INVESTIGATION OF THE INTERFACIAL ENERGY LEVEL WITHIN ORGANIC SEMICONDUCTING DEVICES

WONG WAH SENG

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WONG WAH SENG

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ABSTRACT

This main goal of this research is investigating the interfacial energy level of organic semiconducting devices by correlated to the devices performance as well as physical/chemical change in the blended/mixed organic semiconductor system. The first project reported the high efficiency extra warm white organic light emitting diodes tris(4-carbazoyl-9-ylphenyl)amine (WOLEDs) blending (TcTa) by to poly(vinylcarbazole) (PVK). The hole current for PVK:TcTa (60:40) increased by one order of magnitude in hole only device, but the current efficiency of WOLEDs improved only by 7% compared to pristine PVK. Using Ultraviolet photoelectron spectroscopy discovered the hole injection barrier between poly(3,4-(UPS), it was ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) and PVK:TcTa blend was reduced by merely ~ 0.1 eV. Phase segregation of TcTa is observed using atomic force microscopy (AFM) resulting in percolation path which increases the hole current. However, using ultraviolet-visible (UV-Vis) spectroscopy the PVK:TcTa blend absorption was found redshifted with increasing TcTa suggesting the compactification of PVK which resulted in triplet quenching that limited the increase in current efficiency. The second project demonstrated the lowering of the work function of PEDOT:PSS by mixing with barium acetylacetonate (Ba(acac)₂). The increasing pH, formation of precipitation, disappearance of PEDOT signature in UV-Vis spectroscopy suggested PEDOT was dedoped when mixed with Ba(acac)₂. The work function of PEDOT:PSS was reduced from 4.9 eV to 3.6 eV upon mixing Ba(acac)₂. The n-doped PEDOT:PSS increased the electron current density in electron only device due to the reduced electron injection barrier height. Both UPS and X-ray photoelectron spectroscopy (XPS) suggested the formation of barium polystyrene sulfonate (Ba-PSS) which resulted in the interfacial dipole up to 1.37 eV at indium tin oxide (ITO)/ Ba-PSS interface which result in reduction of PEDOT:PSS:Ba(acac)₂ work function.

Keywords: white organic light emitting diodes, blended/mixed organic semiconductor, work function, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS)

University

PENYELIDIKAN ARAS TENAGA ANTARA MUKA DALAM PERANTI SEMIKONDUKTOR ORGANIK

ABSTRAK

Tujuan utama penyelidikan ini adalah menyiasat hubungkait antara aras tenaga antara muka di dalam peranti semikonduktor organik dengan keupayaan peranti serta perubahan secara fizikal/ kimia selepas campuran/sebatian bagi sistem semikonduktor organik. Projek pertama merekodkan diod pemancar cahaya organik berwarna putih-kekuningan (WOLEDs) dengan kecekapan yang tinggi berasaskan campuran tris(4-carbazoyl-9ylphenyl)amine (TcTa) dan poly(vinylcarbazole) (PVK). Arus lohong bagi peranti berasaskan PVK: TcTa (60:40) bertambah sebanyak sepuluh kali ganda untuk peranti lohong-sahaja, tetapi kecekapan arus WOLEDs hanya meningkat sebanyak 7 % berbanding dengan peranti PVK yang tulen. Ukuran menggunakan Spektrometri Pembebasan Foton Ultra-ungu (UPS) mendapati sebatian PVK: TcTa hanya mengurangkan rintangan penyuntikan lohong sebanyak ~ 0.1 eV. Pengukuran dengan Mikroskop Daya Atomik (AFM) menunjukan pengasingan fasa TcTa yang meningkatkan arus lohong dengan laluan perkolasi. Walau bagaimanapun, analisa spektrometri UV-Vis mendapati penyerapan ke arah anjakan merah bagi serapan PVK selepas mencampurkan TcTa. Anjakan merah ini disebabkan oleh pemadatan PVK yang menurunkan aras tenaga triplet yang menghadkan kecekapan arus peranti. Projek kedua menunjukkan penurunan fungsi kerja poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) dengan mencampurkan barium acetylacetonate (Ba(acac)₂). Peningkatan pH, penghasilan mendakan dan kehilangan serapan PEDOT dalam analisa UV-Vis mencadangkan PEDOT dipisahkan selepas dicampurkan dengan Ba(acac)₂. Fungsi kerja PEDOT: PSS berkurang dari 4.9 eV ke 3.6 eV setelah mencampurkan Ba(acac)₂. Campuran PEDOT:PSS:Ba(acac)₂ meningkatkan ketumpatan arus elektron pada peranti elektron dengan mengurangkan rintangan bagi suntikan elektron. Ukuran menggunakan UPS dan Spektrometri Pembebasan Foton Sinar-X (XPS) mencadangkan pembentukan barium polystyrene sulfonate (Ba-PSS) yang menghasilkan momen dipole sebanyak 1.37 eV antara muka ITO/ Ba-PSS yang menghasilkan penurunan fungsi kerja pada campuran PEDOT:PSS:Ba(acac).

Kata Kunci: diod pemancar cahaya putih organik, campuran/sebatian semikonduktor organik, fungsi kerja, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS)

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LIST OF SYMBOLS AND ABBREVIATIONS

A	:	Absorbance
С	:	Speed of light
С	:	Molar concentration
d	:	Distance
ΔBE	:	Shift of binding energy
Δ	:	Interfacial dipole
Δe	:	Electron injection barrier
ΔΕ	:	Energy interval
Δ_h	:	Hole injection barrier
е	:	Elementary charge
e	:	Electron
Ε	:	Site energy relative to center of the DOS
EB	:	Exciton binding energy
E_F	:	Fermi level
Eg	:	Band gap (for inorganic)/ HOMO-LUMO gap (for OSC)
EHF ^{atom}	:	Hartree-Fock orbital energy for free atom
Еномо, relative to EF	:	HOMO level relative to E_F
Eop	:	Optical gap
EVAC	:	Vacuum level
Е	:	Molar extinction coefficient
E0	:	Vacuum permittivity
Er	:	Dielectric constant
E	:	Electric field

η_{ext}	:	External quantum efficiency
η_{int}	:	Internal quantum efficiency
η_L	:	Current efficiency
η_{out}	:	Out-coupling efficiency
η_P	:	Power efficiency
η_{st}	:	Fraction of luminescent excitations based on spin statistics
f(E)	:	Fermi-Dirac distribution
<i>g</i> DOS	:	Density of state
γ	:	Ratio of hole to electron
h	:	Plank's constant
hv	:	Photon energy
Ι	:	Electric current
Ie	:	Electron beam current stored in storage beam
If	:	Fluorescent-induced current
I_0	:	Initial intensity
Ip	:	Photoelectron current
Is	:	Secondary electron-induced current
<i>I(d)</i>	:	Intensity after travel distance d
IEi	:	IE in orbital i
J	:	Current density
k	:	Boltzmann constant
k	:	Wavevector of X-ray before diffraction
<i>k</i> '	:	Wavevector of X-ray after diffraction
KEmax	:	Maximum kinetic energy
l	:	Path length

L	:	Luminance
λ_{IMFP}	:	Inelastic mean free path for photoelectron.
λ	:	Wavelength
λmax	:	Wavelength when maximum absorbance
т	:	Mass
M_s	:	Z-component of spin angular momentum
μ	:	Linear attenuation coefficient
μ^{I}	:	Absorption length
μm	:	Charge mobility
n	:	Charge carrier density
n	:	Normal vector
Ν	:	Number of states per volume
No	:	Molecular density
р	:	Momentum
Φ	:	Work function
ϕ_{pl}	:	Photoluminescence quantum efficiency of the emitter
φ	:	In plane scanning angle
$\rho(z)$:	Charge density distribution
%T	:	Percentage transmittance
q	:	Charge
q	:	Scattering vector
q_{xy}	:	In plane scattering vectors
q_z	:	Out of plane scattering vectors
R	:	Interatomic distance
Ra	:	Average roughness

Rrms	:	Root means square roughness
Rea	:	Extra-atomic relaxation energy
R _{ia}	:	Intra-atomic relaxation energy
S	:	Spin angular momentum
So	:	Ground state
S_1	:	Singlet state
Sn	:	Higher singlet state
σ	:	Standard deviation of Gaussian distribution
О Н	:	Standard deviation of HOMO distribution
σ_L	:	Standard deviation of LUMO distribution
Т	:	Temperature
T_{I}	:	Triplet state
Tn	:	Higher triplet state
T_{0}	:	Thermometric parameter related to density of localized state
θ	:	Angle
θι	:	Incident angle
$ heta_{f}$:	Diffracted angle
ν	:	Frequency of photon
V	:	Voltage
Vea	:	Shift in E_{HF}^{atom} due to free atom to solid state
Via	:	Shift in E_{HF}^{atom} due to valence charge
Voc	:	Open circuit voltage
V turn-on	:	Turn-on voltage
V(z)	:	Potential within the material
Ζ	:	Distance/depth

Ζ	:	Atomic number
AL	:	Absorption layer
Alq ₃	:	Tris(8-hydroxyquinolinato) aluminium
AFM	:	Atomic force microscope
ASF	:	Atomic sensitivity factor
BA	:	Benzoic acid
Ba(acac) ₂	:	Barium acetylacetonate
Ba-PSS	:	Barium polystyrene sulfonate
BE	:	Binding energy
BGD	:	Bässler's Gaussian disorder
CB	:	Conduction band
CBM	:	Conduction band minimum
CBP	:	(4,4'-bis(n-carbazolyl)-1,1'-biphenyl)
CCT	:	Correlated colour temperature
CE	:	Current efficiency
CIE	:	International Commission on Illumination
СМ	:	Collimating mirror
DCM	÷	Double-crystal monochromator
DFT	:	Density functional theory
DI	:	Deionized
DOS	:	Density of state
EA	:	Electron affinity
EIL	:	Electron injection layer
EL	:	Electroluminescence
EML	:	Emissive layer
EOD	:	Electron only device

EQE	:	External quantum efficiency
ESRF	:	European Synchrotron Radiation Facility
ETL	:	Electron transport layer
ETM	:	Electron transport material
EXAFS	:	Extended X-ray Absorption Fine Structure
FIrpic	:	[bis(4,6-difluorophenyl) pyridinato-N,C ²]picolinate iridium(III)
FLP	:	Fermi level pinning
FM	:	Focusing mirror
FWHM	:	Full-width half maximum
GIXRD	:	Grazing incidence X-ray diffraction
HECO	:	High energy cut-off
Hex-Ir(phq)3	:	Tris[2-(4-n-hexylphenyl)quinoline]]iridium(III)
HIL	:	Hole injection layer
HOD	:	Hole only device
НОМО	:	Highest occupied molecular orbital
HTL	:	Hole transport layer
HTM	:	Hole transport material
IC	÷	Internal conversion
ICT	:	Integer charge transfer
IE	:	Ionization energy
IMFP	:	Inelastic mean free
IQE	:	Internal quantum efficiency
Ir(ppy)3	:	Fac tris(2-phenylpyridine) iridium
ISC	:	Intersystem crossing
ITO	:	Indium tin oxide
JVL	:	Current density- voltage- luminance

KE	:	Kinetic energy			
LECO	:	Low energy cut-off			
LED	:	Light emitting diode			
LUMO	:	Lowest unoccupied molecular orbital			
LVDC	:	Linear variable differential capacitor			
МСР	:	1,3-bis(n-carbazolyl)benzene			
NEXAFS	:	lear edge X-Ray absorption fine structure			
NIST	:	National Institute of Standards and Technology			
NPD	:	N,N'-Di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'- diamine			
OFET	:	Organic field effect transistor			
OLED	:	Organic light emitting diode			
OPV	:	Organic photovoltaic			
OSC	:	Organic semiconductor			
OXD-7	:	1,3-bis[(4-tert-butylphenyl)-1,3,4-oxidiazolyl]phenylene			
Pc	:	Phthalocyanine			
PCS	:	Photoionization cross section			
PE	:	Power efficiency			
PEDOT	:	Poly(3,4-ethylenedioxythiophene)			
PEDOT:PSS	:	Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate			
PES	:	Photoemission spectroscopy			
PhOLED	:	Phosphorescent organic light emitting diode			
PTCDA	:	Perylenetetracarboxylic dianhydride			
PVD	:	Physical vapour deposition			
PVK	:	Poly(vinylcarbazole)			
PSS	:	Polystyrene sulfonate			

PSSH	:	Polystyrene sulfonic acid
RGB	:	Red, green and blue
RISC	:	Reverse intersystem crossing
SBH	:	Schottky barrier height
S-path	:	Singlet path
SCLC	:	Space charge limited current
SLRI	:	Synchrotron Light Research Institute
SOC	:	Spin-orbit coupling
SPPO13	:	2,7-bis(diphenylphosphoryl)-9,9'- spirobi[fluorene]
T-paths	:	Triplet path
TAPC	:	di-[4-(n,n-ditolyl-amino)-phenyl]cyclohexane
ТсТа	:	tris(4-carbazoy1-9-ylphenyl)amine
TEY	:	Total electron yield
TFY	:	Total fluorescent yield
TPBI	:	(1,3,5-tris(2-nphenylbenzimidazolyl) benzene)
TOF	:	Time of flight
ТРО	:	1,3,5-tris(diphenylphosphoryl)benzene
TTF	÷	Tetrathiafulvalene
UHV	:	Ultra-high vacuum
UPS	:	Ultraviolet photoemission spectroscopy
UV	:	Ultraviolet
UV-Vis	:	Ultraviolet-visible
VB	:	Valance band
VBM	:	Valence band maximum
VR	:	Vibrational relaxation
VRH	:	Variable range hopping

VLSPG	:	Varied line spacing plane grating
WOLED	:	White organic light emitting diode
XANES	:	X-ray absorption near edge structure
XAS	:	X-ray absorption spectroscopy
XPS	:	X-ray photoemission spectroscopy
XRD	:	X-ray diffraction

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CHAPTER 1: INTRODUCTION

1.1 Introduction

The first observation of high conductivity anthracene doped with iodine (Akamatu et al., 1956) is often taken as a starting point for the beginning of the organic semiconductor (OSC). It was not until 1987, when C. W. Tang and VanSlyke, from Kodak fabricated the world first practical organic light emitting diode (OLED) by vacuum deposition with low driving voltage and reasonable efficiency (C. W. Tang & VanSlyke, 1987). Nowadays, the OLEDs fabricated by vacuum deposition have comparable efficiency with other lighting sources (light-emitting diodes (LED), compact fluorescent) and starts to domain the display market in mobile device (Zou et al., 2020). Vacuum deposition capable of fabricating multi-layer structure is an essential feature for high efficiency OLEDs but is expensive due to the high cost of vacuum system and material wastage (Duan et al., 2010). Solution processing can produce a large area and flexible device with extremely low cost, but the performance is still lagging far behind the vacuum deposition. The facile synthesis small molecule OSCs has the advantage of well-defined structure, chemical purity and better performance at the expense of high fabrication cost due to vacuum deposition. Meanwhile, polymer based OSCs are typically required in solution processing because polymer can form excellent film with great film morphology stability compared with small molecule (Z. Yang et al., 2009).

Numerous studies had been carried out to improve the device performance of solution processable OSC devices such as OLEDs (Godumala *et al.*, 2020), organic photovoltaics (OPVs) (Borse *et al.*, 2019), organic field effect transistors (OFETs) (Vegiraju *et al.*, 2017), organic memory devices (Goswami *et al.*, 2017) and others, due to its cost-efficient fabrication. The strategies to improve the performance of solution processable OSC devices can be grouped into two approaches: molecular designing and

blending/mixing. Through molecular designing approaches, Hassan *et al.* designed a solution processable hole-transporting host for OLEDs using carbazole dendrimer (highly branched molecule) (Hasan *et al.*, 2017). Meanwhile, blending/mixing approaches are popular in solution processable OSC devices to enhance the electronic, chemical or mechanical properties by mixing small molecules and polymers. Several researchers reported mixing small molecule (such as tris(4-carbazoyl-9-ylphenyl)amine (TcTa) and (4,4'-bis(n-carbazolyl)-1,1'-biphenyl) (CBP)) to polymer hole transport material (such as Poly(9-vinylcarbazole) (PVK)) to improve the charge carrier balance (M. D. Ho *et al.*, 2013; Lee *et al.*, 2010; Talik, Woon, & Yap, 2016). The solution processable small molecules- polymer blends were widely adopted in OFETs such as blending of TIPs-pentacene to poly(α -methyl styrene) (Kang *et al.*, 2008). Blending/mixing shows promising potential to enhance the conductivity and injection properties for high performance OSC devices. However, the understanding of the underlying mechanism behind organic blends remains limited.

