Tuning Singlet and Triplet Excited State Energies and Frontier Orbitals of Imidazole Host/Emitter for Hybrid White OLEDs

Muzzazam Idris,[1] Chan Ho So,[3] Moon Chul Jung,[1] Peter I. Djurovich,[1] Stephen R. Forrest[2,3,4] and Mark E. Thompson[1]

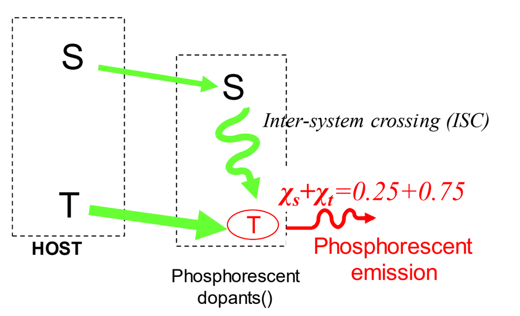
1: Department of Chemistry, University of Southern California, Los Angeles, CA

2: Departments of Physics 3: Electrical Engineering and Computer Science 4: Department of Materials Science and Engineering , University of Michigan, Ann Arbor, MI

Background & Rationale

The efficiencies of monochromatic OLEDs have been pushed to near theoretical limits in both laboratory and commercial applications. This was done in large part by recognizing that both singlet and triplet excitons are formed on hole/electron recombination (ratio = 1:3) and that every exciton counts, such that both the singlet and triplet fraction MUST be efficiently harvested and lead to light emission. The solution to this harvesting problem that is in wide spread use is to use a emissive dopant in the OLED that has a heavy metal ion at its core to promote spin orbit coupling and give efficient ISC from S_1 to T_1 and phosphorescence from the triplet . This heavy metal based approach has lead to nearly 100% efficiency (photons/electrons) across the visible spectrum. Mixing dopants in an OLED can give broadband emission and has been used to prepare white OLED (WOLEDs).

Phosphorescent OLED

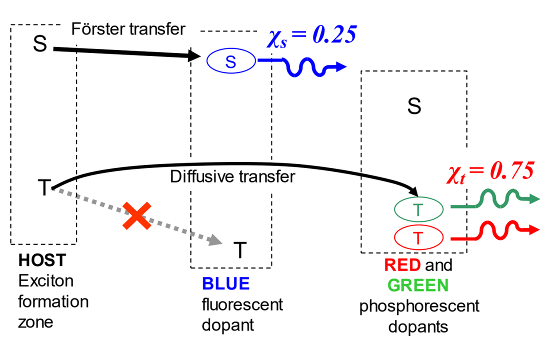


Pros:
- High efficiency possible, up to 100%
- Color tunable UV→NIR
- Low voltage, high lm/W possible

Cons:
- Emitter (color) mixing to achieve white can be complicated, often accomplished by stacking different colored OLEDs
- Lifetime of blue PHOLED is poor, limiting WOLED lifetime
- Exchange energy $S_1 \rightarrow T_1$ is lost, limiting power efficiency

Hybrid fl/ph WOLED

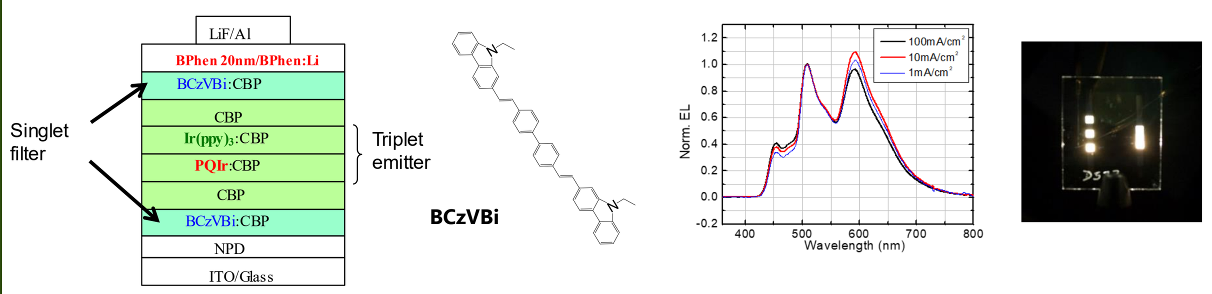
In this research program we ware focusing on an alternate solution that keeps all of the ""Pros" of a phosphorescence based OLED and eliminates the "Cons". The approach being pursued here is to NOT promote ISC $S_1 \rightarrow T_1$, but to collect singlet excitons on a fluorescent dopant and triplets on one or more phosphorescent dopants. We first proposed this approach in 2006 (Y. Sun, *et. al, Nature*, **2006**, *440*, 908-912).



