To my mother and father
ACKNOWLEDGMENTS

First and foremost, I would like give my gratitude to my great parents who are always loving, supporting and patient to me. They never lose faith in me and always help me with their wisdom.

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<td>3TPYMB</td>
<td>Tris[3-(3-pyridyl)mesityl]borane</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscope</td>
</tr>
<tr>
<td>Alq3</td>
<td>Tris(8-hydroxy-quinolinato)aluminium</td>
</tr>
<tr>
<td>AMOLED</td>
<td>Active matrix OLED</td>
</tr>
<tr>
<td>B3PyPB</td>
<td>3,5,3&quot;,5&quot;-tetra-3-pyridyl-[1,1';3',1&quot;]terphenyl</td>
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<td>BETC</td>
<td>3,3&quot;,6,6&quot;-tetrakis(1,1-dimethylethyl)-9&quot;-(ethyl)-(9Cl) -9,3':6'9&quot;-Ter-9H-Carbazole</td>
</tr>
<tr>
<td>BPhen</td>
<td>Bathophenanthroline</td>
</tr>
<tr>
<td>CBP</td>
<td>4,4'-bis(carbazol-9-yl)biphenyl</td>
</tr>
<tr>
<td>CIE</td>
<td>International Commission on Illumination</td>
</tr>
<tr>
<td>CT</td>
<td>Charge Transfer</td>
</tr>
<tr>
<td>DEL</td>
<td>Double Emitting Layer</td>
</tr>
<tr>
<td>DBR</td>
<td>Distributed Bragg Reflector</td>
</tr>
<tr>
<td>EA</td>
<td>Electroabsorption</td>
</tr>
<tr>
<td>EL</td>
<td>Electroluminescence</td>
</tr>
<tr>
<td>EML</td>
<td>Emitting layer</td>
</tr>
<tr>
<td>EQE</td>
<td>External Quantum Efficiency</td>
</tr>
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<td>ETC</td>
<td>9&quot;-ethyl-9,3':6'9&quot;-(9Cl)-Ter-9H-carbazole</td>
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<tr>
<td>ETL</td>
<td>Electron transporting layer</td>
</tr>
<tr>
<td>Firpic</td>
<td>Iridium (III) bis[(4,6-difluorophenyl)pyridinato]picolinate</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>HAT-CN</td>
<td>1,4,5,8,9,11-hexaazatriphenylene-hexacarbonitrile</td>
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<tr>
<td>HIL</td>
<td>Hole injection layer</td>
</tr>
<tr>
<td>HTL</td>
<td>Hole transporting layer</td>
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<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
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<tr>
<td>IC</td>
<td>Internal Conversion</td>
</tr>
<tr>
<td>ISC</td>
<td>Intersystem Crossing</td>
</tr>
<tr>
<td>IQE</td>
<td>Internal quantum efficiency</td>
</tr>
<tr>
<td>Ir(MDQ)2(acac)</td>
<td>Bis(2-methyl-dibenzo[f,h]quinoxaline)(acetylacetonate)iridium (III)</td>
</tr>
<tr>
<td>Ir(ppy)3</td>
<td>Tris(2-phenylpyridine)iridium(III)</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>mCP</td>
<td>1,3-bis(carbazol-9-yl)benzene</td>
</tr>
<tr>
<td>MEH-PPV vinylene</td>
<td>Poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene]</td>
</tr>
<tr>
<td>MoOx</td>
<td>Molybdenum Oxide</td>
</tr>
<tr>
<td>NCs</td>
<td>Nanocrystals</td>
</tr>
<tr>
<td>NPB</td>
<td>N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine</td>
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<tr>
<td>OLED</td>
<td>Organic Light-Emitting Diode</td>
</tr>
<tr>
<td>OPV</td>
<td>Organic Photovoltaic</td>
</tr>
<tr>
<td>PCE</td>
<td>Power Conversion Efficiency</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>Poly(3,4-ethylenedioxythiophene):polystyrenesulfonate</td>
</tr>
<tr>
<td>PhOLED</td>
<td>Phosphorescent organic light-emitting diode</td>
</tr>
<tr>
<td>PLED</td>
<td>Polymer light-emitting diode</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>poly-TPD</td>
<td>Poly(4-butylphenyl-diphenyl-amine)</td>
</tr>
<tr>
<td>PTC</td>
<td>9'-phenyl-9,3':6'9&quot;-(9CI)-Ter-9H-carbazole</td>
</tr>
<tr>
<td>PVK</td>
<td>Poly(N-vinylcarbazole)</td>
</tr>
<tr>
<td>QD</td>
<td>Quantum dot</td>
</tr>
<tr>
<td>SiO2</td>
<td>Silicon oxide</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
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<tr>
<td>SOC</td>
<td>Spin-orbital coupling</td>
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<tr>
<td>TAPC</td>
<td>Di-[4-(N,N-ditolyl-amino)-phenyl]cyclohexane</td>
</tr>
<tr>
<td>TCTA</td>
<td>Tris[4-(carbazol-9-yl)phenyl]amine</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Titanium oxide</td>
</tr>
<tr>
<td>TPBi</td>
<td>2,2',2''-(1,3,5-benzintriyl)-tris(1-phenyl-1-H-benzemidazole)</td>
</tr>
<tr>
<td>UGH2</td>
<td>1,4-bis(triphenylsilyl)benzene</td>
</tr>
<tr>
<td>ZnO</td>
<td>Zinc Oxide</td>
</tr>
<tr>
<td>ZnS</td>
<td>Zinc sulfide</td>
</tr>
<tr>
<td>ZnSe</td>
<td>Zinc selenide</td>
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ON MICROCAVITY AND TRIPLET EXCITON BEHAVIOUR IN ORGANIC AND HYBRID LIGHT EMITTING DIODES

By
Chaoyu Xiang

May 2014

Chair: Franky So
Major: Materials Science and Engineering

Instead of describing the behaviors of ‘free’ carriers in energy diagram formed from periodic lattice structures as in inorganic semiconductors, a strong bonded hole and electron, named exciton, is used as the basic quasi-particle to characterize the properties of organic semiconductors. With the presence of excitons, more interactions occur such as exciton confinement, exciton-exciton annihilation, and exciton-polaron annihilation, which will be discussed in this thesis.

First, microcavity was used to confine the excitons and modify the electroluminescence (EL) characteristics of phosphorescent OLEDs. A systematic study has been conducted on microcavity OLEDs using on green, red and blue phosphorescent emitters to elucidate the microcavity effects for different color emitters. While the luminance enhancements of blue and red phosphorescent microcavity devices are small, the current efficiency as high as 224 cd/A is obtained in green phosphorescent microcavity OLEDs.

Quantum dots are other excitonic materials with strong confinement of electrons and holes. We demonstrated blue/violet emitting hybrid LEDs based on cadmium-free zinc selenide/zinc sulfide core/shell quantum dots. Using poly(N-vinylcarbazole) with a
low lying highest occupied molecular orbital energy for the hole transporting layer, enhanced hole injection and better exciton confinement were observed, resulting in efficient blue/violet emitting devices.

Due to the long lifetime and high density of triplet excitons, exciton-exciton annihilation and exciton-polaron quenching become the dominating loss mechanisms which contribute to the phosphorescent OLED efficiency roll-off. We characterized the interactions of triplet excitons and polarons in blue phosphorescent OLEDs with ter-carbazole host materials and found that these interactions could be modified and the efficiency roll-off is suppressed by changing the host system. Highly efficient blue phosphorescent OLEDs with reduced roll-off at high luminance were demonstrated.

We also show that exciton interaction can further reduce the operating voltage of fluorescent OLEDs with a luminance turn-on below the corresponding bandgap voltage of the emitter. With experiment results from electroabsorption, transient EL and PL measurements, we verified the energy from the charge transfer state of the donor and acceptor can be acquired by the triplet state, which undergoes an up-conversion path and transfers its energy to higher singlet state.
CHAPTER 1
FUNDAMENTALS OF ORGANIC SEMICONDUCTORS

In this chapter, several key concepts governing the processes in organic electronic materials are presented, from the basic molecular orbitals constructions to electronic states, charge carrier transport, and excitons. Basic characterization regarding the performance of OLEDs will follows the introduction of OLEDs. Also theory regarding the microcavity and quantum dots used in this thesis will be discussed.

1.1 Physics of Organic Semiconductors

1.1.1 Molecular Orbitals

Organic semiconductors are organic compounds that can conduct carriers. All of them are sharing the common chemical characteristic: conjugated structure, where are alternating single σ-bounds and double π-bonds between the carbon atoms. The σ-bound is overlapped sp2-hybridized orbitals between two adjacent carbon atoms, which leads to a planar structure of the molecule. π-bounds consist of the overlap of the remaining p-orbitals of the carbon atoms, which are oriented perpendicularly to the molecular plane. Electrons in p-orbitals are delocalized over the whole molecule. The associated higher energy molecular orbitals of σ* and π* are anti-bonding orbitals. Bonding energy of σ-electrons is much stronger than those of π-electrons which correspond to the outmost orbitals of molecule. In condensed organic semiconductors, weak van der Waals interaction bounds all the molecules together. The overlap of π-orbitals create band structure like in the inorganic semiconductors, where the filled band edge forms the highest occupied molecular orbital (HOMO) and the unfilled band edge contributes to the lowest unoccupied molecular orbital (LUMO). As the results, the optical and electronic properties of organic semiconductors are determined by
properties of HOMO and LUMO as well as the bandgap between them. Figure 1-1 shows the molecular orbitals and associated HOMO/LUMO diagram of the most basic conjugated molecule: benzene.

1.1.2 Photophysics of Organic Molecules

External energy (from photons, excitons or injected charges) can excite an organic molecule from ground state to higher energy states. Those excited states have different degrees of freedom: electronic, vibrational, rotational and translational ones which correspond to different molecular orbitals. The relaxation of an excited molecule back to ground state can go via radiative transition which involves the emission of photons or non-radiative transition where energy is transferred to heat. The various energy levels involving in the excitation and relaxation of an organic molecule are classically presented by a Jablonski energy diagram. Figure 1-2 illustrates the Jablonski diagram, the thicker lines represent electronic energy levels, while the thinner lines denote the various vibrational energy states within each vibrational level, a number of rotational and translational sub energy levels exist which are ignored here. Every transition between each energy level is characterized by a rate constant, the number of which varies in different kinds of transition processes.

Due to Pauli exclusion principle, each electronic state forms bonding or antibonding molecular orbital. They will have a total spin number of 0 or 1, which correspond to singlet or triplet state, respectively. In order to preserve the spin conservation, the transitions are allowed within the same total spin number (singlet to singlet or triplet to triplet). As a result, transition from singlet to triplet is ‘spin forbidden’, which, more strictly speaking, is due to a significant low transition rate. In the ground state, the outmost orbital of an organic molecule is filled with two electrons with paired
spins which have a total spin number of 1, forming a singlet. Therefore in photon absorption transition, organic molecule is excited from $S_0$ to $S_n$. The common radiative decays could be singlet to singlet emission so called fluorescence or triplet to singlet emission so called phosphorescence while the nonradiative decay are included internal conversion (IC) - transitions between states of the same multiplicity and intersystem crossing (ISC) - transitions between states of a different multiplicity.

Due to the significant mass difference between electrons and unclear, an electronic transition involves no change in the nuclear coordinates. The transition between each vibrational level follows Franck-Condon principle that is the intensity distribution in the vibronic progression is determined by the overlap between the ground-state vibrational wave function $\psi_{0v}$ and the excited-state vibrational wave function $\psi_{nv}$. In photon absorption, the strongest transition occurs from the vibrational ground state into a vibrational level of the excited state having its maximum wave function over the maximum of the ground state. Also, in the relaxation process, the most probable transition is between vibrational levels of the excited state and ground state that have the maximum overlap of wave functions. These transitions are represented by vertical transitions on the potential energy diagram. Transitions to other vibrational levels are also possible but with reduced probabilities. The starting vibrational level of radiative transition is governed by Kasha's rule. Vibrational relaxations in each electronic state involve non-radiative emission of photon, whose rates are much larger than the radiative transition rate. Therefore the radiative transitions are most likely to start from the lowest vibrational level of an electronic state.
The radiative decay from singlet to ground state is called as fluorescence, while the radiative decay from triplet to ground state is called as phosphorescence. Fluorescence is the spontaneous radiative emission. Once the molecule is excited the fluorescent relaxation of the excitation occurs within few nanoseconds. Phosphorescence is a relatively slow spontaneous emission. Due to the spin forbidden between singlet and triplet, the transition rates from excited singlets to triplets and from triplets to ground state are very low. However, in the presence of additional internal or external force, these transitions may occur. For example, by introducing heavy metal into the molecule, strong spin-orbit coupling enables the mixing of singlet and triplet states. Thus, those forbidden transitions become weakly allowed. Thereby, the rate of triplet decay as well as the probability for intersystem crossing increases, leading to enhanced phosphorescence. There is also another possibility of triplet energy transfer back to singlet which is so called reverse intersystem crossing (RISC). This new formed singlet undergoes delayed fluorescent radiative decay.

1.1.3 Exciton and Intermolecular Exciton Energy Transfer

The intermolecular energy transfer can be a radiative or non-radiative process between molecules, which can be described in term of exciton transfer. The exciton is a bound electron-hole pair by Coulomb force. Due to the small dielectric constant of organic materials, electron and hole are strongly bounded, resulting in a small excitonic radius and localized exciton state. Therefore compared with inorganic semiconductors, organic semiconductors tend to describe exciton behaviors to explain the optoelectronic properties. Depending on the degree of delocalization, the excitons are classified as Frenkel, Wannier-Mott and Charge-Transfer (CT) which are shown in Figure 1-4. In organic materials, strong Coulombic interaction bounds the electron-hole pair localizing
on a single molecule. With its radius comparable to the size of the molecule, the Frenkel exciton is considered as a neutral particle that can diffuse from site to site. Wannier-Mott excitons have the electron-hole distance larger than the lattice constant. Due to the weakly correlated, crystalline semiconductors such as Si, Ge, GaAs, the overlap between neighboring lattice atoms reduces the Coulombic interaction between the electron and the hole. Hence, they are not likely found in organic materials. The CT exciton is an intermediate case between a Frenkel and a Wannier-Mott state, being neither very extended nor tightly bound to a single molecule. It is sometimes regarded as an unrelaxed electron-hole pair with both the positive and negative of the charge pair located on separated but adjacent molecules. Yet, this localized picture is only true for a molecular crystal with weak intermolecular interactions and a small overlap between the neighboring orbitals, i.e. each molecule forms a deep potential well in which the charges are confined.

Excitons can diffuse inside organic solids and transfer energy without transporting net charge. The radiative energy transfer involves the emission and absorption of photons, which is controlled by the emission quantum yield and spectrum of donor and the absorption intensity and spectrum of acceptor. There are two types of non-radiative exciton energy transfer. Förster energy transfer refers to resonance between the dipole-dipole interaction. This kind of interaction requires the conservation of spin, thus typically occurs in singlet-singlet with very fast rate. The transfer intensity depends on the degree of overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor. The transfer rate is proportional to the $r^{-6}$, where $r$ is the distance between donor and acceptor. This distance can be in a long range of 10
nm. Figure 1-5 shows the scheme of Förster transfer between two singlets. The second intermolecular transfer is Dexter transfer which originates from exchange of electrons between molecules, so electron orbitals of donor and acceptor must be overlapped. As a result, the active distance of Dexter transfer is within short length of 1 nm. In the Dexter transfer process, only the total spin of the donor-acceptor system is conserved. Therefore effective energy transfers between triplet states or between singlet and triplet states can occur. Figure 1-6 illustrates the Dexter transfer between a singlet and a triplet.