The understanding of interfacial energy level between organic/organic and organic/metal are of paramount importance to understand the blending/mixing effect of OSC materials. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the OSC blends need to align with the Fermi level of anode and cathode in order to reduce the energy barrier. The blended/mixed OSC may not have similar frontier energy level compared its individual component (P. Li *et al.*, 2019). The interplay between host, dopant and electrode such as: charge transfer between host and guest (W. Li *et al.*, 2018), phase segregation (Z. Zhang *et al.*, 2020), molecular conformations (Hamilton *et al.*, 2018) or molecular packing between two blends (Xu *et al.*, 2015) can significantly alter the π -conjugation and change the interfacial energy level (P. Li *et al.*, 2019). Furthermore, the interplay between host, dopant energetic disorder (Fediai *et al.*, 2019) and mobility (W. Li *et al.*, 2018; Talik, Woon, & Yap, 2016) can

occur too. Hence, the whole picture of interfacial energy level is incomplete without considering the interaction between host and dopant. There have been considerable studies on the interfacial energy level of OSC in blended/mixed system. Further understanding of the correlation between the interfacial energy level with interaction between host and dopant is required, in order to optimize the performance of blended OSC device.

1.2 Motivations and Objectives

Since Tang and VanSlyke fabricated the first practical OLEDs by vacuum deposition, the high-performance OSC devices, especially OLEDs are dominated by the vacuum deposition technology (C. W. Tang & VanSlyke, 1987). Although OLEDs offer better white light quality and more flexible form factors, the vacuum deposition OLEDs are too expensive to use for daily lighting (Pode, 2020). For better market penetration, OLEDs were pushed towards solution processable methods, which permitted low cost and large-scale production for lighting purpose.

Recently researches showed that cool white night lighting can suppress the secretion of melatonin, a hormone that regulates the sleep–wake cycle, leading to insomnia or even cancer (Kozaki *et al.*, 2008; Pauley, 2004; Sato *et al.*, 2005; Srinivasan *et al.*, 2008). This thesis is primarily focused on designing a high efficiency solution processable warm white OLEDs by blending TcTa, a small molecule OSC into PVK, a polymer OSC. Both PVK and TcTa are widely used polymer and small molecule-based hole transport materials (HTMs). As a polymer, PVK able to form excellent film but the hole mobility is two orders lower compared to TcTa. This research aims to the study of interfacial energy level as well as the molecular conformation between PVK and TcTa in order to correlate to the efficiency of blended OLEDs.

PEDOT:PSS is popular as the hole transporting layer in OLEDs (Kumar & Pereira, 2020; Singh *et al.*, 2018) and OPVs (Guo *et al.*, 2019; Whitcher *et al.*, 2014) or as the

electrode in OFETs (S. H. Kim *et al.*, 2017; J. Liao *et al.*, 2019) and supercapacitors (Y. Liu *et al.*, 2015) and many more due to its superior electronic and ionic conductivities, morphology, stability and solution processability. PEDOT:PSS has relative high work function, ranging between 4.85 to 5.15 eV, making it suitable for hole injection rather than electron injection (Park *et al.*, 2012; S. Wu *et al.*, 2011). While there are considerable studies on increase of work function of PEDOT:PSS, the researches on lowering the work function are limited. Recent works reported modified PEDOT:PSS with polyethylenimine can reduce the work function to 4.0 eV (Z. Li, Liang, *et al.*, 2015; S. Zhang *et al.*, 2015). The low work function PEDOT:PSS can be functionalized as electron injection layer (EIL) or cathode, offering a promising new avenue toward full solution processable OSC devices.

Overall, there are four objectives in this research work as below:

- I. To fabricate a highly efficient extra warm white OLEDs by tuning the ratio of 3 primary colour (red, green, blue) phosphorescent dopants in PVK:TcTa blended host.
- II. To investigate relationship of interfacial energy level, molecular conformation in PVK:TcTa blend with the efficiency of OLEDs by synchrotron technique.
- III. To lower the work function of PEDOT:PSS by n-doping with Ba(acac)₂.
- IV. To correlate the lowering of work function in PEDOT:PSS as well as the induced interfacial dipole with the physical and chemical change upon mixing Ba(acac)₂.

1.3 Thesis Outline

This thesis consists of 6 chapters. Chapter 1 covers the history and trend of OSC devices as well as the important of interfacial energy level to optimize the performance of blended OSC device. On top of that, the motivation and objective of this study are discussed.

In chapter 2, the literature reviews begin with the introduction to the fundamental knowledge of OSC such as conjugated, charge transport and mobility. Subsequently, the interfacial energy level, specifically on two important interfaces in this research: metal/organic and organic/organic interface are discussed along with the origin of interfacial dipole. This chapter ended with the brief discussion of interfacial energy level in several popular OSC devices, followed by the history, operation principle, PEDOT:PSS, efficiency and colour temperature of OLEDs.

In chapter 3, the background theory of a number of advance synchrotron techniques, such as UPS, XPS, near edge X-Ray absorption fine structure (NEXAFS) spectroscopy, grazing incidence X-ray diffraction (GIXRD) used in the research are discussed. This chapter also covers the device fabrication and the electrical, optical, morphology and pH measurement for OLEDs.

Chapter 4 studied the limited improvement of the efficiency of extra warm white OLED upon blending PVK with TcTa using synchrotron techniques. The limited improvement of efficiency and colour temperature of white OLEDs were first discussed. The investigation on interfacial energy level by hole only device (HOD), photovoltaic response and UPS revealed the large increase of hole current cannot be explained by the marginal reduction of hole injection barrier when high TcTa ratio was used. Further investigation based on NEXAFS, GIXRD, AFM and UV-Vis suggested the conformation of PVK resulted in the marginal improvement of OLED efficiency when blended with TcTa.

Chapter 5 investigated the work function modification of PEDOT:PSS by doping with Ba(acac)₂. The pH and UV-vis measurement suggested chemical reaction takes place upon doping. The UPS measurement and EOD confirmed the reduction of work function as low as 3.6 eV in doped PEDOT:PSS can reduce the electron injection barrier and improve the electron injection. Lastly, an interfacial dipole model was suggested to explain the work function modification based on the result of UPS, XPS and AFM.

Chapter 6 summarized all the works done and also the possible future works.

CHAPTER 2:LITERATURE REVIEW

2.1 Introduction

In this chapter, the interfacial energy level was reviewed based on OSC devices. The review begins with the concept, history and properties of organic semiconductor. Subsequently, the concept of interfacial energy level and its alignment was explained for two most prominent interfaces: metal/organic and organic/organic, followed by the discussion on the origin of interfacial dipole. The interfacial energy level in 3 common OSC devices: OLEDs, OPVs and OFETs were briefly introduced. The chapter ends with the review of OLEDs, including the history, operating principle, efficiency as well as the colour temperature.

2.2 Organic Semiconductor (OSC)

2.2.1 Introduction to Semiconductor

Semiconductors are materials with electrical conductivity between a conductor and insulator. The electrical conductivity of conductor, semiconductor and insulator can be explained by their electronic energy band structure. Figure 2.1 shows the energy level of a single, as well as double, triple and multiple (10^{23}) of carbon atoms upon interactions. Single atom has discrete energy levels as shown in Bohr's model. However, upon mutual interaction between atoms (in solid), their energy levels will split into different levels, as Pauli exclusion principle states two or more electrons cannot occupy the identical quantum state at the same time. For 1 mole of carbon atoms, there are 6.02×10^{23} of energy states for each energy levels (C1s, C2s and C2p in figure), each energy state is so close to each other, forming a continuously ranges of allowed energy values, known as energy band. The core electrons that occupied the lowest energy level does not involve in chemical bonding, only valence electrons that occupied the outer shell participate in chemical reaction, electron or thermal conductivity. It is particular important to understand the energy band formed by valence electrons in order to understand the electric conductivity.



Figure 2.1: Energy level (denoted by 1s, 2s and 2p) for single, double, triple or multiple (10²³) of interacting carbon atoms. The upward and downward arrow showed in single atom indicate only paired electron spins can occupy in each energy level due to Pauli exclusive principle.



Figure 2.2: The interaction between one or more valence electrons from metal atoms to form the valence band (VB) and conduction band (CB).

Figure 2.2 shows the formation of valence band (VB) and conduction band (CB) from the filling of valence electrons with increased number of atoms interacting with each other. Since electron has a tendency to fill up the lowest available states, the VB always

completely filled with electron, in particularly at absolute zero temperature. The VB and CB are overlapping in metals as shown in Figure 2.2 and Figure 2.3a, even at temperature slightly higher than absolute zero (such as 1K), the KE gained by the electron will enable most of the electrons to move freely in CB. For semiconductors and insulators, the VB and CB are separated by an energy gap called band gap, also known as forbidden energy gap, where no electron are allowed to stay in this band. The value of band gap can be obtained by the difference between conduction band minimum (CBM) and valence band maximum (VBM). Semiconductors show a small bandgap compared to the insulators. At room temperature, a small number of the electrons gain sufficient KE to jump across the band gap (if small) and able to transfer to the CB, leaving a hole in VB. Both charge carriers (electron in CB and hole in VB) contributed to the electric conductivity when subjected under the influence of electric field. The band model explained the increasing conductivity of pristine semiconductor with temperature (which this behavior is opposite to metal), as increasing number of electrons with high KE to overcome the barrier of the bandgap. The insulator has very large bandgap and no electron has sufficient energy to be ionized into CB.

The two common intrinsic inorganic semiconductors, silicon (Si) and germanium (Ge) have band gap of 1.16 eV and 0.67 eV, respectively at absolute zero temperature (Xin, 1986). The electrical properties of semiconductor material can be modified by addition of impurities, known as doping, to tune the energy states between the band gap. Today, doping in silicon and germanium pave the way of the modern electronics such as LEDs (Nakamura, 2015), transistors (Trifunovic *et al.*, 2017), solar cells (Yoshikawa *et al.*, 2017), lasers (D.-C. Wang *et al.*, 2018) and others.



Figure 2.3: The band model for (a) metal, (b) semiconductor and (c) insulator. The minimum energy in CB and maximum energy in VB are denoted as conduction band minimum (CBM) and valence band maximum (VBM), respectively.

2.2.2 Introduction of OSC

OSCs are made up by conjugated (alternating single and double bonds along the hydrocarbon chain) small molecule or polymer consisting of low molecular weight atoms such as carbon, hydrogen, nitrogen, oxygen and Sulphur. OSCs usually behave like insulator due to the relatively higher bandgap. In 1950s, Hideo *et al.* and Kallman & Pope discovered bulk conductivity in anthracene (an insulating organic materials when no charge carrier is injected) (Akamatu *et al.*, 1956; Kallmann & Pope, 1960). The electrical conductivity of anthracene is contributed by the conjugated pi (π) bonding, as shown in the molecular structure of anthracene in Figure 2.4.



Figure 2.4: Molecular structure of anthracene.

Upon this discovery, anthracene drew the attention of scientists worldwide. In 1965, two research teams under Sano *et al.* and Helfrich & Schneider independently discovered the anthracene crystal under intense electrical excitation can generate light, known as electroluminescence (EL) (Helfrich & Schneider, 1965; Sano *et al.*, 1965). However, the EL was impractical due to the requirement of high voltage (100 -1000V for practical brightness), as a consequence of the crystal thickness was in micrometer range. Helfrich & Schneider and Shirakawa *et al.* found doping polyacetylene with iodine resulted in high conductivity polymers and they earned Nobel award in chemistry 2000 for this discovery (Helfrich & Schneider, 1965; Shirakawa *et al.*, 1977).

Afterward, the OSC develops rapidly thanks to the better understanding on the mechanism behind, as well as more and more novel OSC materials discovered yearly. To date, OSC has been used for OLEDs (Y. Chen *et al.*, 2012; K. L. Woon *et al.*, 2019), OPVs (Howells *et al.*, 2018; Whitcher *et al.*, 2014), organic field-effect transistors (OFETs) (S. H. Kim *et al.*, 2017), super capacitor (Y. Liu *et al.*, 2015), organic memory device (Whitcher, Woon, *et al.*, 2016) and many other applications.



Performance



Silicon based semiconductors have the advantage of operating with high performance, high speed and even operating under high temperature as shown in Figure 2.5. Meanwhile, OSCs show the benefit in term of possibility of using printing or coating technology for large scale area fabrication, lower material and processing cost, as well as high flexible, which plays a vital role in wearable electronics. The low temperature synthesis and fabrication process of OSC can reduce the carbon footprint, along with its easily biodegradable property is emerging as a green technology in the future.

By analyzing the number of articles published from year 1970 to 2019 with Web of Science as in Figure 2.6, the publication in "organic semiconductor" field increases exponentially since early 1990s, probably inspired by the successful fabrication of first practical OLEDs device (C. W. Tang & VanSlyke, 1987).



Figure 2.6: Development of the number of publications on "Organic Semiconductor" since 1970. Web of Science keyword: Organic Semiconductor

2.2.3 Property of OSC

2.2.3.1 Conjugated

An OSC must possess π -conjugated chain in the molecule. A conjugated system is a system of connected p orbitals, which usually in the form of alternating single and double bond. Besides, lone pairs, atoms with empty p orbital (carbocations), atoms with half-filled orbital (radicals) can participate in conjugated system as well.

Example of conjugated system

 $\wedge \circ \wedge \Rightarrow \wedge \circ \wedge$

Alternating double bond (1,3 pentadiene)

Lone pairs

Carbocations

Radicals

Example of Non-Conjugated System

1,4-pentadiene

Figure 2.7: Examples of conjugated and non-conjugated system

The continuous array of "p" orbital in conjugated system allows π bonding to interact with the adjacent π bonding, resulting in a system where π bonding spreading over the system, named as delocalization. Such interaction allows electrons to spread over larger area, lowering the energy and increases the stability of the system. Figure 2.7 shows a few examples of conjugated and non-conjugated system. Noted that all the conjugated systems having their resonance forms, where there are more than one combination of molecular structures. The π electron is not "localized" to designated carbon atom as shown in resonance form of conjugated system in Figure 2.7. The conjugated system will be interrupted/broken at position where it does not provide "p" orbital. Hence, 1,4pentadiene is a non-conjugated system as the double bond is localized at 1st and 4th carbon.



Figure 2.8: Molecular orbital of Benzene, approximated by Huckel molecular orbital theory.

The delocalization of the pi electron (conjugation) not only stabilized the system but allowed the charge (π electron) transport along the pi conjugated chain as seen in the resonance mode. The stabilization of the system can be explained by Huckel molecular orbital theory. Figure 2.8 shows the molecular orbital of a common aromatic molecule, benzene. Benzene has molecular C₆H₆ with six carbon arranging in planer ring with each carbon attached to one hydrogen and two adjacent carbons. Each carbon-carbon is bonded via sp² hybridization of 2s, 2p_x and 2p_y atomic orbitals, while the 6 unhybridized perpendicular 2p_z electrons will form the π bonding frameworks. Applying Huckel molecular orbital theory on benzene revealed that there are 6 molecular orbitals with energy: (α -2 β), (α - β), (α + β), (α + β) and (α +2 β), where α is energy of p_z electron before interaction while β is the energy of stabilization experienced by an electron when delocalize. The 6 molecular orbitals of benzene were drawn in Figure 2.8. Noted that all the 6 electrons will occupy the 3 lowest energy levels (α - β and α -2 β) energy to achieve better stability compared to standalone p_z atomic orbital (with energy α).

