

Controlling Photons in Organic Light Emitting Diodes

by

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OCMer's adage (paraphrased):

Another day,
another ... device.

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To my sister

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LIST OF ACRONYMS

B	Blue
B-E	Bottom emitting
BHJ	Bulk heterojunction
CCD	Charge-coupled device
CCT	Correlated color temperature
CGL	Charge generation layer
CIE	Commission Internationale de l'Éclairage
CRI	Color-rendering index
CT	Charge transfer
DC	Direct current
DI	Deionized
EA	Electron affinity
EBL	Exciton (or electron) blocking layer
EEL	External enhancement layer
EIL	Electron injection layer
EML	Emissive layer
EQE	External quantum efficiency
ETL	Electron transport layer
FF	Fill factor
FL	Fluorescent
FRET	Förster resonant energy transfer

G	Green
GIWAXS	Grazing incidence wide-angle scattering
HBL	Hole blocking layer
HIL	Hole injection layer
HJ	Heterojunction
HOMO	Highest occupied molecular orbital
HTL	Hole transport layer
IMF	Index-matching fluid
IC	Internal conversion
I-P	In-plane
IP	Ionization potential
ISC	Inter-system crossing
J-V	Current density-voltage
J-V-L	Current density-voltage-luminance
K-cell	Knudsen cell
LP	Lower polariton (energetic feature) or long pass (optical filter)
LUMO	Lowest unoccupied molecular orbital
MLA	Microlens array
MPP	Maximum power point
NFA	Non-fullerene acceptor
NIR	Near infrared
OLED	Organic light emitting diode
OMBD	Organic molecular beam deposition
OOP	Out-of-plane
OPV	Organic photovoltaic
OVPD	Organic vapor phase deposition
PCE	Power conversion efficiency

PD	Photodiode or photodetector
PEP	Plasmon-exciton-polariton
PES	Photoelectron spectroscopy
PF	Purcell factor
PH	Phosphorescent
PHOLED	Phosphorescent organic light emitting diode
PLQY	Photoluminescent quantum yield
PML	Polymer matching layer
PSF	Phosphor-sensitized fluorescence
QCM	Quartz crystal microbalance
RF	Radio frequency
R/G	Red/green
SEM	Scanning electron microscope
SEMLA	Sub-electrode microlens array
SMU	Source-measuring-unit
SP	Short pass
SPP	Surface plasmon polariton
SxS	Side-by-side
TADF	Thermally-activated delayed fluorescence
T-E	Top-emitting
TE	Transverse electric
TF	Tooling factor
TIR	Total internal reflection
TM	Transverse magnetic
UDC	Universal Display Corp.
UP	Upper polariton
UV	Ultraviolet

VTE	Vacuum thermal evaporation
WG	Waveguide
WOLED	White organic light emitting diode
WVTR	Water vapor transmission rate

LIST OF CHEMICALS

Al₂O₃	aluminum oxide
Alq₃	tris(8-hydroxyquinoline)aluminum
Alucone	poly(aluminum ethylene glycol)
BAlq	bis(2-methyl-8-quinolinolate)-4-(phenylphenolato)aluminium
BHF	or BOE - buffered oxide etch, buffered hydrofluoric acid
BPyTP2	2,7-bis(2,20-bipyridine-5-yl)triphenylene
BT-CIC	(4,4,10,10-tetrakis(4-hexylphenyl)-5,11-(2-ethylhexyloxy)-4,10-dihydro-dithienyl[1,2-b:4,5b]benzodithiophene-2,8-diyl)bis(2-(3-oxo-2,3-dihydroinden-5,6-dichloro-1-ylidene)-malononitrile)
C₇₀	carbon 70
CBP	4,4'-bis(9-carbazolyl)-1,1'-biphenyl
DBP	tetraphenyldibenzoperiflanthene
Etcp2Mg	bis(ethylcyclopentadienyl)magnesium
HATCN	hexaazatriphenylene hexacarbonitrile
HMDS	hexamethyldisilazane
IC-SAM	4-[(1,3-dioxoinden-2-ylidene)methyl]benzoic acid
Ir(dmp)₃	tris[3-(2,6-dimethylphenyl)-7-methylimidazo[1,2-f]phenanthridine] iridium(III)
Ir(ppy)₃	fac-tris(2-phenylpyridine)iridium(III)
ITO	indium tin oxide
IZO	indium zinc oxide
Liq	8-hydroxyquinolinolato-lithium
mCBP	3,3'-Di(9H-carbazol-9-yl) biphenyl

MgO	magnesium oxide
MoO_x	molybdenum oxide
NPD	or α - NPD , N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)-2,2'-dimethylbenzidine
PCE-10	or PTB7-Th , poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b;4,5-b']dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene)-2-carboxylate-2,6-diyl]
PDMS	polydimethylsiloxane
PEDOT:PSS	poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)
PET	polyethylene terephthalate
PQIr	bis(2-phenylquinolyl-N,C ^{2'}) acetylacetonateiridium(III)
TDMAZ	tetrakis(dimethylamino)zirconium(IV)
Teflon	or PTFE , polytetrafluoroethylene
Tergitol	polyethylene glycol mono(branched p-nonylphenyl) ether
TMA	trimethyl aluminum
TPBi	1,3,5-tris(1-phenyl-1Hbenzimidazol-2-yl)benzene
Tris-PCz	9-phenyl-3,6-bis(9-phenyl-9Hcarbazol-3-yl)-9H-carbazole
Triton X-100	polyethylene glycol tert-octylphenyl ether
ZnO	zinc oxide
ZrO₂	zirconium oxide

ABSTRACT

In the nearly 40 years since the demonstration of the first organic light emitting diode (OLED), organic devices have come to make up a 55 billion dollar display industry with increasing demand for organic photovoltaics (OPVs) in energy generation applications that require unique form factors, including transparency and flexibility. Both device systems are constrained by key application requirements: high efficiency and reliable operational lifetime. In this work, we will investigate ways to address these key requirements through the control of photons in OPVs and OLEDs.

We begin by leveraging the reciprocal relationship between OLEDs and OPVs to investigate the emissive internal quantum efficiency (IQE), i.e. emission from the charge transfer (CT) state, when operating an OPV in the dark under forward bias. We relate the degradation of the CT state emission to open circuit voltage through a semi-empirical factor, m , derived from the detailed balance of photon emission and absorption. We apply this relationship to quantify the reliability of archetype OPV structures. We find that the region of degradation within the device can be determined by m , with $m = 1$ corresponding to degradation within the bulk heterojunction for DBP:C₇₀ devices and $m > 1$ corresponding to degradation outside of the bulk heterojunction for PCE-10:BT-CIC devices.

Though phosphorescent OLEDs can achieve high IQE approaching 100%, their practical external efficiency is limited by light trapped within the device. In an archetypal structure, approximately 80% of photons generated in an OLED are trapped within the device in waveguided substrate or organic modes, or coupled to plasmonic modes at metal/organic interfaces. In this work, we investigate methods for extracting photons from both modes. First, we apply sub-electrode microlens arrays (SEMLA) to deep-stacked white OLEDs (WOLEDs). We demon-

strate a $1.9\times$ enhancement in external quantum efficiency for devices with waveguided modes extracted using SEMLA and substrate modes extracted using an external microlens array (MLA). While the SEMLA effectively couples organic waveguided modes to substrate modes, the MLA only couples $\sim 60\%$ of light from the substrate. We then discuss methods for improving MLA substrate mode outcoupling through the use of low-index coatings.

Surface plasmon polariton (SPP) modes, which couple light to the metal cathode surface within the device, are typically lossy modes. We demonstrate that by strongly coupling the SPP to excitons in the adjacent transport layer, forming a plasmon-exciton-polariton (PEP), the outcoupling efficiency of plasmonic modes can be increased from a $1.2\times$ enhancement with outcoupled SPP modes to a $1.4\times$ enhancement with outcoupled PEP modes using the same nanoparticle outcoupling scheme. We then present two WOLED architectures utilizing stacked and side-by-side red, green, and blue emitters. We demonstrate, in side-by-side devices, color-tunability in the 1960 color space from $(u, v) = (0.33, 0.36)$ to $(0.12, 0.32)$ through the use of a micro-scale peel-off patterning method. In the stacked devices, we demonstrate color stability over the course of device aging to 70% of the initial luminance by enhancing the lifetime of the blue emitter using the PEP-enhanced Purcell effect. These two architectures, which are compatible with the outcoupling schemes studied in this work, provide pathways toward achieving highly efficient, long-lived WOLED lighting.

We conclude by presenting an outlook for the field of organic electronics as well as two new questions: 1) a design for maximizing OLED external efficiency using currently available technologies and 2) a pathway for using OLED outcoupling structures to increase OPV IQE, and thus operational power conversion efficiency.

CHAPTER 1

A Background in Organic Semiconductors

As classified by a physicist, organic materials are those composed of molecules containing either C-H or C-C bonds [1]. This serves as a practical definition, with organic materials possessing properties distinct from those found in inorganic materials. In Sec. 1.1, we will describe the electrical and optical properties of organic materials. Then, in Sec. 1.2 we will discuss growth and fabrication of organic materials. This chapter will end by summarizing the state of research into two organic devices: organic photovoltaics (OPVs) and organic light emitting diodes (OLEDs).

1.1 Electrical and Optical Properties

An organic solid is composed of molecules bound by intermolecular van der Waals forces. Inorganic semiconductors contain much stronger intermolecular covalent or ionic bonds, resulting in charges delocalized across many molecules arranged in a crystalline lattice. The weak intermolecular bonds in organic materials confine charges to individual molecules within the solid, which is typically amorphous or polycrystalline. The electronic and optical properties that result provide organic films with many of their unique and useful attributes.

1.1.1 Electrical Properties

Inorganic solids are defined by ground and excited states that behave as insulating and conducting bands, respectively, spanning across many molecules. In contrast, the excited states for organic

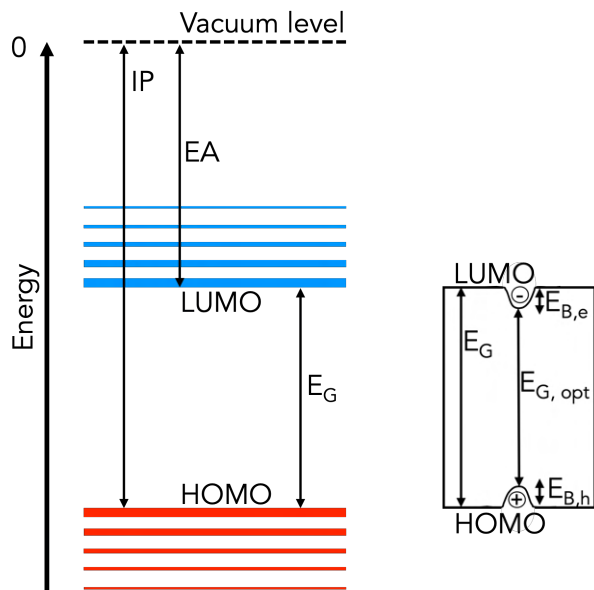


Figure 1.1: **Diagram of organic molecular orbital energies.** Energies are shown relative to the vacuum energy level $E_{vac} = 0$ (*left*). The ionization potential (IP) is the energy between the vacuum level and the highest occupied molecular orbital (HOMO) while the electron affinity (EA) is the energy between the vacuum level and the lowest unoccupied molecular orbital (LUMO). The energy gap, E_G is the difference in HOMO-LUMO energy. The optical energy gap, $E_{G,opt}$, is the energy gap less the charge binding energies. A simplified version illustrating only the HOMO and LUMO is commonly used in depictions of device structure (*right*).

solids remain isolated on single molecules, resulting in levels of molecular orbitals. The Pauli exclusion principle states that no two electrons can occupy the same state. This leads to N electrons in a system filling $N/2$ orbitals, each with a spin up and spin down state. The highest occupied molecular orbital (HOMO) is defined relative to the vacuum energy level, less the ionization potential. The HOMO ground state is separated from the lowest energy excited state, referred to as the lowest unoccupied molecular orbital (LUMO). The LUMO is defined relative to the vacuum level, less the electron affinity, and separated from the HOMO by the energy gap, $E_G \sim 1 - 4$ eV, illustrated in Fig. 1.1. The energy gap is determined by the molecular structure, analogous to the band gap found in inorganic semiconductors, which is defined by the crystal lattice. The wavefunctions of the molecular orbitals can be approximated by assuming a linear combination of atomic orbitals summed over all electrons, i , using the Born-Oppenheimer

approximation to separate out only the electronic interactions:

$$\psi_i(\vec{r}_i) = \sum_{j=1}^M c_{ij} \phi_j(\vec{r}_i) \quad (1.1)$$

where $\phi_j(\vec{r}_i)$ are the individual atomic orbitals with electron positions $\vec{r}_i$, and c_{ij} are weighting coefficients. The corresponding energies arise from Schrödinger's equation, where:

$$\sum_{r=1}^M c_r (\langle \phi_s | \hat{H} | \phi_r \rangle - E \langle \phi_s | \phi_r \rangle) = 0 \quad (1.2)$$

where M is the number of atomic orbitals, s and r index the atomic orbitals [2] and $\hat{H}$ is the Coulombic interaction Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i^N \nabla_{\vec{r}_i}^2 + \frac{q^2}{4\pi\epsilon_e} \left(\sum_{i>j}^N \frac{1}{|\vec{r}_i - \vec{r}_j|} - \sum_{i,I}^{N,M} \frac{Z_I}{|\vec{r}_i - \vec{R}_I|} \right). \quad (1.3)$$

Here, N and M are the number of electrons and atomic nuclei where N is indexed by i, j and M is indexed by I , Z is the atomic number of the nucleus, and $\vec{r}$ and $\vec{R}$ denote the position vectors of electrons and nuclei.

The orbitals can be approximated as Gaussian to aid in calculation of the energies [3]. While arriving at numerical solutions of molecular orbital energies is possible using *ab initio* calculations and other simulation methods enabled by advances in computing, these calculations remain challenging [4, 5].

Experimentally, the orbital structure can be measured using photoelectron spectroscopy (PES). PES uses a high energy optical beam, typically $\lambda = 24 - 58$ nm, to excite an electron from an occupied molecular orbital [6, 7]. The electron is then focused and passes through an electric field. The position of the electron after passing through the electric field determines its energy, which corresponds to the ionization energy of the material. Finding the electron affinity of the material is more challenging but can be done using inverse PES, in which an incident electron beam generates an excited electron on a material surface and measures the energy of photons

emitted as the electrons relax. The electron affinity can also be found electrochemically using cyclic voltammetry [8].

Charges in an organic solid are bound tightly to individual molecules, with the mean free path of a charge being smaller or on the order of the molecular spacing. Charges must then transport between organic molecules via polaron hopping, where energy contained within the lattice is required to mobilize charges. As a result, charge mobility in organics is low, with typical values ranging from $10^0 - 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and decreases with temperature with mobility $\mu \sim \exp(-\Delta E/k_b T)$. At very low T , tunneling dominates transport and $\mu \sim T^{-n}$, where n is defined by the molecular structure. At very high T , transport is dominated by scattering with $\mu \sim T^{-3/2}$. This is different to the condition for inorganic materials that can have high mobilities that increase as temperature decreases. Though van der Waals-bonded organic solids have no lattice-matching restriction and provide other desirable features, such as flexibility, they are not ideal candidate for electronic applications where high mobilities are required to satisfy modern needs for speed and ever-shrinking size. Instead, organic materials are most useful for optoelectronic applications, where their weak intramolecular bonds give rise to unique optical properties.

1.1.2 Optical Properties

Charge localization also results in a high dipole oscillator strength with absorption coefficients ranging from $10^{-5} - 10^{-6} \text{ cm}^{-1}$, an order of magnitude higher than the typical values for inorganic materials. High absorption means that thin organic films can interact strongly enough with light for a variety of optoelectronic applications.

The energy difference between the HOMO and LUMO defines the material energy gap, E_G . In organics, which have tightly bound excited states, the high energy absorption edge, corresponding to the optical energy gap $E_{G,opt}$, is smaller than E_G . The difference in these two energies is equal to the exciton binding energy, $E_{B,e} + E_{B,h}$, illustrated in Fig. 1.1.

The complex index of refraction $n + ik$ determines the group velocity of photons traveling in a

material and material absorption. Most organic materials have $n \sim 1.5-1.8$ with k values varying depending on the application - OPV materials typically have a higher k than OLED materials. The n and k values can be found via ellipsometry, which measures the change in amplitude, ψ , and phase, Δ , of a polarized light beam reflected off a sample surface. First, the material sample thickness, which should be thick enough to be fit reliably (at least $100\text{\AA}$) but thin enough to not be very absorptive, is found by recursively fitting the ψ and Δ curves using the Cauchy approximation and extracting film thickness. This fit must be done for a region of wavelength where $k = 0$, since the Cauchy approximation does not obey the Kramers-Kronig relationship and cannot account for accurate material absorption [9]. Then, with a known thickness, the n and k values can be extracted from a curve fit accounting for non-zero absorption through Gaussian- or Lorentzian-type oscillators over all wavelengths of interest. Ellipsometry can also be used to measure wavelength-, polarization- and angle-dependent reflectance and transmittance, as we will discuss in Sec. 2.3.3.1.

1.1.3 Exciton Dynamics

When charge is injected into a material or a photon is absorbed, electrons will populate the LUMO excited state. When this excited electron is bound to a hole, it is called an exciton. The binding energy of the exciton is defined as:

$$E_B = \frac{-q^2}{8\pi a_0 \varepsilon_r \varepsilon_0 n^2} \quad (1.4)$$

where a_0 is defined as:

$$a_0 = \frac{4\pi \varepsilon_r \varepsilon_0 \hbar^2}{m_r^* q^2} \quad (1.5)$$

and ε_r is the dielectric constant, ε_0 is the permittivity of free space, m_r^* is the reduced mass of the electron, q is the elementary charge, and n is the principle quantum number. Organic materials, which have a low dielectric constant, thus have a large binding energy $\sim 0.5 - 1\text{eV}$ and small exciton radius $\sim 1-5 \text{\AA}$. These tightly bound excitons are known as Frenkel excitons. Un-

like the Wannier-Mott excitons found in inorganic semiconductors and delocalized across many molecules, 10-20 Å diameter, Frenkel excitons are stable at room temperatures, i.e. 300K and higher. Thus, the working mechanisms of real-world organic optoelectronic device applications which demand ambient operation at room temperature are governed by excitons. Once an exciton is formed it will either 1) separate into free charges, 2) recombine either radiatively or non-radiatively, or 3) annihilate.

The diffusion constant is defined as:

$$D = \frac{L_D^2}{\tau_D} \quad (1.6)$$

where L_D is the diffusion length and τ_D is the scattering time. A Frenkel exciton can diffuse to a heterojunction (HJ), discussed further in Sec. 3.1, between two materials with off-set HOMO-LUMO levels. Here the charges separate to form a charge transfer (CT) exciton bound across neighboring molecules. Typically, the molecule hosting the electron in its LUMO is called the acceptor material, while the donor material hosts the hole in its HOMO. If the separated electron hole pair remains within the Coulombic capture radius, r_c :

$$r_c = \frac{q^2}{4\pi\epsilon_0\epsilon_r kT} \quad (1.7)$$

the electron-hole pair can recombine. This is Langevin recombination. When the recombined electron-hole pair originate from the same excited state, this is geminate recombination. When the recombined electron-hole pair originate from different molecules, the recombination is bimolecular. The relatively small dielectric constant of the material, ϵ_r discussed in Sec. 1.1.2, results in a large capture radius. Excitons can radiatively recombine to generate a photon. The radiative recombination rate is governed by Fermi's Golden Rule:

$$k_{if} = \frac{2\pi}{\hbar} |\langle \psi_f | \hat{H} | \psi_i \rangle|^2 \rho(E_{if}) \quad (1.8)$$

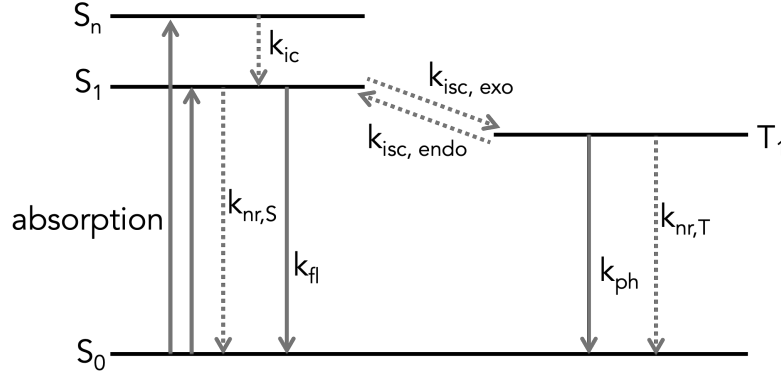


Figure 1.2: **Jablonski diagram.** A Jablonski diagram illustrating internal conversion (ic) and intersystem crossing (isc) transitions between singlet and triplet manifolds. Fluorescent (fl) and phosphorescent (ph) radiative transitions are indicated by solid lines and labeled by their rates, k ; non-radiative (nr) transitions are indicated by dotted lines.

where i and f denote initial and final states, $\rho(E_{if})$ is the joint density of states, and $|\langle \psi_f | \hat{H} | \psi_i \rangle|$ is the transition probability between states. Recombination of a singlet exciton with the singlet ground state is fluorescence while recombination of a triplet exciton with the singlet ground state is phosphorescence. The Jablonski diagram in Fig. 1.2 illustrates the radiative and non-radiative transitions from the singlet and triplet manifolds within the material. The rates of radiative recombination, k_{fl} and k_{ph} , are discussed more in Sec. 2.1.2. Absorption of a photon can excite an electron into the $S_1 - S_n$ orbitals. Higher order excited states will non-radiatively relax to the S_1 state via internal conversion at a rate k_{ic} . Excited states can also transition from the singlet to the triplet manifold via inter-system crossing at a rate k_{isc} . This transition can be endothermic or exothermic, depending on if the initial state is the higher energy triplet state or lower energy singlet state.

The exciton energy can also be transferred. When two molecules are in contact with one another, exciton energy can transfer from one molecule to another by exchanging the excited electron, called Dexter energy transfer. At slightly greater distances, energy can be transferred via Förster resonant energy transfer (FRET). The FRET radius is determined by the overlap integral between two molecules and typically falls between 30-50Å. At distances $>50\text{\AA}$, energy can be radiatively transferred, where one excited state emits a photon that is re-absorbed by

another molecule.

Excitons can also encounter another excited state or polaron and annihilate. These processes involve an exciton (singlet or triplet) gaining energy from annihilation with another singlet (SSA), triplet (TTA), or polaron (TPA or SPA) and promoting to a higher order excited state. In phosphorescent OLEDs, TTA and TPA can generate higher order excited states with energies $\sim 6\text{eV}$, which is sufficient to break intramolecular bonds and lead to material degradation [10, 11].

1.2 Growth and Fabrication

The material properties of organic materials described in Sec. 1.1 dictate the methods by which organic films can be deposited. The weak intermolecular forces binding organic solids and strong intramolecular C-C bonds mean that most organic materials have a sublimation point between 100 - 600 °C, making organic film growth via sublimation a viable option for many organic materials. Amorphous organics can be deposited without requiring a lattice-matched substrate or epitaxial growth. Notably, very large or polymeric organic molecules require sublimation temperatures high enough to break intramolecular bonds and lead to molecular degradation. Alternative methods for deposition will be discussed later in this section. For organic molecules compatible with sublimation, so-called small molecule organics, sublimation must take place with high purity materials in high vacuum conditions to achieve nearly defect-free films with functional mobility and reproducible morphology.

1.2.1 Material Purification

Organic material purity is very important for decreasing defects within devices that can trap charges and instigate material degradation during reliability testing. High purity is achieved through thermal gradient sublimation [12, 13]. A quartz crucible of material is placed within a quartz tube, ideally separated into three sections. Quartz is used both because of its high heat tolerance, and its ability to withstand rigorous cleaning; a 3:1 mixture of H_2SO_4 and H_2O_2 is

used to prepare all quartz parts prior to use, so called Piranha cleaning because of its ability to eat away organic residue with carnivorous efficiency. Each section is aligned to a separate region of a furnace such that a thermal gradient is applied across the glass tube. The tube is kept under low vacuum, $<10^{-5}$ Torr, using a turbo pump. As the furnace temperature is ramped up, unpurified material will sublime from the crucible. The temperature of the center region of the furnace is chosen to be slightly cooler than the sublimation temperature of the material so that purified material will preferentially deposit in this region. Impurities, which may have higher or lower sublimation temperatures than the chosen material, will gather in either the hottest region, closest to the crucible, or the coolest region, farthest from the crucible. This purification process can be repeated as many times as desired; in the first round of purification, a temperature gradient of approximately $\pm 20\text{-}50^{\circ}\text{C}$ is used. The process is deemed complete when all of the raw material from the crucible has been sublimed, or only ash remains, and the material deposited in the center section has formed crystals, for polycrystalline materials, or a uniform glassy area, for amorphous materials.

All purified materials in this work have been purified using thermal gradient sublimation given its relative ease, acceptable yield (generally $>50\%$), reproducibility, and success across a wide range of organic materials. Materials whose decomposition temperatures are close to or higher than their sublimation temperatures cannot be purified thermally, nor can they be deposited thermally. Instead, these materials are typically deposited via solution, see Sec. 1.2.3.2. Materials deposited via solution can be filtered for particle size by forcing solution through filter paper.

1.2.2 Substrates and Substrate Preparation

The versatility provided by organic materials is due in large part to their ability to be deposited on any substrate - amorphous or crystalline, flexible or rigid, opaque or transparent, conductive or insulating. Transparent substrates enable devices to be designed both bottom-up, with light emitted or incident on the “bottom” substrate side of the device, or top-down, with inverted geometry, shown in Fig. 1.3. In this work we will predominantly use soda-lime glass substrates,



Figure 1.3: Schematic of bottom-up and top-down devices. Side view of bottom-up (*left*) and top-down (*right*) devices. The organic areas are indicated in orange. Transparent and opaque contacts are indicated by the pink and gray areas, respectively. The substrate/encapsulation glass and epoxy seal are indicated by light and dark blue, respectively.

which are a common choice given their high transmittance, low surface roughness, and low cost. Glass has an index of refraction $n \sim 1.5$ which can trap light emitted from the organic EML in bottom-up devices, as we will discuss in Sec. 2.3 and Ch. 6. This limit can be circumvented by using a transparent substrate whose index of refraction is closer to that of organics, $n \sim 1.7$, such as sapphire or a metal-doped glass (available from most optical glass manufacturers). These high-index glasses can reduce light trapping in the substrate, but often have undesirable qualities, such as low or wavelength-dependent transmittance, birefringence, and high cost. There has been significant research into substrates engineered to achieve a high index of refraction while maintaining high, wavelength-independent transmittance, low cost, and other specifications. We will discuss some of these engineered substrates in Secs. 6.1 and 5.1. Transparent polymers such as parylene, PDMS, or PET are commonly used for flexible applications. Top-down devices, which typically utilize an opaque bottom electrode material, are typically agnostic to the optical properties of the substrates on which they are grown. Common choices for top-down device substrates are glass or a flexible substrate with a back-surface reflecting layer applied or Si passivated with an insulating layer to prevent shorting between multiple devices on a single substrate.

Prior to device growth, substrates must be cleaned to eliminate any surface contaminants. While CMOS-level cleaning is not required, the high absorption of organic films means that total device thickness is typically on the order of 10-100s of nm. As such, these thin film devices are susceptible to impurities that can short between top and bottom electrodes. The standard cleaning procedure used throughout this work has 7 steps. First, substrates are submerged in a

soap (e.g. Tergitol[™] or Triton[™] X-100)/deionized (DI) water mixture to clean off oils and large particles. A 3 min ultrasonication bath is used to enhance effectiveness of contaminant removal. Substrates are then sonicated in two subsequent acetone baths. These steps remove any organic residue from the surface. Finally substrates are sonicated in two subsequent isopropanol baths to remove any remaining organics and wash away acetone residue. At this stage isopropanol can be heated to $\sim 165^{\circ}\text{C}$ to prevent residue from forming as substrates are dried using ultrapure N_2 .

Modifications can be made to this process, including adding repetitions of each step, extending sonication time, and using other organic solvents as required for specific applications (e.g. methanol is preferred when streak-free optical quality is a priority).

After solvent cleaning an optional snow cleaning step can be added to clear any remaining large debris [14]. This process works by spraying substrates heated to 100°C with high pressure supercritical CO_2 . As the CO_2 leaves the high pressure cylinder, its temperature drops and it nucleates or “snows” on the substrate surface. The CO_2 condensate then immediately evaporates from the heated substrate surface and draws with it any remaining debris via static van der Waals forces. The final cleaning step before device growth is a surface treatment using plasma. The plasma will ash any remaining scum on the substrate and decrease the surface energy of the substrate allowing subsequent layers to wet more easily. This is particularly important for films deposited via solution, see Sec. 1.2.3. In this work we use ozone plasma, which has the added benefit of lowering the work function of ITO, a common bottom contact material.

More rigorous cleaning can be used before these standard cleaning steps. The options for cleaning will depend on the substrate used. For glass, a Piranha clean can be used to remove significant organic contaminants, though a pre-clean with acetone and isopropanol followed by at least 5 DI water rinses is required to prevent a violent reaction between the Piranha solution and the organic contaminants. The first step of an RCA clean (5:5:10 $\text{NH}_4:\text{H}_2\text{O}_2:\text{DI}$ water heated to 80°C) can be used to remove ionic contaminants [15].

Substrates should be cleaned before and after depositing or patterning the bottom contact, so long as the contact will not be damaged by exposure to the cleaning process. For bottom-

down devices requiring a transparent electrode ITO or IZO are commonly used given their high transparency and low sheet resistance. Metals such as Al, Ag, Au, and Mg are commonly used for opaque contacts on either the top of the device stack for bottom-down devices, or as the bottom contact for top-up devices. Transparent top contacts can be made from ITO or thin Ag ($<30\text{nm}$).

The top and bottom electrodes and organic layers are patterned such that the device area is defined as the area where the bottom contact, organic layers, and top contact are overlapping in the vertical direction. A standard pattern, shown from the top view in Fig. 1.4, is composed of a bottom contact patterned into stripes 1-3mm wide under the center of the substrate and extending to larger pads on the edge of the substrate to be used when probing the device. The top electrode has an analogous pattern rotated perpendicular to the bottom contact, with organics overfilling the area between the two electrodes to ensure they do not short. The top contact is typically probed using larger pads extending beyond the device active area, but can also be contacted directly on top of the organic stack by using a gold wire that is conductive, but not hard enough to penetrate through the organic stack.

The example geometry shown in Fig. 1.4 is achieved by patterning the device layers. The inorganic layers deposited before the organics can be patterned using photolithographic masking and selective chemical or plasma etching to achieve nanometer-scale features. Many of the solvents and photoresists used during lithography will degrade or dissolve organics, so organic and any subsequent layers are typically patterned using shadow masks. Very fine and thin shadow masks (referred to as fine metal masks) can pattern micron-scale features, but are most commonly used for millimeter-scale features since even a very small spacing between the substrate and the mask will result in deposition beyond the mask edge. Shadow masks only directionally block material deposition making them incompatible with conformal deposition techniques, such as atomic layer deposition (ALD) and solution processing. In Sec. 8.1, we will discuss additional methods for achieving micron-scale patterning that is not damaging to organics.

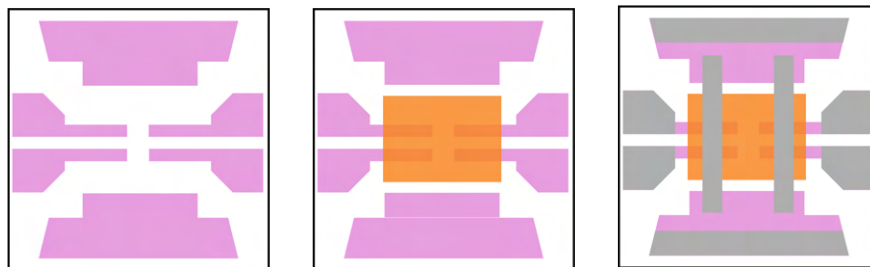


Figure 1.4: Schematic of a patterned anode, organic, and cathode of a standard device. Top view schematic of a patterned anode (pink, *left*), organic (orange, *center*), and cathode (gray, *right*) of a standard device.

1.2.3 Deposition Methods

The relatively weak van der Waals forces between organic molecules lead to two attributes that are particularly relevant to film deposition: 1) ability to be grown amorphously while retaining the desired optical and electronic properties and 2) relatively low sublimation temperatures. In this work we use two methods for depositing organic films each with distinct advantages and disadvantages: thermal evaporation and deposition via solution. Though not utilized in this work, organic materials can also be deposited via the vapor phase in a process similar to physical vapor deposition, called organic vapor phase deposition (OVPD).

1.2.3.1 Thermal Evaporation

Organic material can be deposited via sublimation. In vacuum thermal evaporation, or VTE, material solids (typically powders) are held in a metal boat (usually W or Ta) or ceramic crucible held in a metal basket, referred to as source boats. A current is applied across the source boat that resistively heats the boat and material within. The total power across the boat is monitored as a proxy for boat temperature and set to achieve the desired deposition rate between $0.1\text{-}1.0\text{\AA s}^{-1}$ (note: some source boats are equipped with thermocouples to measure source temperature directly). Sources are contained in a high vacuum chamber and sublimated material travels ballistically to a rotating sample stage where it is deposited on the sample substrates. Vacuum levels of $< 10^{-6}$ Torr are required, with higher vacuum $\sim 10^{-8}$ Torr preferred to minimize contamination and

defect formation from the background pressure.

During deposition, the film thickness is measured by the change in frequency of a quartz crystal microbalance (QCM). The change in QCM frequency corresponds to the deposited layer thickness, density, and Z-factor, which accounts for the difference in acoustic impedance between the deposited material and the QCM. The accuracy of the QCM reading is calibrated by depositing a film $>100\text{\AA}$ and measuring the actual thickness using ellipsometry, see Sec. 1.1.2. The ratio of the measured thickness to the QCM reading is used to scale the QCM reading; this is called the tooling factor (TF). The TF can change based on source placement within the chamber, the type of boat or crucible used, the amount of material in the boat, and the lifetime of the QCM (there is negligible change in the TF when QCM frequency is $>90\%$ of its initial frequency).

Organic molecular beam deposition (OMBD) is analogous to molecular beam epitaxy, a deposition technique commonly used for inorganic semiconductors. In this process a Knudsen cell (K-cell) of organic material is heated to its sublimation temperature. This is similar to the working principle of VTE, but the K-cell is designed to heat very uniformly, allowing for precise sublimation rates. Ultra-high vacuum ($\sim 10^{-9}$ Torr) is required to achieve quasi-epitaxial growth [16]. While OMBD offers the ability to precisely control film morphology *in situ* and can produce single layer films, typical tool size (4-6 K-cells) and the required tool maintenance is not conducive to systems where many different materials are continually exchanged.

While VTE sacrifices some of the morphological control achieved in OMBD and OVPD, it offers a very scalable and reproducible method for film deposition. The majority of devices shown in this work (and sacrificed in failed tests along the way) were grown via VTE. VTE is capable of evaporating many materials, from organics to metals with sublimation temperatures up to $1,500^{\circ}\text{C}$. Many VTE chambers are equipped with 6-10 sources, making it possible to deposit an entire device without breaking high vacuum. In reality, it is advantageous to deposit metals and organics in separate chambers to maintain organic material purity. As such, the ideal setup includes multiple chambers isolated from one another but connected by a high vacuum loadlock.

1.2.3.2 Deposition via solution

The decomposition temperature for some organic materials is similar or lower than their sublimation temperature, meaning none of the previous deposition techniques can be used. For this reason many polymers and some heavy metallorganics must be deposited via solution. An organic solvent, such as chloroform, ethanol, toluene, etc., chosen based on material solubility, is used to dissolve an organic solid in solution. This typically requires heating and mechanical stirring. The solution is deposited by dispensing onto a spinning substrate using a tool called a spin coater. Material thickness is controlled by varying the spin speed and/or concentration in solution.

While solution processing offers a method for depositing materials that are unable to be deposited using evaporation, it is the least controlled and least versatile method of organic deposition. In multilayer films, solvents must be strategically chosen to be orthogonal such that one layer doesn't wash away or damage the layers beneath it. Solution concentration, as a proxy for film thickness, is highly reproducible but requires precision weight and volume measurements. Spin speed is also controllable, but the correspondence between spin speed and film thickness is dependent on the spin coater used, and the ambient pressure and gas flow of its operating environment. Solution processing must be done at atmospheric pressure so a very pure, inert environment is required, typically an N₂ glovebox. Solvents must be fully evaporated before device use to avoid degradation due to outgassing. Additionally, while solution processing can be done at a large scale using tools such as a doctor blade, dip coater, or slot-dye coater, spin coating itself is not scalable for substrates larger than ~8" wafers.

1.2.3.3 Other deposition techniques

Though VTE and solution processing can be used to deposit a range of inorganic materials (e.g. Al and Ag via VTE, and ZnO via solution), this work utilizes additional deposition techniques for certain inorganic films. In particular, radio frequency (RF) sputtering is used to deposit ITO for use in transparent contacts. Sputtering works by ionizing a plasma of inert gas that then bombards a material target and breaks atoms from the target surface to be deposited on

the substrate. Other inorganic materials can also be deposited via electron beam, chemical and plasma-enhanced chemical vapor deposition, physical vapor deposition, and molecular beam epitaxy.

A note on pumps

Though not crucial to understanding the work presented in this dissertation, the existence, use, and maintenance of pumps have occupied significant amount of time during the completion of this work.

The vacuum levels required for defect-free film deposition utilize multi-step pumping. To achieve pressures between 10^{-2} to 10^2 Torr, a so-called rough pump is used. These pumps are categorized by their working mechanism - oil, scroll, or diaphragm pumps. Oil pumps often have the highest pumping speeds and are the best choice for large volume chambers. There is some risk of oil vapor contamination when using oil pumps - scroll and diaphragm pumps are dry and are best for systems where purity is important and a slower pumping speed is acceptable.

Once low vacuum is achieved, higher vacuum can be achieved by switching the system to a high vacuum pump. It is crucial to note that an oil pump should never be connected to the intake side of any other pump, especially a stronger pump, as this can cause oil to back flow through the pump damaging both pumps and anything in between them. High vacuum between 10^{-3} – 10^{-8} Torr can be achieved using a turbo or cryo pump. Cryogenic “cryo” pumps require the use of 99.999% pure He gas, compressed to liquid phase and circulated to cool a high surface area material that is exposed to the chamber. Molecules will be frozen on the pump so cryo pumps must be regularly regenerated to purge trapped molecules, and occasionally serviced to decontaminate the circulating He.

Turbomolecular “turbo” pumps operate like small jet engines with layers of blades spinning at speeds ~ 1200 RPM. While turbo pumps require less routine maintenance than cryo pumps, a turbo pump exposed to pressures $> 10^{-2}$ Torr will be permanently damaged due to too many particles hitting the blades. Cryo pumps exposed to high pressure only require regeneration,

which can be done without uninstalling the pump.

Once high vacuum is achieved, ultra-high vacuum can be reached using another pumping step. Ion pumps are used to achieve vacuum from $10^{-8} - 10^{-11}$ Torr. Ion pumps work by trapping molecules underneath layers of Ti sputtered across two or three electrodes within the pump. The pump requires servicing when the sputtered Ti creates a short between the electrodes.

1.2.3.4 Encapsulation

Organic molecules are susceptible to degradation from water vapor and oxygen, requiring practical devices and devices intended for long-term or environmental testing to be encapsulated. Encapsulation techniques are characterized by their water vapor transmission rate (WVTR), which should be $< 10^{-6} \text{gm}^{-2} \text{day}^{-1}$. Glass satisfies this condition and some plastic films have been engineered to approach the necessary value (e.g. 3M™ Ultra Barrier Solar Film 512, WVTR $\sim 10^{-5} \text{gm}^{-2} \text{day}^{-1}$). For top-down devices, the transparency of the encapsulation film is also important. In this work, devices are encapsulated using a glass slide that fits within the contact area and is sealed to the substrate using a UV-curing epoxy. Inside an inert N₂ glove box, the epoxy is dispensed in a thin line around the edge of the cover glass which is then pressed onto the device substrate. The device active area is shielded while the epoxy is cured to prevent UV degradation.

Thin film encapsulation (TFE) can also be used. Typical TFE designs utilize dyads or triads of materials deposited via ALD, which is both conformal and can be defect-free, repeated until the required WVTR is achieved.

1.3 Open Questions in Organic Optoelectronics

At the start of this work in 2018, much of the research focus in organic optoelectronics could be summarized by two central goals: 1) increase OPV efficiency and lifetime and 2) increase blue emitter efficiency and lifetime. Both goals are governed by the somewhat paradoxical nature of applied research. In OPVs: it is possible to create a high efficiency OPV using non-fullerene

acceptors (NFAs), but they have poor lifetime [17]; fullerene-based OPVs have incredibly long intrinsic lifetimes [18], but have stalled in achieving power conversion efficiencies, $\eta_{PC} > 10\%$. In OLEDs: fluorescent blue emitters acceptable lifetimes for displays, but their internal quantum efficiency (IQE) is capped at 25%; phosphorescent blue emitters can achieve nearly 100% IQE, but do not have commercially viable operational lifetimes. In both cases, the problem is inherently material-based: if we can design an organic molecule with both lifetime and efficiency, all the problems are solved. This is, of course, much easier said than done so much so that it becomes worthwhile to investigate other ways of solving the efficiency/lifetime paradox. This work investigates these two central questions and progresses toward solutions for improving OLED and OPV performance through device design and engineering. In Ch. 4, we study an archetype long-lived fullerene-based OPV alongside a high efficiency NFA OPV and develop an empirical method for understanding device degradation mechanisms. In Ch. 5-Ch. 7 we characterize the coupling efficiencies of photons generated within an OLED to waveguided, substrate-trapped, and plasmonic optical modes, and present three methods for coupling photons trapped in these modes into observable air modes. In Ch. 8 we focus specifically on white OLEDs (WOLEDs) for solid-state lighting applications and discuss two methods for improving WOLED efficiency and reliability through device design. Finally, in Ch. 9, we revisit the main questions existing in the field of organic electronics, and provide an outlook for future work.

CHAPTER 2

Photon Emission and Coupling in Organic Light Emitting Diodes

An exciton in an organic material has some probability of radiatively recombining and emitting a photon, as discussed in Sec. 1.1.3. The IQE accounts for the efficiency of charges reaching or extracted from the active layer and all photons generated or absorbed, regardless of whether or not they can be observed outside the device.

The IQE is dependent on the active layer materials as well as device architecture. The device architecture - namely layer thicknesses and dispersions - affects the coupling efficiency of light into and out of the device, such that the external quantum efficiency (EQE) is defined:

$$\eta_{EL} = \eta_{coupling} \eta_{IQE} \quad (2.1)$$

where $\eta_{coupling}$ is equivalent to η_{oc} , the outcoupling efficiency, when considering light emission, and η_{abs} , the absorption efficiency, for light absorption. **This is the central equation of this work.** The EQE encompasses both optical and electrical losses, and accounts for all photons and charges that enter or exit the device structure. The EQE can be expanded to explicitly account for separated processes contributing to the IQE. For OPVs, in which charge is extracted from the device, EQE is written:

$$\eta_{PV} = \eta_{abs} \eta_{diff} \eta_{diss} \eta_{extr} \eta_{CT} \quad (2.2)$$

where η_{abs} is the overlap between the incident light spectrum (typically AM1.5G) and the absorption spectrum of the device, η_{CT} is the CT state emission efficiency, η_{diff} is the efficiency of exciton diffusion to the heterojunction, η_{diss} is the CT state dissociation efficiency, and η_{extr} is the extraction efficiency of the contacts. η_{PV} is sometimes referred to as EQE_{PV} . OPV operation, light absorption leading to exciton generation and charge extraction, is reciprocal to OLED operation, charge injection leading to exciton formation and light emission, so an equivalent, reciprocal EQE can be written for OLEDs:

$$\eta_{EL} = \eta_{oc}\gamma\chi_{ST}\phi_{PL} \quad (2.3)$$

where η_{oc} is the outcoupling efficiency, γ is the charge balance factor, χ_{ST} is the singlet/triplet ratio, and ϕ_{PL} is the photoluminescent quantum yield. η_{EL} is sometimes referred to as EQE_{LED} . In this work, we will be investigating the light emitting properties of both OLEDs and OPVs, as governed by Eq. 2.3. In Sec. 2.1 we will discuss the physical processes governing IQE for light emitting devices and in Sec. 2.3 we will discuss the optical architectures that determine EQE.

2.1 Photon Generation in Organic Diodes

2.1.1 Spin Statistics

The spin wavefunction of an excited state can either be symmetric, corresponding to a singlet, or anti-symmetric, corresponding to a triplet:

$$\psi_S = |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle, \quad S=0, m_s=0 \quad (2.4)$$

$$\psi_T = |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle, \quad S=1, m_s=0 \quad (2.5)$$

$$\psi_T = |\uparrow\uparrow\rangle, \quad S=1, m_s=1 \quad (2.6)$$

$$\psi_T = |\downarrow\downarrow\rangle, \quad S=1, m_s=-1. \quad (2.7)$$

This defines the probability of forming singlet (25%) vs. triplet (75%) excited states. The Pauli exclusion principle prevents a triplet, whose excited state spin is the same as its ground state, from radiatively decaying. When there is mixing between singlet and triplet states, the triplet can radiatively decay to the singlet ground state, bypassing the spin selection rule that would otherwise prohibit phosphorescence. This can be achieved through spin-orbit coupling, where the electron spin interacts with the orbital angular momentum through the following Hamiltonian:

$$\hat{H}_{SO} = \frac{-Zq^2}{8\pi\epsilon_0 m_e^2 c^2 r^3} \vec{l} \cdot \vec{s} \quad (2.8)$$

where Z is the atomic number of the atom, q is the elementary charge, ϵ_0 is the permittivity of free space, m_e is the electron mass, c is the speed of light, and r is the atomic spacing. The vectors $\vec{l}$ and $\vec{s}$ correspond to the orbital angular momentum and spin, respectively.

The fraction of radiative excited states is included in the IQE as the singlet/triplet ratio, χ_{ST} , where $\chi_{ST} = 0.25$ for fluorescent emitters. In phosphorescent emitters, where emission triplet is allowed, $\chi_{ST} = 1$, to account for both emission from the triplet and intersystem crossing between singlet and triplet manifolds.

In OPVs, the photovoltaic efficiency is not limited by χ_{ST} . All optically generated excited states will form singlets, but subsequent intersystem crossing may form triplet states. When an OPV is operated under forward bias in the dark (see Ch. 4), the emission efficiency is limited by $\chi_{ST} = 0.25$, since the triplet state is non-radiative in standard OPV systems.

2.1.2 Photoluminescent Quantum Yield

The photoluminescent quantum yield, ϕ_{PL} or PLQY, is the number of photons emitted per excited state. For fluorescent emission:

$$\Phi_f = \frac{k_f}{k_f + k_{nr,s} + k_{ISC}} \quad (2.9)$$

where k_f is the radiative rate of fluorescence, typically $\sim 10^7 - 10^9 s^{-1}$, $k_{nr,s}$ is the singlet non-radiative decay rate, and k_{ISC} is the intersystem crossing rate, typically $\sim 10^5 - 10^{10} s^{-1}$. For phosphorescent emission:

$$\Phi_{ph} = \frac{k_{ph}\Phi_{ISC}}{k_{ph} + k_{nr,t}} \quad (2.10)$$

where k_{ph} is the radiative rate of phosphorescence, typically $\sim 10^4 - 10^7 s^{-1}$. For both singlets and triplets, $k_{nr} \sim 10^0 - 10^5 s^{-1}$. The intersystem crossing efficiency, Φ_{ISC} is defined:

$$\Phi_{ISC} = \frac{k_{ISC}}{k_f + k_{nr,s} + k_{ISC}} \quad (2.11)$$

Thus, efficient phosphorescence requires a large intersystem crossing rate. The energetics of these transitions are illustrated in Fig. 1.2. Measurement of PLQY is discussed in Sec. 3.3.1.

