TADF process in blended organic luminescent material

Lu Zhang

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TADF Process in Blended Organic Luminescent Material

ZHANG Lu

A thesis submitted in partial fulfillment of the requirements

for the degree of

Doctor of Philosophy

Principal Supervisor: Prof. CHEAH Kok Wai

Hong Kong Baptist University

August 2016
DECLARATION

I hereby declare that this thesis represents my own work which has been done after registration for the degree of Ph. D. at Hong Kong Baptist University, and has not been previously included in a thesis, dissertation submitted to this or other institution for a degree, diploma or other qualifications.

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Date: August 2016
Abstract

Organic light-emitting diode (OLED) devices have been applied in the fields of display and solid-state lighting. In addition to phosphorescent OLEDs using heavy transition metals, a new approach of harvesting both singlet and triplet excitons generated in the OLED device by using pure organic materials has drawn a lot of attentions in recent years. It is thermally activated delayed fluorescence (TADF) process, which makes it possible to obtain potential 100% internal quantum efficiency (IQE).

TADF is a process existing in certain organic materials with small singlet-triplet exchange energy ($\Delta E_{ST}$), which is generally observed in the molecules with weak-coupled electron-donating (D) group and electron-accepting (A) group. Individual molecule containing D/A, which is named intramolecular exciplex, or intermolecular exciplex with D/A on separated molecules, can fulfill this requirement. Although at present the intramolecular exciplex attracts considerable research interests, it takes a lot of efforts to design an individual molecule with high fluorescent quantum yield as well as small $\Delta E_{ST}$. Intermolecular exciplex, which is achieved by physically blending individual D and A molecules with appropriate selection from present materials, has excellent performance comparable to the phosphorescent emitter.

In this work, we studied the TADF process in an intermolecular exciplex and its application in highly efficient OLED devices. By doping electron-donating material tris(4-carbazoyl-9-ylphenyl)amine (TCTA) with electron-accepting material 2,4,6-tris(3'-(pyridin-3-yl)biphenyl-3-yl)-1,3,5-triazine (Tm3PyBPZ), an exciplex with a
green emission around 514 nm was demonstrated. The time-resolved photoluminescence of the exciplex under different temperatures from 12 K to 300 K demonstrated the existence of temperature-dependent delayed fluorescence. By applying this exciplex as the emissive layer, a highly efficient all-fluorescent organic lighting emitting diode with maximum efficiencies of 13.1% and 53.4 lm/W was realized with an extremely low turn-on voltage of only 2.4 V. The efficiencies of the device have outperformed conventional fluorescent OLED devices due to the contribution of triplet excitons. By doping this exciplex with other conventional green or yellow fluorescent dopants, we observed that the performances of these dopants also surpass the limitation of conventional fluorescent OLED (~5 % external quantum efficiency).
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List of Abbreviations

\( a \) average hopping distance
\( A_0 \) Richardson constant
\( A_1 \) quantity of emission process
\( A_2 \) quantity of emission process
\( A(\lambda) \) absorbance
\( AFM \) atomic force microscopy
\( c \) the speed of light,
concentration
\( CE \) current efficiency
\( CV \) cyclic voltammetry
\( CW \) continuous wave
\( d \) distance between the electrodes,
separation of grating elements
\( D \) diffusion coefficient,
sum of the diffusion coefficients of the fluorophore and quencher
\( DF \) delayed fluorescence
\( e \) charge of an electron,
electrons
\( E \) applied electric field,
effective electric field
\( E_e \) energy of the excited state
\( E_g \) energy of the ground state
\( E_{HOMO} \) energy of HOMO level
\( E_i \) energy of site \( i \)
\( E_j \) energy of site \( j \)
\( E_{LUMO} \) energy of LUMO level
\( E_S \) the energy of the fluorescent emission maximum
\( E_T \) the energy of the phosphorescent emission maximum
\( E_{\text{vac}} \) vacuum level
\( |E_{\text{in}}(\lambda)|^2 \) free-space emission intensity
\( |E_{\text{out}}(\lambda)|^2 \) output intensity
\( EIL \) electron injection layer
\( EL \) electroluminescence
\( EML \) emissive layer
\( EQE \) external quantum efficiency
\( ETL \) electron transport layer
\( FET \) field-effect transistor
\( HOMO \) highest occupied molecular orbital
\( HIL \) hole injection layer
\( HTL \) hole transport layer
\( I \) intensity of the emission,
saturated emission current density,
the intensity of emitted radiation at a later time \( t \)
\( I_\theta \) the emission intensity at angle \( \theta \)
\( I_0 \) the emission intensity at the normal direction of the surface,
the intensity of emitted radiation immediately after excitation
\( IC \) internal conversion
\( ISC \) intersystem crossing
\( ITO \) indium-tin-oxide
\( IQE \) internal quantum efficiency
\( h \) Planck’s constant,
holes
\( J \) the spectral overlap integral between donor and acceptor,
current density
\( k \) Boltzmann constant
\( k_0 \) rate constant of the process
\( k_d \) rate of delayed component
\( k_{\text{DET}} \) rate of Dexter energy transfer
\( k_{\text{diff}} \) diffusion-controlled bimolecular rate constant
\( k_{\text{FET}} \) rate of Föster energy transfer
\(k_{\text{ISC}}\) rate constant of intersystem crossing
\(k_m\) the imaginary part of the refractive index of the metal
\(k_{np}\) rate of non-radiative triplet decay
\(k_{RISC}\) rate constant of reverse intersystem crossing
\(k'_{ic}\) rate constant of internal conversion
\(k'_{nr}\) rate constant of non-radiative decay
\(k'_{r}\) rate constant of radiative decay
\(k_p\) phosphorescence emission rate,
rate of prompt component
\(k_q\) bimolecular quenching rate constant
\(K\) exchange interaction integral,
constant proportional to orbital overlap between donor and acceptor
\(K_{SV}\) Stern-Volmer quenching constant
\(l\) the path length
\(L\) the sum of the van der Waals radii of the donor and acceptor molecules,
total optical length of the cavity,
luminance
\(L_0\) initial luminance
\(LUMO\) lowest unoccupied molecular orbital
\(m\) mass of the electron,
integer
\(m_0\) mass of the free electron
\(m^*\) effective mass of the tunneling carrier
\(n\) number of molecules in vibrational level,
the refractive index of the medium
\(n_m\) the real part of the refractive index of the metal
\(n_o\) the refractive index of organic material in contact with metal
\(N\) Avogadro’s number
\(OLED\) organic light-emitting diode
$P(\lambda)$ spectrum

PE power efficiency

PF prompt fluorescence

PL photoluminescence

$Q$ concentration of the quencher

$R$ collision radius,

reactive field

$R_{DA}$ distance between donor and acceptor molecule

$R_0$ Föster radius

$R_1$ reflectivity of the cathode

$R_2$ reflectivity of the ITO side

RISC reverse intersystem crossing

RMS root mean square

$S_D$ normalized emission of the donor

$S_0$ singlet ground state

$S_1$ first singlet excited state

SCLC space-charge-limited current

SWNIR short wavelength near infrared

t average transient time

$T$ absolute temperature

$T_1$ first triplet excited state

$T_2$ transmittivity

$T_{1/2}$ lifetime of an OLED device

TADF thermally activated delayed fluorescence

THF tetrahydrofuran

TOF time-of-flight

UPS ultraviolet photoemission spectroscopy

UV ultraviolet

$v$ charge hopping rate

$v_{ij}$ hopping rate between an occupied site i and an unoccupied site j

$v_0$ attempt-to-hop frequency
\( V \) the applied voltage
\( x \) the distance between recombination zone and cathode, CIE coordinate
\( x_\lambda(\lambda) \) CIE spectral stimulus function
\( X \) CIE tristimulus value
\( y \) CIE coordinate
\( y_\lambda(\lambda) \) CIE spectral stimulus function
\( Y \) CIE tristimulus value
\( z_\lambda(\lambda) \) CIE spectral stimulus function
\( Z \) CIE tristimulus value
\( \alpha \) constant
\( \beta \) constant
\( \varepsilon(\lambda) \) molar absorption coefficient
\( \eta \) solvent viscosity
\( \eta_{EQE} \) external quantum efficiency
\( \eta_D \) PL quantum efficiency of the donor
\( \eta_{IQE} \) internal quantum efficiency
\( \eta_{out} \) out-coupling efficiency
\( \eta_r \) the ratio of excitons capable of radiative transition
\( \theta \) angle between the direction of the emission and normal to the surface
\( \theta_i \) the incident angle of the light
\( \kappa \) orientation factor
\( \lambda \) wavelength of the light
\( \lambda_{cut off} \) cut-off wavelength
\( \mu \) mobility of charge carriers
\( m_e \) dipole moments of the solute molecule in the excited state
\( \mu_g \) dipole moments of the solute molecule in the ground state
\( \nu_\alpha \) wavenumber of lowest energy peak observed in absorption
\( \nu_e \) wavenumber of the fluorescent emission peak
frequency of the light

0-0 transition frequency of a free molecule

constant determined by dipole alignment and the geometry of OLED device

the absorption cross-section of the acceptor

lifetime of the excited state

PL lifetime of the donor

lifetime of the first excited state

lifetime of the emission process

lifetime of the emission process

work function of the surface

angular frequency

the recombination efficiency of the injected holes and electrons

barrier for the tunneling carrier

the decay length of the electronic wave function

quantum yield

photoluminescence quantum efficiency of the delayed components

fluorescent quantum yield

quantum yield of intersystem crossing

photoluminescence quantum yield

phosphorescent quantum yield

photoluminescence quantum efficiency of the prompt components

wave functions of HOMO level

wave functions of HOMO level

singlet-triplet exchange energy

the distance between i and j
Chapter 1 Introduction

In 1963, electroluminescence (EL) was first discovered in organic material by Pope and coworkers.[1] Above 400 V voltage was applied to the sublimed anthracene crystal to obtain the electroluminescence. Since the applied voltage was extremely high and the efficiency was very low, the electroluminescence in organic material was not well developed until 1987, when C. W. Tang and S. A. VanSlyke fabricated the first organic light-emitting diode (OLED) with a double-layer structure.[2] In their work, vapor-deposited organic thin films were sandwiched between indium-tin-oxide (ITO) anode and an alloyed Mg: Ag cathode. By using aromatic diamine as hole transport layer (HTL) and 8-hydroxyquinoline aluminum (Alq3) as the emissive layer (EML), the driving voltage was greatly reduced below 10 V and the external quantum efficiency (EQE) of the OLED was first over 1 %. Since then, researchers have made continuous efforts in the field of organic electroluminescence. An OLED device with doped organic thin film was reported in 1989, the EQE of OLED was further improved to about 2.5 % by doping other fluorescent emitters into Alq3 host.[3] In 1990, solution-processed conjugated polymer poly-para-phenylene vinylene (PPV) was first introduced into OLED, which expanded the field of OLED.[4] The chemical structures of Alq3 and PPV are shown in Figure 1.1.

In conventional fluorescent OLED devices, the transition between first singlet excited state ($S_1$) and first triplet excited state ($T_1$) is forbidden due to the selection rule as shown in Figure 1.2. Therefore, the fluorescent emitter can only harvest singlet excitons in the OLED device. Generally, the ratio of singlet to triplet excitons formed
by electrical excitation is 1:3, according to the statistics of spin multiplicity as shown in Figure 1.3. As a consequence, the internal quantum efficiency (IQE) for conventional fluorescent OLED is limited to 25% and the EQE is limited to 5%.

Figure 1.1 The chemical structures of (a) Alq3, (b) PPV.

Figure 1.2 Schematic of energy transfer between host and fluorescent guest.

Figure 1.3 The ratio of singlet to triplet excitons formed under electrical excitation.

In order to utilize both singlet and triplet excitons in the OLEDs, phosphorescent materials containing heavy transition metal atom were introduced into OLED devices in the late 1990s. The heavy metal induced strong spin-orbit coupling enables the
radiative transition from $T_1$ to the ground state ($S_0$) at room temperature. By using a phosphorescent emitter, both singlet and triplet excitons formed in an OLED device can be harvested as shown in Figure 1.4. Therefore, a theoretical 100 % IQE can be realized in a phosphorescent OLED device.

The first phosphorescent emitter introduced into an OLED device was 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine platinum(II) (PtOEP) in 1998.[6] As shown in Figure 1.5, a central platinum (Pt) atom was introduced into the molecular structure. This heavy transition metal introduces a strong spin-orbit coupling, leading to intersystem crossing from $S_1$ to $T_1$. Then, a phosphorescent emission around 650 nm was observed at room temperature. The maximum external and internal quantum efficiencies of this red phosphorescent OLED device were 4 % and 23 %, respectively. The phosphorescent lifetime of PtOEP is relatively long, so molecules at $T_1$ cannot efficiently return to $S_0$. As a result, the concentration of triplet excitons was very high and significant efficiency roll-off caused by triplet-triplet annihilation was observed.

![Figure 1.4 Schematic of energy transfer between host and phosphorescent guest.](image-url)
Phosphorescent emitters containing other heavy transition metals were then introduced to improve the efficiencies of the OLED as well as suppress the non-radiative decay, such as iridium complexes with short radiative lifetimes and high luminance efficiencies. The first OLED utilizing iridium complex was reported in 1999.[7] A green phosphorescent emitter tris(2-phenylpyridine) iridium [Ir(ppy)$_3$] was doped into a 4,4’-N,N’-dicarbazole-biphenyl (CBP) host and a maximum EQE of 8.0 % was achieved. The transient decay of Ir(ppy)$_3$ doped in CBP was reported to be a mono-exponential phosphorescent decay with a lifetime of about 500 ns at room temperature, which was much faster than PtOEP doped into Alq$_3$ (~ 35 μs).[8] The chemical structures of Ir(ppy)$_3$ and CBP are shown in Figure 1.6.

Figure 1.5 The chemical structure of PtOEP.

Another approach to harvest both singlet and triplet excitons formed in the OLED was demonstrated in 2009.[9] Six tin(IV) fluoride–porphyrin complexes exhibiting thermally activated delayed fluorescence (TADF) were reported and all these
complexes showed both fluorescence and TADF around 550-650 nm. In a TADF emitter, triplet excitons can be converted to singlet excitons via reverse intersystem crossing (RISC) with the assistance of thermal energy as shown in Figure 1.7. Therefore, an OLED device based on TADF emitter can also realize a theoretical 100 % IQE.

An OLED device based on a copper complex [Cu(PNP-t-Bu)]2 exhibiting TADF was demonstrated in the next year.[10] When this complex was doped into the EML, a maximum EQE of 16.1% was obtained. This results shows that TADF emitters are competitive with phosphorescent emitters.

![TADF Emitter Diagram](image)

Figure 1.7 Schematic of fluorescent emission from a TADF emitter.

A metal-free aromatic compound 2-biphenyl-4,6-bis(12-phenylindolo[2,3-a]carbazole-11-yl)-1,3,5-triazine (PIC-TRZ) exhibiting highly efficient TADF was first developed in 2011.[11] As shown in Figure 1.8, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were designed to be separately located on indolocarbazole and biphenyl triazole units, respectively, which resulted in a small singlet-triplet exchange energy (ΔE_ST) while maintaining a high fluorescent quantum yield. This result demonstrated the efficient TADF process
in metal-free aromatic organic material. It provided another way to utilize both singlet and triplet excitons without use of heavy transition metals.

A series of metal-free TADF materials were synthesized in 2012. This series of materials were based on carbazolyl dicyanobenzene, with carbazole functioning as an electron donor and dicyanobenzene functioning as an electron acceptor.[12] By introducing steric hindrance, the HOMO and the LUMO were localized on the donor and acceptor moieties, respectively. The emission of these materials can be tuned from blue emission to red emission by changing the number of carbazolyl groups or introducing other substituents. The OLED device based on the orange TADF material showed a high EQE of 11.2 %, which was much higher than conventional fluorescent OLED devices. From then on, more and more TADF materials were reported to improve the OLED efficiencies.[13-18] Chemical structures of some reported TADF materials are shown in Figure 1.9.