The maximum energy of the occupied orbital $(\alpha-\beta)$ defined as the HOMO, analogous to VB in inorganic semiconductor. The LUMO of benzene has energy of $(\alpha+\beta)$, which is the lowest energy among the antibonding molecular orbital (π^*) analogous to CB in inorganic counterpart. Thus, when an electron excited by photon or electric field, the pi electron may transit between HOMO and LUMO, with energy equivalent to HOMO-LUMO gap, analogous to band gap.

While the energy level of simple organic molecules like benzene can be calculated using Huckel molecular orbital theory, it is difficult to calculate the shape and energy for complex organic molecules. The development of density functional theory (DFT) by Pople *et al.* and Kohn *et al.* overcomes these difficulties by iteration using computational method, eventually lead to Nobel prize in chemistry in year 1998 (Kohn *et al.*, 1996; Pople *et al.*, 1987). Nowadays, the computational chemistry able to calculate the structure, energy, charge density, dipoles and many other information, complement with the experiment results. Milad *et al.* using DFT to calculate the HOMO and LUMO as well as the molecular structure for Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene] (MEHPPV) and fluorinated MEHPPV (F-MEHPPV) as shown in Figure 2.9, which is impossible to solve using Huckel molecular orbital theory numerically (Milad *et al.*, 2016).



Figure 2.9: An example of DFT simulation for MEHPPV and F-MEHPPV to obtain the HOMO, LUMO as well as the structure of the molecules (Milad *et al.*, 2016).

Increasing the number of conjugated double bonds will increase the delocalization and decrease the HOMO-LUMO gap. Besides, the spatial arrangement of conjugated carbon chain will affect the conjugation as well. Figure 2.9 demonstrate the twisted plane (with torsional angle 45 °) due to the sterically hindrance in F-MEHPPV resulting in breaking of conjugation, hence a higher HOMO-LUMO gap (Milad *et al.*, 2016). The simulation resulted was supported by UV-Vis spectroscopy since the HOMO-LUMO gap correlates directly with the respective molecular electronic transitions in absorption spectroscopy. Interactions between conjugated chains also can reduce the HOMO-LUMO bandgap.

2.2.3.2 Charge Transportation and Mobility

The charge carrier transport in semiconductor describes how the electrons and holes move under the external electrical field, which generate current. The charge transport can be expressed in the Equation 2.1, where J is the current density, q is the elementary charge of a single carrier, n is the number of free charge carrier per unit volume (charge density), μ_m is the charge mobility and \in is the electric field.

$$J = qn\mu_m \epsilon \tag{2.1}$$

As discussed in previous section, HOMO and LUMO are the allowed energy orbital forming upon conjugation in OSC molecules. The HOMO-LUMO gap in OSC is often larger than inorganic semiconductor and hence even at higher temperature, the intrinsic free charge carrier is completely absented. Electric field doping (via injection) is required to generate free charge carrier. The energetic distribution of holes or electrons in a material, also known as density of state (DOS), g_{DOS} is defined as the number of states (available for a charge carrier to occupy) per volume (*N*) within an energy interval (ΔE) as Equation 2.2.

$$g_{DOS}(E) = \frac{N}{\Delta E}$$
(2.2)

The DOS of CB and VB in conventional inorganic semiconductor are parabolic distributed with well define bandgap (E_g) as shown in Figure 2.10 (a). One can see the electron and hole in inorganic semiconductor are localized at band edges. However, most of the OSC (except with molecular crystal) systems show significant disorder (Karki *et al.*, 2019; Tessler *et al.*, 2009). The breaking of conjugation in the long carbon chains

came from the defects such as twists, kinks or chemical defects. This introduces different conjugation lengths giving raise to energetic disorder. Furthermore, the different energetic environment (due to the polarization of the surrounding molecules) on every molecule (energy site) further intensify the energy disorder (Navamani & Senthilkumar, 2017). The weak intermolecular (Van der Waals) interaction between the molecule/polymer also causes the charge carrier to be largely localized in the molecules (Horowitz, 2015). Therefore, the distribution of energy sites, in occupied or unoccupied band of OSC was found to be statistically described by Gaussian distribution of DOS as Equation 2.3, where N_{0} , *E* and σ is the molecular density, site energy relative to center of the DOS and standard deviation (degree of disorder) of gaussian distribution, respectively (Bässler, 1993).

$$g(E) = \frac{N_0}{\sqrt{2\pi\sigma}} \exp\left(-\frac{E^2}{2\sigma^2}\right)$$
(2.3)

Figure 2.10 (b) shows the Gaussian profile of HOMO and LUMO with blue lines and green lines indicated the individual molecular energy levels. The HOMO and LUMO onsets are assigned to energy level with 2 standard deviation (σ_{H} , σ_{L} for HOMO and LUMO) relative to the center of Gaussian peak. The density of the charge carrier (*n*) can be estimated from the product of DOS function with Fermi-Dirac Distribution *f*(*E*) as shown in Equation 2.4. The Fermi–Dirac statistic (Equation 2.5) describes the distribution of particles over energy states in system consists of fermions, such as electrons. The Fermi level, *E_F* refers to the hypothetical energy level where both electron and hole have an equal probability of being occupied at any given time and *kT* is the product of Boltzmann constant and temperature.

$$n = \int_{-\infty}^{\infty} g(E) \cdot f(E) dE \tag{2.4}$$

$$f(E) = \frac{1}{1 + \exp\frac{(E - E_F)}{kT}}$$
(2.5)



Figure 2.10: The DOS of (a) inorganic semiconductors and (b) organic semiconductors. The VBM and CBM for semiconductor are separated by a well-defined band gap. The blue and green line indicated the localized state in HOMO and LUMO, with Gaussian distribution of DOS. The HOMO-LUMO gap is the gap between HOMO and LUMO onset (defined by 2 standard deviations from the center of DOS) (Adapted from (J.-P. Yang *et al.*, 2017)).

The carrier density and the charge mobility for most OSCs are low compared to inorganic semiconductor and dependent on the electrical field strength. Several mechanisms have been proposed to describe the charge transport in OSCs. The "Band Transport Model" which commonly used for high crystallized solids failed to explain the disorder organic system.

Variable range hopping (VRH) transport model proposed by Miller-Abrahams and Marcus for non-crystalline material indeed is one of the widely accepted models to describe the charge transport in OSCs (Marcus, 1965; Miller & Abrahams, 1960). VRH model suggested the charge transportation in OSCs occurs via hopping, a thermally activated tunneling between energetically localized sites.



Figure 2.11: Schematic diagram shows the variable range hopping model in an organic semiconducting device (OLEDs). The hole (electron) is injected from anode (cathode) followed by hopping transport along the thickness (z) of the device before forming exciton and radiatively recombination. Example of swallow and deep trap in LUMO were pointed out with green colour.

Figure 2.11 presents the VRH model in an OSC device, such as OLEDs. The electron (hole) hopping (tunneling) between the adjacent localized energy states in LUMO (HOMO), respectively before forming excitons at recombination zones. The hopping process is thermally activated because upward hopping of electron is assisted by the phonon (vibration of atom) while the downward hopping releasing energy in the form of phonon. Noted that OSCs show disorder in term of energy (energy disorder) as well as position of the energy states (position disorder). The position disorder is illustrated in Figure 2.11 with every energy site has random distance with each other, resulted in "variable range" hopping. The energy states that lying above the center of LUMO (below the center of HOMO) require activation energy in order for hopping, thus forming trap states. These trap states can be either intrinsic (structural defect i.e. conformable

distortion, twist in carbon chain) or extrinsic (chemical defect, i.e. impurities). While shallows traps capture charge carrier for short time because the charge can easily hop to nearby states by thermal activation process, the deep traps will capture the charge carrier for long time, hindering the charge transport resulting in poor performance of OSC device. It is important to note that if the electrons (holes) have higher mobility than hole (electron), the recombination zone will be located nearer to anode (cathodes).

The Mott's formalism VRH model describes the temperature (*T*) dependence of mobility (μ_m) in disorder system as Equation 2.6, where T_0 is a thermometric parameter related to density of localized state (N. F. Mott, 1969). The Bässler formalism VRH model, also known as Bässler's Gaussian disorder (BGD) model relating the mobility with the Gaussian distribution of all localized states where σ related to energetic width of Gaussian DOS and k is the Boltzman's constant as in Equation 2.7 (Bässler, 1993; C. Liu *et al.*, 2017). Both Mott's formalism VRH and BGD model have been successful in modeling the experiment data of mobility in Pentacene, Zinc phthalocyanine (ZnPc), PVK, TcTa and other OSCs (Germs *et al.*, 2012; Schmechel, 2002; Talik, Woon, & Yap, 2016).

$$\mu_m \propto \exp(-\frac{T_0}{T})^{\frac{1}{4}} \tag{2.6}$$

$$\mu_m \propto \exp[-(\frac{2\sigma}{3kT})^2] \tag{2.7}$$

The mobility in OSCs is commonly measured by time of flight (TOF) measurement, space charge limited current (SCLC) measurement, or field effect measurement. Even mobility value obtained from TOF and SCLC measurements reflect the charge conduction in bulk and thin film (~ 100 nm) respectively, literature showed mobility obtained from TOF and SCLC can be different up to one order magnitude (Domercq *et al.*, 2008). Therefore, it is important to compare the mobility of different OSCs only if both of them are measured with similar technique. Field effect measurement calculated the mobility of charge carrier when charge accumulated at the interface

between gate and OSC, thus field effect mobility is sensitive to the trap state at interface as well as morphology between OSC and dielectric layer.

2.2.4 Type of OSC

2.2.4.1 Small Molecule and Polymer

OSC materials can be categorized as small molecules and polymers. Polymers are large molecules which composed of many repeating units, namely monomer. Figure 2.12 illustrates one of the (a) small molecule OSCs and (b) polymer OSCs utilize in this research.



Figure 2.12: Example of (a) small molecule (TcTa) and (b) polymer OSCs (PVK)

Both small molecules and polymer OSCs can be dissolved in appropriate organic solvent. Polymer can be solution processable (such as spin coating, blade coating, inkjet printing) to form a very smooth and uniform film, reducing the variance in term of film thickness and morphology. Meanwhile, forming a uniform thin film with ideal thickness for OSC device (30-100 nm) with small molecule is a challenging task due to the strong molecular aggregation (Höfle *et al.*, 2014). Therefore, devices based on small molecule usually fabricated with vacuum deposition under high vacuum. Vacuum deposition has the advantage of fabrication complicated multiple layers with excellent performance. However, the complexity of vacuum deposition system and underutilization of expensive

OSC materials hinder the market penetration of OSC devices (Duan *et al.*, 2010). In this research, the polymer was blending with small molecule to harvest the advantage of polymer (good morphology) and small molecule (higher mobility) in the extra warm white OLEDs.

Polymer usually has high disorder compared to small molecule OSCs due to the structural disorder that breaking the conjugation (Venkateshvaran *et al.*, 2014). On the other hand, a small molecule can be well organized depend on fabrication parameters such as annealing, type of solvent and others (J.-F. Chang *et al.*, 2004). The high degree of crystallization is crucial for performance of OFETs as it encourages charge transport that gives high mobility (Hwang *et al.*, 2012).

2.2.4.2 n-type and p-type

OSCs can also be categorized according to the charge transport: n-type (electrontransporting), p-type (hole-transporting) and ambipolar (transporting both electron and hole). Figure 2.13 shows the different positions of electrode Fermi level relative to the frontier energy for p-type (left), ambipolar and n-type (right) of OSCs. Noted that p-type has Fermi level close to HOMO, thus the hole injection barrier (Δh) become minimized and facilities the hole injection and transport. The n-type has Fermi level close to the LUMO while the ambipolar has Fermi level close the center of HOMO and LUMO (Quinn *et al.*, 2017).

Most of the OSCs are intrinsically ambipolar, with Fermi level at the center between HOMO and LUMO, capable to conduct both electrons and holes with low mobility (due to the significant large Δ_e and Δ_h) (K. Zhou *et al.*, 2014). There are two common approaches to change the density of charge carrier concentration and Fermi level position of OSCs: electrical doping (Z. Q. Gao *et al.*, 2008; Reiser *et al.*, 2019) or design a new material by introducing electron-deficient (rich) building block (Facchetti *et al.*, 2003; Min *et al.*, 2018; K. Zhou *et al.*, 2014). In fact, electrical doping in polyacetylene by (Shirakawa *et al.*, 1977) earned him the 2000 Nobel prize for the conducting polymer. One of the common hole transport material (HTM) in OSC devices, PEDOT:PSS is a heavily p-doped (oxidized) to facilitate hole transport (S. Zhang *et al.*, 2015).



Figure 2.13: A schematic drawing of the relationship between Fermi level (E_F) of source electrode with HOMO and LUMO for different types of OSC. The Δ_e and Δ_h represent the electron and hole injection barrier and "X" marking denotes the inhabitation of charge transport (Adapted from (Quinn *et al.*, 2017)).

2.3 Interfacial Energy Level

2.3.1 Electronic Properties of Organic Interface

Fermi level, HOMO and LUMO are important interfacial energy levels to control the electronic, transport (electric), optical and redox behavior of OSCs. The energy diagram for OSC-vacuum interface in Figure 2.14 was drawn to relate the energy level above with all the relevant key parameters such as vacuum level (E_{VAC}), work function (Φ), HOMO-LUMO gap (E_g), optical gap (E_{opt}), electron-hole (exciton) binding energy (E_B), ionization energy (IE), and electron affinity (EA). The understanding of the concept of terminology and their mechanisms are of paramount important before further discussion of interfacial energy (energy between two separated phases or matters). The HOMO and LUMO (equivalent to VBM and CBM for inorganic) concept have been introduced in section 2.2.3.1, here the HOMO and LUMO are referring the molecular orbital for single neutral molecule. Noted that interaction between molecule will resulted in disorder and spread the energy state in the form of Gaussian distribution. The E_{vac} is defined as energy level of electron that is free from the bounding of solids, experimentally it can be referred to electron rests at few nm outside solids (Kahn, 2016). The energy required to remove an electron from HOMO to E_{VAC} is known as IE while the energy gain when electron dropping from E_{VAC} to LUMO is definite as EA.



Figure 2.14: Energy diagram of an OSC-Vacuum interface. The frontier orbital edge (HOMO, LUMO), Fermi level (E_F) , HOMO-LUMO gap (E_g) , hole-electron (exciton) binding energy (E_B) , optical gap (E_{opt}) , work function (Φ) , ionization energy (IE), and electron affinity (EA) were defined.

The Fermi level (E_F) is defined as energy level with the 50% probability to be occupied with electron at thermal equilibrium, and work function (Φ) is the energy required to remove an electron from E_F to E_{VAC} . Since metal has overlapping VB and CB, the E_F positioned similar to VBM and CBM, hence metal has equal value for Φ , IE and EA. For OSCs, the HOMO and LUMO are separated from each other with HOMO-LUMO gap (E_g), corresponding to the different between IE and EA. OSCs have E_F located between HOMO and LUMO, hence the Φ has a value fall between IE and EA. The E_F of OSCs was determined with reference with metal (commonly gold) during photoelectron spectroscopy experiment since E_F will align with each other to achieve chemical potential equilibrium.

One of the common methods to estimate the E_g was by determining the optical gap (E_{opt}) using Tauc plot and UV-Vis absorption spectroscopy (Tauc, 1968). While the E_g and E_{opt} almost equivalent for inorganic semiconductor, the E_{opt} from OSCs is substantially different from E_g . Upon photoexcitation in OSCs, the electron and hole are bounded together as a pair by the electrostatic attraction between them. Such electron-hole pair has binding energy (BE) of E_B , which has a value of a few tenth of an eV for OSCs, but only a few meV for inorganic semiconductor due to the significant smaller dielectric constant of OSCs ($\varepsilon_r \sim 3-5$) compared to inorganic ($\varepsilon_r \sim 10$) (Bredas, 2014). Thus, the E_{opt} obtained from UV-Vis is always smaller from the E_g with a deviation of EB. The best method to obtain the true E_g value was by coupling the photoemission spectroscopy (PES) and inverse photoemission spectroscopy (IPES) to measure the occupied and unoccupied state, respectively. Anyway, optical absorption technique is commonly used to estimate the E_g due to the easily accessibility and low cost of UV-Vis spectroscopy (Talik, Woon, Yap, *et al.*, 2016).