In OPVs, the equivalent term is η_{CT} . This distinction arises from the fact that charge generation is governed by the CT state, and so the CT state emission efficiency governs IQE. If excitons recombine before diffusing to the heterojunction, meaning $\eta_{diff} < 1$, this could result in emission from the material singlet state with a radiative efficiency equivalent to ϕ_{PL} of the neat material. These excitons will not contribute to charge generation and thus result in a decreased IQE.

2.1.3 Charge Balance

Finally, IQE is limited by the maximum number of excited electron-hole pairs that can form in the device active region. This is referred to the charge balance factor, γ , defined:

$$\gamma = \frac{\# \text{ excitons formed in EML}}{\# \text{ free charges injected into device}} \quad (2.12)$$

The charge balance factor can be qualitatively estimated by measuring the current generated in single carrier devices for electrons and holes. A well-balanced device should have approximately equivalent currents for both carriers. The EQE spectral shape provides a qualitative indication

of charge balance. Devices with poor charge balance show low EQE at low and high current densities, resulting in a hump-shaped EQE curve. EQE roll-off at high current densities also results from TTA and TPA, so a diagnosis of poor charge balance from EQE shape should be supported by other evidence. The exciton generation profile in the emissive layer (EML) can be more directly compared to injected current using sensing layers [19]. A sensing layer consists of a low energy fluorescent material doped in very thin, $\sim 1\text{\AA}$, layers throughout multiple devices of the same structure. The intensity of electroluminescent (EL) emission from the sensing layer corresponds to the exciton profile at that point in the device.

In an OPV, where charge is extracted, γ is further broken down into η_{diss} and η_{extr} , which account for the efficiency of converting excitons into extracted charges - the reciprocal process to injecting charges and generating excitons.

2.2 Cavity Optics

The reflective contacts and layer thickness of a typical OLED ($\sim 100\text{-}500\text{nm}$) result in the device behaving as a microcavity [20]. In a weak cavity with a transparent contact on one side, the cavity effects are minimal. As the strength of the cavity is increased through a more reflective metal contact or using two metal contacts, the cavity introduces a spectral narrowing and angle dependence [21]. The cavity strength also affects the rate of radiative decay of dipoles contained within it. This phenomenon was first discovered by Edward Purcell in 1946. The amount of change in the radiative decay rate depends on the change in the strength of the cavity. Zhao, et al. have demonstrated that the Purcell factor (PF), defined as:

$$PF = \frac{k_{r,cavity}}{k_{r,0}} \quad (2.13)$$

where $k_{r,cavity}$ is the radiative decay rate and $k_{r,0}$, the natural decay rate, can be increased from $PF = 1.4$ in standard OLED with an ITO/Al cavity to $PF = 2.4$ in devices with a DBR/Ag cavity, corresponding to a $1.4\times\text{-}1.9\times$ increase in $k_{r,cavity}$ for an isotropic dipole distribution.

Additional work has demonstrated that the use of a metal-metal cavity can further increase the PF, even for a tandem structure with a long cavity and multiple EMLs [23]. The Purcell effect can be further enhanced through the generation of plasmon-exciton-polaritons (PEP) at the metal-organic interfaces. This phenomenon, first reported by Zhao, et al., will be discussed in detail in Sec. 2.3.3.1 and further utilized in devices in Ch. 7 and Sec. 8.2.

2.3 Optical Modes

A photon generated in the EML will have some wavelength and wave vector, k , dependent on the orientation of the emissive molecule. The wave vector can be written as a function of the index of refraction and photon wavelength:

$$k = \frac{2\pi n}{\lambda} \quad (2.14)$$

These properties, along with the position of the EML within the device and the index of refraction of the EML material will determine the optical coupling of the photon. We can also write the normalized wave vector, $u = \frac{k}{k_0}$ with k_0 corresponding to the EML. Photon trapping within various modes within the OLED can largely be simplified to a geometric problem depending on: 1) angle of incidence of a photon on an interface and 2) the index of refraction mismatch at that interface. Some fraction of photons generated in the EML will be automatically coupled out of the devices, for $u < n_{air}/n_{org} = u_{air} \sim 0.59$. This fraction of light is equivalent to the outcoupling efficiency of the device, $\sim 20\%$ for a standard device architecture. Photons with $u > u_{air}$ will be trapped within the device coupled to waveguided modes in the organic materials or substrate, or plasmonic modes coupled to metal surfaces. A small fraction of light, typically $< 5\%$ is lost to material absorption.

2.3.1 Waveguided Modes

The index of refraction of organics is typically ~ 1.7 , which is high relative to air and glass. This results in the generation of waveguided modes which trap photons in the organic layers between the lower index glass substrate and reflective top metal contact. The waveguided modes are defined as those with $n_{\text{substrate}}/n_{\text{EML}} < u_{\text{WG}} < n_{\text{EML}}/n_{\text{EML}}$. For a standard glass substrate and a typical organic, $0.88 < u < 1$. The thicker the organic layers, the higher fraction of photons coupled to waveguided modes.

2.3.2 Substrate Modes

Substrate modes are coupled in the same manner as waveguided modes, with light trapped between high-index organics, the device substrate, and air. In this sense, substrate modes can be considered as a specific subset of waveguided modes with $n_{\text{air}}/n_{\text{EML}} < u_{\text{sub}} < n_{\text{substrate}}/n_{\text{EML}}$, corresponding to $0.59 < u < 0.88$. It is useful to distinguish substrate modes from waveguided modes given that they are trapped external to the device organic layers and can be coupled into air modes more easily, as we will discuss in Chs. 5-6.

2.3.3 Plasmonic Modes

Photons can also couple to the metal interfaces in the device to form plasmonic modes. Plasmonic modes have $1 < u$. Most commonly, plasmonic modes are surface plasmon polaritons (SPP), where a photon is coupled to an evanescent mode on the surface of the metal. The SPP mode is trapped along the surface of the metal, and propagates until it is absorbed by the metal or scattered out by an engineered structure, as we will discuss in Ch. 7. The SPP mode can also couple to an exciton in the adjacent organic layer to form a hybrid PEP. The differences between SPP and PEP modes will be investigated further in Ch. 7.

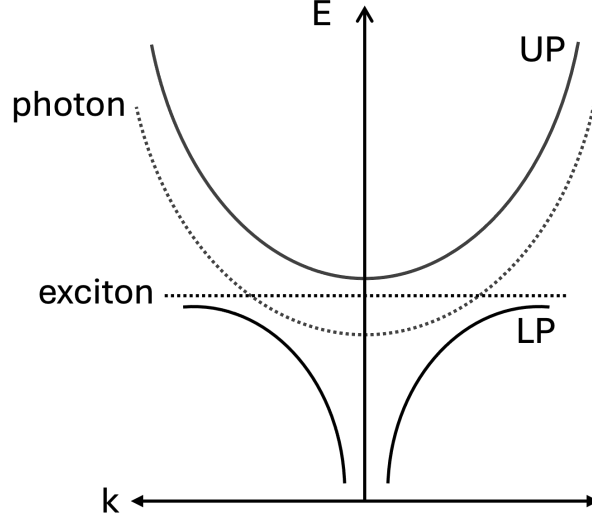


Figure 2.1: **Schematic of a polariton.** The upper and lower polariton (UP and LP) branches are drawn with solid lines, as a function of energy E vs wave vector k . The dashed lines indicate the separate photon and exciton energy.

2.3.3.1 Plasmon-exciton-polaritons

An exciton polariton is a quasi-particle consisting of a photon strongly coupled to an exciton [24]. The polariton consists of a photonic component and an excitonic component, shown in Fig. 2.1, where the photon dispersion and exciton dispersion have resonant energies. When the photon and exciton interact before the decay of either component, the condition for strong coupling is met and a polariton forms. The energies of the coupled state are defined by an anti-crossing centered around the exciton energy and resulting in an upper polariton branch, with energy higher than the exciton, and a lower polariton branch with energy lower than the exciton. The energy splitting between the two branches is referred to as the Rabi splitting, Ω_R , which describes the interaction between the photon and exciton. The polariton can be described by the Hamiltonian from the coupled oscillator model:

$$\begin{pmatrix} E_{ph} & g \\ g & E_{ex} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \quad (2.15)$$

where the E_{ph} is the photon energy, E_{ex} is the exciton energy, $g = \frac{\Omega_R}{2}$ is the interaction

term between the two particles, E represents the eigenvalues and α and β are the Hopfield coefficients of the eigenfunction that describe the photonic and excitonic fractions of the polariton, respectively. Additional excitonic terms can be added to the Hamiltonian to account for multiple vibronic peaks of the material [25].

The condition for strong coupling is quantified by the interaction satisfied when $g > \frac{\gamma + \kappa}{2}$, where γ and κ are the decay rates of the photon and exciton, respectively. Thus, the photon must be confined in order to couple to the excitation. The nature of photon confinement defines the nature of the polariton, with cavity polaritons and Bloch surface wave polaritons commonly formed in optoelectronic devices.

At the metal interface within an OLED, the photon couples to the surface plasmon mode of the metal to create an SPP mode. The coupling between the SPP (part photonic, part plasmonic) and the transport layer exciton creates a hybrid plasmon-exciton-polariton. Formation of a PEP requires that the absorption of the transport layer exciton is resonant with the absorption of the metal layer.

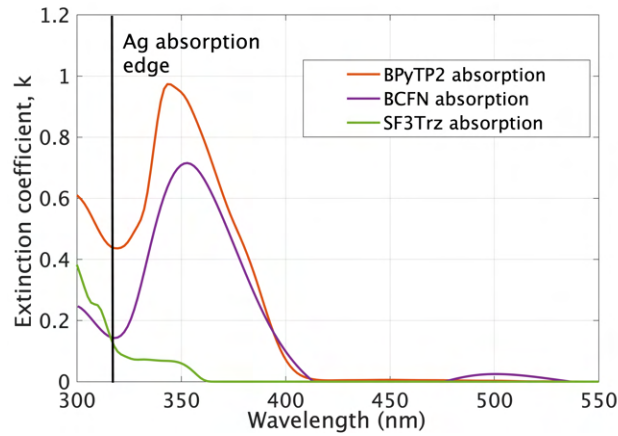


Figure 2.2: Absorption of BPyTP2, BCFN, SF3Trz, and Ag. The extinction coefficients of BPyTP2, BCFN, and SF3Trz, which are proportional to the absorption, are compared to the absorption edge of Ag.

The extinction coefficients, k , as functions of wavelength are shown in Fig. 2.2 for two common electron transporting materials, BPyTP2 and SF3Trz, and BCFN, a hole transporting material. The extinction coefficient, the unitless imaginary component of the complex index of

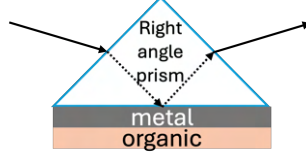


Figure 2.3: **Schematic of reflection measurement samples.** The incidence angle is defined relative to the surface normal.

refraction, is related to the absorption coefficient, α , typically reported in units of cm^{-1} :

$$\alpha = \frac{4\pi k}{\lambda} \quad (2.16)$$

where λ is wavelength. BPyTP2 and BCFN have high absorption at energies slightly below the Ag absorption edge, while SF3Trz has a much lower absorption coefficient. We can measure the formation of a PEP using angle-resolved reflection measurements taken using an ellipsometer. The sample configuration is shown in Fig. 2.3. The polariton branches appear as absorption dips in the reflection spectrum. The angle-resolved reflection is shown in 2.4, where the PEP LP branch of BPyTP2 is red shifted compared to SPP LP branch of SF3Trz as a result of strong coupling between the BPyTP2 exciton and the Ag SPP.

Further, the formation of PEP modes depends on the orientation of dipole emission. Vertical dipoles, also defined as *p*-polarized or transverse magnetic (TM) modes, will preferentially couple to the metal surface. We observe an angle-dependent dispersion for *p*-polarized light, corresponding to vertical dipoles coupled to the metal surface, as shown in Fig. 2.5. No dispersion is present for *s*-polarized light, corresponding to transverse electric (TE) modes emitted from horizontal dipoles, which does not couple to SPP modes. The bilayers shown in Fig. 2.5 consist of Al/BPyTP2. The absorption edge of Al is at a much higher energy than Ag, and couples to a higher order vibronic of the BPyTP2 absorption spectrum. As a result, additional polariton branches can be resolved around 275 and 325 nm for the UP and middle polariton branches, respectively.

Zhao, et al. have demonstrated the use of PEPs in both single junction and tandem blue

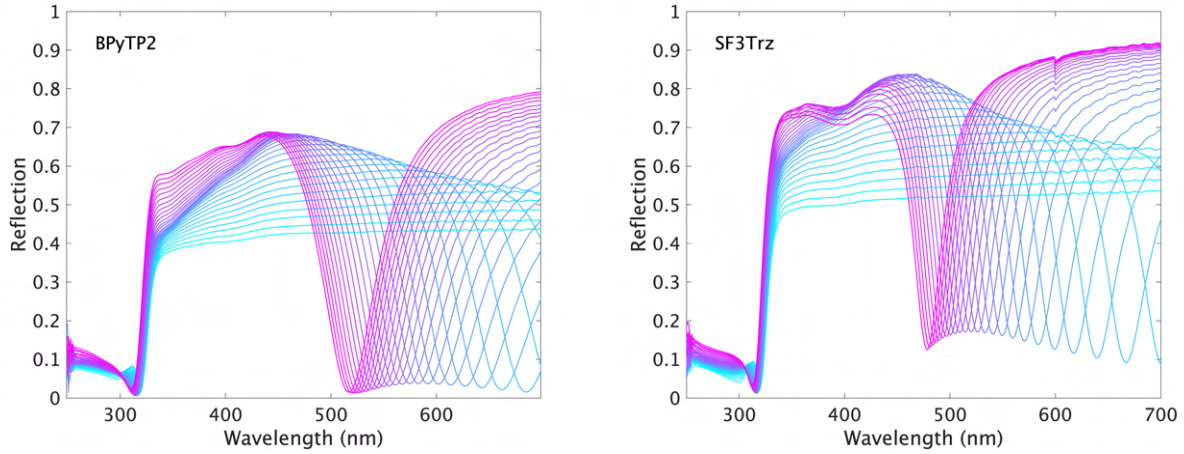


Figure 2.4: Angle-dependent p-polarized reflection for Ag/BPyTP2 and Ag/SF3Trz films. Angle-dependent p-polarized (TM) reflection for Ag/BPyTP2 (*left*) and Ag/SF3Trz (*right*) bi-layer films. The color gradient follows the incidence angle, from 43°(cyan) - 73°(pink).

PHOLEDs [22, 23]. In the tandem device structure PEPs are formed at both the Ag cathode/ETL and anode/HTL interfaces, where the anode is composed of a layered ITO/Ag/ITO stack, such that strong coupling can occur between the Ag and hole transporting material. The use of PEPs in OLEDs will be further developed in Ch. 7 and Ch. 8.2. The effect of PEP on OLED performance has also been investigated for phosphor-sensitized and TADF emitters [26].

2.4 Calculations of Optical Coupling

2.4.1 Green's Function Calculations

The fraction of light coupled to each of the optical modes described in Sec. 2.3 can be computed by modeling the emissive layer with a dipole emitter and solving Maxwell's equations to find the electromagnetic field distribution within the device stack. Throughout this work, these calculations are used to design and characterize device performance.

First, the properties of the device are specified: the wavelength of photon emission, λ , the layers of the device stack, N , the position of the EML within the device stack, n , the thickness of each layer, the complex dielectric constant of each layer, ε , the position of the dipole within the

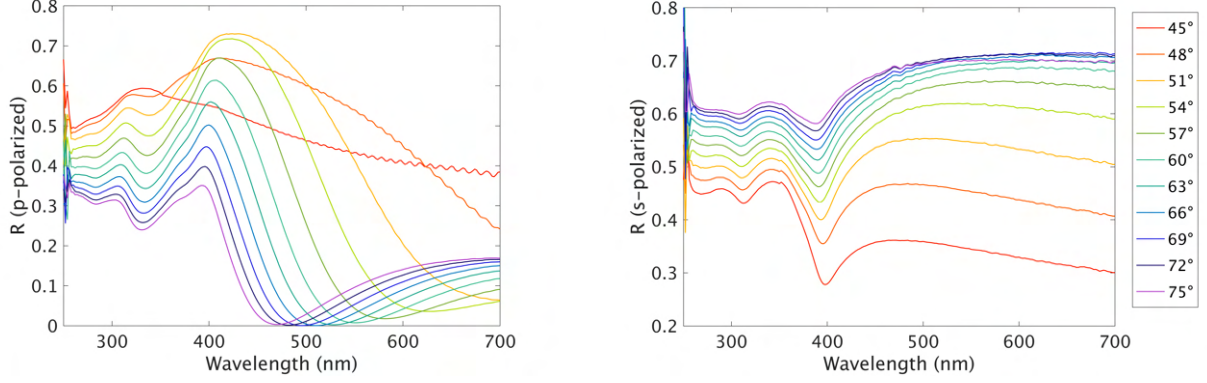


Figure 2.5: Angle-dependent p -polarized and s -polarized reflection for an Al/BPyT2 film. Angle-dependent p -polarized (TM, *left*) and s -polarized (TE, *right*) reflection for an Al/BPyT2 film.

EML, the material PLQY, q , and the fraction of horizontal dipoles in the EML, θ_{hor} . Next, we define a range of test angles, θ from $-\frac{\pi}{2}$ to 0, which correspond to the normalized wave vector $u = \cos(\theta)$. Then we calculate the perpendicular wave vector, h :

$$h = k_0 \sqrt{\frac{\varepsilon}{\varepsilon_0} - \cos^2(x)}. \quad (2.17)$$

Next, we model emission from a dipole in the EML using the Chance, Prock, Silbey model [27]. The electric field due to a dipole oscillator can be written [28]:

$$E(R) = i\omega\mu_0 \int G(R|R') \cdot J(R') d^3 R' \quad (2.18)$$

where ω is the oscillation frequency, μ_0 is the permeability of free space, $J(R')$ is the current, and $G(R|R')$ is the dyadic Green's function [29]. The Green's function can be written in terms of its eigenfunctions, which have coefficients c, f, c' , and f' . They correspond to the eigenfunctions traveling upward, c and f , and downward, c' and f' , from the EML. In this case, “downward” refers to the direction of light emission. Additionally, c' and c refer to the eigenfunction with only a surface parallel (i.e. TE) component, while f' and f contain both a parallel and perpendicular component (i.e. TE and TM). We then numerically solve for the ratio of the coefficients, c'/c

and f'/f in each layer from the top of the device stack to the EML, with the boundary conditions $c_1/c'_1 = f_1/f'_1 = 0$. Then, we do the same from the bottom of the device stack up to the EML, with the condition that $c_N/c'_N = f_N/f'_N = 0$. We set the two ratios (one from solving from bottom up and one from solving top down) at the EML equal and solve for c, f, c' , and f' at the EML. With these values as a starting point we then solve for the coefficients in each layer, moving outward from the EML.

Using these coefficients, we can calculate the dipole decay rate for the parallel and perpendicular dipoles [29]:

$$\frac{b_{\parallel}}{b_0} = 1 - q + q \left(1 + \frac{3}{4} \operatorname{Re} \left[\int_0^{\infty} d\kappa \frac{\kappa}{h_s k_s} \left(c_s + c'_s + \frac{h_s^2}{k_s^2} (f_s - f'_s) \right) \right] \right) \quad (2.19)$$

$$\frac{b_{\perp}}{b_0} = 1 - q + q \left(1 + \frac{3}{2} \operatorname{Re} \left[\int_0^{\infty} d\kappa \frac{\kappa^3}{h_s k_s^3} (f_s + f'_s) \right] \right) \quad (2.20)$$

where κ is the parallel component of the wave vector such that $k^2 = \kappa^2 + h^2 = \cos^2(\theta) + \sin^2(\theta)$, and the subscript s denotes a value in the EML.

The normalized decay rate in the cavity can be used to calculate the Purcell factor, with contributions from the parallel and perpendicular dipole scaled by θ_{hor} :

$$PF = b_{tot} = \theta_{hor} \frac{b_{\parallel}}{b_0} + (1 - \theta_{hor}) \frac{b_{\perp}}{b_0}. \quad (2.21)$$

We can also compute the power generated, P , over some unit area A by integrating the Poynting vector over the infinitesimal cross section in the xy plane, dA [29]. The surface parallel and perpendicular power generated from the corresponding components of the Poynting vector, S , in the z -direction in each layer, j , are defined as:

$$P_{\perp} = \operatorname{Re} \left(\int S_{z,j}^{\perp*} dA \right) = \frac{3q}{4} \operatorname{Re} \left[\int_0^{\infty} du \frac{u^3 (\sqrt{\varepsilon_j})^*}{|1 - u^2| \sqrt{\varepsilon_j}} \left(\frac{\varepsilon_j}{\varepsilon_s} - u^2 \right)^{1/2} (f'_j e^{ih_j z} - f_j e^{-ih_j z}) (f'_j e^{ih_j z} + f_j e^{-ih_j z})^* \right] \quad (2.22)$$

$$\begin{aligned}
P_{\parallel} = \text{Re} \left(\int S_{z,j}^* dA \right) = \\
\frac{3q}{8} \text{Re} \left[\int_0^{\infty} du \frac{u(\sqrt{\varepsilon_j})^*}{\sqrt{\varepsilon_j}} \left(\frac{\varepsilon_j}{\varepsilon_s} - u^2 \right)^{1/2} (f'_j e^{ih_j z} - f_j e^{-ih_j z}) (f'_j e^{ih_j z} + f_j e^{-ih_j z})^* + \right. \\
\left. \int_0^{\infty} du \frac{u \left(\left(\frac{\varepsilon_j}{\varepsilon_s} - u^2 \right)^{1/2} \right)^*}{|1 - u^2|} (c'_j e^{ih_j z} + c_j e^{-ih_j z}) (c'_j e^{ih_j z} - c_j e^{-ih_j z})^* \right] \quad (2.23)
\end{aligned}$$

where z is the position within the device stack and the other variables follow the same definitions provided previously in this section. The power is wavelength-dependent, since $\varepsilon(\lambda)$ for dispersive materials.

As is the case for the total normalized decay rate, the total power generated is scaled by θ_{hor} :

$$P_{tot} = \theta_{hor} P_{\parallel} + (1 - \theta_{hor}) P_{\perp} . \quad (2.24)$$

The dipole energy transfer to each mode is taken to be the fraction of Eqs. 2.22-2.23 that falls within each range of u , defined in Sec. 2.3, for $z = z_0$ where z_0 is the dipole position in the stack. We can also compute the distribution of the Poynting vector throughout the device stack by dividing the total device stack thickness, Z , into sections with thickness dZ , and solving Eqs. 2.22-2.23. The magnitude of the flux at both layer boundaries, normalized by the dipole decay rate, provides the fraction of dipole energy transfer to that layer.

For device stacks with multiple emissive layers, the coupling of emission from each EML is calculated separately (changing the layer index containing the emissive dipole). The emission spectrum for the entire stack is simulated by scaling the spectrum of the individual emitter with the wavelength-dependent outcoupling fraction and summing this with emission from the other EMLs calculated the same way. Calculations of optical coupling using this method are included in Ch. 5, 6, 7, and 8.

2.4.2 Ray Tracing

The Green's function calculations described in the previous section can be used to describe optical features with size $\sim$ nanometers, but cannot be used to account for micron-scale features or geometric features, such as microlenses. To compute the transmittance of these structures, geometric ray tracing is required. This method is modified based on the ray tracing method used in Refs. [30, 31].

Generally, the ray tracing method analyzes individual rays intersecting a boundary between two different mediums (start and exit mediums). Given the incidence angle of the ray at the boundary, the index of refraction mismatch at the boundary, and the absorption of the mediums, the ray is classified as either transmitted, reflected, or absorbed. Transmission and reflection are calculated using the Fresnel equations. The intensity of each ray decreases each time, i , it intersects an absorptive boundary (e.g. metal surface) following, $I_i = I_0 e^{-\alpha}$, where α is the absorption of the boundary. A ray is assumed to be absorbed when $I_i < 0.0001 I_0$.

In this work, we specifically use ray tracing to model a single lens in a hexagonal close-packed array of hemispherical microlenses with a radius, r , and spacing from the center of one lens to its nearest neighbor, s . We assume that the lenses are located on a planar surface of some thickness, l . In this setup, the light source (i.e. the OLED), would be located atop the planar surface. Since the geometric feature size is much large than the wavelength of light, we do not need to specify a specific emission color. The only assumptions we make about the emission source are that 1) it contains two far field planar reflective surface (an opaque and transparent metal contact) which will reflect rays with some efficiency accounting for absorption and 2) there is some angle-dependent emission profile, which we can use to scale the calculated transmission across all tested polar angles, θ . Typically, emission can be assumed to be a Lambertian profile following $\cos(\theta)$, but this can be experimentally verified by measuring the angle-dependent OLED emission (see Sec. 3.3).

First, we define a range of polar and azimuthal angles, θ and ϕ , and a block of N rays. Each ray is given an initial position (x, y, z) , orientation in spherical coordinates ($x_{sph} =$

$\sin(\theta) \cos(\phi)$, $y_{sph} = \sin(\phi) \cos(\theta)$, $z_{ph} = \cos(\theta)$), set to be on the planar side (light incident side) of the lens, and an initial normalized intensity, I_0 . At each ray location (x_n, y_n, z_n) there exist a distribution of rays through all angles θ and ϕ .

Next, we define a counter for the set of rays at a single value of θ and ϕ , which keeps track of 1) the index of the ray being traced n , 2) the number of rays yet to be traced $N - n$, and 3) whether the ray, n , is still traceable (ray was reflected) or if it is terminated (transmitted or absorbed). When a ray is terminated, the total number of rays to be traced $N = N - 1$. The tracing at the specific angles θ and ϕ is complete when $N = 0$. The trace is repeated for each combination of θ and ϕ .

When $N > n > 0$, we determine whether each ray n , is transmitted, reflected, or absorbed by tracing the path of the ray from its initial position and orientation to find its end location. The end location of the lens will fall into one of four cases: 1) the lens will hit the boundary between the start and exit mediums, 2) the ray will be transmitted the exit medium (i.e. beyond the lens boundary), 3) the ray will hit the unit cell boundary of the lens, and 4) the ray is in the spacer layer in the start medium (i.e. above the lens boundary). In each case, some fraction of the ray intensity, I , will contribute to the total transmission, reflection, or absorption, T , R , and A , respectively.

In case 1), we determine the angle of incidence upon the boundary using the geometry of the lens and the orientation of the ray. We then calculate the the transmitted, t , and reflected, r , fraction of the ray intensity I using the Fresnel equations. We update the total transmission $T = T + tI$ and set the remaining ray intensity $I = rI$. If $I < 0.0001I_0$, we terminate the ray, adjust $A = A + I$, and set $N = N - 1$.

In case 2), the entire ray is transmitted so $T = T + I$ and $N = N - 1$. In case 3), the ray intersects the unit cell wall so we update the ray position to satisfy the periodic boundary condition (e.g. ray position (x, y) is now on the opposite side of the lens $(-x, -y)$). In case 4), the ray will be reflected by the planar surfaces of the device (e.g. the opaque and transparent contacts), $R = R + I(1 - \alpha)$. We then update the ray intensity $I = \alpha I$. If $I < 0.0001I_0$, we

terminate the ray, adjust $A = A + I$, and set $N = N - 1$.

We iterate through all rays until $N = 0$, then repeat the trace for each combination of θ and ϕ . We average T , R , and A over all ϕ . For each angle θ , we calculate total T , R , and A , which are normalized such that $T + R + A = 1$. We can scale the transmission using the emission profile of the light sources to calculate a weighted value of T , R , and A over all angles. This calculation method is used in Ch. 6.

CHAPTER 3

Device Operation and Characterization

This chapter will provide a detailed description of OLED and OPV design, and discussion on how these devices are characterized and tested. In Sec. 1.2.2, we introduced a generic architecture scheme for organic optoelectronic diodes separated into the categories of top-down and bottom-up. In both cases, the electrodes and organic stack follow the same general design principle, shown in Fig. 3.1. An equivalent circuit diagram for an OLED and OPV is shown in Fig. 3.2. The components of this diagram will be discussed more in Sec. 3.2. Note that the equivalent OPV circuit includes a current generating element, that generates current opposite to the diode current. This represents the photocurrent.

Holes are injected from the low work function conductive anode into a hole injection layer (HIL) followed by a hole transport layer (HTL). The HIL works by withdrawing electrons from the HTL to the electrode (thus, generating holes) and is designed such that its LUMO aligns to the HTL HOMO. The HTL is chosen to have a high hole mobility and high LUMO to prevent electrons from entering this layer and recombining with holes. If the HTL LUMO is not sufficiently high (e.g. $>$ active layer LUMO), or if the singlet or triplet excited state energies within the HTL are close to or lower than the energy of excitons in the active layer, an additional exciton (or electron) blocking layer, the EBL can be added. Typically, EBL materials, chosen for their high LUMOs, have low hole mobility and thus are very thin $\sim 5\text{nm}$.

Next, is the active layer. In OLEDs, this layer facilitates charge recombination leading to photon emission and is called the EML. Though the first OLED utilized a neat fluorescent layer

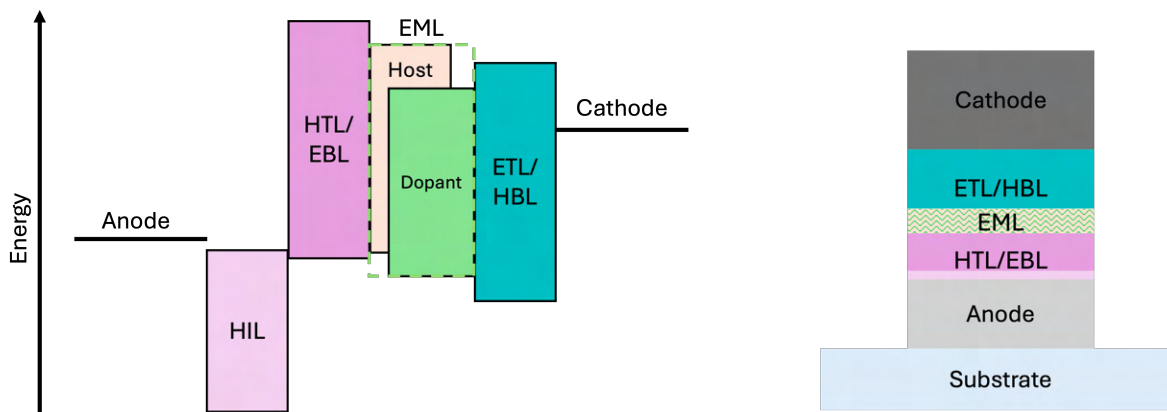


Figure 3.1: Organic material energy diagram. A schematic of the energetic profile of an organic diode with energy on the vertical axis and layer position on the horizontal axis (*left*). Shaded squares indicate the energy gap, with the top and bottom of the rectangle demarcating the LUMO and HOMO, respectively. A vertical version of the same device structure (*right*) with organic and electrode layers drawn to scale for an archetype green OLED structure. The substrate is much thicker than the organic and electrode layers.

of Alq₃, EMLs typically consist of an emitter molecule with the desired emission properties, called the dopant, mixed in a material with a wider energy gap and desirable hole and electron mobilities, called the host. There are many other designs for EMLs, including graded layers where the dopant concentration is varied across the layer, co-host systems where two host materials are chosen with each one preferentially transporting holes or electrons, and managed systems where additional non-terminal emissive molecules are included to aid in exciton transport across the EML. In OPVs, the active layer is considered to be the layers that absorb light and facilitate charge separation, consisting of the acceptor and donor material. The donor and acceptor can form a planar HJ (i.e. two adjacent neat layers) or bulk HJ (i.e. a single layer consisting of two mixed materials), see Sec. 3.1. The primary concern of the active layer is to facilitate exciton formation which requires, for OLEDs, equal distributions of holes and electrons across the EML or, for OPVs, a driving force to separate CT excitons into free charges. On the opposite side of the active layer is the electron transport layer (ETL), which serves the same purpose as the HTL, except that it transports electrons. If the excited state energy in the ETL is not higher than the energy of holes or excitons in the active layer, a hole blocking layer (HBL) should be

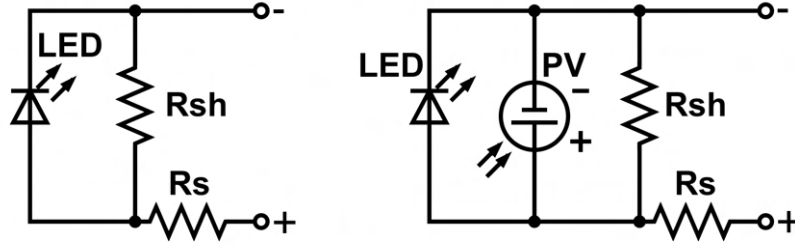


Figure 3.2: Circuit diagrams of an OLED and OPV. Circuit diagrams of an OLED (*left*) and OPV (*right*) with the internal diode (LED), current generating (PV), series resistance (R_s), shunt resistance (R_{sh}) elements. The positive and negative electrodes are labeled corresponding to forward bias operation.

included between the active layer and the ETL. The somewhat ambiguously named EBL can also be defined as an *exciton* blocking layer, which is used to prevent excitons from leaking into the transporting layers. After the ETL, an electron injecting layer (EIL) made up of a material with a low electron affinity is included to generate electrons on the electrode surface. This layer can be very thin, and doesn't need to form a uniform film - typical thickness is 1- 2nm. Finally the device is topped with the high work function cathode.

Additional buffer layers can be used to passivate the interface between metal or metal oxide materials and organic layers, tune the cavity size, or protect organics from subsequent high-energy (e.g. metal) deposition. These layers are particularly important for device reliability, as discussed in Ch. 4. Buffer layers can consist of HBL, EBL, or insulating materials. Typical buffer layer thickness is < 5 nm, such that charges can tunnel through an insulating energy barrier.

3.1 Heterojunctions

The active layer of a device typically consists of a HJ of two materials with offset energy levels. HJs can be defined by their geometry, planar or mixed, or by their energy level offset. The most simple HJ, a planar HJ, consists of two neat films deposited on top of one another. While simple, this geometry results in high density of excitons forming at a single interface. This can be detrimental for both OLED and OPV. In OLEDs, a high density of excitons can result in increased

annihilation. In OPVs, the single interface can decrease η_{diff} , η_{diss} , and η_{extr} by increasing the distance an exciton has to travel to form a CT state, as well as the distance separated charges must travel to reach the transport and contact layers. The mixed HJ, typically referred to as a bulk heterojunction (BHJ), consists of two materials mixed together. In OLEDs, a dopant molecule is typically mixed with a host material at a low ratio, $\sim 5 - 20$ vol%. This helps to spread the exciton density across a 5-25 nm thick layer. Graded doping and a mixed host, where one host preferentially transports electrons and another preferentially transports holes, can be used to further control the exciton distribution [32, 33]. In OPVs, the BHJ decreases the distance excitons must diffuse before reaching an interface where charge separation can occur [34, 35]. There is an optimal ratio of donor/acceptor material that balances the competing interests of decreasing the distance to a donor/acceptor interface and maintaining pathways of donor and acceptor material through which charge can be extracted [36, 37].

One method for characterizing the morphology of the BHJ is grazing-incidence wide-angle X-ray scattering (GIWAXS) [38]. A shallow incidence angle is used for the exciting X-ray beam to control its penetration depth in the sample. The intensity of the scattered signal is measured on a plane perpendicular to the sample. Peaks in the scattered signal occur due to interference resulting from Bragg diffraction off crystalline regions of the sample. A completely disordered sample, such as a powder, will show circular bands. The main features of the scattered signal, peak location and integrated peak intensity, provide information on the spacing between isolated crystalline regions and the degree of crystallinity of said regions, respectively. Isolated crystalline regions, or domains, are identified by the coherence length of regions that diffract coherently. Coherence length is inversely proportional to the full-width half-maximum of the peak features. GIWAXS is used in Ch. 4 to characterize the change in morphology of BHJs after aging under a simulated solar spectrum.

In most cases, the BHJ proves to be more efficient than the planar alternative. The BHJ can be further characterized by the overlap between the energy gap of two (or more) materials. In OLEDs, a host/dopant alignment is used where the singlet and/or triplet energy state of the

emitter material is at higher energy than that of the host. Host/guest alignment can also be used, where the energy of the emitter is nested within the host. In OPVs, the open-circuit voltage, V_{oc} of the device is defined by the offset of the highest energy HOMO, and lowest energy LUMO. Most often, the donor and acceptor material are chosen such that the donor LUMO and HOMO at a higher energy than the corresponding levels in the acceptor to facilitate energetically favorable dissociation of electrons across the acceptor and holes across the donor. In this case, the V_{oc} is defined by the HOMO of the donor and the LUMO of the acceptor, called the HOMO-LUMO gap ΔE_{HL} , less the exciton binding energy, see Eq. 1.4. For both types of devices, more complex BHJ architectures exist to account for specific device performance requirements. For example, ternary structure consisting of two donors and an acceptor or a donor and two acceptors have been used to achieve high efficiency OPVs [39].

3.2 J-V Characteristics and the Ideal Diode Equation

The electronic behavior of a diode is described by allowing directional current flow only after some threshold voltage is surpassed, at which point current increases exponentially with the bias voltage. In a truly ideal diode, the relationship between current and voltage is always exponential for any forward bias voltage; in reality, diodes have some threshold resulting from a small but non-zero reverse bias off current. This relationship is known as the ideal diode law [40–42]:

$$I = I_0 \left(\exp \left(\frac{qV}{kT} \right) - 1 \right) \quad (3.1)$$

where I is the device current, I_0 is the reverse bias current, q is the elementary charge, V is the bias voltage, n is the ideality factor, k is Boltzmann's constant, and T is temperature. The terms in the exponential are such that when the applied bias $\frac{qV}{kT} \leq 0$, the device current $I < 0$, approaching the reverse bias current as $-V$ increases. When $\frac{qV}{kT} > 0$, the device current $I > 0$, rectifies exponentially. At very large reverse bias ($V < 0$), the materials within the diode will breakdown at which point Eq. 3.1 no longer holds. Equation 3.1 defines a so-called “ideal” diode

which has no parasitic resistance, shunt pathways, or non-geminate recombination; in reality, these properties contribute to device performance, which is more accurately described by:

$$I = I_0 \left(\exp \left(\frac{q}{nkT} (V - IR_{series}) \right) - 1 \right) - \frac{V - IR_{series}}{R_{shunt}} \quad (3.2)$$

where n is the ideality factor, R_{series} is the series resistance, and R_{shunt} is the shunt resistance, cf. Fig. 3.2. In an ideal diode, $n = 1$ with diffusion dominating charge transport. As n increases, recombination within the gap affects charge transport. When $n = 2$, Shockley-Read-Hall recombination dominates. Larger values of n do not correspond to a known physical theory. When R_{series} is very small, and R_{shunt} is very large, these terms can be ignored.

When the diode is illuminated, the current generated by photon absorption is given by adding a term, I_{ph} , to the right hand side of Eq. 3.2. Note: I and I_0 in Eq. 3.1 can be replaced with their corresponding current densities, J and J_0 . Current density will primarily be used from this point forward as it provides a better comparison for intrinsic device performance than current, which depends on the extrinsic factor of device area. From this equation, we can extract many useful parameters for PVs. When current through the device is zero, we can solve for the open-circuit voltage, V_{oc} :

$$V_{oc} = \frac{nkT}{q} \ln \left(\frac{J_{ph}}{J_0} - 1 \right). \quad (3.3)$$

Setting $V = 0$, we can find the short-circuit current, J_{sc} :

$$J_{sc} = J_0 - J_{ph} \quad (3.4)$$

where $J_{sc} > 0$, assuming $J_{ph} < 0$. Often, the J-V characteristic is plotted such that $J_{sc} < 0$; in this case Eq. 3.4 still holds but the sign flips for all current densities.

While Eq. 3.1 - 3.4 describe many inorganic diodes well, they do not describe the behavior of organic semiconductors, whose behavior is dominated by excitons, particularly at low temperature. A set of equations of the same form should instead be used for organic diodes in particular

[43, 44], where:

$$J = J_{0,org} \left(\exp \left(\frac{qV}{nkT} \right) - \frac{k_{PPd}}{k_{PPd,eq}} \right) - q\eta_{PPd}J_{ph} \quad (3.5)$$

where q is the elementary charge, n is the ideality factor, k is Boltzmann's constant, T is temperature, k_{PPd} is the CT exciton dissociation rate, and $k_{PPd,eq}$ is the CT exciton dissociation rate with no applied bias or illumination. The subscript PP is used for consistency with the literature, where the CT exciton is referred to as a polaron pair. $J_{0,org}$ is defined as:

$$J_{0,org} = qa_0k_{rec}N_{HOMO}N_{LUMO}(1 - \eta_{PPd}) \exp \left(\frac{-\Delta E_{HL}}{kT} \right) \quad (3.6)$$

where a_0 is the CT exciton radius, k_{rec} is the CT state recombination rate, N is the density of states in the frontier orbitals, η_{PPd} is the CT exciton dissociation efficiency, and ΔE_{HL} is the HOMO-LUMO gap.

Thus, for an organic diode, Eqs. 3.3 and 3.4 become:

$$V_{oc} = \frac{nkT}{q} \ln \left(\frac{q\eta_{PPd}J_{ph}}{J_{0,org}} - \frac{k_{PPd}}{k_{PPd,eq}} \right) \quad (3.7)$$

$$J_{sc} = J_{0,org} \left(1 - \frac{k_{PPd}}{k_{PPd,eq}} \right) - q\eta_{PPd}J_{ph} \quad (3.8)$$

Since we will be reporting organic diode parameters specifically from this point forward, we will use J_0 and J_{ph} to refer to $J_{0,org}$ and $q\eta_{PPd}J_{ph}$. The differences between Eqs. 3.1 and 3.5 result, amongst other physical effects, in both J_0 and J_{ph} having a voltage dependence arising from k_{PPd} and η_{PPd} , which are dependent on the built-in voltage across the device (defined by the difference in anode and cathode work functions) and the applied bias. The implications of this will be discussed in Ch. 4.

3.2.0.1 Experimental measurement

The diode curve, or J-V characteristic, for a device is measured using a source-measuring-unit (SMU) that can either supply current or apply a voltage, while measuring the resulting voltage

difference or generated current, respectively. For organic diodes a standard J-V scan varies the bias between -2 to 2V for OPV and 0 to 12 V for OLEDs. The exact range measured depends on the device properties themselves, such as resistance, material stability, photon energy. For OLEDs, the number of photons emitted, quantified as luminance L in cd m^{-2} , is measured using a calibrated photodiode (PD) with appropriate responsivity for the OLED emission spectrum (Si for 300-900nm, InGaAs or Ge for 800-1700nm), see Sec. 3.3.3. J-V-L can be used to calculate OLED EQE, as discussed in Sec. 3.4. OLED luminance is dependent on J-V, requiring a second SMU to measure the generated photocurrent of the calibrated diode. Typically, a tool called a parameter analyzer, which integrates multiple SMUs and operates them concurrently, is used to measure J-V-L in a single voltage sweep. Voltage is typically measured from negative to positive, though a reverse sweep can be used to determine if the device has any polarity. A reverse sweep can also help to recover J-V if leakage is occurring due to metal electrode migration from the bias-induced electric field. For an OPV, J-V is measured under at least two conditions: dark and 1 sun intensity. The simulated 1 sun intensity is provided by a solar simulator lamp, typically Xe, and the intensity is adjusted before each measurement to achieve the same power density, equivalent to AM1.5G solar power $P_{AM1.5G} = 1\text{kW m}^{-2}$, as measured by a calibrated PD. The AM1.5G spectrum is defined by the American Society for Testing and Materials as a standardized solar cell testing spectrum, defined as the solar spectrum filtered by 1.5 air mass of effective atmosphere [45]. The mismatch between the solar simulator and the AM1.5G spectrum can be accounted for by a mismatch factor, M [46]:

$$M = \frac{\int \Phi_{ref} R_{ref} \int \Phi_{sim} R_{test}}{\int \Phi_{sim} R_{ref} \int \Phi_{ref} R_{test}} = \frac{J_{sc, sim}}{J_{sc, EQE}} \quad (3.9)$$

where Φ is the spectral irradiance for the reference (*ref*) source, in this case AM1.5G, and simulator source (*sim*), and R is the responsivity of a calibrated reference device (*ref*) and test device (*test*). This mismatch is equivalent to the ratio of short-circuit current density measured using the simulator lamp, $J_{sc, sim}$ over the short-circuit current density calculated by integrating

the EQE, $J_{sc, EQE}$, see 3.30. The spectrum and intensity of the solar simulator should be filtered and adjusted such that $\frac{\int \Phi_{ref} R_{ref}}{\int \Phi_{sim} R_{ref}} \rightarrow 1$ to ensure that $0.9 < M < 1.1$.

3.3 Photoluminescence and Electroluminescence

3.3.1 Photoluminescence

Photoluminescence (PL) is measured by exciting a film, device, or solution of material with a laser whose wavelength falls within the absorption spectrum of the material(s) being studied. Typically, a blue diode laser, with wavelength $\lambda = 405\text{nm}$ is used, though materials with very high energy absorption spectra, including many blue emissive materials, require a higher energy light source such as an HeCd laser, $\lambda = 335\text{nm}$. PL can include emission from the singlet or CT states, if a blend is being measured. PL is used to measure emission from the material bulk. Only singlet states can be excited via PL, though this can include emission from the CT state or triplet state, in systems with single/triplet mixing. PL can be measured using a standard $4f$ system [47] to focus the excitation beam onto the sample, with a second set of $4f$ lenses set to collect PL emission and focus it onto a fiber or the slit of a spectrometer, see Fig. 3.3. A long pass filter is used to remove the excitation beam and any harmonics at $n\lambda$. This setup can be easily adjusted to collect angle-resolved spectra, by placing the emission collection optics on a goniometer such that angles from $\sim 10 - 90^\circ$ can be swept.

PL can also be measured in an integrating sphere to collect light emitted from all angles at once, shown to the right in Fig. 3.3. The integrating sphere measurement can be used to calculate the material PLQY by accurately measuring the number of photons absorbed by the sample and the number of photons emitted by the sample:

$$\eta_{PL} = \frac{\# \text{ photons emitted}}{\# \text{ photons absorbed}} = \frac{\int I_{PL}(\lambda) - \int I_{bg}(\lambda)}{\int I_{laser}(\lambda) - \int I_{laser, bg}(\lambda)} \quad (3.10)$$

where I_{PL} is the intensity of the PL signal, I_{bg} is the integrated intensity of any background

signal generated when the laser is illuminating a blank, control substrate within the sphere, and I_{laser} and $I_{laser,bg}$ are the intensity of the laser measured after reflecting off the sample, and before reflecting off the sample. A fraction of the laser power is measured simultaneously with the emitted PL and absorbed laser power to account for any fluctuations. Additionally, N_2 is flowed in the sphere to eliminate absorption losses to air. Time-resolved PL measurements can also be used to determine PLQY through the measurement of radiative rates.