In addition to direct use of TADF materials as emitter, they can also function as an assistant dopant in OLED devices. As shown in Figure 1.10, triplet excitons formed on TADF assistant dopant are converted to singlet excitons via RISC, the energy then
transfers from the TADF assistant dopant to another doped conventional fluorescent emitter. Since the emitter can harvest extra singlet excitons from the TADF assistant dopant, OLED based on this structure can exceed the limitation of EQE in conventional fluorescent OLED device. It was reported that the EQE of OLED device based on conventional blue fluorescent emitter 2,5,8,11-tetra-tert-butylperylene (TBPe) was enhanced to 13.4 % by using a TADF assistant dopant.[19]

![Chemical structures of (a) BFCz-2CN,[14] (b) PXZ-TRZ,[15] (c) BT,[18] (d) 2CzPN,[12]](image)

Figure 1.9 Chemical structures of (a) BFCz-2CN,[14] (b) PXZ-TRZ,[15] (c) BT,[18] (d) 2CzPN,[12]

![Energy transfer schematic](image)

Figure 1.10 Schematic of TADF material functioning as assistant dopant.

TADF materials also provide another way to fabricate highly efficient hybrid white OLED. A white OLED device with the emissive layer employing a blue TADF
material 4,6-di(9H-carbazol-9-yl)isophthalonitrile (DCzIPN) both as emitter and host for yellow phosphorescent dopant, the EQE of this white OLED was as high as 21.0 % with a CIE coordinate of (0.31, 0.33). [20]

Except designing individual TADF materials, some blended donor-accepter systems with pronounced intermolecular charge transfer character also exhibit TADF via an efficient RISC process. Therefore, the intermolecular excited-state complex (exciplex) formed between electron-donating molecule and electron-accepting molecule is another alternative to realize efficient TADF process.[21-23]

The intermolecular exciplex can be formed either at the interface of selected electron-donating layer and the electron-accepting layer or by simply blending these two materials together. The emission of an exciplex based on blended organic materials exhibiting TADF is similar as the individual TADF molecules, as shown in Figure 1.11. When electron-donating material 4,4’,4’’-tris[3-methylphenyl(phenyl)-amino]triphenylamine (m-MTDATA) was doped with electron-accepting material 4,7-diphenyl-1,10-phenanthroline (Bphen), an OLED device with the EQE of 7.8 % was realized.[24] When m-MTDATA was doped with electron-accepting material tris-[3-(3-pyridyl)mesityl]borane (3TPYMB), the OLED device showed a maximum current efficiency of 36.8 cd/A.[25]

The exciplex exhibiting TADF can also function as host material for fluorescent emitters with different emissions. As shown in Figure 2.12, the triplet excitons formed at the exciplex host can be up-converted to singlet excitons via RISC. After this up-conversion process, the energy transfers from the singlet excitons on the
exciplex host to the fluorescent emitter. Since the fluorescent emitter can harvest more singlet excitons from the exciplex host than from the conventional host, the efficiencies of conventional fluorescent emitter are greatly improved. It was reported that the EQE of the OLED device based on the conventional fluorescent emitter 4-(dicyanomethylene)-2-t-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB) was increased to 10.2 % by using the exciplex host based on tris(4-carbazoyl-9-ylphenyl)amine (TCTA) and 2,4,6-tris(3-(1H-pyrazol-1-yl)phenyl)-1,3,5-triazine (3P-T2T). [26]

Figure 1.11 Schematic of fluorescent emission from exciplex exhibiting TADF process.

Figure 1.12 Schematic of exciplex functioning as host for fluorescent dopant.

Since the TADF process can result in a theoretical 100 % internal quantum efficiency (IQE) without use of heavy metals, the performances of OLED devices based on
TADF materials can be greatly improved without complex chemical synthesis involving heavy metals that can generate environmental pollution. In this work, we studied the TADF process in the intermolecular exciplex based on blended TCTA and 2,4,6-tris(3’-(pyridin-3-yl)biphenyl-3-yl)-1,3,5-triazine (Tm3PyBPZ). The properties of TCTA:Tm3PyBPZ and its application in OLED device were studied.
Chapter 2  OLED Fundamentals

Organic solids are composed of molecules held together by van der Waals forces and dipole-dipole interactions.[27] Since both van der Waals forces and dipole-dipole interactions are relatively weak, melting points of organic solids are generally low.[28] In general, organic materials used in optoelectronic devices are conjugated aromatic compounds. The term ‘conjugated’ refers to the molecules in which atoms are connected through p-orbitals, with delocalized electrons in compounds with alternating single and multiple bonds.[27] In highly conjugated systems, the absorption bands shift to longer wavelengths as the extent of conjugation increases.[29] The orbitals and electrons in molecules are responsible for the electronic bands. The energies of the orbitals are determined by the strong bonding interactions between atoms.

The frontier orbitals in organic materials are the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). These orbitals are actively involved in reactions since they are most available to electrophiles and nucleophiles, respectively.[30] The energy difference between HOMO and LUMO is called energy gap. However, the energy of the optical transition is lower than the energy gap, which is due to the exciton binding energy caused by columbic attraction between the excited electron and the hole left behind. Therefore, the electron was excited a little below LUMO and the hole has the energy just above the corresponding HOMO.[31] The HOMO energy level can be experimentally derived using two methods: one is ultraviolet photoemission spectroscopy (UPS); the other is cyclic voltammetry (CV).[32] The LUMO energy level can be calculated using
HOMO energy level and cut-off wavelength ($\lambda_{\text{cutoff}}$) in the absorption spectrum as shown below:

$$E_{\text{LUMO}} = E_{\text{HOMO}} + \frac{1240}{\lambda_{\text{cutoff}}} (eV)$$  \hspace{1cm} (0.1)

### 2.1 Principles of Organic Luminescent Materials

Electronic states and the transitions between them in organic molecules are usually represented using a Jablonski diagram shown in Figure 2.1.[27,33] The singlet and triplet states in organic molecules are derived from the multiplicity of the state which is equal to $2S + 1$, where $S$ is the total spin angular momentum for all electrons. For singlet states $S$ is equal to 0, so the multiplicity is equal to 1. If singlet states are resulted from a coupled electron pair occupying separate orbitals, the spin vectors are antiparallel (\(\uparrow \downarrow\)). For triplet states $S$ is equal to 1, so the multiplicity is equal to 3. If triplet states are resulted from a coupled electron pair occupying separate orbitals, the spin vectors are parallel.[34] According to Hund’s rule which states that the energy of an electronic state with maximum $S$ is lowest, the energy of the triplet state is usually lower than the corresponding singlet state.[35] The energy difference between singlet state and triplet state is called exchange energy $\Delta E_{\text{str}}$, which equals to twice the exchange integral $K$. In each electronic state, there are vibrational energy states. In each vibrational state, there are rotational energy states.[36] The transitions between different states are discussed in the following sections.
2.1.1 The absorption process

The electronic transition to promote an electron from ground state to the excited state by absorbing a photon is called absorption. The absorption usually starts from the lowest vibrational energy level of the ground state where most molecules remain in room temperature according to Boltzmann distribution law shown in Equation 2.2

\[
\frac{n_0}{n_1} = \exp\left(-\frac{E_0 - E_1}{kT}\right) \tag{0.2}
\]

where \( n_0 \) and \( n_1 \) are the number of molecules in two vibrational levels, \( E_0 \) and \( E_1 \) are energies of corresponding vibrational level, \( k \) is the Boltzmann constant (1.38×10^{-23} J/K) and \( T \) is the absolute temperature.[37]

A molecule in singlet ground state can only be promoted to a singlet excited state according to the selection rules, which states that the electron spin in initial and final states should be conserved.[38] This means transitions between singlet-singlet and triplet-triplet are allowed, however, transitions between singlet-triplet are forbidden.
If a photon is traveling at the velocity of light $3 \times 10^8$ m/s, it would remain in the vicinity of a molecule of diameter say, 30 Å for

$$t = \frac{30\text{Å}}{3 \times 10^{18}\text{Å/s}} = 10^{-17}\text{s}$$

(0.3)

If the photon is absorbed by the molecule, then the time required for absorption process is no more than $10^{-17}$ s.[39]

### 2.1.2 Vibrational relaxation

Following the absorption process, an electron was promoted to an excited state, which is usually some higher vibrational level of the electronic excited state. The excess vibrational energy can be released as kinetic energy by collisions. This process is called vibrational relaxation, which is a non-radiative transition and usually occurs immediately following the absorption process. The vibrational relaxation happens very fast and the time-scale is about $10^{-12}$ s.[40] Generally, this process occurs from higher vibrational level to lower vibrational level in the same electronic state, so there is no change in electronic energy.[41]

### 2.1.3 Internal conversion

The transition from a vibrational level in one electronic state to another vibrational level in a lower electronic state with the same multiplicity is called internal conversion (IC). The mechanism of this process is identical to vibrational relaxation, it happens when the vibrational energy levels of two electronic states overlap.[42] According to density of states, the vibrational and electronic energy levels are closer distributed as energies increase.[43] At higher energy levels, there may be overlap
between the vibrational energy levels of two electronic states. This overlap makes it possible for the transition from vibrational levels in higher electronic state to vibrational levels in lower the electronic state. The time-scale of internal conversion is around $10^{-12}$ s which is comparable to that of nuclear vibration.[44] However, internal conversion from first singlet excited state to ground state is much slower due to the much larger energy gap between $S_1$ and $S_0$. This slow transition process for electron returning to the ground state competes with other processes such as, fluorescence and intersystem crossing.

### 2.1.4 Intersystem crossing

Even though the transition between singlet state and triplet state is forbidden due to the selection rule, it may be still observed due to spin-orbit coupling. Spin-orbit coupling is the magnetic mutual interaction between orbital momentum and spin of an electron. It becomes much stronger when a heavy atom is introduced in the molecule. When spin-orbit coupling exists, the transition from $S_1$ to $T_1$ is possible and the transition from $T_1$ to $S_0$ is allowed.

The transition from vibrational level of an electronic state to another vibrational level of an electronic state with different multiplicity is called intersystem crossing (ISC). It is a non-radiative process. The rate constant $k_{ISC}$ of intersystem crossing is defined as the reciprocal of the transition time. It is determined by the strength of spin-orbit coupling and the vibrational overlap between the wavefunctions of the two states. For fluorescent emitters, it is about $10^7$ s$^{-1}$. For phosphorecent emitters the rate $k_{ISC}$ is as fast as $10^{-12}$ s$^{-1}$.[45]
2.1.5 Non-radiative decay

The de-excitation processes from $S_1$ to ground state consist of radiative and non-radiative decay. There is usually one radiative process from $S_1$ which is called fluorescence and will be discussed in the following section. The non-radiative decay pathways are shown in Figure 2.2. For an individual molecule, the non-radiative decay processes that can occur are internal conversion and intersystem crossing. For a condensed phase such as in a solution or a film, the non-radiative decay processes may also include dissociation of excited states into free charge carriers and energy transfer to other molecules.[46]

![Figure 2.2 Schematic of non-radiative decay](image)

The rate constants of IC and ISC follow the energy gap law. It states that the rate constants of IC and ISC decrease exponentially as the energy gap between the two electronic states increases in a series of related molecules.[47]

Dissociation of excitons may occur at internal sites such as defects or impurities, it can also occur in strong electric fields which can be found at the interfaces.[48]
2.1.6 Luminescence processes

2.1.6.1 Fluorescence

The transition from $S_1$ to $S_0$ accompanying with the emission of photons is called fluorescence. Since organic fluorescent molecules consist of electronic states containing a multitude of vibrational and rotational levels, the energy bands are broad and continuous. Therefore, the fluorescent molecules exhibit broad fluorescence and absorption spectra.[49]

2.1.6.1.1 The Stokes shift

The energy of the fluorescent emission peak is lower than the lowest energy peak observed in absorption due to the loss of energy caused by vibrational relaxation. This phenomenon is called Stokes shift.[50] It is expressed in wavenumbers as shown in Equation 2.4:

$$\Delta \nu = \bar{\nu}_a - \bar{\nu}_e$$  \hspace{1cm} (0.4)

where $\bar{\nu}_a$ is the wavenumber of lowest energy peak observed in absorption, $\bar{\nu}_e$ is the wavenumber of the fluorescent emission peak. Wavenumber is converted from wavelength by taking the reciprocal. For example, the absorption and emission spectra of bis(10-hydroxybenzo [h] quinolinato)-beryllium (Bebq$_2$) are shown in Figure 2.3. The $\bar{\nu}_a$ is calculated to be 23697 cm$^{-1}$ and $\bar{\nu}_e$ is calculated to be 19763 cm$^{-1}$, so the Stokes shift is 3934 cm$^{-1}$. 
Figure 2.3 Example of Stokes shift: Bebq₂ on quartz substrate at room temperature.

2.1.6.1.2 Lifetime and quantum yield

The emission of a photon is as fast as absorption of a photon. However, the excited molecules may stay in S₁ for some time before the emission. The lifetime of the first excited state \( \tau_s \) is given by:

\[
\tau_s = \frac{1}{k^s_r + k^s_{nr}}
\]

where \( k^s_r \) is the rate constant for radiative decay, \( k^s_{nr} \) is the rate constant for non-radiative decay. \( k^s_{nr} \) can be calculated by adding up all the non-radiative processes involved in the deactivation process. If only internal conversion and intersystem crossing is involved in the non-radiative decay, then \( k^s_{nr} \) is given by:

\[
k^s_{nr} = k^S_{IC} + k^S_{ISC}
\]
where $k_{ic}^{s}$ is the rate constant for internal conversion and $k_{isc}^{s}$ is the rate constant for intersystem crossing.

$k_{nr}^{s}$ can also be given by energy gap law as shown in Equation 2.7:

$$k_{nr}^{s} = \alpha \exp(-\beta \Delta E) \quad (0.7)$$

where $\alpha$ and $\beta$ are constant.

The quantum yield $\Phi$ for a process is defined as the fraction of the number of molecules undergoing the process to the number of photons absorbed for excitation.[51]

For instance, fluorescence quantum yield $\Phi_F$ is given by the fraction of the number of photons emitted from $S_1$ to the number of photons absorbed for excitation as shown in Equation 2.8

$$\Phi_F = \frac{k_{r}^{s}}{k_{r}^{s} + k_{nr}^{s}} = k_{r}^{s} \tau_{s} \quad (0.8)$$

The quantum yield for intersystem crossing $\Phi_{ISC}$ is given by

$$\Phi_{ISC} = \frac{k_{ISC}}{k_{r}^{s} + k_{nr}^{s}} = k_{ISC} \tau_{s} \quad (0.9)$$

### 2.1.6.1.3 Environmental effects

The surrounding environment such as temperature, quenching, solvent polarity and viscosity have a great influence on the fluorescence of a molecule. Generally, an increase of temperature result in an increase of non-radiative processes related to
thermal agitation. Higher temperature also causes more frequent collisions between molecules. This results in a decrease in fluorescence quantum yield and the fluorescence lifetime.[52]

Quenching is any process which reduces the fluorescence intensity. A collisional quenching process is that a molecule in excited state collides with another molecule (quencher) and transfers its energy to that molecule. The excited state lifetime and quantum yield are also reduced in this case. This process can be expressed by Stern-Volmer equation:

\[
\frac{\Phi_0}{\Phi} = \frac{I_0}{I} = 1 + \tau_0 k_q Q = 1 + K_{SV} Q
\]  

(0.10)

where \(\Phi_0\) and \(\Phi\) are the fluorescence quantum yields in the absence and presence of quencher, respectively; \(I_0\) and \(I\) are the fluorescence intensities in the absence and presence of quencher, respectively; \(\tau_0\) is the fluorescence lifetime in the absence of the quencher; \(k_q\) is the bimolecular quenching rate constant; \(K_{SV}\) is the Stern-Volmer quenching constant and \(Q\) is the concentration of the quencher.[53]

If \(k_q\) occurred through a diffusion-controlled path, the theoretical diffusion-controlled bimolecular rate constant \(k_{diff}\) can be calculated by Smoluchowski equation as a function of temperature:

\[
k_{diff} = \frac{4\pi RND}{1000}
\]  

(0.10)
where $R$ is the collision radius, $N$ is the Avogadro’s number and $D$ is the sum of the diffusion coefficients of the fluorophore and quencher. Diffusion coefficients can be obtained from the Stokes-Einstein equation:

$$D = \frac{kT}{6\pi \eta R} \quad (0.10)$$

where $k$ is the Boltzmann constant and $\eta$ is the solvent viscosity. [54]

Triplet oxygen molecules are well-known quenchers for aromatic fluorophores. The encounter with triplet oxygen molecules causes the singlet excited state molecule becoming a triplet excited state molecule. Then, the triplet excited molecule can be either quenched by oxygen again or return to the ground state by non-radiative decay as shown in Figure 2.4. [55] This process may result from mixed mechanisms including intersystem crossing, charge transfer, and electron exchange. [56, 57] According to Stern-Volmer equation discussed above, the concentration of oxygen has a very big influence on the quenching process.