2.3.2 Interfacial Energy of OSCs

The electronic structure at the interface between two different materials can be significantly different compared with the bulk. The understanding of interfacial energy is important for design efficient OSC devices, for example to stabilize an exciton (for efficient OLEDs) or destabilize an exciton (for efficient OPVs) (J.-S. Kim & Murphy, 2011). OSCs have the advantage to form clean interface (no insulating oxide form on OSC surface) with many different materials, such as metal/organic, organic/organic, organic/dielectric, organic/electrolytes or even organic/biological interfaces (Fahlman *et al.*, 2019). Among all these interfaces, metal/organic and organic/organic interface gains most the interest and have been investigated for past 30 years with consistent fundamental theory nowadays (Gomez & Loo, 2010; Hill *et al.*, 2000; S. Ho *et al.*, 2016). In this chapter, the interface of metal/organic and organic/organic will be discussed as these two interfaces are important for the OSC devices in this research.

2.3.2.1 Metal/Organic Interface

Metal/organic interfaces are of paramount importance in device engineering as it exists in nearly all the OSC devices. The understand of energetic alignment at metal/organic interfaces is a key factor in device performance such as turn on voltage, degradation, efficiency and others. In short, interface physicists and engineers are looking for recipe to minimize the energy barrier between interface of metal and organic, in other word, to obtain an ohmic contact.

In the early day, Mott proposed Schottky–Mott rule for metal/organic interface, where Schottky barrier height (SBH) can be obtained by finding the different between the work function of the metal (Φ) and IE (or EA) of semiconductor, by assuming vacuum level alignment (Nevill Francis Mott, 1939). Figure 2.15 demonstrates the alignment of metal/organic interface based on Schottky–Mott rule, where the hole injection barrier Δ_h and electron injection barrier Δ_e are calculated based with Equation 2.8 and 2.9 below.

$$\Delta_h = IE - \Phi_{metal} \tag{2.8}$$

$$\Delta_e = \Phi_{metal} - EA \tag{2.9}$$

However, the assumption of "vacuum level alignment" become invalid when there is vacuum level offset caused by the presence of interfacial dipole, due to the charge transfer across interface to equilibrate the chemical potential throughout the multilayer structure (Hill *et al.*, 2000; Seki *et al.*, 1996). Moreover, experiments showed that in certain situation the Fermi level always fall between HOMO and LUMO (or VBM and CBM for inorganic) with a constant offset. This phenomenon is known as Fermi level pinning (FLP) (Akaike *et al.*, 2014; Van Dyck *et al.*, 2014).



Figure 2.15: Energy diagram of a Metal-Organic interface based on Schottky–Mott rule (vacuum level alignment). The Δ_h and Δ_e represent the Schottky barrier height for hole and electron, respectively.

The mechanism and origin of FLP had been debated for long time and is still not conclusive yet, but some believed the energy states between HOMO-LUMO gap (gapstates) are induced in semiconductor upon contact with metal tends to pin the Fermi level. Several models have been proposed to explain the FLP. Heine *et al.* suggested the tail end of metal electron states extending into the semiconductor's energy gap, known as metal-induced gap states (MIGS) (Heine, 1990; Sotthewes *et al.*, 2019).

Oehzelt *et al.* proposed a numerical electrostatic model that can be programmed to iteratively solve the electronic potential based on charge density in a monolayer thickness in order to simulate the band bending at metal/organic interface (Oehzelt *et al.*, 2014). The electrostatic model proposed by Oehzelt *et al.* can simulate the FLP by varied the work function of the electrode (Oehzelt *et al.*, 2014). Hence, Oehzelt model suggested FLP resulted from the pinning of gaussian tails of HOMO/LUMO bands and FLP seems to be more severe for more disorder system. Zhong *et al.* proposed the induced density of interface state (IDIS), where the gap states originating from the relatively strong chemical where the gap states originating from the relatively strong chemical interaction between the substrate and the molecule (Zhong *et al.*, 2012). Besides, the FLP can be interpreted based on the extending of DOS of HOMO and LUMO into the energy gap.



Figure 2.16: The left diagram shows the position of E_F of metal substrate relative to LUMO and HOMO of organic layer, the right diagram shows the offset between E_F and LUMO or HOMO versus electrode work function (Φ_{sub}) (Adapted from (J.-P. Yang et al., 2017))

While there are various prototypes trying to model the FLP, experiment found Schottky–Mott rule (vacuum level alignment) are in good agreement with FLP when electrode work function (Φ_{sub}) is near the mid-gap (middle of bandgap) position (J. X. Tang *et al.*, 2007; J.-P. Yang *et al.*, 2017). Figure 2.16 shows the relationship between Fermi level position in the HOMO-LUMO gap with Φ . The slope parameter, *S* indicate the change of E_F relative to the change of Φ as Equation 2.10. Noted that the FLP (*S*~0) occurs when the Φ is less than EA, or greater than IE, and transits to Schottky-Mott limit $(S\sim1)$ when near the middle of the gap. The E_F - LUMO and HOMO- E_F distance represent the electron injection barrier (Δ_e) and hole injection barrier (Δ_h) respectively.

$$S = \frac{dE_F}{d\Phi} \tag{2.10}$$

Hence, choosing a high work function metal (such as gold, platinum) are good for hole injection and low work function metal (such as calcium, magnesium) are good for electron injection (X. Peng *et al.*, 2018). Besides Φ of electrode, many researchers found the energy disorder of organic layer plays a main role to energy level alignment (P. Li *et al.*, 2019; Whitcher, Woon, *et al.*, 2016; J.-P. Yang *et al.*, 2017). Yang *et al.* reported the minimum limit of hole and electron injection barrier are proportional to Gaussian width of HOMO (σ_H) and LUMO (σ_L) as Equation 2.11 and 2.12. In other words, narrowing the DOS of frontier energy is essential to minimize the injection barrier (J.-P. Yang *et al.*, 2017).

$$\Delta_h \sim 2\sigma_H \tag{2.11}$$

$$\Delta_e \sim 2\sigma_L \tag{2.12}$$

The charge injection barrier can be tuned by choosing metal with suitable work function and organic layer with narrow DOS (less disorder). However, the selection of organic layer usually prioritizes on other properties (mobility, triplet energy, energy of HOMO, LUMO) for better device performance rather than degree of disorder. Inserting of ultra-thin interlayer between metal and organic layer seems a promising approach to resolve the above issue (Y. Gao, 2010). Inserting LiF between aluminum contact and organic layer can reduce Δ_e (Hung *et al.*, 1997), and many mechanisms were suggested to explain the role of LiF in this reduction (Hung *et al.*, 1997). Besides, PEDOT:PSS with high work function were commonly found as hole injection interlayer to reduce the Δ_h (de Kok *et al.*, 2004; S. Wu *et al.*, 2011).

2.3.2.2 Organic/Organic Interface

The evolution of the universal fundamental rule from Schottky–Mott rule to FLP provides a guidance to optimize metal/organic interface. As a comparison, there is no universal rule for the interfacial energy alignment in organic/organic interface. In most cases, the outcome of the literature can only be adapted for limited organic/organic interfaces. Hence, the best method to understand the energetic of organic/organic interface still rely on the PES measurement, to reveal the vacuum shift (interfacial dipole), HOMO onset as well as the band bending (Forsythe *et al.*, 1999; Whitcher, Wong, *et al.*, 2016).

Figure 2.17 shows the organic/organic interface of (a)Alq₃/NPB and (b) PEDOT:PSS/PVK obtained by PES measurement. Noted that Fermi level always aligned at the interface driving by the chemical potential equilibrium. The interfacial dipole and HOMO onset can be measured by the onset of HECO and LECO of ultraviolet photoemission spectroscopy. XPS is used to measure the degree of band bending in Figure 2.17. Upon measurement, the LUMO between Alq₃ and NPB is as large as 0.8 eV, hence confines the electron in emissive Alq₃ layer. By taking into account of the downward band bending of 0.20 eV between PEDOT:PSS and PVK, hole injection barrier disappeared hence explaining the superior device performance when inserting a PEDOT:PSS interlayer before PVK.

For OLEDs, the small offset between HOMO and LUMO are desirable for hole and electron to transport between the interfaces, respectively as seen in Figure 2.17 (b). On the other hand, a large offset between LUMO (HOMO) can confine the electron (hole) as demonstrated in Figure 2.17 (a). Izawa found open circuit voltage of OPVs is affected by the vacuum level shift due to the band bending between organic/organic interface (Izawa *et al.*, 2018). A lot of researches have been carrying out to understand the mechanism of organic/organic interface alignment due to the need of multilayer structure in OSC devices, especially OLEDs and OPVs.



Figure 2.17: Examples of band diagram for organic/organic interface between (a) Alq and NPB (Forsythe *et al.*, 1999) and (b) PEDOT:PSS and PVK (Whitcher, Wong, *et al.*, 2016)

Ishii *et al.* found two weakly interacting (almost no interaction) OSCs usually have interfacial dipole <0.1 eV, indicating vacuum level alignment (Hisao Ishii *et al.*, 1999). For organic/organic interface with greatly different of IE and EA referred as Donor/Acceptor, electron can transfer from low IE donor to high EA acceptor, known as integer charge transfer (ICT), forming charge transfer complex, resulted in large interfacial dipole. Hill *et al.* reported twelve organic/organic interfaces and found most of them showed vacuum-level alignment, as chemical bonding and charge exchange unlikely to happen due to the closed-shell nature of the molecules at heterointerface (Hill *et al.*, 2000). However, the Perylenetetracarboxylic dianhydride (PTCDA)/ N,N'-Di(1naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPD) interface is predicted to form charge transfer complex but showed negligible interfacial dipole, contradicts with the finding of Ishii. Besides, three interfaces with high interfacial dipole were explained by pinning due to impurity induced gap states, but it failed to explain 0.5 eV dipole observed at the PTCDA/ Tris(8-hydroxyquinolinato)aluminum (Alq3) interface. Recently, Oehzelt *et al.* proposed a self-iterative electrostatic model for the energy level alignment at metal/organic/organic interface based on Poisson equation as Equation 2.14 below, where *z*, V(z), $\rho(z)$, ε_r , ε_0 and ∇ are the distance from metal electrode, potential within the material , charge density distribution, static dielectric constant, vacuum permittivity and Del operator, respectively (Oehzelt *et al.*, 2015).

$$\nabla[\varepsilon_r \,\nabla \,V(z)] = -\frac{\rho(z)}{\varepsilon_0} \tag{2.14}$$

Figure 2.18 demonstrates an example of iteration of band bending for 10 nm of copper phthalocyanine (CuPc) on 10 nm of Alq₃, both deposited on magnesium coated ITO (Oehzelt *et al.*, 2015). The energy distribution of HOMO (orange) and LUMO (blue) of organic layer are obtained from UPS and IPES, respectively before iteration begin as shown in Figure 2.18 (a). Figure 2.18 (a) shows the vacuum aligned CuPc and Alq₃ with Fermi level of metal electrode (green dash line) before deposition, hence the alignment vacuum level (black solid line) remains unknown as indicated by the question mark. During iteration, the band bending function V(z) which initially set as zero will calculate an initial guess of charge density function $\rho(z)$, resulted in a new value of V(z) for subsequent iteration. The iteration is repeated until convergence is reached. Figure 2.18 (b) and (c) shows the final result of iteration for band bending and charge density of Mn/Alq₃/CuPc interface versus the distance from Mn electrode, *z*.

The energy level in Mn/Alq₃/CuPc was simulated based on FLP and agreed well with the experiment (J. X. Tang *et al.*, 2007), hinted that alignment of interfacial energy level in organic/organic is very dependent on work function of electrode. Besides, Oehzelet's work demonstrated that the origin of charge accumulation/depletion (that caused the band bending). The finding of Oehzelt *et al.* provides a universal approach for alignment between organic/organic (Oehzelt *et al.*, 2015). However, the electrostatic model still required the PES measurement to obtain the HOMO (LUMO) before iteration. Besides, this model was unable to predict interfacial dipole (vacuum shift) accurately as

interfacial dipole is caused by a variety physical or chemical process at the interface as discussed later (Whitcher, Wong, *et al.*, 2016).



Figure 2.18: Demonstration of the energy level alignment of the Mn/Alq₃/CuPc interface according to simulation based on electrostatic model proposed. (a) Before deposition, all the interfaces are arranged according to vacuum level alignment. The blue box, orange box, black solid line and green dash line represented the DOS of LUMO, DOS of HOMO, vacuum level and Fermi level of electrode, respectively. The simulated result of (b) band bending function eV(z) and (c) charge density function, $\rho(z)$ of Mn/Alq₃/CuPc interface versus the distance from Mn electrode (z) (Oehzelt *et al.*, 2015).

Recently, researches observe energetic disorder is closely related to the energetic of organic/organic interface. Recently, Li *et al.* correlated the energy disorder with the interfacial energy between host-dopant (P. Li *et al.*, 2019). Whitcher *et al.* also found the degree of disorder can be used to predict band bending between organic/organic interface (Whitcher, Wong, *et al.*, 2016). Such a finding can help chemists and physicists to design or chosen a suitable organic material to optimize the organic/organic interface.

Since PES measurement still the best way to probe the organic/organic interface, hence UPS measurement was carried out with synchrotron light source in SLRI, Thailand to probe the interfacial energy level of the devices in this research.

2.3.3 Interfacial Dipole

The concept of interfacial dipole arises when the vacuum level alignment failed to explain the energy level alignment. As the discussion in section 2.3.2.1, Schottky–Mott rule agrees well when work function of metal, Φ_{metal} in the range of EA< Φ_{metal} < IE for most of the metal/organic interfacial. However, the Fermi level of metal always pinning near to LUMO happen when $\Phi_{metal} \approx$ EA or pinning near to HOMO when $\Phi_{metal} \approx$ IE, known as FLP (Tanaka *et al.*, 2009). For organic/organic interface, vacuum level alignment can be applied on weak interaction interface only. According to section 2.3.2.2, the interplay between organic/organic are not completely understood. The interfacial dipole (vacuum level shift) when FLP shift on metal/organic/organic interface is shown in Figure 2.19. The induced interfacial dipole (Δ) due to FLP are similar to the offset of E_F as illustrated in Figure 2.19.



Figure 2.19: The interfacial dipole induced (Δ) by FLP for metal/organic/organic interface similar to the offset of Fermi level (E_F) inside organic layer

The direction of interfacial dipole commonly assigned by two ways. The first way is by telling the direction of the negative side of dipole with reference to interface, for example, the interfacial dipole in Figure 2.19 is pointed away from organic (Whitcher, Wong, *et al.*, 2016). The second way is by assigned upward (downward) dipole as positive (negative), which the interfacial dipole in Figure 2.19 is a negative dipole for change moving from left to right (Alloway *et al.*, 2003). There are several mechanisms on how interfacial dipole created at heterojunction, such as charge transfer across interface, Pauli push back, permanent or temporary dipole, image charge or combination of them. The section below will discuss about origin of interfacial dipole in detail.

2.3.3.1 Origin of Interfacial Dipole

The vacuum level misalignment is resulted from the interfacial dipole at interface. The possible interfacial dipole formation such as: charge transfer across interface, Pauli push-back, permanent dipole of molecule or image charge, are briefly introduced as below.

2.3.3.2 Charge Transfer across Interface

Chemical interaction at the interface can lead to chemical bond, accompanied with the charge transfer across the interface, which shifts the vacuum level and induce interfacial dipole (Crispin *et al.*, 2002; Helander *et al.*, 2016). Charge transfer induced interfacial dipole is observed in both metal/organic and organic/organic interfaces. Even adsorption of small molecule such as CO, benzene to metal surface can lead to chemical bonding at the interface (Hisao Ishii *et al.*, 1999).