Pros:
- High efficiency possible, up to 100% for white
- Color tunable white emission (CCT) by tuning dopants
- Constant color with changing drive voltage
- Low voltage, high lm/W possible (no exchange energy loss)
- Emitter (color) mixing to achieve white is built into structure
- Blue from a fluorescent emitter, does not limit device lifetime

Cons:
- As pictured the triplet level of the fl-dopant is a trap
- Phosphorescent dopants can trap carriers: S_1:T_1 imbalance

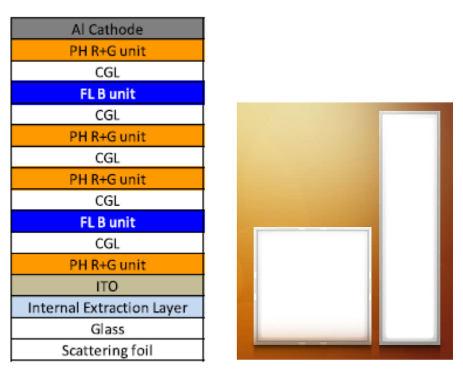
Proof of concept



Efficiency = 24 lm/W at 500 nits, CIE = (0.40, 0.41), CRI = 85, CCT = 3750K

Separated OLED stacked approach to fl/ph

OLED Works has commercials WOLEDs that utilize both fluorescent dopants for blue and phosphorescent dopants for green→red (https://www.oledworks.com/products/ and J. Spindler et al., *SID Int. Symp. Dig. Tech.*, **2016**, 47). The structure is shown below and is composed of isolated blue and green/red OLEDs in a stack. Color temperature can be tuned by varying the number of each OLED type. This approach give good efficiency and excellent lifetime, but suffers from an ultimate limit of 25% on the blue emission and is a somewhat complicated structure to fabricate.

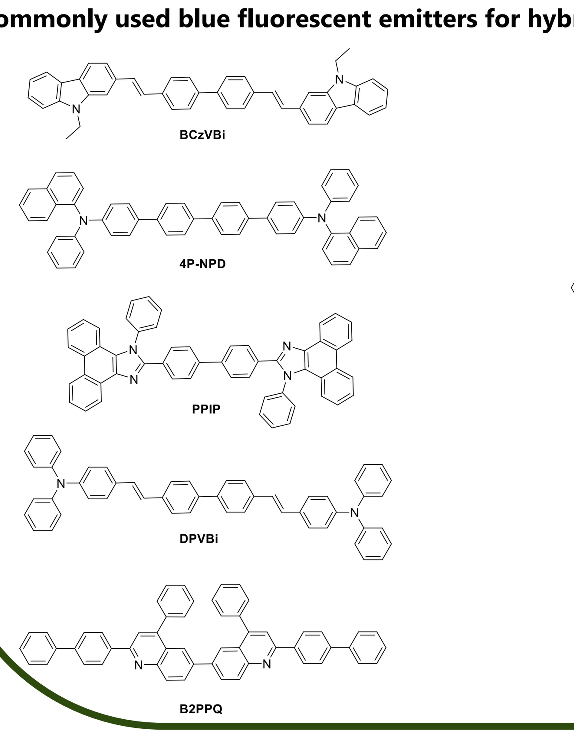


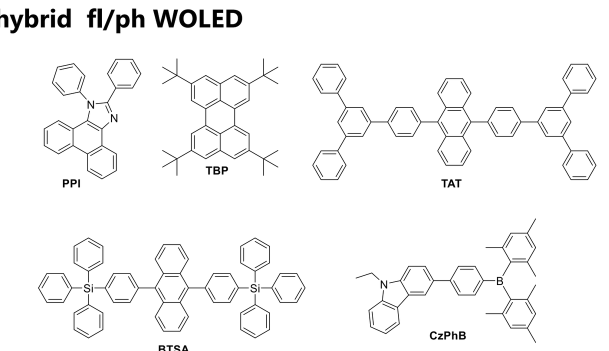
Pros:
- Color tunable white emission with high CCT
- Constant color with changing drive voltage
- Stacking improves efficiency of PHOLED at high drive current leading to good lm/W at high brightness
- Emitter (color) mixing to achieve white is built into structure
- Excellent lifetime at high brightness