1.1.4 Charge Transport

Presence of charges inside of organic semiconductors leads to polarization of the adjacent environment due to the weak van der Waals interactions. This polarization is much faster than the transfer time of a charge carrier from site to site. This instantaneous following polarization with the moving charge carrier can be treated as a quasiparticle called polaron. Those polarons have their unique transporting properties and can interact with excitons and phonons. There are two types of charge transport mechanism in organic materials. If the phonon scattering time is relatively small and the mean free path of a charge carrier is large compared to the lattice constant, band transport like inorganic semiconductors can be observed. For example, the mobility in molecular crystals such as pentacene reaches up to 40 cm$^2$/V sec. However, most organic semiconductors are amorphous, which fails to meet the requirement of band transport. The charge transport is dominated by the hopping transport model. The carrier hops from one molecule to another with the assistant of energy. This thermally activated process, can be expressed as
Here, $\mu_0$ is the intrinsic mobility at $T = 0$ and $E_A$ is the average activation energy needed to move the charge carrier from one localized state to the next site.

The lower mobility for organic semiconductors is due to the fact that intermolecular interactions in organic electronic materials are weak causing electronic states to be localized on individual molecules or polymer chains. This causes narrower transport bands that are easily disrupted by disorder. The variation of local environments, including molecular orientation and chemical defects, results in energetically disordered electronic states. In order to fully understand charge conduction, we need to understand that adding or removing a charge from a molecule will result in structural relaxation of the molecule and its surrounding environment including changing the bond lengths. Therefore, as a charge moves through a disordered organic solid, it hops between molecules since it is easily localized by defects and disorder.\(^{10}\) Charge transport in organic semiconductors is a result of hops between localized states. The resulting field-dependent mobility follows the universal Poole-Frenkel form

$$
\mu = \mu_0 \exp(\beta \sqrt{\frac{V}{d}})
$$

$\mu_0$ is the zero field mobility in the materials, $V$ is the applied voltage and $d$ is the thickness of the device, $\beta$ is Poole-Frenkel factor related to temperature and materials.

### 1.2 Fundamental of OLED

OLED uses multilayer structure, where the organic layers are sandwiched between two electrodes. When voltage is applied, electrons and holes are injected from
cathode and anode respectively, transported to emitting layer (EML) under electric field and recombine. Usually a hole injection layer (HIL) and a hole transporting layer (HTL) are inserted between anode and EML, an electron transporting layer (ETL) and an electron injection layer (EIL) are inserted between cathode and EML, in order to lower the barrier for carrier injection and facilitate carrier transport. EML is usually doped with emitter to form a guest-host system. Emitters serve as trap-sites for electron-hole recombination, and provide a wide range of emitting color to fulfill the need for full-color display or white light illumination. Figure 1-7 shows a general operation of OLEDs.

During recombination, electrons and holes bound with each other by Coulomb force and form a quasi-particle called ‘exciton’. The radiative decay path of excitons will emit photons. Since electron and hole can have a spin of $\frac{1}{2}$ or $-\frac{1}{2}$, four spin configurations can occur. Combination of antiparallel spins results in a singlet (total quantum spin number $S=0$, $M_S=0$), while combination of parallel spins results in triplet ($S=1$, $M_S=0,\pm 1$). According to spin statistics, the four configurations have equal chance (25%) to occur, therefore singlets and triplets are generated in a ratio of 1:3 under electrical excitation.

Excitons transit back to ground state ($S_0$) through radiative or non-radiative processes. Depending on different radiative pathway, OLEDs are categorized into fluorescent OLEDs and phosphorescent OLEDs. In fluorescent OLEDs, the lifetime of singlets is in the scale of nanoseconds, and the lifetime of triplets are very long, ranging from several microseconds to seconds$^{11}$. Therefore only singlets can go through efficient radiative decay to the ground state (called fluorescence), while most of the triplets go through non-radiative decay and generate heat. The internal quantum
efficiency (IQE), defined as the ratio of generated photons to the injected carriers, has a maximum value of 25% in fluorescent OLED, since only singlets are harvested. In phosphorescent OLEDs, phosphorescent materials incorporating spin-orbit coupling (SOC) are used as emitter. SOC relaxes the transition spin-forbiddeness between singlet state and triplet state, enabling transition between first excited singlet state ($S_1$) and first excited triplet state ($T_1$) as well as the radiative decay between $T_1$ and $S_0$\textsuperscript{12}. The transition between $S_1$ and $T_1$ is intersystem crossing (ISC), usually in a time scale of picoseconds\textsuperscript{13}, which transfers singlets to the $T_1$ state right upon generation, not to be observed as fluorescent light. Triplets then go through radiative decay (usually in a time scale of microseconds) to $S_0$, called phosphorescence. In this scenario both singlets and triplets are harvested, and a 100% maximum IQE can be achieved.

1.3 Terminology of Photometry

Light energy can be characterized by radiometry which measures the radiation of electromagnetic wave in terms of absolute power unit; or by photometry which calculates the relative response from human eyes. Since the human eye is a specific detector that only response to the range of visible spectrum (400-700 nm) and its sensitivity varies significantly within the spectral range, it is easier to use photometric units for daily appliance such as lighting panel and display screen. In this section, a few basic concepts of photometry related to OLED characterization are introduced.

Luminosity Function is the normalized sensitivity of human visual perception of brightness. There are two luminosity functions. At low brightness such as dark night, scotopic luminosity describes the light response of human eye, while at high brightness such as daylight level, the photopic luminosity function is used as the best approximation of the response of the human eye. The photopic luminosity is the CIE
The standard curve used in the CIE 1931 color space. The standard photopic luminosity function \( y(\lambda) \) is normalized to a peak value of unity at 555 nm. The luminosity curve is shown in Figure 1-9.

Luminous intensity represents the perceived light intensity of a light source, the unit of which is candela (cd). 1 cd is defined as an optical power of 1/683 W of a monochromatic light at 555 nm into a solid angle of 1 steradian (sr).

\[
I_v = 683 \int_0^\infty y(\lambda) \frac{dI_v(\lambda)}{d\lambda} d\lambda
\]

Luminous flux represents the total emitted power of a light source over all directions, the unit of which is lumen (lm). 1 lm is defined as the luminous flux of a monochromatic light at 555 nm with an optical power of 1/683 W.

\[
F = 683 (\text{lum/W}) \int_0^\infty y(\lambda)J_v(\lambda) d\lambda
\]

Therefore, according to the definitions of candela and lumen, 1 cd equals 1 lm/sr.

In OLED measurement, the luminance of a device is the ratio of the luminous intensity per the projected area of the device in a certain direction. The unit is cd/m^2 or nit.

CIE color coordinates are mathematical color space recommended by International Commission on Illumination (CIE). The very first one was given in 1931. The coordinates in the CIE 1931 color space is based on the three tristimulus values \( X, Y, \) and \( Z \) defined as

\[
x = \frac{X}{X + Y + Z}.
\]

\[
y = \frac{Y}{X + Y + Z}.
\]

\[
z = \frac{Z}{X + Y + Z} = 1 - x - y.
\]
The tristimulus values of a color are calculated by integrating the radiant power of the light source and the spectral color matching functions over the all visible wavelength. The CIE XYZ color space was deliberately designed so that the Y parameter was a measure of the brightness or luminance of a color. Figure 1-10 shows the CIE 1931 color space with different color regions.

1.4 Optical property in OLEDs

1.4.1 Snell’s Law and Fresnel Equations

When incident light propagates to the interface of two different refractive indexes media, the relationship between the incident angle and the refractive index is described by Snell’s law

\[
\frac{\sin \theta_i}{\sin \theta_t} = \frac{n_t}{n_i}
\]

where \( n_i \) is the refractive index of medium i, \( n_t \) is the refractive index of medium t, \( \theta_i \) is the incident angle of the light ray (with respect to the normal), \( \theta_t \) is the refracted angle (with respect to the normal). There exits an angle that will then approach 90° for some critical incident angle \( \theta_c \), and for incident angles greater than the critical angle there will be total internal reflection. The critical angle can be calculated from Snell's law by setting the refraction angle equal to 90°. Total internal reflection is important in out-coupling efficiency in OLEDs, due to the refractive index difference between organic layers and other layers such as ITO and substrate.

The fraction of the incident power that is reflected from the interface (reflectance \( R \)) and transmitted through the interface (transmittance \( T \)) can be calculated by Fresnel equation. The calculations of \( R \) and \( T \) depend on polarization of the incident ray. The s-polarized light is defined as its electric field perpendicular to the
plane containing incident and reflected light. The reflection coefficient of $s$-polarized light is given by:

$$R_s = \left| \frac{n_1 \cos \theta_i - n_2 \cos \theta_r}{n_1 \cos \theta_i + n_2 \cos \theta_r} \right|^2$$

where $\theta_r$ can be derived from $\theta_i$ by Snell's law. The $p$-polarized light is defined as its electric field parallels to the plane containing incident and reflected light. The reflection coefficient of $p$-polarized light is given by:

$$R_p = \left| \frac{n_1 \cos \theta_i - n_2 \cos \theta_r}{n_1 \cos \theta_i + n_2 \cos \theta_r} \right|^2$$

The transmission coefficient in each case is given by $T_s = 1 - R_s$ and $T_p = 1 - R_p$. If the incident light is unpolarized, the reflection coefficient is $R = (R_s + R_p)/2$. In OLEDs, these combinations of refraction and reflection always happen at every boundary of organic/ITO, ITO/glass, and glass/air. Hence the Fresnel reflection is fundamental reason of weak microcavity effects on OLEDs.

### 1.4.2 Fabry-Perot Interference

Due to the different refractive indices layers in OLED structure, interference from the Fresnel reflection plays an important role in optical property of OLEDs. This interference is an analogy to Fabry-Perot interference where a beam of light propagates through a space between two reflectors. Constructive interference occurs if the transmitted beams are in phase, and this corresponds to a high-transmission peak while destructive interference corresponding to a transmission minimum occurs when the transmitted beams are out-of-phase. The phase difference between each succeeding reflection is given by $\delta$: 
\[ \delta = \left( \frac{2\pi}{\lambda} \right) 2n\ell \cos \theta. \]

where are the wavelength \( \lambda \) of the light (in vacuum), the angle the light travels through the etalon \( \theta \), the thickness between the two reflectors \( \ell \) and the refractive index of the material between the reflecting surfaces \( n \). If both surfaces have a reflectance \( R \), the transmittance function is given by

\[ T_e = \frac{(1 - R)^2}{1 + R^2 - 2R \cos \delta} = \frac{1}{1 + F \sin^2(\delta/2)}, \]

where

\[ F = \frac{4R}{(1 - R)^2} \]

is the coefficient of finesse. Maximum transmission \((T_e = 1)\) occurs when the optical path difference \((2n\ell \cos \theta)\) between each transmitted beam is an integer multiple of the wavelength. In the absence of absorption, the reflectance \( R_e \) is the complement of the transmittance, such that \( T_e + R_e = 1 \). The maximum reflectivity is given by:

\[ R_{\text{max}} = 1 - \frac{1}{1 + F} = \frac{4R}{(1 + R)^2} \]

and this occurs when the path difference is equal to half an odd multiple of the wavelength.

### 1.4.3 Theoretical Analysis of Strong Microcavity

Based on the concept of Fabry-Perot etalon, one can create microcavity by using multilayers of dielectric materials with different refractive indices. Each layer's optical path meets the requirement of the maximum reflectivity. With the presence of microcavity, the density of optical modes will be modified compared with non-cavity devices. Microcavity only allows light with resonance wavelength propagating along its
optical axis, which redistributes density of photons from free space into normal direction of device. Consequently, more light can be extracted from thin film guided mode and substrate mode. The resonance wavelength at normal direction is determined by the optical length of microcavity,

\[ m\lambda = 2L_{optical} \]

\( \lambda \) is the resonance wavelength. \( m \) is the mode order which usually equals to 1 in OLEDs. \( L_{optical} \) is the optical length related to the refractive index of each layer, the thickness of device, phase shift at the interface and light penetration depth into back metal reflector. In the meantime, in order to form a stable resonance inside cavity, standing wave condition must be satisfied, which requires to place the emitting zone at the middle position of the cavity. At the resonance wavelength, the enhancement of emission intensity is calculated as\(^{14}\)

\[ G_e = \frac{\xi}{2} \frac{(1+\sqrt{R_2})^2(1-R_1)}{(1-\sqrt{R_1R_2})^2} \frac{\tau_{cav}}{\tau} \]

\( \xi \) is the antinodes enhancement factor, which equals to 2 at standing wave condition in OLEDs. \( R_1 \) and \( R_2 \) refer to the reflectivity of back metal mirror and front semitransparent mirror, respectively. The ratio, \( \frac{\tau_{cav}}{\tau} \), between radioactive lifetime in cavity device and in noncavity device equals to 1 under first order approximation.

Another effect of microcavity on OLEDs comes from the modifying profile of emission spectrum. The spectral width (\( \Delta \lambda \)) of cavity resonance can be calculated by the uncertainty relation and the photon lift time in the cavity\(^{14}\)
The spectral width is usually much smaller in microcavity than that of free space spectrum. For example, a typical microcavity has $R_1=100\%$ and $R_2=70\%$. With the optical cavity length setting up to the antinodes, the spectral width is calculated as 35 nm with a resonance wavelength at 540 nm. As comparison, one of the most commonly used green emitter Alq₃ with a spectral peak at 540 nm has a full width at half maximum (FWHM) of 120 nm. Thus light from the spectrum overlapping within the spectral width of cavity resonance can only be enhanced. The emitting spectrum of a microcavity device shows a significantly reduced FWHM. On the other hand, by tuning the cavity length, the cavity resonance wavelength can be shifted.

1.5 Optical Simulation

1.5.1 Transfer Matrix Formalism for Passive Layers

Since OLEDs are based on multilayer structure, the light propagation through the stack can be calculated by the method of transfer matrix. Transfer matrix is describing passive optical properties of propagation of the electromagnetic waves (for example light) of a given frequency through a stack. The transfer matrix formalism is an extremely useful method to calculate the reflectivity $R$ and the transmission $T$ of a multilayer structure. The electrical field $E$ and magnetic field $F$ of a light passing through a passive layer with a distance $L$ into the positive $z$ direction are described by the matrix

$$
M = \begin{pmatrix}
\cos kL & \frac{1}{k} \sin kL \\
-k \sin kL & \cos kL
\end{pmatrix},
$$

and
Such a matrix can represent propagation through a layer if $k$ is the wave number in the medium and $L$ the thickness of the layer. For a system with $N$ layers, each layer $j$ has a transfer matrix $M_j$, where $j$ increases towards higher $z$ values. The system transfer matrix is then

$$M_s = M_N \cdots M_2 \cdot M_1.$$ 

Therefore by calculating the system transfer matrix, we can easily get the relation between the incident and transmitted light.