Charge transfer can occur at both metal/organic and organic/organic interface. Hu *et al.* reported an interfacial dipole of 0.21 eV pointed from self-assembly molecule BA-CN (Benzoic acid with CN moiety) layer to aluminum metal due to the negative charge transfer from Al to CN (Z. Hu *et al.*, 2017). Researcher also found charge transfer between the metal and the organic molecule that contributes to the interface dipole when a monolayer of tetrathiafulvalene (TTF) deposit on gold, which modifies the work function of the system (Martínez *et al.*, 2012). Chen *et al.* revealed that the vacuum level
shift (interfacial dipole) of up to 0.45 eV when deposited acceptor-like copperhexadecafluoro-phthalocyanine ($F_{16}CuPc$) on the donor-like CuPc, originated from the interfacial charge transfer involving electron transfer from CuPc to $F_{16}CuPc$ (W. Chen *et al.*, 2008).

2.3.3.3 Pauli Push-back

For a clean metal, while positive charge density from nuclei abruptly drops to zero at the surface, the electron doesn't, rather it spills out into the vacuum. Such a negative charge at the vacuum side creates a surface dipole which couple to the bulk chemical potential, corresponding to the work function on metal surface (Otero *et al.*, 2017). When molecule absorbs on metal, the electron that "spilling out" are pushing back by electron cloud of the adsorbate. Due to the Pauli principle, this push-back effect named as Pauli push-back (Hofmann *et al.*, 2008)(Hofmann 2008), will decrease the "surface dipole" and work function, resulted in interfacial dipole between metal and the adsorbate. Similar effect also named as pillow effect (Vázquez *et al.*, 2007) or cushion effect (Witte *et al.*, 2005). Pauli push-back can explain the interaction between benzene or cyclohexane with copper (Bagus *et al.*, 2005). Besides, Witte *et al.* also reported Pauli repulsion dominates in the case of aromatic molecules on Cu and Au surfaces (Witte *et al.*, 2005). Figure 2.20 represented the Pauli push-back where absorbed molecules reduce the surface dipole with moment of (μ), resulted in the interfacial dipole (Δ) and hole barrier height (Δh) compared with free molecule (based on vacuum level alignment, draw on the right)



Figure 2.20: Illustration of Pauli push-back when molecule adsorbed on metal, a surface dipole of metal reduced with moment of μ , resulted in interfacial dipole (Δ) and hole injection barrier (Δ_h) (Bagus *et al.*, 2005).

2.3.3.4 Permanent Molecular Dipole

A molecule with permanent dipole can contribute to interfacial dipole. Even a non-polar molecule can change the work function, but the net molecular dipole will be more significant if the adsorbed molecules are preferentially oriented (Gomez & Loo, 2010; J.-P. Yang *et al.*, 2017). In order to lower the vacuum energy level on metal, depositing OSCs with ionic or polar pendant group, such as PEIE, ethylene glycol, amino, ammonium salt, and phosphonate functional groups on metal (or ITO, or even PEDOT:PSS) will create a strong interface and molecular dipoles onto the metal surface , lowering the work function of the electrode (X. Peng *et al.*, 2018). Hu *et al.* also found that through Lewis acid–base interactions, the amino groups can push electrons toward the metal (Pauli push-back), creating a dipole layer that effectively reduces the cathode WF (Z. Hu *et al.*, 2017). Recently, Peng *et al.* reported a dipole originated from the positively charged amines (protonated amines) of the cationic nonconjugated polyelectrolytes interacting with the negatively charged terminal oxygen ions of the ITO surface (X. Peng *et al.*, 2018).

The surface engineering by molecular dipole has been successful applying on various OSC devices. An inverted OLED was fabricated by modifying ITO or ZnO with self-assembly molecules, PEI for reduced electron injection barrier (Di *et al.*, 2017; Y.-H. Kim *et al.*, 2014). Single layer of self-assembly molecules with polar tail groups adsorbed on the SiO₂ dielectric layer on OFETs to induce interfacial dipole, in order to tune the turn-on voltage (Zojer *et al.*, 2019). Besides, the dipole molecule, trimethylamine oxide inserted between TiO₂ and perovskite induces the improved energy level alignment for the efficient organic-inorganic perovskite solar cell (Y. Yang *et al.*, 2019).

2.3.3.5 Image Charge

Image charge is a kind of dipole induced by molecule on electrode. Researchers found the adsorption of Xenon (Xe) atoms on various metal surfaces will change the work function of the surface (Knupfer & Paasch, 2005; Zangwill, 1988). Since Xe is an inert gas, there is neither chemisorption nor chemical dipole, which mean interacting weakly with metal. The vacuum level offset is explained by image charge induced inside metal surface by the valence electron of Xe, resulted in electric double layer (Wandelt & Hulse, 1984).

Van Reenen *et al.* suggested the mechanism of image charge relying on the movability of the charge in work function modification layer (WML) as in Figure 2.21 (Van Reenen *et al.*, 2014). Figure 2.21 (a) shows the charge carriers in WML has similar ability to move, hence no dipole is formed. In case (b), the charges in WML have different movability, the negative charge approaching the interface, forming an image charge in the metal substrate. The image charge creates a double electric layer, enhancing the interfacial dipole.



Figure 2.21: (a) The charges in a work function modification layer (WML) always move together (b) The formation of an interfacial dipole when charges in WML has different movability, the interfacial dipole generated by the dipole caused by both WML and image charge. The black line shows the change of work function along with generated dipole (Van Reenen *et al.*, 2014).

Noted that the interfacial dipole at the heterojunction may be the summation of the contribution of any of the combination of charge transfer across interface, Pauli pushback, permanent dipole of molecule or image charge. The dipole must be added or subtracted depend on its direction of the moment.

2.4 OSC Device

2.4.1 Introduction

OSCs have many advantages compared to inorganic as the discussion in early chapter. Among all these advantages, the low-cost of OSCs is the driving force to commercialize the OSC devices, such as OLEDs, OPVs, OFETs, super capacitors, memory devices and many other. The market research conducted by Market Research Future® predicted the global OSC market is expected to grow 22 % yearly from 2018 to 2024, expected the market size will be expanding from USD 53.3 billion in 2018 to USD 179.4 billion in 2024 (MarketResearchFuture®, 2020).

Among all the OSC devices, OLEDs are among the 1st OSC devices to commercially available in the market, and have been adopted in many applications such as, mobile phones, televisions, wearable devices nowadays. Commercial OPVs is available with similar cost compared to silicon-based technology nowadays, however the inferior efficiency and lifetime limited its market to application where silicon-based technology does not fit well such as curved surface (Freitas *et al.*, 2019). At the meantime, researchers had fabricated pressure sensors, wearable electronic prototypes based on OFETs (J. Yang *et al.*, 2018). Besides, the commercialize of OSCs are not limited to OLEDs, OPVs, OFETs, but also on super capacitors (Z. Li *et al.*, 2019) or even biosensors (Hopkins *et al.*, 2019) which are under intense research nowadays.

2.4.2 Interfacial Energy Level in OSC Devices

The basic principles and interfaces in the 3 common OSC devices, OLEDs, OPVs, and OFETs will be briefly discussed in this session. Figure 2.22 shows the device structure and the interfacial energy level for (a) OLED, (b) OPV and (c) OFET.

The simplest OLED device consists of 3 layers, where emissive layer (EML) sandwiches between anode and cathode. Hole transport layer (HTL) and electron transport layer (ETL) are inserted between EML with anode and cathode in order to lower the hole and electron injection barrier, improving the device efficiency. During operation, hole (electron) is injected from anode (cathode) to the HOMO (LUMO) of the transport layer, and subsequently transport to EML. The exciton (hole-electron pair) formed in the EML layer and relaxed by emitting a photon (labeled as "*hv*" in the figure). Noted that upward movement of electron (and downward movement of hole) required extra energy. Therefore, reducing the offset between Fermi level of anode and HOMO of EML by inserting interlayer HTL can reduce the Δ_h (Yeoh *et al.*, 2013). Similar mechanism applied to reducing the Δ_e between cathode and LUMO and EML(Hung *et al.*, 1997). Besides, device engineers prefer large LUMO-LUMO offset between EML and HTL (and HOMO-HOMO offset for EML and ETL) to confine the hole and electron in the EML, so the exciton can be form in EML to harvest all the excitons as photons (Forsythe *et al.*, 1999).



Figure 2.22: The device structure (left) and interfacial energy level (right) for (a) OLED, (b) OPV and (c) OFET. The movement of electron (e) and hole (h) were labelled with dashed arrow. The photon with energy (hv) was labelled to indicate (a) EL in OLED and (b) photoexcitation process in OPV. (Adapted from (Fahlman *et al.*, 2019; Greiner & Lu, 2013; C. Kim *et al.*, 2014))

For OPV, the device structure looks alike with OLED except the absorption layer. The absorption layer (AL) usually consists of a blend of donor and acceptor, where sunlight usually absorbed by donor, generated a photogenerated exciton has a BE up to 1 eV (Cusumano *et al.*, 2020). The exciton can separate into hole and electron only at interface between donor and acceptor, driving by the offset of LUMO-LUMO between donor and acceptor. The open circuit voltage of solar cell correlated to the offset between LUMO of acceptor and HOMO of donor. Therefore, the LUMO of acceptor has to be as high as possible for high open circuit voltage but comes with sufficient degree of offset relative to donor's LUMO to drive the charge separation (Facchetti, 2013). The location of LUMO of ETL between acceptor and cathode, and HOMO of HTL between donor and anode can facilitate the stepwise charge transport. Both OPVs and OLEDs always use transparent conductive oxide such as ITO as anode, due to its optical transparency to visible wavelength, high electric conductivity as well as acceptable high work function (Sohn & Han, 2011).

There are three contacts: source, drain and gate in an OFET. For a p-type OFET as shown in the example, the majority carrier hole will be able to propagate along OSC layer between source and drain only when gate is negatively biased. The negative bias of gate will encourage the hole accumulation at organic/dielectric interface, forming conducting path along the channel indicated by the red dashed arrow in Figure 2.22 (c). The two energy diagrams in the figure shows the interfacial energy level between source-drain (middle) and source-gate regime (right) during charge accumulation regime. The offset between Fermi level of metal and HOMO of OSC indicated a hole injection barrier (Greiner & Lu, 2013). The negative bias on gate electrode bend the HOMO of dielectric and OSC, to facilitate the hole injection toward OSC/dielectric interface (C. Kim *et al.*, 2014).

In this research, OLED was selected as the OSC device to study the effect of blending small molecule HTM to polymer HTM due to the relatively simple of fabrication and testing compared to OPVs and OFETs. Besides, the selected HTMs (PVK, TcTa) are suitable as the host for OLEDs (Lee *et al.*, 2010; Talik, Woon, & Yap, 2016), opens the opportunity to study the effect on the fully solution processable extra warm white OLEDs. Hence, the OLEDs will be discussed in detail in the coming section.

2.4.3 **OLEDs**

2.4.3.1 History of OLEDs

The first OSCs based EL demonstrated in 1960s paved the way for the development of OLEDs (Helfrich & Schneider, 1965; Pope *et al.*, 1963; Sano *et al.*, 1965). However, until late 1970s, the reported EL by OSCs required high voltage (> 100 V) for significant light output due to the limitation of crystal thickness (> 1 mm). The early researches also based on small molecule crystal such as anthracene (Roberts *et al.*, 1979; Wittmer & Zschokke - Gränacher, 1975), Porphyrin (Kampas & Gouterman, 1977), Pyrene (Basurto & Burshtein, 1975) and others. In 1974, Kaneto *et al.* reported first EL based on polymer, by applying 1 kV pulse voltage on 25 μ m of polyethylene terephthalate (Kaneto *et al.*, 1974). The early development of OLEDs not only hindered by the high driving voltage, but also the poor efficiency (external quantum efficiency (EQE ~0.05 %)) and lack of long-term stability (Vincett *et al.*, 1982).

In 1987, Tang & Vanslyke from Kodak fabricated the first practical OLED with direct voltage of less than 10 V but brightness higher than 1000 cd/m² and EQE as high as 1 %, by sandwiching HTL (diamine based compound) and EML (Tris(8-hydroxyquinolinato) aluminum) between ITO anode and Mg:Ag cathode using vacuum deposition (C. W. Tang & VanSlyke, 1987). Three years later, the first practical polymer LED (PLED) was invented by Burroughes *et al.* using 100 nm thick films of poly (p-phenylene vinylene) with operating voltage of 15 V (Burroughes *et al.*, 1990).

A breakthrough in OLEDs was made by Forrest and his team in 1998 to fabricate the phosphorescence OLEDs (PhOLEDs) by doping organometallic complex with heavy metal center (such as Pt, Ir) in the host to harvest the triplet energy by its large spin-orbit coupling (SOC), increasing the internal quantum efficiency (IQE) up to 3 times higher compared to fluorescent based OLEDs (Adachi *et al.*, 2001; Baldo *et al.*, 1998). Since 2009, many researchers reported OLEDs materials based on thermally activated delayed fluorescence (TADF), first discovered by Adachi group (Endo *et al.*, 2009; Endo *et al.*, 2011; Uoyama *et al.*, 2012). TADF materials featured small singlet-triplet energy gap, increased the reverse intersystem crossing (RISC) to harvest all the triplet energy but the cost is much lower compared to PhOLEDs, which required the precious metal such as Pt and Ir.

Besides, the advance of OLEDs also can be seen in term of efficiency too. The first white OLEDs (WOLEDs) was fabricated by Kido *et al.*, with power efficiency of 0.83lm/W (Kido *et al.*, 1994). In 2009, the world first WOLEDs with power efficiency (PE) higher than 100 lm/W was reported, which is comparable to efficiency of fluorescent tube (Reineke *et al.*, 2009). Recently a WOLED with extremely high PE of 168.5 lm/W and excellent EQE of 72.4 % was reported (Xiang *et al.*, 2018). The high efficiency WOLEDs have a potential to replace fluorescent tubes and LEDs as next generation of solid-state lighting in future.

However, the efficiency achieved by vacuum deposition is still far exceed solution process (wet process). To date, the solution processable WOLEDs with efficiency as high as 34.9 lm/W (Jou *et al.*, 2012) and EQE as high as 24.5 % (Singh *et al.*, 2018) were reported. Compared to vacuum deposition which required expensive ultra-high vacuum system, solution process offers numerous advantages, such as low cost, saving material, high throughput, large-area sample size as well as able to produce on flexible substrate. In this work, the WOLED fabrication in this research was based on solution processing.

2.4.3.2 Operational Principle of OLEDs

The operation of OLEDs is based on 4 processes: (a) charge injection, (b) charge transportation, (c) charge recombination and (d) light emission as illustrated in Figure 2.23. Optimizing all these processes will be of paramount important for device efficiency. The detail of the processes will be depicted in section below.



Figure 2.23: The illustration of the working principle of OLED based on the energy diagram. The hole (electron) is first (a) injecting from electrode to HTL (ETL), then (b) transporting along HTL (ETL) before injected to EML. The hole and electron (c) recombine in EML, forming an exciton and subsequent (d) radiative decay by emitting a photon. The horizontal line at HOMO and LUMO indicated the occupied (unoccupied) sites, the energy sites distribution with a Gaussian distribution due to the energetic disorder. The red and blue arrow indicate the transfer route of hole and electron, respectively.

2.4.3.2.1 Charge Injection

Referring to device structure and energy band diagram of OLED in Figure 2.23, the hole (electron) is first injected from anode (cathode) to HTL (ETL). The hole and electron then transported across the HTL and ETL before injected again into EML. The metal/organic and organic/organic interface will determine the injection properties. The HTL(ETL) is chosen so its HOMO (LUMO) is between Fermi level of electrode and

EML to reduce the injection barrier between electrode and EML as shown in Figure 2.23 (a). Choosing an anode with high work function, or cathode with low work function can reduce the injection barrier (P. Li *et al.*, 2019; X. Peng *et al.*, 2018), by pinning the Fermi level near the HOMO and LUMO, respectively.