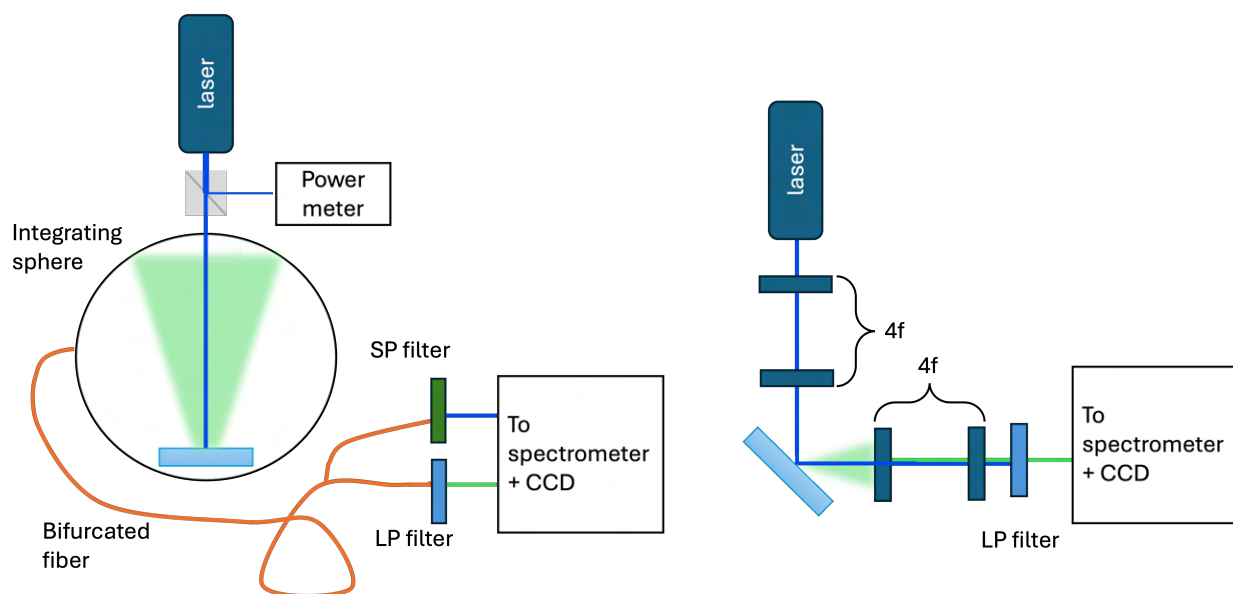


Figure 3.3: **PL measurement setups.** Diagrams of PL measurement set up for the forward viewing direction (*right*) and using an integrating sphere (*left*). The short pass (SP) and long pass (LP) filters are used to isolate the PL signal from the excitation signal.

3.3.2 Electroluminescence

EL is measured by injecting current into a device under forward bias and collecting the emitted spectrum. The emissive side of a device is aligned over a fiber, which is connected to a spectrometer. An optical setup similar to the collection side of the PL setup shown in the left panel of Fig. 3.3 can be used to measure the angle-resolved spectra. EL is most commonly measured at a constant current density ranging from $0.1 - 10 \text{ mA cm}^{-2}$ for an OLED. An EL measurement of an OPV is essentially a measurement of the OPV as an OLED, although the emission intensity

is typically much lower. Because EL results from recombination of electrically injected charges, both singlet and triplet emission can be measured. The EL spectrum is required for extracting the number of photons or photon power from measurements taken with a PD, which integrates all photons collected within some wavelength range and reports total optical power. In OPVs, CT state emission can also be measured. This will be studied in detail in Ch. 4.

3.3.3 OLED Color

The color of an OLED is determined by its outcoupled EL spectrum. Because color is primarily of interest as an observed quality, OLED color is quantified by a spectrum scaled to the photopic response of the average human eye. There are three color-perceiving cone cells in the human eye whose responsivities are quantified by the color-matching functions in Fig. 3.4. The integral of these curves convolved with the EL spectrum over all visible wavelengths yields the tristimulus values X , Y , and Z . These values can be used to calculate the color coordinates defined by the Commission Internationale de l'Éclairage (CIE):

$$x = \frac{X}{X + Y + Z} \quad (3.11)$$

$$y = \frac{Y}{X + Y + Z} \quad (3.12)$$

$$z = \frac{Z}{X + Y + Z} \quad (3.13)$$

where X , Y , and Z are computed from the convolution of the color matching functions $\bar{x}$, $\bar{y}$, and $\bar{z}$, and the radiance of some source, L_e :

$$X = \int_{380}^{780} L_e(\lambda) \bar{x}(\lambda) d\lambda \quad (3.14)$$

$$Y = \int_{380}^{780} L_e(\lambda) \bar{y}(\lambda) d\lambda \quad (3.15)$$

$$Z = \int_{380}^{780} L_e(\lambda) \bar{z}(\lambda) d\lambda. \quad (3.16)$$

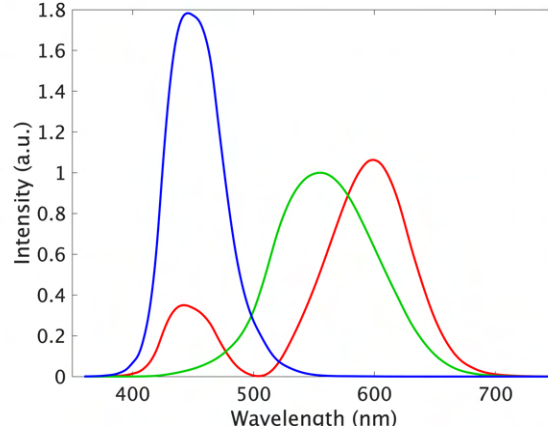


Figure 3.4: **Color matching functions of the standard observer.** Color matching functions of the three cone cells $\bar{x}$ (red), $\bar{y}$ (green), and $\bar{z}$ (blue) of the standard human observer.

The color matching function $\bar{y}$ describes the photopic response of the human eye, with the peak responsivity corresponding to 683 A W^{-1} at 555 nm. Luminance, the perceived brightness of the OLED, is calculated from the PD photocurrent, I_{PD} :

$$L = \frac{I_{PD}}{A\pi} \frac{\int 683 \phi(\lambda) \bar{y}(\lambda) d\lambda}{\int \phi(\lambda) R(\lambda) d\lambda} \quad (3.17)$$

where A is the device area, ϕ is the EL spectrum of the device, R is the PD responsivity, and the factor of π arises from the conversion of lumens to candelas, with $1 \text{ lm} = \pi \text{ cd}$ for a Lambertian emitter. The radiance of a source, L_e , does not depend on the human eye or emission profile and can be calculated following Eq. 3.17, omitting $\frac{683}{\pi} \bar{y}$. The luminous efficiency, with units of cd A^{-1} , is:

$$\eta_L = \frac{L}{I_{OLED}} A. \quad (3.18)$$

The CIE has defined several versions of the color gamut visible to the average human observer. The most commonly used gamuts are CIE 1931, CIE 1976, and CIE 1960, defined by (x, y) , (u, v) , and (u', v') respectively and shown in Fig. 3.5. The projection of one set of color coordinates onto another color gamut can be computed simply adjusting the tristimulus values

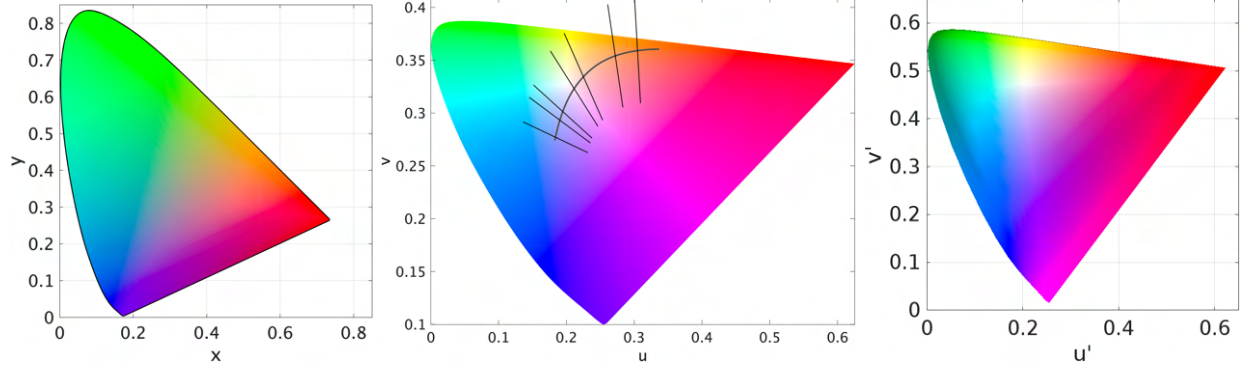


Figure 3.5: Color gamuts. CIE 1931 (*left*), 1976 (*center*), and 1960 (*right*) color gamuts. The Planckian locus is drawn on the 1960 color gamut in black, along with color isotherms from 2000 - 20000K.

[48], where:

$$U = \frac{2}{3}X \quad (3.19)$$

$$V = Y \quad (3.20)$$

$$W = -\frac{1}{2}X + \frac{3}{2}Y + \frac{1}{2}Z \quad (3.21)$$

corresponding to the color coordinates:

$$u = \frac{U}{U + V + W} \quad (3.22)$$

$$v = \frac{V}{U + V + W} \quad (3.23)$$

$$w = \frac{W}{U + V + W} \quad (3.24)$$

Similarly (u', v') can be computed from X , Y , and Z , but these coordinates are not used in this work. The three color gamuts are shown in Fig. 3.5. The 1931 color gamut is the standard for quantifying the color of emitters in display applications. Within each color gamut we can define the Planckian locus, which is given by the CIE coordinates of blackbody emitters at some temperature T . The 1960 color gamut is preferred for assessing lighting applications where the color temperature is a specification of interest because the gamut is defined such that the Planckian

locus falls perpendicular to the isothermal color lines. Though device CIE coordinates will not necessarily fall on the Planckian locus, the correlated color temperature (CCT) for a device can be given by finding the closest blackbody temperature to the device CIE [49]. The accuracy of the color temperature assignment is given by the distance from the device CIE to the Planckian locus, Δuv , given by Eq. 3.25:

$$\Delta uv = \sqrt{(u - u_{bb})^2 + (v - v_{bb})^2} \quad (3.25)$$

where (u_{bb}, v_{bb}) are the CIE coordinates of a black body whose coordinates define the locus. CCT can only be reliably reported when $\Delta uv < 0.1$. CCT is an important metric for classifying the suitability of a WOLED for lighting applications, where CCTs that are too hot (appearing blueish) or cold (appearing reddish) will distort the color of the subjects they illuminate. This effect is called color-rendering and can be quantified by the color-rendering index (CRI). The CRI is defined out of 100 and accounts for the spectral overlap between the photopic device spectrum and 9-16 standard illumination sources. A CRI > 80 is required for high-quality lighting applications, though CRI > 90 is preferred.

3.3.3.1 Photometric vs. radiometric parameters

Parameters quantifying emission from a light source can either be photometric, accounting for the responsivity of the average human eye as defined earlier in this chapter, or radiometric, accounting for photon number only. Table 3.1 serves as a reference and sorts all the emission parameters used in this work as either radiometric or photometric.

3.3.3.2 A note on OPV color

Transparent OPVs are becoming increasingly promising given recent demonstrations of stability and efficiency in NIR NFA-based devices. Applications requiring transparency also require characterization of the transparent appearance, specifically color tint and opacity. As the reciprocal of OLED characterization, this depends on the absorption spectrum of the device. Similar

to the calculations performed for OLED color, color coordinates for OPV color appearance can be calculated the same way, exchanging the emission spectrum for the absorption spectrum. Though CIE_{xy} or CIE_{uv} could be used, the related CIE_{LAB} and CIE_{LUV} coordinates account for both color appearance and opacity, by comparing X , Y , and Z , or U' , V' , and W' values to the corresponding values for a standard daytime illuminant [50].

Table 3.1: Photometric and radiometric parameters. Units are indicated in []

Radiometric	Photometric
EL and PL [counts], Radiance, L_e [W sr-m^{-2}]	Luminance, L [cd m^{-2}]
Power conversion efficiency, PCE or η_{PC} [$\frac{W}{W}$]	Luminescent power efficiency, LPE or η_{LP} [lm W^{-1}]
External Quantum Efficiency, EQE [%]	Luminous efficiency, η_L [cd A^{-2}]

3.4 Quantum Efficiency

EQE, defined previously in Eq. 2.1, can also be written in terms of easily measured parameters:

$$\eta_{EL} = \frac{\# \text{ photons extracted}}{\# \text{ electrons injected}} \quad (3.26)$$

for OLEDs, and the reciprocal Eq. 3.27:

$$\eta_{PV} = \frac{\# \text{ electrons extracted}}{\# \text{ photons incident}} \quad (3.27)$$

Equations 2.1, 3.27, and 3.26 are the general definitions of EQE for all organic diodes. η_{EL} is measured by placing the emissive side of a device in contact with a calibrated large area PD, shown in Fig. 3.6. Ideally, the PD should have an area greater than the device active area and a dark current much less than the expected device photocurrent, $I_D \leq 10^{-9} \text{ A}$.

η_{EL} is calculated by the following equation [51]:

$$\eta_{EL} = \frac{q}{hc} \frac{\int \phi_{LED}(\lambda) \lambda d\lambda}{\int R(\lambda) \phi_{LED}(\lambda) d\lambda} \frac{I_{PD}}{I_{LED}} = Q \frac{I_{PD}}{I_{LED}} \quad (3.28)$$

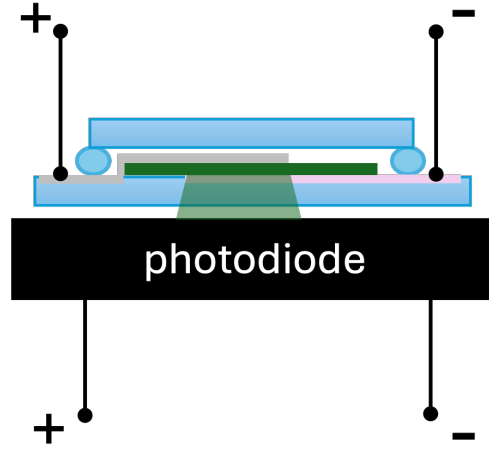


Figure 3.6: **Schematic of the LED EQE measurement setup.** The device substrate and encapsulation glass are drawn in blue. The device transparent bottom contact, organic layers, and opaque top contact are shown in pink, green, and silver, respectively. For this architecture, the opaque top contact is the device cathode (electron injecting in forward bias).

where q is the elementary charge, h is Planck's constant, c is the speed of light, R is the calibrated responsivity of the PD, ϕ_{LED} is the emission spectrum of the OLED, I_{PD} is the photocurrent generated in the photodiode, and I_{LED} is the current measured within the device. The terms aside from the measured currents are constant for the same measurement setup and EL spectrum and are sometimes referred to as the EQE factor, Q . Index matching fluid (IMF) can be used between the device and the PD to collect all substrate modes from the device, providing an upper limit to EQE that can be reached using substrate mode outcoupling structures, see Ch. 6. Additionally, EQE can be measured using an integrating sphere to account for emission from the full 4π solid angle surrounding the device. When the substrate area is much greater than the device active area, the EQE measured in the integrating sphere can underestimate the EQE due to reabsorption in the substrate. While this provides a more accurate estimate for the practical EQE for some devices (e.g. lighting sources which are expected to be housed in a reflective luminaire), it is important that use of such methods are clearly reported.

η_{PV} is measured by illuminating a small area within the device active area with monochromatic

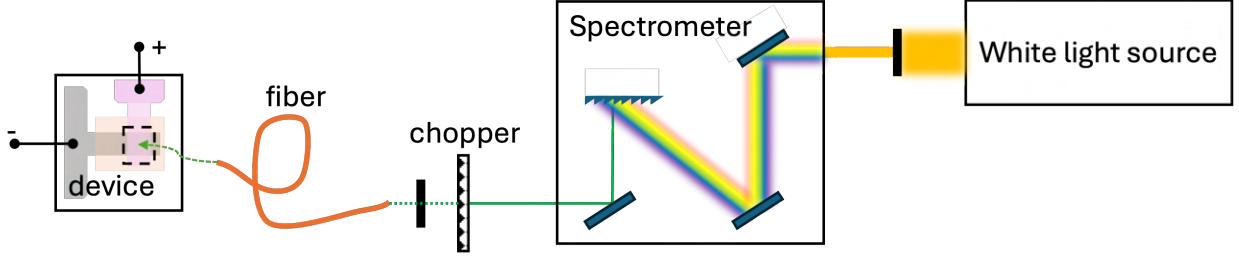


Figure 3.7: **Schematic of a PV measurement setup.** A broadband white light source is separated into monochromatic light using a spectrometer or monochromator. The light beam passes through a chopper and fiber aligned to underfill the device active area. The pulsed generated current is measured using a lock-in amplifier.

beam of light of known intensity and measuring the current generated. An example set-up is shown in Fig. 3.7. Monochromatic light is selected from a white light source using a spectrometer and then chopped so that the light incident on the device is pulsed. This generates a pulsed photocurrent signal which can be measured with a lock-in amplifier. The locked-in detection serves two purposes: 1) enables the measurements of small currents generated from an under-filled excitation beam and 2) filters out any DC light signal from parasitic sources to prevent an overestimate of η_{PV} . The EQE is calculated via the following equation:

$$\eta_{PV}(\lambda) = \frac{hc}{q\lambda} \frac{I_{ph}(\lambda)(\lambda)}{I_{PD}(\lambda)R_{PD}^{-1}(\lambda)} \quad (3.29)$$

where I_{ph} is the photocurrent generated by the OPV, I_{PD} is the photocurrent in a calibrated photodiode generated from the same monochromatic source, and R_{PD} is the calibrated responsivity of the photodiode. J_{sc} can be found by integrating the convolution of η_{PV} with the AM1.5G solar spectrum via

$$J_{sc} = \frac{q}{hc} \int_0^\infty \lambda \eta_{PV}(\lambda) \phi_{AM1.5G} d\lambda \quad (3.30)$$

where $\phi_{AM1.5G}$ is the solar flux.

3.5 Power Efficiency

Power conversion efficiency (PCE) defines the efficiency with which, for OPV operation, incident light generates electrical power or, for OLED operation, input electrical power generates emitted optical power. PCE is defined in units of W/W. Under one sun illumination and at the device maximum power point (MPP) for a solar cell:

$$\eta_{PC} = \frac{V_{oc}J_{sc}FF}{P_{inc}} \quad (3.31)$$

where P_{inc} is the incident solar power during the measurement and FF is the fill factor. $V_{oc}J_{sc}FF = P_{MPP}$ since FF is defined as:

$$FF = \frac{V_{MPP}J_{MPP}}{V_{oc}J_{sc}} \quad (3.32)$$

where V_{MPP} and J_{MPP} are the voltage and current corresponding to the maximum power point. The PCE for an OLED is:

$$\eta_{PC} = \frac{\int d\Omega d\theta \int L_e d\lambda}{V_{OLED}I_{OLED}} \quad (3.33)$$

where the numerator is integrated over wavelength, λ , and the total solid angle of emission collected (4π for all solid angles, 2π for emission in the forward viewing direction). In an OLED, it is more common to report the luminous power efficiency, in units of brightness per watt. LPE considers not only photons that escape the device but also those that are visible to the average human observer - i.e. taking into account the responsivity of the average human eye:

$$\eta_{LP} = \frac{I_{PD} \int R_{observer} \phi_{LED} d\lambda}{V_{OLED}I_{OLED} \int R_{PD} \phi_{LED} d\lambda} \quad (3.34)$$

where $R_{observer}$ is equivalent to the color matching function $\bar{y}$ and is normalized to a peak responsivity of 683 lm W⁻¹ at 555nm.

3.6 Device Reliability

Organic materials are susceptible to intrinsic degradation, from high energy charges and excitons (generated from absorption of photons or injection of charge) that can break intramolecular bonds, and extrinsic degradation from water vapor, oxygen, and heat. Standardized reliability measurements and testing conditions are essential for understanding the limitations and progress of organic device lifetime. Here, we explain the experimental setups used for OLED and OPV reliability tests in this work.

3.6.1 OPV Lifetime

The standard testing environment for intrinsic OPV reliability is under a 1 sun solar simulator. The device can be aged under the open circuit condition or at its MPP. Standard reliability tests track the change in V_{oc} , J_{sc} , FF , and η_{PC} over aging time. These parameters can be measured *in situ*, without removing the device from the aging setup since the light source aging conditions match the measurement conditions. The 1 sun simulator must be calibrated regularly with a calibrated photodiode so that any changes in lamp intensity and spectrum (i.e. lamp dimming with age) are accounted for. The typical metric for overall device reliability is the time to reach 80% of the initial PCE performance, T_{80} . OPV reliability will be discussed in Ch. 4.

In very stable systems, the aging time under one sun can be very slow. This introduces a need for high-intensity aging setups. In this work, we use high-intensity white LEDs calibrated with a photodiode and collimated to fall on the device surface. The intensity of the aging source relative to the solar spectrum, $I_{x \text{ sun}}$, is found by taking the ratio of the short-circuit current of a reference device, $i_{sc, x \text{ sun}}$, under the high intensity source, filtered by a neutral density filter to protect the device, to the 1 sun short-circuit of the same device, $i_{sc, 1 \text{ sun}}$, measured under an AM1.5G solar simulator. Thus, following the Beer-Lambert law:

$$I_{x \text{ sun}} = \frac{i_{ph, x \text{ sun}} 10^\alpha}{i_{ph, 1 \text{ sun}}} \quad (3.35)$$

where α is the absorption of the neutral density filter.

Previous empirical studies of OPV degradation have showed that an Arrhenius model with separable terms to account for thermal and irradiant degradation can provide a reasonable fit for device degradation [18, 52, 53]. Thus, to isolate intensity-related degradation, devices are cooled by cycling chilled water through a metal back plate.

3.6.2 OLED Lifetime

Unlike OPV reliability testing, which is standardized based on the AM1.5G solar spectrum, OLED reliability testing does not have standardized test conditions. The operating J-V of an OLED is determined by the desired application luminance, typically 500-3000 nits. At comparable luminance, however, individual devices may have significantly different operating currents, especially for devices deploying outcoupling structures or multi-EML stacks. In this work, we have controlled for this discrepancy by aging separate devices at the same current density for multiple test current densities, typically 0.1 and 0.2 mA cm⁻², and reporting lifetime extrapolated to the same luminance following Eq. 3.36. This method is suitable for comparing devices with similar photon energy (i.e. emission spectra). Luminance is, however, a photometric quantity and so equivalent luminances at very different The acceleration factor, ξ , is found by solving:

$$T_x(L_0) = T_x(L_{0,test}) \left(\frac{L_{0,test}}{L_0} \right)^\xi \quad (3.36)$$

where L_0 is the initial test luminance, e.g. 1000 cd m⁻², $L_{0,test}$ is the initial luminance at some other current density of interest, and T_x is the time at which the device has lost (1-x)% of its initial luminance.

The luminance decay curve can be fit with an empirical stretched exponential function [54]:

$$\frac{L(t)}{L_0} = e^{(-\frac{t}{\tau})^\beta} \quad (3.37)$$

where $L(t)$ is the luminance at some time, t , and τ and β are empirical fit parameters correspond-

ing to the characteristic decay time to T_0 and the curvature of the stretched exponential.

An OLED lifetime test setup consists of a calibrated photodiode to measure device luminance and an SMU to provide constant current injection or bias. Typically the devices are aged under constant current, supplied by a SMU, and device luminance is measured at 1-3 min intervals using a photodiode. Devices are typically aged to T_{95} or T_{70} , which correspond to the reliability metrics used in the display and lighting industries, respectively.

CHAPTER 4

Charge Transfer State Electroluminescence in Organic Photovoltaics

Developments in the field of organic electronics have led to an increase in potential applications including lighting, displays, and solar energy harvesting. OPVs are well-suited for applications underserved by conventional solar cell technologies, including those that require visibly transparent, lightweight, and flexible modules [55, 56]. The viability of OPV applications relies on both achieving high efficiency and extrapolated lifetimes of at least 10-15 yrs [57]. Efficiencies $< 17\%$ have been achieved in solution-processed NFA OPVs, while vacuum-deposited small molecule OPVs have demonstrated extrapolated intrinsic lifetimes as long as 27,000 years [18, 58–65]. Unfortunately, high efficiency and long lifetime have yet to be achieved in the same materials system and device architecture. Specifically, very high efficiency OPVs based on NFAs often have shorter operational lifetimes than analogous fullerene-based cells [66–71]. Previously, a correlation between a reduction in the V_{oc} and the charge transfer CT state EL efficiency under forward bias over the course of aging of the cell has been identified [18, 72]. In this work, we develop a semi-empirical, quantitative analysis starting from detailed balance that connects these parameters in both fullerene and NFA-based OPVs [72–75]. A voltage-loss ideality factor, m , is introduced that establishes the deviation from the thermodynamic limit while revealing the relative importance of degradation of the photoactive region and interfacial layers over time. Depending on whether the m -factor used to fit the change in V_{oc} , $\Delta V_{oc}(t)$, is greater than or equal to 1, we establish that degradation primarily occurs outside of, or within the bulk active region, respectively,

for archetype vacuum- and solution-processed devices. Further, we observe that the inclusion of a buffer layer into the solution-processed device structure decreases rate of degradation external to the HJ, which correspondingly leads to a decrease in m . This analysis is useful in pinpointing the source, and ultimately increasing the stability of high efficiency OPVs.

4.1 Relationship Between CT State EL and Device Reliability

This section was previously published, in part, as [76] C. Arneson, X. Huang, X. Huang, D. Fan, M. Gao, L. Ye, H. Ade, Y. Li, and S. R. Forrest, “Relationship between charge transfer state electroluminescence and the degradation of organic photovoltaics.” *Appl. Phys. Lett.* (2021). DOI: [10.1063/5.0037710](https://doi.org/10.1063/5.0037710)

Optoelectronic processes can be generally divided into two categories: charge injection leading to light emission and light absorption leading to charge generation. For organic diodes, OLEDs are primarily characterized by the former, while OPVs are primarily categorized by the latter. These processes are reciprocal - OLED and OPV operation are governed by the same diode equation, as discussed in Sec. 3.2. An organic diode at equilibrium thus follows the principle of detailed balance in which every instance of charge injection leading to photon emission is balanced by an instance of photon emission leading to charge generation when the device is at thermal equilibrium. From this relationship, we get the seemingly bold claim that “A great solar cell also needs to be a great LED” [77]. In this chapter, we investigate the relationship between CT state EL, that is the OPV operating as an OLED, and the reliability of the OPV.

4.1.0.1 A note on variable naming conventions

In this chapter, we operate OPVs as OLEDs and report their “OLED efficiencies”. The convention of η_{EL} and η_{CT} are chosen to avoid any ambiguity between when we are discussing the external quantum efficiency, η_{EL} , and the internal emission efficiency, η_{CT} . However, some work in the literature uses the $ELQY$ and EQE_{LED} to refer interchangeably to the external quantum

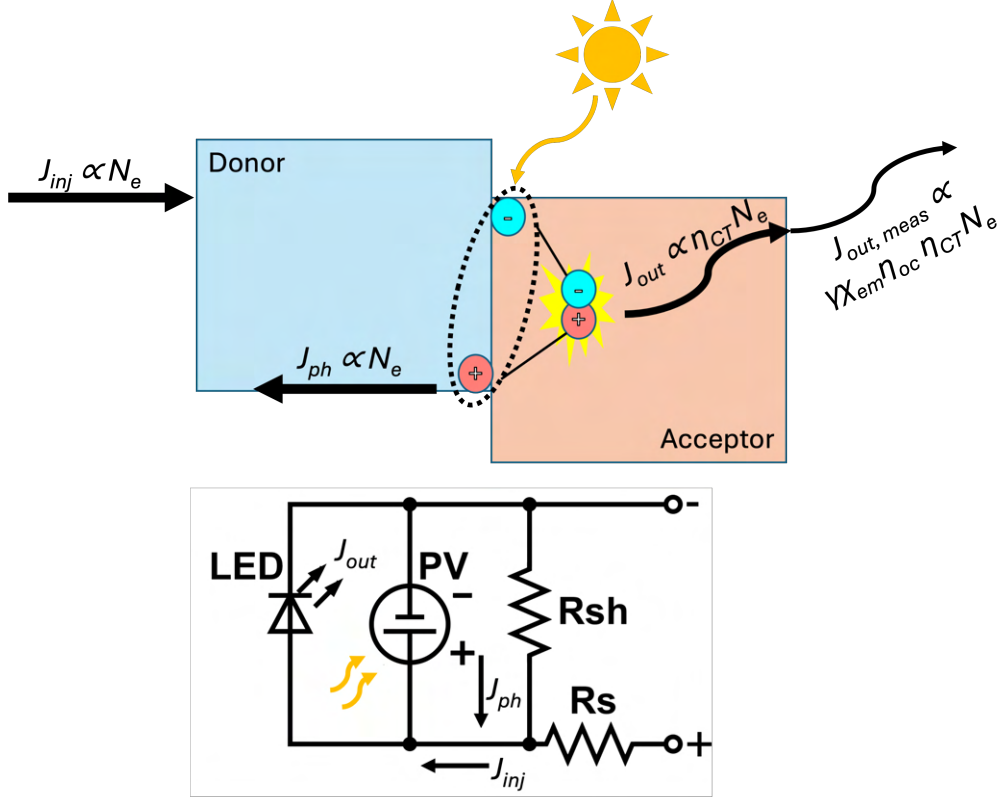


Figure 4.1: Illustration of the detailed balance condition and equivalent circuit. The shaded rectangles outline the donor and acceptor energy gaps in the detailed balance condition (*top*). N_e is the number of electrons injected, which is equivalent to the number of electrons generated by photon absorption under 1 sun. The number of photons generated in the dark with N_e injected is $\eta_{CT}N_e$. The equivalent circuit diagram (*bottom*) illustrates the same generated and injected currents.

efficiency and internal efficiency.

4.1.1 Theory

Three mechanisms that determine the magnitude of V_{oc} are: (i) radiative recombination of optically generated excited states, or excitons, within the donor or acceptor regions; (ii) radiative recombination due to CT state relaxation; and (iii) non-radiative recombination due to defect states or other diode non-idealities. This latter process may result in a voltage loss over time. To quantify these effects, the non-radiative voltage loss, ΔV_{nr} , is defined as the difference between the open-circuit voltage in the presence of only radiative processes (the radiative limit), V_{oc}^{rad} , and

the actual V_{oc} of the cell, viz. [72]:

$$\Delta V_{nr} = V_{oc}^{rad} - V_{oc} = \frac{kT}{q} \ln \left(\frac{J_{sc}}{J_0^{rad}} \right) - V_{oc} \quad (4.1)$$

Here, J_{sc} is the short circuit current density, J_0^{rad} is the dark saturation current density in the radiative limit (i.e. in the absence of non-radiative effects, it is the lower limit of the experimental value, J_0), k is the Boltzmann constant, T is the temperature, and q is the elementary charge. The theory of detailed balance requires that in equilibrium, i.e. the open circuit condition, the photocurrent is balanced by an equal and opposite injection current, resulting in a total current of zero within the device. This concept is illustrated in Fig. 4.1. Previously, detailed balance has been invoked to relate ΔV_{nr} to the forward-biased external emission efficiency [72]. Other works have, incorrectly, assumed that the external emission efficiency is equal to the EL external quantum efficiency, η_{EL} , and asserted that in the radiative limit $\eta_{EL} = 1$ [73–75, 78–83]. For an organic device where emission is dominated by the CT state, however, the current resulting from non-radiative recombination will be exactly zero when the emissive CT state efficiency, η_{CT} , is unity, which is not equivalent to $\eta_{EL} = 1$. For organics, CT state emission is confined to donor/acceptor junctions, thus η_{CT} can only account for non-radiative defect sites occurring within the active region. Rather, the measured EL efficiency is dependent on several factors, as discussed in Ch. 2, Eq. 2.3 and Sec. 3.26, Eq. 3.26.

First, the charge balance, γ , determines the efficiency of electron-hole recombination in the EML. The ratio of emissive CT states vs total excited states formed by electrical injection, χ_{em} , depends on whether the states reside in the singlet or triplet manifold. That is, if the CT states are singlets and the triplets are non-emissive, $\chi_{em} = 0.25$. Alternatively, χ_{em} may assume a value as high as 1 if the CT states are emissive triplets or a mixed state. Only a fraction of the photons generated by CT state recombination will be coupled out of the device, corresponding to $\eta_{oc} < 1$. Thus, η_{EL} must account for η_{oc} , χ_{em} , and γ when determining the magnitude of η_{CT} .

Under open-circuit conditions, the ideal diode equation for an OPV is written [43]:

$$J_0 \left(\exp \left(\frac{qV_{oc}}{nKT} \right) - \frac{k_{PPd}}{k_{PPd,eq}} \right) = -J_{ph} \quad (4.2)$$

where J_0 is the dark saturation current, n is the ideality factor (which is well-defined only for purely diffusion, $n = 1$, and mid-gap recombination, $n = 2$, currents), k_{PPd} is the polaron pair dissociation rate at V_{oc} , $k_{PPd,eq}$ is the polaron pair dissociation rate in thermal equilibrium, and J_{ph} is the photocurrent. An OPV in thermal equilibrium requires that the photocurrent due to thermal excitation is balanced by current injection, J_{inj} , leading to recombination at the CT state, $J_{out} \propto \# \text{ photons generated}$. Thus, in the dark:

$$J_{out}(V_{oc}) = J_0^{rad} \left(\exp \left(\frac{qV_{oc}}{nKT} \right) - 1 \right) \approx J_0^{rad} \left(\exp \left(\frac{qV_{oc}}{nKT} \right) \right) \quad (4.3)$$

where J_0^{rad} is the saturation current generated by excitation from a room temperature blackbody, and J_{out} is the photon current density equivalent to radiative recombination generated from the CT state. For simplicity, we assume $k_{PPd} \approx k_{PPd,eq}$ in Eq. 4.3. Returning to η_{CT} , which is defined as the number of photons emitted per electrons injected, we can write:

$$\eta_{CT} = \frac{J_{out}(V_{oc})}{J_{inj}(V_{oc})} \quad (4.4)$$

from which it follows:

$$\eta_{EL} = \frac{J_{out}(V_{oc})}{J_{inj}(V_{oc})} \gamma \chi_{em} \eta_{oc} = \frac{J_{out,meas}(V_{oc})}{J_{inj}(V_{oc})} \quad (4.5)$$

where $J_{out,meas}$ is the measured photon current density equivalent to radiative recombination generated from the CT state, i.e. $J_{out,meas} \propto \# \text{ photons collected}$. Equations 2.1, 2.3, 3.26, and 4.4 provide a physical understanding for the origin of OLED efficiency, while Eq. 4.5 is defined in terms of measurable quantities from the OPV cell operated as an OLED. In a photovoltaic

cell, the open circuit condition requires that the total current is zero. Therefore, $J_{inj}(V_{oc})$ must be balanced by an equal and opposite photocurrent, i.e. $J_{inj}(V_{oc}) = J_{ph}(V_{oc})$; an equality that allows us to relate η_{EL} to V_{oc} . For OPVs, it cannot be assumed that $J_{ph}(V_{oc}) = J_{sc}$, because J_{ph} is dependent on voltage, see Eq. 3.8. This is due to the fact that in an ideal junction, k_{PPd} is dependent on electric field at the HJ [43]. Thus,

$$J_{inj}(V_{oc}) = J_{ph}(V_{oc}) = J_{sc} - J_{\Delta} \quad (4.6)$$

where J_{Δ} accounts for the difference between $J_{ph}(V_{oc})$ and J_{sc} . Combining Eqs. 4.3, 4.5, and 4.6, and solving for V_{oc} gives the following expressions:

$$V_{oc} = V_{oc}^{rad} + \frac{kT}{q} \ln \left(\frac{J_{ph}(V_{oc})}{J_{sc}} \right) + \frac{mkT}{q} \ln(\eta_{CT}) \quad (4.7)$$

$$V_{oc} = \frac{kT}{q} \ln \left(\frac{J_{sc} - J_{\Delta}}{J_0^{rad}} \right) + \frac{mkT}{q} \ln \left(\frac{\eta_{EL}}{\gamma \chi_{em} \eta_{oc}} \right) \quad (4.8)$$

Because η_{CT} already accounts for non-radiative defect sites occurring within the HJ, we have introduced the factor, m , in Eq. 4.8 to account for nonradiative losses occurring outside the HJ. The first term of Eq. 4.7 does not include the m -factor because nonradiative losses occurring both within and external to the HJ are not present in the radiative limit, where $\eta_{CT} = 1$. The lower bound for this factor is, therefore, $m = 1$, which is defined by the ideal diode equation in the absence of traps [43]. The second term of Eq. 4.7 accounts for the voltage dependence of J_{ph} , and the third term is equivalent to ΔV_{nr} , which accounts for all nonradiative losses. Losses that occur within the HJ lead to $\eta_{CT} < 1$ and are accounted for by the calculation of V_{oc} from detailed balance. Losses that are not already contained within η_{CT} , corresponding to $m > 1$,

occur external to the HJ. Thus, the change in V_{oc} is given by:

$$\Delta V_{oc} = V_{oc}(t) - V_{oc}(0) = [V_{oc}^{rad}(t) - V_{oc}^{rad}(0)] + \frac{kT}{q} \ln \left(\frac{J_{ph}(V_{oc}, t) J_{sc}(0)}{J_{ph}(V_{oc}, 0) J_{sc}(t)} \right) + \frac{mkT}{q} \left(\ln \left(\frac{\eta_{EL}(t) \gamma(0)}{\eta_{EL}(0) \gamma(t)} \right) + \ln \left(\frac{\eta_{oc}(0) \chi_{em}(0)}{\eta_{oc}(t) \chi_{em}(t)} \right) \right) \quad (4.9)$$

where m can be found by fitting Eq. 4.9 to the observed value of ΔV_{oc} . The last term of Eq. 4.9 will be 0 if η_{oc} and χ_{em} do not change over time. Because χ_{em} arises from spin statistics of the molecule, it is not likely to change in most applications. We can assume η_{oc} for devices that exhibit color-stability over time, since η_{oc} primarily depends on layer thickness and index of refraction, see Sec. 2.4. Dipole orientation can also affect η_{oc} and in devices with a change in BHJ morphology, this may change over time. For example, in OPVs with polar acceptor materials, it has been shown that device degradation is linked to the reorganization of dipole orientation [84].

4.1.2 Methods and Experimental Set-up

Vacuum- and solution-processed devices are grown on 150 nm thick, 15 Ω /sq. ITO on glass pre-patterned anode contacts. Prior to fabrication, the substrates and cover glass slides are sonicated in the following solutions for 10 min each: tergitol:DI water (1:100), DI water, acetone (2 $\times$), isopropanol (2 $\times$). Substrates are dried with N_2 and undergo snow-cleaning on a 100°C hotplate for 30 s [14], after which they are exposed to UV-ozone for 10 min.

Vapor-deposited layers are grown via thermal evaporation in a system with a base pressure of $\sim 5 \times 10^{-7}$ Torr. Organic layers (C_{70} , DBP, and TPBi) and MoO_3 are deposited at rates ranging from 0.2 to 1.6 $\text{\AA s}^{-1}$, and the Al cathode is deposited at a maximum rate of 0.6 $\text{\AA s}^{-1}$. Patterned ITO, and the source DBP and TPBi materials were purchased from Luminescent Technology Corp. (Lumtec). C_{70} was purchased from SES Research, and MoO_3 was purchased from Sigma-Aldrich. Aluminum was purchased from Alfa Aesar. The device structure is as follows: 150 nm ITO anode/10 nm MoO_3 HIL/54 nm DBP: C_{70} 1:8 mixed BHJ/9 nm C_{70} ETL/10 nm TPBi: C_{70} EBL/3 nm TPBi cathode buffer layer/100 nm Al cathode. The device area (9 mm²)

is defined by the overlap of 3 mm wide pre-patterned ITO strips and 3 mm wide shadow mask openings used during Al deposition.

For the solution-processed devices, the control device structure is: 150 nm ITO/30 nm ZnO/80 nm PCE-10:BT-CIC mixed BHJ/10 nm MoO₃/100 nm Al. The structure with the anode buffer includes a 2 nm thick C₇₀ layer between the BHJ and MoO₃ layer. The ZnO is spin cast onto ITO/glass substrates from a sol-gel precursor solution, and thermally annealed at 160°C for 30 min in air. The PCE-10:BT-CIC (purchased from 1-Material, Inc. with a molecular weight $M_w \approx 180,000$ for PCE-10) HJ blend is dissolved in 9:1 chlorobenzene:chloroform solution with a 1:1.5 weight ratio in 16 mg mL⁻¹ and stirred overnight at 65°C before deposition via spin-coating. MoO₃ and Al are vapor-deposited using the same conditions as for the vacuum-processed devices. The 4 mm² device area is defined by the overlap of 2 mm wide pre-patterned ITO strips and 2 mm wide shadow mask openings used during Al deposition. Following fabrication, all devices are encapsulated in a N₂ glove box with H₂O < 0.1 ppm and O₂ < 0.1 ppm using a cover glass slide and ultraviolet-curing epoxy. Vacuum-deposited OPVs were aged for 75 h under high-intensity (10 to 27 suns) white LEDs, see 3.2.0.1. Note that while UV is absent in these spectral sources, it has been found that DBP:C₇₀ OPV lifetimes are insensitive to UV [18]. During aging, substrates are placed, cover glass side down, on a cooling stage held at 5°C, with the surface temperature following the trend shown in Ref. [18]. Solution-processed devices were aged under a 1 sun intensity Xe arc lamp at 55 ± 5°C. The intensity of each light source is calibrated by measuring J_{sc} illuminated in the aging setup compared to that under 1 sun intensity.

The EL and PL spectra, η_{PV} , η_{EL} , and J-V characteristics were measured in 1-15 h increments. The emission spectra were measured using a Princeton 2300i monochromator equipped with a Si CCD. For EL measurements, vacuum-processed devices are driven at 4 mA cm⁻², and solution-processed devices at 500 mA cm⁻². For PL measurements, a 325 nm He-Cd continuous wave laser is focused on the active area, and the output is coupled to the CCD via an optical fiber and monochromator, see Sec. 3.3.1. The device J-V characteristics, are measured from -2 to 2 V using a parameter analyzer (Agilent) and a Xe solar simulator (Asahi, HAL-320, JIS class

AAA). The spectral mismatch factor $M = 0.98$. The photovoltaic EQE, η_{PV} , is measured using a lock-in amplifier (Stanford Research Systems SR830), which measures photocurrent from a device that is illuminated by an underfilled monochromatic beam from a calibrated Xe arc lamp (Oriel). η_{EL} is measured using a Si photodetector under voltage bias ranging from 0 to 2 V for vacuum-processed devices, and 0 to 3 V for solution-processed devices. J_{sc} , FF , V_{oc} , and η_{PC} are calculated following the procedures detailed in Sec. 3.4. J_0^{rad} is calculated using the blackbody spectrum at 300 K [72]:

$$J_0^{rad} = q \int_0^\infty \eta_{PV} \phi_{BB}(E) dE \quad (4.10)$$

where q is the elementary charge, ϕ_{BB} is the blackbody spectrum as a function of photon energy, E . This follows from the usual definition of Planck's law as a function of frequency, ν :

$$d\phi_{BB}(\nu) = \frac{2\pi h \nu^2 d\nu}{c^2 (\exp(\frac{h\nu}{kT}) - 1)} \approx \frac{2\pi E^2}{c^2 h^3} \exp\left(\frac{-E}{kT}\right) dE \quad (4.11)$$

where h is Planck's constant, k is Boltzmann's constant, and c is the speed of light in air. The approximation $e^x - 1 \approx e^x$ holds since $kT < E$ at room temperature.

GIWAXS measurements employed 54 nm thick DBP:C₇₀ blends deposited on a Si substrate precoated with a layer of PEDOT:PSS purchased from Heraeus. Samples were aged under high-intensity white LEDs calibrated to 30 sun intensity for 10 and 100 h. GIWAXS measurements were performed at the Advanced Light Source at Lawrence Berkeley National Laboratory. Absorbance is measured using a Perkin-Elmer 1050 UV-Vis spectrometer.