Cons:
- Complicated structure
- Efficiency loss in blue (singlet limit is 25%)
- Stacking improves efficiency, but leads to high drive voltage

Brite2: CCT = 3000K, CRI = 90, 63 lm/W and L70 > 50K hours at 3000 nits.

Commonly used blue fluorescent emitters for hybrid fl/ph WOLED





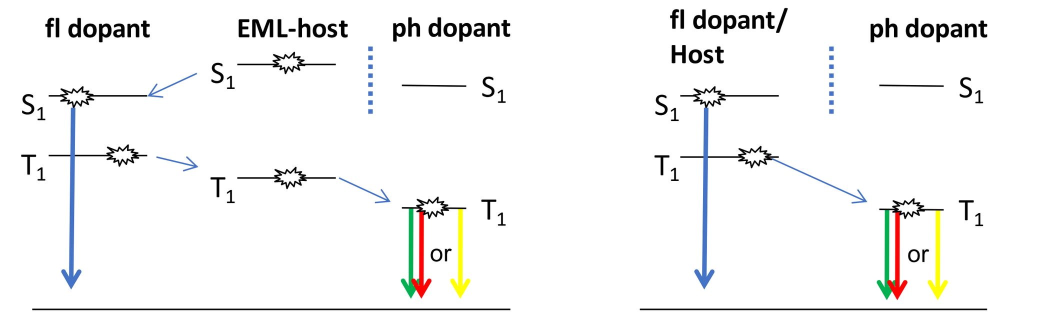
Pros:
- Highly emissive as isolated molecules

Cons:
- Efficiency loss in the solid-state due to aggregation
- Low triplet energies (<2.3 eV) due large π systems
- High singlet energy (e.g. **PPI**) limiting WOLED to cool white emission
- Difficult synthesis (e.g. **4P-NPD**)

Chem. Soc. Rev., 2013, **42**, 4963--4976

Objectives

- Our first objective is to find **fluorescent dopants that have small S_1/T_1 energy gaps**, so we can achieve efficient blue fluorescence and have a sufficiently high triplet energy to transfer triplet to the host or directly to a phosphor.
- We also aim to **develop host materials with wide S_1/T_1 energy gaps** so that the energy levels of the fluorescent dopant can be nested within the host.
- We will also investigate materials that give **strong blue fluorescence in the solid state to act as a host material**.



Dopant/Host WOLED

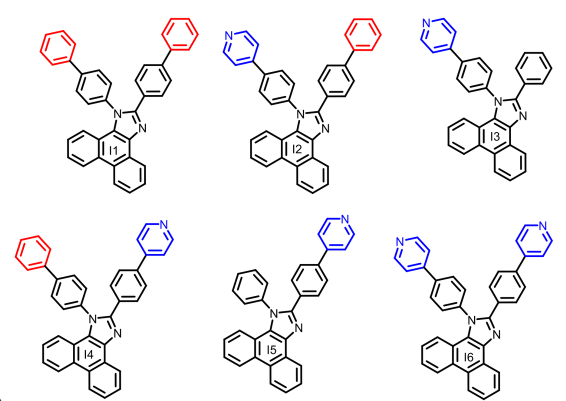
fl dopant is Host WOLED

Modeling Studies of fl-dopants and hosts

Density Functional Theory (DFT) calculations have been employed to screen through prospective libraries of compounds (depicted below) to assess their likelihood of success based on critical parameters, *i.e.* S_1, T_1, HOMO/LUMO energies and S_1-T_1 gap, $\Delta(S_1/T_1)$ (B3LYP/6-31G** level of theory using Qchem.). The DFT calculations on the fl-dopant libraries indicate that incorporating acceptor (pyridyl) and/or donor (phenyl) moieties at the N1 and/or C2 positions of the phenanthro[9,10-*d*]imidazole varies the S_1/T_1, HOMO/LUMO and oscillator strength of singlet transition (f) on account of HOMO/LUMO overlap.