However, the injection barrier can be affected by many factors, such as FLP, interfacial dipole as well as bend banding at metal/organic interface (Q.-H. Wu, 2013; J.-P. Yang *et al.*, 2017; Y. Zhou *et al.*, 2012). Yang *et al.* found the injection barrier at metal/organic cannot minimize to 0 eV due to FLP (J.-P. Yang *et al.*, 2017). The minimal injection barrier can be approximated to twice the DOS of HOMO (σ_H) and LUMO (σ_L) for organic/anode and organic/cathode interface, respectively (J.-P. Yang *et al.*, 2017). Hence reducing the DOS of frontier energy seemed to be a promising step to achieve ohmic contact.

The injection barrier between HTL (ETL) and EML generally can be predicted by vacuum level alignment if the interaction between organic/organic interface weakly. However, vacuum level alignment was found to be valid only when Fermi level of OSC near the middle of HOMO-LUMO gap position (J. X. Tang *et al.*, 2007). Since the theoretical framework for organic/organic still under developing, the best way to validate the injection barrier of organic/organic interface still rely on photoemission experiment.

2.4.3.2.2 Charge Transportation

The hole and electron transport along HOMO of HTL and LUMO of ETL, respectively by hopping. The occupied (unoccupied) energy sites are represented by horizontal line at HOMO (LUMO) as shown in Figure 2.23 (b). Due to the positional disorder and energy disorder exhibited by hopping sites, the charge transport in OSCs can be described by VRH or BDG model as discussed in section 2.2.3.2. The VRH and BDG model can correlate the mobility of the OSCs with the Gaussian disorder in both position

and energy. The mobility of OSCs can be experimental determined by TOF, SCLC or field effect measurement.

Noted that the electron located at higher energy level has a higher potential energy, hence upward hopping is thermal activated while downward hopping can occur spontaneously as it is an energy releasing process. For similar reason, the downward hopping for hole is thermal activated. Therefore, the large energy barrier between electrode and EML will reduce the charge carrier significantly. For the design of OLEDs, the selection of HTL (ETL) are based on three criterions. Firstly, the HOMO of HTL (LUMO of ETL) need to locate between and Fermi level of electrode and HOMO (LUMO) of EML in order to reduce the injection barrier (Yeoh et al., 2013). Secondly, the large LUMO-LUMO (HOMO-HOMO) offset between HTL (ETL) with EML is preferred in order to block the electron (hole) from reaching the electrode, thus confine the charge carrier in the EML (S.-Y. Lu et al., 2018). Thirdly, high mobility for hole in HTL (electron in ETL) for effective charge transport. The hole mobility (in HTL) need to match the electron mobility (in ETL) for a balance charge injection (Negi et al., 2018). The time taken for carrier to reach EML depends on mobility and thickness. The thickness of HTL can vary in case there is slightly mismatch in mobility in order the charge recombination to occur at the center of EML. Narayan et al. reported recombination near to electrode leading to a higher probability of non-radiative decay (Narayan et al., 2013).

2.4.3.2.3 Charge Recombination

When an electron and a hole reach the recombination zone (design to be located at the center of EML), an exciton will form immediately (due to the significant large BE). Exciton is a type of quasi-particle, an electron-hole pair bounded together by electrostatic force, which can migrate as a whole. The BE of exciton is in the order of 0.1 eV to 1 eV (Knupfer, 2003), one order higher than inorganic semiconductor (~0.01 eV) (Burgelman *et al.*, 2006) due to the low dielectric constant of OSC. Besides, while the excitons of

inorganic semiconductor are delocalized over many lattice spaces, the exciton of OSCs are localized on molecules. The exciton can only migrate to neighboring molecule through hopping.



Figure 2.24: (a) Two different spin states of exciton: singlet (S_1) and triplet (T_1) , when hole and electron are coulombically bounded. The direction of arrow indicates the spin state of electron. (b) Vectoral diagram of two electron spins for singlet and triplet states. The $\alpha\beta$ denoted spin wavefunction of electron and the subscript 1 and 2 refer to first and second electron, respectively. (Adapted based on (Köhler & Bässler, 2009))

When electron and hole recombine, the generated excitons have two different spin states: singlet (*Si*) and triplet (*Ti*), both excited states have energy higher than ground state (*So*) as shown in Figure 2.24 (a). However, the triplet state has a lower energy than the singlet, as maximum spin multiplicity has the lowest energy as stated in Hund's rule (Atkins & De Paula, 2006). Figure 2.24 (b) shows the vector diagram of the spin configuration of two electrons system. The $\alpha\beta$ denoted spin wavefunction of electron and the subscript 1 and 2 refer to first and second electron, respectively. Noted that two-electron system can have four possible spin states: $\alpha_1\beta_2-\beta_1\alpha_2$, $\beta_1\beta_2$, $\alpha_1\beta_2+\beta_1\alpha_2$ and $\alpha_1\alpha_2$. The resultant eigenstate for two-electron system can described by eigenvalues *S* and *Ms*, where *S* is the spin angular momentum and *Ms* is its z-component. Both $\alpha_1\beta_2-\beta_1\alpha_2$ and $\alpha_1\beta_2+\beta_1\alpha_2$ configurations look similar in term of *Ms* =0 but only the spin in $\alpha_1\beta_2-\beta_1\alpha_2$ configuration is 180° out of phase. Hence, $\alpha_1\beta_2-\beta_1\alpha_2$ is the only arrangement with singlet states (*S*=0) and other 3 with *S*=1 are denoted as triplet states. Therefore, the probability of excitons in singlet and triplet state are 25% and 75%. Both singlet and triplet states can

radiatively decay by emitting photon, known as fluorescence and phosphorescence, which will be described in next section.

2.4.3.2.4 Radiative Decay

The exciton formed by charge recombination can decay by a few routes with different lifetimes, either radiatively decay (fluorescence, phosphorescence) or non-radiatively decay, such as: intersystem crossing (ISC), internal conversion (IC) and vibrational relaxation (VR) as shown by Jablonski diagram in Figure 2.25.





The singlet and triplet states are divided to left and right panels, respectively in Jablonski diagram. The singlet exciton can radiatively decay via fluorescence easily as the lifetime in ns scale. However, the phosphorescence (radiative decay of triplet exciton) comes with the lifetime in ms scale (at low temperature \sim 77K), as it is spin forbidden for triplet excitons to return to singlet ground state, according to Pauli exclusion principle.

The dash line in Figure 2.25 shows the vibrational energy level above singlet and triplet state. The VR has a lifetime ~ ps. Hence, fluorescence always occurs with a longer wavelength after vibration energy dissipation to the surrounding often involves molecular reorganization, known as Stokes shift. A higher singlet state (S_n) or triplet state (T_n) can undergo IC to a higher vibrational level of lower singlet or triplet state and continue VR routes until reaching the ground state. Besides, a singlet state can transform to triplet state by ISC when vibration level of these two states overlapping.



Figure 2.26: The working principle of PhOLEDs by illustration the dynamic of exciton formation. (Adapted from (Yersin, 2004))

Since phosphorescence comes with the longest lifetime among all the processes, phosphorescence is unable to compete with IC and VR as relaxation path. Therefore, 75% of the energy in exciton (triplet exciton) are lost into heat in fluorescence OLEDs, limited the maximum IQE to 25 % (Segal *et al.*, 2003). In 1998, PhOLED was first fabricated by doping organometallic complex with transition metal to harvest light from both singlet and triplet, resulting in IQE of nearly 100 % (Adachi *et al.*, 2001). Figure 2.26 shows the working principle of PhOLEDs (Yersin, 2004). The hole is trapped at doped phosphorescent emitter (host) while electron in the LUMO of the matrix (guest). When

electron-hole separation reduced, exciton formed in the matrix due to Coulombic attraction, with singlet: triplet ratio of 1:3. The S_n and T_n in the matrix then transfers to the S_n and T_n in emitter via S-path and T-path, respectively. Noted that PhOLEDs do not show fluorescence due to the large SOC facilitating the efficient ISC, turning the singlet state into triplet state. Due to the large SOC, the lowest triplet state (T_l) can easily radiatively decay (phosphorescence) in time scale of ~µs, which is competitive with other non-radiative decay.

The charge transfer from host to guest (S-path and T-paths) are based on two different mechanisms, long-range Förster and short-range Dexter energy transfer. The singlet exciton in the host (S-path in the diagram) can transfer energy to guest through both Förster and Dexter energy transfer. Meanwhile, the energy in triplet exciton of the host can only be transferred to guest by Dexter energy transfer only (T-path in the diagram). Hence, it is of paramount important to optimize both Förster and Dexter energy transfer to approach 100% IQE.

The mechanism of (a) Förster energy transfer and (b) Dexter energy transfer are illustrated in Figure 2.27 above. For Förster energy transfer, when the exciton (S_1) in host return to ground state (S_0), the energy is released as a virtual photon, which immediately received by guest and subsequently form an exciton in guest. The columbic interaction between host and guest will be enhanced by the overlapping of emission spectra of host and the absorption spectra of guest. The Dexter energy transfer takes place by exchanging electron, which required the overlapping of wavefunction (electron cloud) between host and guest. Hence the Dexter energy transfer required interatomic distance (<0.5 nm) (Olaya-Castro & Scholes, 2011), much shorter than effective distance of Förster energy transfer, which is 2-10 nm (Deniz *et al.*, 1999).



Figure 2.27: Mechanism of (a) Förster energy transfer and (b) Dexter energy transfer from host (donor) to guest (acceptor). The top and bottom vertical bar indicated the lowest excited state $(S_1 \text{ or } T_1)$ and ground state (S_0) , respectively. The blue and red symbol represents the excited electron in the host and the ground state electron, respectively. The star symbol represents the electron that undergo energy transfer process. (Adapted from (Martins *et al.*, 2018))

Since triplet exciton consist of 75 % of total exciton according to spin statistics, it is important to ensure adequate concentration of phosphorescent dopant in PhOLEDs to ensure efficient Dexter energy transfer. While increasing dopant concentration can reduce the distance between host and guest to facilitate Dexter energy transfer, however further increase of dopant concentration may deteriorate performance due to triplet-triplet annihilation between closely separated dopant-dopant (Kwon *et al.*, 2009)(Kwon 2019). Beside concentration of dopant, the efficiency of PhOLEDs are depending on several factors such as: the overlapping of emission spectra of host with the absorption spectra of dopant, the triplet energy level of host must be higher compared to the guest to prevent energy back transfer (Kai Lin Woon *et al.*, 2015). The efficiency of OLEDs will be further discussed in coming session.

2.4.3.3 **PEDOT:PSS**

PEDOT:PSS is one of the most successful conductive p-type polymers, widely used in OSC devices nowadays. The relative high work function, electrically conductive, optical transparency to visible light, thermally stable and electrochemical stable of solution processable PEDOT:PSS make it a suitable candidate for HTL in OLEDs and OPVs.

The highly conductivity of PEDOT:PSS are contributed by the oxidized (doped) conjugated backbone of PEDOT. The oxidized poly (3,4-ethylenedioxythiophene (PEDOT) has maximum one positive charge per three monomer units, with the hole polaron delocalized over the three monomers forming a quinoid structure (D. Kim & Zozoulenko, 2019) as shown in Figure 2.28 (a). However, PEDOT alone is insoluble in most solvents, affecting its processability. By doping PEDOT with water soluble poly (4-tyrenesulfonic acid) (PSS), the PEDOT oligomers can intermix with PSS chain by the electron located at the deprotonated sulfonate side group and coils up to form a colloidal structure as shown in Figure 2.28 (b).



Figure 2.28: (a) The chemical structure of PEDOT and PSS, (b) The colloidal structure formed by doping PEDOT with PSS (L. Hu, Song, Yin, Zhen, *et al.*, 2020).

Unmodified PEDOT:PSS has work function 4.85 eV - 5.15 eV depending on the type of PEDOT:PSS (Park *et al.*, 2012; S. Wu *et al.*, 2011) commonly serves as anode modifier material. However, the host of the EML typically have wide HOMO-LUMO gap and high triplet energy to facilitate energy transfer to guest, especially blue phosphor. The common host materials for blue PhOLEDs (Jung & Lee, 2020) usually showed

HOMO (IP) deeper than 5.5 eV and LUMO (EA) swallower than 3.0 eV as shown in Table 2.1. Therefore, device engineers are looking for the anode with work function higher than 5.5 eV, or cathode with work function lower than 3.0 eV to reduce the injection barrier with EML.

Much efforts had been devoted on deepening the work function of PEDOT:PSS, such as metal oxide doping (Kanwat & Jang, 2016), surface treatment with alkyl alcohol (Lenze *et al.*, 2015) or additional of Nafion (Mauger *et al.*, 2014; Yeoh *et al.*, 2013) to increase the work function of PEDOT:PSS to as high as 6 eV. Meanwhile, the research on lowering the work function of PEDOT:PSS is underway, including surface modified with polyethylenimine to reduce the work function to 4 eV (Z. Li, Liang, *et al.*, 2015; S. Zhang *et al.*, 2015). In this research, the PEDOT:PSS was n-doped in order reduce the work function to as low as 3.6 eV, potentially served as ETL in full solution processable OSC devices.

Common Host Materials in PhOLEDs	HOMO	LUMO	Reference
	(eV)	(eV)	
PVK	5.8	2.2	(Kumar & Pereira, 2020)
CBP	5.6	2.3	(T. Zhang <i>et al.</i> , 2013)
MCP (1,3-bis(n-carbazolyl)benzene)	6.1	2.4	(Kumar & Pereira, 2020)
ТсТа	5.7	2.4	(Y. Chen <i>et al.</i> , 2012)
TPBi (1,3,5-tris(2- nphenylbenzimidazolyl) benzene)	6.7	2.7	(Anthopoulos <i>et al.</i> , 2003)
TPO (1,3,5- tris(diphenylphosphoryl)benzene)	7.1	2.8	(Ban <i>et al.</i> , 2016)
TAPC (di-[4-(N,N-ditolyl-amino)- phenyl]cyclohexane)	5.5	2.0	(Jou <i>et al.</i> , 2015)

 Table 2.1: HOMO and LUMO for common materials for Host in blue PhOLEDs.

2.4.3.4 Efficiency

The efficiency of OLEDs is widely evaluated by several parameters, such as: IQE, external quantum efficiency (EQE), current efficiency (CE) or power efficiency (PE).

IQE (η_{int}) is given by the ratio between number of photons generated and the number of injected charge carrier as shown in Equation 2.15. Hence, IQE measures the efficiency of conversion of electrons to protons. IQE depends on 3 variables: photoluminescence quantum efficiency of the emitter (ϕ_{pl}), ratio of hole to electron (γ) and fraction of luminescent excitations based on spin statistics (η_{sl}). The photoluminescence quantum efficiency of the emitter can be close to unity by optimizing the emitter molecule. The ratio of hole to electron is depending on the mobility and thickness of HTL, ETL as well is EML. By choosing phosphorescent or TADF emitter, the η_{sl} can be improved from 25 % to 100 % by harvesting light from nearly all the excitons, Adachi *et al.* fabricated a PhOLEDs with IQE nearly unity by optimized all the 3 parameters above (Adachi *et al.*, 2001).

$$\eta_{int} = \frac{number \ of \ photon \ generated}{number \ of \ injected \ charge \ carrier} = \phi_{pl} \ \gamma \ \eta_{st}$$
(2.15)

Equation 2.16 shows that EQE (η_{ext}) is given by the ratio of number of photons emitted from the surface of the OLEDs to the number of injected charge carrier. The EQE is the product of both η_{int} and out-coupling efficiency (η_{out}). While η_{int} can be optimized to unity, the out-coupling efficiency are typically below 0.3 for OLEDs before optimization (Gather & Reineke, 2015; Youn *et al.*, 2015). The losses are mainly caused by the total internal reflection due to the variation of refractive index of different layer, which trapping the light in substrate (~23 %), in organic layer via waveguide mode (~15 %) as well as surface plasmon at cathode (~40 %) in OLEDs (Zou *et al.*, 2020). Efforts such as refraction index matching, corrugate structure on substrate and additional of micro lens on the substrate can enhance the EQE up to 63 % (Youn *et al.*, 2015).

$$\eta_{ext} = \frac{number \ of \ photon \ emitted \ from \ surface \ of \ OLEDs}{number \ of \ injected \ charge \ carrier} = \eta_{int} \ \eta_{out}$$
(2.16)

CE(η_L) and PE (η_P) are commonly used to measure efficiency of OLEDs, especially WOLEDs. Both CE and PE take into account the response of human eye over wavelength of light, known as spectral luminosity efficiency. Figure 2.29 is the normalized spectral luminosity efficiency standardize, $K(\lambda)$ for photopic vision (well-lit condition) published by International Commission on Illumination (CIE) in 1924. Noted that human eyes are more sensitive to green light than other colours, as shown by the peak at 555 nm in the diagram. CE are calculated based on luminance (*L*) over current density (*J*) as shown in Equation 2.17. For a Lambertian surface such as OLED, which apparent brightness is same regardless of angle of view (Kawabata & Ohno, 2013), the PE can be obtained from η_L and applied voltage (*V*) as Equation 2.18. In this research, the efficiency of the fabricated extra warm WOLEDs was evaluated with both CE and PE.