4.1.3 Results

Prior to aging, the DBP:C₇₀ OPV device parameters were $FF = 55.0 \pm 0.3\%$, $J_{sc} = 11.18 \pm 0.04 \text{ mA cm}^{-2}$, $V_{oc} = 0.900 \pm 0.001 \text{ V}$, and $\eta_{PC} = 5.5 \pm 0.4\%$. Substrates aged under 10, 18, and 27 sun exhibit stable J-V characteristics for over 75 h. The η_{PC} is reduced by $3.4 \pm 0.1\%$ (relative) for the 10 sun devices, $3.9 \pm 0.2\%$ for the 18 sun devices, and $4.4 \pm 0.1\%$ for the 27 sun devices, consistent with previous results [18, 85, 86]. The stability in PCE is due, in part, to

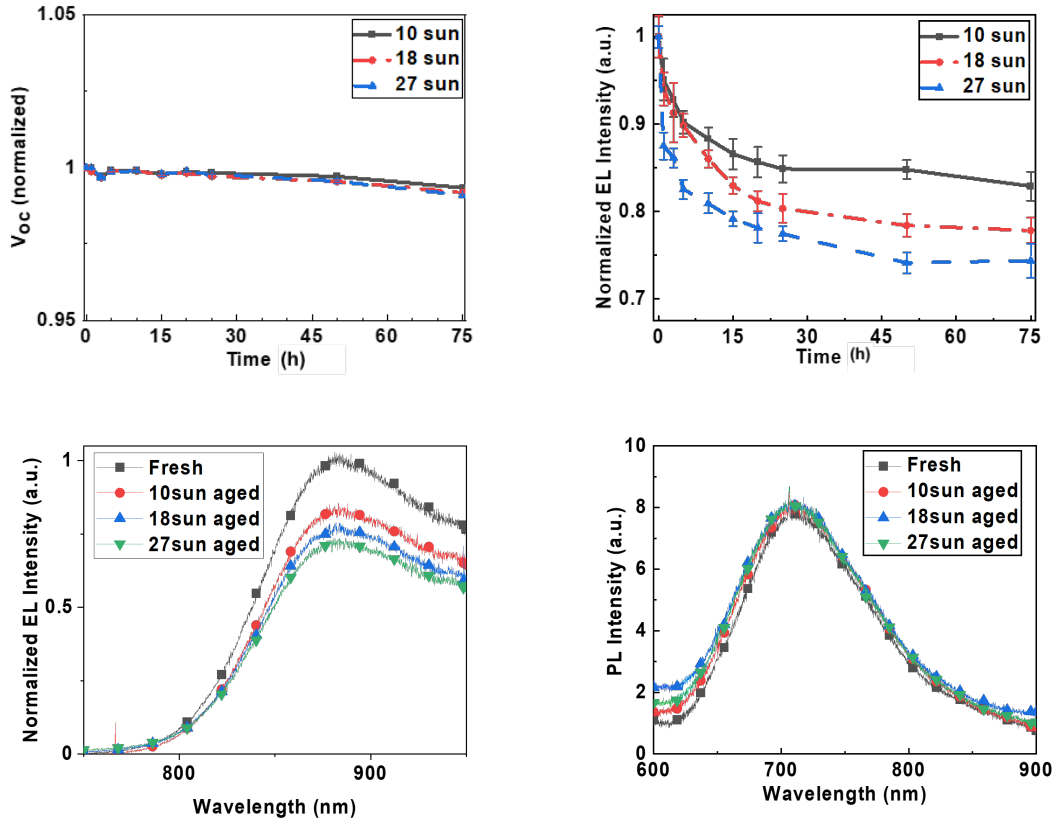


Figure 4.2: Peak EL and V_{oc} for vacuum-processed devices. Normalized (*top left*) open-circuit voltage (V_{oc}) and (*top right*) peak EL intensity over time for vacuum-processed devices aged under 10, 18, and 27 sun white illumination. Devices are encapsulated with a cover glass slide and ultraviolet curing epoxy. Error bars represent one standard deviation of measured EL for 3 devices per substrate aged under 10, 18, or 27 suns. (*bottom left*) The EL and (*bottom right*) PL spectra at 0 and 75 h of aging for vacuum-processed devices exposed to 10, 18, and 27 suns white illumination.

the very stable V_{oc} , which is shown in Fig. 4.2. After 75 h aging, V_{oc} degrades by $0.66 \pm 0.01\%$ under 10 suns, $0.80 \pm 0.04\%$ under 18 suns, and $0.82 \pm 0.02\%$ under 27 suns. In contrast, the reduction in EL intensity is $17 \pm 2\%$ for the 10 sun devices, $22 \pm 1\%$ for the 18 sun devices, and $26 \pm 2\%$ for the 27 sun devices, as shown in Fig. 4.2. The change in EL over time is consistent with η_{EL} degradation taken at $J_{inj} = J_{ph}(V_{oc})$, which indicates that the decrease in η_{EL} is due to a decrease in CT state emission, as shown in Fig. 4.2. After 75 h of aging there was no difference in the shape or magnitude of the PL spectra between fresh and 10, 18, or 27 sun-aged, as shown in Fig. 4.2. Additionally, η_{PV} does not show any change in shape over the course of aging, which

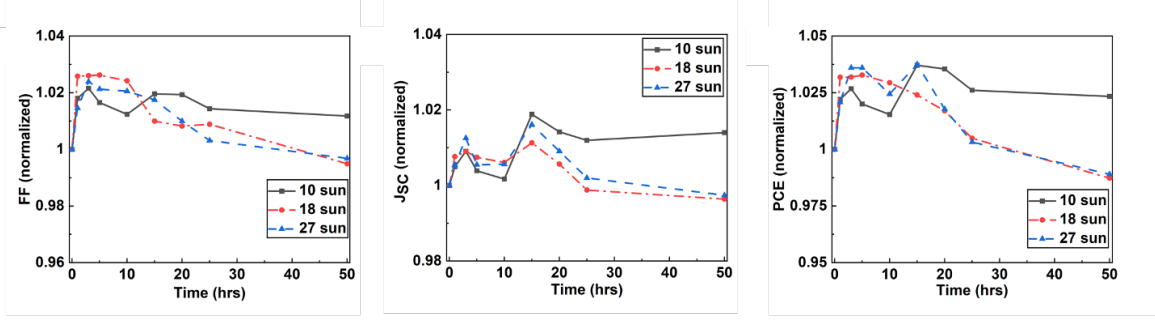


Figure 4.3: Normalized parameters for vacuum-processed devices. Normalized FF (left), J_{sc} (center), and η_{PC} (right) over time for vacuum-processed devices aged under 10, 18, and 27 sun white light illumination.

is reflected in a stable J_{sc} . After 75 h of aging, J_{sc} decreases by $0.9 \pm 0.2\%$ under 10 suns, $2.1 \pm 0.5\%$ under 18 suns, and $2.3 \pm 0.1\%$ under 27 suns. FF , J_{sc} , and η_{PC} vs. time are plotted in Fig. 4.3. Device microstructure is investigated through GIWAXS, whose 1D profiles show peaks at

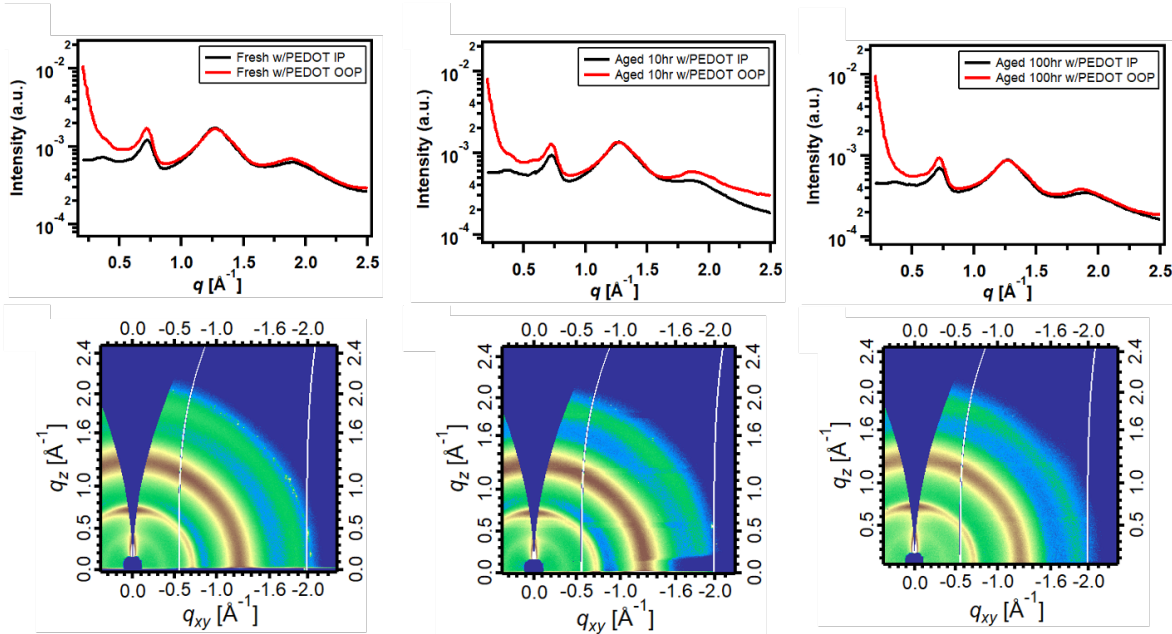


Figure 4.4: GIWAXS for fresh and aged DBP:C₇₀. 1D (top row) and 2D (bottom row) GIWAXS patterns for fresh (left column), 10 h aged (center column), and 100 h aged (right column) samples of DBP:C₇₀. Aged devices were exposed to 30 sun intensity white light.

0.71 and $1.87 \text{ \AA}^{-1}$ characteristic of C₇₀, while the peak at $1.28 \text{ \AA}^{-1}$ results from the DBP:C₇₀ blend, see Figs. 4.4 and 4.5 [38, 87]. The out-of-plane (OOP) peak location is unchanged over

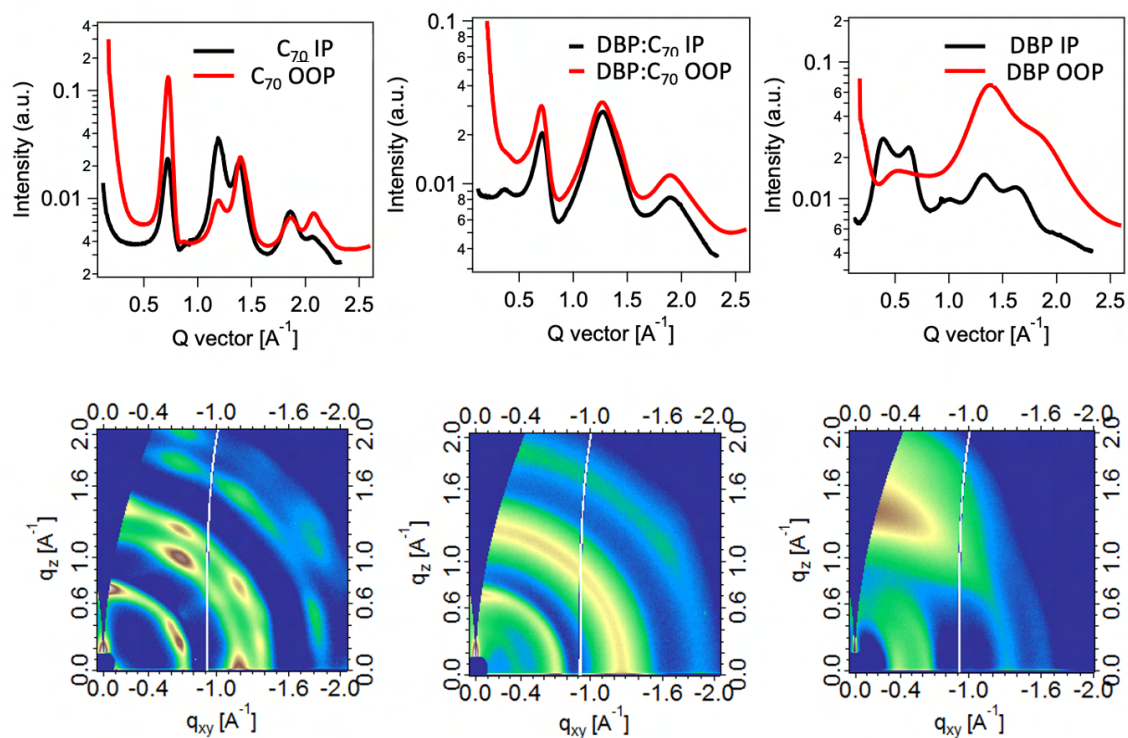


Figure 4.5: GIWAXS for fresh DBP:C₇₀, DBP, and C₇₀. 1D (*top row*) and 2D (*bottom row*) GIWAXS patterns for fresh and neat C₇₀ (*left column*), DBP:C₇₀ 1:8 (*center column*), and DBP (*right column*) films.

the course of aging, which indicates that the $\pi - \pi$ stacking distance between C₇₀ molecules, and between DBP and C₇₀ molecules, is stable.

Table 4.1: GIWAXS peak fit analysis for fresh and aged DBP:C₇₀ BHJs.

		Normalized Area			Coherence Length (Å)		
Sample		Peak 1 0.71 Å ⁻¹	Peak 2 1.28 Å ⁻¹	Peak 3 1.87 Å ⁻¹	Peak 1 0.71 Å ⁻¹	Peak 2 1.28 Å ⁻¹	Peak 3 1.87 Å ⁻¹
OOP	Fresh	1	3.8.8.8	1.81.8	56.2	18.3	11.5
	Aged 10 hr	0.65	2.9	1.4	57.6	18.5	11.0
	Aged 100 hr	0.47	1.8	0.9	57.1	18.4	10.9
I-P	Fresh	0.7	3.6	1.3	51.7	19.6	11.0
	Aged 10 hr	0.48	2.7	1	52.9	19.3	9.0
	Aged 100 hr	0.35	1.5	0.4	51.3	20.4	13.9

The structural coherence length and normalized peak area are calculated from the peak fit for OOP and in-plane (I-P) directions, with results provided in Table 4.1. During aging, the I-P and OOP diffraction peak intensities gradually decrease. In contrast to vacuum-processed devices, solution-processed devices have demonstrated performance instabilities over the short term [67–71]. Prior to aging, the measured solution-processed control device parameters were: $FF = 68.6 \pm 0.6\%$, $J_{sc} = 21.4 \pm 0.5 \text{ mA cm}^{-2}$, $V_{oc} = 0.689 \pm 0.001 \text{ V}$, and $\eta_{PC} = 10.0 \pm 0.2\%$. The initial parameters for devices with a C₇₀ buffer layer were: $FF = 65 \pm 1\%$, $J_{sc} = 21.2 \pm 0.1 \text{ mA cm}^{-2}$, $V_{oc} = 0.654 \pm 0.004 \text{ V}$, and $\eta_{PC} = 9.0 \pm 0.6\%$.

Control devices aged for 540 h under 1 sun simulated AM1.5G spectra, shown in Fig. 4.6, exhibit a decrease in η_{PC} of $66.3 \pm 0.6\%$, V_{oc} of $17.7 \pm 0.3\%$, FF of $42 \pm 1\%$, and J_{sc} of $29.9 \pm 0.4\%$, as shown in Fig. 4.6 and 4.7. This is compared with relative changes in the buffer device performance corresponding to a decrease in η_{PC} of $56.2 \pm 0.6\%$, V_{oc} of $8.7 \pm 0.3\%$, FF of $38 \pm 1\%$, and J_{sc} of $22.9 \pm 0.5\%$. The C₇₀ buffer device shows less degradation than the control, while degradation in both solution-processed systems is an order of magnitude greater than for the vacuum-processed cell aged under 10 suns, corresponding to an equivalent of approximately 750 h under 1 sun intensity. A significant decrease in the CT state EL peak intensity of $86 \pm 1\%$

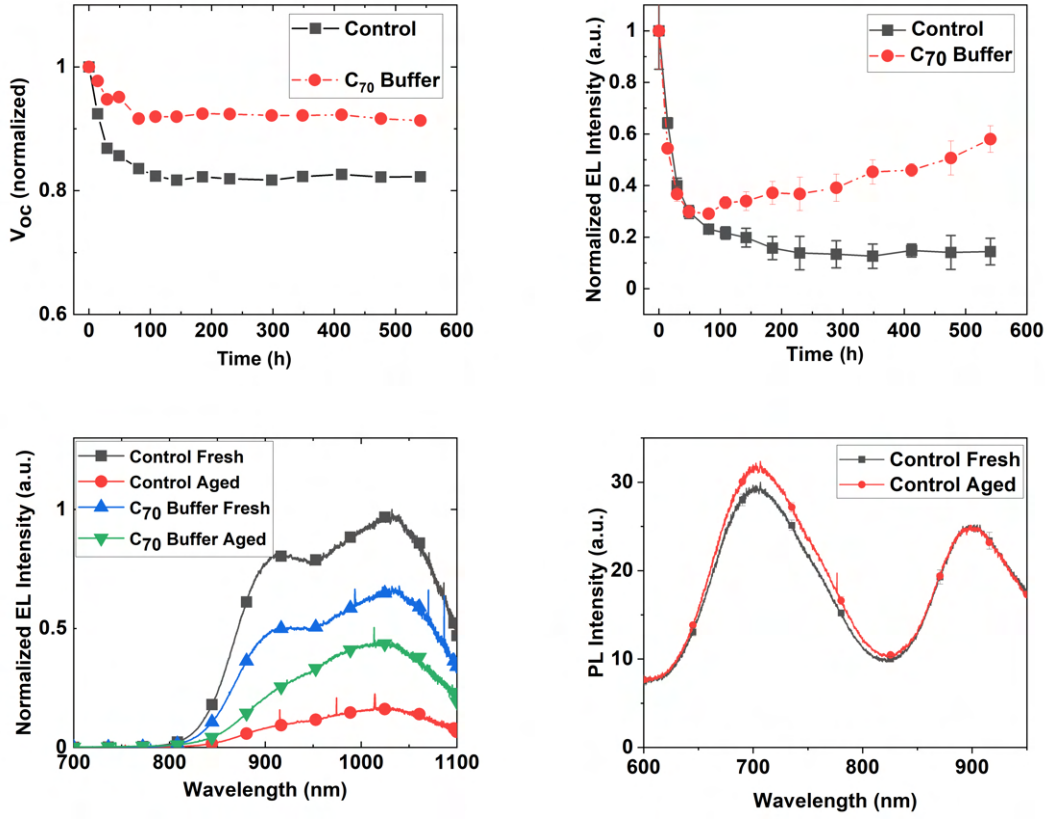


Figure 4.6: Peak EL for solution-processed devices. Normalized (*top left*) V_{oc} and (*top right*) peak EL intensity over time for encapsulated solution-processed devices aged under 1 sun, AM1.5G simulated solar illumination intensity. Devices are encapsulated with a cover glass slide and ultra-violet curing epoxy. Error bars represent one standard deviation of measured EL for 3 devices. The EL (*bottom left*) and PL (*bottom right*) spectra at 0 and 33 h of aging for solution-processed devices exposed to 1 sun, AM1.5G simulated solar illumination intensity.

and $42 \pm 5\%$ are also observed for the control and C_{70} buffer systems, respectively, see Fig. 4.6. The EL spectrum for the solution-processed cell contains both the CT state peak at a wavelength of 1025 ± 5 nm, and singlet emission peak of 915 ± 5 nm, as is shown in Fig. 4.6. Due to the low CT state emission intensity, the EL is measured at $J_{inj} = 500 \text{ mA cm}^{-2}$. The EL of the unaged device was measured at $J_{inj} = J_{ph}(V_{oc})$ and $J_{inj} = 500 \text{ mA cm}^{-2}$, and showed no dependence on injected current density. Thus, we assume that the change in η_{EL} measured at $J_{inj} = 500 \text{ mA cm}^{-2}$ is equivalent to the change in η_{EL} at the detailed balance condition, $J_{inj} = J_{ph}(V_{oc})$. The PL spectrum in Fig. 4.6 shows singlet emission peaks from the donor and acceptor materials at 700

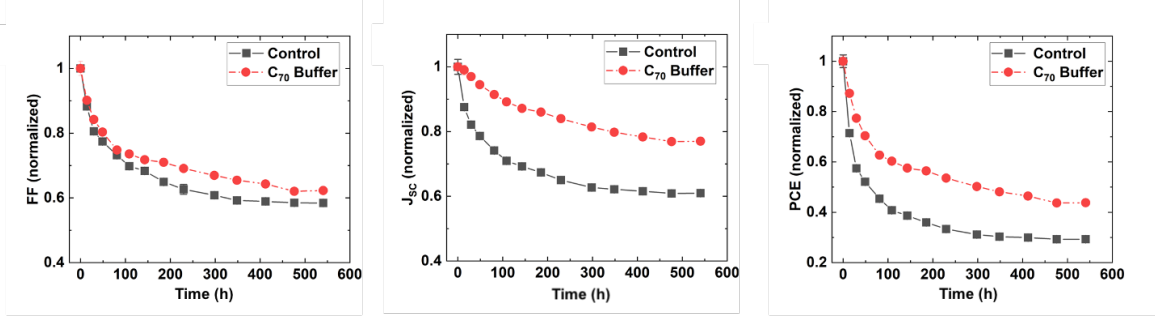


Figure 4.7: **Normalized parameters for solution-processed devices.** Normalized FF (left), J_{sc} (center), and η_{PC} (right) over time for solution-processed devices aged under 1 sun illumination without any buffer layers (control) and with a C_{70} buffer layer.

± 5 nm and from the acceptor 890 ± 5 nm. The PL intensity was measured after 33 h of aging, and shows no change, which is in contrast to the EL intensity that decreases by over 50% over a similar time span. Additionally, the absorbance of a PCE-10:BT-CIC film shows no change over 680h aging under 27 sun intensity white light, see Fig. 4.8.

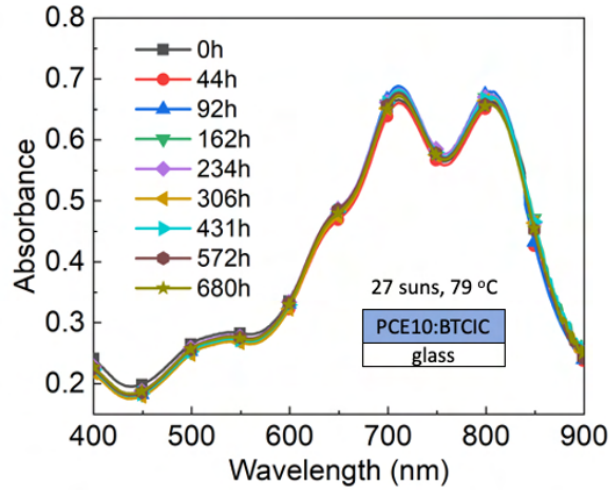


Figure 4.8: **Solution-processed BHJ absorbance.** Absorbance of a neat PCE-10:BT-CIC BHJ aged under 27 suns at 79°C .

4.1.4 Discussion

The difference between the magnitude of the changes in EL and PCE during aging can be reconciled by fitting Eq. 4.9 to the measured ΔV_{oc} to obtain m for the vacuum- and solution-processed

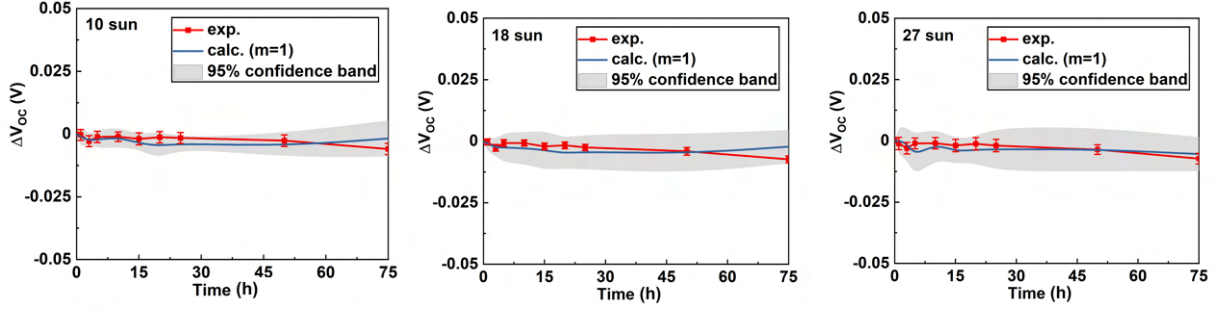


Figure 4.9: ΔV_{oc} for vacuum-processed devices. Change in V_{oc} over time for vacuum-processed devices aged under (*top*) 10 sun, (*middle*) 18 sun, and (*bottom*) 27 sun intensity white illumination. Experimental data for ΔV_{oc} are plotted alongside ΔV_{oc} calculated from Eq. 4.9 in text, with $m = 1$. Error bars represent one standard deviation of measured V_{oc} for 3 devices per substrate aged under 10, 18, or 27 suns. The 95% confidence interval for the calculated ΔV_{oc} is shown in grey.

devices. The m -factor for vacuum-processed devices aged under 10 suns, 18 suns, and 27 suns, shown in Fig. 4.9, are $m_{10} = 1.030 \pm 0.002$, $m_{18} = 1.010 \pm 0.002$, and $m_{27} = 1.010 \pm 0.003$. For solution-processed devices, the best fit is found at $m = 2.93 \pm 0.09$ for the control and $m = 1.90 \pm 0.01$ for the C₇₀ buffer device, shown in Fig. 4.10. For the vacuum-processed devices and the control solution-processed device, we assume the change in charge balance over time is negligible. This is justified since a 50% change from $\gamma(0)$ to $\gamma(t)$ results in a change in ΔV_{oc} only on the order of 50 mV, which falls within the 95% confidence interval of the fit. In the C₇₀ buffer device, however, an increase in EL is observed after a 100h burn-in period. This trend is not observed in V_{oc} , indicating that while η_{EL} increases, η_{CT} remains unchanged. Thus, since χ_{em} does not change and the absorbance and thus η_{oc} are stable over aging, we deduce that the increase in η_{EL} is due to an increase in γ . We find that the best fit corresponds to a linear increase in γ from $\gamma = 0.48$ to 0.96 after 540 h. Since charge balance is controlled by the buffer layer, this result provides direct evidence for our argument that (i) $\eta_{CT} \neq \eta_{EL}$, and (ii) $m > 1$ is due to change in regions peripheral to the BHJ.

In both vacuum- and solution-processed devices, the PL spectral shapes are unchanged over the course of aging. Because the PL spectrum is dominated by singlet rather than CT state emission, its stability indicates that the material bulk morphology is stable. In the solution-

processed system, the stability of the material bulk, along with the observation of $m > 1$, suggest that the primary source of degradation is located outside the boundaries of the active region, i.e. at the interfaces with the buffer layers, within the buffers themselves, or at the contacts. This is confirmed by the absorbance data, which shows no change over the course of aging under white light. In contrast to the control device, we observe that the inclusion of the C_{70} buffer layer improves device lifetime. The decrease in m relative to the control system indicates increased stability is afforded by the buffer layer. The degradation of V_{oc} in the vacuum-processed system is, conversely, characterized by $m = 1$, suggesting that degradation is confined to the active region. The GIWAXS data indicate that the structural coherence length of the BHJ is stable over the course of aging, suggesting that morphological changes in the active region bulk are not the cause of increased non-radiative recombination. Similarly, charge transport within the active

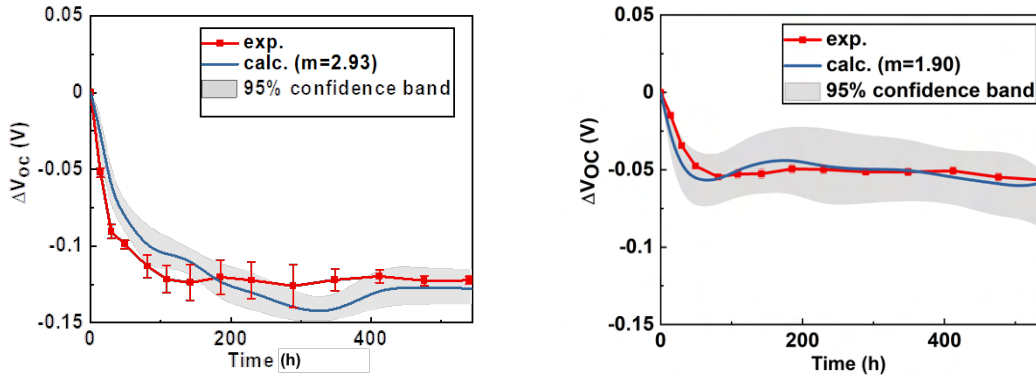


Figure 4.10: ΔV_{oc} for solution-processed devices. Change in V_{oc} over time for control (*left*) and C_{70} buffer (*right*) solution-processed devices aged under 1 sun intensity, AM1.5G simulated illumination. Experimental data for ΔV_{oc} are plotted alongside ΔV_{oc} calculated from Eq. 4.9 in text, with $m = 2.93$ and $m = 1.90$ in the left and right, respectively. Error bars represent one standard deviation of measured V_{oc} for three devices. The 95% confidence interval for the calculated ΔV_{oc} is shown in gray.

region is also unaffected by changes in morphology over the course of aging [88]. The stability of the bulk C_{70} morphology is further supported through calculation of the CT state energy (E_{CT}) [89]. Here, E_{CT} is taken to be the 0-0 crossing point of the η_{PV} normalized to the lowest energy absorption peak, and the EL spectra normalized to the highest energy emission peak. This yields

$E_{CT} = 1.56$ eV, which remains constant over time. A significant morphology change occurring in the bulk would result in a decrease in E_{CT} due to an increasing rate of inverse Marcus transfer [74, 90]. These observations are in agreement with previous experiments on DBP:C₇₀ blends, which also feature stable device performance and active area morphologies [91]. The decrease in I-P and OOP diffraction peak intensities indicates that the crystalline volume within isolated C₇₀ or DBP domains decreases over the course of aging. Because DBP concentration is only 12% that of C₇₀, the observed changes result from decreased C₇₀ crystallinity; i.e. the DBP may diffuse into, and disrupt the C₇₀ domains. This, in turn, can decrease radiative CT state recombination. In summary, the lack of changes in exciton absorption and PL, coupled with the absence of morphological changes supports the hypothesis that $m = 1$ indicates a lack of non-radiative defect sites within the active region.

4.2 Conclusions and Further Advances

In this study, we have presented an empirical method for quantitatively associating the change in open circuit voltage and the change in CT emission efficiency in organic photovoltaic cells. We introduce a quantity, the m -factor, that arises due to deviations of the V_{oc} from its radiative, or thermodynamic limit. We have used this analysis to explore voltage losses in both solution- and vacuum-processed OPVs, and relate these losses to the changes in CT state emission during extended device operation. Furthermore, we relate CT state emission to the observable external luminescence efficiency, η_{EL} , as a means to determine the impact of non-radiative recombination. We find that $m = 1$ corresponds to degradation within the device active region, whereas $m > 1$ indicates that the primary source of aging is either at the BHJ interfaces, or in the regions peripheral to the active region.

By elucidating that device degradation in efficient, archetype PCE-10:BT-CIC OPVs occurs primarily at the interfaces, Li, et al. were able to integrate an additional interface buffer on the cathode side of the device made of IC-SAM. Devices with both cathode and anode buffers

have demonstrated an extrapolated intrinsic lifetime of $T_{80} > 56,000$ h [17]. Additional studies have shown that this reliability persists in semi-transparent and outdoor applications, further demonstrating the usefulness of OPV technology in commercial applications [52, 92]. This result has also been used to understand OPV degradation under exposure to proton radiation, an initial test necessary for determining the suitability of organics in outerspace applications [93].

Contributions: Claire E. Arneson (C.E.A.) and Xiaheng Huang (X.H.H.) designed experimental protocols. C.E.A. and Xinjing Huang (X.J.H.) fabricated all vacuum-processed samples. X.H.H. fabricated solution-processed samples. X.J.H. and X.H.H. performed the device characterization. C.E.A., X.J.H., X.H.H., Deiju Fan, and Stephen R. Forrest (S.R.F.) analyzed the data and developed the theory. Yongxi Li fabricated samples for absorbance measurements and neat film samples for GIWAXS. Mengyuan Gao, Long Ye, and Harald Ade performed GIWAXS measurements.

CHAPTER 5

Waveguided Mode Outcoupling in Deep-Stacked OLEDs

Waveguided modes, as discussed in 2.3.1, account for the majority of photon trapping in devices where the emissive layer is very far from either metal electrode (i.e. very low coupling to plasmonic modes). This is a particular issue in so-called deep-stacked OLEDs, which deploy multiple emissive layers and very thick organic layers on the order of microns. Deep-stacked OLEDs are common in industry applications, particularly for WOLEDs, where the stacking of multiple emissive layers achieves high efficiency and allows for color quality to be tuned to match desired specifications. In this chapter, we will discuss existing strategies for outcoupling waveguided modes. Then, we will discuss the application of one of these technologies, the subelectrode microlens array (SEMLA), to deep-stacked WOLEDs on thin glass substrates.

5.1 Waveguided Mode Outcoupling Designs

Waveguided mode outcoupling schemes work primarily by adjusting the angle of photon emission as it exits the high index organic layers of the stack. The most successful waveguide outcoupling architectures are summarized in Table 5.1. Some of these methods, including random nanostructures and 2D gratings, rely on imparting a vertical pattern throughout the organic stack. While effective in scattering waveguided modes, the texture throughout the organic stack introduces potential avenues for degradation or decreased yield of the organic stack. Other structures, such

as the diffuse scatterer and sub-anode grid are designed with scattering features embedded in a substrate or polymer such that OLED growth on top of these structures is planar. As such, these designs are only compatible with devices that using the bottom substrate as a scatterer and emit light from the top surface (i.e. top-down architecture). Both the 2D grating and scattering grid include periodic features of wavelength-scale size, which can lead to wavelength-dependent outcoupling.

Outcoupling can be improved through material design, in addition to modifications of the device geometry. The dipole orientation of the emissive molecule also plays a role in the fraction of light coupled to waveguided modes. As the horizontal dipole fraction increases, coupling into waveguide and SPP modes decreases and into air modes naturally increases [32, 94]. Some work has been done to demonstrate ways of controlling the dipole orientation within the EML, but so far this strategy is only applicable to a limited selection of materials and, thus, is impractical at this time [95]. Waveguided modes are only supported when $n_{EML} > n_{sub}$, so another method for outcoupling waveguided modes is to design lower index EML materials with $n \sim 1.5$. Emissive materials doped in PDMS have achieved $n = 1.48$ for optical applications, but such schemes are not suitable for optoelectronic applications requiring specific electrical properties in addition to optical properties [96]. Lowering the index of the transporting layers has been used to improve outcoupling efficiency as well [97, 98]. Waveguided modes can also be suppressed by modifying the cavity length so that only SPP and substrate modes are supported [99]. This technique has limited usefulness in commercial device stacks requiring multiple emissive layers in order to achieve color, efficiency, and lifetime specifications. The outcoupling of SPP modes is, in some ways, more difficult than outcoupling waveguided modes. This will be discussed in Ch. 7.

5.1.1 Sub-Electrode Microlens Arrays

The SEMLA offers a solution for waveguided mode outcoupling that is both external to the organic stack and wavelength-independent. The SEMLA, designed by [Qu, et al.] improves upon an earlier outcoupling scheme, called the built-up light extraction substrate, which includes

Table 5.1: Summary of waveguide (WG) mode outcoupling schemes.

Extraction Method	Extracted Modes	Enhancement Factor	Ref.
Random Nanostructures	WG and SPP	2.4	[100]
Sub-electrode Microlens Array	WG	1.7	[31]
Diffuse Reflector	WG	2.5	[30]
Scattering Grid	WG	1.5	[101]
2D Grating	WG and SPP	1.48	[102]



Figure 5.1: **Illustration of SEMLA substrate preparation.** Planar glass is coated with photoresist and patterned to allow selective wet-etching of a hexagonal close-packed array of hemispheres. A PML is then coated to planarize the etched surface prior to device growth.

a high index microlens array (MLA) substrate placed atop a standard glass substrate [103]. The high index MLA works to outcouple waveguided modes, while the planar glass slab beneath extracts light from the MLA. This design introduces air gaps between the MLA and the glass slab, decreasing the extraction efficiency. In the SEMLA, the MLA pattern is etched directly into glass and planarized with a high index polymer matching layer (PML) to fully extract waveguided modes, see Fig. 5.1 [31]. This method has achieved green phosphorescent (PHOLED) efficiencies up to 47% using a SEMLA with an external MLA corresponding to a $1.7\times$ enhancement in EQE. The SEMLA achieves this with minimal impact on the OLED light quality: there is no wavelength dependence, the Lambertian emission profile is maintained, and there is minimal image blurring. As such, the SEMLA is a promising technology for achieving high efficiency lighting-quality light. In Sec. 5.2, we will analyze the use of SEMLA in a deep-stacked WOLED.

5.2 High Efficiency, Deep-stacked WOLED Utilizing SEMLA

In collaboration with an OLED lighting manufacturer, OLEDWorks, we expand upon the initial characterization of SEMLA (see Ref. [31]) by studying the stability of SEMLA substrates and characterizing their efficiency in commercial-quality WOLED stacks. We investigate the effectiveness of waveguided mode outcoupling in a deep-stacked WOLED consisting of four separated phosphorescent EMLs. We find that $\sim 80\%$ of waveguided modes are coupled into substrate modes in both a single EML green PHOLED and a deep-stacked WOLED, with a calculated maximum EQE, $\eta_{EL} = 333\%$ for the WOLED. Experimentally, with the use of an external MLA, we achieve $\eta_{EL} = 161\%$, corresponding to a SEMLA efficiency of $\sim 80\%$ and an MLA outcoupling efficiency of $\sim 60\%$. Because SPP modes are significantly suppressed in the deep stack, substrate mode outcoupling is the main limiting factor to achieving the calculated maximum EQE.

5.2.1 Methods and Experimental Design

Willow[®] glass substrates pre-cut into 2.5” squares measuring 0.2mm thick are cleaned in piranha solution for 20 min to remove organic residue. Substrates are then sonicated in DI water, acetone, and isopropanol. Next, HMDS is deposited in a vapor prime oven (YES-310TA) to increase the hydrophobicity of the glass surface. This aids in adhesion between the substrate and photoresist. A $0.97\mu\text{m}$ thick layer of SPR 955 photoresist is spin-coated onto the glass at a rate of 2880 kRPM for 45 s (CEE 200x). Thin glass squares are supported during spin coating by a 2” diameter chuck. Substrates are baked for 90s on a 90°C hotplate to evaporate solvent that is present in the photoresist. Next, samples are exposed for 0.43s via projection exposure (GCA AS200 AutoStep). The exposed pattern is a hexagonal array of $1.7\mu\text{m}$ circles with $10\mu\text{m}$ spacing. Following exposure, samples are baked for 90s on a 110°C hotplate. Next, the photoresist is developed by spin coating AZ 726 developer onto the substrate two times, puddling for 25 s each time, followed by a rinse in DI water (CEE Developer). Substrates are then baked at 115°C

for 40 minutes immediately prior to wet etching for 60 mins. in a mixture of Triton X-100:DI water:BHF 1:75:437 mL. Following the wet etch, substrates are diced into 1 in. squares using a dicing saw and resin blade (ADT 7100, 00777-1030-008). Then, substrates are sonicated in DI water, acetone, and isopropanol to remove debris from dicing and any remaining photoresist. A microscope image of etched SEMLA glass is shown in Fig. 5.2. Substrates then undergo the first RCA cleaning step for 20 minutes, see Sec. 1.2.2. Next, NOA-170 is spin coated onto the etched side of 1" squares at 7000 RPM for 30 s, and cured using pulsed UV light until hard, for two intervals of 300s (XENON Corp.).

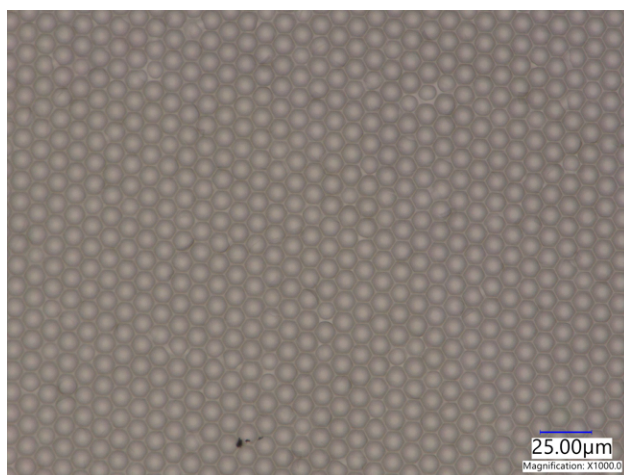


Figure 5.2: **Image of SEMLA.** Microscope image of an etched glass SEMLA prior to planarization

Green PHOLED: ITO is deposited 70nm thick at $0.1\text{-}0.2 \text{ \AA s}^{-1}$ via RF magnetron sputtering using an ITO target and Ar plasma at 15-20 W at 2mTorr. Immediately before depositing organics, the substrates are baked at 150°C for 15 mins in an N_2 environment, and ramped down to room temperature slowly to prevent cracking. A green OLED stack consisting of 5nm HATCN/ 40nm NPD/ 5nm Tris-Pcz/ 25 nm 8% Ir(ppy)₃:mCBP/ 60nm BPyTP2/ 1.5nm Liq/ 100nm Al was deposited via VTE. The device active area is 2mm². All control and NOA-170 coated substrates were encapsulated using a 1.2cm×1.2cm cover glass slide and UV curing epoxy (OG-159, EPO-TEK).

Deep-stacked white PHOLED: The devices structure fabricated at OLEDWorks consists of: (1)

140nm ITO anode/(2) 10nm HIL/(3) 60nm HTL/(4) 10nm EBL/(5) 20nm phosphorescent red/green (R/G) EML/(6) 42nm HBL/(7) 7nm ETL/(8) 10nm HIL/(9) 56nm HTL/(10) 10nm EBL/(11) 20nm phosphorescent R/G EML/(12) 22nm HBL/(13) 7nm ETL/(14) 10nm HIL/(15) 24nm HTL/(16) 5nm EBL/(17) 15nm phosphorescent blue (B) EML/(18) 15nm phosphorescent green (G) EML/(19) 5nm HBL/(20) 12nm ETL/(21) 10nm HIL/(22) 25nm HTL/(23) 10nm EBL/(24) 20nm phosphorescent RG EML/(25) 57nm HBL/(26) 8nm ETL/(27) 140nm Ag cathode. Layer numbers are included for reference. This contains four separate EMLs, each separated by a charge generation layer (CGL) consisting of the HBL/ETL/HIL/EBL. This means the maximum possible EQE, assuming there is no electrical loss, is 400% for the stack. The device active area is 2cm^2 . A standard OLEDWorks MLA is used to outcouple substrate modes. Indices of refraction for each layer were provided by OLEDWorks. Devices were characterized using a PR655 spectrophotometer by OLEDWorks.

Optical simulations: Calculations of emission spectra, power distribution, and EQE are performed using Green's function analysis. For the green PHOLED, we calculate the mode coupling at $\lambda = 540\text{nm}$ assuming the ratio of horizontal dipoles $\theta_{hor} = 0.77$. For the WOLED, we estimate the emission spectra from the RG, B, and G EMLs by fitting the measured EL with a set of Gaussians and extracting three separate spectra, shown in Fig. 5.3. We assume an isotropic distribution of dipole orientation, $\theta_{hor} = 0.67$, for all EMLs. We calculate the mode coupling for $\lambda = 430 - 775\text{nm}$. The dipole distribution in the device is calculated at $\lambda = 475$ and 600nm . Full details of the optical calculations are available in Sec. 2.4.

5.2.2 Results

The performance of a standard green PHOLED on thin glass SEMLA achieves $\eta_{EL} = 24.5\%$, a $1.3\times$ enhancement over the control, $\eta_{EL} = 19.4\%$ with no external enhancement layers. With IMF, the control achieves $\eta_{EL} = 39.8\%$ and SEMLA reaches $\eta_{EL} = 44.8\%$. The green device efficiency data is summarized in Table 5.2 and plotted in Fig. 5.5.

The reliability of the green PHOLED on control and SEMLA substrates is tested by aging

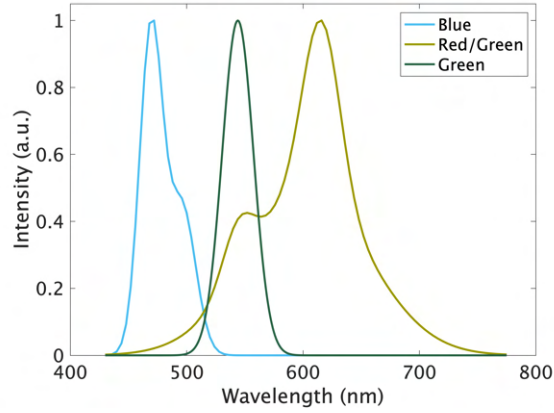


Figure 5.3: **Estimated emission spectra for individual EMLs.** Estimated emission spectra for individual blue, green, and red/green emitters extracted from the measured WOLED spectrum using Gaussian fits.

Table 5.2: Green PHOLED efficiencies with and without SEMLA.

	η_{LP} (lm W ⁻¹)	η_{EL} (%) Measured	η_{EL} (%) Simulated	Measured En- hancement
Control	36.2	19.4	20	–
Control + IMF	82.4	39.8	40	2.05
SEMLA	48.9	24.5	20	1.3
SEMLA + IMF	98.4	44.8	57	2.3

the devices continuously at constant current. The control device is aged at $J = 6\text{mA cm}^{-2}$, corresponding to an initial luminance $L_0 = 4200\text{cd m}^{-2}$. The SEMLA is aged at a slightly lower current, $J = 5\text{mA cm}^{-2}$ to achieve a similar brightness, $L_0 = 4500\text{cd m}^{-2}$. The luminance decay vs. time is shown in Fig. 5.6. The devices reach 80% of their initial luminance at $T_{80} = 6.2\text{h}$ and 10.1h for control and SEMLA substrates, respectively. Assuming an acceleration factor of 1.7, this corresponds to $T_{80} = 71\text{h}$ and 130h using Eq. 3.36 to scale the initial luminance to $L_0 = 1000\text{ cd m}^{-2}$.

The deep-stacked WOLED devices demonstrate $\eta_{EL} = 84.4\%$ and 85.5% and $\text{CRI} = 82.7$ and 85.5 for control and SEMLA substrates, respectively, at 3000 cd m^{-2} without any external enhancement layers (EELs). The full device parameters at 3000 cd m^{-2} are shown in Table 5.3. With an external MLA, the control substrate shows a $1.54\times$ enhancement while the SEMLA

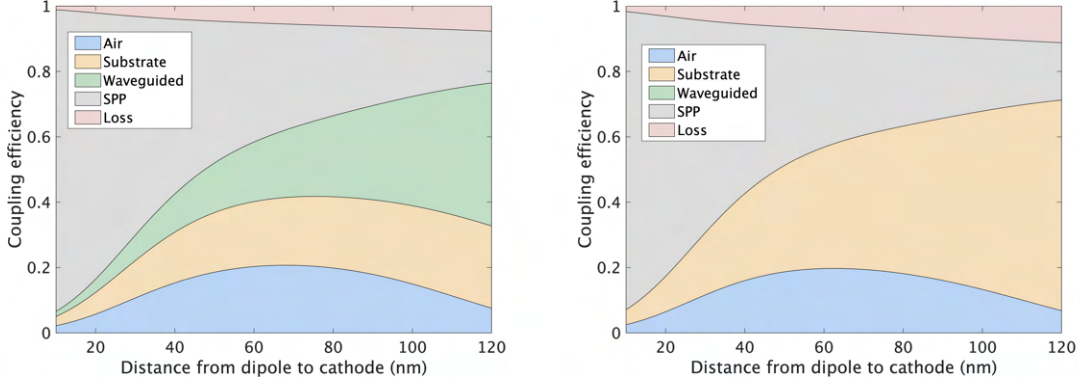


Figure 5.4: **Optical mode coupling for a green PHOLED.** Optical mode coupling for a green PHOLED with (*right*) and without (*left*) SEMLA as a function of the ETL thickness (i.e. distance from the EML to the metal cathode) at 540nm for a horizontal dipole fraction of 0.77.

improves by $1.91\times$, achieving $\eta_{EL} = 130\%$ and 161% , respectively. The device efficiencies and enhancements are summarized in Table 5.4, alongside the calculated EQE values. The measured and simulated EL spectra for the SEMLA substrate with and without an external MLA are shown in Fig. 5.7.

Table 5.3: Deep-stacked WOLED device parameters.

	V (V)	J (mA cm ⁻²)	η_L (cd A ⁻¹)	η_{LP} (lm W ⁻¹)	η_{EL} (%)	CIE (x,y)	CRI	CCT (K)
Control	10.9	–	179	51	84	(0.48, 0.40)	83	2348
Control + MLA	10.8	–	305	112	130	(0.46, 0.45)	82	2954
SEMLA	10.9	1.6	185	53	86	(0.48, 0.40)	86	2413
SEMLA + MLA	10.6	0.8	377	89	161	(0.46, 0.45)	82	3026

5.2.3 Discussion

The theoretical limit of light that can be extracted by the SEMLA is measured using IMF, which will outcouple 100% of substrate modes. In the SEMLA device, where the SEMLA couples up to 100% of waveguided light into the substrate, the IMF will also extract these modes. We can verify the efficiency of the SEMLA by comparing the IMF results to the simulated outcoupling

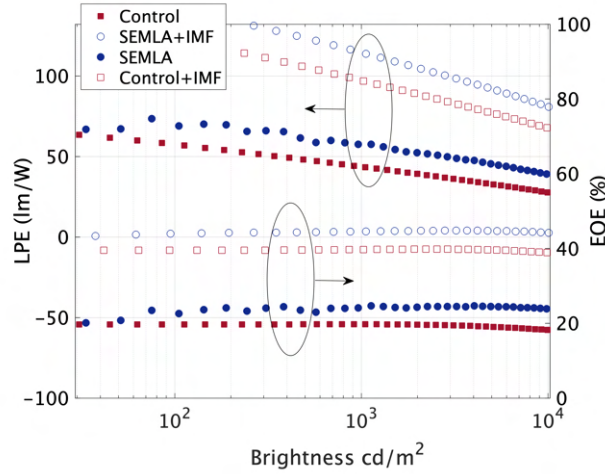


Figure 5.5: **Green PHOLED efficiencies.** External quantum efficiency and luminous power efficiency for a green PHOLED on control and SEMLA substrates.

Table 5.4: Measured and calculated WOLED EQE and enhancement.

	η_{EL} (%) Measured, 3000 nits	η_{EL} (%) Simulated	Measured Enhancement
Control	84.4	83	–
Control + MLA	130	190	1.54
SEMLA	85.5	82	1.01
SEMLA + MLA	161	333	1.91

efficiencies of the green control and SEMLA devices, see Fig. 5.4. For the control and control with IMF, the calculations agree within a percent, see Table 5.2. For the SEMLA device, we simulate a maximum $\eta_{EL} = 57\%$ assuming all substrate modes are outcoupled. This suggests that $\sim 80\%$ of the waveguided modes are coupled into the SEMLA. In the deep-stacked WOLED, the MLA couples out 46% of the simulated EQE. We assume that the SEMLA efficiency in the WOLED is consistent with the simple green PHOLED. Thus, we estimate that the MLA is only outcoupling $\sim 60\%$ of substrate mode photons, which is consistent with the control device reaching 56% of the simulated EQE. These results indicate that the efficiency of the external MLA remains a limiting factor in realizing high outcoupling efficiency. In the next chapter, we will discuss these limitations and present a pathway for improving MLA performance.