### 1.5.2 Optics of Emissive Multilayer Structures

The emission characteristic of a single molecule is similar to that of a Hertzian dipole. However, in an infinite medium consisting of isotropically oriented molecules, the emission from the multitude of molecules is homogeneous in all directions. If, on the contrary, the molecules are embedded in a thin layer, interference effects of electromagnetic waves reflected at layer interfaces dominate the emission characteristics. In general, the emissive layer of an OLED is part of a multilayer system and the device emission is subject to interference effects. Based on a classical theory, the calculation of the emission of a Hertzian dipole antenna describes the influence of optical interfaces on the radiative dynamics of (fluorescent) molecules. Consider the molecules as driven damped harmonic dipole oscillators. The dynamics of the oscillating dipole moment $\vec{p}$ is described by the following equation:

$$\frac{d^2}{dt^2} \vec{p} + b_0 \frac{d}{dt} \vec{p} + \omega^2 \vec{p} = \frac{e^2}{m} \vec{E}_R(\omega).$$
with $\omega$ as the oscillator frequency in the undamped case, $b_0$ is the initial dipole intensity, $e$ the elementary charge, $m$ the effective mass of the dipole, and $E_r(\omega)$ the interface-reflected field at dipole position. The intrinsic power of the dipole is therefore given by the sum of a radiative and a non-radiative fraction, respectively. These are not affected by the optical feed-back onto the dipoles, therefore the dynamics of the dipole within an optical structure in terms of the intrinsic quantum efficiency $q_0$ and the optical feedback $F$ can be expressed as

$$b = q_0 b_0 \cdot F + (1 - q_0) b_0$$

$F$ can be expressed by means of a generalized parameterization of the emission angle from the passive method, simply speaking, from the Snell’s law.

$$F = \int_0^\infty f(u) du$$

the total dissipated power from the dipole is proportional to the electromagnetic feed-back strength $F$ and therefore, a stepwise integration this equation based on the index limits for total internal reflection allows to determine the fractional radiated power that can be assigned to out-coupled, guided (in the organic materials), and evanescent modes. The integration limits are given by:

$$u = 0 \sim n_t / n_e \quad \text{radiative modes}$$

$$u = n_t / n_e \sim 1 \quad \text{waveguided modes}$$

$$u = 1 \sim \infty \quad \text{evanescent modes}$$

$n_t$ and $n_e$ are the refractive indices of the top and the emissive medium, respectively.
1.6 Optical Properties of Colloidal Quantum Dots

Quantum dots are semiconductor nanocrystals whose sizes reduced into nanoscale dimensions. In this dimension scale, unique optical properties due to a combination of their material band gap energy and quantum well phenomena exhibits. According to quantum theory, only discrete values of energy are allowed to exist within a quantum well. Every particle has a deBroglie wavelength based upon its mass and energy, and the energy states allowed in a quantum well correspond to the energy levels that cause the deBroglie wavelength to form a standing wave. In a three dimensional cubic well, standing waves, or modes, can exist in all three dimensions independent of one another. Thus, the expression for allowed energies is modified and now contains three values for $n$, one corresponding to each direction

$$E_n = \frac{\hbar^2 (n_1^2 + n_2^2 + n_3^2)}{8md^2}$$

When the electrons and holes are confined in such a limited volume and dimension of quantum dot that comparable to the average separation between an electron and a hole, known as exciton Bohr radius, this quantum dot confinement leads to the discrete density of states, which gives unique properties in their optical, electronic, magnetic and chemical properties from bulk crystals. The optical band gap of the QDs becomes different from that of bulk materials. While its intrinsic energy properties are still determined by the bulk material, the QD has emerging new absorption and emission energies near the band gap related to nanocrystal's quantum confined size. As with any crystalline semiconductor, a QD's electronic wave functions extend over the crystal lattice. Similar to a molecule, a QD has both a quantized energy spectrum and a quantized density of electronic states near the edge
of the band gap. As the results, the QDs of the same material, but with different sizes, can emit light of different colors. Due to the quantum confinement, the bandgap energy that determines the energy (and hence color) of the fluorescent light is inversely proportional to the size of the QD. The emission peak is quite narrow due to the small size distribution. Quantum confinement can also be enhanced by introducing larger bandgap semiconductor as the shell outside the core QD. These core/shell QDs have shown improvement to the spectroscopic properties of the particles like stability, lifetime and emission intensity.

1.7 Characterization of Organic Materials and Devices

1.7.1 Terms of Efficiency of OLEDs

The most fundamental measurement of OLEDs is L (luminance)-J (current density)-V (voltage) characteristic which measures the electroluminescence of a device with applied voltage by a photometer and a source meter. With the data from L-J-V measurement, one can calculate the efficiency of OLEDs including the current efficiency, external quantum efficiency (EQE) and power efficiency. Current efficiency, also called luminous efficiency is the ratio of forward luminance to the injected current to the device. It is measured in units of cd/A.

EQE is the percentage ratio of the number of photons emitted out of the device to the number of charge carriers injected into the device. The internal quantum efficiency (IQE) is defined as the ratio of the number of photons generated from the recombination zone inside of the OLED to the number of charge carriers injected into the device. The difference between the IQE and EQE is the out-coupling efficiency which characterizes how much of the generated photons can emit to free space. Therefore the EQE $\mu_{\text{ex}}$ of
OLEDs, can be expressed as product of IQE $\mu_{\text{int}}$ and external out-coupling efficiency $\mu_{\text{outcoupling}}$

$$\mu_{\text{ext}} = \mu_{\text{int}} \mu_{\text{outcoupling}} = \gamma \mu_{\text{exc}} \phi_p \mu_{\text{outcoupling}}$$

The IQE is related to the charge carrier balance factor ($\gamma$), exciton generation ratio by singlet and triplet decay ($\mu_{\text{exc}}$), and intrinsic quantum efficiency for radioactive decay ($\phi_p$).

The relation between the EQE and current efficiency is given by considering the photopic response of the spectrum and the spatial emission distribution. Finally convert EQE in terms of the energy which is characterized by Power efficiency. The power efficiency is the ratio of the luminous power of the device to the electrical power required to drive the device. It is expressed in units of lm/W.

### 1.7.2 Electroabsorption (EA) Spectroscopy

Electroabsorption (EA) spectroscopy is a non-invasive method to probe the internal electric fields in organic semiconductor devices.

EA spectroscopy is based on externally applied electric fields influencing the interaction of molecules with light. The change in absorption of a molecule with an applied electric field can be explained by the Stark Effect which is illustrated in Figure 1-3. Under an applied electric field, dipoles will be present in materials which are dependent on its polarization. This causes a splitting in energy levels and previously forbidden transitions become allowed as well as a red shift in the $1A_g \rightarrow 1B_u$ transition. The excitonic Stark shift follows:

$$\Delta E = \mu \cdot F + \frac{1}{2} \cdot \Delta P \cdot F^2$$
where $F$ is the externally applied electric field and $\Delta P$ represents the polarizability of the material. The polarization is the dipole unit per volume and is described as:

$$P = \varepsilon_0 \cdot \chi \cdot E \cdot l$$

where $\varepsilon_0$ is the dielectric constant of the vacuum and $\chi$ is the polarizability of the material. The field dependent susceptibility is nonlinear and for molecules and polymers with inversion symmetry, all even terms of $\chi$ disappear. Since the imaginary part of the susceptibility $\text{Im}\chi$ is directly proportional to the absorption constant $\alpha(E)$, where $E$ is the energy of the photon, the change in transmittance $\frac{\Delta T}{T}$ can be described as:

$$\frac{\Delta T}{T} \propto \text{Im}\chi^{(3)}(E) \cdot F^2$$

If the applied electric field $F$ is a superposition of both AC and DC biases ($V$), as well as an internal electric field $V_{bi}$, the change in transmittance is:

$$\frac{\Delta T}{T}(\omega) \propto (V_{DC} - V_{bi}) \cdot V_{AC} \sin(\omega t)$$

Therefore, when the $V_{DC}$ is of equal magnitude but opposite direction as the $V_{bi}$, the EA response vanishes. Experimentally, the $V_{AC}$ amplitude is kept constant while changing the applied $V_{DC}$ until $V_{DC}$ exactly cancels out $V_{bi}$.

### 1.7.3 Transient Photoluminescence Analysis

In transient PL (setup in Figure 1-11), a pulse generator is connected to both $N_2$ laser source and storage oscilloscope, to generate periodic laser pulse and receive PL signal. $N_2$ laser has a peak wavelength of 337.1 nm which is within the absorption spectrum of materials. Laser pulse is focused by a focal lens onto a spot of emitting layer. The sample should be placed in vacuum or nitrogen atmosphere to avoid
quenching from O$_2$. The excited PL signal will go through a filter to screen out reflected laser pulse, second harmonious generated laser pulse and substrate modes. The filtered signal is then received by a photomultiplier tube (PMT). The amplified signal will then be received by oscilloscope which is tuned by the same pulse generator.

During the very short time of optical excitation, excitons will be formed in EML. When the pulse is removed, singlets will go through fast fluorescent decay and cause prompt fluorescence (decay time ~ns), whereas triplets go through the slow RISC to singlet state, and contribute to delayed fluorescence (decay time μs~ms). The two phased decays can indicate that triplet harvesting mechanisms exist in a device.
Figure 1-1. Molecular orbitals and associated band diagram of benzene ring\textsuperscript{15}

Figure 1-2. The Jablonski diagram indicates the energy level of each excitation state and the possible transitions between them\textsuperscript{16}
Figure 1-3. Potential energy diagram and Franck-Condon transitions ($E_{(F\,C)a}$ for absorption and $E_{(F\,C)f}$ emission) between electronic ground $S_0$ and excited $S_1$ states. Dashed lines represent the vibrational energy sublevel.\textsuperscript{17}

Figure 1-4. Frenkel, Wannier-Mott and CT excitons in terms of relative bounding distances.\textsuperscript{17}
Figure 1-5. The scheme of Föster transfer between two singlets

Figure 1-6. The scheme of Dexter transfer between a singlet and a triplet.
Figure 1-7. Energy diagram of a common multilayer OLED device

Figure 1-8. Exciton transitions in (a) fluorescent and (b) phosphorescent OLEDs
Figure 1-9. Comparison of eye sensitivity functions for the photopic and scotopic vision regime.\textsuperscript{18}

Figure 1-10. CIE 1931 (x, y) chromaticity diagram. White light is located in the center. Also shown are the regions of distinct colors\textsuperscript{18}
Figure 1-11. Transient photoluminescence measurement: (a) Setup and (b) transient PL signal.
CHAPTER 2
MANIPULATION OF EXCITON BY MICROCAVITY IN OLEDS

In this chapter, we modified the exciton emission from PhOLEDs by microcavity. A systematic study has been conducted on microcavity organic light emitting diodes based on red, green and blue phosphorescent emitters to elucidate the microcavity effects for different color emitters. We found that the luminance output is determined by the reflectivity of the semitransparent electrode and the photopic response of the red, green and blue emitters. While the luminance enhancements of blue and red phosphorescent microcavity devices are small, a current efficiency as high as 224 cd/A is obtained in the green phosphorescent microcavity OLEDs.

2.1 Background and Motivation

The spectral characteristics of an OLED can be manipulated using a microcavity structure to produce saturated colors and enhance the color gamut, and therefore microcavity OLEDs are widely used in active matrix OLED (AMOLED) displays today\(^{19-21}\). In addition, it has been reported that microcavity structure can be used to enhance the light extraction of an OLED by modifying the light distribution within the device\(^{22-25}\). However, closely examining the previous reports, there is a significant difference in luminance enhancements in different microcavity OLEDs. While two times enhancement in current efficiency has been observed in green microcavity OLEDs, no significant improvements were reported in blue microcavity devices\(^{26-28}\). Moreover, there is a discrepancy between enhancement in current efficiency and enhancement in quantum efficiency\(^{29}\). It is apparent that the difference in quantum efficiency and luminance enhancements cannot be due to the difference in photon out-coupling. It is
therefore important to take into account the photopic luminosity due to the microcavity effects.

In this chapter, we report on a systematic study of the microcavity effects on the light out-coupling efficiency and luminance output in red, green and blue phosphorescent OLEDs. Specifically, we investigated two important parameters in microcavity OLEDs: the reflectivity of the semitransparent electrode and the cavity length. A high reflectivity and low absorption semitransparent electrode is required in microcavity OLEDs so as to control the luminance characteristics. We demonstrated that the enhancement in photon out-coupling in the microcavity devices can be greatly affected by the reflectivity of the electrodes. By tuning the cavity length, we found the change of photopic luminosity within the microcavity device leads to a difference in enhancements of current efficiency and quantum efficiency. Finally a green microcavity OLEDs with a current efficiency of 224 cd/A was demonstrated by optimizing both the photon out-coupling efficiency and photopic luminosity.

2.2 Experiments

ITO coated distributed Bragg reflector (DBR) substrates composing of two pairs of quarter-wave stacks of alternating layers of titanium oxide (TiO₂) and silicon oxide (SiO₂) were used for OLED fabrication. The reflectance maxima of the DBR substrates for red, green and blue emitting devices were tuned to 610, 550, and 474 nm respectively. After UV ozone treatment for 15 minutes, a 25-nm-thick poly(3,4-ethylenedioxythiophene)–polystyrenesulfonic acid (PEDOT:PSS) (AI 4803) as a hole injection layer was spin-coated onto ITO substrates and baked at 180 °C for 15 minutes in air. To fabricate the devices, the following layers were sequentially deposited by thermal evaporation: a 20 to 45-nm-thick 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane
(TAPC) as a hole transport layer (HTL), a 20 to 30-nm-thick 4,4'-N,N'-dicarbazole-biphenyl (CBP) doped with 7 wt% tris(2-phenylpyridine)iridium (Ir(ppy)_3) as a green emitter, a 15-nm-thick 3,5'-N,N'-dicarbazolebenzene (mCP) doped with 15 wt% iridium (III)bis [2-methyl dibeno-(f,h) quinoxaline](acetylacetonate) (Ir(MDQ)_2(acac)) and a 15-nm-thick 2,2',2''(1,3,5-benzenetriyl)tris-(1-phenyl–1H-benzimidazole) (TPBi) doped with 15 wt% Ir(MDQ)_2(acac) as a red emitter, a 20-nm-thick mCP doped with 5 wt% iridium(III) bis[(4,6-difluorophenyl)pyridinato-N,C2'] picolinate (Flrpic) as a blue emitter, a 45 to 60-nm-thick tris[3-(3-pyridyl)-mesityl]borane (3TPYMB) as an electron transporting layer (ETL) for the green and red emitting devices, a 45 to 55-nm–thick 3,5,3",5"-tetra-3-pyridyl-[1,1';3',1"]terphenyl (B3PyPB) as an ETL for the blue emitting devices, a 1-nm-thick LiF layer as an electron injection layer and a 100-nm-thick aluminum as a cathode. To extract the substrate mode, a macrolens was attached to the substrate using an index matching gel. Current–luminance–voltage characteristics were measured using a Keithley Series 2400 source meter and a Keithley Series 6485 picoammeter with a calibrated Newport silicon photodiode. The luminance was calibrated using a Konica Minolta luminance meter (LS-100). The electroluminescence spectra were obtained with an Ocean Optics HR4000 spectrometer.

2.3 Results and Discussion

2.3.1 Relation between Resonant Enhancement and Reflectivity of DBR

The resonant emission enhancement $G_{e}$ along the normal direction in a microcavity structure is related to the reflectivity of the semitransparent mirror based on the following relationship:\textsuperscript{30}

$$G_{e} \propto \frac{(1+\sqrt{R_2})^2(1-R_1)}{(1-\sqrt{R_1R_2})^2}$$
$R_1$ and $R_2$ refer to the reflectivities of the front semitransparent mirror and back metal mirror, respectively. In order to enhance the light output from a microcavity, a front semitransparent electrode with high reflectivity and low absorption loss is preferred. A semitransparent metal electrode such as a thin Ag layer is mostly commonly used due to its simple fabrication steps.\textsuperscript{22,29,31-33} However a thin Ag layer does not provide a high enough reflectivity for a microcavity device. Because of the large extinction coefficient of a metal and of the presence of surface plasmon mode at the organic/metal interface, the use of semitransparent metal electrodes is not favorable for microcavity OLEDs.

On the other hand, the use of dielectric DBR has the advantages of high reflectivity and low absorption loss\textsuperscript{34}. Here we chose SiO$_2$/TiO$_2$ DBRs for our microcavity OLED fabrication. Figure 2-1 shows the measured reflectivity of the DBR substrates for blue, green, and red microcavity devices. The peak reflectivities of the blue, green and red DBR substrates were tuned to 474, 550, and 610 nm respectively. Due to the dispersion of refractive indices of SiO$_2$ and TiO$_2$, the maximum reflectivities of the DBR substrates are different. The reflectivities are 62, 75, and 65% for blue, green and red DBR substrates respectively, corresponding to a calculated enhancement ratio of 0.581:1.00:0.685 normalized by green enhancement according to equation 1. Because the higher reflectivity of the semitransparent electrodes, they give rise to a stronger microcavity effect with higher resonance peak intensity, it is expected that the green microcavity device will give a higher efficiency enhancement than the blue and red devices. We fabricated blue, green and red emitting OLEDs on DBR substrates along with devices on non-DBR substrates which were used as references. Figure 2-2A shows the structures of the optimized devices with and without microcavity
structure. Figure 2-2 B shows the normalized electroluminescent (EL) spectra of the microcavity devices and the EL spectra of the reference devices driven at a constant current density. Compared to the non-cavity devices, the DBR devices show significantly enhanced luminance output along the normal direction with narrow FWHMs due to the strong microcavity effects. The intensity enhancements of the blue, green and red devices at optimized wavelength are 3.5, 6.0, and 3.9 respectively. The ratio of those enhancements is 0.583:1.00:0.650 for blue, green and red devices, which match the calculation from the reflectivity of each substrate.