Figure 2.29: The spectral luminous efficiency for photopic vision versus wavelength (nm), standardize by CIE in 1924 (Modest, 2003).

2.4.3.5 Colour Temperature

The colour of lighting is commonly defined by 2 dimensional chromaticity coordinates (x, y) based on CIE 1931 standard. Figure 2.30 illustrated the CIE 1931 xy chromaticity space with all the visible colour contained inside the horseshoe-shaped locus. The boundary of colour space covering all the monochromatic colour with wavelength ranging from 380 nm – 700 nm as seen in the diagram. The line joining blue end (380 nm) and red end (700 nm) formed "line of purple" in figure, as purple is colour resulted from mixing two monochromatic blue and red. Hence, the white colour, resulted from mixing of red, green and blue (RGB) located at the center of colour space.

In case of white lighting, correlated colour temperature (CCT) are commonly employed to compare the colour temperature of the device with reference to the colour temperature of ideal blackbody radiator. The corresponding CIE coordinate for the locus of CCT, known as Planckian locus are overlay with CIE 1931 colour space in Figure 2.30. Noted that CCT only valid if the light source has small deviation of CIE coordinate with Planckian locus. The light with CCT between 2700 – 3500 K appears as warm white, while a cool white light has CCT between 4500- 7500 K (Choudhury 2014). Generally, warmer colour can promote relaxation and comfortable, while cooler colour can enhance concentration. The studies conducted recently showed that cool white night lighting can suppressed the secretion of melatonin, a hormone that regulates the sleep–wake cycle, leading to insomnia or even cancer (Kozaki *et al.*, 2008; Pauley, 2004; Sato *et al.*, 2005; Srinivasan *et al.*, 2008). Therefore, a high efficiency warm WOLEDs become an especially attractive option as night lighting. In this research, an extra warm WOLEDs with CCT around 2500 K was successful fabricated by optimized the ratio between three primary colour phosphorescent dopants.



Figure 2.30: The colour space illustrated by CIE 1931 xy chromaticity space. The correlated colour temperature are overlay with the colour space (adapted from (Kunkel *et al.*, 2016)).

CHAPTER 3: METHODOLOGY

3.1 Introduction

In this chapter, the characterization technique and device fabrication are presented. This chapter begins with the description of four types of synchrotron based measurement technique applied in this research included: UPS, XPS, NEXAFS Spectroscopy and GIXRD. All the synchrotron-based techniques are conducted in Thailand once/twice a year as this advanced characterization system is not available locally and usually required booking as early as six months before. All these synchrotron-based techniques are important in this research to explore the electronic energy, chemical composition, chemical environment, crystallinity and many more in OSC devices. All the techniques above are presented based on the sequence as below: the system setup, basic principles, data acquisition system and data analysis of the measurement system. The device (OLEDs) fabrication as well as the electrical measurement are also described. This chapter ends with the explanation of other characterization techniques such as: UV-Vis measurement, EL measurement, pH measurement, Surface Profiler and AFM.

3.2 Introduction of the Synchrotron System

The early UPS experiment use helium gas discharge lamp, which emitting photon with energy 21.2 eV. The development of synchrotron light source allows very brilliant (high number of photons per area), highly focus and intense of ultraviolet light to study our sample. By bending high speed electron (99.99999% of the speed of light for electron with energy of 1.2GeV) using strong magnet, coherent light can be produced before directing to beamlines (end station). All the UPS measurements in this work were performed by beamline 3.2a:PES in Synchrotron Light Research Institute (SLRI), Thailand.



Figure 3.1: The layout of Synchrotron facilities in SLRI, Thailand.

Figure 3.1 shows the layout of the synchrotron light source in SLRI. The electron generated by electron gun (1) was pulled toward linear accelerator (2) to accelerate the electron to 40 MeV by microwave radiation. Subsequently, the electron was fed to booster ring (3) to accelerate the electron in circular motion by radio frequency (RF) wave to 1GeV. Then, the electron was transferred to storage ring to further increase the energy of electron to 1.2GeV. Storage ring consists of various type magnets to focus and align electron beam and RF booster to recover the energy of the electron after losing energy in

term of light for every circulation. Bending magnets, and other insertion devices (series of magnet), such as undulator or wiggler are installed before beamline (5) to bend the path of electron beam, where the acceleration (due to bending) of electron will generate light necessary to perform experiments at end station (6). There are multiple of optics, including diffraction grating and monochromator along the beamline to choose the wavelength appropriate for the technique required for the end station (such as ultraviolet for UPS). Noted that the storage ring is keeping under ultra-high vacuum of 10⁻¹⁰ torr to minimize the loss of electron due to the collision of electron with air particle.

3.3 Ultraviolet Photoelectron Spectroscopy (UPS) Measurement

UPS are used to determine the surface state and valence state of matter. As implied by its name, UPS uses ultraviolet as light source to induce photoelectron from the sample, so an electron analyzer can be used to measure its KE spectra. UPS using ultraviolet with energy ranging from 10 to 124 eV (Naik, 2017).

3.3.1 Introduction of the UPS System

Figure 3.2 shows the schematic diagram of beamline 3.2a, illustrates how the light paths originated from undulator (U60) to sample chamber (label as UPS/XPS) along with various mirrors (label as M), slits (label as S) and Varied Line Spacing Plane Grating (VLSPG) Monochromator. The light supplied to beamline 3.2a contains photon with energy between 40 eV to 1040 eV. The selection of photon energy was done by rotating VLSPG Monochromator with 600, 1200 and 2400 lines/mm diffraction grating corresponding to 40-160 eV, 220-520 eV and 440-1040 eV respectively. The first order of diffracted light (with desired energy) will pass through the slit and to be focused with mirror before radiated on sample inside sample chamber (label UPS/XPS). The UPS in this experiment was performed with photon energy of 39.5 eV, due to the minimum photon energy of 40 eV at beamline 3.2, limited by minimum undulator gap of 26mm (Songsiriritthigul *et al.*, 2007).



Figure 3.2: Schematic diagram of beamline 3.2a in SLRI

The UPS/XPS sample chamber in beamline 3.2a was shown in Figure 3.3 (a). Figure 3.2 (b) shows 6 different organic samples on ITO adhering to the sample holder by carbon tape before loading to transfer chamber prior to UPS measurement. The sample was prepared in University of Malaya 2-3 days before departing to SLRI to minimize the degradation. The sample spin coated on pre-patterned ITO, which were ultrasonically cleaned using DI water, acetone, isopropyl alcohol and DI water again for 10 min, followed by oxygen plasma treatment for 5 min. The fabricated samples were then annealed in glovebox with 120 °C for 10 min. Each sample was adhered to the base of sample container with double sided tape to avoid flipping during transportation. Finally, all the samples were vacuum sealed with home vacuum sealer to mediate degradation.

The sample holder is a stainless-steel plate with dimension 28 mm x 94 mm x 2 mm. The sample must be prepared on a conductive surface, such as ITO coated glass, gold, copper tape to avoid charging (the deficient of electron) due to photoelectron during UPS. As ITO coated glass is only conductive on surface, ITO coated glass must form a conductive path with the sample holder by carbon taping between them when mounting different samples on holder as shown in Figure 3.3 (b), to allow compensation of loss electron on sample after photoelectron.

The sample holder was sliding to manipulator (HPT xyz translator) inside transfer chamber and the gas in the chamber was removed (by pumping down to $1x 10^{-5}$ mbar, which take about 30 minutes) before transferring to UPS/ XPS chamber (with around 1x 10^{-9} mbar). The orientation of the sample can be manipulated by HPT xyz translator. The pressure inside the chamber is in an ultra-high vacuum (UHV) for few reasons, including avoid the contamination of sample due to the adsorption of residual gas on sample during the experiment, avoid the scattering of photoelectron with gas molecule and to prolong the lifetime of electron analyzer. The light source from synchrotron will be incident on sample inside UPS / XPS chamber. The position of each sample was first determined by incident with zero-order (the direct reflection light on the diffraction grating), which contains all visible, ultra-violet and x-ray, and recorded on logbook for UPS measurement later. The Gold sample (prepared by vacuum deposited of gold on ITO coated glass, as shown in the right most sample in Figure 3.2 b) is the most common pristine sample for UPS or XPS. LabVIEW program (as shown in Figure 3.3 c) was used to control and data acquisition for UPS measurement.



Figure 3.3: (a) The UPS/XPS chamber (coupled with electron analyzer Thermo CLAM2), (b) the sample holder, (c) LabVIEW program for beamline control and data acquisition for UPS.

3.3.2 Introduction of UPS Data Acquisition

The schematic diagram of UPS measurement system in beamline 3.2a is illustrated on Figure 3.4. To begin the UPS measurement, the position of grating (determined by the photon energy), pass energy, the range, step and number of scan for KE were pre-set on the home developed LabVIEW program before pressing "Start" to initiate measurement. The photon energy for UPS was chosen to be 39.5 eV because the photon energy in beamline 3.2a can range from 40 eV to 1040 eV due to the design of undulator, thus the minimum value of photon energy was selected. The pass energy with 81.92 eV was chosen for all the UPS measurement. The KE will be setting to 6-12 eV (step 0.02 eV), 0-50 eV (step 0.1 eV) and 36-46 eV (step 0.02 eV) for high energy cut-off (HECO), wide scan and low energy cut-off (LECO) respectively. The number of scan was pre-set to one and can be increase to improve the signal - noise ratio.



Figure 3.4: Schematic diagram of UPS measurement system in beamline 3.2a

During measurement, the photoelectron emitted when ultra-violet incident on sample will be transmitted to angle-integral electron analyzer (model CLAM2, Thermo VG Scientific). The electron analyzer applied retarding potential before entrance slit to filter electron and only electron with specific KE can pass through the exit slit of analyzer at once. A single channel electron multiplier installed at the exit slit measures the amount of electron and output the count to LabVIEW. By varying retarding potential, the count of electron over different KE can be obtained and feedback to computer. LabVIEW will display the real time data in term of electron count versus KE of electron. The data will automatically be logged as ASCII formatted file in computer to be further analysis with dedicated software.

3.3.3 Principle of UPS

The working principle of UPS measurement is based on photoelectric effect, described mathematically by Albert Einstein on 1905. According to Einstein's photoelectric law, the maximum KE of photoelectron (KE_{max}) for metal (such as gold) can be described by Equation 3.1, where *h* is the Plank's constant, *v* is the frequency of photon (light source) and Φ is the work function of metal.

$$\Phi = h\nu - KE_{max} \tag{3.1}$$

This photoelectric law basically is based on conservation of energy and the properties of light as a particle (photon), where the work function (minimum work required to eject an electron for metal) is equal to the different between photon energy and maximum KE of the photoelectron.

The advance of technology in instrumentation, engineering and physics allowed the KE of electron to be studied in depth beside its maximum KE (KE_{max}). The electron analyzer in beamline 3.2a using retarding potential to record the count of electron over different KE of electron. As lower photon energy of ultraviolet used in UPS, only the electrons around the VB are excited. The acquired spectral provides two electronic information including work function and VB for OSC. Figure 3.5 illustrates the working principle of UPS with energy level alignment for (a) metal and (b) metal/organic layer interface. The spectrum displays the count of electron over KE in the vertical axis. Noted that the e^{-} symbol in the diagram indicates the maximum occupied state of electron for metal and OSC.



Figure 3.5: The principle of UPS for metal/organic interface. The photoemission of (a) metal and (b) metal/organic layer interface was shown with the *e*⁻ symbol indicated the highest occupied state. The spectrum displays the electron count versus KE of electron while the inset shows the magnified view for Fermi edge of metal. The HECO and LECO is labelled on the spectrum (H. Ishii & Seki, 1997).

For metal (such as gold in this thesis), UPS measurement started by incident

ultraviolet light with photon energy hv on metal surface, the electron beneath Fermi level (E_F) are excited and emitted to vacuum with KE reflected the DOS of occupied states. The spectrum contains HECO and LECO, corresponding to E_F and Vacuum level (E_{Vac} (*Metal*)), respectively. The work function of metal (Φ_{Metal}) is obtained by finding the different between hv and KE_{max} as photoelectric law (Equation 3.1). For metal, the E_F can be easily identified by observing the Fermi-Dirac distribution of Fermi edge (the magnified spectrum shown in the inset). In short, the Fermi level and work function for metal can be determined by UPS.

For metal/OSC interface, the excited electron originated from HOMO level in organic material. Noted OSC don't have any electron at Fermi level, as the last electron fills up the molecular orbital at HOMO. Figure 3.5 (b) shows the photoemission from organic layer deposited on the metal substrate. The UPS spectrum for OSC is originated from occupied state below HOMO. Therefore, the HECO corresponds to the electron emission from HOMO, while the LECO corresponds to the vacuum level. The difference of LECO between metal and organic material implies the existence of different vacuum level, known as interfacial dipole, Δ . The work function is defined as the different between potential energy at vacuum level relative to E_F (Schulte, 1977). Noted that organic material doesn't have any occupied state at E_F , thus UPS cannot measure the location of E_F from organic layer. However, electrical circuit having similar E_F occurs when chemical potential equilibrium is reached through charge redistribution, named as Fermi level equilibration (Peljo et al., 2016). Therefore, it is critical for UPS to connect all the samples and reference (commonly gold) with carbon tape on metallic sample holder as in Figure 3.3 (b). Afterward, the work function of organic layer (Φ_{Organic}) can be calculated with reference to Fermi level of metal by adding or subtracting Δ from Φ Metal, when interfacial dipole is pointing away or toward the organic layer, respectively. The HECO of metal and organic layer represent the tail of DOS resulted from electron emission from Fermi level of metal and HOMO from organic layer respectively. Therefore, the HOMO level relative to $E_F(E_{HOMO, relative to E_F})$ can be found by finding the different of HECO onset between metal and organic layer. The IE defined as the minimum energy to remove the most loosely bounded valence electron to vacuum, corresponding to the energy difference between HOMO and Evac (Organic). IE can be calculated from $\Phi_{Organic}$ and $E_{HOMO, relative to E_F}$ using Equation 3.2.

$$IE = \Phi_{Organic} + E_{HOMO, relative to E_F}$$
(3.2)

According to Koopman's Theorem (Koopmans, 1934), the BE of electron in orbital i (E_i) is equal to the negative of IE in orbital i (IE_i) as expression by Equation 3.3. Thus, the HOMO (the BE of electron in the highest occupied state) is equal to the first IE.

$$E_i = -IE_i \tag{3.3}$$

3.3.4 Data Analysis of UPS

After UPS measurement, the spectrum raw data will automatically save as CSV format. The raw file contains all the UPS information including the photon energy, KE, count of electron and other information as shown in Figure A. The raw file can be further processed by Microsoft Excel, OriginPro or other software.