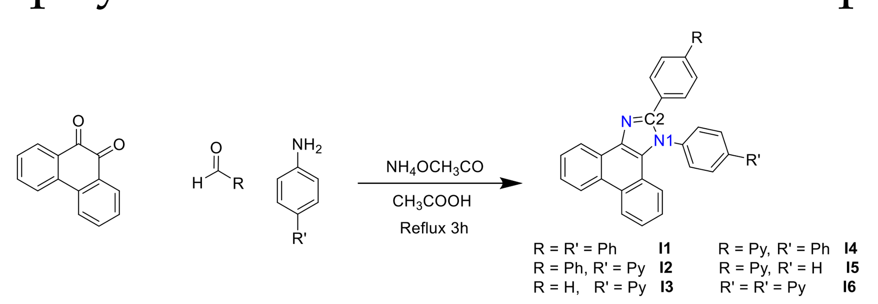
Promising candidates based on DFT calculations

Based on DFT calculation, host materials with wide S_1/T_1 energy gaps that can nest the fluorescent and phosphorescent dopants are synthesized and characterized.



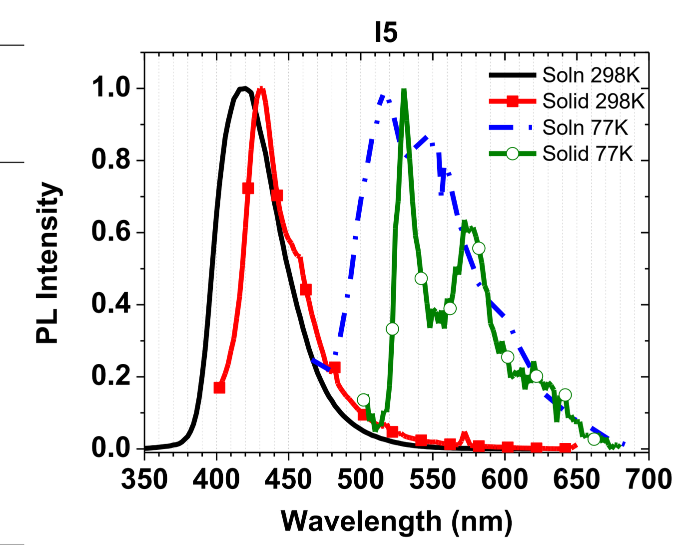
	S_1	T_1	HOMO	LUMO	f
I1	3.36	2.65	-5.15	-1.31	0.854
I2	3.08	2.64	-5.25	-1.69	0.361
I3	3.12	2.72	-5.29	-1.68	0.169
I4	3.34	2.60	-5.29	-1.56	0.502
I5	3.37	2.60	-5.30	-1.56	0.576
I6	3.12	2.60	-5.39	-1.78	0.947