2.3.2 Relation between Resonant Enhancement and Cavity Length

In order to study the cavity length effect, devices with three different cavity lengths were fabricated on DBR substrates for red, green and blue OLEDs. The cavity length of these devices is based on the device structures of each emitting color as shown in Figure 2-2A. For the green emitting devices, we tuned the thicknesses of the TAPC and emitting layers. Device G1 has a 35-nm thick TAPC layer and a 30-nm thick CBP:Ir(ppy)_3 layer, device G2 has a 30-nm thick TAPC layer and a 25-nm thick CBP:Ir(ppy)_3 layer and device G3 has a 30-nm thick TAPC layer and a 20-nm thick CBP:Ir(ppy)_3 layer. Figure 2-3A shows the electroluminescent (EL) spectra of the devices with and without DBR driven at a current density of 0.1 mA/cm². The noncavity devices showed broad EL spectra with FWHMs of about 80 nm and the intensity of shoulder peak in EL spectra is slightly reduced as the optical length decreases from device G1 to device G3 due to the weak microcavity effect. On the other hand, in addition to the significantly enhanced intensity along the normal direction and narrow FWHMs in the microcavity devices, the peak wavelength of the DBR device decreases from 572 nm to 528 nm with decreasing thicknesses of the TAPC and emitting layers.
While the main peak emission wavelength of Ir(ppy)₃ is around 515 nm, the G2 DBR device exhibits a higher EL intensity than the G1 DBR device along the normal direction because the DBR substrate for green devices has the highest reflectivity at 550 nm. We calculated the enhancement ratio due to microcavity effects by integrating the EL intensity of each device over all wavelengths and considering the ratio of the integrated intensity of the DBR device to that of the noncavity device, and the results are shown in Table 2-1. DBR devices G1, G2, and G3 show enhancement ratios of 60.1, 101, and 70.2%, respectively, indicating the enhanced out-coupling efficiency due to the microcavity effects. However, the current efficiency shows different enhancement ratios from the number of outcoupled photons. The current efficiencies for devices G1, G2, and G3 with and without DBR as shown in Figure 2-3 B are 115, 175, and 104 cd/A, and 65, 73, and 53 cd/A at 0.1 mA/cm², respectively, representing enhancements of 75, 140, and 97% due to microcavity effects. While the G2 DBR device shows the highest quantum efficiency and current efficiency, the enhancement ratio of the current efficiency is higher than that of the quantum efficiency along the normal direction. This discrepancy in enhancement ratio is caused by the difference in luminosity. The normalized photopic luminosity ($L$) of each spectrum is calculated according to equation

$$L = \int_{400}^{750} V(\lambda)S(\lambda)d\lambda$$

$S(\lambda)$ is the normalized electroluminescent spectrum of OLEDs, $V(\lambda)$ is the standard photopic luminosity function with an unity value at 555 nm, $\lambda$ is wavelength. The integrating region is over all visible wavelengths. We calculated enhancement ratio of the luminosity in the G1, G2, and G3 DBR devices from their references. The results are shown in Table 2-1. Because the narrow EL spectra of the DBR devices are peaked at
around 550 nm where the photopic luminosity has a highest value, all DBR devices show higher luminosities than the noncavity devices and the G2 DBR device having a maximum EL intensity at 550 nm represents the highest enhancement of luminosity. By considering both enhancements from the quantum efficiency along the normal direction and the luminosity, the total enhancement ratios of 78, 146, and 95% can be calculated for the G1, G2, and G3 DBR devices, respectively, and they are in agreement with the measured enhancement ratios of the current efficiencies.

We also examined the cavity length effects on red emitting phosphorescent microcavity OLEDs. Keeping the rest of the device structure the same as the red device shown in Figure 2-2A, we fabricated devices with different 3TPYMB thickness: device R1 has a thickness of 52 nm, device R2 has a thickness of 55 nm and device R3 has a thickness of 61 nm. Figure 2-3C shows the normalized EL spectra of the devices with and without DBR driven at a constant current density along the normal direction. With a significantly reduced FWHM, the emission peak decreases from 599 nm to 630 nm. The R2 DBR device having a resonant wavelength at 612 nm, corresponding to the peak reflectivity of red DBR, shows the highest enhancement of 66.8% by integrating all wavelengths, while the shorter and longer microcavity devices showed an enhancement of 46.6% and 31.4% respectively due to the mismatch of the DBR reflectivity. Figure 2-3D shows the current efficiencies of the devices with and without DBR. At a current density of 0.1 mA/cm², devices R2 with and without DBR show the highest current efficiencies of 29 and 55 cd/A, respectively, indicating a 89% enhancement due to microcavity effects, while the R1 DBR device shows a lower current efficiency of 50 cd/A and the R3 DBR device has the same current efficiency as the R3 noncavity
device. Compared to an enhancement of 66.6% in the EL intensity along the normal direction, a larger enhancement of 89% in current efficiency for the R2 DBR device is attributed to an increase in luminosity (Table 2-1). The importance of the luminosity is apparent in the R3 DBR device. While the R3 DBR device shows an enhancement of 31.4% for the integrated EL intensity along normal direction over the R3 noncavity device, a decrease of the luminosity by 23.7% in the R3 DBR device leads to insignificant changes in current efficiency even there is an enhancement in outcoupled photons.

Finally, we investigated the microcavity effects on the blue emitting phosphorescent OLEDs. B3PyPB having high triplet energy and high mobility was used as the electron transporting layer. Devices B1, B2 and B3 have the thicknesses of B3PyPB layer as 45 nm, 49 nm and 53 nm respectively. Figure 2-3E shows the normalized EL spectra of the DBR devices with along the normal direction compared with the corresponding devices without DBR. With the increase of cavity length, the DBR devices showed a peak emission wavelength change from 470 nm to 498 nm. While all DBR devices showed enhancements of 40.1, 29.4 and 23.2% in the integrated intensity, the B1 DBR device shows the highest enhancement with a resonant wavelength at 470 nm which corresponds to the peak reflectivity of blue DBR. However, device B3 DBR is the only device which shows an enhancement in current efficiency (Figure 2-3 F) and devices DBR B1 and B2 showed the same current efficiencies as the non-cavity B1 and B2 devices. This is due to the significantly decreasing luminosity as the resonant wavelength of the emitting light shifts toward shorter wavelengths away from 550 nm. According to Table 2-1, the luminosity in the B1, B2, and B3 DBR devices
decrease by 28.7, 19.5, and 10.6%, respectively. Even if the B3 DBR device exhibited 12% enhancement in the current efficiency, the Commission Internationale de L'Eclairage (CIE) coordinates of its EL spectrum is (0.06, 0.51), indicating that the emitting color is no longer blue. Therefore in order to achieve deeper blue from Firpic, one has to force the microcavity peak to shorter wavelengths, which is demonstrated in device B1 DBR. Consequently, it causes a greater mismatch between the cavity resonance wavelength and the Firpic emission spectrum, resulting in a lower enhancement in quantum efficiency. Therefore, it is difficult to enhance the efficiency of the Firpic-based blue emitting OLED device while pushing the emission peak to shorter wavelengths to generate a deeper blue color. Figure 2-4 shows the CIE coordinates for the R, G, and B EL spectra from the noncavity devices and optimized microcavity devices. Because of the reduction of the EL spectral width in the microcavity devices, the CIE coordinates of the R, G, and B emitters moved towards the boundary of CIE chart, from (0.617, 0.373), (0.321, 0.624), (0.148, 0.345) to (0.636, 0.350), (0.289, 0.692), (0.138, 0.170), respectively, enlarging the color gamut in the microcavity devices.

2.3.3 High Efficiency Green OLEDs with Microcavity

To further enhance the device efficiency, we demonstrate the microcavity effects through a highly efficient OLED device using double emitting layer (DEL). It has been demonstrated that the DEL structure can confine the emitting zone of OLEDs within the center of the emitting layer\textsuperscript{37,38}. Figure 2-5A shows the device structure and the energy level diagram of the DEL OLEDs. The resonant peak wavelength of the DBR device was tuned to 555 nm to maximize the luminance enhancement. TCTA was selected as a host due to its energy band edge off-set regarding CBP. While TCTA has a hole
mobility of $3 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ and a very low electron mobility of $10^{-8}$ cm$^2$ V$^{-1}$ s$^{-1}$, CBP has high electron and hole mobilities of $3 \times 10^{-4}$ and $2 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively. As a result, exciton generation zone is confined at the TCTA/CBP interface, preventing the quenching of excitons at the interface between the emitting layer and the electron transport layer. Additionally, the DEL structure also facilities carrier injection into the emitting layer due to the low lying highest occupied molecular orbitals (HOMO) of TCTA. Figure 2-5B shows the current density-voltage characteristics of the single and double emitting layer devices with and without DBR. It is apparent that DEL devices have an order of magnitude higher in current density than that of the single emitting devices. Figure 2-5C shows the current efficiency of the DEL OLEDs with and without DBR. The device with and without DBR show the maximum current efficiencies of 93 cd/A and 224 cd/A, respectively, which corresponding to an enhancement of external quantum efficiency from 21% to 27%. While the enhancement of 140% in the DEL OLEDs with DBR was the same as that in the #2 DBR device with single emitting layer, the current efficiency increases to 224 cd/A which, to our knowledge, is the highest current efficiency for single emitting unit devices without light extraction ever reported$^{25,26}$. Figure 2-5D shows the angle dependence of emitting light for the noncavity device and the DBR device with and without macrolens. Both of the DBR devices with and without the macrolens showed strong forward emission distribution and with macrolens another 89% enhancement was achieved by integrating intensity at all angles. Thus, the total enhancement by a factor of 2.4 ($=1.28 \times 1.89$), promising an EQE of 50%, can be achieved by the microcavity and macrolens in the DEL device with DBR. Figure 2-5E shows the angle dependence of peak wavelengths for non-cavity
device and DBR devices with and without macrolens. Both DBR microcavity devices show blue shift with the increasing of viewing angle, while the peak wavelengths of non-cavity device stay the same.

2.4 Conclusions

In summary, through a systematic study, we investigated the effects of the electrode reflectivity and cavity length on the performance of microcavity phosphorescent green, red and blue emitting OLEDs. We found the luminance output is a strong function of the reflectivity of the electrodes as well as the EL spectral luminosity in microcavity OLEDs. The resulting enhancement in current efficiency is a combined effect of luminescence efficiency and luminosity. By optimizing both factors, a high current efficiency of 224 cd/A was demonstrated in a double-emitting-layer green microcavity OLED.
Table 2-1. Enhancement from spectra was percentage change between integrated intensities of non-cavity and microcavity having same organic structure.

| Device | Enhancement from quantum efficiency | Change of luminosity | Current efficiency enhancement
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Green</td>
<td>G1 60.1%</td>
<td>11.3%</td>
<td>78%</td>
</tr>
<tr>
<td></td>
<td>G2 101%</td>
<td>22.7%</td>
<td>146%</td>
</tr>
<tr>
<td></td>
<td>G3 70.2%</td>
<td>14.8%</td>
<td>95%</td>
</tr>
<tr>
<td>Red</td>
<td>R1 46.6%</td>
<td>32.6%</td>
<td>94%</td>
</tr>
<tr>
<td></td>
<td>R2 66.8%</td>
<td>14.2%</td>
<td>90%</td>
</tr>
<tr>
<td></td>
<td>R3 31.4%</td>
<td>-23.7%</td>
<td>0%</td>
</tr>
<tr>
<td>Blue</td>
<td>B1 40.1%</td>
<td>-28.7%</td>
<td>-1%</td>
</tr>
<tr>
<td></td>
<td>B2 29.4%</td>
<td>-19.5%</td>
<td>4%</td>
</tr>
<tr>
<td></td>
<td>B3 23.2%</td>
<td>-10.6%</td>
<td>11%</td>
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Figure 2-12. Reflectivity of DBR substrates for blue, green, and red.
Figure 2-2. Microcavity devices: (a) Device structure of green red and blue OLEDs (b) normalized EL spectra of green, red and blue devices, spectra were normalized to the peak intensities of their non-cavity devices with same organic structure.
Figure 2-13. Microcavity device performance: normalized EL spectra (a) and current efficiency (b) of green PhOLEDs, normalized EL spectra (c) and current efficiency (d) of red PhOLEDs, normalized EL spectra (e) and current efficiency (f) of blue PhOLEDs.
Figure 2-3. Continued.
Figure 2-3. Continued.
Figure 2-14. The Commission Internationale de L’Eclairage coordinates (1932) of noncavity devices (black) and optimized microcavity devices (yellow) EL spectra
Figure 2-15. Double-emitting layer device performance: (a), device structure of double-emitting layer OLED; (b) current density vs voltage of DEL and SEL devices; (c) current efficiency with and without microcavity; (d) angle dependence of integrated intensity; (e) angle dependence of peak wavelength.
Figure 2-5. Continued
Figure 2-5. Continued
CHAPTER 3
EXCITON CONFINEMENT IN MULTILAYER CADMIUM-FREE BLUE EMITTING QD-LEDS

In this chapter, we demonstrate blue/violet emitting devices based on cadmium-free zinc selenide/zinc sulfide core/shell quantum dots. Using poly(N-vinylcarbazole) with a low lying highest occupied molecular orbital energy for the hole transporting layer, enhanced hole injection was observed, resulting in efficient blue/violet emitting devices. The device charge balance was enhanced by tuning the thicknesses of the hole transporting layer and quantum dot emitting layer. An external quantum efficiency of 0.65% for these devices was achieved.

3.1 Background and Motivation

Recently quantum dot light emitting diodes (QD-LEDs) are considered as the devices for the next generation displays because of their color tunability and highly saturated emitting colors\textsuperscript{40-45}. The electroluminescent spectra of typical QD-LEDs have a full-width at half-maximum (FWHM) of 20 nm and by tuning the size of nanocrystals, they can cover the full color gamut of the CIE chromaticity diagram\textsuperscript{40-42}. Furthermore, these devices can be fabricated by solution processes which are favorable for low cost and large area manufacturing\textsuperscript{45}. Thus far the most efficient light emitting QD-LEDs are green and red with external quantum efficiencies (EQEs) less than 10\%\textsuperscript{46,47}. While the EQEs of orange and red emitting QD-LEDs are comparable with the efficiencies of organic LEDs\textsuperscript{48}, the EQEs of blue/violet emitting QD-LEDs are substantially lower\textsuperscript{49-51} because of the low photoluminescence (PL) yields of blue/violet emitting cadmium (Cd)-based QDs. Although CdSe/ZnS core/shell QDs have high PL quantum yields in the green and red regions, the uniformity of the blue emitting QDs is difficult to control due to the lattice mismatch between CdSe and ZnS\textsuperscript{52} resulting in defect formation and low
PL quantum yields in these nanocrystals (NCs). For example, the EL spectra of CdS QD-based LED have a relatively wide FWHM of ~30 nm along with a broad background emission at longer wavelengths due to emission from the trap states. Moreover, the Cd-based QDs are not environmental friendly and heavy metal-free QDs are desirable for future applications. Recently, zinc-based compound semiconductors have been developed as candidates for efficient blue/violet emitting NCs.

Specifically, ZnSe is a large gap semiconductor with a bulk bandgap energy of 2.8 eV and its QDs emit in the range between UV and blue. Although there are several studies on PL of ZnSe NCs, blue/violet emitting ZnSe/ZnS QD-LEDs have not been reported. Here, we report on efficient solution processed blue/violet emitting QD-LEDs using ZnSe/ZnS core/shell QDs.