![Figure 2.4 Fluorescence quenching by molecular oxygen.](image)

When a solute molecule is excited in a solution, the excited molecule interacts to a vary degree with the solvent molecules before returning to the ground state. These interactions influence the spectral position, shape of the emission bands and the lifetime of the excited states. This change in fluorescent spectra caused by solvent is
included in the term solvatochromism.[58] The elementary cell to analyze is solvate which is defined as a fluorescent organic molecule and its immediate surroundings.

The electronic transition frequency of the solute molecule as a function of the reactive field of the solvate can be written as:

\[ h\nu = h\nu_0 - \Delta\mu R = h\nu_0 - (\mu_e - \mu_g)R \quad (0.11) \]

where \( \mu_g \) and \( \mu_e \) are the dipole moments of the solute molecule in the ground and excited states, respectively, \( \nu_0 \) is the 0-0 transition frequency of a free molecule, \( R \) is the reactive field which is determined by the geometric configuration of dipole solvent molecules in the solvation shell.[59]

For most fluorescent molecules the dipole moment of the excited state is larger than it in the ground state. In this case, a redshift of the fluorescence band is observed. The stronger the interaction between the solute and the solvent, the lower the energy of the excited state and the larger redshift of the emission is.

**2.1.6.2 Phosphorescence**

The radiative transition from \( T_1 \) to the ground state is phosphorescence as shown in Figure 2.1. It cannot be observed in fluorescent organic material at room temperature due to the low transition probability and the dominant non-radiative decay from triplet state. However, it can be observed at very low temperature due to the significantly reduced non-radiative decay. Since the triplet state is usually at lower energy than the corresponding singlet state, the phosphorescent spectrum is usually located at longer wavelength than fluorescent spectrum.
Although transition between states with different multiplicity is forbidden, introducing spin-orbit coupling makes it possible. Strong spin-orbit coupling can be realized by introducing heavy metal atoms such as iridium and platinum. When a molecule with strong spin-orbit coupling is excited by optical excitation, the molecule is at a singlet excited state. Then, the molecule may stay at singlet state for some time and transfer to a triplet state by intersystem crossing. Finally, the radiative transition from T\textsubscript{1} to the ground state occurs and phosphorescence emission is observed.

The phosphorescence quantum yield (\(\Phi_P\)) can be calculated by Equation 2.14:

\[
\Phi_P = \Phi_{ISC} \frac{k_p}{k_p + k_{np}}
\]

where \(k_p\) is the phosphorescence emission rate and \(k_{np}\) is the rate of non-radiative triplet decay.

### 2.1.6.3 Thermally-activated delayed fluorescence

In conventional fluorescent materials, the energy difference between S\textsubscript{1} and T\textsubscript{1} is relatively large and the transition probability from S\textsubscript{1} to T\textsubscript{1} is very low. Therefore, only singlet excitons can contribute to the fluorescence. In recent years, many studies show that triplet excitons can also make a great contribution to the fluorescence through thermally-activated delayed fluorescence (TADF). TADF is also known as E-type delayed fluorescence since it was first observed in eosin in 1961.[60] At that time, this long-lived luminance is very weak and it is considered to decrease the device efficiencies in the following years.[61,62] Ever since the work of Adachi and co-workers in recent years, OLED devices employing TADF materials are greatly
developed.[9] Since TADF process is very sensitive to temperature and oxygen, materials exhibiting TADF can also be used for temperature and oxygen sensors.[63]

To achieve an efficient TADF process, the singlet-triplet exchange energy ($\Delta E_{ST}$) should be very small. The schematic of TADF under optical and electrical excitation is shown in Figure 2.5. The reverse intersystem crossing (RISC) from $T_1$ to $S_1$ occurs with the assistance of thermal energy and then there is repopulation of $S_1$, followed by delayed fluorescence (DF). In addition to prompt fluorescence (PF) happened immediately after the excitation from $S_1$ to $S_0$, DF can make an extra contribution to the total fluorescent quantum yield. Under electrical excitation, both singlet and triplet excitons can be utilized to the luminance leading to a theoretical 100% internal quantum efficiency. The PF usually occurs within nanoseconds, whereas the lifetime of DF can be as long as microseconds.

The PL quantum efficiencies of PF and DF can be given by:

$$\Phi_{PF} = \frac{k^s_r}{k_r^s + k^s_{nr} + k_{ISC}} = \frac{k^s_r}{k_{PF}} \quad (0.13)$$

$$\Phi_{DF} = \frac{\Phi_{ISC} \Phi_{RISC}}{1 - \Phi_{ISC} \Phi_{RISC}} \Phi_{PF} \quad (0.14)$$

The rate of RISC ($k_{RISC}$) is related to $\Delta E_{ST}$ according to the energy gap law as shown in Equation 2.17.

$$k_{RISC} \propto \exp \left( \frac{\Delta E_{ST}}{k_B T} \right) \quad (0.15)$$
\( \Delta E_{ST} \) is scaled with the overlap between HOMO and LUMO as shown in Equation 2.18,[64]

\[
\Delta E_{ST} = 2K \propto \int \psi_{HOMO}(r)\psi_{LUMO}(r) \, d^{3}r
\]  

(0.16)

Here, \( K \) is the exchange interaction integral, \( \psi_{HOMO}(r) \) and \( \psi_{LUMO}(r) \) are wave functions of HOMO and LUMO, respectively.

Figure 2.5 Schematic of TADF under (a) optical excitation. (b) electrical excitation. Therefore, materials with a small \( \Delta E_{ST} \) should have weak-coupled electron-donating group and electron-accepting group situated on well separated locations either in the same molecule or in different molecules.[65] In the former case, it is called intramolecular exciplex as shown in Figure 2.6a, and in the latter case, it is called intermolecular exciplex as shown in Figure 2.6b.[66,67]
To design an efficient TADF material based on intramolecular exciplex, the $\Delta E_{ST}$ should be smaller than 100 meV and the radiative decay rate should be larger than $10^6$ s$^{-1}$ to compete with the non-radiative decay.\[12\] By introducing large steric hinderance structure, the HOMO and LUMO are localized on the donor and acceptor moieties, respectively. In addition to directly use of TADF materials as emitters in OLED, it can also function as an assistant dopant.\[19\] Triplet excitons formed on TADF assistant dopant can transfer to singlet excitons via RISC, the energy then transfers from the TADF assistant dopant to a fluorescent emitter by Föster energy transfer. As a result, the fluorescent quantum yield of the emitter is increased.

To design an efficient TADF material based on intermolecular exciplex, the selected donor and acceptor molecules are physically blended together. The exciplex forms at the heterojunctions with charge-transfer character.\[68\] The donor and acceptor molecules emit in a cooperative manner with one molecule at the excited state and the other one at the ground state. It is important to distinguish exciplex from ground-state complex. In a ground-state complex, two molecules absorb in a cooperative manner at their ground state. The emission of the exciplex is determined by the HOMO level of the donor and LUMO level of the acceptor as shown in Figure 2.7. The energy of the exciplex can be determined by HOMO level of the donor, LUMO level of the acceptor and the exciplex binding energy.\[69,70\]
It is noted that triplet-triplet annihilation can also result in delayed fluorescence. However, the theoretically maximum IQE is only 62.5 % and the maximum EQE is limited to just 12.5 %.[71,72]

2.2 Mechanisms of OLED under Electrical Field

Figure 2.8 shows basic structure of an OLED device. It consists of multiple organic layers either solution-processed or vacuum-deposited sandwiched between anode and cathode. Indium tin oxide (ITO) is the most common used material for anode which consists of SnO$_2$ and In$_2$O$_3$. The transmission of an 80-nm-thick ITO layer at UV-Vis region is around 90 %.[73] Hole injection layer (HIL) and hole transport layer (HTL) are deposited onto the ITO substrate to achieve a balanced hole transport into emissive layer (EML). A metal cathode with suitable work function is selected to benefit the electron injection into the electron transport layer (ETL). A very thin electron injection layer (EIL) is inserted between cathode and ETL to reduce the electron injection barrier and prevent the chemical reactions between ETL and cathode.[74] When a forward bias voltage is applied to the OLED device, holes and electrons are injected from anode and cathode, respectively. The carriers are then drifted by the internal electric field towards the electrode with opposite polarity. When an electron passes close to a hole, they could attract each other to form an
exciton. Then the electroluminescence occurs during the radiative decay of the excitons.

Figure 2.8 Basic structure of organic light-emitting device.

2.2.1 Charge injection

Figure 2.9 shows an energy diagram for a molecular solid. The vacuum level ($E_{\text{vac}}$) is defined as the energy required for an electron to escape from the solid. The energy difference between LUMO and vacuum level is electron affinity which is defined as the energy released when an electron is added to a neutral atom or molecule to form a negative ion. The energy difference between HOMO and vacuum level is ionization potential which is defined as the energy required for removing an electron from a neutral atom or molecule. When a strong electric field is applied to an OLED device, electrons are injected from the cathode to the LUMO level of the ETL and holes are injected from the anode to the HOMO level of the HTL.
Figure 2.9 Energy diagram of a molecular solid.

Generally, there are two important approaches for charge carrier injection: thermionic emission and the Fowler-Nordheim tunneling injection processes.

2.2.1.1 Thermionic emission

For thermionic emission, the charge carriers are thermally excited to overcome the potential barrier to exit the electrode surface. The electric current density of thermionic emission is given by Richardson-Dushman equation:

\[ I = A_0 T^2 \exp\left(-\frac{\varphi}{kT}\right) \]  

(0.17)

where \( I \) is the saturated emission current density, \( \varphi \) is the work function of the surface, \( k \) is the Boltzmann constant, \( T \) is the temperature and \( A_0 \) is the Richardson constant which is given by:

\[ A_0 = \frac{4\pi em^2}{h^3} = 1.2 \, A \, m^{-2} \, K^{-2} \]  

(0.18)

where \( e \) is the charge of an electron, \( m \) is the mass of the electron, \( h \) is Planck’s constant.
The current emitted from the metal cathode into the vacuum is determined by the thermionic work function of the metal. When an electric field is applied, the work function is reduced. This change of barrier caused by electric field is called Schottky effect. The Richardson-Dushman equation can be corrected for the Schottky effect and the equation is expressed as follows:

$$ J = A_0 T^2 \exp \left( -\frac{\varphi - E^2}{kT} \right) $$

where $E$ is the applied electric field. This equation is applied for electric filed lower than $10^8$ Vm$^{-1}$. [75,76]

### 2.2.1.2 Fowler-Nordheim tunneling injection

The tunneling effect is another way for carrier injection. The Fowler-Nordheim model is applicable under high electric field. The probability for Fowler-Nordheim tunneling through a triangular barrier is given by:

$$ P = \exp \left( -\frac{4 \sqrt{2em^*} \phi^3}{3 \ h \ E} \right) $$

where $\hbar$ is the Planck’s constant, $m^*$ is the effective mass of the tunneling carrier, $\phi$ is the barrier for the tunneling carrier, and $E$ is the effective electric field inside the dielectric.[77] This equation indicates that the Fowler-Nordheim model is affected by the electric field rather than temperature.

The current flow caused by Fowler-Nordheim tunneling is given by:
\[ J = \frac{e^3 V^2 m_0}{8\pi\hbar\phi m^*} \exp\left(-\frac{4\sqrt{2m^*}\phi^2}{3\hbar V}\right) \]  

where \( V \) is the applied voltage, \( m_0 \) is the mass of the free electron.[78]

### 2.2.2 Charge transport

When charge carriers move in amorphous organic solids, they can be localized by defects, disorder or potential. Since the energy sites with the organic material are strongly localized, the charge carriers transport by intersite hopping between localized states. This charge carrier hopping process between adjacent molecules is caused by thermal-activated lattice vibrations. The rate of hopping transport is given by Miller-Abraham formula:

\[ \nu_{ij} = \nu_0 \exp\left(-2\Delta R_{ij}\zeta\right) \begin{cases} \exp\left(-\frac{E_j - E_i}{k_B T}\right); & E_j > E_i \\ 1; & \text{else} \end{cases} \]

Here, \( \nu_{ij} \) is the hopping rate between an occupied site \( i \) and an unoccupied site \( j \), \( \nu_0 \) is the attempt-to-hop frequency, \( \Delta R_{ij} \) is the distance between \( i \) and \( j \), \( \zeta \) is the decay length of the electronic wave function, \( E_i \) and \( E_j \) are energies of site \( i \) and site \( j \).[79,80]

Unlike inorganic semiconductors, the mobility of organic material is relatively low. The charge mobility \( \mu \) can be estimated by Einstein-Smoluchowski equation:

\[ \mu = \frac{eD}{k_B T} \]  

Here, \( D \) is the diffusion coefficient and is given by:
\[ D = a^2 \nu \quad (0.24) \]

where \( a \) is the average hopping distance and \( \nu \) is the charge hopping rate. [81]

The charge mobilities can be experimentally determined by several methods such as time-of-flight (TOF), space-charge-limited current (SCLC) and field-effect transistor (FET).[82]

Schematic of time-of-flight is shown in Figure 2.10. An organic layer with the thickness of several microns is sandwiched between two electrodes. The organic layer is first excited by a pulsed laser to generate charge carriers. The charge carriers then migrate in the organic layer toward the electrode under the applied bias. The current at the arriving electrode is recorded by an oscilloscope as a function of time. The mobility of holes or electrons is given by:

\[ \mu = \frac{d^2}{Vt} \quad (0.25) \]

where \( d \) is the distance between the electrodes, \( V \) is the applied voltage and \( t \) is the average transient time.
2.2.3 Excitons

When an electron is excited to an excited state, a hole is created and left behind. The excited electron is attracted to a hole nearby by Coulomb’s electrostatic force and they form an electron-hole pair. This electron-hole pair is called exciton.

Excitons can be generated by absorption of light or by charge carrier injection under electric field. If the excitons are generated by absorption of light, there are only singlet excitons generated due to the singlet ground state and the conservation of the spin. If the excitons are generated by charge carrier injection under electric field, there are both singlet and triplet excitons generated. The ratio of singlet excitons and triplet excitons generated by this method is generally believed to be 1:3 due to the spin statistics.

There are generally three types of exciton determined by the distance between the electron and the hole in the exciton: Frenkel exciton, charge transfer exciton and Wannier exciton as shown in Figure 2.11.[83,84] The radius of a Frenkel exciton is very small (~10 Å), so the electron and hole in a Frenkel exciton usually located on the same molecule and the binding energy is about 1 eV. For the charge transfer exciton, the electron and hole are separated in two adjacent molecules. This kind of
excitons is usually observed in donor-acceptor molecule with electron-donating moiety and electron-accepting moiety located in different places of the molecule. The radius of a Wannier exciton is relatively large (~100 Å). They are normally observed in inorganic semiconductors.

![Diagram](image)

Figure 2.11 Types of exciton. (a) Frenkel exciton. (b) charge transfer exciton. (c) Wannier exciton.

2.2.4 Energy transfer

Energy transfer between excitons can be classified as radiative or non-radiative energy transfer. A photon emitted by one molecule can be then absorbed by another molecule. This energy transfer process is called radiative energy transfer. There are mainly two kinds of non-radiative energy transfer in organic semiconductor: Föster energy transfer and Dexter energy transfer.