One of the main attributes of the SEMLA is its position within the device stack - external to

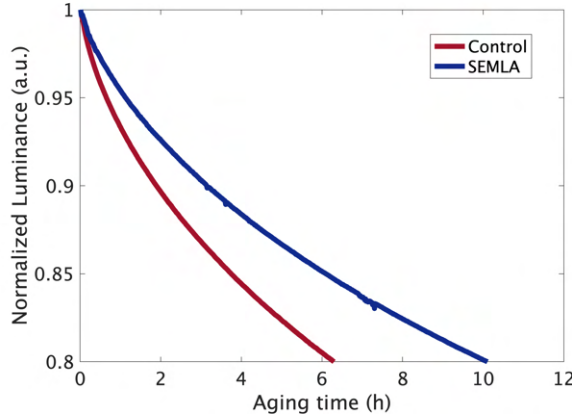


Figure 5.6: **Normalized luminance decay vs. time for control and SEMLA substrates.** Green PHOLED devices are aged at a constant current density chosen such that $L_0 \sim 4300$ is comparable across both substrates.

all device layers. This makes SEMLA easy to integrate into existing device structures. The planar surface of the SEMLA allows for planar organic layers to be maintained unlike in many other waveguide outcoupling schemes, which introduce texture throughout the device stack and potentially create degradation pathways. Here we test the device lifetime on a simple green PHOLED to determine if the SEMLA planarization layer contributes to any external degradation pathways. This device structure is not optimized for stability, but the control and SEMLA devices were grown in the same batch to provide the most even comparison in lifetime. We find that by degassing the polymer matching layer after anode deposition and immediately before organic deposition, we eliminate any extrinsic degradation from the SEMLA substrate. Additionally, the efficiency enhancement provided by SEMLA enables devices to achieve an equivalent brightness at a lower operational current.

The high enhancement in both EQE and lifetime are desirable for commercial applications, and the WOLED results show that the SEMLA is compatible with commercial deep-stacked structures. In a deep-stacked device, the mode coupling changes significantly with the position and wavelength of the EML in the stack. Using the estimated spectra shown in Fig. 5.3, we can predict the emission spectrum for the deep-stacked device by calculating the wavelength-dependent coupling efficiency to air and substrate modes separately for each EML. The total

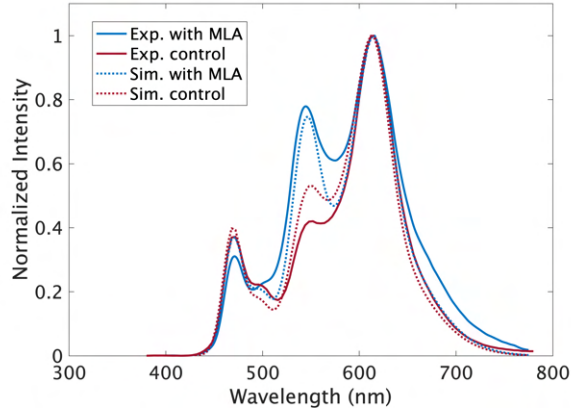


Figure 5.7: **Measured and simulated spectra for SEMLA devices.** Device spectra are measured with and without external MLAs, outcoupling substrate+air modes and air modes only, respectively.

wavelength-dependent coupling profile is shown in Fig. 5.8, and corresponds to the calculated spectra shown in Fig. 5.7. In Fig.5.9 we show the modal power distributions from 430-775 nm for the three RG EMLs in layers 5, 11, and 24, with and without the SEMLA.

The very long cavity created by the deep stack (490 nm between the two electrodes) allows for multiple strong waveguided modes to exist within the cavity. This is shown across the top row of Fig. 5.9. Light generated in layer 24 couples to 6 strong waveguided modes, for $u = 0.77 - 1$. The proximity of layer 24 to the cathode allows an SPP mode to form at $u > 1$. As the EML position shifts closer to the transparent anode, the SPP mode is nearly eliminated, with layer 11 hosting a weak SPP tail at $\lambda > 650\text{nm}$. The number of waveguided modes is constant across the three EMLs, though the relative strength changes. Emission from layer 11 couples weakly to the low- u waveguided modes, while emission from layer 5 recovers these modes but loses the middle two waveguided modes. The use of the SEMLA substrate shifts the lower- u limit of the waveguided modes to $u = 0.88$. The waveguided mode boundaries are drawn with dashed white lines in the center plots of Fig. 5.9. The curvature of the lines arises from the dispersion of the EML, with $n = 1.94 - 1.78$ from $\lambda = 430 - 775\text{nm}$. This effectively squeezes out all the waveguided modes in the SEMLA device, where the leakage into substrate and air modes can be seen at low u . There is a small window of waveguided modes allowed from 430-550 nm, at which

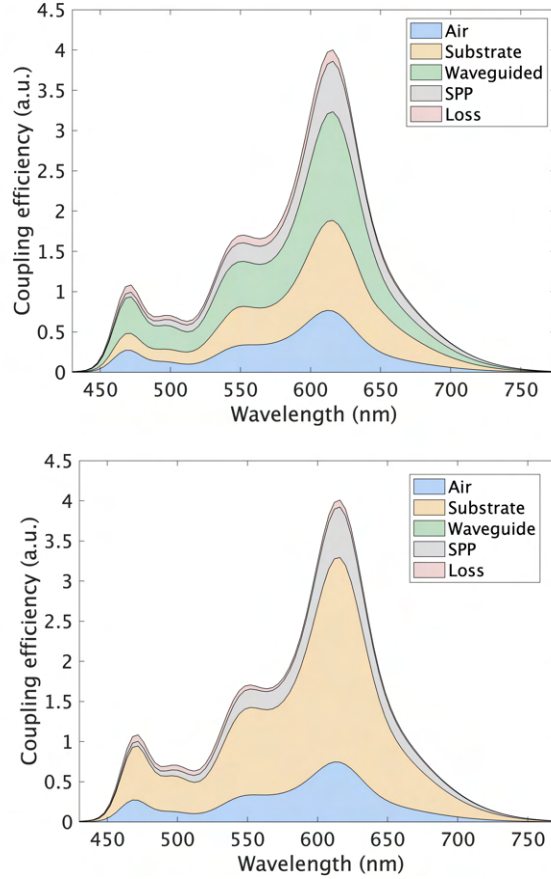


Figure 5.8: **Wavelength-dependent mode coupling for control and SEMLA.** Coupling to air (blue), substrate (yellow), waveguided (green), SPP (gray), and loss (red) modes for WOLEDs on control and SEMLA substrates.

point the index of the EML is greater than the index of the SEMLA.

The B EML has the highest index within the organic stack. As a result we see that at 475nm, there exist multiple channels of organic waveguided modes following layers of the relatively low index HIL/HTL/EBL between other, higher index layers. This illustrates the impact of EML index on coupling to waveguided modes, indicating there is a potential pathway for outcoupling waveguided modes by decreasing the EML index. For emission from the adjacent G EML, $\lambda = 600\text{nm}$, which has a lower index, we see that light travels easily out of the organics and to the metal surface and high index ITO, see Fig. 5.10.

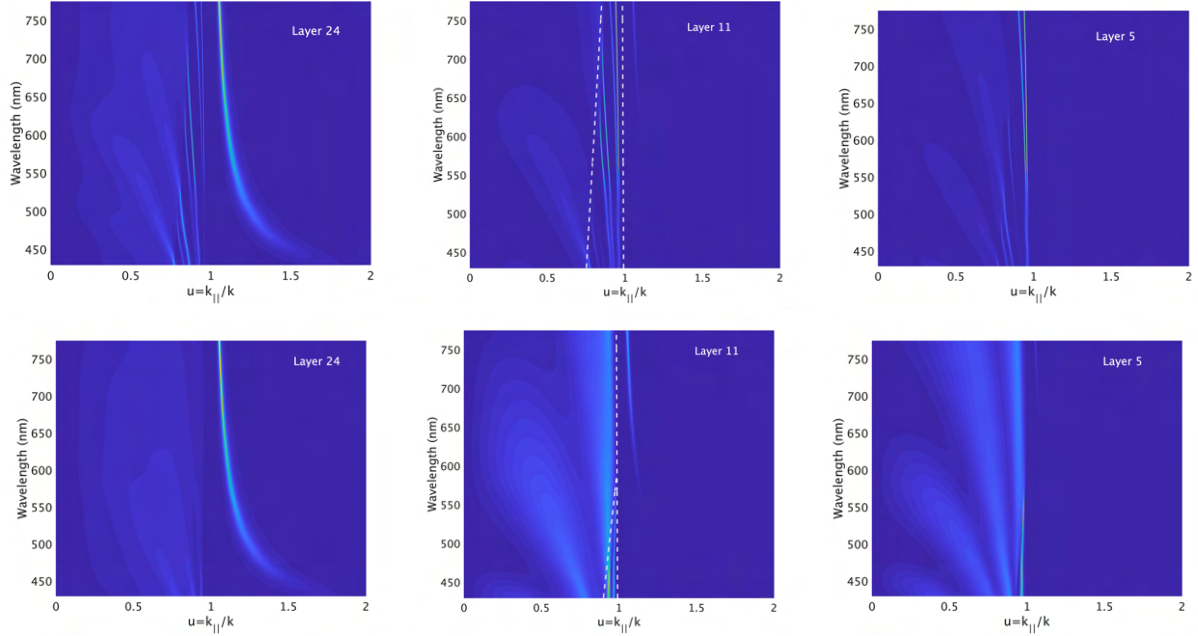


Figure 5.9: **Modal power distributions for deep-stacked WOLED.** Modal power distributions of emission from the RG EMLs without (*top*) and with (*bottom*) SEMLA for layer 24 (*left*), layer 11 (*center*, and layer 5 (*right*)). The boundaries of the waveguided modes in layer 11 are indicated by dashed white lines.

5.3 Conclusions

We demonstrate that the SEMLA is effective at outcoupling waveguided modes, even from very deep organic stacks with high-index EML materials. The distribution of outcoupled waveguided modes changes as a function of wavelength and EML position within the deep stack, suggesting that a deep-stack design which aligns EML position and color to locations within the microcavity with the highest outcoupling could further improve external device efficiency [104]. Using a SEMLA substrate with an external MLA, we achieve an $\eta_{EL} = 161\%$ corresponding to a $1.9\times$ enhancement over control devices. We estimate that $\sim 80\%$ of waveguided modes are coupled into more easily accessible substrate modes. Additionally, nearly all SPP modes are naturally suppressed by the deep stack, accounting for only $\sim 10\%$ of photon coupling. Thus, the main limiting factor to efficiency enhancement is the external MLA.

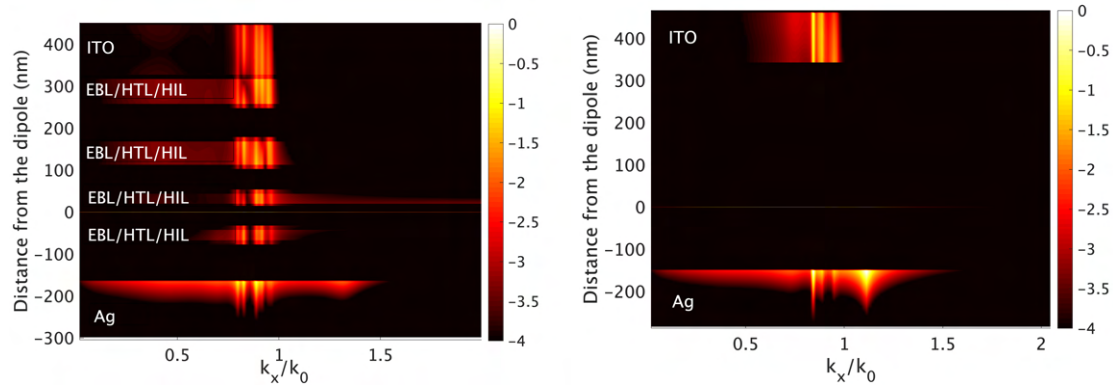


Figure 5.10: **Deep-stacked WOLED dipole distribution.** Dipole distribution throughout the device stack for 475nm emission from the B EML in layer 17 (*left*) and 600nm emission from the G in layer 18 (*right*).

Contributions: C.E.A. and Xinyi Zhou prepared all SEMLA substrates. C.E.A. fabricated and characterized the green single EML OLED. The team at OLEDWorks- Jeff Spindler, Marina Kondakova, Mike Andre, Ryan Mashack, Dustin Comfort, and Nick Leykin- conducted all device fabrication and characterization for the deep-stacked WOLEDs. C.E.A. performed all calculations and data analysis.

CHAPTER 6

Methods for Substrate Mode Extraction

Substrate modes can be thought of as a subset of waveguided modes referring to photons trapped specifically in layers external to the device contacts. Though the moniker “substrate” may seem to imply these modes are only a concern for bottom-up OLEDs, substrate mode trapping can occur in top-down devices that employ any structure adjacent to the top device contact, whether for outcoupling organic waveguided modes, encapsulation, or some other purpose. In this chapter we will use substrate to refer to any layer external to the device contacts, on the top or bottom of the stack.

Substrate mode trapping occurs because of index of refraction mismatches at the air/substrate and substrate/organic interface. In this chapter we will first address current technologies for outcoupling substrate modes. We will then present a method for loosening the trade off between the air/substrate and substrate/organic interface through optical design.

Table 6.1: External substrate mode outcoupling schemes.

Ref.	Geometry	Modes out-coupled	Enhancement	TE or BE	Wavelength dependence
[105]	Crystalline organic scatterer	Substrate	1.3	BE	yes
[106]	High-contrast scattering matrix	Substrate	1.7	BE	no
[107]	MLA	Substrate	1.5	BE	no
[108]	MLA	Substrate	1.5	TE	no
[109]	Silica aerogel	Substrate	1.8	BE	no

6.1 External Enhancement Structures

Substrate mode outcoupling structures, often referred to as EELs or external enhancement structures, modify the device substrate by either 1) reducing the index of refraction mismatch between air/substrate or substrate/organics, or 2) changing the angle of light incident on the air/substrate interface.

Two well-developed EELs are MLAs and diffuse light scatterers. Both technologies utilize transparent materials that decrease total internal reflection (TIR) at the substrate/air interface by changing the exit angle of photons leaving the device. Additional structures providing a variation on the same concept are summarized in Table 6.1. In laboratory measurements, IMF (see Sec. 5.2) and high index half-ball lenses can be used to couple out 100% of substrate modes, typically achieving enhancement factors > 2 [110]. These methods are not practical for applications beyond the laboratory but they demonstrate the need for improving substrate mode outcoupling architectures.

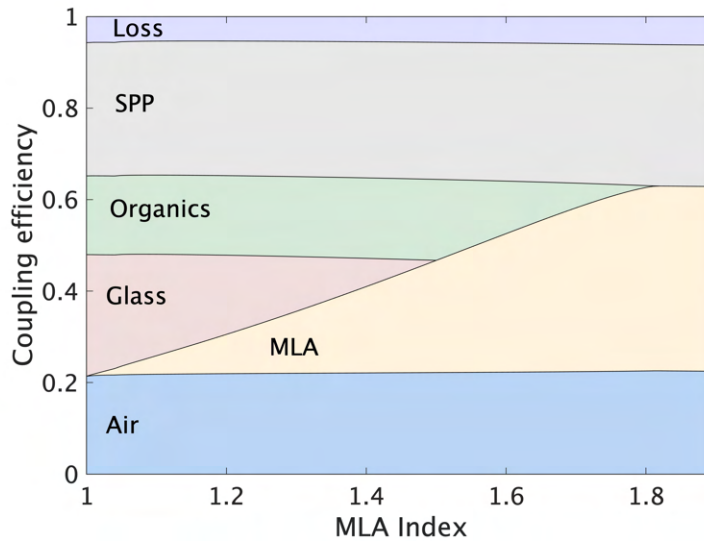


Figure 6.1: Coupling modes as a function of MLA index. Fraction of light coupled to air (blue), MLA (yellow), glass (red), organic (green), metal/SPP (gray) layers, and loss (light blue) modes as a function of MLA index for a standard green PHOLED (see Sec. 5.2.1) with an isotropic dipole distribution at 520nm.

6.2 Optically Engineered Designs for Improving External MLA Performance

The outcoupling efficiency, η_{oc} of an MLA can be described by the following equation:

$$\eta_{oc} = \eta_{air} + (\eta_{MLA,in} T_{MLA}) \quad (6.1)$$

where η_{air} is the fraction of photons coupled directly to air modes, $\eta_{MLA,in}$ is the fraction of photons coupled into the MLA layer, and T_{MLA} is the transmission of the MLA. We can calculate $\eta_{MLA,in}$ using the dyadic Green's function described in Sec. 2.4. For a standard green device, see Sec. 5.2.1, we show, in Fig. 6.1, that as the index of refraction of the MLA decreases, so does $\eta_{MLA,in}$. This suggests that the optimal MLA has $n_{MLA} \geq n_{organics}$. To compute T_{MLA} , we use geometric ray tracing to calculate the transmission through a hexagonal close-packed array of $10\mu\text{m}$ diameter lenses following the method used in Refs. [30, 31] for 100 rays at angles $\theta = 5 - 85^\circ$ and $\phi = 0 - 30^\circ$. We assume that ITO and Al absorb 4% and 10% on each pass, respectively. We calculate transmission for a range of starting mediums with $n = 1 - 2$. The exit medium is air, $n = 1$. The ray tracing calculation is described in detail in Sec. 2.4.2. In Fig. 6.2, we see that as the index of refraction of the MLA increases, T_{MLA} decreases. This suggests that the optimal MLA has $n_{MLA} \rightarrow 1$.

This creates a trade off in the optimal substrate index of refraction- as the substrate index increases, TIR at the air/substrate interface increases; as the substrate index decreases, TIR at the substrate/organic interface increases. Most current MLA technology utilizes polymers such as PMMA or PDMS, with $n \sim 1.5$. This optimizes neither interface, and leads to a typical MLA extraction efficiency of $\sim 60 - 70\%$. To increase the efficiency of MLA outcoupling, two schemes may be utilized. In the first scheme, the MLA has an index approximately equal to or higher than the substrate index, and the index mismatch between air and MLA must be decreased through additional structures. In the second scheme, the MLA is composed of a material with an

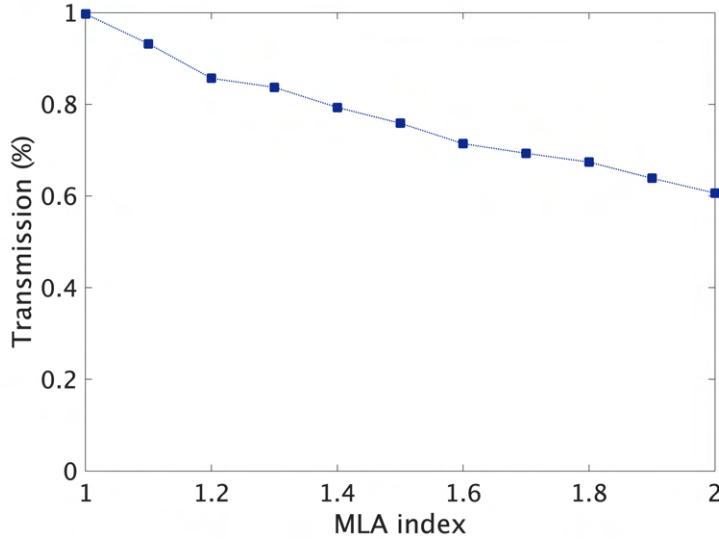


Figure 6.2: **Transmission of an MLA.** Transmission of a hexagonal close-packed hemispherical MLA as a function of MLA index.

index approaching that of air, and the index mismatch between the substrate and MLA must be decreased.

6.2.1 Low-index Coatings

Here, we discuss designs, preliminary work, and limitations for creating optical coatings to decrease reflection at index-mismatched interfaces.

Very low-index materials with $n \rightarrow 1$ can be fabricated by creating a porous structure of a low-index material, $n \sim 1.3 - 1.4$. The pores of air result in a material with an effective index between air and the host medium. Such structures can be fabricated through a variety of methods, including aerogels, high-angle deposition, and etched structures [109, 111–113].

While direct write X-ray and E-beam lithography have been used to fabricate nano-structures and pores in polymer and organic films, this technology has not yet been used for the purpose of constructing low-index porous films [114, 115]. To realize porous structures using direct write X-ray or E-beam lithography, small pores throughout the bulk film are exposed by focusing the electron or x-ray source at various depths throughout the film, and removed exposed areas using

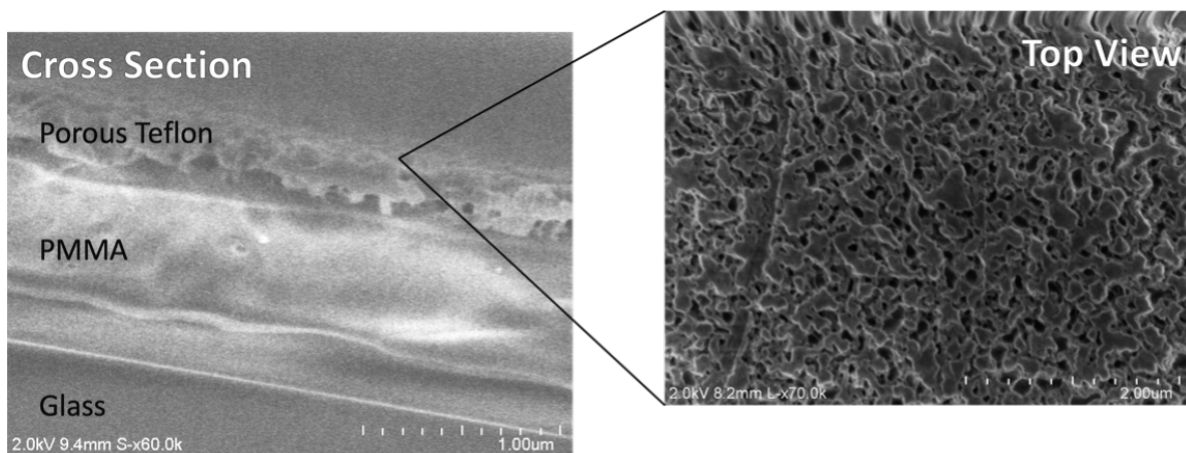


Figure 6.3: **Images of porous Teflon.** Cross-sectional (*left*) and top view (*right*) SEM images of porous Teflon on planar PMMA. A thin Au layer ($< 5\text{nm}$) is sputtered on the sample surface to improve conductivity for imaging.

a wet etch.

Previous work has used porous Teflon to fabricate graded index anti-reflection coatings (ARC) for photovoltaic applications [113]. In this process, Teflon is co-deposited alongside an organic molecule via VTE. After deposition, the organic porogen is removed by washing the substrate in isopropanol to leave behind a porous scaffold of Teflon. This coating is demonstrated on a macro-scale acrylic dome.

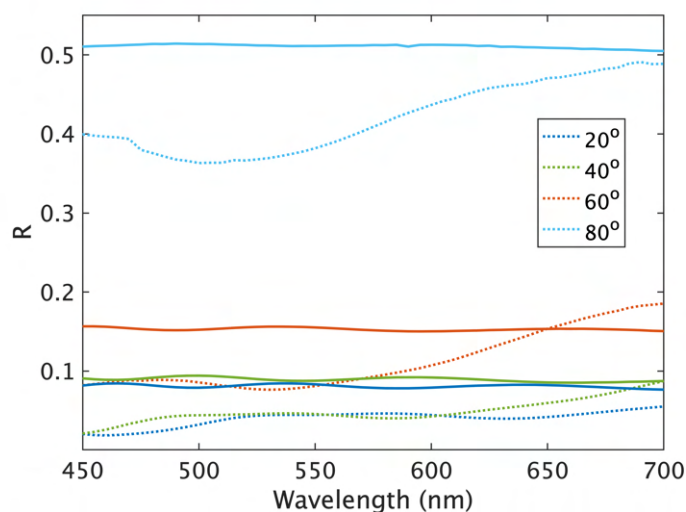


Figure 6.4: **Reflection of coated and uncoated PMMA.** Measured reflection of a three layer ARC on planar PMMA (dotted lines) compared to neat, planar PMMA (solid) from 20-80°.

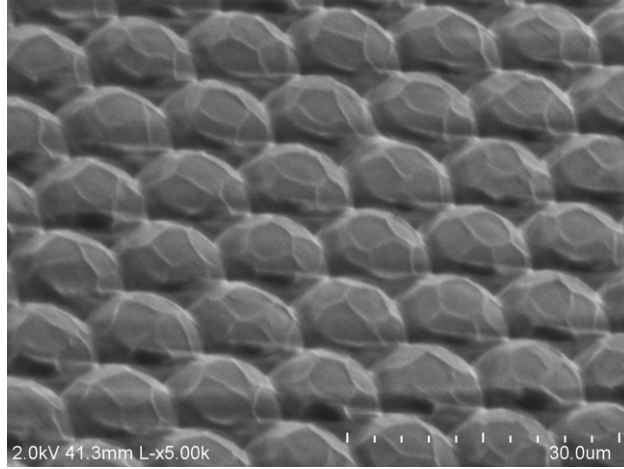


Figure 6.5: **SEM image of a porous Teflon-coated MLA.** The MLA is coated with a $<5\text{nm}$ thick layer of gold to improve surface conductivity.

As a test for the applicability of porous Teflon as an ARC for MLAs, we designed a three-layer coating consisting of neat Teflon 117 nm with $n = 1.31$ / 1:1 Teflon NPD 129 nm with $n = 1.15$ / 1:4 Teflon NPD 149 nm with $n = 1.05$ using a genetic optimization algorithm [116]. This coating is optimized for a standard green phosphorescent emitter with a peak wavelength at 540nm and a PMMA MLA, with $n_{MLA} = 1.48$. An SEM image of the porous Teflon surface and cross-section is shown in Fig. 6.3. We find that, while the low index ARC performs as expected on planar PMMA substrates, see Fig. 6.4, we do not observe a comparable enhancement for an ARC deposited on an MLA. Under SEM, we observe that the coated lenses show a soccer ball-like texture, see Fig. 6.5 which we suspect arises from the small, steep features of the MLA. Additionally, the directionality of VTE deposition may lead to uneven coatings between the top of the MLA domes and crevices between lenses.

6.2.1.1 Low-index ALD coatings

ALD offers one potential solution to coating uniformity on MLA features, given its conformal coating quality. Calcination and etching in water have been used to generate porous alumina films from neat Alucone films [117]. Here, we demonstrate porous Al_2O_3 on PMMA films. Al_2O_3 is chosen given that the alumina precursor, TMA, has a high reactivity and is able to react

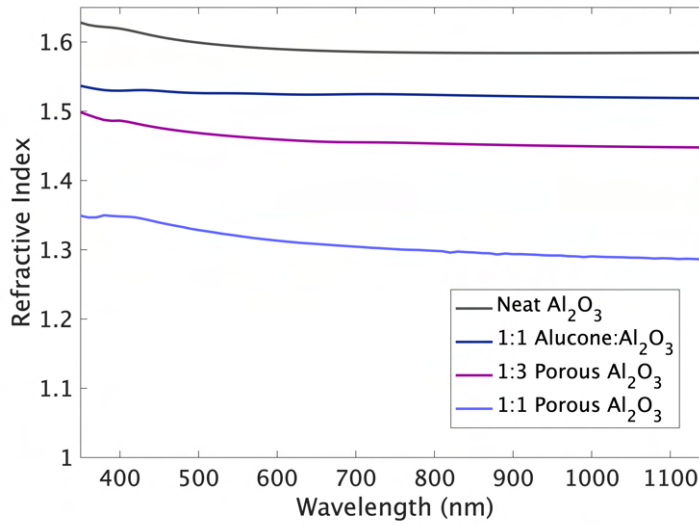


Figure 6.6: **Alumina film indices of refraction.** The index of refraction of various alumina films; neat Al_2O_3 (gray), 1:1 alucone: Al_2O_3 (dark blue), 1:3 porous Al_2O_3 (purple), and 1:1 porous Al_2O_3 (light blue) from high to low index, respectively.

and deposit on the surface of PMMA. Additionally, Alucone, the metal-alkoxide counterpart to Al_2O_3 , etches in HCl $10\times$ faster than Al_2O_3 . We can generate porous Al_2O_3 by alternatively depositing Al_2O_3 and Alucone, then etching in HCl to remove the Alucone, leaving a porous Al_2O_3 scaffold. We deposit both Alucone and Al_2O_3 at 80°C . Each cycle consists of 15 ms H_2O /10s wait/15ms TMA/10s wait and 10 ms EG/10s wait/15ms TMA/10s wait for Al_2O_3 and Alucone, respectively. We are able to achieve a decrease in $n = 1.60$ for neat Al_2O_3 to $n = 1.33$ at 500nm, see Fig. 6.6 for a 1:1 ratio of alternating Al_2O_3 :Alucone cycles, etched in 6% HCl:DI water. A film with intermediate index, $n = 1.47$, can be achieved using a 1:3 ratio of Al_2O_3 :Alucone cycles. Each cycle deposits approximately $0.75\text{-}1.2\text{\AA}$ of material.

Porous ALD is a promising option for conformally coating low-index materials over micro-scale lens features. Lower index polymer films could be achieved by using a lower index scaffold material, such as SiO_2 , which can be deposited via ALD using silane-based precursors [118]. The slow growth rate of ALD poses a challenge for the scalability of this technique for films 100s nm thick, which maybe required for multi-layer optical coatings.

6.3 Conclusions

Substrate mode outcoupling efficiency remains limited by the use of external enhancement structures that only satisfy one index matching condition, either between air and the substrate, or between the substrate and organics. Periodic anti-reflection coatings could reduce reflection at the MLA/air interface, but also introduce a strong angle and wavelength dependence [119]. Low-index coatings and materials offer one solution for creating aperiodic and graded index coatings to decrease TIR in MLAs index matched to organics, with little to no wavelength dependence. However, overcoming the fabrication challenge presented by low-index coatings remains a challenge in designing a practical solution for overcoming MLA loss.

Contributions: C.E.A. prepared and measured all films and MLAs. Hafiz K.M. Sheriff, Jr., designed the 3-layer ARC structure.

CHAPTER 7

Understanding and Improving Plasmonic Mode Outcoupling Efficiency

In Ch. 5, we present challenges and solutions for outcoupling light from deep-stacked structures which are dominated by waveguided mode coupling. There is a trivial solution to this problem as well: thin the organic stack enough to suppress most of the waveguided modes. The result is not a high EQE OLED, but rather an OLED dominated by coupling to plasmonic modes. There exist a variety of strategies for outcoupling plasmonic modes, which we will discuss in Sec. 7.1. Recent work by Zhao, et al. has demonstrated the presence of hybrid plasmon-exciton modes, PEPs, in OLEDs. In Sec. 7.2, we will examine the difference between SPP and PEP modes, and the implications this has for outcoupling efficiency. We will revisit PEP modes in Sec. 8.2, where PEP coupling is used to enhance color stability in stacked WOLEDs.

7.1 Plasmonic Mode Outcoupling Designs

Many OLED designs incorporate one or more metal contacts, typically made of Al or Ag. When dipole emission occurs close enough to a metal surface, the photon energy is coupled to an evanescent mode in the metal. This state is called a surface plasmon polariton. SPP modes are typically lossy because their evanescent nature prevents them from dissipating energy radiatively. Many of the outcoupling strategies discussed in Ch. 5 and 6 rely on far-field structures or using index-matched materials, with a maximum $n \sim 1.7$. Such technologies are not useful in accessing SPP

Table 7.1: Summary of plasmonic mode outcoupling schemes.

Ref.	Geometry	Modes outcoupled	Enhancement	T-E or B-E
[100]	Random nanostructures	SPP and WG	2.4	B-E
[120]	Curved mirror array	SPP	2	T-E
[101]	Subanode grid	SPP and WG	1.5	T-E
[121]	Photonic crystal	SPP	1.5	B-E
[122]	Corrugated metal	SPP	1.2	B-E
[123]	Corrugated metal	SPP	1.2	TE

modes that are locally coupled to the metal surface, and have high k . Instead, outcoupling SPP modes relies on structures that directly scatter SPP modes, typically through nano-scale metal patterns which have a feature size $\sim \lambda_{SPP}$, the SPP wavelength. A summary of these outcoupling schemes is provided in Table 7.1. Bottom-emitting (B-E) and top-emitting (T-E) devices, (referred to as bottom-up and top-down architectures in Sec. 1.2.2, respectively), can often utilize the same type of outcoupling structure but the outcoupling efficiency and implications on device performance and reliability may depend on the device orientation. Plasmonic mode coupling can be nearly eliminated by using non-metal contacts such as ITO on both electrodes, though this constrains design of the OLED stack.

7.2 Improving Plasmonic Mode Outcoupling in Top-emitting OLEDs

Recent work by Zhao, et al. has demonstrated that devices with an increased Purcell factor can extend the lifetime of notoriously unstable blue phosphorescent emitters by up to $14\times$ [22]. The Purcell factor, discussed in detail in Sec. 2.2, is increased by increasing the strength of the cavity formed by the device electrodes by replacing one or both with Ag. In conventional device design, the thickness of the transporting layer adjacent to a metal electrode is selected to suppress SPP modes and maximize outcoupling to visible air modes, $\sim 300\text{nm}$ for blue emitters and $\sim 600\text{nm}$ for red/green emitters. The Purcell factor, which is defined as the ratio between the radiative

decay of a dipole in a cavity to the natural dipole decay rate (see Sec. 2.2), decreases the farther the dipole is from the metal surface. This requires the device EML to be close to the metal electrode, $\sim 15\text{nm}$ spacing, which results in a large fraction of dipole emission coupled to SPP modes. Methods for outcoupling SPP modes are needed to achieve the lifetime improvement from the Purcell effect without sacrificing η_{oc} , particularly in T-E geometries which are the standard geometries used in display applications. Previously, nanoparticle scattering layers have been used to outcouple SPP modes, demonstrating a nearly $8\times$ increase in T-E EQE [124, 125].

Zhao, et al. have also demonstrated that the nature of the SPP can be modified through the choice of the adjacent organic transport layer [22]. When the transport layer singlet exciton energy overlaps with the low energy absorption edge of the metal, the transport layer excitation can couple to SPP modes on the metal surface to form a hybrid plasmon-exciton-polariton mode, discussed in detail in Sec. 2.3.3.1. This mode is both excitonic and photonic (contributed from the SPP mode) in nature and has been demonstrated to have nearly $100\times$ brighter PL than SPP modes [22]. This suggests that, given the SPP-like nature, typical SPP outcoupling structures can also be used to outcouple PEPs and, given the exciton-like nature, the efficiency of these structures may be higher as a result of the luminescent nature of the PEPs.

In this work we deploy a nanoparticle scattering layer to T-E+B-E OLEDs with a thin Ag top contact and either a SPP-hosting ETL material, SF3Trz, or a PEP-hosting ETL material, BPyTP2. We refer to these OLEDs as SPP devices and PEP devices, respectively, from now on. We find that the PEP devices have a larger enhancement in luminance and EQE than the SPP devices. This disparity is confirmed through optical measurements of bilayer ETL/Ag films, with and without nanoparticles, which show that the PEPs scatter a higher fraction of high- k light into visible, low- k modes. We then investigate T-E only devices using a reflective bottom Al anode and thin top Ag cathode. In both SPP and PEP devices we find that the addition of nanoparticles decreases device EQE, since the majority of plasmonic modes are trapped on the anode, far from the scattering layer. Finally we demonstrate that a high-index MLA applied directly to the top emitting surface can enhance EQE in PEP devices by factor of 2 by outcoupling both waveguide

and plasmonic modes.

7.2.1 Methods and Experimental Set-up

T-E + B-E substrates: The bottom ITO contact is prepared on 0.7mm thick Corning Eagle XG glass (Colorado Concepts). The substrates are cleaned in Tergitol:DI water 1:100, DI water, and acetone 2× in an ultrasonic bath followed by isopropanol 2×, heated to 165°C, for 5 min. each. The surface is exposed to UV-ozone (UVOCS Inc.) for 15 min. Then a neat layer of 70nm ITO is sputtered on the glass surface (Kurt J. Lesker). After the deposition, ITO is thermally annealed at 450°C in forming gas for 3 min (JetFirst 100). The sheet resistance of the ITO is 20-30 $\Omega \text{ sq}^{-1}$. Then, HMDS is spin coated on the ITO surface at 4000RPM to help the photoresist wet to the surface. Photoresist S1813 is spincoated at 4000RPM and soft baked at 115° for 90s. The photoresist is exposed for 20s to form 6 isolated 1mm wide bars (Karl Suss MJB3 contact aligner). The photoresist is developed in AZ726 for 30s, 2×. Then, the exposed ITO is etched in a 1:1 HCl:DI water mixture for 15 min. The remaining photoresist is removed in PRS2000. Following this patterning process, substrates are cleaned in Tergitol:DI water 1:100, DI water, and acetone 2× in an ultrasonic bath followed by isopropanol 2×, heated to 165°C, for 3 min. each. The ITO surface is exposed to UV-ozone for 15 min. immediately before organic deposition.

T-E only substrates: Bare glass slides, 1” sq. and 0.2 mm thick are cleaned following the same procedure as for the T-E + B-E substrates. A shadow mask is used to define 1mm wide anode contacts. A 120 nm thick Al layer is deposited via VTE at $1\text{\AA s}^{-1}$. The Al deposition is done immediately before organic deposition, and the substrates are exclusively handled in a pure N_2 environment to prevent oxidation.

Device fabrication On both substrates, the following organic layers are deposited via VTE at rates 0.08 - 1.0 $\text{\AA s}^{-1}$: 5nm HATCN/40nm NPD/5nm Tris-PCz/25nm mCBP:Ir(ppy)₃ 8% vol/15 nm ETL/1.5nm Liq, where the ETL is either SF3TRz (SPP devices) or BPyTP2 (PEP devices). HATCN, NPD, and mCBP were provided by Universal Display Corporation (UDC).

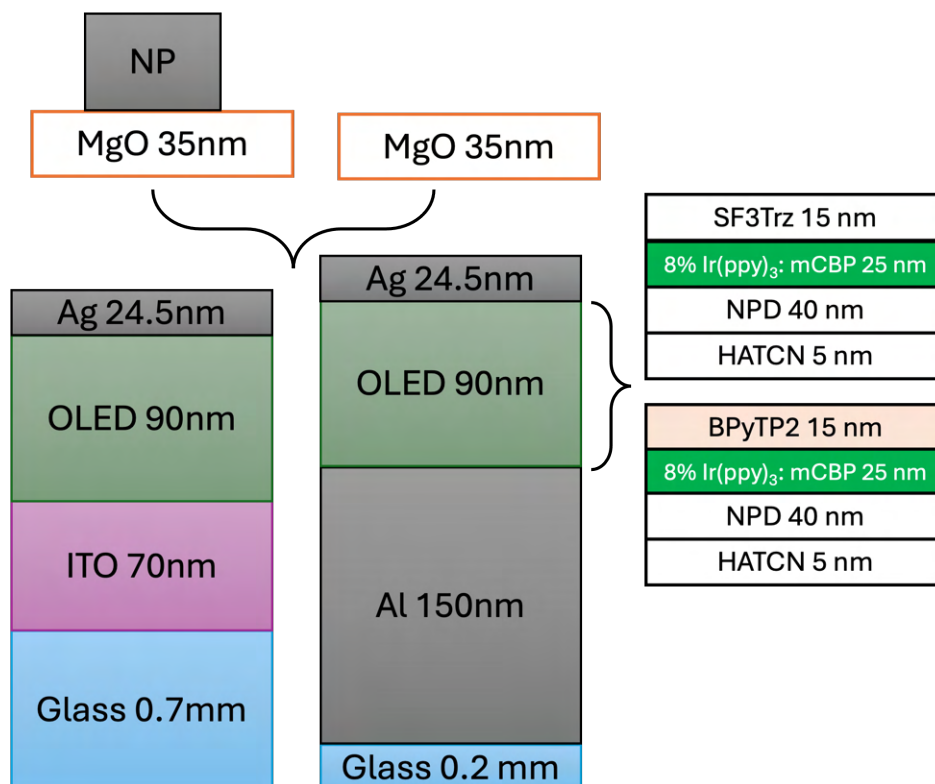


Figure 7.1: **Schematic of device structures.** The left stack shows the T-E + B-E device while the right shows the T-E only device. All features are drawn to scale, except for the individual organic layers and the glass substrates.

All other organic materials were purchased from Lumtec and purified via thermal gradient sublimation (see Sec. 1.2.1). Following the organic layers, the cathode is deposited via VTE using a 2mm wide shadow mask to define a device active area of 2mm^2 . The cathode consists of 3nm Al followed by 20nm Ag, deposited at $0.1 \text{ \AA s}^{-1}$ to prevent Ag penetration into the thin ETL. Devices are then transferred in a pure N_2 environment for deposition of the MgO cathode capping layer via ALD (Veeco Savannah). The ALD chamber is held at 80°C to prevent degradation of the organic layers. The Mg precursor, Etcp2Mg (STREM Chemical), is held at 90°C , while the H_2O precursor is held at room temperature. Each cycle consists of 0.015s H_2O /30s wait/1s Etcp2Mg/30s wait, depositing $1.3 \text{ \AA}$ per cycle. For nanoparticle devices, a 35nm (263 cycles) capping layer is deposited. For MLA devices, a 145nm (1046 cycles) capping layer is deposited. Schematic drawings of the device structures are shown in Fig. 7.1.

Nanoparticle scattering layer: We purchased 75nm Ag nanocubes, suspended in ethanol at 1 mg mL⁻¹ from Nanocomposix. To achieve the desired density, the solution is centrifuged at 5.2 krcf for 10min, and the excess solution is decanted to create a 10 mg mL⁻¹ solution (Eppendorf Mini Spin Plus). The solution is sonicated for 10 min. before and after centrifuging to ensure the nanoparticles are well-mixed. The solution is coated on top of the capping layer at a constant spin speed of 250 RPM, maintained for 2 min after dispensing in an N₂ glove box (G3P Spin Coat, Specialty Coating Systems Inc.). Devices are then encapsulated using a thin glass slide 0.2 mm thick and UV-curing epoxy. The device active area and nanoparticle area are shielded from UV exposure using a 0.5mm thick Si piece. Spin coating and encapsulation are performed in a pure N₂ glove box. Nanoparticles are imaged using SEM, see Fig. 7.2, and the deposited nanoparticle density is counted in ImageJ.

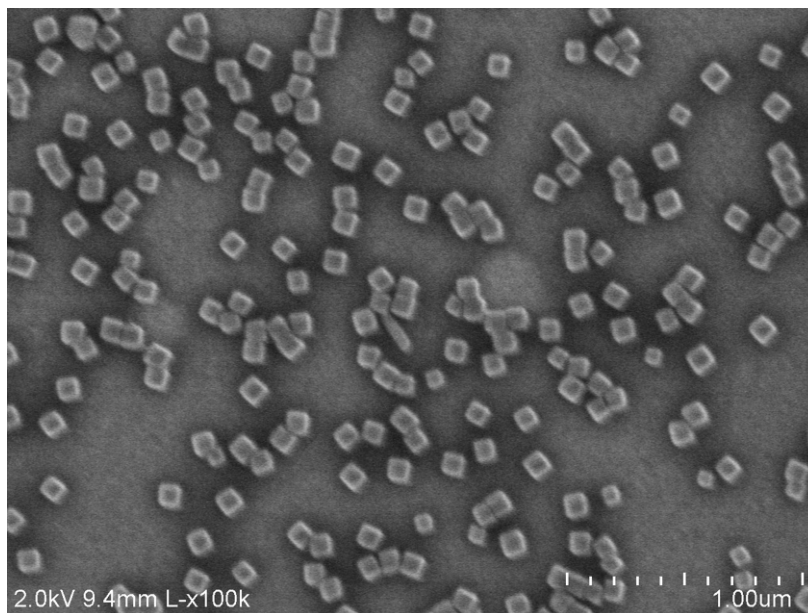


Figure 7.2: **SEM image of nanoparticles.** An SEM image of nanoparticles coated on the surface of a T-E OLED.

MLA preparation: Glass MLA molds are fabricated following the procedure described in Sec. 5.2.1 to form 10 μ m diameter hemispherical concavities in a hexagonal close-packed array. A mixture of Micro 90:isopropanol:DI water 1:10:10 is spin coated onto the MLA mold at 4500 RPM for 45s to aid in the release of the MLA from the mold. Then, a high-index polymer

(PixNIL SFT1, Pixelligent) is spin coated onto the mold at 500 RPM for 45s (Laurell WS-650MZ-23NPP). The coated mold is then degassed under vacuum for 15mins to prevent air bubbles from forming. Inside an N_2 glove box, the coated mold is pressed onto the surface of a device with a thick capping layer. With the mold still in place, the MLA is cured for 200s under 365nm pulsed UV light (Xenon Corp.). Then, the mold is released from the MLA by applying light upward pressure. A microscope image of the MLA is shown in Fig. 7.3.

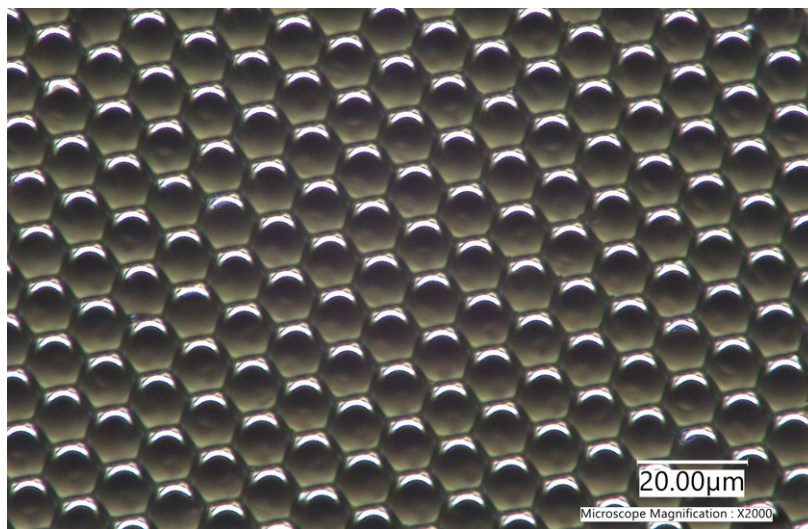


Figure 7.3: Image of an MLA. A microscope image of a MLA made of PixNIL SFT1.

Device measurements: The device J-V-L, EQE, and spectra are measured following the standard procedure outlined in Sec. 3.2.0.1. Voltage is scanned from 0 to 8V. Average device data is reported for 2-4 devices, with the error bar calculated from the standard deviation of the data.

Optical samples and measurements: Optical samples are prepared by cleaning a thin glass slide, 0.15mm thick, following the procedure above. A 5nm ZrO_2 layer is deposited via ALD to aid in wetting the nanoparticles to the substrate surface. The ALD chamber is held at 80°C. The Zr precursor, TDMAZ (STREM Chemical), is held at 75°C and the H_2O precursor is held at room temperature. Each cycle consists of 0.015s H_2O /30s wait/0.25s TDMAZ/30s wait, depositing 1.4Å per cycle. The nanoparticles are coated following the procedure described previously, such that half of the substrate is coated with nanoparticles and half is bare. This allows for controlled measurements of substrates with and without nanoparticles. Substrates are then capped with a

30nm ZrO_2 (217 cycle) layer. Then the bilayer is deposited via VTE under the same conditions used for device growth: 30nm Ag/30nm ETL, where the ETL is either BPyTP2 or SF3Trz. A shadow mask is used when depositing Ag to define 1mm diameter circles. The substrate is then encapsulated in the same manner as the devices.