### 3.2 Experiment

We fabricated QD-LEDs on glass substrates coated with ITO with a sheet resistance of ~20 Ω sq⁻¹. The substrates were cleaned with deionized water, acetone and isopropanol, consecutively, for 15 min each, and then treated for 15 min UV-ozone cleaner. The first layers of PEDOT:PSS (Al 4803) were spin-coated and annealed at 180 °C for 15 min in air. The coated substrates were then transferred to a N₂-filled glove box for spin-coating of the Poly(4-butylphenyl-diphenyl-amine)(poly-TPD) (American Dye Source), PVK (American Dye Source), ZnSe/ZnS QD and ZnO nanoparticle layers. The HTL (20 mg ml⁻¹ in chlorobenzene) was spin-coated at 6000 r.p.m. for 30 s, followed by annealing at 120 °C for 15 min. Then spin-coated ZnSe/ZnS QDs (10 mg ml⁻¹ in toluene) spin speed varied from 500 to 2,000 r.p.m to achieve different layer thickness and annealed at 180 °C for 30 min. ZnO nanoparticles (30 mg ml⁻¹ in ethanol) [14] was spin-coated at 8,000 r.p.m. and annealing at 80 °C for 30 min. These
multilayer samples were then loaded into a custom high-vacuum deposition chamber (background pressure, \( \sim 3 \times 10^{-7} \) torr) to deposit the top Al cathode (100 nm thick) patterned by an \textit{in situ} shadow mask to form an active device area of 4 mm\(^2\).

3.3 Results and Discussion

3.3.1 Characterizaion of Cd-free QDs

ZnSe/ZnS core/shell QDs were synthesized according to the previous reports \cite{56,59}. In our synthesis of Zn-based QDs, highly toxic reagents which are required for Cd-based QD synthesis are avoided. The size of the ZnSe core was tuned to violet emission. In order to confine the exciton, additional ZnS layers were grown as a shell to form the core-shell structure. Our hydrodynamic size measurement shows our core/shell ZnSe/ZnS QDs have an average size of 9.3 nm. From the PL measurements, ZnSe/ZnS QDs suspended in toluene showed a high quantum yield of 40\%, similar to that of the deep blue emitting ZnCdS alloy QDs reported previously \cite{60}. Figure 3-1 shows the optical absorption and PL spectra of the QDs. While the absorption peak of the QDs is at 406 nm, the PL emission peak is at 420 nm with a FWHM of 16 nm, which is significantly narrower than that for blue emitting Cd-based QDs, indicating that the quality of our ZnS QDs is indeed better than most Cd-based QDs.

3.3.2 Deep Blue QD-LEDs

There are two configurations of EML of QD-LEDs. One approach is to blend the QDs with a wide gap conjugated polymer matrix \cite{42,61} which is responsible for carrier transport. However, in case of wide gap QDs such as ZnSe or CdS, it is difficult to find a wide gap conjugated polymer capable of both transporting carriers and confining excitons in the QDs. As a result, the polymer matrix can sometime contribute to EL thus lowering the efficiency of the emitting QDs. Another approach is to fabricate multilayer
LEDs, wherein a close-packed QD layer is sandwiched between a wide gap HTL and a wide gap ETL. The photo-generated excitons can be effectively confined in the QD layer by the HTL and ETL, resulting in light emission from the QD layer \(^{41,52,57,62}\). In this work, we used the multilayer approach to fabricate our ZnSe/ZnS QD-LEDs.

Figure 3-2A shows the current density and optical power density as a function of applied voltage for devices with a 40-nm-thick QD layer on the poly-TPD and the PVK layers, respectively. Poly-TPD has been widely used as a HTL material for solution processed organic light emitting devices due to its low process temperature and good chemical resistance to organic solvents used for subsequent QD layer deposition \(^{47}\). However, our device with poly-TPD layer shows low current density and low optical power density over a wide voltage range. Based on the energy band diagram shown in Figure 3-2B, ZnSe/ZnS has a low lying ionization potential at -6.6 eV and poly-TPD has a highest occupied molecular orbital (HOMO) level of -5.2 eV. Hole injection from the poly-TPD layer into the QDs layer can be significantly suppressed by a hole barrier of 1.4 eV at the poly-TPD/QDs layer interface, whereas electron injection is more efficient due to a better matching of the conduction bands between the ZnSe QDs (-3.7 eV) and ZnO (-4.2 eV) \(^{63}\) layers. Notice that there are two turn-on voltages shown in the current-voltage curve in Figure 3-2A. The first current turn-on at 1.2 V corresponds to the onset of electron injection and the second turn-on at 4.4 V corresponds to the onset of hole injection and light emission. Such a difference in carrier injection causes a severe charge imbalance in our devices, resulting in low electron-hole recombination efficiency. Moreover, it is reported that an imbalanced charge transport leads to strong non-radiative Auger recombination, where an exciton recombines and donates its energy to
an unpaired carrier which then relaxes to the ground state via interactions with phonons\textsuperscript{64}. In our poly-TPD devices, generated excitons were likely to be quenched by excess electrons.

In order to improve hole injection, the poly-TPD layer was replaced by PVK\textsuperscript{61,65}. With a HOMO level at -5.8 eV, PVK reduces the hole injection barrier from 1.4 eV to 0.8 eV, resulting in an enhancement in charge balance and an increase in hole current as shown in Figure 3-2A. The enhancement in hole injection also leads to a reduction of optical power density turn-on voltage from 4.4 V to 3.5 V. At an applied voltage of 8 V, the device with the PVK layer shows an optical power density of 46 mW/cm\textsuperscript{2}, which is significantly higher than 7.5 × 10\textsuperscript{-3} mW/cm\textsuperscript{2} of the device with the poly-TPD layer.

Figure 3-3 A and B show the EL spectra of the poly-TPD and PVK devices, respectively. The poly-TPD device shows a strong band edge emission peaked at 425 nm with a broad background emission from 400 nm to 700 nm. Considering the insufficient hole injection from the poly-TPD into the QDs layer due to the large energy barrier of 1.4 eV, exciplex formation can lead to the background emission from the poly-TPD device or emission through the surface states of the QDs, which gives rise to the broadband emission in Figure 3A. Moreover, the band gap of poly-TPD is not sufficient to effectively confine the excitons in the QDs layer. Exciton energy can be transferred from the QD layer to the poly-TPD layer resulting in a low quantum efficiency of QD emission. In contrast to the poly-TPD device, the PVK device only shows band edge emission from the QDs with no background emission as shown in Figure 3-3B. The deep HOMO level of PVK lowers the hole injection barrier and facilitates hole injection into the QDs, thereby shifting the charge recombination zone from the HTL/QDs.
interface to the bulk of the QDs layer. Compared to poly-TPD, PVK also provides better exciton confinement due to its higher exciton energy.

In order to achieve the best device performance, we fabricated devices with different QD layer and PVK layer thicknesses. Figure 3-4A shows the EQE vs. current density for the devices with different QD layer thicknesses of 20, 30, and 40 nm. Spinning coating a QD layer with thickness larger than 40 nm leads to non-uniform thickness and poor device performance. It is apparent that the EQE increases with the QD layer thickness and the device with the 40-nm-thick QD layer has an EQE as high as 0.65% with a low roll-off up to a current density of 500 mA/cm². Increasing the thickness of the QD layer, the distance between the emitting zone and the HTL/QD interface becomes larger, resulting in a reduction of non-radiative recombination of excitons at the interface and enhancement in device efficiency. We also fabricated devices with different PVK thicknesses. Figure 3-4A shows the EQE vs. current density of devices with different PVK layer thicknesses. With the decrease in PVK layer thickness from 40 nm to 20 nm, the EQE increases from 0.3% to 0.65%. PVK has a deep HOMO level but with a substantially lower hole mobility (10⁻⁶ cm²/Vs) compared with the electron mobility in ZnO (2.0 × 10⁻³ cm²/V·s)⁴⁷. Based on the above discussion, QD-LED devices are electron dominated and decreasing the HTL thickness leads to improved charge balance and higher efficiency, confirming our discussion in the previous section that the charge balance is critical to the device performance.

3.4 Conclusion

In summary, we demonstrated that efficient cadmium-free violet emitting QD-LEDs can be fabricated using PVK as an HTL. Because of its deep HOMO energy, hole injection into ZnSe/ZnS core-shell structured QDs is enhanced, resulting in an increase
in exciton recombination in the active layer. Our device data show that the thickness of QDs layer plays a critical role in determining the charge recombination efficiency. With an optimized QDs layer, we reported an EQE of 0.65\%, suggesting a solution based cadmium-free ZnSe/ZnS QD-LED is a promising candidate for short wavelength LEDs.
Figure 3-16. Absorption and PL spectra of ZnSe/ZnS QDs in solution (toluene)
Figure 3-2. Device performance: (a) Current density – voltage (black) and optical power density – voltage (blue) characteristics of poly-TPD and PVK devices; (b) Energy band diagram of multilayer QD-LED devices with poly-TPD or PVK as HTL. The unit for the energy levels is in eV.
Figure 3-3. EL spectra of (a) poly-TPD device and (b) PVK device.
Figure 3-4. EQE as a function of (a) emitting layer thickness and (b) PVK thickness.
CHAPTER 4
TRIPLET EXCITONS IN HIGH EFFICIENT LOW ROLL-OFF BLUE EMITTING PhOLEDs WITH TERCARBAZOLE HOSTS

Long lifetime and high density of triplets are big problems in PhOLEDs, which cause problems like large roll-off and unstable devices. In this section, we studied the triplet dynamic in blue PhOLEDs with three new ter-carbazole-based host materials designed and synthesized. These hosts exhibited high triplet energy levels (2.90–3.02 eV) and high glass transition temperatures (> 147 °C), which promised high efficiency and improved thermal stability compared with the commonly used carbazole-based host material, mCP. Comparable maximum efficiency and improved thermal stability were achieved in the blue emitting PhOLEDs using ETC as the host material doped with the iridium(III) bis (4,6-difluorophenylpyridinato)-picolinate (FIrpic). All OLEDs with ter-carbazole hosts showed suppressed roll-off of efficiency at high luminance due to the low triplet-triplet annihilation and triplet-polaron quenching revealed by the device physics study. Our study also indicated that not only the mobility of BETC is nearly 2 order magnitudes lower than that of ETC, but also the BETC device is carrier injecting limited.

4.1 Background and Motivation

Phosphorescent emitting systems improved the efficiency of organic light emitting diodes (OLEDs) enormously and promoted their wide applications in display and lighting.\(^{25,66,67}\) While the green and red emitting phosphorescent OLEDs have achieved high efficiency and long lifetime, the performance of blue emitting counterpart is still a bottleneck.\(^{68-70}\) In order to realize the high performance of blue phosphorescent OLEDs, several critical issues are noted and partially addressed, such as triplet exciton confinement, charge balance, and injection.\(^{36,71-75}\)
In order to prevent the energy back transfer from the high triplet energy ($E_T$) emitters, both transporting and host materials with higher $E_T$ are therefore needed.\textsuperscript{36,71,72} With a high $E_T$ electron transporting material used in the ETL, 100% internal quantum efficiency was reported in blue phosphorescent OLEDs.\textsuperscript{73} The second concern comes from the charge balance inside the emitting zone. The imbalanced electron and hole carriers will result in a dropped excitation generation rate which leads to low quantum efficiency and excessive polarons within the devices. Therefore, ETLs with a mobility larger than $10^{-4}$ cm$^2$/V·s such as 1,3,5-Tri(m-pyrid-3-y1phenyl)benzene (TmPyPB) were applied.\textsuperscript{75} In the aspect of host materials, it is also important to consider the matching of the front molecular orbitals of host materials with respect to transporting material molecules, so as to ensure a better charge injection into the host materials.\textsuperscript{76}

In addition to high $E_T$, mobility and suitable energy levels, a good host for blue phosphorescent emitters also requires the high glass transition temperature (Tg) and high energy transfer rate which lead to high stability and quantum yield for blue dopant emission. Aryl silanes and phosphine oxides are potential candidates.\textsuperscript{77,78} However, due to the large band gap, low PL quantum yield and poor charge transfer properties, devices showed low efficiency and large roll-off.\textsuperscript{79,80}

Carbazole derivatives are very good candidates as host materials for efficient blue phosphorescent emitters. Due to the high ionized potential of carbazole functional group, the derivatives share high $E_T$. And large π-conjugated structure promises high hole mobility ($\mu_h$). For example, 1,3-Bis(N-carbazolyl)benzene (mCP) has a $\mu_h$ as high as $5\times10^{-4}$ cm$^2$/Vs and a triplet energy up to 2.9 eV.\textsuperscript{81} Previous studies have reported
over 90% PL quantum yield in iridium (III) bis(4,6-(di-fluorophenyl)pyridinato-N,C²) picolinate (FIrpic) doped mCP. Another advantage arises from the singlet and triplet energy split of carbazole derivatives. Due to the strong electron acceptor character of the carbazole, the energy split is small in their n-π* transitions. This energy split can be as small as about 0.3-0.5 eV. As a result, a lower luminance turn-on in blue phosphorescent OLEDs can be achieved, which promises high power efficiency. However, compared with aryl silanes and phosphor oxides, mCP does not have a proper Tg. Due to the flat molecular shape of mCP, Tg of mCP is only 60 °C. This drawback makes the OLEDs thermally unstable under operation.

Suppressing efficiency roll-off plays a critical role in the application of OLEDs on display and lighting which require high luminescence of operation. Due to the long lifetime and high density of triplet excitons, the triplet-triplet annihilation and triplet-polaron quenching become the dominating loss mechanisms that contribute to the efficiency roll-off, which lead to the increase of power consumption and eventually reduce the device operating lifetime. Therefore it is very important to characterize the reactions of triplet excitons and polaron so as to reduce the efficiency roll-off in PhOLEDs. Emitting layers (EMLs) of most PhOLEDs are based on host-guest system, thus changing the host system could help modify these interactions and suppress efficiency roll-off.

Here, we demonstrated blue phosphorescent devices with three ter-carbazole host materials doped with FIrpic. High efficiency, small roll-off and low luminance turn-on were achieved in PTC device. Device physics studies were conducted in order to characterize and rationalize the different performance rising from different side chains.
The result and conclusion of our study could provide more information to the materials engineering for further realizing efficient and stable blue phosphorescent materials.

4.2 Experiment

4.2.1 Synthesis and Characterization of Ter-carbazole Hosts

The reaction scheme for synthesizing ter-carbazole hosts are shown in Figure 4-1. By using an optimized Buchwald Hartwig reaction condition, the final host materials were synthesized and purified with high yields of 85%-89%. The synthetic procedures were designed according to industrial scale protocols with considerations on procedure simplification and safety issues. tBu₃P was replaced by a less pyrophoric reagent HP₃Bu₃BF₄. In the workup steps, the solvents were directly distilled out from the flask and the solutions were purified by passing a silica filtration which have reduced a large amount of solvent transfer, extraction and filtration steps. These reactions has been scaled up to 200 g batches and believed to be reaching kilogram scale with small modifications.

All chemicals and solvents were purchased from Sigma Aldrich Corp. without further purification. A round bottom flask was degassed for 30 mins. Palladium Acetate (0.08 eq.) and tri-tert-butylyphosphonium tetrafluoroborate (0.31 eq.) were added respectively into the flask under nitrogen, followed by the addition of sodium tert-butoxide powder (2.8 eq.) into the flask. o-xylene (20 eq.) was first pressured and transferred into the addition funnel and later slowly added into the flask resulting in a brown solution. The mixture was stirred at the room temperature for 1 hour. In the meantime, carbazole or 3,6-Di-tert-butylcarbazole (2.1 eq.) was dissolved in o-xylene. This solution was transferred into the addition funnel and slowly added into the previous solution. The color of the reaction slowly turned yellowish orange. 3, 6-dibromo-9-
phenylcarbazole powder or the 3, 6-dibromo-9-ethylcarbazole powder (1 eq.) was weighed and added into the flask in 5 portions when stirring. The reaction mixture was heated up to 130 °C and refluxed overnight. 80% of the o-xylene was distilled off under vacuum. Enough amount of DCM was added into the flask to dissolve all the soluble materials. DCM solution was passed via a silica gel column. The filtrate was collected and methanol was added for a recrystallization. A lot of white solids formed overnight. The white solids were collected in a frit funnel after a reduced pressure filtration. The solids were washed by DI water, ethanol and TBME to give the pure product as a white solid. 1H NMR, HPLC purity and elemental analysis data of these compounds are shown in Table 4-1.