Photophysical and electrochemical Properties

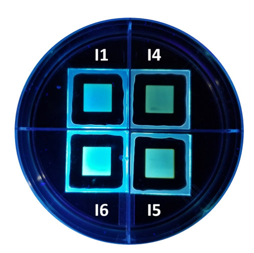


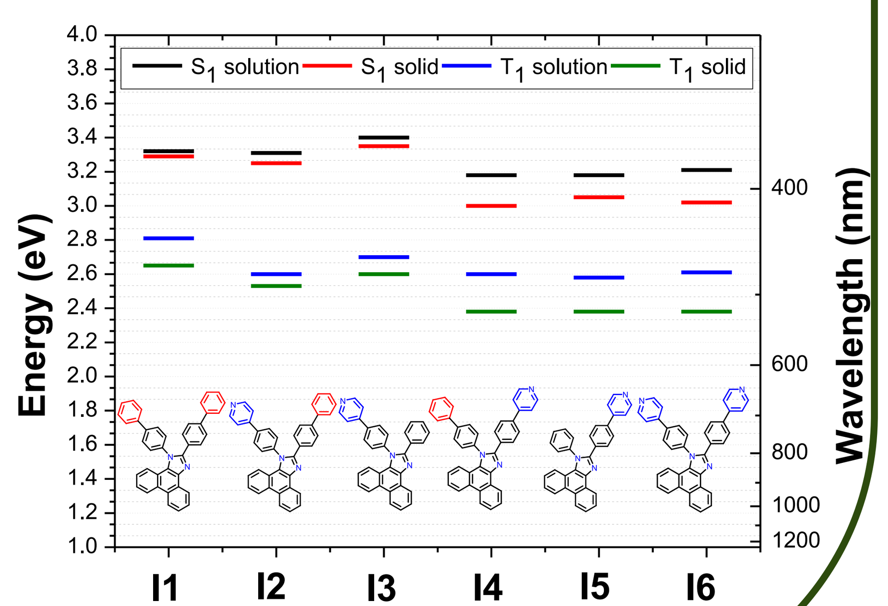
	E_{ox} (V)[a]	E_{red} (V)[a]	HOMO(eV)[b]	LUMO(eV)[b]	PLQY[c]	PLQY[d]
I1	+0.86	-2.61	-5.81	-1.70	1	0.95
I2	+0.87	-2.44	-5.82	-1.89	0.28	0.10
I3	+0.90	-2.44	-5.86	-1.89	0.28	0.10
I4	+0.91	-2.32	-5.87	-2.03	1	0.55
I5	+0.91	-2.35	-5.87	-2.00	1	0.81
I6	+0.96	-2.36	-5.94	-2.00	1	0.83

a: reference to ferrocene b: experimental values in eV c: measured in solution using an integrating sphere d: measured as neat material in films using an integrating sphere

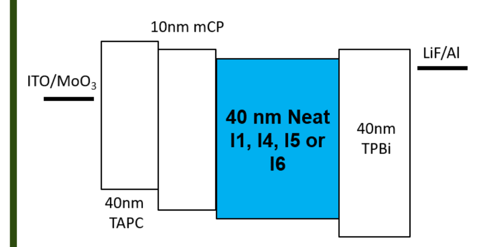


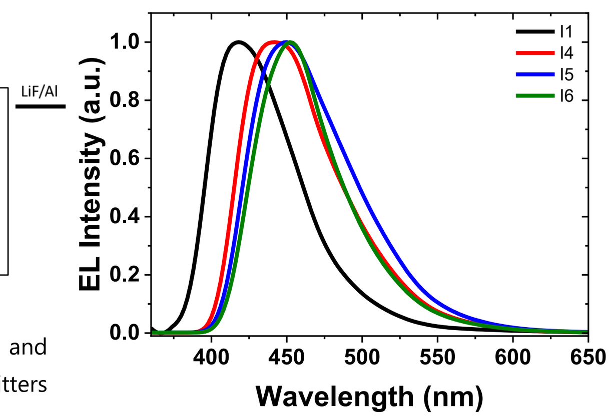
- Phenanthro[9,10-*d*]imidazoles (**I1** – **I6**) are synthesized in two high yielding steps (yield>90%)
- Their frontier orbitals, singlet and triplet energies are fine tuned by incorporating acceptor (pyridyl) and/or donor (phenyl) moieties at the N1 and/or C2 positions of the phenanthro[9,10-*d*]imidazole
- Their singlet and triplet energies redshift in the solid state giving appropriate singlet energies for blue emission and high triplet energies for hosting green, yellow and red phosphors
- Deep LUMO levels ideal for electron injection and transport
- Strong blue fluorescence in solution and in the solid-state (**PLQY > 80%**)