The optical measurements are performed using an Olympus microscope equipped with Fourier-space imaging optics [25, 126]. A pulsed 405 nm laser diode (Thor Labs NPL41B) with a 38 ns pulse width and 10 MHz repetition rate is used as the excitation beam. The microscope is set up in the transmission configuration the focused excitation beam falls on the ETL surface of the sample and emission is collected through the sample substrate. The bottom glass substrate is coupled to a 100x objective using $n = 1.5$ immersion oil. PL emission is collected from the bottom of the sample, which passes through a set of lenses in the $4f$ configuration. Immediately after the last focusing lens, a polarization filter set to 0° (i.e. allowing only TM light through) and 450nm longpass filter are installed. The PL signal is measured by a spectrometer and Si CCD (Princeton Instruments). A schematic of the device structure and measurement orientation are shown in Fig. 7.4.

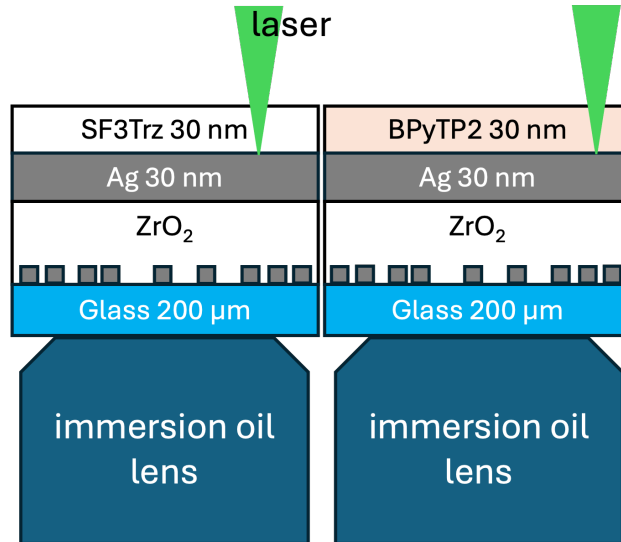


Figure 7.4: **Schematic of optical samples and measurement orientation.** The excitation laser is incident from the top of the device, while PL emission is collected from the bottom using a $100\times$ immersion oil objective.

Table 7.2: J-V-L and EQE data for T-E + B-E SPP and PEP devices.

	T-E only					T-E + B-E	
	V (V)	J (mA cm ⁻²)	L (cd m ⁻²)	EF	η_{EL} (%)	L (cd m ⁻²)	η_{EL} (%)
SPP	11.2	93 ± 8	5540 ± 10	–	1.7 ± 0.1	–	–
PEP	7.93	153 ± 6	5450 ± 70	–	1.02 ± 0.04	–	–
SPP + NP	11.25	100 ± 10	6600 ± 400	1.2	2.0 ± 0.5	25000	7
PEP + NP	7.73	158 ± 5	7680 ± 200	1.4	1.4 ± 0.08	24000	4.3

Optical calculations: We use the dyadic Green’s function method to simulate dipole emission for the device stacks described previously and calculate the energy flux coupled to each layer of the device [29]. Full details of the optical calculations are provided in Sec. 2.4. The device n and k values are measured for neat films on Si substrates using ellipsometry (J.A. Woollam). We use $q = 0.95$ and $\theta_{hor} = 0.77$. The flux calculations are performed at $\lambda = 500\text{nm}$.

7.2.2 Results

The T-E J-V-L for T-E + B-E devices with and without nanoparticles are shown in Fig. 7.5. Considering T-E only, the control SPP devices demonstrate $L = 5540 \pm 10 \text{ cd m}^{-2}$ and $\eta_{EL} = 1.7 \pm 0.01\%$ at $J = 93 \pm 8 \text{ mA cm}^{-2}$ and $V = 11.20\text{V}$. At the same luminance, the control PEP devices demonstrate $L = 5450 \pm 70 \text{ cd m}^{-2}$ and $\eta_{EL} = 1.02 \pm 0.04\%$ at $J = 153 \pm 6 \text{ mA cm}^{-2}$ and $V = 7.93$. The addition of nanoparticles results in $L = 6600 \pm 400 \text{ cd m}^{-2}$ and $\eta_{EL} = 2.0 \pm 0.5\%$ at $V = 11.25\text{V}$ and $J = 100 \pm 10 \text{ mA cm}^{-2}$ for SPP devices and $L = 7680 \pm 200 \text{ cd m}^{-2}$ and $\eta_{EL} = 1.40 \pm 0.08\%$ at $V = 7.73 \text{ V}$ and $J = 158 \pm 5 \text{ mA cm}^{-2}$ for PEP devices. This results in a 1.2 $\times$ enhancement in L for the SPP devices and a 1.4 $\times$ enhancement in L for PEP devices. These results are summarized in Table 7.2. The applied nanoparticles are shown in Fig. 7.2 and cover $\sim 14\%$ of the cathode surface.

To characterize the observed enhancement, we measured the Fourier space PL emission for optical samples with and without nanoparticle enhancement layers. Figure 7.6 shows the PL emission at $k_{\perp} = 0$ integrated over all wavelengths as a function of the in-plane wave vector, $k_{\parallel}$, and arbitrary intensity. PL is collected with an integration time of 10s for all samples such

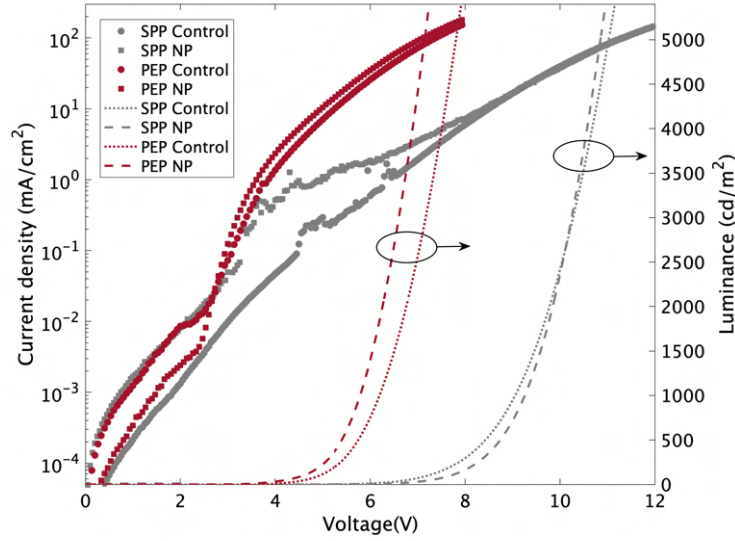


Figure 7.5: T-E + B-E device J-V-L. J-V-L characteristics for T-E + B-E devices with and without nanoparticles. Luminance accounts for top emission only.

that the contrast in PL intensity can be compared directly. The PEP sample shows an average $1.53\times$ enhancement across the low- k range, $k = 0.45 - 1$, with the addition of nanoparticles, while the peak at $k \sim 1.3$ is decreased by $0.93\times$ relative to the control. For the SPP samples, the enhancement across low- k is $1.05\times$, while the peak intensity with nanoparticles decreases $0.78\times$ relative to the control.

The PEP- vs. SPP- nature of the PL signal can be observed through wavelength-resolved k -space measurements for devices with nanoparticles, shown in Fig. 7.7. In both samples, the high- k signal of the plasmon PL decreases with increasing wavelength. The SPP sample shows the intensity of light scattered to $k < 1$ is independent of wavelength, while the PEP sample shows decreased scattering to $k < 1$ as wavelength increases. Additionally, the PEP signal is $> 3\times$ brighter than the SPP signal.

In T-E only devices, the control J-V-L $J = 1.54 \pm 0.08$ and $10.1 \pm 0.01 \text{ mA cm}^{-2}$, $L = 250 \pm 10$ and $1300 \pm 200 \text{ cd m}^{-2}$, $\eta_{EL} = 4.1 \pm 0.1$ and $3.3 \pm 0.6\%$ at $V = 7.93 \text{ V}$ for the SPP and PEP devices, respectively. With the nanoparticle layer at the same voltage, $L = 220 \pm 10$ and $920 \pm 40 \text{ cd m}^{-2}$, $\eta_{EL} = 3.6 \pm 0.1$ and $2.7 \pm 0.2\%$ at $J = 1.7 \pm 0.1$ and $9.3 \pm 0.3 \text{ mA cm}^{-2}$ for the SPP and PEP

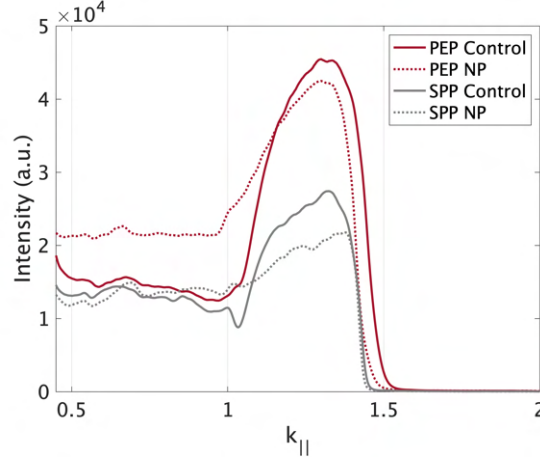


Figure 7.6: Comparison of k -space PL for optical samples with and without nanoparticles. PEP and SPP devices are plotted in red and gray, respectively, with dashed lines indicating the addition of nanoparticles. The integration time for all samples is 10s.

devices, respectively. This corresponds to a $0.9\times$ drop in EQE for the SPP device, and a similar $0.8\times$ drop for the PEP device. The J-V-L characteristics for these devices are shown in Fig. 7.8. The strong microcavity formed by the metal-metal electrodes of the T-E only device results in a narrowed emission spectrum for both SPP and PEP control devices, shown in Fig. 7.9.

In addition to nanoparticle scattering layers, we test the effectiveness of a high-index MLA. The high index polymer, purchased from Pixelligent, contains a polymer base doped with 20nm diameter TiO_2 nanospheres. The J-V-L and EQE for the control, MLA, and nanoparticle PEP devices are shown in Fig. 7.10. A summary of the device parameters is included in the inset table. We observe the largest enhancement for devices with the MLA. The device emission spectra are shown in Fig. 7.11. The spectra for both nanoparticle and MLA devices are broadened relative to the control, with the nanoparticle device showing slightly broader emission than the MLA.

7.2.3 Discussion

The device structure used in this work is designed with a thin ETL to maximize coupling to the top cathode plasmonic mode in order to characterize the difference between SPP and PEP devices. We choose SF3Trz and BPyTP2 for the SPP and PEP devices, respectively, because of

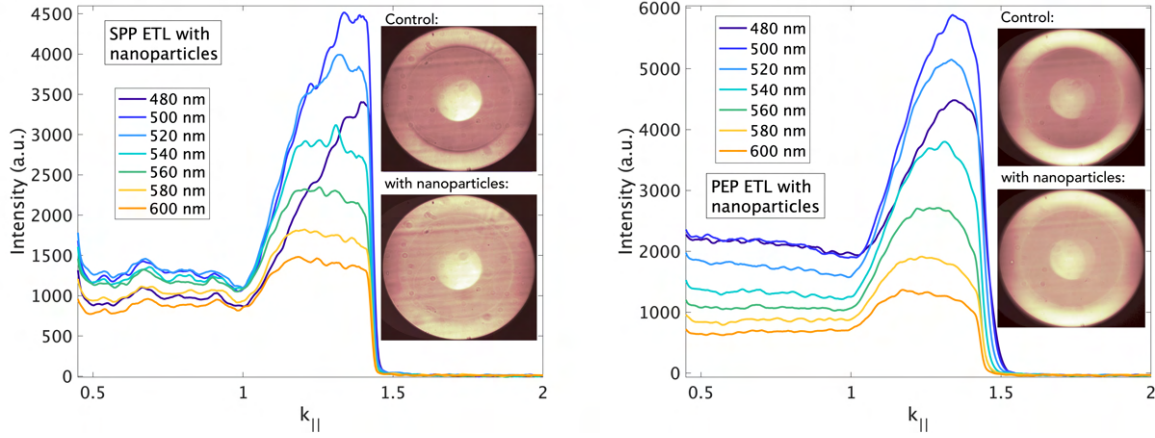


Figure 7.7: **Wavelength-resolved k -space measurements.** PL of SPP (*left*) and PEP (*right*) samples at single wavelengths, measured with integration times of 30s and 10s, respectively. *Inset:* Integrated PL intensity in Fourier space, $k_{\perp}$ vs. $k_{\parallel}$, for SPP and PEP samples with (*bottom*) and without (*top*) nanoparticles.

their well-characterized polaritonic behavior described in Sec. 2.3.3.1 and Ref. [22]. We use MgO deposited via ALD for the cathode capping layer because it has an index of refraction matching that of the EML and the ALD provides conformal coating to protect the organic layers during application of EEL. We use a transparent ITO anode and thin Ag cathode, enabling both T-E and B-E, to isolate the outcoupling enhancement from the top contact plasmonic modes. As a result the observed EQE for all devices is quite low. We observe a significant $1.4\times$ enhancement in PEP device EQE with the addition of nanoparticles, which is a $1.2\times$ greater than the enhancement observed in SPP devices, $1.2\times$. This indicates that the PEP device achieves a higher outcoupling efficiency enhancement from nanoparticles than comparable SPP devices.

Using dyadic Green's function calculations, we calculate the energy flux from a radiative dipole centered in the EML to the top cathode, capping layer, and a single nanoparticle for $\lambda = 500$ nm. This flux is shown in Fig. 7.12 for SPP and PEP devices. The intensity of plasmon peaks at $u \sim 1.2$ and 1.7 is similar for both devices, but the plasmonic mode in the PEP is shifted to slightly higher u . This is the result of the anti-crossing between the metal SPP and the ETL exciton. At wavelengths closer to the BPyTP2 exciton energy, the PEP dispersion flattens out, pushing the coupled plasmonic mode to slightly higher k . Typically, a higher k , i.e. farther from

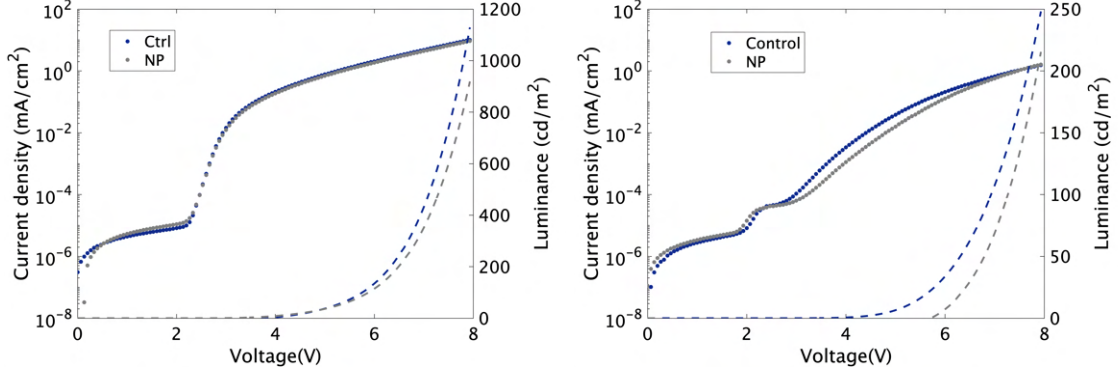


Figure 7.8: J-V-L data for T-E only devices. PEP (*left*) and SPP (*right*) device J-V-L characteristics with (gray) and without nanoparticles (blue).

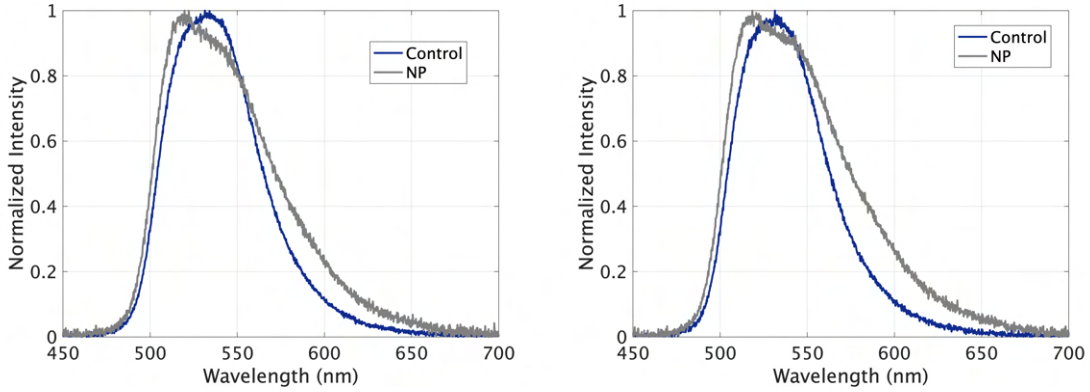


Figure 7.9: EL spectra for T-E only devices. PEP (*left*) and SPP (*right*) devices with (blue) and without nanoparticles (gray).

the light cone, evanescent mode would be more difficult to outcouple. Thus, we attribute the observed outcoupling enhancement in PEP devices to the PEP-nature of the plasmonic modes. To characterize the PEP outcoupling, we measure optical samples, where the ETL exciton PL is excited directly. The control samples show that the PEP has a much stronger PL signal than the SPP, shown by the signal at $k > 1$. The measured k cuts off at $k \sim 1.5$ as this is the limit of the microscope's numerical aperture. In nanoparticle samples, the $k > 1$ signal for both samples decreases slightly as the nanoparticles scatter light into visible low- k modes. We see from Fig. 7.6 that the enhanced scattering ($1.5\times$ and $1.05\times$) between the control and nanoparticle samples agrees with the observed luminance enhancements ($1.4\times$ and $1.2\times$) for PEP and SPP devices, respectively.

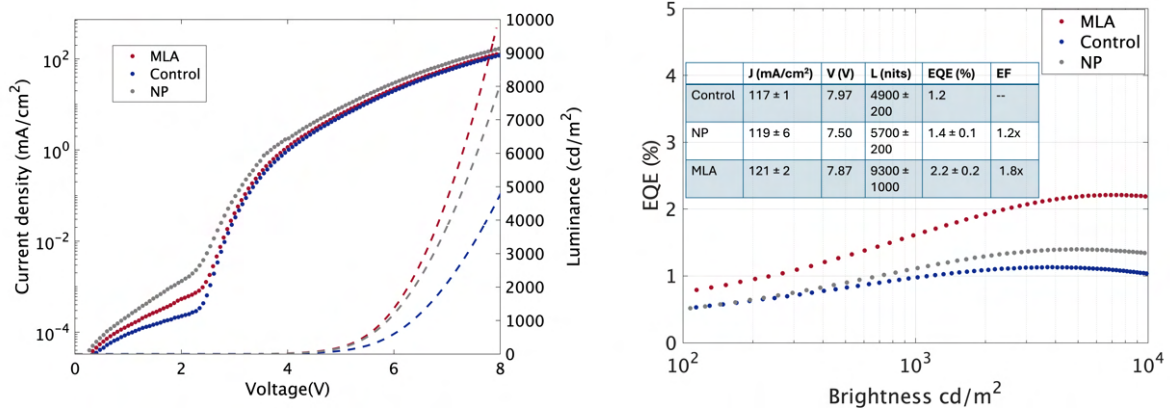


Figure 7.10: **Summary of J-V-L and EQE for PEP devices.** J-V-L (*left*) and EQE (*right*) for PEP control, MLA, and nanoparticle devices. The inset table summarizes the enhancement of each structure.

The improved outcoupling efficiency in the PEP device is the result of strong coupling between the metal SPP mode and the ETL exciton, characteristic of the PEP mode. This is observed in the wavelength-dependent PL shown in Fig. 7.7. The full Fourier space $k_{\perp}$ vs. $k_{\parallel}$, integrated over all wavelengths, is shown in the insets. At lower wavelengths, the cathode SPP is strongly coupled to the BPyTP2 exciton. The coupling strength decreases at longer wavelengths, further from the BPyTP2 exciton energy. Thus, at long wavelengths the plasmonic mode becomes more SPP-like. In the SF3Trz, whose exciton sits at a higher energy than the low-energy absorption edge of silver, there is no strong coupling between the ETL and metal. As a result, we observe no wavelength-dependent scattering behavior. Additionally, the observed scattering is comparable between the SPP sample and the PEP sample at long wavelengths. This provides evidence that the observed improvement in PEP vs SPP devices is due to coupling between the metal plasmonic modes and organic ETL excitons.

We also investigate the performance of a nanoparticle enhancement layer on a T-E only device with a reflective bottom Al contact. We find that the nanoparticle layer leads to a decrease in η_{EL} and L in both PEP and SPP devices. A large fraction of SPP modes are coupled to the thick, bottom Al and cannot be extracted by the distant nanoparticle layer. In practical applications, such as displays, where T-E is required or preferred, nanoparticle structures should be used with

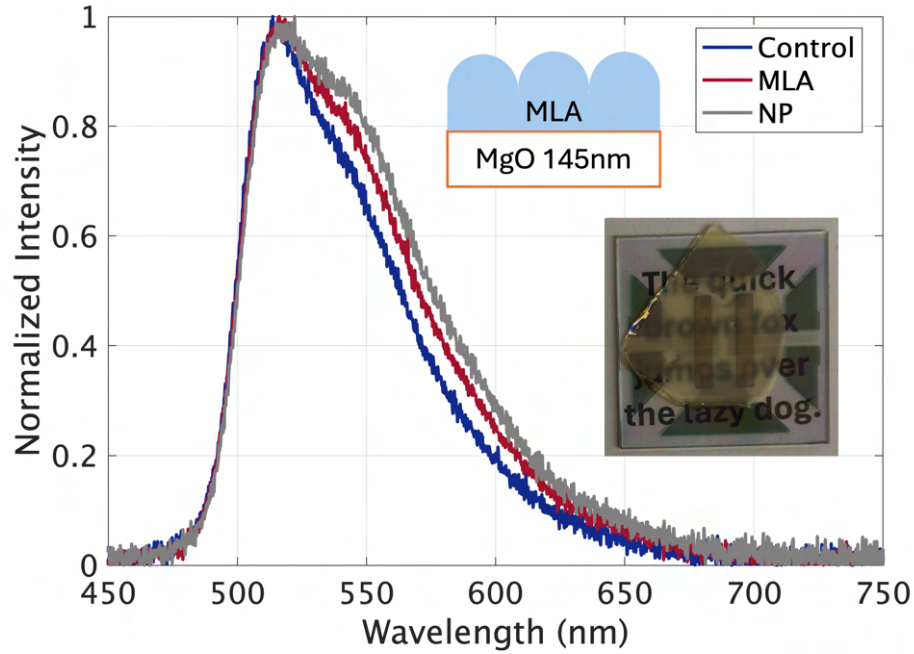


Figure 7.11: EL spectra for PEP devices. Emission spectra for control (blue), MLA (red), and nanoparticle (gray) PEP devices at $J = 2\text{mA}$. The inset figures show a schematic of the MLA and capping structure (*top*) and a photograph of an MLA applied to a T-E + B-E device (*bottom*).

engineered anode structures to prevent SPP loss at the bottom contact, such as a sub-anode grid, or transparent electrode paired with a backsurface reflector [30, 101]. Additionally, engineered bottom contacts, such as ITO/Ag/ITO structures which have previously demonstrated operational stability and PEP coupling, could be modified to satisfy T-E only architectures [23]. The observed change in emission spectrum is expected since scattering structures inherently decrease the strength of the cavity, weakening the cavity effects on emission. The addition of nanoparticle scattering centers effectively disrupts the cavity, recovering the standard $\text{Ir}(\text{ppy})_3$ emission spectrum, with visible vibronic modes. This potentially poses a problem for display applications where a narrow spectrum is preferred, but it is an unavoidable consequence of plasmon outcoupling structures which require scattering of the trapped mode.

We also investigate the use of an MLA attached directly to the capping layer of the device. We increase the thickness of the MgO capping layer to protect the device from the MLA polymer prior to curing. Previous work using a MLA on T-E devices has achieved EQE enhancements

ranging from $1.1\text{--}1.5\times$ for MLAs with $n = 1.5 - 1.7$ [108, 127, 128]. Here, we use a high index polymer (see 7.2.1) with $n \sim 1.85$. We see that the $1.9\times$ outcoupling enhancement of the MLA outperforms the nanoparticle enhancement layer and provides greater enhancement than in previous works. The width of the spectrum for MLA devices falls between the control and nanoparticle devices since the scattering is increased with the 75 nm nanocubes.

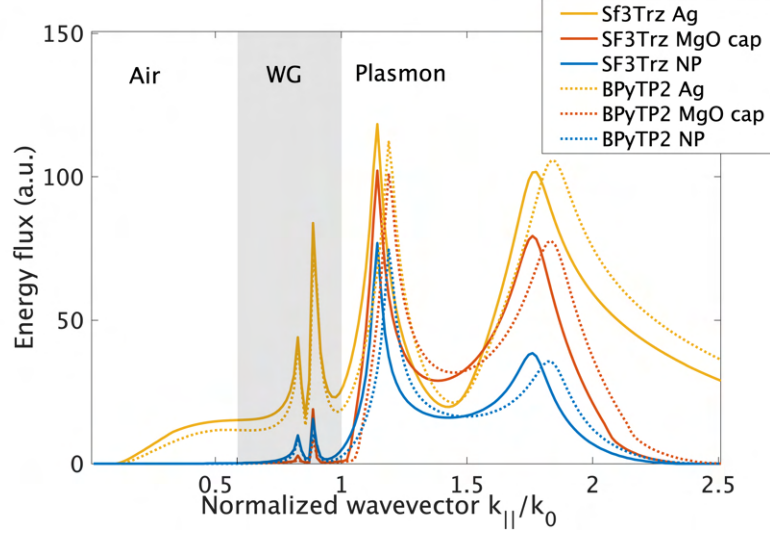


Figure 7.12: **Calculated energy flux for SPP and PEP devices.** Calculated energy flux into the cathode (yellow), capping layer (orange), and nanoparticle (blue) for SPP (solid) and PEP (dotted) devices for 500 nm photons. The plasmonic modes in the PEP device are shifted to a higher k .

The thin ETL structure completely suppresses waveguided modes between the ITO anode and Ag cathode. Instead, they couple to the plasmonic mode. The MgO capping layer does trap some waveguided modes, $0.58 < u < 1$, which are then propagated into the higher index MLA for devices with the additional external enhancement layer. The calculated flux to the top layers of the control and MLA-enhanced stack are shown in Fig. 7.13. When the MLA is added, the fraction of light waveguided in the MgO/MLA layer decreases from 15% to 10%. In the control device, however, waveguided light cannot be extracted; the MLA can scatter these modes into visible modes, thus leading to the observed enhancement. The majority of the modes outcoupled by the MLA modifies the exit angle of these modes, thus leading to increased extraction to air and the observed enhancement. The majority of the modes outcoupled by the MLA are waveguided

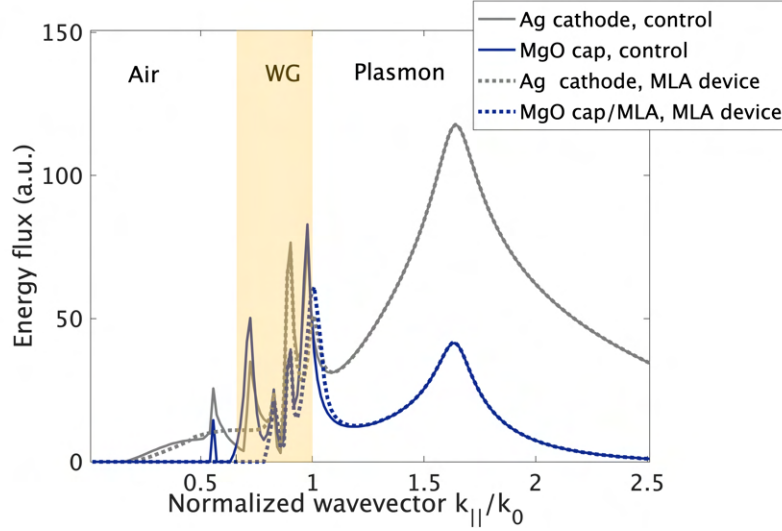


Figure 7.13: Calculated energy flux in the PEP device cathode, capping, and MLA. The flux is computed for $\lambda = 500\text{nm}$.

modes with $u < 1$, but it is possible that some plasmonic modes are outcoupled as well. The commercial high-index polymer used is doped with 20nm diameter TiO_2 nanospheres. The optimal diameter for nanoparticle scatterers is on the order of $\sim 100\text{nm}$, so scattering from within the MLA is likely low. The performance of the MLA could potentially be enhanced by replacing the scattering centers with larger diameter nanoparticles, which has been demonstrated in B-E devices previously [129].

7.3 Conclusions and Further Advances

We demonstrate that plasmonic mode outcoupling efficiency can be improved by utilizing PEP-forming materials at the metal-organic interface. In devices with nanoparticle scattering layers applied to the top contact, PEP devices demonstrate a $1.4\times$ enhancement in L , while SPP devices only show $1.2\times$ enhancement. Additionally, the SPP devices show significant degradation of the J-V characteristic after nanoparticle coating. In T-E only devices, the addition of nanoparticles leads to a slight drop in device luminance since nanoparticles can only outcouple local plasmonic modes. Both limitations suggest that alternative outcoupling

designs may be needed for practical applications, including ways to integrate PEP-scattering architectures to the reflective bottom contact. We demonstrate that a high-index MLA doped with 20nm diameter nanospheres can achieve an EQE enhancement of $1.9\times$. We expect this enhancement could be improved by tuning the size and material of doped nanoparticles in the MLA.

Contributions: C.E.A. fabricated all devices, MLAs, and optical samples. Sritoma Paul fabricated the low-angle sidewall ITO substrates. Haonan Zhao (H.Z.) built the optical set-up. C.E.A. collected all device and optical data. C.E.A. and S.R.F. analyzed the data.

CHAPTER 8

Engineered Solutions for White OLEDs

As of the writing of this work, OLEDs comprise a 55 billion dollar industry, primarily dealing in portable displays. Many of the attributes that make PHOLEDs desirable for display applications, such as a high internal quantum efficiency, wide color gamut, and accurate color rendering, are also desirable for solid-state lighting applications, which require white light [1, 130–134]. The choice of lighting source has been shown to impact room aesthetics and building power consumption, with the studies showing that the quality of environmental lighting can affect psychological functioning, such as moods [135, 136]. WOLED illumination sources can provide diffuse light suitable for luminaires desired to be large area, flexible, and transparent [1, 137]. The tunability of emissive organic molecules enables a range of aesthetic qualities, including a high CRI and color temperature tunability, without sacrificing efficiency [138–141]. White light is generated by exciting a combination of red, green, and blue emitting molecules placed in close enough physical proximity that individual colors cannot be resolved. This can be achieved by either vertically stacking separate color emitters, a “stacked” geometry, or by placing individual emissive layers next to one another horizontally, a “side-by-side” (SxS) geometry.

Given the promising physical attributes and previously tested device designs used for achieving quality white light, one might expect the WOLED lighting industry to be as far along the path to commercialization as the display industry, and, in fact, WOLED lighting is currently commercially available. An architectural OLED luminaire, created by the haute couture lighting firm BLACKBODY®, installed at Hotel Le Louis Versailles Château in Paris, France, is shown

in Fig. 8.1. It is perhaps fitting that a beautiful OLED fixture can be found installed in a luxury hotel meters from the opulent Château de Versailles, while OLED lighting remains uncommon in most lighting applications.



Figure 8.1: **OLED lighting fixture.** An OLED lighting fixture at Hotel Le Louis Versailles. Photo courtesy of BLACKBODY®.

Inorganic LEDs already account for many solid-state lighting needs, meaning that OLEDs must be competitive in cost to penetrate the existing market [142]. Lighting cost, typically reported as \$/klm, can either be reduced by decreasing manufacturing throughput costs, or by increasing the luminance per lighting fixture. Additionally, blue PHOLED lifetime still remains an issue for all-color OLED applications. In this chapter, we will describe two different solutions for generating white light using OLEDs that offer pathways for increasing WOLED luminance, improving color-stability, and extending lifetime. In Sec. 8.1 we will introduce a method for SxS positioning of monochromatic blue and yellow phosphorescent OLED stripes that are combined to create tunable white light, using a high-resolution mechanical peel-off patterning method. In Sec. 8.2 we will demonstrate a white emitting PHOLED comprising stacked red, green, and blue elements that exploits PEPs to extend the operational lifetime of the blue element such that all color emissive layers degrade at the same rate. Both of these methods make progress in addressing

the issues that currently limit OLED lighting. In Sec.8.3 we will expand upon ways these two technologies can be further developed.

8.1 Side-by-side OLEDs

This section was previously published, in part, as [143] C. Arneson, X. Huang, and S.R. Forrest, “Solid-State Lighting Using Side-by-Side White Phosphorescent Organic Light-Emitting Diodes” *ACS Photonics* (2023). DOI: [10.1021/acsphotonics.2c01698](https://doi.org/10.1021/acsphotonics.2c01698)

A SxS geometry, in which two or three separately energized monochromatic emitter stripes are horizontally positioned relative to one another, enables color tunability under normal device operating conditions, while also affording the possibility of 100% internal efficiency when triplet-controlled emitting molecules are employed in the individual color elements [144–147]. Color tunability has also been achieved in devices where emission color is dependent on applied voltage [148, 149]. To generate the desired colors, high voltage or alternating current may be required. Current methods for SxS organic device patterning include vacuum deposition through fine metal shadow masks, direct patterning via organic vapor-jet printing, solution processing using ink-jet printing or microchannels, film transfer via laser-induced thermal imaging, and post-deposition processing via chemical lift-off [144–147, 150–162]. A somewhat less complex and damage-free method that can achieve photolithographic resolution is mechanical peel-off, which has recently been demonstrated for patterning organic photovoltaics and perovskite light-emitting devices [163, 164]. In this work, we demonstrate two-color, SxS WOLEDs deposited via vacuum thermal evaporation and subsequently patterned using mechanically peeled-off films. This method allows for multi-layer patterning with micron-scale resolution while avoiding precise alignment of shadow masks, or exposing the individual color-emitting stripes to destructive solvents used in conventional photolithography. That is, in contrast to photolithographically patterned, chemical lift-off methods, all chemical processing steps occur

prior to organic deposition [151]. As such, material solubility and solvent orthogonality do not need to be considered [165], thus eliminating many processing constraints. We demonstrate all-phosphorescent white emission from electrically isolated, parallel blue and yellow emissive stripes whose CCT can be tuned from 2000 – 8000 K while maintaining CRI > 75. There is no sacrifice to device efficiency or operational device lifetime for the patterned device stripes when compared to control devices patterned using conventional, millimeter-scale shadow masks.

8.1.1 Methods and Experimental Set-up

Glass substrates (0.7 mm thick) with pre-patterned, 150 nm thick ITO anodes ($15 \Omega/\text{sq}$, Lumtec) were cleaned for 3 min each in sonicated tergitol:water (1:100, Sigma Aldrich), DI water, acetone ($2\times$), and isopropanol solution at 160°C ($2\times$), and dried with ultrapure N_2 gas. A Micro90:isopropanol:DI water 50:475:475 μL mixture was sonicated for 20 min and then deposited on substrates for peel-off patterning via spin coating at 3000 rpm. Polyimide (PI2611, HD Microsystems) was spin-coated at 5000 rpm, and soft-cured at 90°C and 150°C for 90 s each, followed by a hard bake ramped from 50 to 350°C at a rate of 450°C h^{-1} , and held at 350°C for 30 min. Next, HMDS was applied to improve wetting between the polyimide surface and photoresist. Photoresist (SPR220-7.0, MEGAPOSITTM) was spin-coated at 3000 rpm and soft-baked for 5 min at 115°C . Samples were then exposed via contact lithography using a mask aligner (Karl Suss MJB-3) and a custom chrome mask plate. The photoresist was developed (AZ[®]726, MicroChemicals) for 80 s ($2\times$). The samples were then exposed to $\text{C}_4\text{F}_8:\text{He}:\text{O}_2$ 14:56:50 sccm plasma in a 30 mTorr chamber with a transformer coupled plasma power of 500 W, and 25 W bias power (LAM 9400 SE, LAM Research Corp.) for 990 s. Following polyimide etch, samples were dipped in acetone for 30 s to remove excess photoresist. The initial cleaning process was repeated without sonication to prevent premature polyimide peeling.

Control and SxS devices were grown via VTE (Ångström Engineering). The ITO edge contacts were shielded by a centimeter-scale shadow mask during organic film deposition. All organics were deposited at rates ranging from 0.1 to 1.0 Å s^{-1} at a base vacuum of $< 2\times 10^{-7}$ Torr.

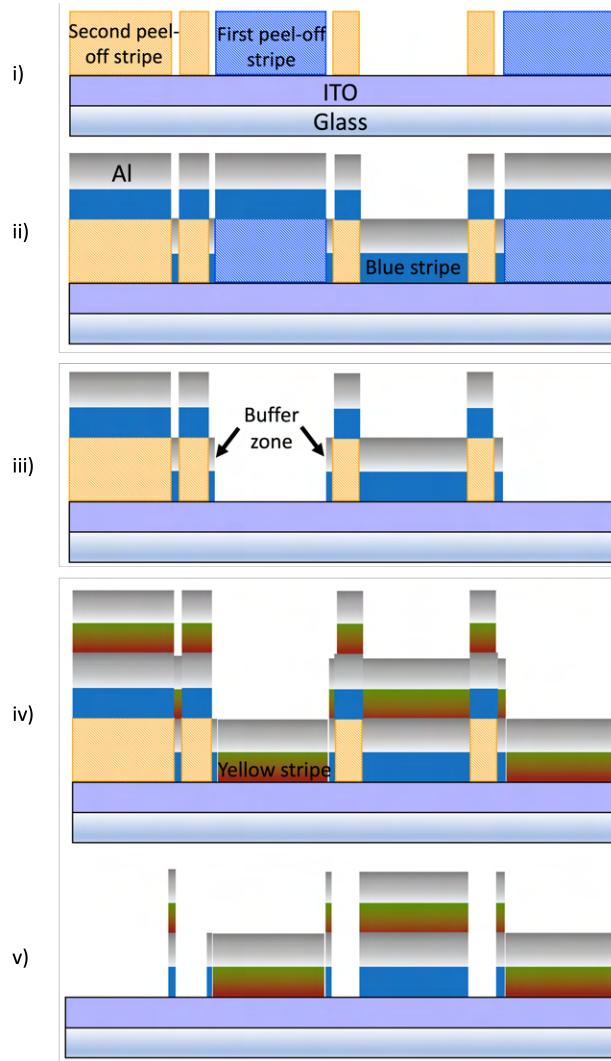


Figure 8.2: **Peel-off patterning process flow.** A schematic side view of the 2-stripe peel-off patterning of a side-by-side WOLED. i) Polyimide peel-off stripes are deposited and patterned on an ITO-coated glass substrate. ii) The blue organic stack and metal cathode are deposited. iii) The first polyimide stripe is peeled off. iv) The yellow organic stack and metal cathode are deposited. v) The final polyimide stripes are peeled off, separating the individual color elements, and anode and cathode contacts.

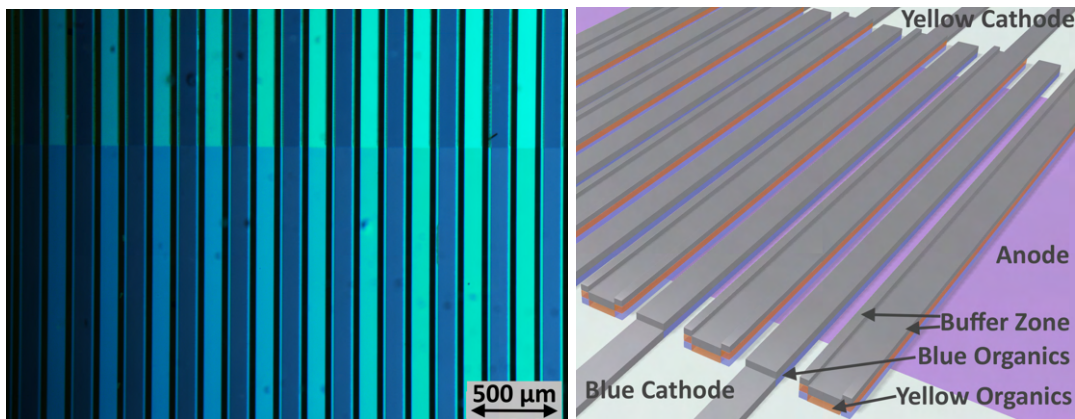


Figure 8.3: **Microscope image of SxS OLED.** Microscopic image (*left*) of the top edge of the striped device active area under fluorescent illumination. The blue stripe, (appearing lighter), is completely isolated from the yellow stripe (appearing darker), by a 25 μm space and a 25 μm electrically isolated buffer stripe. Illustration of the device active area (*right*).

First, the blue sub-element and control device were grown as follows: 10 nm HATCN (UDC) HIL/50 nm mCBP (UDC):Ir(dmp)₃ (UDC) 8-18 vol% blue EML/5 nm BAq (UDC) buffer layer/40 nm BPyTP2 (Lumtec) ETL/1.5 nm Liq (Lumtec) EIL/100 nm Al (Alfa Aesar) cathode. During cathode deposition, a millimeter-scale shadow mask covered the anode contacts to define the area of the control devices. Control device area, defined by the overlap between the ITO substrate pattern and an Al mask, was 0.2 mm². SxS device area, defined by the overlap between the ITO pattern and peel-off pattern was 0.3 and 0.33 mm² for yellow and blue elements, respectively. The first peel-off stripe was removed in a N₂-filled glove box with < 0.1 ppm H₂O and O₂ gripped at the substrate edges using tweezers (see Fig. 8.2).

Next, the yellow sub-element was deposited on control and SxS devices with the blue sub-element as follows: 5 nm HATCN HIL/30 nm NPD (UDC) HTL/5 nm Tris-PCz (Lumtec) exciton blocking layer/12 nm mCBP:PQIr (UDC) 10 vol% red EML/12 nm mCBP:Ir(ppy)₃, Lumtec) 7.5 vol% green EML/5 nm BAq buffer layer/12 nm mCBP:PQIr 10 vol% red EML/60 nm BPyTP2 ETL/1.5 nm Liq EIL/100 nm Al cathode. The following materials were purified via thermal gradient sublimation (see Sec. 1.2) prior to deposition: Ir(dmp)₃, mCBP, BPyTP2, and Tris-PCz. The second peel-off stripe was removed in the glove box, and the control and striped devices were encapsulated using a 0.5 mm thick cover glass slide sealed along

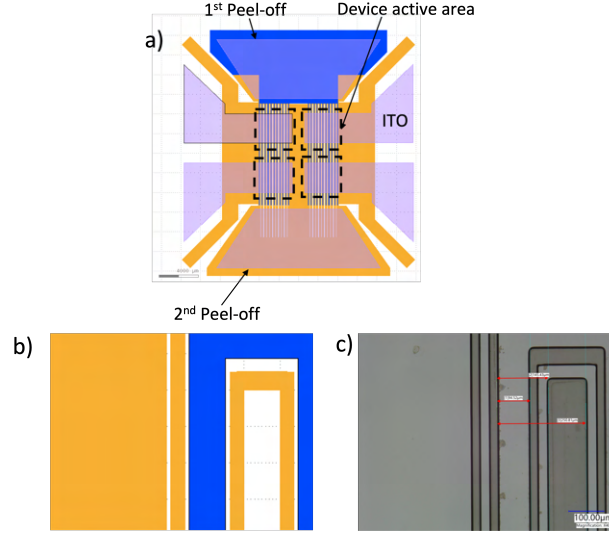


Figure 8.4: Schematic drawing and microscope image of patterned polyimide. Top view of the patterned substrate (a, *top*). Zoomed in view of the stripe schematic top view (b, *bottom left*). Microscope image of patterned polyimide of the same area shown in the schematic (c, *bottom right*).

its periphery with UV-curing epoxy (OG159-2, EPO-TEK®) for 99 s ($2\times$) under a pulsed UV lamp (RC-500B, XENON Corp.). An Al foil was used to protect the device active area from UV exposure.

Current-voltage-luminance characteristics and device spectra were measured following the procedure detailed in Sec.3.2. Error bars were calculated from the standard deviation from four devices. Since the photodiode area is larger than the device active area, we assume all light emitted in a 2π solid angle from the bottom of the glass substrate is collected. To account for light emitted in a 4π solid angle, a scaling factor is calculated from the ratio of device efficiency with and without an integrating sphere. The parameter analyzer is equipped with 4 source-measuring units to allow the yellow and blue sub-elements to be separately and concurrently probed. SxS devices are biased using a separate cathode probe for each color, and a common anode probe. Devices were aged following the procedure detailed in Sec. 3.6.2. Microscope images were taken using a Nikon SMZ25 stereoscope equipped with a fluorescent light source with a 375 nm bandpass excitation filter and a 435 nm long pass emission filter and a Keyence VHX microscope.

The micrograph in Fig. 8.3 shows a detailed image of a two-color SxS WOLED with isolated,

individually addressable, $100\text{ }\mu\text{m}$ wide blue and yellow emissive stripes at a $50\text{ }\mu\text{m}$ pitch, and fabricated using peel-off patterning. To realize two peel-off stripes necessary to sequentially pattern both color emitters, a $25\text{ }\mu\text{m}$ wide buffer zone is included between the stripes, as illustrated in Fig. 8.3. The full device structure is shown in Figs. 8.2 and 8.4.

When forward biased and viewed in the far-field, the emission from individual stripes cannot be resolved, resulting in diffuse white light shown in Fig. 8.5. Illumination of a printed image by a 0.63 cm^2 device is also shown.

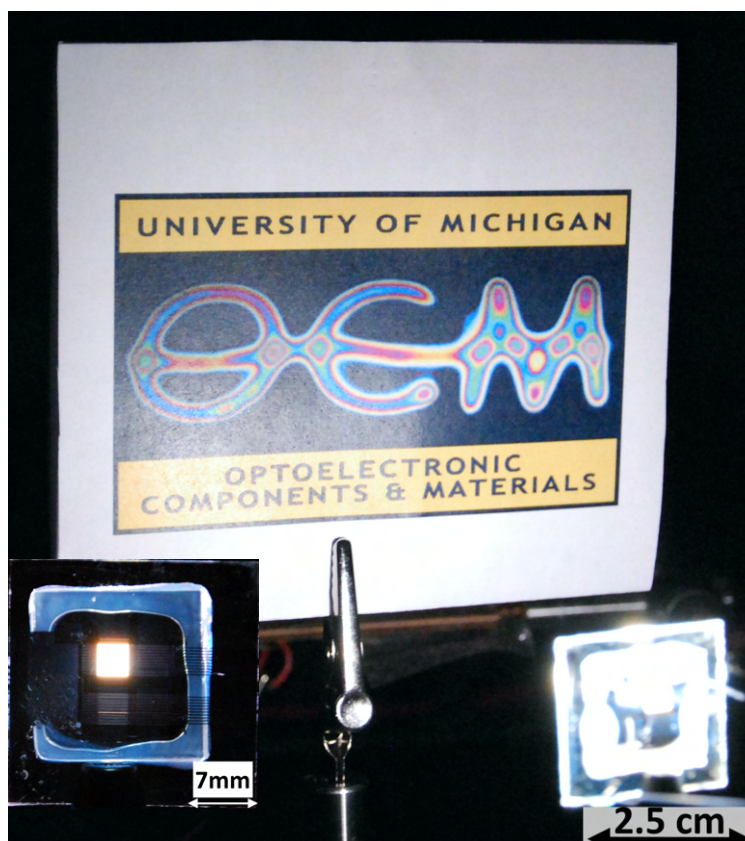


Figure 8.5: Images of illuminated devices. Photograph of the Optoelectronic Components and Materials group logo illuminated by a 0.63 cm^2 device. *Inset*: Photograph of the device in forward bias.