The UV spectra were measured by Agilent 8453 UV-Vis spectrophotometer. Fluorescent emission spectra were measured by PerkinElmer LS55 Fluorescence spectrometer. Surface morphology was measured by Veeco diInnova Scanning Probe Microscopy 004-1005-000.

4.2.2 Device Fabrication and Characterization

Blue emitting phosphorescent OLEDs were fabricated by the following procedures. Patterned ITO substrates were under UV ozone treatment for 15 minutes. A 25-nm-thick PEDOT:PSS (Al 4803) as a hole injection layer was spin-coated baked at 180 °C for 15 minutes in air. After that, the following layers were sequentially deposited by thermal evaporation: a 18 to 25-nm-thick TAPC as a hole transport layer, a 20 to 30-nm-thick host doped with 6% to 25% FIrpic as a blue emitting layer, a 35 to 40-nm-thick TmPyPB as an electron transporting layer for the green and red devices, a 1-nm-thick LiF layer as an electron injection layer and a 100-nm-thick aluminum as a cathode.
The hole only device used for extracting mobility consisted of a spincoated 25-nm-thick PEDOT:PSS and thermal evaporated 200-nm-thick host materials and 4-nm-thick MoOₓ and 100-nm-Al as electrode. For hole single carrier devices, 20-nm-thick TAPC and 50-nm-thick host doped 6% FIrpic were thermal evaporated between 25-nm-thick PEDOT:PSS and 4-nm-thick MoOₓ/100-nm-thick Al cathode. While for electron single carrier devices, 15 TmPyPB was first evaporated on top of cleaned ITO but with no UV-Ozone treatment serving as hole blocking layer, followed by 50-nm-thick host doped 6% FIrpic, 30-nm-thick TmPyPB and a 1-nm-thick LiF and a 100-nm-thick aluminum.

Current–luminance–voltage characteristics were measured using a Keithley Series 2400 sourcemeter and a Keithley Series 6485 picoammeter with a calibrated Newport silicon photodiode. The luminance was calibrated using a Konica Minolta luminance meter (LS-100). The electroluminescence spectra were obtained with an OceanOptics HR4000 spectrometer.

**4.2.3 Transient Measurement**

Transient PL measurement was conducted on 100 nm FIrpic doped mCP and ETC thin films on quartz glass substrates were put under low vacuum of 17 mTorr. A nitrogen pulse laser (Stanford Research System NL100) with emission of 337 nm and 3.5 ns pulse width was used to excite the thin films. A Hamamastu PMT was put behind a low pass filter (> 400 nm) to detect the PL signals, which was analyzed and recorded by an oscilloscope from Terktronix.

PL quenching measurement was conducted by an UV light from a high power LEDs with a peak of 365 nm and FWHM of 30 nm was focus on the device pixel. A Hamamastu PMT was put behind a low pass filter (> 400 nm) to detect the PL signals. A
function power generator controlled the electrical pulse driving the pixel. Data were
analyzed and recorded by an oscilloscope from Terktronix.

4.3 Results and Discussion

4.3.1 Designing of Ter-carbazole Molecules

In the aspect of molecular design, one way to increase the Tg is to manipulate
the steric hindrance of a molecule by adding side chains to it. Side chains will increase
the twisted configuration of the molecules, leading to higher Tg and more stable
amorphous thin films. Suppression of the electronic coupling between molecules can
be achieved by linking of bulky and large-gap moieties into the 3,6-positions of a
carbazole, resulting in only a small reduction in the triplet energy. Improved
performance of blue phosphorescent OLEDs with this family of host materials have
been reported by several groups. Here, we designed and synthesized three
carbazole-based host materials, 9'-phenyl-9,3':6'9"-(9Cl)-Ter-9H-carbazole (PTC), 9'-
ethyl-9,3':6'9"-(9Cl)-Ter-9H-carbazole (ETC) and 3,3",6,6"-tetrakis(1,1-dimethylethyl)-
9'-(ethyl)-(9Cl)-9,3':6'9"-Ter-9H-carbazole (BETC). Figure 4-2 shows the molecular
structures of them. When keeping the same peripheral carbazole groups, the phenyl
group of PTC was replaced with an ethyl group, which creates a new molecule ETC
with a different functional group at the 9' position on the core carbazole. Phenyl group is
an electron donor, which will extend the local π conjugated bonds. On the other hand,
the ethyl group is unlikely to have a strong affection on the electron state of bone
structure. Moreover, it has been long believed that adding alkyl functional groups can
improve the solubility of organic molecules. When keeping the same core as the 9-
ethyl carbazole, tert-butyl groups were incorporated onto the 3 and 6 position of the
peripheral carbazole. Due to the limit of the content, the solution processed devices

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fabricated from these materials will be discussed elsewhere. The HOMO and LUMO energies for PTC, ETC and BETC were calculated using Titan software to the 6-31G* level. The LUMOs of these molecules are localized on the core carbazole and the HOMOs are mostly localized on the two peripheral carbazoles. There is no obvious influence from the 9-position substituent on their HOMO or LUMO orbitals as shown in Figure 4-3. While the amorphous characteristics of alkyl groups could provide a better film homogeneity by reducing crystal boundaries and islands which help increase the charge hopping, its insolation between π systems could also reduce charge transportation. With this molecular design strategy, we could easily compare the contribution of alkyl group on either the core carbazole or the peripheral to the materials properties and the device performance.

4.3.2 Characterization of Ter-carbazole Materials

The UV-vis absorption spectra of the three materials in Tetrahydrofuran (THF) were measured at room temperature as shown in Figure 4-4. All materials shared similar shape of absorption spectra which can be attributed to the core bone of carbazole. The lowest energy absorptions of PTC and ETC were very similar which locate at about 341 nm. Due to the non-conjugated tert-butyl side chains, the lowest energy absorption of BETC had an 8 nm red shift showing a peak at 349 nm suggesting a little smaller optical gap than PTC and ETC.

Good phosphorescent host materials should have the higher ET than the guests. Also the efficient energy transfer to emitters is demanded, which requires a good overlap between the host PL emission and the absorption of the guests. One of the neat Flrpic absorption peak locates at 388 nm. We measured the PL emissions of all three host materials. Figure 4-5 shows the PL emissions of all three neat host materials as
well as their emissions doped with the same concentrations of FIrpic used in the device fabrication. Because of the same core bone molecular structure, the shapes and peak wavelengths of neat host materials are very close. Therefore, the differences of them indicate the side chain effects. Compared with ETC and BETC, the PL of neat PTC is red shifted. This is due to the phenyl group extended the π bound of PTC, lowering the energy of the excited state. Another significant difference comes from the shapes of PL spectra. The number and the electron affinity of the side chains can influence the vibration states. Therefore the transition rates from vibration states between HOMOs and LUMOs varied, which led to the changes of the PL spectral shapes. Above all, due to the emission overlap with the absorption of FIrpic, all hosts showed good energy transfer to FIrpic. From the PL spectra of the doped layers, we observed clear FIrpic emissions with sharp cutoff at 440 nm. The peak intensities at 470 nm and 500 nm are different with three hosts, which also come from the effect of side chains.

4.3.3 Blue Emitting Phosphorescent OLEDs

Blue PhOLEDs were fabricated with these three host materials and compared with OLED with mCP. The device structure is ITO/PEDOT:PSS/TAPC/new host: FIrpic/TmPyPB/Lithium Fluoride (LiF)/Aluminum. PEDOT:PSS is hole injecting layer. TAPC and TmPyPB are hole and electron transporting materials, with mobility of $10^{-2}$ cm²/Vs and $10^{-4}$ cm²/Vs respectively. The thicknesses and doping concentrations of each optimized device were:

ITO/PEDOT:PSS/TAPC (25 nm)/mCP (30 nm): FIrpic(6%)/ TmPyPB(38 nm)/LiF/Al,
ITO/PEDOT:PSS/TAPC(22 nm)/PTC(25 nm): FIrpic(10%)/ TmPyPB(40 nm)/LiF/Al,
ITO/PEDOT:PSS/TAPC(22 nm)/ETC(25 nm): FIrpic(7%)/ TmPyPB(37 nm)/LiF/Al,
ITO/PEDOT:PSS/TAPC(20 nm)/BETC(20 nm): FIrpic(25%)/TmPyPB(37 nm)/LiF/Al.
Figure 4-6 A shows the electroluminescent spectra of the devices with different hosts. All of them showed only Flrpic emission. The different intensities of shoulder peaks at 500 nm, which corresponds to their PL emissions, come from the effect of side chains and weak microcavity of different device thicknesses. The small red shifts of the PTC and mCP spectra compared with others are due to the longer device thicknesses. Figure 4-6 B shows the plots of current density vs. applied voltages of each device. Reference device with mCP shows an electrical turn-on at 3.1 V. The lowest turn-on, 2.9 V, comes from the ETC device, which indicates a good carrier injection into the emitting layer. Meanwhile the PTC device has a turn-on voltage of 3.1 V. The highest turn-on voltage belongs to BETC device, which is 5.1 V. The luminance turn-on voltage of each device corresponds to their electrical turn-on voltage as showed on Figure 4-6 C. ETC device shows a very rapid rise of luminance, from 1 cd/m² to 1000 cd/m² within 0.8 V, while it takes 1.4 V and 1.3 V for PTC and BETC devices to raise the luminance within the same range respectively. mCP device shows slow rises of both current density and luminance. Figure 4-6 D shows the current efficiency of devices studied. ETC devices exhibit the highest current efficiency which is comparable to mCP device, but their efficiency roll-off significantly reduces at higher luminance. And all other ter-carbazole host devices also achieve very low roll-off. We can define a critical luminance ($L_{90}$) where the current efficiency reduces to 90% of its maximum value. The higher $L_{90}$ is, the lower roll-off the OLED has. In mCP device, the maximum efficiency of 49.4 cd/A is achieved at 113 cd/m² with a $L_{90}$ of 850 cd/m². As comparison, a maximum efficiency of 48.4 cd/A at 260 cd/m² with a higher $L_{90}$ of 3300 cd/m² was obtained from ETC device. The PTC device has a maximum efficiency of 35.8 cd/A at 200 cd/m² with an
improved $L_{90}$ at 4500 cd/m$^2$. Even though the maximum efficiency of BETC device, 30.6 cd/A at 124 cd/m$^2$, is the lowest among all ter-carbazole hosts, its $L_{90}$ reaches 1540 cd/m$^2$.

4.3.4 Annealing Effects on mCP and ETC

Due to the low thermal conductivity of organic materials and glass, the heat dissipation in an OLED is a problem, especially under continuous operation. Local heat will be accumulated and the device temperature can go over 50°C in 30 s at high current density. Considering the $T_g$ of mCP is only 60°C, phase transition could easily happen with the elevation of temperature, which will eventually affect the electrical and optical properties of OLEDs. Therefore increasing the $T_g$ of organic materials can improve the stability of OLEDs. First we verified that due to the high $T_g$ of ETC, less effect comes under thermal stress. We measured the morphology of neat mCP and ETC films as deposited and annealed at 45°C for 30 min. Figure 4-7 shows the AFM images of them. Both mCP and ETC showed a smooth surface of as deposited films. The roughness of mCP is 1.4 nm while the roughness of ETC film is 2.0 nm. After annealing at 45°C for 30 min, the changes of film morphology were quite different. The roughness of mCP significantly increased to 24 nm after annealing. Within 500 nm$^2$ scanning area, clear ‘valleys’ and ‘hills’ were observed. The maximum vertical distance between them was over 100 nm. Even worse, clear pikes were observed on annealed mCP film. Those dramatic changes in the morphology of annealed mCP contributed to the unstable voltage fluctuation of elevated temperature measurement. On the other side, due to the high $T_g$ of ETC, the change of the morphology of annealed film was not significant. Even though, aggregations were also observed, the maximum vertical distance between
valleys and hills was only 19 nm which was comparable to 11 nm of as deposited ETC. Besides, no pike existed within the 500 nm$^2$ scanning range. As a result, the roughness of annealed ETC was 3.1 nm. We also made hole only devices of mCP and ETC and measured the \(J-V\) characteristics before and after 45$^\circ$C annealing, which are presented in Figure 4-8. Due to the dramatic change of morphology of mCP during the annealing, the interfaces between organic layers become fuzzy along with the change of compositions. As a result, the current density of mCP hole only device reduced.

4.3.5 Hole Mobility and Injection into Hosts

We conducted further experiment to study the device transport property to explain the difference in the electrical properties of those materials. First we extracted the field dependence mobility from the hole only devices. These devices had the same structure, ITO/PEDOT:PSS(20 nm)/host materials(200 nm)/MoOx(4 nm)/Al(100 nm). MoOx has low lying electron affinity and can align the work function of Al to the HOMO of host materials so as to prevent electron injection.$^{95}$ Hole only devices showed a space charge limited current (SCLC). According to Mott-Gurney’s law,$^{96}$ \(J_{\text{SCLC}}\) can be expressed as

\[
J_{\text{SCLC}} = \frac{9}{8} \varepsilon \varepsilon_0 \mu_0 \exp(0.89 \beta \sqrt{\frac{V}{d}}) \frac{V^2}{d},
\]

\(\varepsilon_0\) is the permittivity and \(\varepsilon\) relative permittivity which is \(\approx 3\) in most small molecular semiconducting materials.$^{96,97}$ \(\mu_0\) is the zero field mobility in the materials, \(V\) is the applied voltage and \(d\) is the thickness of the device, \(\beta\) is Poole-Frankel factor related to temperature and materials. By fitting the \(J-V\) characteristics, the \(\mu_0\) and \(\beta\) can be extracted. The Poole-Frankel field dependence mobility can be calculated according to
\[ \mu = \mu_0 \exp(\beta \sqrt{\frac{V}{d}}) \]

However, this apparent mobility extracted from SCLC is based on the assumption of ohmic contact. We fabricated hole only devices to investigate the hole injection into each host. The hole unipolar devices have the same structure: ITO/PEDOT:PSS(25 nm)/TAPC(20 nm)/hosts(50 nm)/MoOx(4 nm)/Al. Figure 4-9 B hole only current density for each device. mCP, ETC and PTC have very similar turn-on while BETC device shows a turn-on voltage of 4 V. This indicates a larger injection barrier from TAPC to BETC. In case of host material with deep lying HOMO like BETC, current density of hole only device is limited by injection. Therefore, carrier mobility can be extracted from the fitting of injection limited current (ILC). Based on the solution of drift diffusion equation and considering the equilibrium contributions to the current density for charge carriers recombining with their own image in analogy with Langevin bimolecular recombination, the ILC current density with field-dependent mobility is

\[ J_{ILC} = 4N_0\psi^2e\mu \frac{V}{d}\exp(-\frac{e\phi_B}{k_BT})\exp(f^{1/2}) \]

where \( N_0 \) is the density of states in the organic film, \( \phi_B \) is the barrier height, \( k_B \) is the Boltzmann constant, \( e \) is the electron charge, \( T \) is the temperature, and \( \psi \) is a function of reduced electric field \( f = \frac{e^3V}{4\pi\varepsilon dk_B^2T^2} \), and can be expressed as

\[ \psi = f^{-1} + f^{-1/2} - f^{-1}(1 + 2f^{1/2})^{1/2} \]

Figure 4-9 A shows the mobility of host materials used in this study. The mobility of BETC is nearly two orders lower than ETC. The low mobility of BETC also increases the
voltage drop across itself. Therefore we can conclude that not only the mobility of BETC is low, but also there are large barrier heights for both carriers injection into BETC.