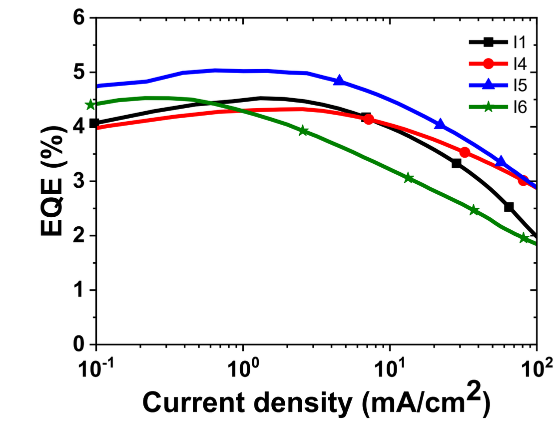




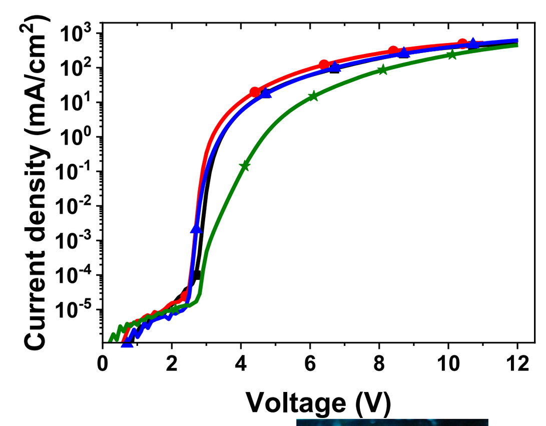
Monochromatic OLED Devices

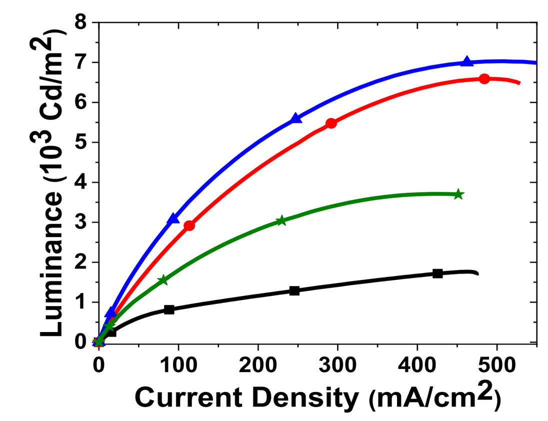


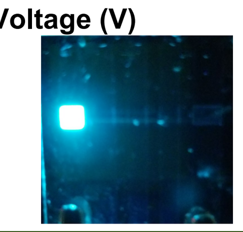




- Monochromatic devices of **I1** and **I4–I6** as neat fluorescent emitters were fabricated
- Effective singlet exciton confinement on the emitters
- Excellent transport properties
- Moderate luminance achieved
- Due to their high PL efficiency (80%) in neat films, monochromatic devices with **I1** and **I4–I6** as neat blue fluorescent emitters achieved close to theoretical maximum efficiency (**5%**)