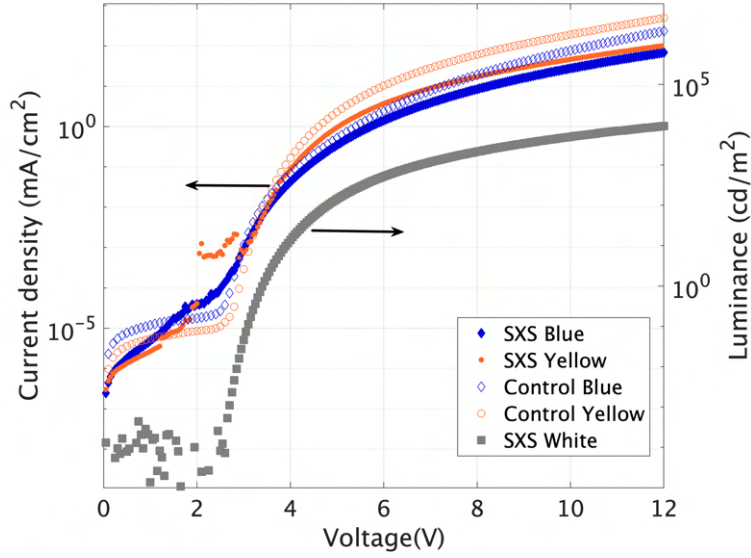


Figure 8.6: **J-V characteristics for SXS OLED.** J-V characteristics for single color control devices and for striped devices under concurrent bias. Luminance for the total SxS white device is also shown.

8.1.2 Results

The J-V-L characteristics for simultaneously biased sub-elements, and discrete control devices consisting of only a single color emitter patterned using standard millimeter-scale shadow mask techniques, are shown in Fig. 8.6.

The J-V scan is taken concurrently for the separate colors, with the same bias voltage applied to all stripes. We observe no significant differences in the J-V characteristic between the SxS devices and the control. The forward-viewing luminance for the SxS WOLED reaches 3000 cd m^{-2} at $8.6 \pm 0.3 \text{ mA cm}^{-2}$, with LPE and EQE of $\eta_{LP} = 5.3 \pm 0.2 \text{ lm W}^{-1}$ and $\eta_{EL} = 8.5 \pm 0.6 \%$, respectively. The EQE for white emission falls between that calculated for each separate sub-element, as expected (see Fig. 8.7). A more accurate characterization for lighting appliances is their total emission, not just that in the forward-viewing direction. For this purpose we measure the efficiency using the addition of IMF between the substrate and the detector, to achieve $\eta_{EL} = 22.4 \pm 0.6 \%$ and $\eta_{LP} = 16.0 \pm 0.2 \text{ lm W}^{-1}$ at 3000 cd m^{-2} .

When the luminance is reduced to 1000 cd m^{-2} , $\eta_{EL} = 25.1 \pm 0.2 \%$ and $\eta_{LP} = 22.3 \pm 0.3$

Table 8.1: Device efficiencies at various L , for both 2π and 4π collection angles.

L_0 (cd m ²)	V (V)	J (mA cm ⁻²)	η_{EL} (%)	η_{EL} w/ IMF (%)	η_{LP} (lm W ⁻¹)	η_{LP} w/ IMF (lm W ⁻¹)
1000	6.6 ± 0.1	5.4 ± 0.1	11.7 ± 0.2	25.1 ± 0.2	9.0 ± 0.3	22.3 ± 0.3
2000	7.6 ± 0.2	12.5 ± 0.3	9.6 ± 0.1	23.6 ± 0.1	6.7 ± 0.1	18.5 ± 0.1
3000	8.4 ± 0.8	22 ± 2	8.1 ± 0.6	22.4 ± 0.6	5.2 ± 0.2	16.0 ± 0.2

lm W⁻¹. These results are summarized in Table 8.1. At both 1000 and 3000 cd m⁻², the current ratio through the blue and yellow sub-elements is $I_B/I_Y \sim 0.5$, corresponding to a CRI ~ 78 .

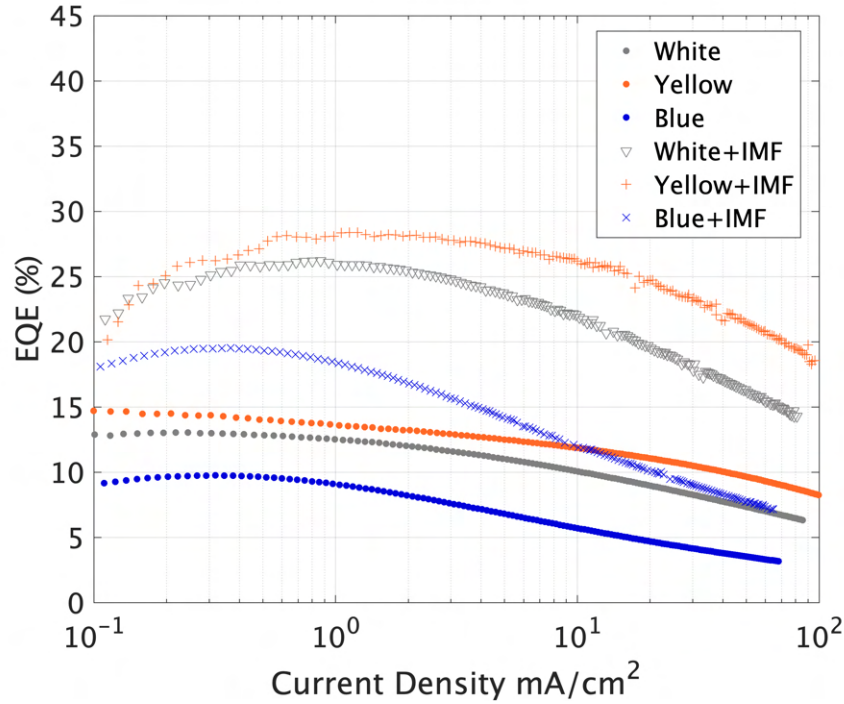


Figure 8.7: SxS device EQE. External quantum efficiency with and without IMF for striped devices under concurrent bias.

The spectra for individual color elements, with equivalent injection currents, are shown in Fig. 8.8, with CIE 1960 color coordinates [166] of $(u, v) = (0.12, 0.31)$ and $(0.33, 0.36)$ for the blue and yellow sub-elements, respectively. The spectral shift vs. current across both sub-elements is shown in Fig. 8.9. The CIE coordinates are $(0.23, 0.34)$ at 1000 cd m⁻² and $(0.21, 0.34)$ at 3000

cd m^{-2} , resulting in a nearly imperceptible color shift of $(\Delta u, \Delta v) = (0.014, -0.002)$. At 100 mA cm^{-2} , $\text{CRI} = 81 \pm 1$ and $\text{CCT} = 3800 \pm 600 \text{ K}$.

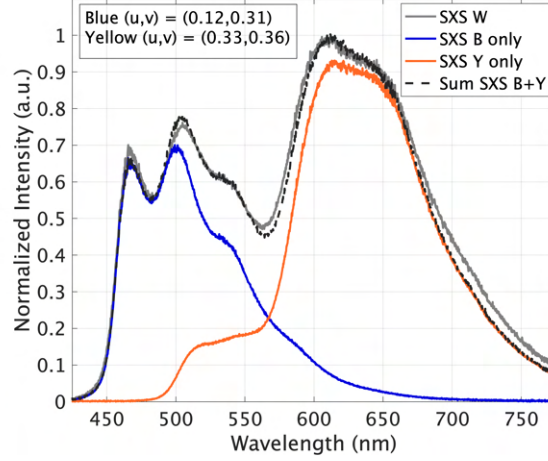


Figure 8.8: **SxS device EL spectra.** Electroluminescent spectra for SxS blue stripes only, SxS yellow stripes only, and all stripes simultaneously energized. The SxS white spectrum is normalized to the maximum intensity, while the SxS blue and SxS yellow stripes are normalized such that the sum of the two spectra matches the white spectrum.

By varying the ratio of current applied to the blue and yellow stripes, the chromaticity coordinates are linearly translated between the colors of the individual blue and yellow sub-elements while keeping the luminance constant at 1000 cd m^{-2} , as shown in Fig. 8.10.

As the proportion of blue emission increases, CCT also increases, as shown by the plot of CCT and CRI vs. the ratio of the blue to yellow current, I_B/I_Y , in Fig. 8.11. Emission spectra at each point are shown in Fig. 8.12.

At $I_B/I_Y < 3$ corresponding to $\text{CCT} < 6000 \text{ K}$, the shortest distance between the SxS CIE coordinates and the Planckian locus is $\Delta uv \leq 0.004$, defined in Eq. 3.25. At the point of intersection between CRI and CCT in Fig. 4b, $\text{CRI} = 78 \pm 1$ and $\text{CCT} = 3800 \pm 600 \text{ K}$, with color coordinates $(0.23, 0.34)$. The maximum $\text{CRI} = 86 \pm 1$ is reached at $\text{CCT} = 2000 \pm 200 \text{ K}$ and color coordinates $(0.30, 0.36)$ with $\Delta uv = 0.0007$ due to the dominance of the yellow stripe emission.

The SxS white device was aged under a constant current density of $J_{\text{SxS}} = 7.6 \text{ mA cm}^{-2}$,

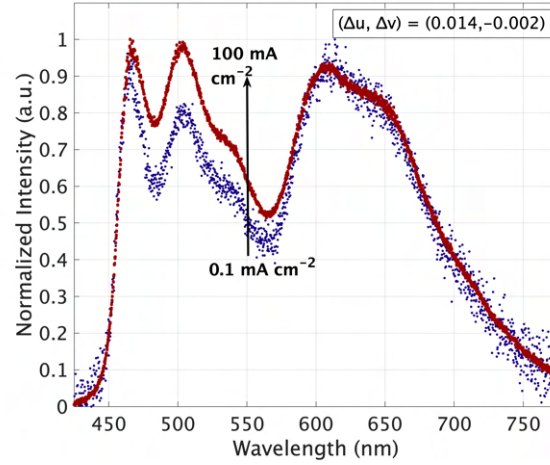


Figure 8.9: Current-dependent EL spectral shift. EL spectral shift from low to high current in SxS devices.

corresponding to an initial luminance of $L_0 = 1000 \pm 70 \text{ cd m}^{-2}$, until at time, T_{95} , the total luminance was reduced to $0.95 \times L_0$. Luminance decay is normalized to 0.98 to account for an observed 2% burn-in. To further accelerate degradation, from this point on, the current density was increased to $J_{SxS} = 50 \text{ mA cm}^{-2}$, which corresponds to a current ratio $I_B/I_Y = 0.02$, bringing the initial luminance back to $L_0 = 3000 \pm 70 \text{ cd m}^{-2}$. The control devices are aged under the same conditions, with $J_B = 4.5 \text{ mA cm}^{-2}$ and $J_Y = 6.0 \text{ mA cm}^{-2}$ for 1000 cd m^{-2} and $J_B = 17.6 \text{ mA cm}^{-2}$ and $J_Y = 19.6 \text{ mA cm}^{-2}$ for 3000 cd m^{-2} . An empirical acceleration factor [54, 167] is used to scale the test conditions to $L_0 = 1000 \text{ cd m}^{-2}$, conditions, see Eq. 3.36 and Table 8.2.

Figure 8.13 shows $L(t)$, where t is the aging time. We find that $T_{95,SxS} = 22.7 \pm 0.05 \text{ h}$ for the SxS white device, and $T_{95,B} = 7.9 \pm 0.05 \text{ h}$ and $T_{95,Y} = 22.9 \pm 0.05 \text{ h}$ normalized to $L_0 = 1000 \text{ cd m}^{-2}$, for the blue and yellow control devices, respectively. The spectral shift of the SxS device at T_{95} is $(\Delta u, \Delta v) = (0.005, 0.0002)$, see Fig. 8.14 5b, increasing to $(\Delta u, \Delta v) = (0.04, 0.004)$ at T_{65} .

From these data and their fits, we obtain $T_{70,Blue} = 265 \pm 2 \text{ h}$, $T_{70,Yellow} = 656 \pm 6 \text{ h}$, and $T_{70,SxS} = 330 \pm 3 \text{ h}$ for $L_0 = 1000 \text{ cd m}^{-2}$ (see Eq. 3.37, Table 8.2, and Fig. 8.15 for details).

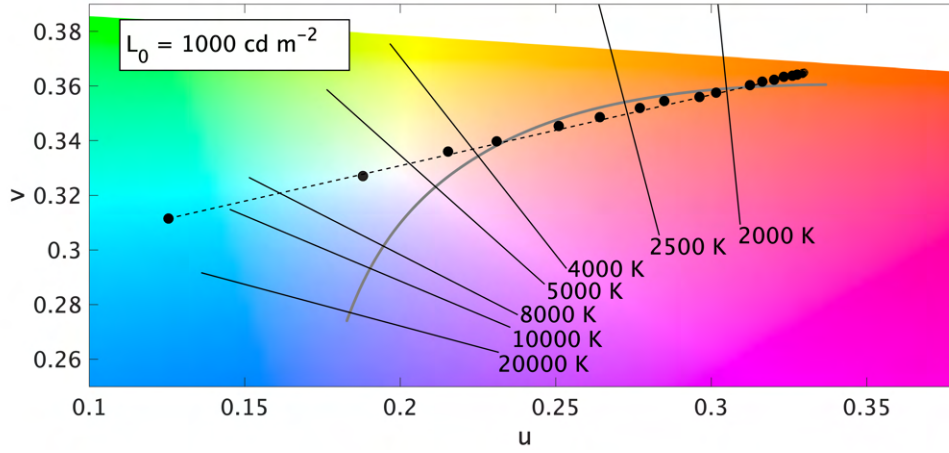


Figure 8.10: CIE and CRI color tunability of the SxS device. The color tuning range of the SxS white PHOLED across the CIE 1960 chromaticity color gamut at a luminance of 1000 cd m^{-2} . The Planckian locus is shown as the gray curve. The maximum CRI is achieved at the intersection of the Planckian locus and the dashed line. CCT isotherms are indicated by the solid black lines.

Table 8.2: Fitting parameters for Eq. 3.37.

	τ	β	ξ
Blue Control	$6.438 \times 10^6 \text{ s}$	0.5367	1.85
Yellow Control	$1.15 \times 10^7 \text{ s}$	0.653	1.25
SxS	$3.411 \times 10^6 \text{ s}$	0.9774	1.21

8.1.3 Discussion

The mechanical peel-off method for patterning SxS WOLEDs offers a non-destructive approach to high resolution, multi-resist-level patterning of striped devices. The peel-off approach has previously been used to pattern organic photovoltaics on substrates as large as 25 cm^2 , and can be scaled up to larger substrates using a roller to minimize stress on thin peel-off stripes [164]. Such equipment can be readily incorporated into a N_2 environment, which is essential to prevent contamination during the device fabrication process [152].

The individual color elements patterned into SxS striped emitters show no difference in spectral, J-V-L, or lifetime characteristics compared to devices prepared using conventional shadow mask patterning technology. Furthermore, peel-off avoids exposure to potential degradation from

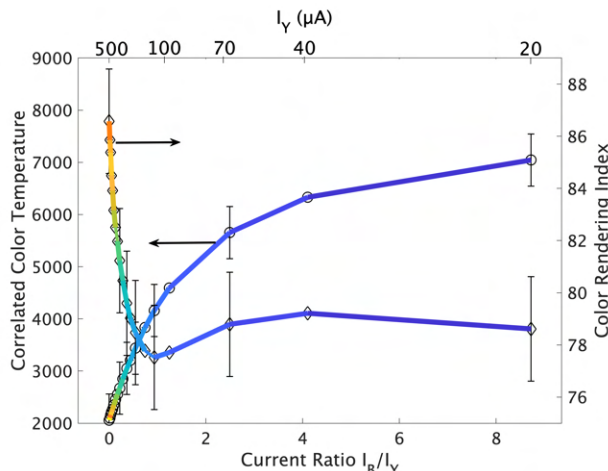


Figure 8.11: **CRI and CCT vs I_B/I_Y .** Color parameters as a function of the ratio of current separately applied to the blue and yellow stripes, respectively. The total luminance is held constant at 1000 cd m^{-2} . The top horizontal axis shows the corresponding values of I_Y .

solvents used in lithographic patterning of the OLED active area. By patterning two separate peel-off stripes before the organics are deposited, we fabricated two isolated color stripe arrays without exposing the devices to atmosphere or chemical release agents. Additionally, the striped device design eliminates color bleeding due to electrical crosstalk [151] from unintended current paths from one color element to its neighbor. This allows the concurrently contacted color elements to maintain a high EQE, color purity and consequently a high CRI. Because the peel-off stripes are patterned prior to device deposition, adding multiple peel-off steps does not introduce additional processing steps, as are required for photolithographically patterning two-color devices.

There is apparently no increase in leakage current when an additional peel-off stripe to isolate color elements is included in the process. This is in contrast to, chemical lift-off patterning where increasing the number of patterning iterations tends to increase the opportunity for device exposure to solvents, thus further degrading device performance. Thus, peel-off enables a flexibility in organic device and process design unavailable to more conventional methods of patterning. In this context, previous work demonstrating a SxS perovskite LED geometry and peel-off patterning [163] exhibit a $> 103\times$ increase in leakage current attributed to electrical cross-talk and imperfect edges [151, 152].

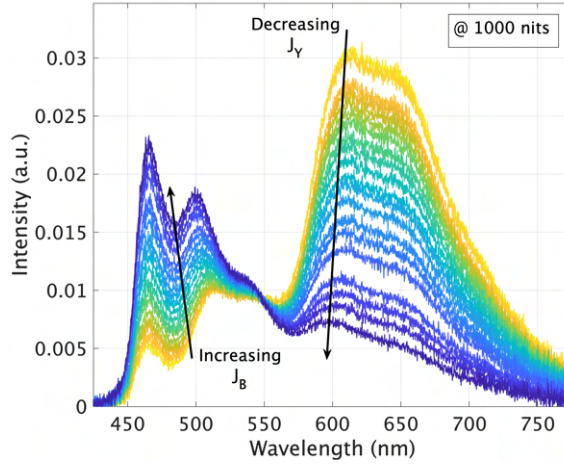


Figure 8.12: **Spectrum tunability.** EL spectral shift vs. current ratio of the blue to the yellow PHOLEDs.

Figure 8.8 shows that there is no mixing between blue and yellow spectra when a single color stripe is activated. The $50\ \mu\text{m}$ pitch provides uniform white light, as is shown in Fig. 8.3, although we find that the pitch of the emissive stripes can be decreased to $10\ \mu\text{m}$. Using IMF, we achieve an increase in EQE of $2.6\times$ compared to the device lacking external optical outcoupling structures. The peak shift in EQE measured with IMF is the result of increased outcoupling, and thus increased luminance at low current densities. In lighting applications, an external outcoupling structure such as a MLA can be used to achieve an increase in EQE of up to $1.5\times$, while also color mixing to create uniform white light [168, 169]. Luminaires and other lighting fixtures are used to direct all light emitted in a 4π solid angle into the half-space occupied by the room it illuminates [1]. In our demonstration, the SxS device area is $0.063\ \text{cm}^2$ is much less than the substrate area of $6.5\ \text{cm}^2$; hence light trapped and reabsorbed by the emitting layers and contacts in this non-optimized configuration results in an underestimate of light available for illumination. To account for emission in all directions, J-V-L is measured using an integrating sphere, resulting in an increase in EQE of $1.2\times$. Accounting for both an external outcoupling structure and a luminaire, we estimate $\eta_{EL} \sim 30\%$ and $\eta_{LP} \sim 27\ \text{lm W}^{-1}$ for the devices if employed in conventional lighting environments.

The separated stripes allow each individual color element to be independently optimized.

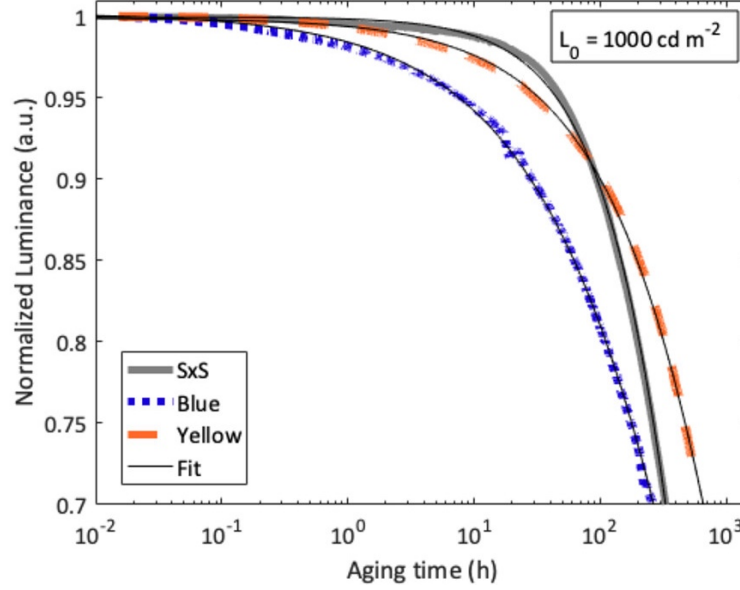


Figure 8.13: **Normalized change in L vs. aging time.** Devices are aged at an initial luminance of $L_0 = 1000 \text{ cd m}^{-2}$, with until the SxS device reaches T_{95} . From that point on, devices are aged at $L_0 = 3000 \text{ nits}$. Luminance decay curves are fit with a stretched exponential function.

Indeed, the striped elements show no significant difference when compared to the discrete control devices, indicating that the OLED structure using conventional shadow masks can be similarly optimized by peel-off patterning. Through the use of a stacked structure, we achieve a higher CRI than conventional two-color white devices provided by the increased spectral coverage from combining red and green phosphors in the yellow sub-element [148, 151, 168, 170]. Since only two emitters are employed, color-tunability is limited to a straight line extending between the blue and yellow element CIE coordinates, whereas a considerably larger color gamut can be achieved by using three isolated red, green and blue color stripes [155, 157, 171]. Employing a yellow element with current-dependent emission [139] that can be tuned from green to red can also cover a larger gamut at the sacrifice of a constant chromaticity and efficiency with brightness. Because the yellow and blue stripes are electrically isolated from each other, the spectral dependence on current density for each stripe are also independent. Thus, we are able to maintain only a small shift in chromaticity of $\Delta u, \Delta v < 0.015$ over a range of brightness from 20 to $>9000 \text{ cd m}^{-2}$ [172].

The color temperature of the striped array can be tuned over a 6000 K range to produce light

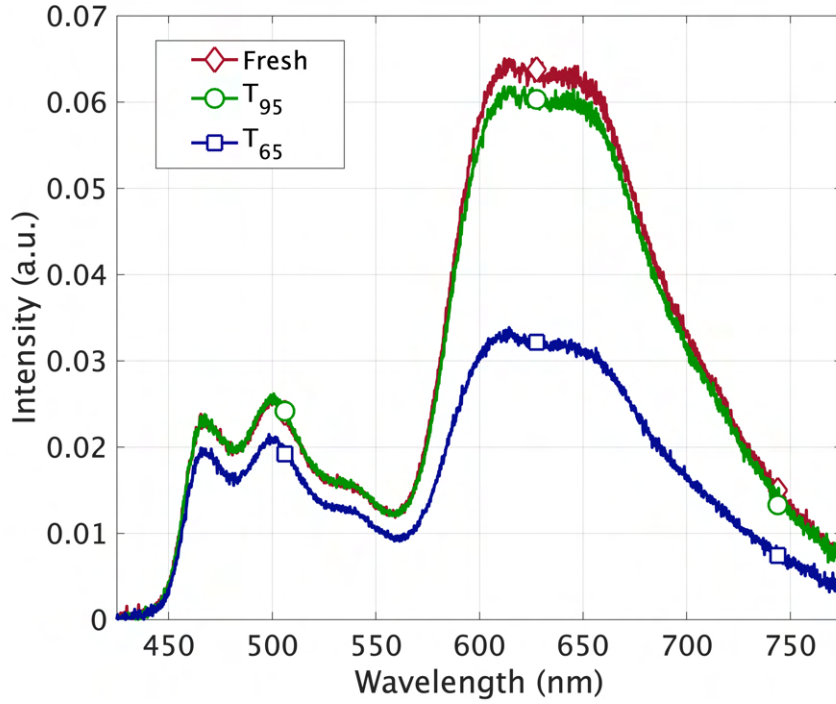


Figure 8.14: Aged SxS spectra. EL spectral shift from T_{100} (“Fresh”) to T_{65} .

suitable for various moods or times of day. The CCT isotherms, calculated for $\Delta uv < 0.05$ [173], indicate the range of (u, v) within which the emission color temperature can be accurately reported. The maximum CRI shown in Fig. 8.11 is attained along the line between the blue and yellow (u, v) coordinates that is closest to the Planckian locus [163]. For this device, with $(u, v) = (0.33, 0.36)$ and $(0.12, 0.31)$ for the yellow and blue elements, respectively, the maximum CRI occurs at CCT = 1935 K, with a secondary maximum at CCT = 3471 K. The CRI at the secondary point is lower due to reduced spectral coverage of the red and green.

Through direct comparison between shadow mask-patterned devices, and SxS devices, we find that device lifetime is unaffected by the striped patterning process. This represents a significant improvement over photolithographically patterned devices, where a single chemical lift-off step has been shown to decrease lifetime by nearly 50% compared to conventionally patterned devices, while the deposition of photoresist further decreases lifetime by over 90% [152]. While the spectral shift is relatively stable over the course of aging, we observe a larger shift in the yellow,

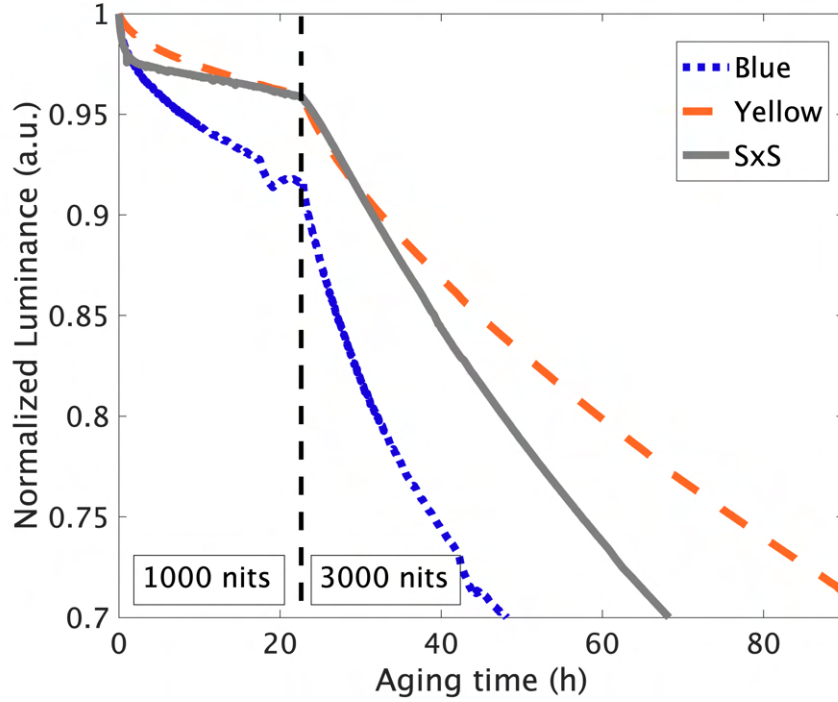


Figure 8.15: **Aged SxS luminance.** Raw luminance decay data for the extracted equivalent luminance decay shown in Fig.8.13

which comprises $\sim 75\%$ of the white emission. This is the result of the particular bias condition chosen to achieve CRI ~ 85 . The luminance decay for the SxS device exhibits a different shape than the controls because it consists of two, separate devices aging simultaneously at different rates resulting in a T_{70} for the SxS falling between the two equivalent control devices. The control blue device has a shorter lifetime than the control yellow device as a result of increased triplet energy in blue PHOLEDs [167]. Because the lifetime is limited by the blue phosphor [167, 174–176], the SxS geometry can be used to extend device lifetime by increasing the ratio of the number or widths of blue-to-yellow stripes, allowing the blue sub-element to be driven at a lower current.

8.2 Stacked OLEDs

This section was previously published, in part, as [177] C.E. Arneson, H. Zhao, and S.R. Forrest, “Color-Stable, All-Phosphorescent White Organic Light Emitting Diodes Using the

The short operational lifetimes of high efficiency PHOLEDs has long been a limiting factor in their use in displays and lighting. For ambient lighting in particular, it is necessary for the lifetime of each element to be stable and importantly, comparable such that the color quality of the device does not noticeably change over its lifetime. In Sec. 8.1, we describe a method for designing WOLEDs with independently-addressed subelements that can be operated at different current densities to compensate for lifetime differences. Though effective, this method restricts the flow of device fabrication, requiring multi-step peel-off patterning. Previous work using a stacked WOLED geometry consisting of multiple emissive layers has achieved efficient white light and a CRI as high as 89 [178, 179]. This geometry has been used in industry applications for achieving high efficiency, as shown in Ch. 5. Stacked WOLEDs comprising individually contacted red, green, and blue, or blue and yellow sub-elements allow for independent tuning of both emission color and intensity, although this architecture presents challenges in contacting metal electrodes within the organic stack [148, 171, 180–182]. Color-stability remains a challenge in series connected, all-phosphorescent devices. Though problem can be avoided by using less efficient fluorescent blue devices in separately biased red, green, and blue emissive elements to achieve stable full color emission, at the sacrifice of efficiency.

Currently, both phosphorescent and fluorescent red and green OLEDs at $L = 1000 \text{ cd m}^{-2}$ can achieve commercially acceptable operational lifetimes of $>180,000 \text{ h}$ before reaching 70% of their initial luminance (T_{70}) [1]. However, the lifetimes of blue phosphorescent emitters have lagged relative to their lower energy emitting red and green analogs, with light blue emitters demonstrating commercial operational lifetimes of 20,000 when aged at 1000 cd m^{-2} to T_{50} [1, 183]. Previous studies have shown blue PHOLED lifetimes are limited by the generation of high energy excited states produced by TTA and TPA. These states have energies greater than the bond dissociation energies within the molecules, thus leading to molecular fragmentation [10, 11]. For this reason, improved stability is achieved using less efficient fluorescent blue coupled with

phosphorescent red and green emitters in WOLEDs [184–189]. To achieve all-phosphorescent WOLEDs it is necessary to compensate for the short blue emitter lifetime through the choice of materials and EML design, such as graded doping or hot excited state management [167, 190]. Despite achieving high efficiencies while maintaining a high CRI, to our knowledge a color-stable all phosphorescent WOLED has not yet been reported in the literature [132, 178, 191–195]. Recently, Zhao, et al. demonstrated the improvement of blue PHOLED operational lifetimes by more than a factor of four compared to conventional devices through the PEP-enhanced Purcell effect. Here, PEPs result in an increase in Purcell factor, and improved coupling of energy from the EML to plasmonic modes on the metal cathode; both of which contribute to an enhancement in device lifetime [22]. The PF is defined as the cavity-enhanced triplet emission rate k_r to the natural triplet radiative rate, k_{r0} , see Eq. 2.21. This phenomenon, known as the Purcell effect, is used to increase the radiative optical density of states within the PHOLED, thereby reducing the radiative lifetime of triplets. This, in turn, reduces their density within the EML, and thus the probability to produce high energy and damaging hot excited states. The Purcell effect is amplified by energy transfer to PEP modes formed at the interface between the ETL and the cathode. Coupling of plasmons in the Ag cathode adjacent to polaritons in the ETL significantly strengthens the Purcell effect compared to conventional PHOLEDs with an Al cathode. In Sec. 8.1, we demonstrated that the blue emissive element in a side-by-side WOLED degrades approximately $2.5\times$ faster to T_{70} than the red/green pixel operated at the same current density [143]. This suggests that the PEP-enhanced Purcell effect can stabilize the blue emission to the point where its lifetime is comparable to the red and green elements.

Here, we demonstrate an all phosphorescent stacked WOLED comprising a blue element adjacent to the cathode that is connected via a charge generation layer to a red/green emitting element, shown in Fig. 8.16. We compare conventional devices employing an Al cathode (the control), to devices in which the radiative lifetime of the blue element is modified by PEPs through use of an Ag cathode (the Purcell-enhanced device) and an exciton-polariton coupling layer of BPyTP2. The BPyTP2 singlet emission spectrum overlaps with both the Ag plasmon absorption while

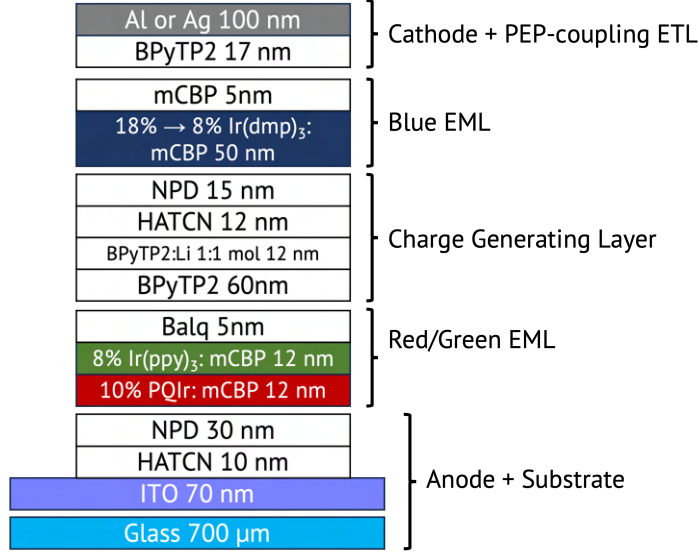


Figure 8.16: Schematic illustration of the device structure. The device stack consists of two EMLs (red/green and blue) separated by a charge generation layer.

its absorption spectrum overlaps with the blue emission from the EML. The resulting strongly coupled polariton serves to decrease the triplet density in the EML by enhancing energy transfer from the EML to Ag plasmonic modes. We achieve an initial EQE of $\eta_{EL,4\pi} = 19.1 \pm 0.4\%$ measured at 4π sr with a CRI = 76 and a correlated color temperature of CCT = 6100 K for the Purcell-enhanced device. This is compared with $\eta_{EL,4\pi} = 13.0 \pm 0.4\%$ with CRI = 74 at 6900K for the control.

We observe no measurable change in the colorimetric values for both devices at T_{70} , maintaining 1960 CIE coordinates $(u, v) = (0.17, 0.32)$ for the control and $(0.18, 0.33)$ for the Purcell-enhanced devices. These latter WOLEDs exhibit an extrapolated $T_{70} = 2900 \pm 100$ h at an initial luminance of 1000 cd m^{-2} , which is a $2.9\times$ improvement over the control device lifetime, as predicted by simulations [22]. By using the PEP-enhanced Purcell effect, we demonstrate a WOLED with CRI >75 that show a significant improvement in the stability of all color emission over the course of aging when compared to previously reported, summarized in Table 8.3.

8.2.1 Methods and Experimental Set-up

Prior to organic layer deposition, pre-patterned ITO anodes ($15 \text{ } \Omega/\text{sq}$) on glass substrates (Lumtec) are sonicated in detergent, DI water, acetone ($\times 2$), isopropanol (165°C , $\times 2$), and dried using pure N_2 . The 2 mm^2 device is defined by the 1 mm width of the ITO stripes and the 2 mm width of the shadow mask placed perpendicular to the ITO used for cathode metal patterning.

Table 8.3: Compilation of WOLED lifetime and color from the literature. All device data is reported without outcoupling structures. For references with multiple devices, the device with the most comparable CIE coordinates was chosen for comparison.

Ref.	Year	Emitter type	# of EMLS	η_{EL}^* (%)	CRI	(u, v)	Lifetime	ΔCRI	$(\Delta u, \Delta v)$
This work	2024	PHOLED	2	12.7	76	(0.18, 0.33)	1600h T_{70}	0.6	(0.00, 0.00)
[132]	2009	PHOLED	1	13.1	80	(0.23, 0.36)	1-2h T_{50}	-	(0.03, -0.02)
[191]	2014	PHOLED	1	23.6	-	(0.18, 0.35)	-	-	-
[196]	2014	PHOLED	1	21.3	63	(0.17, 0.33)	-	-	-
[192]	2017	PHOLED	1	21.5	-	(0.20, 0.36)	-	-	-
[178]	2018	PHOLED	4	50.8	81.2	(0.27, 0.35)	9000 h T_{70}^*	-2.5	(0.03, -0.01)
[193]	2018	PHOLED	1	19.3	81.4	(0.31, 0.36)	-	-	-
[197]	2018	TADF	1	9.9	-	(0.18, 0.36)	580 h T_{70}^*	-	-
[194]	2018	PHOLED	1	16.1	77.1	(0.19, 0.35)	-	-	-
[187]	2020	Hybrid	1	15.8	-	(0.29, 0.35)	100 h T_{70}^*	-	-
[188]	2020	Hybrid TADF	2	45.2	78	(0.25, 0.36)	1900 h T_{50}^*	-	-
[189]	2020	Hybrid TADF	1	19.7	92	(0.20, 0.33)	-	-	-

[198]	2020	TADF	1	17.8	~ 80	(0.15, 0.36)	338 h $T_{80}^\dagger$	-	-
[199]	2021	PSF	1	7	-	(0.21, 0.33)	-	-	-
[195]	2023	PHOLED	1	7.2	59	(0.21, 0.33)	836 h T_{95}^*	-	-

* Measured at 1000 nits

† Measured at 5000 nits

Vacuum thermal evaporation is used to deposit the organic layers. As shown in Fig. 1a, the layers comprise 10 nm thick HATCN (UDC), 30 nm thick NPD (UDC), 12 nm thick 10%vol PQIr (UDC) doped into mCBP (UDC), 12 nm thick 8%vol Ir(ppy)₃ (Lumtec) doped into mCBP, 5 nm thick BALq (UDC), 10 nm thick 10%vol PQIr:mCBP, 60 nm thick BPyTP2 (Lumtec), 12 nm thick 1:1 mol BPyTP2:Li (Kurt J. Lesker), 12 nm thick HATCN, 15 nm thick NPD, 50 nm thick 18 to 8%vol Ir(dmp)₃:mCBP (UDC), 5 nm thick mCBP, 17nm BPyTP2, and 1.5 nm thick Liq (Lumtec). Control devices have a 100 nm thick Al (Alfa Azar) cathode, and Purcell-enhanced devices have a 120 nm thick Ag (Sigma Aldrich) cathode. Organic materials from Lumtec are purified via thermal gradient sublimation, see Sec. 1.2. The devices are encapsulated in ultrapure N₂ with glass cover slide attached using UV-curing epoxy (Epotek).

The forward, 2π , J-V-L characteristics are measured using a parameter analyzer (Keysight) and a large area Si photodetector (Hamamatsu). The 4π measurements use an integrating sphere with a commercial external MLA (Lumtec). Error reported is the standard deviation from a population of four devices. Electroluminescence and angle-dependent spectra are measured via fiber coupling to a spectrometer (Ocean Optics). Device spectra are fit to Gaussian functions using MATLAB. The devices are aged under constant current, supplied by a SMU (Agilent), and device luminance is measured at 1-3 min intervals using a photodiode. The coupling efficiencies are calculated using Green's function methods, see Sec. 2.4 [29], for the stacked structure shown in Fig. 8.16. The layer thicknesses and complex indexes of refraction are measured by ellipsometry (J.A. Woollam). PF is calculated with 1 nm resolution throughout the EML, and report the average PF, is weighted

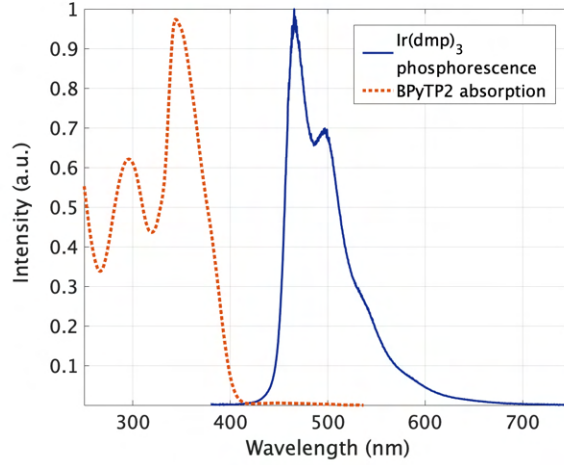


Figure 8.17: **Comparison of ETL and dopant spectra.** Normalized intensity of the BPyTP2 absorption spectrum and Ir(dmp)₃ emission spectrum.

by the doping concentration across each EML. We assume that the exciton concentration is proportional to the dopant concentration [167]. We assume $\theta_{hor} = 0.77$ and $q = 0.45$ for the B EML and $q = 0.95$ for the R/G EML. The peak emissive wavelengths of $\lambda = 600$ nm and $\lambda = 475$ nm are used for the R/G and B EML calculations, respectively.

8.2.2 Results

The stacked WOLED in Fig. 8.16 comprises two emissive layers, one R/G and the other B, separated by a CGL. The control structure employs an Al, cathode, and the other a Purcell-enhanced, Ag, cathode. In both structures, BPyTP2 is used as the ETL. Overlap between the blue triplet and the BPyTP2 singlet exciton absorption spectra shown in Fig. 8.17, and the BPyTP2 emission and the Ag plasmonic mode absorption enables efficient energy transfer to PEPs [22]. This is not observed in the control, where Al has only a weak plasmon resonance in the blue.

The coupling efficiencies into various available WOLED modes for photons emitted from the B and R/G elements calculated using Green's function methods are shown in Fig. 8.18 [29]. The distances of the B EML to the cathode, and the

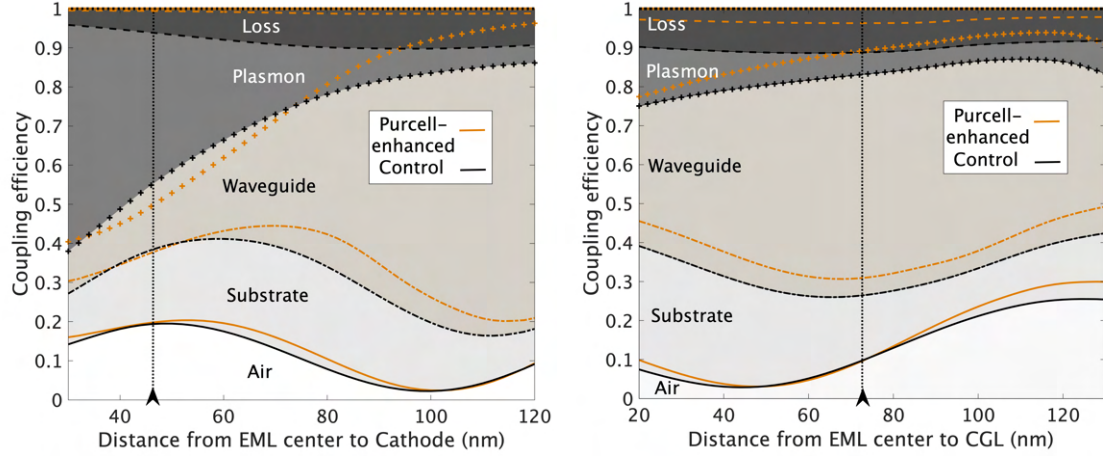


Figure 8.18: Mode coupling efficiencies for blue and red/green subelements. Coupling efficiencies to lossy, surface plasmon polariton, organic waveguide, substrate, and air modes are calculated using Green's function methods for the blue, left, and red/green, right, elements for the control device are indicated by the shaded areas and black lines, and Purcell-enhanced structures are indicated by the orange lines. The horizontal axis shows the results for various spacings between the blue EML and the cathode, left, and the red/green EML and the CGL, right. The dotted vertical lines correspond to the structures used in this work. The vertical axis shows the fractional coupling efficiency into each mode, where the total of all modes is equivalent to 1. The fraction of coupling to each mode can be found by the vertical distance between black lines for the control, and orange lines for the Purcell-enhanced structure.

R/G EML to the CGL used in optimized devices are shown by dashed vertical lines.

The calculated weighted average PF = 0.95 and 1.7 for the R/G and B layers within the control device, respectively, are compared with 0.91 and 2.2, respectively in the Purcell-enhanced device. Details on the calculation of the PF are included in Sec. 2.4. The PF average, which depends on the position in the EML and the exciton concentration at each EML position, is weighted by the distribution of dopant throughout the EML. That is, dopant emission closer to the cathode has a higher PF than emission near the HTL/EML interface.

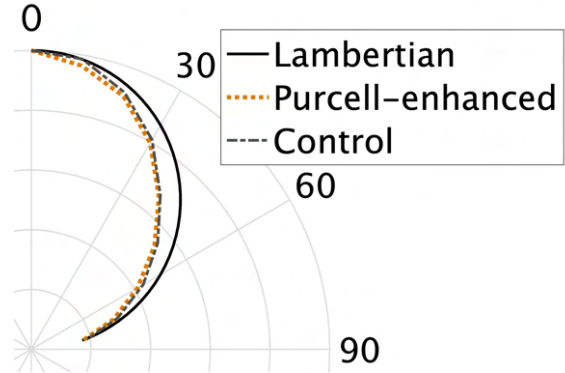


Figure 8.19: Angular device emission profile. Purcell-enhanced (orange dots) and control (gray dashes) device emission profile. A Lambertian profile is indicated by the black line for reference.

From Fig. 8.18, there is a negligible change in the peak outcoupling efficiency between the control and Purcell-enhanced structures, from 16% to 17% for R/G, and no change for B. Coupling to plasmonic modes is increased from 37% to 48% for B in the control and Purcell-enhanced devices, respectively.

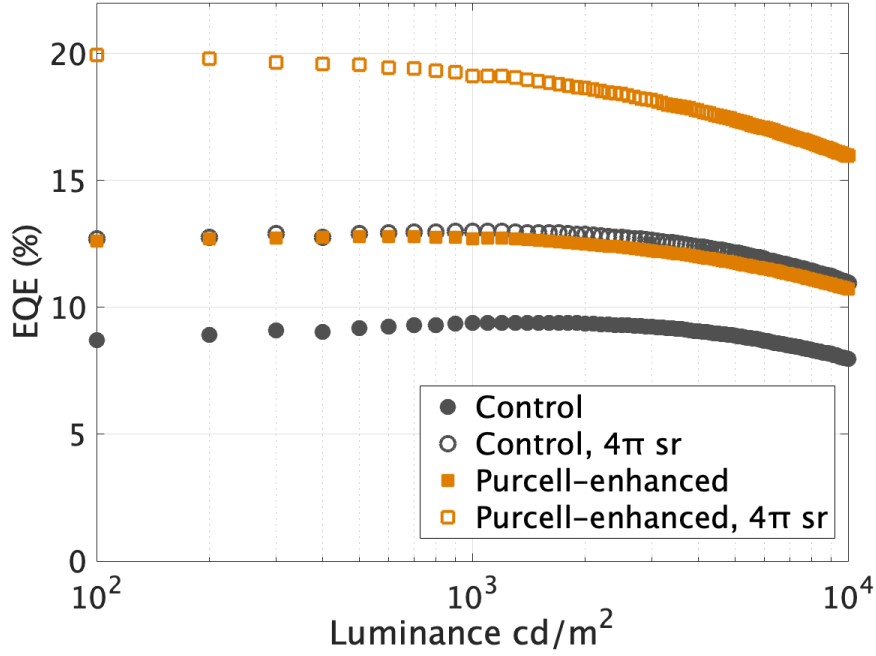


Figure 8.20: Stacked WOLED EQE. Device EQE for forward viewing in 2π solid angle (filled symbols) and 4π solid angle with an external MLA (open symbols) as a function of brightness.