2.2.4.1 Föster energy transfer

Föster energy transfer is a resonant energy transfer between two molecules by dipole-dipole interaction. As shown in Figure 2.12. The excited donor molecule will interact with the ground state acceptor molecule. After the energy transferring from the donor to the acceptor, the donor returns to the ground state and the acceptor is excited. This energy transfer requires overlap between the PL spectrum of the donor molecule and
the absorption spectrum of the acceptor molecule. The rate of Förster energy transfer $k_{FET}$ between a donor molecule and an acceptor molecule is determined by:

$$k_{FET} = \frac{1}{\tau_D} \left( \frac{R_0}{R_{DA}} \right)^6$$  \hspace{1cm} (0.26)

Here, $\tau_D$ is the PL lifetime of the donor, $R_{DA}$ is the distance between donor and acceptor molecule, $R_0$ is known as Förster radius and can be calculated by:

$$R_0^6 = \frac{9c^4 \kappa^2 \eta_D}{8\pi n^4} \int_{-\infty}^{\infty} \frac{S_D(\omega)\sigma_A(\omega)}{\omega^4} d\omega$$  \hspace{1cm} (0.27)

where $c$ is the speed of light, $n$ is the refractive index of the medium, $\kappa$ is the orientation factor, $\eta_D$ is the PL quantum efficiency of the donor, $S_D$ is the normalized emission of the donor, $\sigma_A$ is the absorption cross-section of the acceptor and $\omega$ is angular frequency.[85] The Förster radius is usually in the range of several nanometers. Förster energy transfer is generally observed between donor in singlet excited state and acceptor in ground state.

![Figure 2.12 Schematic of Förster energy transfer.](image)
2.2.4.2 Dexter energy transfer

Dexter energy transfer occurs with the exchange of electrons between excited donor molecule and the ground state acceptor molecule as shown in Figure 2.13. After the exchange of electrons, the donor returns to the ground state and the acceptor is excited. The rate of electron exchange is related to the orbital overlap between the donor and the acceptor, which decreases exponentially with increasing distance between donor and acceptor. Therefore, Dexter energy transfer is a short-range interaction and the distance between donor and acceptor for Dexter energy transfer to occur is smaller than Förster radius (~ 1 nm). The rate of Dexter energy transfer is given by:

\[
k_{DET} = KJ \exp\left(-\frac{2R_{DA}}{L}\right)
\]  

where \( K \) is a constant proportional to orbital overlap between donor and acceptor, \( J \) is the spectral overlap integral between donor and acceptor, \( L \) is the sum of the van der Waals radii of the donor and acceptor molecules.[86]

Dexter energy transfer also requires overlap between the PL spectrum of the donor molecule and the absorption spectrum of the acceptor molecule. This energy transfer process can efficiently transfer energy between triplet states or singlet states provided that the total spin symmetry is conserved. Since Dexter energy transfer is a short-range transfer, the doping concentration of acceptor should be high for this process to occur.[87]
2.2.5 Exciton quenching

In OLED devices, excitons may interact with each other leading to exciton quenching and decreasing of efficiency. Singlet exciton can be quenched by singlet exciton through singlet-singlet annihilation as shown in Equation 2.31. A singlet exciton may return to the ground state by transferring its energy to another singlet exciton to assist that exciton to a higher singlet excited state. Then, the exciton at higher singlet excited state quickly relaxes to the first singlet excited state.[88]

\[ S_1 + S_1 \rightarrow S_1 + S_0 \]  \hspace{1cm} (0.29)

Singlet exciton can also be quenched by triplet exciton through singlet-triplet annihilation as shown in Equation 2.32. A singlet exciton may return to the ground state by transferring its energy to a triplet exciton to assist that exciton to a higher triplet excited state. Then, the exciton at higher triplet excited state quickly relaxes to the first triplet excited state.

\[ S_1 + T_1 \rightarrow T_1 + S_0 \]  \hspace{1cm} (0.30)
Triplet exciton can be quenched by triplet exciton through triplet-triplet annihilation as shown in Equation 2.33 and Equation 2.34. The mechanism is similar to singlet-singlet annihilation.

\[ T_1 + T_1 \rightarrow T_1 + S_0 \]  
\[ (0.31) \]

\[ T_1 + T_1 \rightarrow S_1 + S_0 \]  
\[ (0.32) \]

Holes \((h)\) or electrons \((e)\) can interact with both singlet and triplet excitons and cause excitons returning to the singlet ground state. [89]

\[ S_1 + h \rightarrow S_0 + h \]  
\[ (0.33) \]

\[ S_1 + e \rightarrow S_0 + e \]  
\[ (0.34) \]

\[ T_1 + h \rightarrow S_0 + h \]  
\[ (0.35) \]

\[ T_1 + e \rightarrow S_0 + e \]  
\[ (0.36) \]

Excitons can also be quenched by electric field and dissociate into free charge carriers. [90]

### 2.3 Microcavity effect

Figure 2.15 shows structures of a bottom emission OLED device and a top emission OLED device. For a bottom emission OLED, light is emitted through a transparent anode and a highly reflective metal layer is functioned as cathode. For a top emission OLED, a highly reflective metal layer is functioned as anode and a semitransparent cathode is deposited on the organic layers. The light is emitted through the
semitransparent cathode. Since organic layers are sandwiched between two highly reflective layer in the top emission OLED, there are strong microcavity effects such as spectral narrowing, spectral shift and angular dependence.\cite{91,92} Even in a bottom OLED device, there is also weak microcavity effect to influence the luminescence properties.

![Figure 2.14 Structures of OLED devices. (a) a bottom emission OLED device. (b) a top emission OLED device.](image)

An OLED device can be considered as a Fabry-Perot cavity. It is a cavity in which emitting dipoles are located between two mirrors. One or both of the mirrors can be semitransparent to let the light emitted go out of the cavity. The direct outgoing light can interfere with the light reflected by the mirror and then influence the out-coupled light emission. For bottom OLED devices, the emission intensity in the normal direction at wavelength $\lambda$ can be given by:

$$|E_{out}(\lambda)|^2 = |E_{in}(\lambda)|^2 \times \frac{T_2 \times \left[ 1 + R_1 + 2\sqrt{R_1} \cos \frac{4\pi x}{\lambda} \right]}{1 + R_1 R_2 - 2\sqrt{R_1 R_2} \cos \frac{4\pi L}{\lambda}} \quad (0.37)$$
where $|E_{\text{out}}(\lambda)|^2$ is the output intensity; $|E_{\text{in}}(\lambda)|^2$ is the free-space emission intensity; $T_2$ and $R_2$ are transmittivity and reflectivity of the ITO side, respectively; $R_1$ is the reflectivity of the cathode; $x$ is the distance between recombination zone and cathode; $L$ is the total optical length of the cavity.[93] The weak microcavity effect of an bottom OLED is shown in Figure 2.15.

The phase shift at the reflective metal cathode is given by the following equation:

$$\varphi = \tan^{-1}\left(\frac{2n_o k_m}{n_o^2 - n_m^2 - k_m^2}\right)$$  \hspace{1cm} (0.37)

where $n_o$ is the refractive index of organic material in contact with metal, $n_m$ is the real part of the refractive index of the metal, $k_m$ is the imaginary part of the refractive index of the metal.[78]

![Diagram](image)

Figure 2.15 The weak microcavity effect of a bottom OLED device.

### 2.4 Lambertian emission pattern

Generally, light distribution emitted from a bottom OLED device is considered to be a Lambertian emission pattern as shown in Figure 2.16. The Lambertian pattern is derived from Lambert’s cosine law of emission which is given by:
where \( \theta \) is the angle between the direction of the emission and normal to the surface, 
\( I_\theta \) is the emission intensity at angle \( \theta \), \( I_0 \) is the emission intensity at the normal direction of the surface.[94] This equation indicates that the emission intensity is at maximum along the normal direction to the surface and it falls to zero at the direction parallel to the surface.

\[
I_\theta = I_0 \cos \theta
\]  

(0.38)

Figure 2.16 Lambertian emission pattern.

2.5 External and Internal Quantum Efficiency

The internal quantum efficiency (IQE) of an OLED device is defined as the ratio of the photons emitted over the number of electrons injected. The external quantum efficiency (EQE) is defined as the ratio of the photons escaped from the OLED device over the number of electrons injected. The EQE can be calculated from IQE as shown in Equation 2.42.

\[
\eta_{\text{ext}} = \eta_{\text{int}} \eta_{\text{out}}
\]  

(0.39)

where \( \eta_{\text{int}} \) is the internal quantum efficiency and \( \eta_{\text{out}} \) is the out-coupling efficiency of an OLED device.
Since the refractive index of ITO layer is relatively high \( n = 1.8 \sim 2.1 \), there is total internal reflection occurred at the interface of ITO and substrate \( n = 1.5 \) according to the Snell’s law. This is waveguide mode as shown in Figure 2.17. At the interface of substrate and the air, there is also total internal reflection which is called the substrate mode.[95] These total internal reflections result in that only a small fraction of light can escape from the OLED device and the out-coupling efficiency is relatively low.

The out-coupling efficiency can be calculated from refractive index as shown in Equation 2.43.

\[
\eta_{out} = \frac{1}{\xi n^2} \quad (0.40)
\]

where \( \xi \) is a constant determined by dipole alignment and the geometry of OLED device.[96] If only reflections at the interface of glass and air is considered, then only 20% of the emitted light can go out of the OLED device taking \( \xi = 2 \).[97,98]
2.6 Degradation of OLED devices

The degradation of OLED devices is the decrease of efficiencies of OLED devices during the operation. A main parameter to evaluate the degradation of an OLED is the behavior of the luminance over time under given environment and current density. This luminance versus time characteristic is called the lifetime of the OLED devices. Generally, the lifetime ($T_{1/2}$) is defined as the time when the luminance ($L$) decreases to half value of the initial luminance ($L_0$) under a constant current density as shown in Figure 2.18.[99]

![Figure 2.18 Schematic of the lifetime of an OLED device.](image)

The growth of non-emissive area in OLED device known as dark spot degradation has a great influence on the lifetime of the OLED device. Dark spots can be caused from several reasons such as large surface roughness of the ITO layer, contamination of the substrate surface and penetration of oxygen and moisture.[100,101,102]

Except dark spots degradation caused by the extrinsic factors, there are also intrinsic factors which can also influence the lifetime of OLED devices. It was reported that organic materials with high glass transition temperatures can benefit the device stability. The reason is that organic materials with high glass transition temperatures
are more stable and not easy to recrystallize under the Joule heat produced during the device operation.[103]

A wider recombination zone in the emissive layer can also lead to a longer device lifetime.[104] It was reported that three different materials with the same HOMO energy level were used to evaluate the device stability. The OLED device employing the organic compound with a higher hole mobility exhibited a wider recombination zone and a longer device lifetime.

Other intrinsic factors such as electrochemical reactions, photochemical reactions can also cause the degradation of an OLED device.[105,106]
3.1 Absorption spectra measurement

Since a charged particle (e.g., an electron) in the path of light is capable of absorbing energy from the light. Once the electron in the ground state absorbing energy from the light, it will be promoted to an unoccupied higher energy orbital and the molecule will be in an electronically excited state. A necessary condition for this process to occur is that the energy difference between the ground state and the excited state of the molecule should be exactly equal to the energy of the light. This condition can be expressed by the equation

\[ E_e - E_g = h\nu \]  

(0.41)

where \( E_e \) and \( E_g \) are the energies of the ground state and excited state, respectively; \( h \) is Planck’s constant and \( \nu \) is the frequency of the light. If this condition is not met, the absorption will not occur.

The absorption intensity of a molecule as a function of frequency (or wavelength) of the light can be represented by the electronic absorption spectrum. In the spectrum, regions where high intensity of light is absorbed are called strong absorption bands; regions where low intensity of light is absorbed are called weak absorption bands. If concentration-dependent aggregation is not observed in an absorbing species, the absorbance \( A(\lambda) \) is determined by the Beer-Lambert law.[107]

\[ A(\lambda) = \varepsilon(\lambda)cl \]  

(0.42)
where \( e(\lambda) \) is molar absorption coefficient; \( c \) is the concentration in molarity and \( l \) is the path length usually measured in centimeters.

Experimentally, absorption spectrum can be obtained using a spectrophotometer. Figure 3.1 illustrates a typical optical system of the spectrophotometer. The radiation source is a combination of a deuterium-discharge lamp and a tungsten lamp. The deuterium lamp is the light source for the ultraviolet (UV) wavelength range (~190 nm to 800 nm). The low-noise tungsten lamp is the light source for the visible and short wavelength near infrared (SWNIR) range (~370 nm to 1100 nm). The deuterium lamp and the tungsten lamp share the same axis with the source lens. The light emission passes through source lens and then forms a single, collimated beam of light. The beam first passes through the shutter/stray-light correction filter area then through the sample. Finally, the beam passes through the spectrograph lens and slit and is dispersed onto the diode array by a holographic grating. The absorption spectrum of the sample at each wavelength is acquired.[108]

In this work, HP 8453 UV-visible spectrophotometer is used to obtain the absorption spectra of the organic thin films. The sample is prepared by depositing organic layer on quartz substrate via thermal evaporation under vacuum condition.
3.2 Photoluminescence spectra measurement

When a molecule is excited by absorbing the energy of light, it can then return to the ground state with the emission of light. The spectrum of the emitted light is called photoluminescence (PL) spectrum. The equipment required for the measurement of PL spectrum and the experiment setup are discussed in this section.

3.2.1 The helium-cadmium laser

The helium-cadmium laser (He-Cd) is a typical well-developed metal vapor laser. It is a continuous wave (CW) source with ultraviolet (325 nm) and violet (442 nm) lines output. Cadmium is a metal which is solid at room temperature. It must be evaporated for lasing to occur. A reservoir containing cadmium is heated to produce the vapor in the discharged tube. The excited helium atoms will collide with cadmium atoms in their ground state and result in an energy transfer from helium atoms to cadmium
atoms. After the collision, the cadmium atoms will be ionized and excited to the higher energy level.[109] This process can be expressed as follows:

\[ \text{He}^* + \text{Cd} \rightarrow \text{He} + (\text{Cd}^+)^* + e^- \]  

(0.43)

The construction of a He-Cd laser is shown in Figure 3.2. The He-Cd laser (Kimmon IK3151R-E) emitting at 325 nm is used in this work and the specification of the laser is listed in Table 3.1.

Figure 3.2 The construction of a He-Cd laser.

Table 3.1 Specifications of the He-Cd laser (Kimmon IK3151R-E) used in this work.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Power (mW)</th>
<th>Transverse mode</th>
<th>Polarization</th>
<th>Polarization Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>325</td>
<td>15</td>
<td>TEM(_{00})</td>
<td>Linear</td>
<td>&gt;500:1</td>
</tr>
</tbody>
</table>

3.2.2 Monochromator gratings

The monochromators used in most spectroscopic research use diffraction gratings. A diffraction grating is a periodic structure that can split and disperse incident light into
individual wavelength of light travelling in different directions. The intensity maxima at angles $\theta_m$ is given by the equation 3.4

$$d (\sin \theta_m + \sin \theta_i) = m \lambda$$

(0.44)

where $\theta_i$ is the incident angle of the light; $d$ is the separation of grating elements; $m$ is an integer; $\lambda$ is the wavelength of the light.

The schematic outline of monochromator is shown in Figure 3.3. The incident light from the entrance slit is reflected by the collimating mirror. Then, the collimated light is dispersed from the grating and collected by another focusing mirror. Finally, the light is reflected onto the exit slit.

![Schematic outline of monochromator using diffraction grating.](image)

Figure 3.3 Schematic outline of monochromator using diffraction grating.

3.2.3 Photomultiplier tubes

Photomultiplier tubes (PMT) is used to detect light. The device is generally a vacuum tube consisting of a photocathode, a number of dynodes and an anode, plus a resistor
chain biased by a high voltage power supply. When a photon impacts on the photocathode, an electron is generated from it. Therefore, individual photons can be detected by PMT and each detected photon produces a current pulse. These pulses will result in an average current, which is usually the processed PMT signal.[110]

3.2.4 The lock-in amplifier

A lock-in amplifier is an amplifier which only amplifies received signals which is in phase with the reference signal, e.g. signal from a chopper. By using a pulsed laser or a chopped CW laser, the sample can be excited with pulsed light signal. The lock-in amplifier can be tuned to the same frequency received by the sample via the triggering signal provided by the pulsed laser or the chopper. In that case, noise resulting from light source intensity fluctuation and mechanical vibrations disturbing optical arrangements can be suppressed greatly.