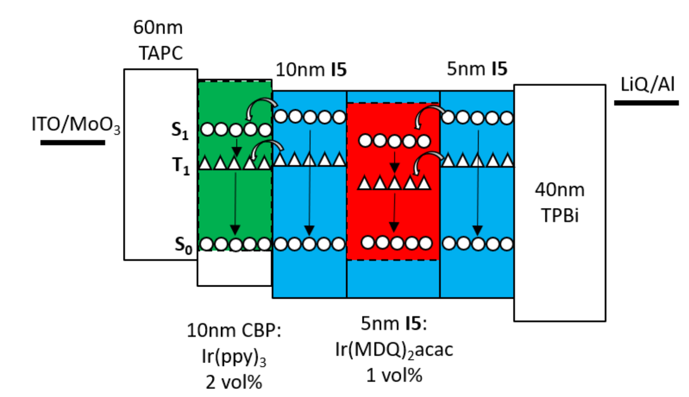


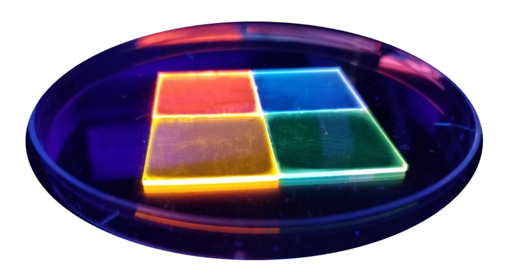


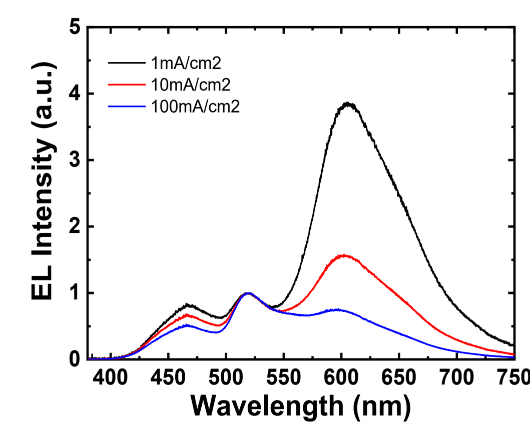


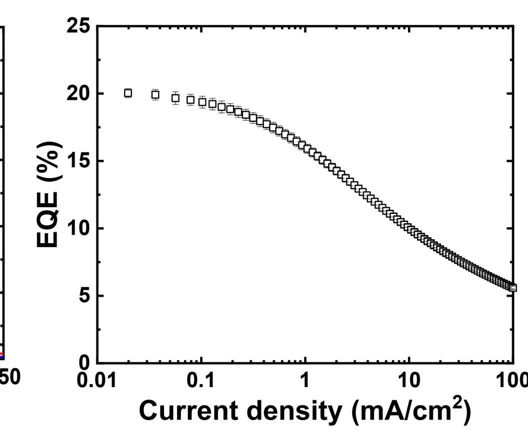
Hybrid White OLED

PLQY	I1	I2	I3	I4	I5	I6
10 wt% $Ir(ppy)_3$	0.65	0.49	0.56	0.39	0.30	0.36
10 wt% $Ir(bt)_2acac$	0.80	0.66	0.84	0.83	0.80	0.78
10 wt% PQIr	0.70	0.69	0.67	0.64	0.69	0.66

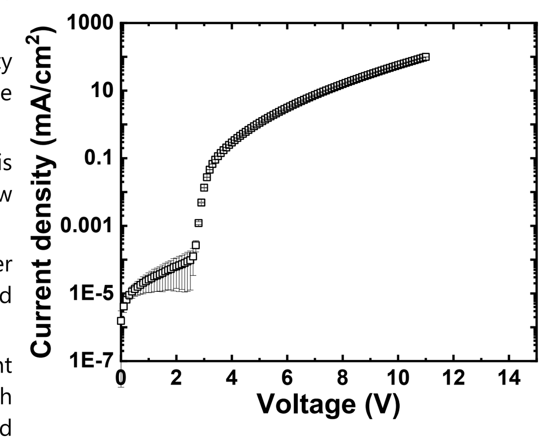


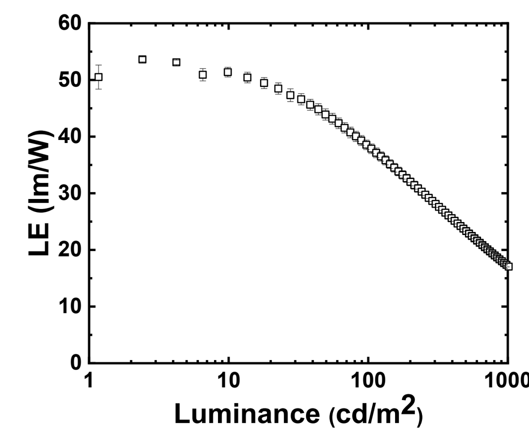






- Due to its broad PL spectrum, **I5** was used as a neat fluorescent emitter to fabricate WOLED
- Due to low efficiency of $Ir(ppy)_3$ in **I5**, CBP was used to host $Ir(ppy)_3$.
- The recombination zone at low current density is mainly at the ETL side but shifts to HTL side at high current densities
- At low current density, the EL spectrum is dominated by the red emission resulting in low CRI and CCT
- A well-balanced spectrum is obtained at higher current densities with CRI as high as 94 and CCT of 4015
- High EQE and Luminous efficacy at low current density, but significantly decrease at high current densities due charge build-up caused by saturation of the dopants
- Attempt to alleviate the roll-off is in progress





	CIE	CCT	CRI
0.1mA/cm^2	(0.55,0.39)	1684	68.1
1mA/cm^2	(0.52,0.40)	1979	76.4
10mA/cm^2	(0.45,0.39)	2734	87.4
100mA/cm^2	(0.38,0.39)	4015	93.6

Acknowledgements

This project is supported by:

U.S. DEPARTMENT OF ENERGY

Energy Efficiency & Renewable Energy

Universal Display Corporation