The EQEs in the forward viewing and 4π viewing directions are shown in Fig. 8.20. We approximate the operating conditions of a white lighting fixture by accounting for emission from 4π sr and adding an external MLA. Under these conditions, $\eta_{EL, 4\pi} = 12.8 \pm 0.1\%$ and $19.1 \pm 0.3\%$, and $\eta_{LP, 4\pi} = 7.8 \pm 0.1 \text{ lm W}^{-1}$ and $10.8 \pm 0.2 \text{ lm W}^{-1}$ for control and Purcell-enhanced devices, respectively, corresponding to $L = 3300 \pm 20$ and $4330 \pm 60 \text{ cd m}^{-2}$.

The L-V characteristics of the control and Purcell-enhanced devices are nearly identical, as shown in Fig. 8.21. Similarly, there are no significant changes in the J-V characteristics between devices employing a Ag or Al cathode, whose turn on voltages are approximately 5.3 V. This is nearly double the voltage observed for single junction devices, since the B, with a turn on of 3

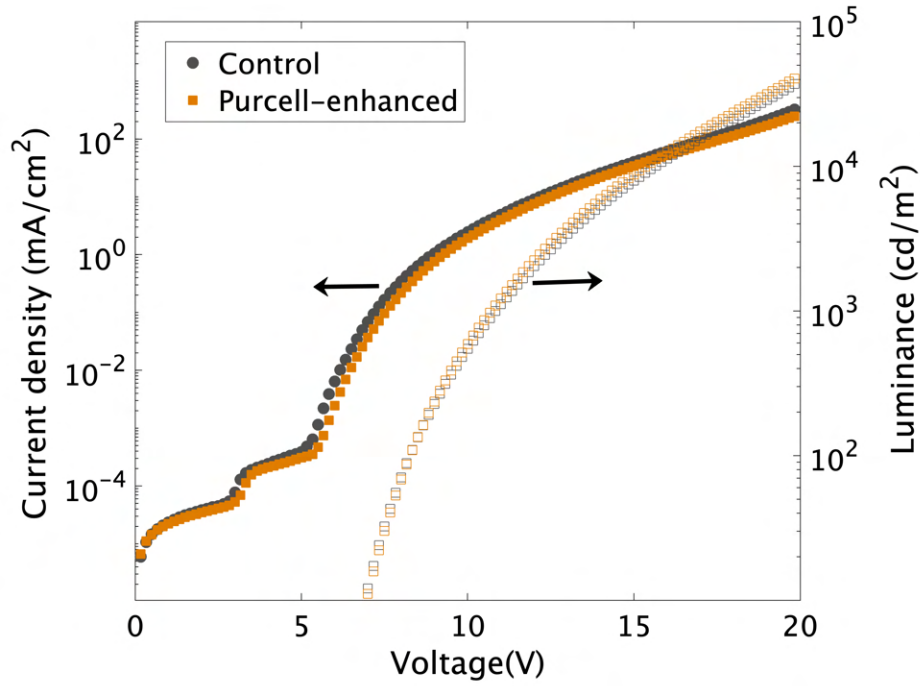


Figure 8.21: Stacked WOLED J-V-L. Current density (filled) and luminance (unfilled) vs. voltage for the control (gray circles) and Purcell-enhanced devices (orange squares).

V, and R/G, with a turn on of 2.5 V, subelements are connected in series [143]. The emission spectra both before and after aging at $J = 10 \text{ mA cm}^{-2}$, are shown in Fig. 8.22.

The control and Purcell-enhanced devices cover 92% and 94% of the Lambertian profile, respectively, see Fig. 8.19. This results in a shift in 1960 CIE (u, v) chromaticity coordinates of $(\Delta u, \Delta v) = (0.04, 0.01)$ from viewing angles of 0° to 80° , as the effective cavity length decreases with increasing viewing angle [20]. The colorimetric coordinates, CRI, CCT, and the distances from the Planckian locus (Δuv) for the devices are provided in Table 8.4. The devices were aged at $J = 10 \text{ mA cm}^{-2}$, corresponding to an initial luminance of $L_{0,4\pi} = 3300 \pm 20 \text{ cd m}^{-2}$ and

Table 8.4: As-prepared device colorimetric parameters.

	1960 CIE (u, v)	CRI	CCT	Δuv
Control	(0.17, 0.32)	74	6900	0.031
Purcell-enhanced	(0.18, 0.33)	76	6100	0.025

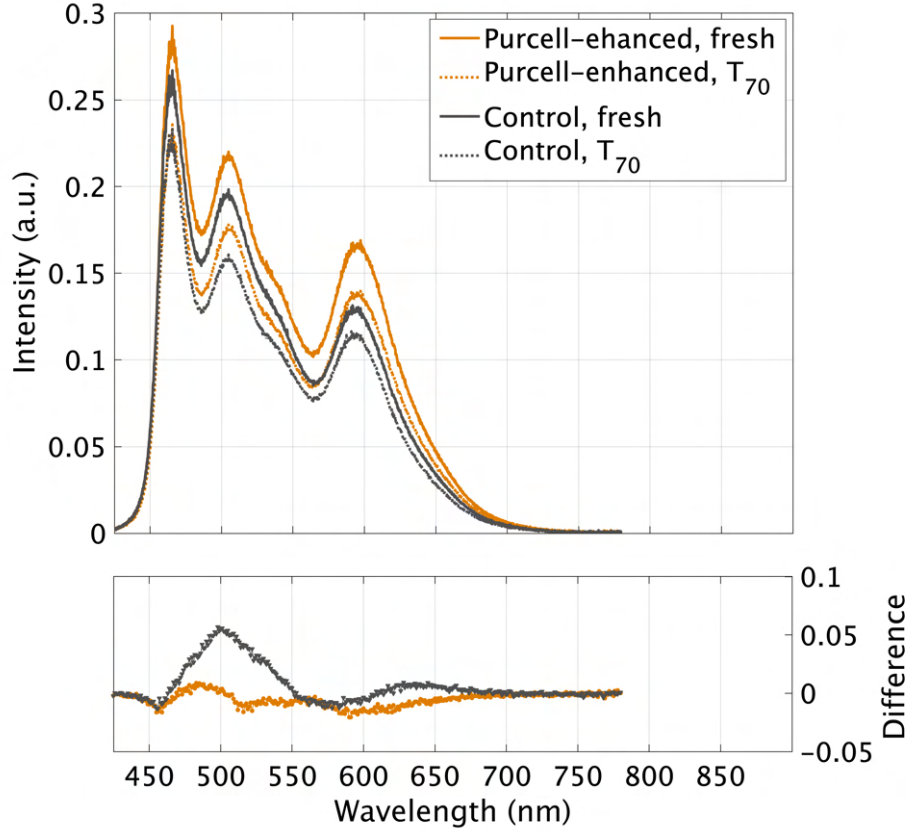


Figure 8.22: **Device spectra over the course of aging.** Device spectra measured at normal incidence for both control and Purcell-enhanced devices before aging (fresh) and at T_{70} . The differences between normalized spectra for control and Purcell-enhanced devices are indicated on the right axis of the lower plot.

$4330 \pm 60 \text{ cd m}^{-2}$ for control and Purcell-enhanced devices with results shown in Fig. 8.23. We obtain the times to reach 70% of their initial luminance of $T_{70} = 1030 \pm 20 \text{ h}$ and $2900 \pm 100 \text{ h}$, with a corresponding increase in voltage at a constant J of $\Delta V = 1.36 \pm 0.03$ and $1.13 \pm 0.01 \text{ V}$ for the control and Purcell-enhanced devices, respectively.

At T_{70} there is no measurable change in device (u, v) chromaticity coordinates and CRI for either device, although the control electroluminescence spectrum exhibits a small change in wavelength dependence with aging corresponding to a red shift in CCT, $\Delta\text{CCT} = 100\text{K}$, while there is no measurable wavelength or CCT shift for the Purcell-enhanced device (see Fig. 8.22). The wavelength changes are characterized by fitting the white spectrum to the sum of the individual spectra of the separate red, green, and blue emitting materials provided in Fig. 8.24, correspond-

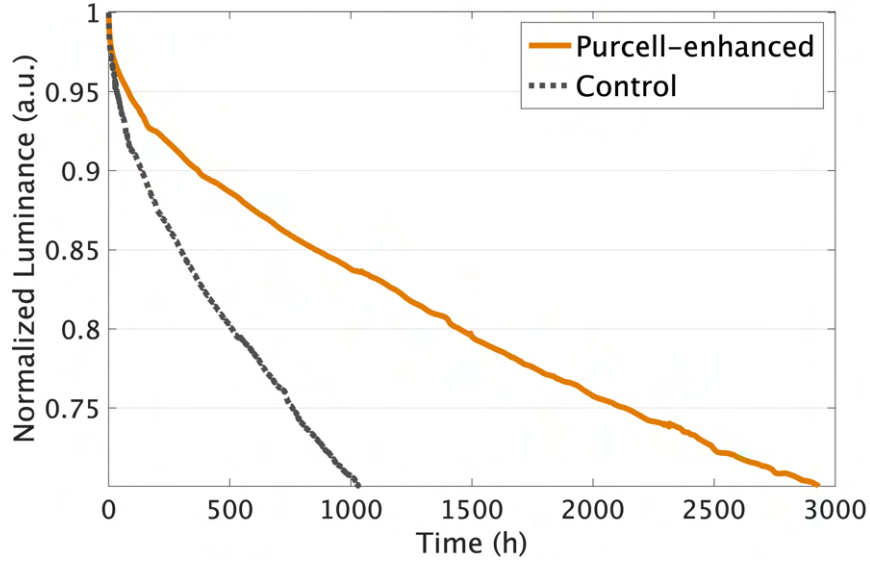


Figure 8.23: **Luminance decay curves for stacked WOLEDs.** Change in luminance vs. time for control and Purcell-enhanced devices, normalized to aging at an initial luminance of 1000 cd m^{-2}

ing to three peaks from Ir(dmp)_3 and Ir(ppy)_3 , and two from PQIr.

Fits for the fresh and aged Purcell enhanced devices and controls are shown in Fig. 8.25, with a summary of all fit parameters found in Table 8.5. Using these fits, we can determine the change in spectra from their differences shown in Fig. 8.22. The Purcell-enhanced devices shows a nearly uniform, $<6\%$ change in peak magnitude across all wavelengths, while the control exhibits a 47% decrease in the 524 nm vibronic of Ir(dmp)_3 , and a $>8\%$ change across red and green. The lifetime is normalized to an initial luminance of $L_0 = 1000 \text{ cd m}^{-2}$ using the acceleration factor, $\xi = 1.3 \pm 0.1$ for the control and $\xi = 1.5 \pm 0.1$ for the Purcell-enhanced device.

The acceleration factor is found by solving Eq. 3.36 using the lifetime and initial luminance of devices aged at $J = 5 \text{ mA cm}^{-2}$ and $J = 10 \text{ mA cm}^{-2}$, with data compiled in Table 8.6. We find that for $L_0 = 1000 \text{ cd m}^{-2}$, the operational lifetime is $T_{70} = 1030 \pm 40 \text{ h}$ for the control and $2900 \pm 60 \text{ h}$ for the Purcell-enhanced devices, demonstrating a $2.9\times$ enhancement. Raw data for devices aged at equivalent current densities before normalizing to constant luminance are shown in Fig. 8.26. The data for the Purcell-enhanced device at 5 mA cm^{-2} is fit with a stretched

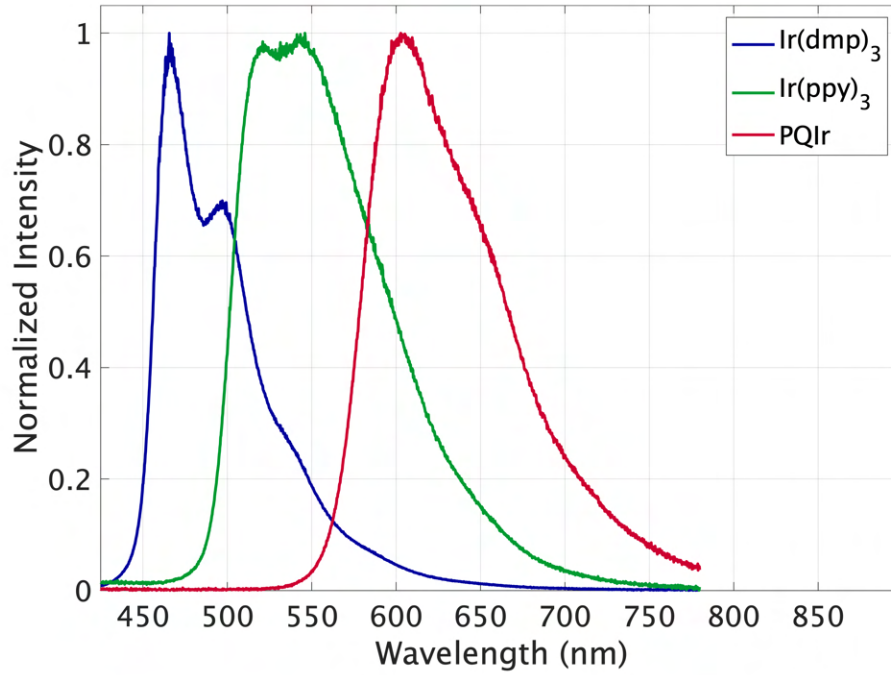


Figure 8.24: **Individual phosphor spectra.** Ir(dmp)₃ (blue), Ir(ppy)₃ (green), and PQIr (red) phosphors electroluminescence spectra in mCBP host devices.

exponential, Eq. 3.37 with $\tau = 2.9 \times 10^{-7} s$ and $\beta = 0.48$.

8.2.3 Discussion

The device stack in Fig. 8.16 employs a 17 nm thick BPyTP2 ETL to optimize coupling between the blue EML and plasmonic modes formed on the metal cathode surface, and outcoupling to air modes of emission from both the B and R/G EMLs. A thinner ETL suppresses outcoupling to air modes as shown in Fig. 8.18, while a thicker ETL decreases coupling to the SPP modes formed at the control ETL/Al interface and PEP modes at the ETL/Ag interface [22]. The outcoupling efficiency of the R/G element is optimized for a 100 nm thick ETL; in this work, we use a thickness of 60 nm, which is sufficient to provide outcoupling efficiencies of approximately 17% for both the Purcell-enhanced and control devices, with 20% for the blue element, and is sufficiently thin to assure a low operating voltage.

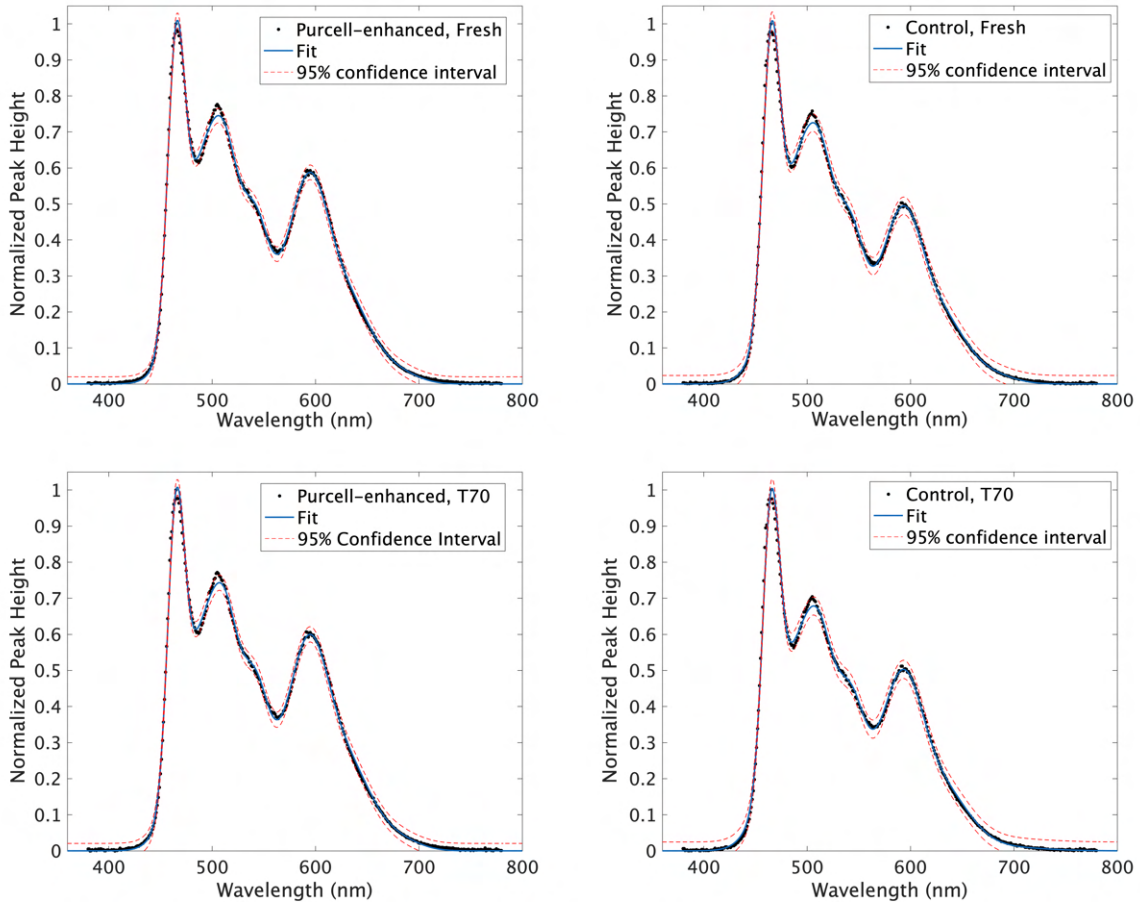


Figure 8.25: **WOLED spectra fitting.** Fitting using the individual emitter spectra for the normalized fresh Purcell-enhanced device (*top left*), fresh control device (*top right*), Purcell-enhanced device at T_{70} (*bottom left*), control devices at T_{70} (*bottom right*).

Additional fresh data for a device with an 80nm thick R/G ETL is shown in Table 8.7 and Fig. 8.27, which demonstrates a red shift in its spectrum because of the increased ETL thickness. The red shift with thicker R/G ETL is the result of higher coupling to air modes from the R/G layer, shown in Fig. 8.18. However, there is not a significant difference in the electrical performance between 60 and 80 nm ETL devices, indicating that the charge balance is better for the device with the thinner ETL. The cathode/ETL structure is optimized for the B element. Because R/G emission is generated far from the cathode, the dependence of R/G outcoupling on B ETL thickness, shown in Fig. 8.28, varies by only $\sim 7\%$ across a 15 nm range of B ETL thicknesses, which is less than half the observed change in plasmon coupling for emission from the B EML

Table 8.5: Spectral fitting parameters.

		Normalized Peak Height					
		Purcell-enhanced			Control		
		Fresh	T ₇₀	Δ%*	Fresh	T ₇₀	Δ%
R-squared value		0.9988	0.9987		0.9982	0.9979	
RMS Error		0.01	0.01		0.01	0.01	
Dopant	Center wavelength (nm)						
Ir(dmp)3	465	0.73	0.72	-1.2	0.70	0.70	-1.2
	491	0.55	0.55	-1.2	0.54	0.53	-1.2
	524	0.25	0.24	-5.4	0.20	0.10	-47.5
	513	0.16	0.17	5.9	0.16	0.19	17.9
Ir(ppy)3	543	0.21	0.22	5.9	0.21	0.25	17.9
	584	0.32	0.32	1.4	0.29	0.31	8.5
PQIr	631	0.21	0.22	3.4	0.17	0.15	-10.9
	596	0.23	0.24	3.4	0.18	0.16	-10.9

*Δ% is defined as the percent change in peak intensity from the fresh to T₇₀ fit

across the same range. Thus, the choice of B ETL thickness is can be optimized independent of the R/G subelement. In the blue EML, the Purcell-enhanced structure increases PF by a factor of 1.4 relative to the control. The CGL between the B and R/G elements enables each injected electron to generate two photons. The measured forward direction $\eta_{EL} = 12.2\%$, therefore, is low due to the relatively low quantum efficiencies of both the B and R/G emitting sections. That is, the blue discrete blue-emitting Ir(dmp)3 devices have $\eta_{EL} = 9.5\%$, and R/G devices have $\eta_{EL} = 12\%$ [143, 167]. Indeed, conventional WOLEDs used in lighting have up to 5 or 6 emitting sections to achieve high efficiency and brightness, see Sec. 5.2. Nevertheless, this relatively simple archetype device achieves CRI = 76 at a high color temperature of CCT = 6100 due to strong blue emission, CCT = 6100, that is unchanged over the course of aging. The chromaticity coordinates have a minimal viewing angle dependence, showing a slight blue shift from a viewing angle of 0° to 80°. The corresponding change in the distance from the (u, v) coordinates to the closest point on the Planckian locus, Δuv , shifts $\delta\Delta uv = -0.033$ for the control and -0.035 for the Purcell-enhanced devices, where $\delta\Delta uv$ is defined as the change in Δuv corresponding to a viewing angle shift from 0° to 80° [143]. Stability of the blue emission is due to the reduced radiative lifetime

Table 8.6: Lifetime and aging parameters for stacked WOLEDs.

	5 mA cm ⁻²			10 mA cm ⁻²			
	L ₀ (cd m ⁻²)	L ₀ * (cd m ⁻²)	T ₉₀ (h)	L ₀ (cd m ⁻²)	L ₀ * (cd m ⁻²)	T ₉₀ (h)	T ₇₀ (h)
Control	1120	1550	73	2240	3300	29	219
Purcell-enhanced	1389	2270	125	2940	4330	41	325

	PF	n	T ₇₀ ⁺ (h)	T ₇₀ ^{+, *} (h)
Control	1.6	1.3	640	1030
Purcell-enhanced	2.2	1.5	1600	2940

* Measured using an external MLA and integrating sphere

+ Normalized to L₀ = 1000 cd m⁻²

Table 8.7: Fresh device performance for a stacked device with an 80nm thick R/G ETL.

	V	J (mA cm ⁻²)	L (cd m ⁻²)	η_{EL} (%)	CIE (<i>u</i> , <i>v</i>)	CRI	CCT (K)	Δuv
Control, 80nm RG ETL	12.8	10.0 ± 0.3	2660 ± 70	11.70 ± 0.07	(0.20, 0.33)	78	5349	0.0123
Purcell-enhanced, 80nm RG ETL	12.5	10.2 ± 0.3	2760 ± 80	11.90 ± 0.04	(0.21, 0.33)	77	4768	0.0096

resulting from coupling between the triplets and SPP modes in the control device. In comparison, previously demonstrated long-lived stacked WOLEDs have shown noticeable red shifts at T_{70} , corresponding to a 50% decrease in luminance from the blue, despite the use of triplet managers to extend the blue emitter lifetime [178]. In work that utilizes the same EML structures in a side-by-side rather than stacked geometry, a red shift of $(\Delta u, \Delta v) = (0.014, -0.002)$ is observed, while here $(\Delta u, \Delta v) = (0.002, 0.000)$ falls within the margin of error [143]. This demonstrates a significant improvement over previous WOLEDs with both phosphorescent and fluorescent blue emitters for which either $(\Delta u, \Delta v)$ is 10× greater or color stability has not been reported [132, 178, 187–189, 191–194, 196–199]. A summary of reported WOLED data in the literature is included in Table 8.3. In the Purcell-enhanced device, blue triplets are strongly coupled to PEP

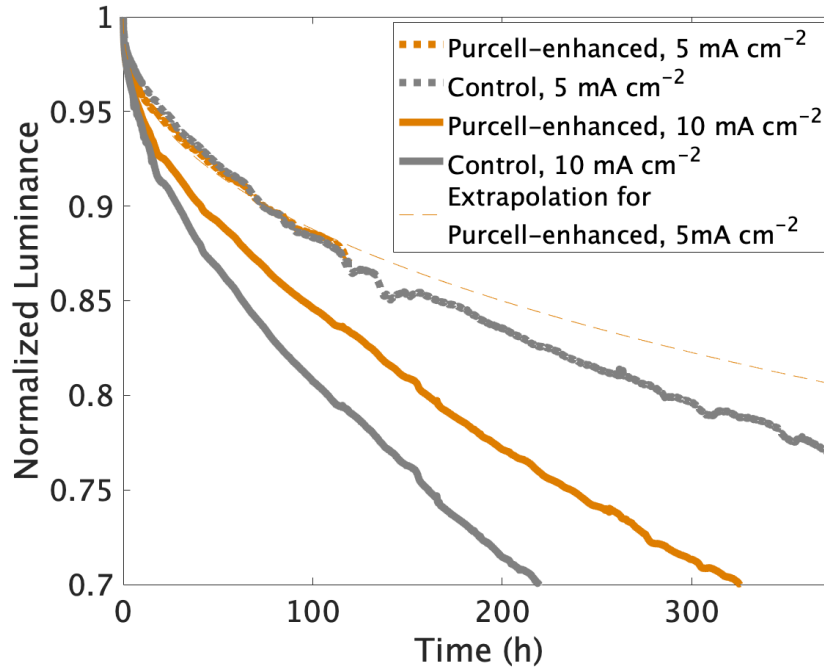


Figure 8.26: **Stacked WOLED aging.** Normalized luminance decay for control and Purcell-enhanced devices aged at 5 and 10 mA cm⁻², before normalizing to a constant luminance.

modes, resulting in improved spectral stability (cf. Fig. 8.22) along with a significant increase in lifetime. Use of the PEP-enhanced Purcell effect results in a reduction in the voltage rise over the course of aging by 0.23V compared to the control, and a $2.9\times$ increase in T_{70} . This operational lifetime enhancement is in agreement with the $2.9\times$ enhancement expected at T_{70} based on the power law, $m = 1.7 \pm 0.1$, dependence between PF and operational lifetime (i.e. $T_x \sim PF^m$), as previously reported [22].

8.3 Conclusions and Further Advances

In Sec. 8.1, we demonstrate a method for patterning SxS WOLEDs that exhibit color tunability and color stability at high currents over the course of the device lifetime, as a result of the non-destructive nature of the patterning process. We show that a yellow PHOLED stack comprising red and green phosphorescent emitting molecules, used alongside a blue PHOLED can achieve CRI > 74 across color temperatures that can be tuned from 2000 to 8000 K without sacrificing

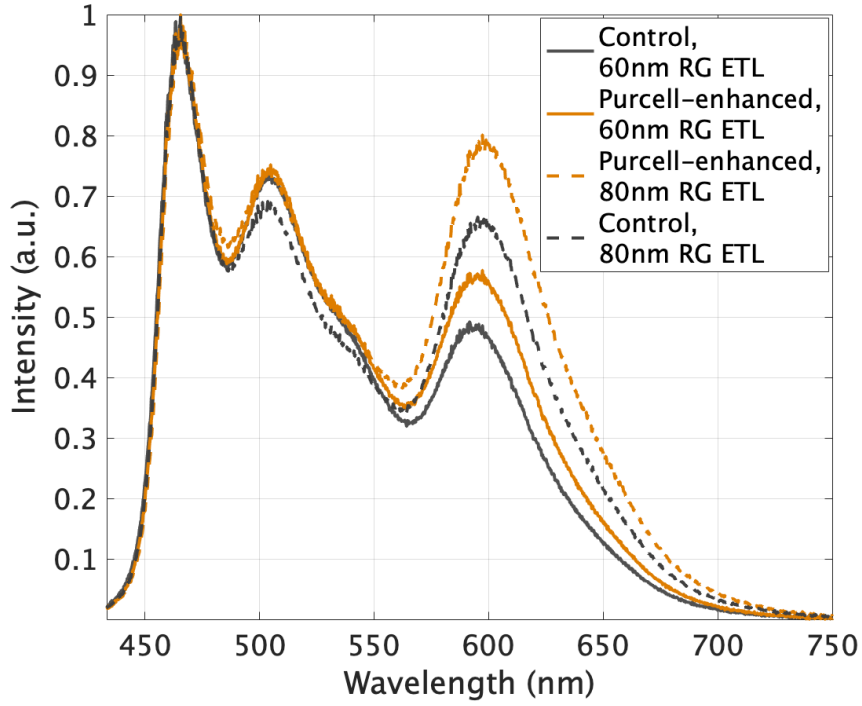


Figure 8.27: **Emission spectra for ETL thickness variation.** Emission spectra for fresh control (gray) and Purcell-enhanced (orange) devices with 60nm (solid) and 80nm (dashed) R/G ETL thicknesses.

lifetime or efficiency when compared to analogous conventional, shadow-mask patterned devices.

In Sec. 8.2, we demonstrate a single stacked white-emitting PHOLED with improved operational lifetime due to exciton-plasmon-polariton coupling that increases the optical density of states within the OLED cavity of the blue subelement. This, in turn, decreases the blue triplet lifetime, thereby reducing the probability for generating high energy excited states via triplet annihilation processes that lead to molecular dissociation. We observe no change in emission color across the entire white spectrum for Purcell-enhanced devices, demonstrating that the polariton-enhanced Purcell effect improves B subelement lifetime such that it degrades at the same rate as the R/G subelement. While this work demonstrates a relatively simple device design with a high CRI and operational stability, the color quality and lifetime can be further improved by increasing the strength of the Purcell effect with a sub-anode reflector and increasing EQE using more efficient blue phosphorescent material. Furthermore, high

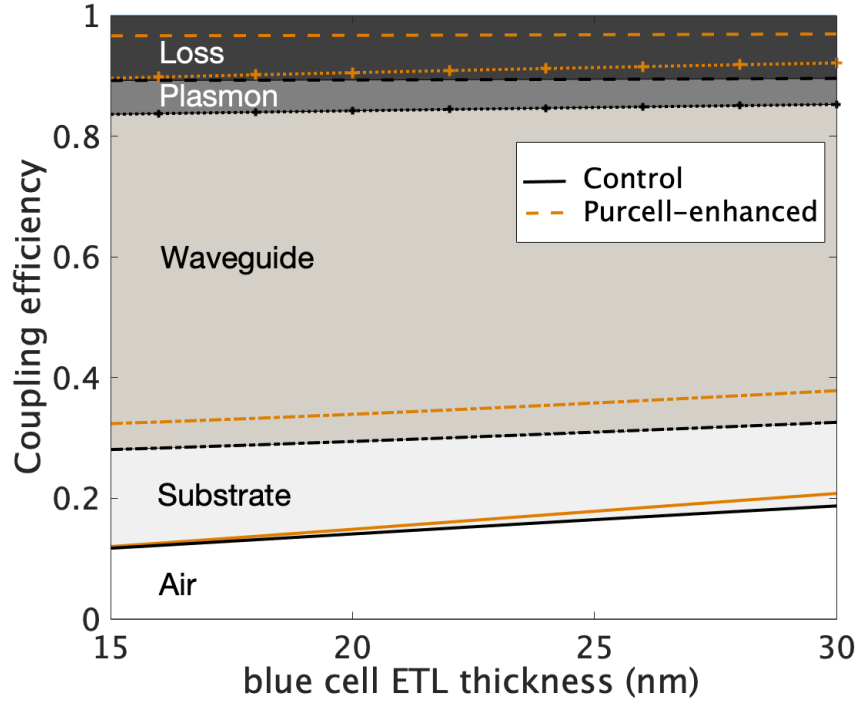


Figure 8.28: **Mode coupling vs. B ETL thickness.** Coupling efficiency for emission from R/G ETL as a function of B ETL thickness.

brightness and efficient stacked PHOLEDs typically are comprised of at least 3 – 5 R/G elements to improve both lifetime and CRI [178]. The design introduced here only affects the single blue emitting subelement in the stack near the cathode, and hence does not preclude the addition of more R/G elements to achieve practical long-lived, bright, and color-balanced emission.

Contributions to Sec. 8.1: C.E.A. and X.J.H. designed the peel-off pattern, C.E.A. fabricated samples and performed measurements, and C.E.A. and S.R.F. analyzed the data.

Contributions to Sec. 8.2: C.E.A. fabricated and measured all devices. C.E.A. and H.Z. designed the devices. C.E.A., H.Z., and S.R.F. analyzed the data.

CHAPTER 9

Conclusions and Outlook

9.1 Summary

In this dissertation, we have used the well-defined parameters of OLED efficiency to investigate optoelectronic diode systems governed by photon emission and absorption, and charge extraction and injection. Our work on OLEDs, discussed in Ch. 5-7, builds on a large body of prior work that has established OLEDs in ubiquitous commercial applications, namely portable displays. The work in Ch. 4 utilizes previously defined OLED efficiency parameters to quantify EL degradation in a reciprocal system, OPV.

In Ch. 4, we demonstrate that by measuring the change in CT state emission for an OPV we can identify degradation within the device. This empirical relationship has since been used to motivate OPV interface design that has further improved OPV stability [17] and understand OPV degradation under extreme conditions [93].

In Ch. 5-8, we focus on OLEDs and methods for achieving desired device specifications of efficiency, reliability, and color through the control of photons within the device. In Ch. 6, we discuss remaining limitations to achieving 100% substrate mode outcoupling efficiency. In Ch. 7, we characterize the outcoupling efficiency of plasmon-exciton-polariton modes and introduce a device architecture that demonstrates both improved device efficiency and reliability. In Chs. 5-8, we investigate lighting-quality WOLEDs and methods for achieving high efficiency, color stability, and color tunability.

9.2 Is the Outcoupling Problem Solved?

Since the discovery of Ir(ppy)₃, the first known 100% IQE OLED emitter, the goal has been to achieve 100% EQE. Nearly 30 years later, it is time to ask the question - is the outcoupling problem solved? In Ch. 5 - 7 we have summarized the existing technologies for outcoupling each mode. In Tables 5.1, 6.1, and 7.1, we summarized the leading technologies for outcoupling. There are two main limits to the realizing a 100% EQE device with existing outcoupling technology- 1) many outcoupling structures that would need to be combined to achieve 100% outcoupling efficiency are incompatible with one another. 2) industrial requirements or preferences for device architecture may not be compatible with outcoupling architectures; conversely, outcoupling architectures may not satisfy application requirements for low cost, low haze, Lambertian angle dependence, and operational stability.

Here, we propose two OLED designs that are sufficient to solve the outcoupling problem for the two main OLED industries: lighting and display.

Lighting: For lighting applications there is no preference for top or bottom emission. Most importantly, OLEDs for lighting should provide diffuse light with a Lambertian profile and a broad spectrum of emission. The SEMLA presented in Ch. 5 nearly achieves all of these metrics, but is limited by a small amount of SPP coupling, $\sim 20\%$ of photons remaining in the waveguided modes, and the approximately 60% outcoupling efficiency of the external MLA.

First, the remaining light trapped in waveguided modes is likely the result of a small fraction of waveguided modes remaining for $0.93 < u < 1$ between 430-550nm, where $n_{EML} > n_{SEMLA}$. To extract these modes, either a slightly lower index EML or slightly higher index polymer should be used. Options for both exist, though the blue emitter hosts must satisfy both optical and operational specifications for color, efficiency, and reliability. As such, it may be easier to switch to a slightly higher index polymer, such as those from Pixelligent (see Ch. 7). These polymers may introduce some absorption losses compared to NOA170.

Additionally, a slightly deeper hemispherical SEMLA feature could increase the SEMLA waveguide outcoupling efficiency closer to its theoretical limit. This can be achieved by more

carefully controlling the etch profile of the glass SEMLA substrate using grayscale lithography or laser-enhanced wet etching [200, 201].

Next, to address the light trapped in substrate modes an MLA that has an index matched to the SEMLA glass substrate, $n = 1.5$ is required. Many MLA material options exist that satisfy this condition, including PMMA, PDMS, and many optical epoxies. The MLA interface with air should have a graded index approaching $n = 1$. Possible options for this include designing coatings such as those discussed in Ch. 6, but, as discussed in this chapter, there are a variety of issues with achieving such coatings. Another option is to fabricate an MLA whose index gradually decreases from $n = 1.5$ on the planar, OLED side, to $n = 1$ at the peak of the lens hemisphere. Such a structure could be possible to achieve in a polymer such as PMMA, which can be selectively exposed using E-beam lithography to generate a graded porous structure. The polymer could also be deposited in a multi-layer structure within an MLA mold using an orthogonal porogen which can be etched away after the lens structure is cured.

Finally, the device must include a scheme for outcoupling SPP modes. For lighting applications, the OLED will be equipped with a luminaire and so a top surface SPP outcoupling scheme can be implemented to eliminate SPP losses. SPP modes can be outcoupled using a transparent top contact paired with a reflector layer spaced $\sim$ nm from the top contact with an index-matched polymer. This would require capping the top contact of the device with TFE protective layers before adhering the back surface reflector. The reflector can be planar, a 2D grid, or a diffuse reflector, depending on the desired light quality and choice of transparent electrode material. A schematic of this device is shown in Fig. 9.1.

Display: For display applications, T-E is preferred. Additionally, color purity, no angle dependence, and no blur are required.

First, to efficiently generate T-E only, a specular back surface reflector should be used along with a transparent non-metal bottom contact. Then, to maximally couple out T-E, a transparent top electrode should also be used. Note, in some applications, such as in blue PHOLEDs where emitter lifetime remains a primary issue, use of a transparent metal top and bottom contact

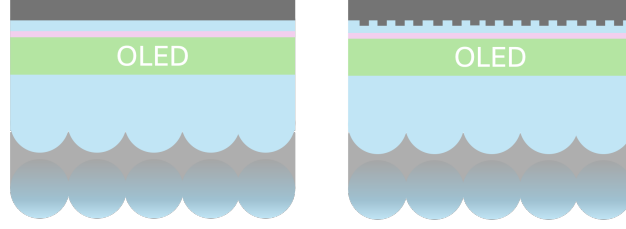


Figure 9.1: **Schematic of a high-efficiency B-E OLED designed for lighting applications.** A schematic of an OLED designed to achieve 100% efficiency for lighting applications. The layers, from top to bottom are: 1) a planar (*left*) or textured (*right*) metal top surface reflector (*dark gray*), 2) a spacer layer (*blue*), 3) a non-metal transparent top contact (*pink*), 4) organic layers (*green*), 5) a transparent non-metal bottom contact (*pink*), 6) a high-index SEMLA substrate (*blue*), 7) graded high (*gray*) to low (*blue*) index MLA.

paired with a PEP-hosting material might be preferred. In this case, lifetime improvement would be gained while some outcoupling efficiency is sacrificed. However, assuming high outcoupling is the primary goal, transparent non-metal contacts are preferred. The top contact is then coated with a TFE whose index should be graded from $n_{TFE} > n_{EML}$ to $n_{TFE} \sim n_{LIpolymer}$, where $n_{LIpolymer}$ is a low-index polymer that can be doped with optimally sized nanoparticles to scatter out waveguided and plasmonic modes. Alternatively, a high-index polymer with low-index scattering centers can be used to scatter waveguide modes. To minimize blur, a planar polymer capping layer is preferred, though an MLA-patterned capping layer could provide improved outcoupling efficiency with potentially manageable blur. A schematic of this device is shown in Fig. 9.2.

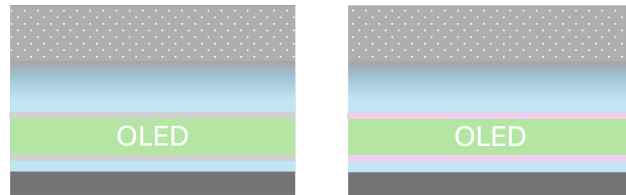


Figure 9.2: **Schematic of a high-efficiency T-E OLED designed for display applications.** A schematic of an OLED designed to achieve 100% efficiency for display applications. The layers, from top to bottom are: 1) a planar low-index encapsulation layer with scattering centers (*gray with white dots*), 2) a graded low (*gray*) to high (*blue*) index capping layer, 3) a metal (*gray, left*) or non-metal (*pink, right*) transparent top contact, 4) organic layers (*green*), 5) a metal (*gray*) or non-metal (*pink*) transparent bottom contact, 6) a spacer layer (*blue*), and 7) a planar metal back surface reflector (*dark gray*).

These two solutions leverage largely existing technologies and are agnostic to the organic stack used. They outline a potential pathway to the solution to the OLED outcoupling problem based solely on changes to device architecture. The efficiency of each outcoupling technology is summarized in Table 9.1. The exact outcoupling efficiency achieved by these two architectures depends on the fraction of coupling to each mode, which results from the design of the organic stack. To achieve the highest EQE, the organic stack should be optimized to couple preferentially to the modes with the most efficient outcoupling (i.e. air and waveguide modes). We estimate that, following the outcoupling efficiency estimates in Table 9.1 and assuming the devices couples 20% to air, 15% to the substrate or capping layer, 45% to waveguided modes, 15% to plasmonic modes, and 5% to loss, that we could achieve $\eta_{oc} \sim 80\%$ for the BE and $\eta_{oc} \sim 75\%$ for the TE architecture. Thus, the outcoupling problem remains, particularly in improving plasmonic mode outcoupling and optimizing the combination of outcoupling structures that can address all trapped modes in a device, as opposed to just one or two.

Table 9.1: Summary of outcoupling technologies.

Technology	Mode outcoupled	Fraction of mode outcoupled		Ref.
		TE	BE	
SEMLA	Waveguide to Substrate	–	80-100%	[31], Sec. 5.2
MLA	Substrate to Air	60%	60%	Sec. 5.2
Graded MLA	Substrate to Air	>90%	>90%	Estimated based on Ch. 6
Mirror BSR	Waveguide to Air	~10%	–	[30]
Diffuse BSR	Waveguide to Air	~30%	–	[30]
Scattering Grids	SPP to Air	50-75%	–	[101]
Graded Planar Coupling Layer	Waveguide to Substrate/Capping Layer	>90%	>90%	Estimated based on Ch. 6
Planar Scattering Polymer Layer	Substrate to Air	45%	45%	[202]

For more specific application needs, different outcoupling technologies may be needed. Some

applications include displays where high brightness is needed, such as AR/VR and LED walls for virtual film production [203]. In both applications, many attributes of OLEDs are useful, including true black pixels, wide and tunable color gamuts, flexible form factor, and energy efficiency. At high brightness, OLED efficiency drops as a result of TTA and TPA, which can also lead to reduced lifetime. Different outcoupling solutions that are tuned for these specific applications may be needed.

One avenue for increasing OLED brightness utilizes a stacked or tandem structure. Such designs are commonly used in industry, as is shown in Ch. 5, and tandem structures have been shown to reach very high EQE, reliability, and brightness [23, 178]. The tandem Purcell work, which leverages PEP modes on both the cathode and anode sides of the device, when combined with PEP outcoupling schemes as described in Ch. 7, may be particularly useful for very bright, stable displays. The use of two metal contacts provides PEP enhancement but also limits the materials that can be used for both contacts and ETLs. One concept for loosening this restriction is the use of nanoparticle-doped transport layer materials for achieving local coupling to PEP modes.

Modification the morphological and optical properties of emissive materials provides another pathway to achieving high EQE without requiring heavily engineered substrates. Outcoupling improvements through materials design must either increase the fraction of horizontal dipoles or lower the index of refraction of the EML without compromising material stability or efficiency. Morphological control of the active area of both OLEDs and OPVs could aid in increasing efficiency, lifetime, and outcoupling. Demonstrations of active layer morphological control have relied on specific materials and growth conditions, which have limited general use.

The blue tandem structure could also be useful in lighting applications, particularly those using a SxS architecture where the B EML can be engineered separately from the R/G EML. One challenge to SxS patterning with Purcell-enhanced devices is the patterning of the bottom reflector, either DBR or metal cavity, which is wavelength-dependent and could require a separate design for B vs. R/G elements. Additionally, outcoupling structures such as SEMLA are incompatible

with the current peel-off technology, in which polyimide is released from glass. Engineering ways to integrate peel-off patterning with engineered substrates could provide many additional avenues for device design. Another challenge is the steep sidewall generated by peel-off patterning. This does not pose an issue for devices with an Al top contact, but the use of an Ag, which migrates within the device more easily, for the top contact could potentially lead to shorting of the device. The deep tandem stack may be sufficient at protecting the device from shorting along the sidewall.

9.3 Increasing the EL Efficiency of OPVs

In Ch. 4, we use the reciprocity relationship to understand device degradation. The reciprocity relationship relates the theoretical maximum $V_{oc,th}$ to the realized V_{oc} , where the difference between the two is a function of the CT emission efficiency and external quantum efficiency, η_{CT} and η_{EL} . The V_{oc} and thus device performance can be improved by improving these efficiencies.

One way to do this is through improving the OPV charge balance within the EML. In Ch. 4, we show that the CT state emission recovers over aging as a result of improved charge balance. In OLEDs, many strategies exist for improving charge balance. One solution that could benefit OPV is the co-host structure, which uses separate electron and hole transporting materials to host the dopant material. In an OPV, a similar structure could be used to drive charge separation, which is somewhat reciprocal to the charge balance. One challenge would be to find co-host materials that form appropriate CT states with the primary OPV active donor or acceptor materials, while not sacrificing the high absorption necessary for photocurrent generation. Additionally, the co-host architecture is sensitive to material ratio, which could be a challenge to achieve in solution processed, polymer OPVs. OPV quantum efficiency is also limited by the triplet states, which remain dark and do not contribute to CT state emission. Utilizing OLED EML architectures to enable single/triplet mixing could provide an avenue for increasing η_{EL} .

Another option to increase OPV efficiency does not directly improve η_{EL} , but does utilize

OLED outcoupling architectures. The OPV active layers could be sandwiched between two low index layers to more effectively confine incident solar radiation within the device and increase absorption. This has been used in OLEDs to increase electrode reflectivity [204].

9.4 Understanding OPV Degradation

The empirical factor m introduced in Ch. 4 provides a useful metric for understanding the observed degradation of OPVs and providing insight on how to improve existing designs. Understanding the physical origin of m could expand upon this and potentially provide a theoretical pathway for improving OPV reliability, as has been done for OLEDs [11, 205]. The lower bound where $m = 1$ is physically described by the ideal diode equation in the absence of traps, where:

$$V_{oc} = V_{oc}^{rad} + \frac{kT}{q} \ln \left(\frac{J_{ph}(V_{oc})}{J_{sc}} (\eta_{CT})^m \right) \quad (9.1)$$

By defining a physical meaning for $m > 1$, we can better understand the intrinsic origins of OPV degradation and better inform future material design for OPV stability.

9.5 Outlook for Organics

Applied technologies evolve from the research and development stage to deployment in practical applications and a eventually disposal at the end of their useful lifetime. Early-stage research and development has indicated that organic PVs and LEDs currently offer promising solutions for solving the energy efficiency and energy generation problems facing our society. At this time, however, there is also a need for optoelectronic devices whose operational metrics not only satisfy those required for specific use applications, but also whose material attributes are conducive to wide-scale deployment and whose disposal is as environmentally neutral as possible. Metrics have been designed to assess the potential impact technologies in early-stage research would have throughout their operational lifetime and disposal [206]. These are useful questions for organic

optoelectronics in particular, since many organics already have benefits in these areas given their large-area manufacturability, relatively low environmental toxicity, and tunable form factors, especially as compared to competitor materials sets such as perovskites and CdTe.

The two central goals we initially posed in Ch. 1, 1) increase OPV efficiency and lifetime and 2) increase blue emitter efficiency and lifetime, are still open problems in the field of organic optoelectronics, even as progress is made to improve the metrics. Future work in organic optoelectronics has the potential to expand beyond these operational questions to consider the broader applications and ramifications of deploying and using organic light emitting diodes.

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