3.2.5 Experiment setup

The experiment setup of PL spectra measurement is illustrated in Figure 3.3. The thermal-evaporated organic thin film on the quartz substrate is excited by the chopped He-Cd laser. The light emitted by the organic thin film passes through the optical lenses and then into the monochromator (SpectraPro 500i monochromator). The detected light produces a current which is proportional to the incident light intensity. The lock-in amplifier can collect the electrical signal in phase with the triggering signal from the optical chopper. Finally, the electrical signal is recorded and analyzed by a program and the PL spectrum is obtained. The diagram of the PL measurement setup is illustrated in Figure 3.4.
3.3 Time-resolved photoluminescence measurement

A molecule in its excited state can undergo a series of energy deactivation processes. The ending state of the excited molecule is determined by both possible intramolecular and inter-molecular processes. Once the surrounding environment changes, the behavior of the excited state may change as well. One of the indicators represent the changes is the time a molecule remaining in the excited state. Measurement of this decay lifetime makes it possible to have a better understanding of the molecule behavior. In this section, a method to measure the lifetime of the excited state is introduced.

Figure 3.4 The experiment setup of photoluminescence (PL) spectra measurement.
3.3.1 Nitrogen laser

The nitrogen (N$_2$) laser is another kind of gas laser. Ultra-violet light generated by pulsed N$_2$ laser at room temperature was first demonstrated in 1963.[111] This laser typically operates at 337.1 nm. The excitation of the upper laser level is from electron-impact collisions with ground-state N$_2$ molecules, so the laser can be excited by a pulsed bias.[112] In the laser, nitrogen is usually filled up with helium to quasi-atmospheric pressure. Specifications of N$_2$ laser (SRS NL 100) used in this work are listed in Table 3.2.

<table>
<thead>
<tr>
<th>Laser wavelength</th>
<th>337.1 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical bandwidth</td>
<td>0.1 nm</td>
</tr>
<tr>
<td>Pulse repetition rate</td>
<td>1-20 HZ, internal trigger; 0-20 HZ external trigger</td>
</tr>
<tr>
<td>Pulse width</td>
<td>&lt;3.5 ns (FWHM)</td>
</tr>
<tr>
<td>Pulse energy</td>
<td>170 μJ at 10 HZ</td>
</tr>
<tr>
<td>Average power</td>
<td>3.4 mW</td>
</tr>
<tr>
<td>Beam size</td>
<td>3×7 mm</td>
</tr>
</tbody>
</table>

3.3.2 Oscilloscope

Signals can be displayed graphically by using an oscilloscope. The signals are shown on the screen of oscilloscope and the magnitude of the signals plotted versus time is observed. There are two types of oscilloscope: analog oscilloscope and digital oscilloscope. A cathode ray tube was used in analog oscilloscopes. It works similarly
with the television display. By applying voltage to an electron beam, it moves across the oscilloscope screen. The voltage applied deflects the electron beam up and down proportionally. An immediate picture of the waveform is obtained.

In contrast, digital oscilloscopes use an analog-to-digital converter. Waveform are analyzed and converted into digital information. Then, this digital information reconstructs the waveform on the screen. Digital oscilloscopes make it more flexible to display, manipulate, and store the signals. The model of oscilloscope used in this work is Agilent 54830B and the specifications are listed in Table 3.3.

<table>
<thead>
<tr>
<th>Table 3.3 Specifications of oscilloscope used in this work.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bandwidth</td>
</tr>
<tr>
<td>Channels</td>
</tr>
<tr>
<td>Maximum Sample Rate</td>
</tr>
<tr>
<td>Standard Acquisition Memory</td>
</tr>
<tr>
<td>Optional Maximum Acquisition Memory</td>
</tr>
</tbody>
</table>

### 3.3.3 Experiment setup

The experiment setup of time-resolved photoluminescence measurement is illustrated in Figure 3.5. The thermal-evaporated organic thin film on the quartz substrate is excited by the pulsed N₂ laser. The light emitted by the organic thin film passes through the optical lenses and then into the monochromator (SpectraPro 500i monochromator). The oscilloscope analyzes and records the waveform at specific wavelength of detected signal with the same frequency of the laser. Different ambient
temperatures of the sample are realized using EDWARDS Cryodrive 3.0 connected with Intelligent Temperature Controller.

**Figure 3.5** The experiment setup of time-resolved photoluminescence measurement.

### 3.4 Time-delayed photoluminescence spectra measurement

The use of time-delayed PL spectra enables further understanding of the emission signature of a material. This method allows temporal evolution of the emission to be monitored. The spectra of species with short lifetime will be predominantly found at shorter times, while the spectra of longer-lived species should be found at longer times. Thus, it is possible to distinguish the spectra of species with different lifetimes. In this section, the equipment and experiment arrangement of the time-delayed PL spectra measurement is discussed.
3.4.1 Nd:Yag laser

In 1960, Theodore H. Maiman built the first laser. A pink ruby crystal was optically pumped by a helical flashlamp and the output wavelength was 694 nm. [113] Robert W. Hellwarth introduced a new method called Q-switching in 1961 and a single pulse from the ruby laser is realized. Since then, several refinements were made and more efficient neodymium doped yttrium aluminum garnet (Nd:YAG) laser replaced ruby laser. Pure yttrium aluminum garnet (Y₃Al₅O₁₂) is a colorless, optically isotropic crystal. In Nd:YAG about 1% of Y³⁺ is substituted by Nd³⁺. [114]

Nd:YAG laser is an important solid-state laser due to its high gain and good thermal and mechanical properties. It is a four-level laser system. For a three-level laser system, the pump transition extends from the ground state (E₀) to a wide absorption band (E₃). Then, a rapid transition the sharply defined level E₂ undergoes. The laser transition is the transition from E₂ to a fourth, terminal level E₁, which is situated above the ground state E₀. The efficiency of a three-level system is relatively low. In a true four-level laser system, the terminal laser level E₁ will be empty and the non-radiative radiation is small. [115]

The Nd:YAG laser (Quantel Brilliant B) used in this work is operated in 355 nm. The 355nm is generated from third harmonics generation using OPO (Optical Pumped Oscillator).

3.4.2 The boxcar averager

The boxcar average is similar to a gated photon counter, receiving a triggering signal and measure after a specific time. The signal is averaged over the gate width intervals.
The boxcar averager (SRS Model SR250) used in this work consists of a gate generator, a fast gated integrator, and exponential averaging circuitry. An adjustable delay from a few nanoseconds (ns) to 100 milliseconds (ms) and continuously adjustable gate of 2 ns to 15 ms are provided by the gate generator. This device can be used to detect weak emission with long lifetime when it is buried under a strong emission with long lifetime. The emission at specific wavelength can be monitored on an oscilloscope. Users can adjust the delay and gate width to obtain the PL spectra at the required time range. The oscilloscope display in the time-delayed PL spectra measurement is shown in Figure 3.6.

![Figure 3.6](image)

**Figure 3.6** The oscilloscope display in the time-delayed PL spectra measurement.

### 3.4.3 Experiment setup

The experiment setup of time-delayed PL spectra measurement is illustrated in Figure 3.7. The thermal-evaporated organic thin film on the quartz substrate is excited by the pulsed Nd:YAG laser. The light emitted by the organic thin film passes through the optical lenses and then into the monochromator. The emission is detected by PMT and monitored on an oscilloscope. Users can adjust the delay and gate width to obtain
the PL spectra at the required time range by using the boxcar averager. Different ambient temperatures of the sample are realized using EDWARDS Cryodrive 3.0 connected with Intelligent Temperature Controller.

![Diagram](image)

Figure 3.7 The experiment setup of time-delayed PL spectra measurement.

### 3.5 OLED device fabrication

There are several steps to fabricate an OLED device. First step is to deposit patterned anode. A suitable anode material should possess several properties, such as good electrical conductivity, good stability, proper work function and high transparency in the UV-Vis range. Commonly used transparent conducting oxides are indium tin oxide (ITO), zinc oxide (ZnO) indium zinc oxide (IZO) and aluminum doped zinc oxide (AZO), etc.[117,118] Second step is to deposit patterned organic layers in
sequence. Organic layers can be deposited using different techniques. Thermal evaporation is usually used to deposit small molecular weight material, while spin coating is commonly utilized to deposit polymer material.[119] Third step is to deposit patterned cathode. The cathode materials with low work function are selected to benefit the electron injection, such as aluminum (Al), silver (Ag) and magnesium doped silver (Mg:Ag). After the deposition, the OLED devices are transferred to a nitrogen protected glove box to encapsulate. In the following sections, the preparation and device fabrication procedures are presented in detail.

3.5.1 Materials used in this work

1,4,5,8,9,11-hexaazatriphenylenehexacarbonitrile (HAT-(CN)6) is commonly used as a buffer layer between ITO and organic hole transport layer. HAT-(CN)6 is a deep HOMO material (~9.7 eV) resulting in a large hole injection barrier at the HAT-(CN)6/ITO interface, it can reduce drive voltage, improve voltage stability, and improve power efficiency in in tandem OLED devices.[120] The HAT-(CN)6 layer was reported as a charge generation layer which excites electron from organic hole transport layer to HAT-(CN)6 and generates electron-hole pairs at the interface. The electrons then move towards the ITO anode, holes move towards the hole transport layer.[121]

1,1-bis(4-(N,N-di(p-tolyl)-amino)phenyl)cyclohexane (TAPC) is widely used as a hole transport layer in OLED devices because of its high hole mobility (~1.0×10⁻² cm²V⁻¹s⁻¹). It has a HOMO energy level of 5.5 eV and LUMO energy level of 2.0 eV.[122] Since the triplet energy level of TAPC (~2.87 eV) is very high preventing
reverse energy transfer, it can be used as hole transport layer for both fluorescent and phosphorescent dopant.[123]

Tris(4-carbazoyl-9-ylphenyl)amine (TCTA) is a hole transporting material. It has a HOMO energy level of 5.7 eV and LUMO energy level of 2.3 eV.[124] The triplet energy level of TCTA is around 2.8 eV.[125] It can function as both hole transport layer and host material for fluorescent and phosphorescent dopant.

2,4,6-tris(3′-(pyridin-3-yl)biphenyl-3-yl)-1,3,5-triazine (Tm3PyBPZ) is an electron transporting material first synthesized by Kido group.[126] The HOMO energy level, LUMO energy level and triplet energy level are 6.7 eV, 3.1 eV and 2.7 eV, respectively.

8-hydroxy-quinolinato lithium (Liq) is usually used as a buffer layer between electron transport layer and the cathode. It was reported that a thin layer of Liq can react with the underlying aluminum surface leading to a new gap state of electron transport material Alq3. This effect is believed to lower the barrier height for electron injection from the cathode to Alq3.[127] The chemical structures of the above OLED materials are illustrated in Figure 3.8.

All the materials used in this work were purchased from Lumtec Corp. and e-Ray Optoelectronics Technology Co., Ltd and were used as received.
Figure 3.8 The chemical structures of materials used in this work.

### 3.5.2 Substrate preparation

The commercial pre-coated ITO substrates were used as the anode in this work. The 100-nm-thick ITO layer was deposited by standard sputtering technique onto a 1.1 mm-thick glass substrate. The sheet resistance was about $18 \, \Omega / \text{square}$ and the ITO pattern was illustrated in Figure 3.9.
Since the contamination on substrates can severely affect the performance of the OLED devices, the ITO substrates were thoroughly cleaned before the deposition of the organic layers.\cite{128} The cleaning procedures included several sequential cleaning in an ultrasonic bath (Branson Ultrasonic Cleaner Model 1210) with substrates immersed in diluted glass detergent (TDF4), and then in distilled water (DI water) for three times to further rinse the surface of the substrate. Each cleaning step took 30 minutes. After the cleaning procedures, the substrates were put into an oven (Binder Universal Drying and Heating Oven Model ED23-UL benchtop) heated at 110 °C for at least one hour to remove the remaining moisture.

Prior to the deposition of the organic layers, the cleaned ITO substrates were transferred to a vacuum chamber for plasma treatment (Junsun Tech Co. Ltd.). The base pressure was under $3 \times 10^{-4}$ Torr and the processing power was 100 W. The substrates were treated by oxygen plasma for 5 minutes then followed by treatment tetrafluoromethane (CF4) for 7 seconds. Oxygen plasma treatment can improve the work function of ITO anode and benefit hole injection from anode to hole transport layer.\cite{129} That means the hole injection efficiency, the carrier concentration and the
mobility of an ITO anode are improved as well.[130,131] The lifetime of the OLED device also increases under constant current with oxygen plasma treatment.[132] The CF4 plasma treatment can also increase the work function and decrease the resistance of ITO anode. With a thin CFx buffer layer formed between the ITO and organic layer, the performance of the OLED devices are improved as well.[133]

3.5.3 Thin film deposition

After the cleaning procedure and the plasma treatment, the ITO substrates were loaded into a ten-source thermal evaporation system (JunSun Tech, Model OM2000R) immediately. Schematic of thermal evaporation system is shown in Figure 3.10. The materials are put into a metal boat or crucible and are heated by Joule effects. The chamber is under high vacuum condition (below 4×10⁻⁶ Torr) to reduce reactions between the vapor of the material and atmosphere. At these low pressures, the mean free path of vapor atoms is long enough, so they travel in straight lines from the evaporation source towards the substrate. The material vapor finally condenses on the cold substrate surface and forms an amorphous thin film. The coating rate of the vapor is monitored by a crystal thickness monitor. It is usually 1Å/s for depositing organic layer. For depositing aluminum, the rate is in the range of 1Å/s to 8 Å/s. Shadow masks are used to pattern the organic layers and the metal layers. Figure 3.11 shows the different pattern of shadow masks used for the deposition of organic layers and metal layer. The configuration of the OLED device after fabrication is illustrated in Figure 3.12. The size of the active area is about 0.1 cm².
Figure 3.10 Schematic of thermal evaporation system.

(a) Organic Mask  (b) Metal Mask

Figure 3.11 Pattern of the shadow masks. (a) Organic mask. (b) Metal mask.

Figure 3.12 The configuration OLED device.

Doping layer can be realized by co-evaporating two materials at the same time (Figure 3.13). Each material is monitored by one thickness monitor. A vapor phase
mixture is then formed and condensed on the surface of the substrate simultaneously. The doping concentration can be controlled by adjusting the current for each source.

Figure 3.13 Schematic diagram of co-deposition.

3.5.4 Device encapsulation

Since the organic materials are very sensitive to oxygen and moisture, the encapsulation process is necessary to avoid degradation of the OLED device. After the deposition procedures, the OLED devices were transferred into a glove box under nitrogen atmosphere. A piece of desiccant was added in the middle of a 2.2 cm×2.2 cm squared cover glass which was applied with UV curing epoxy at the four edges. The OLED device was put on the cover glass and exposed in a UV lamp for four minutes to finish the encapsulation.

3.6 OLED device characterization

Current density-voltage (J-V) measurement, Luminance-voltage (L-V) measurement and CIE color Coordinates are usually used to characterize the efficiency, brightness and chromaticity of an OLED device.
For the J-V measurement, a forward bias voltage is applied to the electrodes of the device and the corresponding current is recorded. The applied voltage starts from 0 V and increases gradually until reaching the stopping voltage. The J-V curve is obtained by plotting the voltages on the x-axis and the corresponding current density (in the unit of mA/cm²) on the y-axis. The carrier injection and carrier transportation of the device can be analyzed using the J-V curve.

The setup of L-V measurement is illustrated in Figure 3.14. A gradually increasing voltage is applied to the OLED device (Keithley 236 source measure unit). After the voltage reaches turn-on voltage of the device, the luminance is measured by a spectrometer (Spectrascan PR650) and the luminous intensity in a direction normal to the substrate surface under given voltage is obtained. This process is repeated until reaching a preset stopping voltage. The L-V curve is obtained by plotting the voltages on the x-axis and the corresponding luminous intensity on the y-axis. The L-V curve may saturate at high applied voltage.

