Lighting

Marina Kondakova, Director and founding member of OLEDWorks, discussed how OLED tech can be used in many exterior lighting applications (rear combination tail light, turn signal, indicator, logo or emblem branded lighting) in automobiles. The use of OLEDs is aesthetic and practical. Automaker Audi reports 35% power consumption reduction with OLED use as compared to LED along with reduction in weight, space, cost and ease of recycling. Dr. Kondakova explained how materials for automotive lighting are different compared to general illumination. Materials for automotive applications have to exhibit high glass transition temperature (Tg) (>120C) and high brightness up to 20,000 nits. This requires stacked devices with low voltage and hence low absorption charge generation layers, which is also important for white OLEDs for general illumination and displays. Kondakova concluded by emphasizing that any new materials need to be cost-effective and need to be tested in a state-of-the-art OLED lighting stack so that performance improvements can be verified.

Michele Ricks, EMD Electronics: Host and Transport Materials for OLED

Michele Ricks, Business Development Manager of OLED Materials for EMD Performance Materials, discussed key R&D needs for OLED materials. She agreed with other attendees that high efficiency blue lighting is the highest priority. At EMD, they are working on the full range of materials, but are focusing on hole transport materials. Hole transport materials are a critical layer in the OLED stack used to adjust the energy barriers from anode to emissive layer. New hole transport materials can improve drive voltage, lifetime, and efficiency. She showed how hole transport materials (HTM) used as a common layer, as an electron blocking layer (EBL), and as a common HTM and EBL combined can improve performance. Finally, Ricks discussed pre-mixed hosts for red and green materials and how these host concentrations can be tailored to achieve optimal performance for different applications.

David Wheeler, Kebotix: Discovery of New OLED Emitters Using Machine Learning

David Wheeler, Device Engineer at Kebotix, talked about rapid discovery and creation of advanced materials using a machine learning closed-loop platform. The platform integrates artificial intelligence control and data collection. Kebotix is applying this approach to target the problem of aggregation in emissive layers, focusing on soluble host-free and blue materials. Wheeler showed that they were able to take a set of 7 million molecules, filter this down to 100,000 with specific desirable electroluminescent properties, and then through materials expertise, pick 10 molecules to synthesize and test. Sorting through these 7 million molecules took just 30 days. Future work is needed to expedite synthesis and shipping of materials and establish device fabrication and testing procedures.

Russ Holmes, University of Minnesota: Spontaneous Orientation Polarization in OLEDs – Impact on Stack Design and Performance

Russell Holmes, Professor at the University of Minnesota, discussed the importance of spontaneous orientation polarization (SOP) in transport layers, which arises when the molecular dipole moments are out-of-plane. SOP leads to enlarged surface potentials and modifies the internal electric fields, which can enhance or frustrate charge injection. The Minnesota group has shown that SOP can cause bi-molecular quenching, even at very low current densities. These effects can be ameliorated by depositing the organic materials at high temperature or by increasing the deposition rate.

Chris Giebink, Pennsylvania State University: Improving OLED Performance via Semiconductor Dilution

Chris Giebink, Professor of Electrical Engineering at Pennsylvania State University, summarized his team's work on the influence of semiconductor diluents on the performance of the organic stack. The motivation for this research was his observation that very few organic molecules are active in the stack. The major goal of dilution is to simplify light extraction by reducing the effective refractive index of the organic layers towards that of the substrate. He has identified molecules that, when added to the hole transport layer, can lead to a significant reduction in the index without degrading the hole mobility.

Homer Antoniadis, Nanosys: QDEL for Diffuse Light

Homer Antoniadis, Chief Technology Officer of Nanosys, presented on quantum dot electroluminescence (QDEL) as a diffuse light source. Dr. Antoniadis contended that QDEL is the perfect diffuse light source as it offers high efficiency, low voltage, spectral tuning, high brightness, solution processability, and low cost. He presented a summary of recent advances in Cd-free QDEL technology, showing EQE over 20% for red and green and ~ 14% for blue. The main challenge for QDEL has been lifetime, but in the past year, Nanosys has made great strides. LT50 (100 nits) for their blue QDs was only around 350 hours in 2020. In the past 12 months, they have improved this metric to 2000 hours. For further advancements in lifetime, they will work on eliminating crystal defects, impurities, and quenching by charge transport layers. They will also explore particle shape to achieve stable facets, search for electrochemically stable ligands, and enhance uniformity of ligand shell coverage.

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