4.3.5 Triplet Lifetime and TTA of mCP and ETC EMLs

In order to study the different roll-off behaviors in the efficiency of FIrpic OLEDs with these host materials, we measured and characterized different mechanisms that can determine the efficiency roll-off in the OLEDs. We focused on the OLEDs with mCP and ETC hosts, because they share the same highest current efficiency, similar device thickness and doping concentration of the optimal conditions. Due to the long lifetime of phosphorescent emitter, triplet-triplet annihilation (TTA) plays an important role in phosphorescent OLEDs. One of the significant influences is on the roll-off due to the TTA. First, we study the transient PL decay of mCP and ETC doped with FIrpic. The concentrations of FIrpic are the same used in the optimal OLEDs. Figure 4-10 shows the transient PL decay of mCP and ETC doped with FIrpic. The differential equation of triplet density after the excitation is

\[
\frac{dT}{dt} = -\frac{T}{\tau} - \gamma_{TT} T^2
\]

the triplet lifetime \( \tau \) characterizes to the conventional and ideally radiative monoexcitonic decay with \( T \), and the TTA rate, \( \gamma_{TT} \), describes the biexcitonic annihilation where TTA increases non-linearly with increasing triplet densities. The equation is solved as

\[
T(t) = \frac{T_0}{(1+T_0 \gamma_{TT} \tau) e^{\gamma_{TT} \tau} - T_0 \gamma_{TT} \tau}
\]

By fitting the transient PL intensity, we can obtain the \( \tau \) and \( \gamma_{TT} \) and compare them in mCP and ETC EMLs. The triplet lifetime in mCP and ETC hosts are 1.517±0.006 \( \mu \)s
and 1.420±0.007 μs respectively. The lifetime we measured are corresponding to FIrpic triplet lifetime reported before. By estimating the initial $[T_0]$ from excitation power density and the absorption constant, we calculated the $\gamma_{TT}$ in mCP and ETC hosts as $2.0±0.6 \times 10^{-13}$ cm$^3$ s$^{-1}$ and $1.6±0.5 \times 10^{-13}$ cm$^3$ s$^{-1}$ respectively. The triplet lifetime is longer and the $\gamma_{TT}$ rate is larger in mCP host. However, the difference of $\tau$ and $\gamma_{TT}$ between mCP and ETC cannot fully explain the dramatic roll-off in the mCP OLED device.

### 4.3.7 Triplet-polaron Quenching in mCP and ETC Devices

Another factor contributes to the roll-off of an OLED is the polaron. We measure the unipolar devices of them in order to study the charge balance inside of OLEDs. Due to the different electrical field dependence of hole and electron mobility, charge balance could reduce at high applied electrical field which results in the efficiency drop. The unipolar devices are ITO/PEDOT:PSS/TAPC/host:FIrpic(50 nm)/MoOx/Al and ITO/TmPyPB/host:FIrpic(50 nm)/TmPyPB/LiF/Al which are based on the optimal devices for hole and electron only devices, respectively. The increased thickness of EML is for the consideration of device stability and reliability. The purpose of TmPyPB between ITO and EML in electron only devices is to block holes. Figure 4-11 shows the current density vs. applied electrical field of mCP and ETC devices. It is obvious that hole only devices have much higher current density than electron only devices in both mCP and ETC devices. This is due to the intrinsic hole domination of transport property of carbozle molecules. Comparing between mCP and ETC devices, $J-E$ characteristics agree with the devices $J-V$ characteristic and hole mobility calculation discussed in the previous section. Even though, hole currents of both device are in the same range, the
electron currents of mCP and ETC device behave differently. In mCP electron only device, we observed a slow increasing current which is more than three orders lower than its hole counterpart in the whole measuring range. In ETC electron only device, there is a clear current turn-on at 0.3 MV/cm, after which follows a faster current increase. This indicates a better LUMOs matching between ETC and TmPyPB. As a result, electron current is higher in ETC device than mCP device, especially at high electrical field. Consequently the reduction charge balance at high electrical field in ETC OLED is less than that in mCP OLED. Moreover, those excessed polarons in mCP will lead to greater quenching of excitons.

Triplet polaron quenching (TPQ) is another significant annihilation of excitons in phosphorescent OLEDs due to interaction between polarons (hole polaron $P^+_h$ and electron polaron $P^-_e$) and triplet excitons ($T_1$). This annihilation by free or trapped charge carriers is possible via the following processes

$$T_1 + P^+_h \rightarrow S_0 + P^+_h^*$$
$$T_1 + P^-_e \rightarrow S_0 + P^-_e^*$$

The annihilation rates for hole and electron are $k_{TP,h}$ and $k_{TP,e}$ respectively. Since the hole is the dominated carrier in our OLEDs and the previous study of Iridium based phosphor dye shows that TPQ from electron polarons is smaller than hole polarons$^{100}$, our study will focus on the hole polaron quenching. In order to characterize the TPQ, we first measured the steady PL quenching of unipolar devices with increased current injection. We used a short pulse to inject the electrical current into the device so as to eliminate the heating effect. The pulse width is 50 microseconds with a frequency of 20
Hz, which corresponds to a duty cycle of 0.1%. Figure 4-12 A and B show the time resolved PL quenching of mCP and ETC hole only device with different injected current densities. The PL intensity of both mCP and ETC devices reduced with the increasing of injected current. And the quenching from mCP device is stronger than ETC device.

Under low PL excitation, only considering the triplet decay, time differential equation of triplet density can be expressed as

$$\frac{d[T]}{dt} = [T_{\text{excited}}] - \frac{[T]}{\tau}$$

When time is much larger than $\tau$, the equilibrium excitation density $[T_0]$ is

$$[T_0] = \tau [T_{\text{excited}}]$$

$[T_{\text{excited}}]$ is the initial triplet density from the excitation of light source. When there is current injection, the time differential equation of triplet exciton density under the PL excitation is

$$\frac{d[T]}{dt} = [T_{\text{excited}}] - \frac{[T]}{\tau} - k_{TP,h}[T][P]$$

$[P]$ is the polaron density. Solving this equation, we can find the relation between the final triplet density $[T_{\text{final}}]$ and $[T_{\text{excited}}]$ under steady equilibrium PL excitation is

$$[T_{\text{final}}] = \frac{[T_{\text{excited}}]}{1 / \tau + k_{TP,h}[P]}$$

Therefore the ratio of triplet density before and after current injection can be

$$\frac{[T_{\text{final}}]}{[T_0]} = \frac{1}{1 + \tau k_{TP,h}[P]}$$
Assuming the SCLC inside the EML, the polaron density \([P]\) is proportional to 
\[
(3\varepsilon_0 V)/(2ed^2),
\]
then we find the relative triplet density difference is proportional to the electrical voltage:

\[
\frac{[T_0] - [T_{\text{final}}]}{[T_{\text{final}}]} = \frac{[\Delta T]}{[T_{\text{final}}]} \propto \frac{3\varepsilon_0 \tau k_{TP,h} V}{2ed^2}.
\]

We plot the relative reduced PL intensity vs. the voltage in Figure 4-12 C and D. Both devices show good lineal dependence. From the slopes of the phosphorescence quenching vs electrical field, we extracted the \(k_{TP,h}\) for mCP and ETC devices are 2.0±0.1 \times 10^{-13} \, \text{cm}^3 \, \text{s}^{-1} and 7.8±0.6 \times 10^{-14} \, \text{cm}^3 \, \text{s}^{-1}, respectively. \(k_{TP,h}\) of mCP is within the same range of other Ir-based phosphor dye studied before\(^\text{100,101}\). ETC shows \(k_{TP,h}\) three times lower than that of mCP. The large \(k_{TP,h}\) of mCP is one of the factors contribute to the great efficiency roll-off at high current density.

We are also interested in the polaron quenching under continuous driving condition where joule heat becomes an inevitable factor especially at higher current density. Here instead using a short pulse to drive the device, we conducted a steady measurement on the PL intensity reduction under a long pulse injected current of 1 s. The hole only device structures are the same in previous discussion. Figure 4-13 shows the relative reduced PL intensity under hole current density from 1 mA/cm to 200 mA/cm which is within the common range of operating an OLED device. For comparison, we put the data under short pulse quenching in the same plots. In both mCP and ETC devices, the PL reduction before 50 mA/cm\(^2\) is close under long and short electrical pulse. However at higher current, significantly larger PL intensity
quenching appears, especially in mCP device. At 200 mA/cm², an additional 64% reduction was observed with long pulse quenching in mCP while this further reduction from long pulse quenching in ETC is about 40%. The lower T_g of mCP makes device more vulnerable to heating under the device operation.

4.4 Conclusion

We designed and synthesized three different ter-carbazole based host materials, PTC, ETC and BETC with different side chains for blue phosphorescent OLEDs. All of them exhibit high triplet energy, high glass transition temperature and good energy transfer to phosphorescent emitter FIrpic. Improved thermal stability on the morphology was demonstrated compared with mCP which has low Tg. The PhOLED devices with those hosts showed high efficiency and low roll-off. Device physics study confirmed the suppressed roll-off comes from the shorter lifetime, low TTA and TPQ rates with FIrpic doped ETC as the EML. Device transporting property study showed the different side chain effects on the mobility. Due to the alkyl group, BTEC device by thermal evaporation exhibited low mobility and poor carrier injections.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield</th>
<th>$^1$H NMR (CDCl$_3$, 400Hz)</th>
</tr>
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<tbody>
<tr>
<td>BETC</td>
<td>91%</td>
<td>8.18-8.19 (2H, Ar-H), 8.15-8.16 (4H, Ar-H), 7.64-7.65 (4H, Ar-H), 7.43-7.46 (4H, Ar-H), 7.30-7.32 (4H, Ar-H), 4.53-4.58 (2H, Et-H), 1.61-1.64 (3H, Et-H), 1.46 (36H, tbu-H). Anal. calcd. for C$<em>{54}$H$</em>{59}$N$_3$: C 86.47 H 7.93 N 5.60; Found: C 85.52 H 7.96 N 5.58. m.p.: 310 °C; HPLC: 98.7%</td>
</tr>
</tbody>
</table>
Figure 4-1. Synthesis route of PTC, ETC and BETC.
Figure 4-17. Structures of host molecules
Figure 4-3. DFT calculated HOMO and LUMO orbitals for PTC (top), ETC (middle) and BETC (bottom).
Figure 4.4. Absorption spectra of PTC, ETC and BETC
Figure 4-5. PL spectra of neat PTC, ETC and BETC as well as the spectra of PTC, ETC and BETC doped with Flrpic.
Figure 4-6. Device performance: (a) EL spectra, (b) J-V curves, (c) L-V curves, (d) current efficiency
Figure 4-7. AFM of mCP as deposited (a) and after annealed (b) and ETC as deposited (d) and after annealed (d).

Figure 4-8. J-V characteristics of mCP (a) and ETC (b) hole only devices before and after 45°C annealing.
Figure 4-9. Host materials characterization: (a) mobility of host materials used, (b) $J-V$ of hole only devices

Figure 4-180. Transient PL decay of mCP and ETC doped with FIrpic
Figure 4-11. Unipolar devices with mCP (a) and ETC (b).
Figure 4-12. TPQ on the PL intensity of mCP (a) and ETC (b) hole only devices; and relative reduced PL intensity vs. applied voltage of mCP (c) and ETC (d) devices.
Figure 4-13. TPQ under different current injection of long and short electrical pulse.
CHAPTER 5
SUB BANDGAP TURN-ON OF ELECTROLUMINESCENCE AT RUBRENE/FULLERENE INTERFACE

The efficiency of fluorescent OLED is limited by the spin statistic, which only allows 25% of the formed excitons decay through radiative process. One possible process to take the advantages of 75% triplets is through TTA. In this section, we are going to show that TTA can further reduce the operating voltage by a luminance turn-on below the corresponding bandgap of the emitter. Experiment was conducted to verify the energy transfer from the charge transfer state to triplet state. It gives a proof to the fundamental mechanism of the sub bandgap luminance phenomenon.

5.1 Background and Motivation

Since the invention of OLEDs, efforts have been made on the improvement of the efficiency.\textsuperscript{25,37,66-68} Besides improving the internal quantum efficiency by using the phosphorescent emitters,\textsuperscript{66,102,103} more light can be out-coupled by using photonic structures,\textsuperscript{25,67} Also new materials with higher mobility were synthesized to improve the power efficacy\textsuperscript{76}. Another way to reduce the power consumption is operating the device at low voltage. However the lowest turn-on voltage of a LED is determined by the bandgap of the emitting layer. This rule governs most of OLEDs where carriers are directly injected in to HOMOs and LUMOs.

Fortunately, several groups reported a few organic systems show an EL turn-on lower than the bandgap of emitting semiconductors.\textsuperscript{63,104} It opens a new door to improve the power efficiency in OLEDs. One of those sub bandgap systems is 5,6,11,12-Tetraphenylnaphthacene (rubrene)/fullerene bilayer structure.\textsuperscript{104} Both rubrene and fullerene are widely studied semiconductors, which have the highest field-effect mobility for holes and electrons, respectively.\textsuperscript{105,106} Rubrene is a material of great interest for
organic optoelectronic research and practical applications with its exceptional properties mobility and crystal structure. Organic field effect transistors have confirmed that hole mobility of rubrene single crystals can be as large as \( \sim 20 \text{ cm}^2/\text{Vs} \). It has also been demonstrated that a significant improvement of the OLED efficiency can be achieved by adding a thin layer of rubrene. Other work also shows with rubrene doping, the position of the recombination zone can be turned, as well as the stability of the devices been improved. Fullerene was demonstrated with good electron transporting and accepting properties. The electron mobility of \( \text{C}_60 \) up to 0.15 \( \text{cm}^2/\text{Vs} \) is possible in devices. With its excellent electron accepting ability, fullerene derivatives are used as the acceptors in organic photovoltaic solar cells and demonstrated high power converted efficiency.

By applying the rubrene/fullerene heterostructure to OLEDs, the device behaves like a compound semiconductor device. Surprisingly, the EL turn-on voltage is about 1 V which is about half the value of the rubrene bandgap (2.2 eV). The EL spectrum of only rubrene emission was observed. (Shown in Figure 5-2) This sub bandgap EL cannot be explained with models of charge injection into organic semiconductors. Figure 5-1 shows the molecules structures of rubrene and \( \text{C}_60 \) as well as the energy band diagram of rubrene/\( \text{C}_60 \) OLEDs. We fabricated rubrene/\( \text{C}_60 \) device and compared it to different electron injection layers. The L-V curves are shown in Figure 5-2. Device with no electron injecting layer, shows the highest turn-on voltage. With the presence of LiF, the luminescence turn-on approaches to the corresponding bandgap. However, by using \( \text{C}_60 \) as the injecting layer, the turn-on voltage reduces to 1 V which is only half of the
bandgap (2.1V). The EL spectra below and above bandgap voltage are identical from the rubrene/C₆₀ heterojunction, which indicates a up conversion process.

A physical interpretation, Auger fountain mechanism, was proposed to explain this sub bandgap phenomenon at this heterojunction. During the EL process in heterojunction devices, holes and electrons are injected from the rubrene and C₆₀ layers, respectively. They then recombine near the interface to raise another electron at the LUMO of C₆₀, which overcomes the energy barrier between the LUMOs of rubrene and C₆₀. After injected into the LUMO of rubrene, this Auger electron recombine with the hole in the HOMO and emits photon with the emission characteristic of rubrene. Several researches were conducted in order to support this hypothesis. A dual functional device using rubrene and C₆₀ was fabricated. While applying voltage, it started emitting light at a sub bandgap voltage. Under illumination it also generates electrical power. The solar power conversion efficiency reaches 3% with a 5.3 mA/cm² short-circuit current density and almost 1 V open-circuit voltage under AM 1.5 illumination. This large Vₐc corresponds to the EL turn-on in OLED device. However, further analysis was not given on how the large Vₐc can be related to Auger electrons. Studies also focus on the exciplex emission from this heterojunction. The exciplex formation in rubrene based heterojunctions is important because it can indicator of the recombination process of bifunctional devices, since efficient exciplex emission implies efficient charge transfer (CT) across the interface and their recombination. In order to distinguish the exciplex formation dependencence on the molecular organization in the film, bulk heterojunction devices and planar heterojunctions were studied comparatively. Even
though near IR emission was observed in the planar heterojunction with a thin mixed layer between the rubrene and C$_{60}$, no evidence of Auger electron was reported.