![OLED characterization setup](image)

Figure 3.14 OLED characterization setup

The electroluminescent (EL) spectrum of the OLED device can be obtained by the spectrometer during the measurement. With the EL spectrum, the CIE coordinates
can be calculated. The CIE coordinates is a standard created in 1931 by the Commission internationale del’Eclairage. It converts all visible color space to a two-dimensional map as x and y coordinates given by the equations

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

and

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

where X, Y and Z are CIE tristimulus values. These values are calculated by integrating the spectrum \( P(\lambda) \) and experimentally determined CIE spectral stimulus functions \( x(\lambda), y(\lambda) \) and \( z(\lambda) \) over the visible range.

\[
X = \sum_{\lambda=380 \text{ nm}}^{780} x(\lambda) P(\lambda) \Delta \lambda
\]

\[
Y = \sum_{\lambda=380 \text{ nm}}^{780} y(\lambda) P(\lambda) \Delta \lambda
\]

and

\[
Z = \sum_{\lambda=380 \text{ nm}}^{780} z(\lambda) P(\lambda) \Delta \lambda
\]

The calculated CIE coordinates can be shown in the 1931 CIE chromaticity diagram (Figure 3.15). The monochromatic light on specific wavelength is shown by the
points on the perimeter of the figure. The point with the coordinates (0.33, 0.33) represents white light.

Figure 3.15 The 1931 CIE chromaticity diagram.
Chapter 4  Properties of intermolecular exciplex

TCTA:Tm3PyBPZ

In this chapter, we demonstrated the intermolecular exciplex formed between electron donor TCTA and electron accepter Tm3PyBPZ and studied the optical and properties of this exciplex, as well as the atomic force microscopy image of the exciplex.

4.1 Optical Properties of TCTA:Tm3PyBPZ

In this section, we studied the absorption and PL spectra of the neat TCTA, neat Tm3PyBPZ films and the exciplex. The time-resolved PL characteristics of the exciplex at peak wavelength were studied at different temperatures. The time-delayed PL spectra of the exciplex at specific time range were examined. Since the triplet excitons are very sensitive to oxygen, we also studied the PL spectra of the exciplex in the solution with or without oxygen.

4.1.1 Absorption and PL spectra

Firstly, we measured the absorption and PL spectra of the organic thin films. Samples of 40-nm-thick organic layer were fabricated by thermally evaporated on quartz substrates. We prepared three samples which were neat TCTA, neat Tm3PyBPZ and blended TCTA: Tm3PyBPZ (1:1) organic films. The experimental results are shown in Figure 4.1. As shown in Figure 4.1a, TCTA, Tm3PyBPZ and TCTA: Tm3PyBPZ exhibit absorption peaks at 237 nm, 258 nm and 247 nm, respectively. There is no new absorption feature observed in TCTA:Tm3PyBPZ compared with neat TCTA and Tm3PyBPZ, indicating that no ground-state charge transfer complex was formed between TCTA and Tm3PyBPZ.
As shown in Figure 4.1b, the PL peak wavelengths of TCTA, Tm3PyBPZ and TCTA:Tm3PyBPZ are located at 388 nm, 413 nm and 514 nm, respectively. The PL spectrum of TCTA:Tm3PyBPZ is significantly redshifted compared to the neat TCTA and Tm3PyBPZ. The observation of this broad and structureless emission, which is also redshifted compared to the emissions of the individual donor and acceptor molecules indicates that there is exciplex formed between TCTA and Tm3PyBPZ molecules.[134] The energy of the emission maximum in exciplex is calculated to be about 2.4 eV, which is corresponding to the energy difference between the HOMO energy level of TCTA and the LUMO energy level Tm3PyBPZ.

Figure 4.1 (a) The absorption spectra of TCTA, Tm3PyBPZ and TCTA: Tm3PyBPZ (1:1) at room temperature. (b) The PL spectra of TCTA, Tm3PyBPZ and TCTA: Tm3PyBPZ (1:1) at room temperature.

4.1.2 Time-resolved PL characteristics

In order to investigate the existence of TADF process in the exciplex, time-resolved PL characteristics of thermally evaporated 40-nm-thick blended TCTA: Tm3PyBPZ (1:1) organic layer on quartz substrates were measured at different ambient
temperatures. The time-resolved PL characteristics were recorded at the feature peak of TCTA:Tm3PyBPZ (~514 nm), as shown in Figure 4.2.

If a sample is excited by a very short pulsed laser, the photoluminescence intensity of the sample decreases exponentially with time, which can be expressed by:

\[ I = I_0 e^{-\frac{t}{\tau_0}} \]  

(0.50)

where \( I_0 \) and \( I \) are the intensities of emitted radiation immediately after excitation and at a later time \( t \), respectively. \( \tau_0 \) is the lifetime of the excited state.[135] The rate constant of the process \( k_0 \) is calculated by taking the reciprocal of \( \tau_0 \):

\[ k_0 = \frac{1}{\tau_0} \]  

(0.51)

If several emission processes with different lifetimes are involved in the relaxation process from singlet excited state to singlet ground state, the photoluminescence intensity may exhibit multi-exponential decay characteristic. In our work, the time-resolved PL characteristics of TCTA:Tm3PyBPZ shown in Figure 4.2 was well analyzed using bi-exponential decay according to Equation 4.3.

\[ I = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} \]  

(0.52)

Here, \( I \) is the photoluminescence intensity, \( A_1 \) and \( A_2 \) are the quantities of each emission process, and \( \tau_1 \) and \( \tau_2 \) are the lifetimes of the corresponding emission process. The derived parameters, which are listed in Table 4.1, show that there are two emission components with different lifetimes. One is prompt component with the
lifetime around nanosecond order; the other is delayed component with the lifetime around microsecond order.

Figure 4.2 The time-resolved PL of TCTA:Tm3PyBPZ (1:1) thin film at different ambient temperatures.

Table 4.1 Summary of $A_1$, $A_2$, $\tau_1$ and $\tau_2$ derived from the time-resolved PL of TCTA:Tm3PyBPZ (1:1) film at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\tau_1$ (ns)</th>
<th>$A_1$</th>
<th>$\tau_2$ (µs)</th>
<th>$A_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>48.8</td>
<td>0.78</td>
<td>2.9</td>
<td>0.08</td>
</tr>
<tr>
<td>80</td>
<td>78.4</td>
<td>0.78</td>
<td>4.6</td>
<td>0.12</td>
</tr>
<tr>
<td>150</td>
<td>73.8</td>
<td>0.73</td>
<td>3.8</td>
<td>0.16</td>
</tr>
<tr>
<td>300</td>
<td>53.7</td>
<td>0.69</td>
<td>2.3</td>
<td>0.23</td>
</tr>
</tbody>
</table>

The intensity ratios of the prompt ($r_1$) and delayed ($r_2$) components are determined by emission lifetimes ($\tau_1$ and $\tau_2$) and fitting parameters ($A_1$ and $A_2$) using Equation 4.4 and Equation 4.5, and the derived values are shown in Table 4.2.[136]
Table 4.2 The intensity ratios of the prompt component \( r_1 \) and delayed component \( r_2 \).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( r_1 ) (%)</th>
<th>( r_2 ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>13.3</td>
<td>86.7</td>
</tr>
<tr>
<td>80</td>
<td>9.7</td>
<td>90.3</td>
</tr>
<tr>
<td>150</td>
<td>8.4</td>
<td>91.6</td>
</tr>
<tr>
<td>300</td>
<td>6.6</td>
<td>93.4</td>
</tr>
</tbody>
</table>

From Table 4.2, the ratio of the prompt component increased from 6.6 % to 13.3 % with decreasing temperature from 300 K to 12 K, while the ratio of delayed component was reduced from 93.4 % to 86.7 %. Since the radiative transition from \( S_1 \) to \( S_0 \) is in competition with other non-radiative losses which may result from intramolecular and external losses related to the ambient temperature, the suppression of non-radiative losses at low temperature could result in the increase in prompt component.[137,138] On the other hand, the RISC process from \( T_1 \) to \( S_1 \) is thermally activated, so the delayed component was suppressed at low temperature.

We also studied the time-resolved PL characteristics of neat TCTA and neat Tm3PyBPZ at their emission peak wavelengths at room temperature and the results are shown in Figure 4.3. The time-resolved PL of neat TCTA exhibits mono-exponential decay with the lifetime of 8.5 ns, whereas the time-resolved PL of neat Tm3PyBPZ exhibits bi-exponential decay with the lifetimes of 7 ns and 70 ns.
time-resolved PL of these two materials are compared with that of TCTA:Tm3PyBPZ, we can realize that both neat TCTA and neat Tm3PyBPZ exhibits much shorter lifetimes than the exciplex. The long-lived and temperature-dependent delayed component exhibiting in the exciplex formed between TCTA and Tm3PyBPZ should be thermally activated delayed fluorescence.

The rate constant of reverse intersystem crossing $k_{RISC}$ from triplet excited state to singlet excited state is very crucial for TADF process and it can be given by the following equation:

$$k_{RISC} = \frac{k_p k_d \Phi_d}{k_{ISC} \Phi_p}$$  \hspace{1cm} (0.53)

Here, the rate of prompt component $k_p$ and delayed component $k_d$ can be calculated according to Equation 4.2 and shown in Table 4.3; $\Phi_p$ and $\Phi_d$ are the photoluminescence quantum efficiencies of the prompt and delayed components, which are determined from the absolute PL efficiency ($\Phi_{PL}$) which is measured by an integrated sphere photoluminescence measurement system and the intensity ratios of the prompt ($r_1$) and delayed ($r_2$) components as shown in Equation 4.7 and Equation 4.8.[139]

$$\Phi_p = r_1 \Phi_{PL}$$  \hspace{1cm} (0.53)

$$\Phi_d = r_2 \Phi_{PL}$$  \hspace{1cm} (0.53)
Figure 4.3 The time-resolved PL of TCTA, Tm3PyBPZ and TCTA: Tm3PyBPZ (1:1) films at room temperature.

According to the energy gap law discussed in section 2.1.6, $k_{RISC}$ is proportional to $\exp(-\Delta E_{ST}/k_BT)$. Therefore, the $\Delta E_{ST}$ can be estimated by using the calculated $k_{RISC}$ from Equation 4.6 at different temperatures and with the assumption that $k_{ISC}$ is independent with temperature.\[140\] $\Delta E_{ST}$ can also be estimated experimentally using the fluorescent spectrum and phosphorescent spectrum as shown in Equation 4.9.

$$\Delta E_{ST} = E_S - E_T \quad (0.54)$$

Here, $E_S$ is the energy of the fluorescent emission maximum; $E_T$ is the energy of the phosphorescent emission maximum.

Since the HOMO and the LUMO in intermolecular exciplex are mainly located on the electron donor and electron acceptor molecules, respectively, $\Delta E_{ST}$ which is proportional to the overlap between HOMO and LUMO is smaller in an intermolecular exciplex than in an intramolecular exciplex. As a result, the triplet
energy levels are very close to the singlet energy levels in an intermolecular exciplex. It was reported that the $\Delta E_{ST}$ in an intermolecular exciplex based on m-MTDATA:Bphen was almost zero (~1.12 meV).[24]

Table 4.3 Summary of $k_p$ and $k_d$ at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$k_p$ ($s^{-1}$)</th>
<th>$k_d$ ($s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>2.05×10&lt;sup&gt;7&lt;/sup&gt;</td>
<td>3.45×10&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
<tr>
<td>80</td>
<td>1.28×10&lt;sup&gt;7&lt;/sup&gt;</td>
<td>2.17×10&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
<tr>
<td>150</td>
<td>1.36×10&lt;sup&gt;7&lt;/sup&gt;</td>
<td>2.63×10&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
<tr>
<td>300</td>
<td>1.86×10&lt;sup&gt;7&lt;/sup&gt;</td>
<td>4.35×10&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

For fluorescent materials excited by light absorption, molecules are excited to singlet states due to the conservation of electron spin. Therefore, triplet excitons can only be generated from singlet excitons via intersystem crossing or fission of singlet excitons.[141] The rate of intersystem crossing depends on the strength of the spin-orbit coupling and the vibrational overlap between the wavefunctions of the $S_1$ and triplet state involved. The quantum yield of intersystem crossing ($\Phi_{ISC}$) ranges from less than 1 % to nearly 100 % in different organic materials. It was reported that the delayed fluorescence in the exciplex formed between m-MTDATA and 3TPYMB was significantly enhanced under electrical excitation due to the high triplet-exciton production efficiency (~75 %).[139] Therefore, we assume that the number of triplet excitons contributed to the delayed fluorescence under optical excitation is much fewer than those contributed to the delayed fluorescence under electrical excitation. As a consequence, the contribution of delayed component to the total fluorescent quantum yield should be more significant in electrically excited OLED device. To confirm the contribution of delayed component under electrical excitation, the time
resolved EL characteristic of the OLED device should be performed with a voltage excitation pulse.[142]

4.1.3 Time-delayed PL spectra

In addition to the time-resolved PL characteristics showing the PL intensity change at specific wavelength after the excitation, we also studied the time-delayed PL spectra of TCTA: Tm3PyBPZ taken in consecutive time slots spanning its entire lifetime to see whether there is any spectral shift in the long lifetime of the exciplex. The measurement method of time-delayed PL spectra was discussed in section 3.4. Sample was thermally evaporated 40-nm-thick blended TCTA: Tm3PyBPZ (1:1) organic layer on quartz substrates. The results shown in Figure 4.4 were recorded in different time ranges in four different ambient temperatures.

As the increase of delayed time, the redshift of emission was observed at all the temperatures. At 300 K, the emission peak shifted from 492 nm to 525 nm as the delayed time increasing from 20 ns to 5 \( \mu \)s. Generally, the excited states in an exciplex are considered to be with variable degrees of charge transfer.[143] The higher the extent of the charge transfer, the lower the coupling between the excited state and ground state. This dispersion in charge transfer will result in redshift of emission as the charge transfer character increases, and the concomitant reduced coupling will decrease the radiative rate constant of the exciplex. As a result, the emission with a longer lifetime is more redshifted. This phenomenon was also found in other exciplex based on m-MTDADA: PBD.[144]
Another time-delayed PL spectra of TCTA:Tm3PyBPZ with more detailed gate widths were measured at room temperature and shown in Figure 4.5. An emission around 380 nm was observed within 250 ns, which should originate from the excited TCTA and Tm3PyBPZ molecules rather than the exciplex (Figure 4.1a). This emission was no longer observed after 250 ns, which was consistent with the lifetime characteristics of neat TCTA and Tm3PyBPZ films shown in Figure 4.3. The energy of emission maximum shown in Figure 4.5 is plotted against the median of the time range and shown in Figure 4.6. After the excitation, the energy of emission maximum dropped very fast from 2.53 eV, whereas it remained around 2.38 eV after 175 ns.
Figure 4.5 The time-delayed PL spectra of TCTA:Tm3PyBPZ (1:1) film under 355 nm excitation at room temperature. (a) 0-100 ns. (b) 100ns-4μs.

Figure 4.6 The energy of peak wavelength versus the median of the time range.

4.1.4 The PL spectra of TCTA:Tm3PyBPZ in oxygen-free solvents

The TADF process is very sensitive to oxygen since the long-lived triplet excitons involved in TADF are easily quenched by ground state triplet oxygen molecules, resulting in luminance quenching and singlet oxygen.[145] Therefore, the PL spectra
of TCTA:Tm3PyBPZ measured with or without oxygen can show if there are triplet
excitons involved in the luminance process. In air-saturated organic solvents, oxygen
concentration is limited to \(2.5\times10^{-4}\) mol/L.\[146]\ Bubbling of inert gas can remove the
dissolved oxygen from solution.

Figure 4.7 shows the PL spectra of TCTA, Tm3PyBPZ and TCTA:Tm3PyBPZ in
chlorobenzene and tetrahydrofuran (THF) without nitrogen bubbling. The
concentration of each solution was around \(10^{-3}\) mol/L. The emission of
TCTA:Tm3PyBPZ solution was mostly from the emission of TCTA and almost no
emission from Tm3PyBPZ was observed. Two reasons could be responsible for that:
one is that the absorption of Tm3PyBPZ at 325 nm is much lower than TCTA which
means more TCTA molecules are excited, the other one is the lifetime of TCTA is
much shorter than Tm3PyBPZ which means the luminance process is more
competitive than other quenching processes happened in the solution. There was also
no emission of the exciplex observed around 514 nm in the solution, which could be
totally quenched by oxygen.