Another well-known up conversion phenomenon in rubrene is triplet-triplet annihilation (TTA).$^{122,123}$ This TTA reaction can either go through non radiative decay or transfer the energy to a singlet which can radiatively recombine. Due to two triplet excitons being involved, this fusion does not violate the spin statistics. The triplet energy of rubrene is just the half of its singlet state.$^{124}$ Therefore this kind of triplet fusion is more efficient. From transient studies this fusion contributing to a delayed fluorescent emission in rubrene was observed.$^{122}$ OLEDs with as much as half of their EL from annihilation of triplet states generated by recombining charge carriers were demonstrated.$^{125,126}$ The magnitude of TTA contribution in combination with the remarkably high total EQE [$>11\%$] indicates that the absolute amount of EL attributing to TTA substantially exceeds the limit imposed by spin statistics, which was independently confirmed by studying magnetic field effects on delayed luminescence. The value of 1.3 for the ratio of the rate constants of singlet and triplet channels of annihilation is indeed substantially higher than the value of 0.33 expected for a purely statistical annihilation process.$^{125}$

By considering the evidence of exciplex from the heterojunction of rubrene and C$_{60}$ interface and the strong triplet fusion capability of rubrene, we propose another mechanism based on the TTA of rubrene that leads to the sub bandgap EL emission. Up conversion has been demonstrated in solution of rubrene and a sensitizer who has lower absorption band gap than rubrene but with higher triplet energy.$^{127-129}$ The photoexcited sensitizer transferred energy to the triplets of rubrene which undergo
fusion process giving energy to the singlet. In case of rubrene/C₆₀ heterojunction, the energy source becomes the exciplex, the charge transfer state formed with LUMO of C₆₀ and HOMO of rubrene. Due to the large barrier height at between the LUMOs and HOMOs of rubrene and C₆₀, electrons and holes are accumulating at the interface, which is bonded and forms charge transfer exciton. Because of the separation of donor and acceptor, the energy split between singlet and triplets is small. Through Dexter transfer, large amount of triplet formed at rubrene molecules.

In this study, we investigated the charge transfer exciton by the electroabsorption measurement, and showed from the transient EL measurement that delayed fluorescent emission dominating the EL of rubrene/C₆₀ OLED. Finally, the increase of triplet density was observed with the present of rubrene/C₆₀ heterojunction.

5.2 Experiment

The heterojunction devices consist of 40 nm thick rubrene and 20 nm thick C₆₀ layers sandwiched between transparent indium tin oxide (ITO) and 100 nm thick metal electrodes. A 30 nm thick layer of poly-(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT: PSS) at the ITO/rubrene interface was used as buffer layer. For reference, rubrene-only devices were also sandwiched between 30 nm thick PEDOT and 100 nm Al metal cathodes.

Transient measurement

100 nm rubrene and rubrene/C₆₀ (2:1) thin film on glass substrates were put under low vacuum of 17 mTorr. A Nd:YAG pulse laser with emission of 527 nm and 10 ns pulse width was used to excite the thin films. A Hamamastu PMT was put behind a band pass filter (peak at 584 nm, FWHM of 20 nm) to detect the PL signals, which was analyzed and recorded by an oscilloscope from Tektronix. Transient EL measurement
was conducted on encapsulated devices in air atmosphere. Lenses were used to focus EL emission onto the PMT, which also was placed behind the band pass filter.

5.3 Results and Discussion

5.3.1 Unipolar Devices

First, we characterized the carrier transporting property using unipolar devices. The thicknesses of each layer are ITO/PEDOT(30nm)/Rubrene(60nm)/C_{60}(35nm)/Au and ITO/Rubrene(90nm)/C_{60}(35nm)/Al for hole and electron only devices respectively. No-UV Ozone treated ITO was used to increase the hole injecting barrier in electron only devices while, high work function metal Au was applied to block electron injection in hole only devices. Figure 5-3 shows the J-V characteristics of both devices. The current density of hole only device is more than two orders larger than that of electron only device, which indicated in this bilayer OLED, hole is the dominating carrier. Due to the large excessive hole carriers accumulated at the interface, a free electron that could play the role of ‘Auger electron’ is less likely to exist. This is another reason that Auger fountain mechanism is not suitable here.

5.3.2 TTA in Sub bandgap EL

Due to the long lifetime of triplet excitons, a delayed fluorescent EL emission is expected in TTA up conversion OLEDs. A detail analysis of the triplet dynamics has been given based on small molecule such as rubrene^{122} and polymer such as F8BT^{124}. We also conducted transient EL measurement based on rubrene OLEDs with and without C_{60} layer. The device structures are ITO/PEDOT/rubrene/Al and ITO/PEDOT/rubrene/C_{60}/Al. The rubrene only device has a luminance turn-on at 2V, while the rubrene/C_{60} heterojunction device shows a low luminance turn-on at 1 V. We first measured the EL transient decay after electrical current shut down from different
voltages. The decay data are presented in Figure 5-4 A. It is clear that there is a fast decay less than 100 ns after current shut down following a long time decay in microsecond. Our data show the same TTA figure print decay curves as previous report\textsuperscript{122}. The fast decay comes from the short lifetime singlet excitons forming directly from the charge recombination. Due to the spin statistic, 75\% recombination leads to triplets, parts of which undergo TTA process and give energy to singlet. With the increase of the voltage, we observed a decrease of decay time of delayed component. Long living triplet is more easily quenched by injected polarons. When there is current injection, the time differential equation of triplet exciton density can be expressed as

\[
\frac{d[T]}{dt} = -\frac{[T]}{\tau} - \gamma_{TT}[T]^2 - k_{TP}[T][P]
\]

\([T]\) is the triplet density, \(\tau\) is the triplet lifetime, \([P]\) is the polaron density, \(\gamma_{TT}\) is the TTA rate and \(k_{TP}\) is the triplet-polaron quenching (TPQ) rate. TPQ is not significant at low current density. Therefore if we only consider the first two terms in the equation at low current density, we obtained a \(\tau = 30 \pm 5\) μs, which is in the same range as previous report\textsuperscript{130}. In case of rubrene/C\textsubscript{60} heterojunction device, we also measured the EL decay after current shut down from sub band gap region to high voltage. The data were presented in Figure 5-4 B. We did not observe obvious fast decay component. Long time delayed fluorescent decay dominates all curves. With the increase of voltage, decay time decreases as expected from the increasing of TPQ. At the sub bandgap region, TTA is the only mechanism for the rubrene emission. We only consider the second term in the triplet time resolve equation, the triplet density is given as

\[
[T] = \frac{[T_0]}{1 + \gamma_{TT}[T_0]t}
\]
The EL intensity which is resulted only from TTA is

\[ I_{TTA} \sim \gamma_{TTA}[T]^2 \sim t^2 \]

Therefore, we expected the time resolved EL decay has a slope of -2 in logarithm plot. Figure 5-5 shows the fitting of EL decays driven in the sub bandgap region where TPQ is not significant. Both EL decays driven at 1.2 V and 1.8 V show a slope of -2, which indicates the TTA is the reason for the EL under the excitation of sub bandgap.

5.3.3 CT States at the Rubrene/fullerene Heterojunction

The energy of triplet contributes to the sub bandgap emission comes from the CT state. In order to prove the existence of CT state at the interface of rubrene and C_60, we measured the electroabsorption (EA) signal of pristine rubrene, pristine C_60 and mix rubrene/C_60 (2:1) blend. The quadrature signal from EA can distinguish the exciton and CT state due to slow response of CT state to the AC electrical field. Figure 5-6 shows the EA signal and its quadrature signal of rubrene/C_60 blend. There is an EA peak at 1220 nm, which corresponds to the charge transfer state energy calculated from the energy band diagram. Its quadrature signal follows the EA signal. Before 1150 nm, there is no quadrature signal. When the EA signal turns positive, the quadrature signal also starts and reaches the peak at 1220 nm. After the peak, both signals reduce. The negative signal of quadrature indicates the slow response to the AC electrical field. Therefore, the EA single at NIR region is from the CT states, which also agrees with the energy (1 eV) calculated from band diagram (Figure 5-1).

5.3.4 Energy Transfer to Triplets

We further conducted the transient PL measurement on the rubrene and rubrene/C_60 blend (2:1). We focus on the decay fluorescent component from rubrene
emission, which is related to the triplet and charge transfer state. Rubrene also shows an efficient singlet fission process. Under high intensity excitation, significant amount of triplets can be generated which go through the triplet fusion and give energy back to singlet. As a result, a delayed fluorescent emission is also expected in PL measurement. Here we used a green pulse laser (527 nm) to excite the thin film. The excitation wavelength is overlap one of the absorption peak of rubrene. Figure 5-7 A shows the transient PL at shorter time (< 500 ns). The laser signal shows a good Gaussian shape with a Full width at Half Maximum (FWHM) of 10 ns, which is longer than the decay time of rubrene singlet. Therefore, there is no fast fluorescent component but only the delayed component in in both rubrene and rubrene/C_{60} blend. And the intensity of delayed component becomes larger in the rubrene/C_{60} blend. We show the EL decay in longer time scale and plot them in log-log scale in Figure 5-7 B. These two lines are paralleled to each other over 3-order magnitudes. Again as in the sub bandgap EL decay, this delayed fluorescent signal solely comes from the TTA, whose intensity is proportional to the square of triplet density. Considering the first two terms in the time resolved differential equation, the time dependence of triplet density is

\[ [T] = \frac{[T_0]}{\gamma_{TT} \tau e^\gamma \tau - [T_0] \gamma_{TT} \tau} \]

We fitted both decays according to \( I_{TTA} \sim \gamma_{TTA}[T]^2 \), and extracted the initial triplet density of them. Our fitting shows good agreement over 3-order of magnitudes in both films. And we found out (23±3) % times more triplets state in rubrene/C_{60} blend than pristine rubrene. Due to the large band offsets of HOMOs and LUMOs of rubrene and C_{60}, non-geminated recombination can be ruled out. Thus we attribute this increase of
delayed rubrene fluorescent emission coming from the charge transfer states which created more initial triplet under photoexcitation.

5.4 Conclusion

We proposed a mechanism based on the TTA property of rubrene to explain the sub bandgap EL phonominoun of rubrene/C\textsubscript{60} heterojunction. The holes are the dominating carriers through this heterojunction, where free electrons are less likely to exist. Transient EL decay of sub bandgap emission shows the characteristic of TTA. And charge transfer state is found with EA measurement. Finally transient PL decay links them together, demonstrating the increase of triplet density is coming from the energy of charge transfer state.
Figure 5-1. The molecular structures of (a) rubrene and (b) $C_{60}$; (c) the energy band diagram of OLEDs with different electron injecting layers.

Figure 5-2. The L-V curves of rubrene OLEDs with different electron injecting layers (left) and EL spectra below and above band gap voltage (right).
Figure 5-19. The $J-V$ characteristics of unipolar devices of rubrene/C$_{60}$ heterojunction.

Figure 5-4. Transient EL decay of (a) rubrene OLED and (b) rubrene/C$_{60}$ OLED
Figure 5-5. Log-log scale of EL decay before bandgap operation. Blue lines are fitting lines having slope of -2.

Figure 5-6. EA and its quadrature signal of rubrene/C₆₀ blend.
Figure 5-7. Transient PL of rubrene and mix rubrene/C\textsubscript{60} blend shorter than 500 ns (a) and over 500 ns (b).
CHAPTER 6
SUMMARY AND FUTURE WORK

In this thesis, series studies have been conducted on the triplet exciton behaviors in organic electronic materials and devices. Due to van de Waals bonding force, small dielectric constants and amorphous structures, excitons are the dominating quasi-particles that determine the properties of organic semiconductors. In the chapter one, I gave a brief introduction of exciton and its related concepts used in organic electronics research. From there we focused on the exciton emission manipulation, exciton confinement, exciton-exciton annihilation, and exciton-polaron annihilation on the microcavity OLEDs, quantum dot LEDs, phosphorescent and fluorescent OLEDs.

First we turned the exciton emission of green, red and blue phosphorescent emitters with the help of microcavity. After the systematic study, we elucidated the microcavity effects for different color emitters. We found that the luminance output is determined by the reflectivity of semitransparent electrode and the photopic response of the green, red and blue emitters. While the luminance enhancements of blue and red phosphorescent microcavity devices are small, current efficiencies as high as 224 cd/A is obtained in green phosphorescent microcavity OLEDs.

Second we study the exciton confinement in QD-LEDs. Enhanced hole injection and better exciton confinement were demonstrated with the low lying HOMO energy for the HTL, PVK. By tuning the thicknesses of the HTL and quantum dot emitting layer, we managed the device charge balance and demonstrated 0.65% EQE blue/violet emitting hybrid LEDs based on cadmium-free zinc selenide/zinc sulfide core/shell QDs.

In order to suppress efficiency roll-off in phosphorescent OLEDs, we introduced three new ter-carbazole hosts. We characterized the triplet lifetime, TTA rates and TPQ
rates of them and compared with mCP. With ter-carbazole host, phosphorescent emitter FIrpic shows short lifetime, reduced TTA and TPQ interaction, resulting highly efficient blue PhOLEDs with reduced efficiency roll-off at high luminescence.

Finally, we proposed the TTA is responsible for the sub bandgap EL of rubrene fluorescent OLEDs. This unique property could reduce the power consumption of OLEDs. With experiment results from electroabsorption, transient EL and PL measurements, we verify the energy from the charge transfer state of the donor and acceptor can be transferred to triplet state, which undergoes an up conversion path and transfer the energy to higher singlet state.

The presence of excitons separates apart the organic semiconductors from their inorganic counterparts. Excitons bring problems which researchers are trying to overcome. It also opens other possibilities leading to the new frontiers and applications. In the future, microcavity OLEDs will be applied to build lighting panels. The increase of the color expression due to the enlargement of primary color triangle in CIE gives the advantages of larger tunable range of color temperature. A detailed relationship between color temperature, CRI and intensity of RGB microcavity OLEDs is needed. Another interesting topic regarding the microcavity is to investigate the exciton behaviors in very strong microcavities. Those very strong cavities provide strong exciton confinement, where coupling between excitons and other particles are tremendously enhanced. More complicated exciton dynamics will occur within those cavities.

Based on the excellent results of blue PhOLEDs with ter-carbazole hosts, we expect good device performance when we adapt them into solution processes. Compared with the thermal evaporation deposition, solution process promises low cost
and large scale fabrication. The high T\textsubscript{g} of those new hosts are suitable for the annealing step in solution process. First, we are going to use those materials as the hosts for green phosphorescent emitters then extend their application to other emitting colors.

My thesis covers a very small area and generates a few interesting results. It is the end of my PhD carrier, but definitely not the end of my pursuing of knowledge and truth. I, was the boy playing on the seashore, am going to discover the great ocean of truth with the power gained in my PhD study.
LIST OF REFERENCES

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BIOGRAPHICAL SKETCH

Chaoyu Xiang (向超宇) was born in Kunming, Yunnan province, China. After graduating from high school attached to Yunnan Normal University, he attended Fudan University in Shanghai, China for his B.S. degree in optical science and technology. In 2009, he came to United States and started graduate school at the University for Florida. In his PhD program, he focused on the device and physics of organic semiconductors in the materials science and engineering department.