The PL spectra of TCTA:Tm3PyBPZ dissolved in chlorobenzene and tetrahydrofuran
(THF) without oxygen were also measured. The oxygen-free solutions were obtained
by two-hour nitrogen bubbling. As shown in Figure 4.8a, we can observe an emission
around 550 nm besides the emission of TCTA in the oxygen-free solutions, which
should be from the exciplex. Normalized spectra of the exciplex emission were
shown in Figure 4.8b. The peak wavelengths of the exciplex in oxygen-free
chlorobenzene and THF were around 553 nm and 558 nm, respectively, which
redshifted about 40 nm compared to the emission maximum in the solid state. This
should arise from the change of dipole moment of exciplex in the ground and excited states caused by a polar solvent.[147]

The PL spectra of TCTA:Tm3PyBPZ in solution state before and after nitrogen bubbling further confirms the participation of triplet excitons in the emission of the exciplex.

Figure 4.7 The PL spectra of TCTA, Tm3PyBPZ and TCTA:Tm3PyBPZ in solvents without nitrogen bubbling. (a) in chlorobenzene, (b) in THF.

Figure 4.8 (a) The PL spectra of TCTA:Tm3PyBPZ in oxygen-free chlorobenzene and THF. (b) The normalized exciplex emission in oxygen-free chlorobenzene and THF.
4.2 Atomic force microscopy image of TCTA: Tm3PyBPZ

Since exciplex is formed at the heterojunction with charge-transfer character, C3-symmetry feature of TCTA and Tm3PyBPZ can provide better conformational compatibility for the exciplex formation.[148] We studied the topography of the surface of TCTA:Tm3PyBPZ using atomic force microscopy image (AFM) by scanning over a desired region with the cantilever. Sample was prepared by thermally evaporated 30-nm-thick TCTA:Tm3PyBPZ (1:1) layer onto clean silicon wafer substrate. The AFM image was shown in Figure 4.9. The root mean square (RMS) surface roughness value of the film is only 0.32 nm. This low RMS value is indicative of the highly smooth and continuous nature of the composite film.

Figure 4.9 AFM image of 30-nm thick mixed TCTA:Tm3PyBPZ (1:1) film.
Chapter 5  OLED devices based on TADF process

After the investigation of the optical properties of the exciplex formed between TCTA and Tm3PyBPZ, OLED devices were fabricated to investigate the performance of the exciplex under electrical excitation. Since the emission of the exciplex is located at 514 nm (~ 2.4 eV), it can be used as the emissive layer itself or functioned as the host materials for some green or red fluorescent emitters.

5.1 TCTA:Tm3PyBPZ as the emissive layer

To investigate the performances of OLED devices employing TCTA:Tm3PyBPZ as the emissive layer, three devices with different doping ratio of TCTA:Tm3PyBPZ were fabricated. The device structures are shown in Figure 5.1 and the materials used were already discussed in section 3.5.1. Since hole mobilities, electron mobilities and energy level alignment of TCTA and Tm3PyBPZ are different, changing the doping ratio of the emissive layer will alter the carrier injection, carrier transport and carrier balance in the OLED devices.

<table>
<thead>
<tr>
<th>Device A</th>
<th>Device B</th>
<th>Device C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (100 nm)</td>
<td>Al (100 nm)</td>
<td>Al (100 nm)</td>
</tr>
<tr>
<td>Liq (2 nm)</td>
<td>Liq (2 nm)</td>
<td>Liq (2 nm)</td>
</tr>
<tr>
<td>Tm3PyBPZ (40 nm)</td>
<td>Tm3PyBPZ (40 nm)</td>
<td>Tm3PyBPZ (40 nm)</td>
</tr>
<tr>
<td>TCTA:Tm3PyBPZ (3:7, 30 nm)</td>
<td>TCTA:Tm3PyBPZ (1:1, 30 nm)</td>
<td>TCTA:Tm3PyBPZ (7:3, 30 nm)</td>
</tr>
<tr>
<td>TAPC (55 nm)</td>
<td>TAPC (55 nm)</td>
<td>TAPC (55 nm)</td>
</tr>
<tr>
<td>Hat(CN)6 (5 nm)</td>
<td>Hat(CN)6 (5 nm)</td>
<td>Hat(CN)6 (5 nm)</td>
</tr>
<tr>
<td>ITO glass substrate</td>
<td>ITO glass substrate</td>
<td>ITO glass substrate</td>
</tr>
</tbody>
</table>

Figure 5.1 Device structures of OLED devices employing TCTA:Tm3PyBPZ as the emissive layer.
The energy level diagram was shown in Figure 5.2. The deep HOMO material Hat(CN)$_6$ functioned as a charge generating layer and benefited the current density-voltage characteristics of the OLED device. Hole-electron pairs are generated at the interface of Hat(CN)$_6$/TAPC, then holes move towards the cathode and excitons are formed in the emissive layer. Finally, the radiative transition occurs and the OLED devices emit green light. The deep HOMO of Tm3PyBPZ can effectively block the holes and confine them in the emissive layer.

![Energy level diagram](image)

Figure 5.2 Energy level diagram of OLED devices employing TCTA:Tm3PyBPZ as the emissive layer.

The OLED devices were characterized after fabrication and the results were plotted in Figure 5.3. Figure 5.3a shows current density versus voltage (J-V) characteristics. All the devices were turned on around a rather low voltage (~2.3 V) which indicating a well carrier injection. With the increase of the TCTA doping concentration in the emissive layer, the applied driving voltage also increased. The current densities of Device A, B and C at 10 V were 304.5, 253.8, and 203.6 mA/cm$^2$, respectively. This result shows that the high concentration of Tm3PyBPZ in the emissive layer benefited the carrier transport in the OLED device leading to a good J-V characteristic.
Although Device A showed the best J-V characteristic among the three devices, Device B showed the highest EQE as shown in Figure 5.3b. The reason may be due to that the emissive layer with doping ratio 1:1 enhanced the exciplex formation, so the TADF process contributed more to the luminance than in the other two devices. The maximum EQE of Device B is 13.1 %, which is almost three times higher than the conventional fluorescent emitters.

Device B with doping ratio 1:1 also showed the highest current efficiencies and power efficiencies as shown in Figure 5.3c and Figure 5.3d. The maximum current efficiency was 44.2 cd/A, which was obtained at 2.6 V with the current density of 0.06 mA/cm². The maximum power efficiency was 54.5 lm/W, which was obtained at 2.4 V with the current density of 0.01 mA/cm². All the three devices exhibited efficiency roll-off under high current density, which originated from triplet-triplet annihilation and singlet-polaron annihilation.[149,150] The higher the current density is, the higher the exciton densities is-leading to a severer quenching in the OLED device. However, introducing host matrix with random orientation may suppress the efficiency roll-off in the TADF OLED devices.[151]

Luminance was plotted as a function of voltage as shown in Figure 5.3e. Device B showed a clear improvement in luminance compared to the other two devices. The maximum luminance was 12800 cd/m², which was obtained at 9 V with the current density of 188.4 mA/cm². The luminance curve saturated at high voltage, which was resulted from current saturation and efficiency roll-off.[152]
Figure 5.3 Device performances of OLED devices employing TCTA:Tm3PyBPZ as the emissive layer. (a) current density versus voltage characteristics. (b) EQE versus current density. (c) CE versus current density. (d) PE versus current density. (e) luminance versus voltage. (f) EL spectra of the OLED devices.
The EL spectra of the three devices were shown in Figure 5.3f. The peak wavelengths of the three devices were located at 540 nm, 528 nm and 528 nm, respectively. The EL spectrum shift could be due to the shift of the recombination zone in the three devices, which resulted from the different carrier balance and carrier transport in the emissive layer. The EL spectrum was also redshifted compared with the PL spectrum of TCTA:Tm3PyBPZ (~514 nm) which could attribute to the weak microcavity effect of the OLED device.[153]

The device performances of OLED devices employing TCTA:Tm3PyBPZ as the emissive layer are summarized in Table 5.1. The CIE values of the three devices at 1 mA/cm² were (0.36, 0.57), (0.33, 0.58) and (0.32, 0.57), respectively.

Table 5.1 Luminance (L), current efficiencies (CE), power efficiencies (PE) and external quantum efficiencies (EQE) of the OLED devices employing TCTA:Tm3PyBPZ as the emissive layer.

<table>
<thead>
<tr>
<th>Device</th>
<th>Maximum at 100 cd/m²</th>
<th>at 100 cd/m²</th>
<th>at 1000 cd/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L</td>
<td>CE cd/A</td>
<td>PE lm/W</td>
</tr>
<tr>
<td>A</td>
<td>7606</td>
<td>30.6</td>
<td>40.1</td>
</tr>
<tr>
<td>B</td>
<td>12800</td>
<td>44.2</td>
<td>54.5</td>
</tr>
<tr>
<td>C</td>
<td>10420</td>
<td>28.7</td>
<td>32.2</td>
</tr>
</tbody>
</table>

According to Equation 2.42, EQE can be further expressed by the following equation:

$$\eta_{ext} = \eta_{int}\eta_{out} = \gamma \eta_{r} \Phi_{PL}\eta_{out}$$  \hspace{1cm} (0.55)

where, \(\gamma\) is the recombination efficiency of the injected holes and electrons, \(\eta_{r}\) is the ratio of excitons capable of radiative transition (\(\eta_{r}=0.25\) for conventional
fluorescent emitters), $\Phi_{PL}$ is the photoluminance quantum yield $\eta_{out}$ is the out-coupling efficiency of an OLED device.

Since the maximum EQE of Device B was 13.1 %, $\Phi_{PL}$ is calculated to be 0.8 with the assumption of $\eta_r=0.8$ when $\gamma=1.0$, and $\eta_{out}=0.2$.

5.2 TCTA:Tm3PyBPZ as the host material for fluorescent emitters

In addition to using the exciplex formed between TCTA and Tm3PyBPZ directly as the emissive layer, it can be also used as host material for some green and red fluorescent emitters. Since materials exhibiting TADF process can achieve high internal quantum efficiency, the performance of conventional fluorescent OLED devices can be greatly improved by introducing certain TADF material as host material. In this section, OLED devices using TCTA:Tm3PyBPZ as host for c545t and rubrene are discussed.

5.2.1 Green fluorescent OLED devices based on c545t

2,3,6,7-tetrahydro-1,1,7,7,-tetramethyl-1H,5H,11H-10-(2-benzothiazolyl)quinolizinono-9,9a,1igh coumarin (c545t) is a well-known green fluorescent dopant with its chemical structure illustrated in Figure 5.4. It is synthesized from coumarin 6 which is a common organic laser dye.[154] By using tris(8-hydroxyquinolinolato)aluminum (Alq₃) as the host material, the current efficiency of OLED device employing c545t is 12.8 cd/A.[155] With optimized carrier balance, the EQE of OLED device can be further improved to be 7.5 %.[156] Here, we investigate the performances of OLED devices employing c545t as the dopant and TCTA:Tm3PyBPZ as the host material.
Figure 5.4 Chemical structure of c545t.

When a TADF material is used as the host in the OLED device, the electrically excited triplet excitons of the host are converted to singlet excitons via reverse intersystem crossing. The energy of singlet excitons on the host then are transferred to the dopant through Förster energy transfer. An important criterion for Förster energy transfer to occur is that the fluorescence emission spectrum of the host molecule must overlap the absorption of the dopant molecule. Figure 5.5 shows an appreciable spectral overlap between the emission spectrum of TCTA:Tm3PyBPZ and absorption spectrum of c545t. The Förster energy transfer between TCTA:Tm3PyBPZ and c545t could be efficient.

Two OLED devices were fabricated with the structures shown in Figure 5.6. The doping concentrations of c545t in Device A and Device B were 0.5 % and 1 %, respectively. The ratio of TCTA:Tm3PyBPZ was 1:1 in both devices. Changing the doping concentration in the host-guest system can also influence the efficiency of Förster energy transfer by changing the distance between host and guest molecules. The energy level diagram of the OLED device is shown in Figure 5.7. The HOMO and LUMO levels of c545t are located inside the energy gap of TCTA and Tm3PyBPZ.
Figure 5.5 Spectral overlap between PL spectrum of TCTA:Tm3PyBPZ and absorption spectrum of c545t.

Figure 5.6 Device structures of OLED devices employing TCTA:Tm3PyBPZ as the host for c545t.

<table>
<thead>
<tr>
<th>Device A</th>
<th>Device B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (100 nm)</td>
<td>Al (100 nm)</td>
</tr>
<tr>
<td>Liq (2 nm)</td>
<td>Liq (2 nm)</td>
</tr>
<tr>
<td>Tm3PyBPZ (50 nm)</td>
<td>Tm3PyBPZ (50 nm)</td>
</tr>
<tr>
<td>TCTA:Tm3PyBPZ:c545t (0.5 %, 10 nm)</td>
<td>TCTA:Tm3PyBPZ:c545t (1 %, 10 nm)</td>
</tr>
<tr>
<td>TAPC (65 nm)</td>
<td>TAPC (65 nm)</td>
</tr>
<tr>
<td>Hat(CN)6 (5 nm)</td>
<td>Hat(CN)6 (5 nm)</td>
</tr>
<tr>
<td>ITO glass substrate</td>
<td>ITO glass substrate</td>
</tr>
</tbody>
</table>

The OLED devices were characterized after fabrication and the result was plotted in Figure 5.8. Figure 5.8a shows current density versus voltage (J-V) characteristics. Both the devices were turned on around a rather low voltage (~2.4 V) which indicating a well carrier injection. Device B with 1 % doping concentration shows
better J-V characteristics than Device A. The current densities of the devices at 10 V were 300 and 352 mA/cm$^2$, respectively. This result shows that the c545t concentration can affect the carrier transport in the emissive layer by changing the carrier mobility in the emissive layer.\cite{157} The increase of the c545t doping concentration from 0.5 % to 1 % assisted the carrier transport in the emissive layer and resulted in a lower applied driving voltage at certain current density.

Figure 5.7 Energy level diagram of OLED devices employing TCTA:Tm3PyBPZ as the host for c545t.

EQE versus current density is shown in Figure 5.8b. Device A showed higher EQE when the current density was below 1 mA/cm$^2$. However, when the current density was higher than 1 mA/cm$^2$, Device B showed a better EQE. The maximum EQE of the two devices were 11.9 % and 10.4 %, respectively. The performance is significantly improved than the OLED devices employing normal fluorescent host.

Current efficiencies and power efficiencies are plotted and shown in Figure 5.8c and Figure 5.8d. The maximum current efficiency of Device A was 39.6 cd/A, which was obtained at 2.4 V with the current density of 0.04 mA/cm$^2$. The maximum power
efficiency of Device A was 51.9 lm/W obtained at 2.4 V. Both the devices exhibited efficiency roll-off under high current density, which also originated from triplet-triplet annihilation and singlet-polaron annihilation under high exciton density.

Luminance was plotted as a function of voltage as shown in Figure 5.8e. Device B showed a clear improvement in luminance compared to Device A. The maximum luminance of Device B was 20640 cd/m², which was obtained at 10 V with the current density of 352 mA/cm². The better luminance of Device B should be due to a better J-V characteristic.

The EL spectra are shown in Figure 5.8f. The peak wavelengths of both the devices were located at 508 nm. The different intensities of shoulder peak around 536 nm could originate from the recombination zone shift and the weak microcavity effect in the OLED device.

The device performances of OLED devices employing TCTA:Tm3PyBPZ as host for c545t are summarized in Table 5.2. The CIE coordinates around 1 mA/cm² of the two devices were (0.25, 0.62) and (0.24, 0.64), respectively.

Table 5.2 Luminance (L), current efficiencies (CE), power efficiencies (PE) and external quantum efficiencies (EQE) of the OLED devices employing TCTA:Tm3PyBPZ as host for c545t.

<table>
<thead>
<tr>
<th>Device</th>
<th>Maximum L (cd/m²)</th>
<th>Maximum CE (cd/A)</th>
<th>Maximum PE (lm/W)</th>
<th>Maximum EQE (%)</th>
<th>at 100 cd/m²</th>
<th>at 1000 cd/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L</td>
<td>CE</td>
<td>PE</td>
<td>EQE</td>
<td>CE</td>
<td>PE</td>
</tr>
<tr>
<td>A</td>
<td>15870</td>
<td>39.6</td>
<td>51.9</td>
<td>11.9</td>
<td>35.4</td>
<td>42.8</td>
</tr>
<tr>
<td>B</td>
<td>20640</td>
<td>34.6</td>
<td>45.3</td>
<td>10.4</td>
<td>30.8</td>
<td>37.3</td>
</tr>
</tbody>
</table>
Figure 5.8 Device performances of OLED devices employing TCTA:Tm3PyBPZ as host for c545t. (a) current density versus voltage characteristics. (b) EQE versus current density. (c) CE versus current density. (d) PE versus current density. (e) luminance versus voltage. (f) EL spectra of the OLED devices.
5.2.2 Yellow fluorescent OLED devices based on rubrene

In this section, OLED devices employing TCTA:Tm3PyBPZ as host for 5,6,11,12-tetraphenyltetracene (rubrene) are investigated. Rubrene is a yellow fluorescent dopant material and its structure is shown in Figure 5.9. It was reported that rubrene can be used as an assistant dopant for some red dopants, such as DCJTB and RC545T, since this narrow band gap material (~2.2 eV) can assist the energy transfer from the host to the red dopant and improve the optical and electrical properties of the OLED devices.\[158\] In this work, it is used as yellow dopant because its absorption spectrum is perfectly overlapped with the PL spectrum of TCTA:Tm3PyBPZ as shown in Figure 5.10. The absorption maximum of rubrene is located at 533 nm.

Two OLED devices were fabricated with the structures shown in Figure 5.11. The doping concentrations of rubrene in Device A and Device B were 0.5 % and 1 %, respectively. The ratio of TCTA:Tm3PyBPZ was 1:1 in both devices and the energy level diagram is shown in Figure 5.12.

![Chemical structure of rubrene](image)

Figure 5.9 Chemical structure of rubrene.

The OLED devices were characterized after fabrication and the result was plotted in Figure 5.13. Figure 5.13a shows current density versus voltage (J-V) characteristics. Both the devices were turned on around a rather low voltage (~2.4 V) which
indicating a well carrier injection. Device A with 0.5 % doping concentration shows better J-V characteristics than Device B. The current densities of the devices at 10 V were 303 and 247 mA/cm$^2$, respectively. This result shows that the rubrene molecules can trap charge carriers and alter the J-V characteristics. It was reported that a large increase in driving voltages was observed with the increase of rubrene doping concentration from 0.5 % to 5 %.[159]

Figure 5.10 Spectral overlap between PL spectrum of TCTA:Tm3PyBPZ and absorption spectrum of rubrene.

<table>
<thead>
<tr>
<th>Device A</th>
<th>Device B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (100 nm)</td>
<td>Al (100 nm)</td>
</tr>
<tr>
<td>Liq (2 nm)</td>
<td>Liq (2 nm)</td>
</tr>
<tr>
<td>Tm3PyBPZ (50 nm)</td>
<td>Tm3PyBPZ (50 nm)</td>
</tr>
<tr>
<td>TCTA:Tm3PyBPZ:rubrene (0.5 %, 10 nm)</td>
<td>TCTA:Tm3PyBPZ:rubrene (1 %, 10 nm)</td>
</tr>
<tr>
<td>TAPC (65 nm)</td>
<td>TAPC (65 nm)</td>
</tr>
<tr>
<td>Hat(CN)6 (5 nm)</td>
<td>Hat(CN)6 (5 nm)</td>
</tr>
<tr>
<td>ITO glass substrate</td>
<td>ITO glass substrate</td>
</tr>
</tbody>
</table>

Figure 5.11 Device structures of OLED devices employing TCTA:Tm3PyBPZ as the host for rubrene.
Figure 5.12 Energy level diagram of OLED devices employing TCTA:Tm3PyBPZ as the host for rubrene.

Although higher EQE, power efficiency and current efficiency were observed in Device A, it should be noted that there was the emission from the host in the EL spectra as shown in Figure 5.13f. With the increase of rubrene doping concentration from 0.5 % to 1 %, the shoulder peak around 500 nm decreased. In fact, this shoulder peak was from the emission of TCTA:Tm3PyBPZ due to the incomplete energy transfer from the host to the dopant under low doping concentration. The EL peak wavelength of rubrene was located around 556 nm and almost no PL shift was observed in the two devices.

EQE versus current density is shown in Figure 5.13b. The EQE of the two devices at 1 mA/cm² were 10.2 % and 9.1 %, respectively. The maximum EQE of Device B was 10.0 % observed at 2.6 V. The performance was greatly improved by using a TADF material as a host material.

Current efficiencies and power efficiencies were plotted and shown in Figure 5.13c and Figure 5.13d. The maximum current efficiency of Device B was 34.5 cd/A,
which was obtained at 2.6 V with the current density of 0.2 mA/cm$^2$. The maximum power efficiency of Device B was 43.6 lm/W obtained at 2.4 V with the current density of 0.03 mA/cm$^2$. Both the devices exhibited efficiency roll-off under high current density, which also originated from triplet-triplet annihilation and singlet-polaron annihilation under high exciton density.

Luminance was plotted as a function of voltage as shown in Figure 5.13e. Device A showed a higher luminance from 3.2 V to 9.6 V, which may result from the different charge carrier balance in the two devices. The maximum luminance of Device A was saturated around 9.8 V and the value is 21620 cd/m$^2$. The maximum luminance of Device B was 22170 cd/m$^2$, which was obtained at 10 V with the current density of 247 mA/cm$^2$.

The device performances of OLED devices employing TCTA:Tm3PyBPZ as host for rubrene are summarized in Table 5.3. The CIE coordinates around 1 mA/cm$^2$ of the two devices were (0.41, 0.55) and (0.44, 0.54), respectively.

Table 5.3 Luminance (L), current efficiencies (CE), power efficiencies (PE) and external quantum efficiencies (EQE) of the OLED devices employing TCTA:Tm3PyBPZ as host for rubrene.

<table>
<thead>
<tr>
<th>Device</th>
<th>Maximum L (cd/m$^2$)</th>
<th>CE (cd/A)</th>
<th>PE (lm/W)</th>
<th>EQE (%)</th>
<th>at 100 cd/m$^2$</th>
<th>CE (cd/A)</th>
<th>PE (lm/W)</th>
<th>EQE (%)</th>
<th>at 1000 cd/m$^2$</th>
<th>CE (cd/A)</th>
<th>PE (lm/W)</th>
<th>EQE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>21620</td>
<td>44.4</td>
<td>58.1</td>
<td>13.0</td>
<td>40.2</td>
<td>48.5</td>
<td>11.6</td>
<td>34.0</td>
<td>33.4</td>
<td>26.9</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>22170</td>
<td>34.5</td>
<td>41.6</td>
<td>10.0</td>
<td>34.5</td>
<td>41.6</td>
<td>10.0</td>
<td>29.1</td>
<td>26.9</td>
<td>8.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.13 Device performances of OLED devices employing TCTA:Tm3PyBPZ as host for rubrene. (a) current density versus voltage characteristics. (b) EQE versus current density. (c) CE versus current density. (d) PE versus current density. (e) luminance versus voltage. (f) EL spectra of the OLED devices.
5.3 OLED devices based on intramolecular exciplex 3DPA3CN

1,3,5-tris(4-(diphenylamino)-phenyl)-2,4,6-tricyanobenzene (3DPA3CN) was synthesized and reported by Adachi’s group in 2015.[160] It is an intramolecular exciplex exhibiting efficient thermally activated delayed fluorescence. As shown in Figure 5.14, it was designed with separated HOMO and LUMO mainly located on diphenylamino groups and tricyanobenzene group, respectively, while maintaining a moderate overlap between them. The emission of 3DPA3CN in degassed toluene is around 506 nm. It was reported the lifetime of prompt component was 6.2 ns and the lifetime of delayed component was as long as 550 µs. In their work, OLED device with the structure of (ITO)-coated glass/ N,N’-di-(1-naphthalenyl)-N,N’-diphenyl-(1,10-biphenyl)-4,40-diamine (α-NPD)/ 3,3’-bis(N-carbazole)-1,10-biphenyl (mCBP)/3DPA3CN (6 wt%) in DPEPO/ 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi)/ LiF/Al was fabricated and the EQE of the device was as high as 21.4 %.

![Chemical structure of 3DPA3CN.](image)

Figure 5.14 Chemical structure of 3DPA3CN.
To compare the performance of OLED device based on this intamolecular exciplex with the intermolecular exciplex in our work, we purchased 3DPA3CN from Lumtec Corp. and used it as received. A wide band gap material 1,3-Bis(carbazol-9-yl)benzene (mCP) was selected to function as the host material for 3DPA3CN since 100% PL quantum efficiency was reported in their work. The HOMO level and LUMO level of mCP are 5.9 eV and 2.4 eV, respectively.[161] We have fabricated a series of OLED devices to find the optimum doping concentration of 3DPA3CN in mCP to be 7%. Three devices are discussed below with their structures shown in Figure 5.15. The thicknesses of HTL and ETL are different in Device A and Device B with the total thickness of organic layers remaining the same. For Device C, charge generation layer of Hat(CN)₆ was inserted between ITO substrate and N,N-Bis(naphthalen-1-yl)-N,N-bis(phenyl)benzidine (NPB) to tune the J-V characteristics of the device. A 5-nm-thick of mCP was introduced between NPB and emissive layer to block the excitons in the emissive layer.[162]

<table>
<thead>
<tr>
<th>Device A</th>
<th>Device B</th>
<th>Device C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (100 nm)</td>
<td>Al (100 nm)</td>
<td>Al (100 nm)</td>
</tr>
<tr>
<td>LiF (1 nm)</td>
<td>LiF (1 nm)</td>
<td>LiF (1 nm)</td>
</tr>
<tr>
<td>TPBi (60 nm)</td>
<td>TPBi (50 nm)</td>
<td>TPBi (50 nm)</td>
</tr>
<tr>
<td>mCP:3DPA3CN (7 %, 10 nm)</td>
<td>mCP:3DPA3CN (7 %, 10 nm)</td>
<td>mCP:3DPA3CN (7 %, 10 nm)</td>
</tr>
<tr>
<td>mCP (5 nm)</td>
<td>mCP (5 nm)</td>
<td>mCP (5 nm)</td>
</tr>
<tr>
<td>NPB (55 nm)</td>
<td>NPB (60 nm)</td>
<td>NPB (60 nm)</td>
</tr>
<tr>
<td>ITO glass substrate</td>
<td>ITO glass substrate</td>
<td>ITO glass substrate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hat(CN)₆ (5 nm)</td>
</tr>
</tbody>
</table>

Figure 5.15 Device structures of OLED devices employing intramolecular exciplex 3DPA3CN as the dopant material.
The OLED devices were characterized after fabrication and the result was plotted in Figure 5.16. Figure 5.16a shows current density versus voltage (J-V) characteristics. The turn-on voltage of the three devices were around 4 V. The increase in driving voltage should be resulted from the introduction of wide band gap material mCP (~3.5 eV). Material with wide energy band gap usually possesses deeper HOMO level and shallower LUMO level, which makes it more difficult for hole and electron injection due to the large energy barrier. The current densities of the devices at 10 V were 216, 233 and 260 mA/cm², respectively.

Although Device C with charge generation layer showed best J-V characteristic, Device A showed much higher EQE value than the other two devices. The carrier balance in Device A was much better than the other two devices. A maximum EQE of 7 % was obtained at 0.2 mA/cm² in Device A. When the current density was below 0.2 mA/cm², the efficiencies dropped. That could be due to that carrier injection under low current density is suppressed.

Current efficiencies and power efficiencies were plotted and shown in Figure 5.16c and Figure 5.16d. The maximum current efficiency of Device A was 23.6 cd/A, which was obtained at 4.6 V with the current density of 0.2 mA/cm². The maximum power efficiency of Device A was 16.4 lm/W obtained at 4.4 V. All the devices exhibited efficiency roll-off under high current density.

Luminance was plotted as a function of voltage as shown in Figure 5.16e. Although three devices showed different J-V characteristics and efficiencies, the differences in
the L-V characteristic were quite small. The luminance values of the three devices at 10 V were 12300, 11410 and 12030 cd/m², respectively.

The EL spectra are shown in Figure 5.16f. The peak wavelengths of all the devices were located at 520 nm. There was a very small shoulder peak around 440 nm. This emission was from NPB whose peak wavelength is around 440 nm.[163] Some excitons may form at the interface of NPB/mCP and resulted in the emission of NPB despite the use of exciton blocking layer mCP. Increasing the thickness of neat mCP layer or replacing the HTL with a high triplet energy level can solve this problem.

The device performances of OLED devices employing intramolecular exciplex 3DPA3CN as the dopant are summarized in Table 5.4. The CIE coordinates around 1 mA/cm² of all the devices were (0.26, 0.60).

Table 5.4 Luminance (L), current efficiencies (CE), power efficiencies (PE) and external quantum efficiencies (EQE) of the OLED devices employing TADF emitter 3DPA3CN.

<table>
<thead>
<tr>
<th>Device</th>
<th>Maximum at 100 cd/m²</th>
<th>at 1000 cd/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L (cd/m²)</td>
<td>CE (cd/A)</td>
</tr>
<tr>
<td>A</td>
<td>12300</td>
<td>23.6</td>
</tr>
<tr>
<td>B</td>
<td>11410</td>
<td>15.5</td>
</tr>
<tr>
<td>C</td>
<td>12030</td>
<td>14.0</td>
</tr>
</tbody>
</table>

Although the OLED device based on 3DPA3CN was reported with an excellent performance, the performance of OLED based on this material discussed in this section was not that high. This may be caused by different OLED structure and different host material.
Figure 5.16 Device performances of OLED devices employing intramolecular exciplex 3DPA3CN as the dopant. (a) current density versus voltage characteristics. (b) EQE versus current density. (c) CE versus current density. (d) PE versus current density. (e) luminance versus voltage. (f) EL spectra of the OLED devices.
Chapter 6  Conclusions and Future Work

In conclusion, we have successfully demonstrated an exciplex with the emission around 514 nm formed between electron-donating material TCTA and electron-accepting material Tm3PyBPZ. These two OLED materials are commercially available and were not initially designed as TADF materials. The time-resolved PL showed the existence of TADF in the exciplex. The lifetimes of prompt fluorescence and delayed fluorescence at 300 K were analyzed to be 53.7 ns and 2.3 μs, respectively. The lifetime of the delayed fluorescence in the exciplex was much longer than the neat TCTA and neat Tm3PyBPZ, which were all analyzed to be around nanosecond order. Since the triplet excitons involved in the TADF process are very sensitive to the oxygen, we studied the emission of the exciplex in solution with or without oxygen. In the solution with oxygen, the emission of the exciplex was totally quenched. In the solution without oxygen, there was weak exciplex emission which was redshifted due to the change of dipole moment in a polar solvent. An OLED device employing this exciplex as the emissive layer was studied. The maximum efficiencies were 44.2 cd/A, 54.5 lm/W and 13.1 % which were much higher than the conventional fluorescent OLED devices due to the TADF process. OLED devices based on the exciplex host and fluorescent dopants also showed higher efficiencies than fluorescent OLED devices based on conventional host material. The reason is that the number of singlet excitons formed at this exciplex was larger than the conventional host due to the RISC process, so the energy transferred from the exciplex to the fluorescent dopants was increased.
After this work, I will try to explore some exciplex with both blue emission and efficient TADF process for fabricating highly efficient hybrid white OLED devices. Moreover, the time-resolved EL characteristic of the exciplex under an electrical excitation pulse will be measured to confirm the contribution of triplet excitons under electrical excitation. We have yet to obtain the phosphorescent spectrum of the exciplex at present, so the energy difference between singlet state and triplet state is still needed to be investigated in the future.
References


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Tong Lin, Fuhua Hou, Blue exciplex emission and its role as a host of phosphorescent emitter, Org. Electron. 2015, 24, 1–6.


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