While the raw data of UPS informs user about the count of electron versus KE, it is common practice to evaluate UPS spectra with BE since the photoemission peak is a function of BE. The relationship between BE and KE are shown in Equation 3.4 where hv is the photon energy and $\Phi_{\text{Spectrometer}}$ is the work function of spectrometer. However, the hv and $\Phi_{\text{Spectrometer}}$ may vary slightly depending on instrument environment, causing uncertainty in the converting KE to BE. The issue can be solved by spectra calibration if the spectra contain certain features with designated energy, such as the Fermi level of metal can be assigned as BE of 0 eV.

$$BE = h\nu - KE - \Phi_{Spectrometer} \tag{3.4}$$

Figure 3.6 shows an example of UPS spectra, with (a) HECO and (b) LECO represents the work function and HOMO, respectively for PEDOT:PSS and PVK. Noted that the UPS spectra is converted to BE from KE via Equation 3.4. The UPS spectra is first calibrated with gold to locate the E_F, determined by the Fermi-Dirac distribution of Fermi edge before analysis. The HECO onset of PEDOT:PSS and PVK was 34.70 eV and 35.10 eV respectively, determined via linear extrapolation as shown in Figure 3.6 (a). The higher HECO of PVK compared to PEDOT:PSS indicated the formation of interfacial dipole Δ , 0.4eV directed toward PEDOT:PSS. The work function of

PEDOT:PSS and PVK can be found by the difference between photon energy (39.5eV) and HECO onset, which is 4.8 eV and 4.4 eV respectively. Figure 3.6 (b) shows the LECO onset for PVK is 1.86 eV, indicated the HOMO of PVK is 1.86eV below E_F . The HOMO of PVK can be calculated from Equation 3.2 and Equation 3.3 by summation of work function and $E_{HOMO, relative to EF}$, hence, the HOMO_{PVK}= -(4.4+1.86)= -6.26 eV.



Figure 3.6: Example of UPS spectra with (a) HECO and (b) LECO for PEDOT:PSS and PVK

3.4 X-ray Photoelectron Spectroscopy (XPS) Measurement

Both XPS and UPS techniques are different in term of photon energy, where UPS uses UV light source with photon energy 10 - 124 eV (Naik, 2017) while XPS uses X-ray with photon energy ranging from soft x-ray (100 - 2000 eV) to hard x-ray (2500 - 10000 eV) (Starr *et al.*, 2017). The high energy of X-ray radiation can excite the electrons in core-level. The KE of ejected electron is a function of core-level BE, which carries the chemical information such as chemical composition, chemical bonding as well as oxidation state.

3.4.1 The XPS System

The XPS measurement in this thesis was measured with PHI 5000 Versa Probe II, a standalone XPS system belong to the SUT-NANOTEC-SLRI joint research facility at beamline 5.3, SLRI in Thailand. Noted that beamline 3.2a also carries out XPS measurement with Synchrotron as light source. However, due to the limited beam time allocated for UPS measurement in beamline 3.2a, all XPS measurements were carried out via beamline 5.3.

Figure 3.7 shows the (a) XPS system and (b) sample holder of model PHI 5000 Versa Probe II. The schematic diagram of XPS system is quite identical to the UPS system as in Figure 3.4 except the light source of XPS system is Al Ka (1486.6 eV) radiation. The Al Ka refers to the characteristic photon emission when electron transit from "L" shell to "K" shell of Al after Al anode was bombarded by high energy electron beam. A quartz crystal Monochromator was used to reflect and focus the X-ray onto the sample in XPS chamber. Photoelectron will be emitted in all the direction upon the incident of xray. PHI 5000 Versa Probe II using an input lens to attract and focus the photoelectron, enhancing the number of electrons that can get into electron analyzer. The electron analyzer is a hemispherical spherical analyzer, the analyzer applies potential difference across the inner and outer sphere to generate electrostatic field (known as pass energy) to filter the electron according to its KE. Electron with selected range of energy can reach the 16-channel multi-channel detector, where the number of electrons is recorded and converted as XPS spectra at computer. One of the advantages of PHI 5000 Versa Probe II system compared with beamline 3.2a is the availability of Argon ion gun and low energy electron neutralizer to resolve the charging issue, allowing XPS measurement on non-conductive sample (such as polymer). Besides, the Argon ion gun can be used for surface cleaning or sputtering to carry out XPS depth profiling measurement. Similar to UPS, the XPS are running in ultra-high vacuum as low 4.2 x 10⁻⁹ mbar to avoid collision of photoelectron with air molecule as well as to avoid surface contamination due to adsorption of air molecule on sample, since XPS is very surface sensitivity.

During sample preparation, samples will stick to sample holder by double sided tape as shown in Figure 3.7 (b). Compared to sample preparation of UPS as shown in Figure 3.3 (b), the standalone XPS doesn't need to create conductive path between samples and sample holder due to two reasons. Firstly, the electron neutralizer and Argon ion gun is capable to neutralize charging. Secondly, the adventitious carbon was used as reference instead of Fermi level of Gold, where the C1s peak of adventitious carbon was set as 284.8 eV, by default. The number of samples on sample holder in single measurement depends on the size of sample, where 14 samples with size approximate 15 mm x 20 mm can be loaded as shown. The sample holder was loaded inside the transfer chamber and pumping down to high vacuum before transferring to XPS chamber.



Figure 3.7: (a) PHI 5000 Versa Probe II XPS system and (b) preparation of sample on sample holder before transfer to XPS chamber.

3.4.2 Principle of XPS

XPS is a surface sensitivity technique where most of the photoemissions without energy loss are limited to the first few nanometers from the surface layer. Noted that the absorption length of x-ray (the length where X-ray intensity drop to 1/e of its incident flux) depend on element as well as X-ray energy. For X-ray energy of 1.5 keV, the absorption length is quite long, which is between 100 nm (for heavy element) and few μ m (for light element). The absorption length for carbon was calculated to be 10 μ m based on X-ray linear attenuation coefficients database from NIST as shown in Figure B (a). X-ray can penetrate deep into the solid material and initiate photoelectrons there, but
only the photoelectron from the top few atomic layers can escape without losses, which can be seen as the XPS photoelectron peak. The probability of a photoelectron to escape from sample after travel distance *d* without losing energy can be written in terms of Beer-Lambert law as shown in Equation 3.5, where I(d) is the intensity of photoelectron escape without losing energy after travel distance *d*, I_0 is the initial intensity of primary electron, λ_{IMFP} is the inelastic mean free path (IMFP) for photoelectron.

$$\frac{I(d)}{I_0} = e^{-d/\lambda_{IMFP}}$$
(3.5)

Noted that the probability becomes 0.37 (1/e), 0.13 (1/e²) and 0.05 (1/e²) for the photoelectron emitted from λ_{IMFP} , $2\lambda_{IMFP}$ and $3\lambda_{IMFP}$ below the surface, respectively. This equation implies that 37%, 13% and 5% of photoelectron can emerge at surface without losing energy originating from λ_{IMFP} , $2\lambda_{IMFP}$ and $3\lambda_{IMFP}$ depth below the surface. At the meantime, most of the photoelectrons collide with atom or electron inelastically, losing energy and contribute to the background, which will be further discussed later.

The IMFP (λ_{IMFP}) is average distance which an emerging photoelectron can travel before losing energy due to collisions. The universal curve in Figure B (b) shows how IMFP varies across electron KE. Noted that IMFP is a function of photoelectron KE. For Al K-alpha radiation with photon energy of 1486.6 eV, the XPS peaks in terms of K.E usually ranges between 20 eV to 1400 eV, which mean the IMFP varies between 0.5 nm to 2 nm by referring to the Figure B (b). The sampling depth defined as depth from which 95% of all photoelectrons are inelastic scattered when they reach the surface is equal to 3λ . Thus, the sampling depth for XPS system is in the range of 1.5 -6.0 nm. Therefore, XPS using Al k α as a radiation source is commonly quoted to have surface sensitivity up to 10 nm from top of the layer.

For XPS, photoelectrons with different KEs are emitted from core levels. The relationship between KE, BE and hv is given in Equation 3.4. In XPS spectra, the sharp peaks and broad peaks corresponding to photoelectron originated from core level and

Auger electron peaks, respectively, with inelastic collision of electron emerging from the surface as a background. The deeper from the surface, the higher chance of photoelectron generated to suffer inelastic collision with atom or electron before reaching the surface. Such collisions causing the electrons to have a lower KE (but higher BE on XPS spectrum) and hence losing information about chemical states. Noted that every photoelectron that lose its KE will contribute to the background, thus the background will aggregate toward lower KE (higher BE).

Figure C (a) shows the energy level diagram of oxygen atom with vertical arrow representing the XPS photoelectron and Auger electron. The white and black circles represented the hole and the electron on the energy level of an oxygen atom, respectively. Noted that the XPS photoelectron always correlates to the BE, depending on the element and orbital, thus O1s and O2s always show the BE of 543.1 eV and 41.6 eV, respectively, regardless of any value of the photon energy. The Auger electrons is an ejected outer shell electron as a result of relaxation of an inner shell electron into deeper energy level to fill up a hole in core level thereby transferring the excess energy to another shell-electron. Thus, the KE of Auger electron equal to energy gap between outer electron transition downward and the BE of the shell where the electron originated, which is independent on photon energy. Using Figure C (a) as example, the transition of electron from orbital O2s (L₁) to O1s (K) provides an excess energy to eject an Auger electron in orbital O2p (L₂), known as Auger O KLL. The Auger O KLL always has a fix range of KE between 468 eV to 503 eV regardless of photon energy.

Survey scan is a wide scan with complete energy range spectra of low energy resolution. It is always performed before narrow scan to accurately quantify the chemistry composition of the sample. Figure C (b) shows the survey scan of XPS spectra for ITO/PEDOT:PSS sample, which contains carbon, Sulphur and oxygen. The spectra were plotted with the electron counts against vertical axis of KE and BE. There are several

sharp peaks labelled as C1s, O1s and S2p contributed by PEDOT:PSS while In3d, In4d and Sn3d are contributed by the ITO substrate. At low KE side, board peaks were observed corresponding to the Auger electron of oxygen, carbon and indium. The VB can be observed at low BE in XPS spectra too, however the band structure is hard to resolve (compared to UPS) because the low signal to noise ratio, due to the decreasing photoionization cross section (PCS) with increased photon energy (S.-L. Liu, 2016). It is clearly observed that the background increases toward high BE (low KE) as shown in Figure C (b). The dashed arrows relate the photoelectron O1s and Auger electron O KLL in the spectrum to the transition of electron between energy level in oxygen atom.

One of the problems during XPS measurement is the Auger peaks may superpose with the XPS photoelectron peaks. Noted that Auger electron peak and XPS photoelectron are function of KE and BE respectively. Synchrotron based XPS can resolve the issue above by varying the diffraction grating to change the X-ray photon energy peak, hence changing the KE of XPS photoelectron without affect Auger electron. However, the photon energy of PHI 5000 Versa Probe II XPS system with Al kα radiation source is fixed at 1486.6 eV. Figure D shows the KE of Auger Electron for different elements. (Palmberg & Industries, 1972).

It is important to ensure there are no spectral overlapping between the Auger electron and XPS photoelectron for common organic element such as C, N, O, P and S for OSC samples. Table 3.1 tabulates the KE and BE of Auger Electron for Al k α , and BE of photoelectron for common organic molecule. The BE of Auger Electron is obtained by Equation 3.4 (based on hv=1486 eV for Al k α and assume spectrometer work function is zero). There is no overlapping between Auger electron and photoelectron for common organic elements since all the photoelectron located at low BE side (<600 eV) while Auger electron reside to high BE (>900 eV). Noted that the table 3.1 only shows the position of Auger Electron emission and photoelectron for common organic elements,

there are chances of overlapping in case the sample or substrate contain other elements

than listed.

Element	KE of Auger	BE of Auger Electron	BE of XPS		
	Electron Peak (eV)	for Al ka Peak (eV)	Photoelectron Peak (eV)		
С	263 (KLL)	1223 (KLL)	285 (C1s)		
Ν	380(KLL)	1107 (KLL)	398 (N1s)		
0	509(KLL)	978 (KLL)	531(O1s)		
Р	151 (LMM)	1367 (LMM)	130 (P2p1/2)		
S	183 (LMM)	1336 (LMM)	164 (S2p1/2)		

Table 3.1: The peak for KE and BE of Auger Electron, and BE of XPS photoelectron for common organic elements when irradiated with Al kα source.

During XPS measurement, narrow scan with high resolution will be measured on the photoelectron peaks right after the survey scan. The narrow scan is useful for in depth study of the chemical composition, chemical shifts (chemical bonding) in different chemical environments, as well as the oxidation states. The area under the peak is a function of atomic percentage of element as well as PCS. PCS refers to the probability of an electron being emitted from its electronic state when excited by a photon. Various theoretical method for PCS had been proposed based on the approximation of frozen nuclei approximation (Frank-Condon principle suggested electronic transition is most likely to occur without changes in nuclei position) (Cacelli *et al.*, 1992). PCS are dependent on photon energy, elements as well as the electron's energy level. For Al ka source, the PCS is used to normalize peak for various elements with C1s as reference are summarized as in Figure E (a) (Scofield, 1976).

Another alternative method to normalize XPS peak is atomic sensitivity factor (ASF), which values were determined by experiment with F1s as reference. ASF was slightly different compared to PCS due to the spectrometer transmission function, which is machine dependent. Figure E (b) shows both PCS (left axis) and ASF (right axis) agree well to each other, indicating a good agreement of calculation with experiment (Wagner *et al.*, 1981). In this thesis, the area under the peak is converted to the atomic percentage by dividing with ASF, to obtain the chemical composition (or even empirical formula).

$$BE = -E_{HF}^{\ atom} + V_{ia} - R_{ia} + V_{ea} - R_{ea} - \phi \tag{3.6}$$

E_{HF}^{atom}	=Hartree-Fock orbital energy for free atom	
V _{ia}	=shift in E_{HF}^{atom} due to valence charge	Correction due
R _{ia}	=intra-atomic relaxation energy	to intra-atomic
V _{ea}	= shift in E_{HF}^{atom} due to free atom to solid state	Correction due
R _{ea}	=extra-atomic relaxation energy	to extra-atomic
φ	=work function of sample	Correction due to work function

To explore how the shift of BE reveals information about chemical shift or oxidation state, one must understand all the parameters contributed to the BE. The BE of the orbital for atom in condense phases is expressed as Equation 3.6 (Delgass *et al.*, 1979; Fadley, 1973). Noted that without consider any correction factor, the expression $BE=-E_{HF}^{atom}$ is merely an expression of Koopman's Theorem. Koopman's theorem predicted BE of an individual atom (such as gas state) with good agreement, but not accurate for condense state as it ignores neighboring electrostatic potential. Hartree-Fock orbital energy for free atom (E_{HF}^{atom}) calculated the energy of orbital for isolated atom assuming the electron orbitals are frozen during photoemission. However, this assumption is not true in realistic, where energy shift due to change of the valence charge (V_{ia}) and the relaxation energy when the electrons rearrangement (R_{ia}) arose after photoemission. Figure F compares the theoretical and experiment BE of C1s for carbon containing molecule (free atom/molecule as in gaseous state), always showed a deviation of 15 eV (Fadley, 1973), indicating the intra-atomic correction factor of V_{ia} and R_{ia} are quite significant.

For condense phase, there are inter-atomic correction factor, including V_{ea} and R_{ea} corresponding to energy shift between free atom and solid state, and relaxation

energy between atoms after photoemission, respectively. Finally, the work function of the sample, ϕ also needs to consider too.

While E_{HF}^{atom} , R_{ia} and ϕ are fixed for a specific orbital of an element, the chemical shift (due to neighbouring electrostatic potential) can be expressed by the BE shift (ΔBE) as Equation 3.7 below. ΔR_{ea} is governed by polarization of surrounding atoms. The term Δ ($V_{ia} + V_{ea}$) corresponds to the displacement of electron density due to the immediate environment factors such as the presence of electron withdrawing group next to the atom investigated, the removal of electron of that atom and just to name a few. For intra-atomic relaxation, the core hole can be delocalized (due to inflow of charge) when the electrons (valence) are weakly bounded in particularly true for a metal where the electrons (valence) can screen the core holes. Intra-atomic relaxation energy, R_{ia} must be taken into account when interpreting the photoelectron's kinetic energy of conductor. For OSC, ΔR_{ea} should be negligible since the valance electrons are strongly bounded.

$$\Delta BE = \Delta \left(V_{ia} + V_{ea} \right) \tag{3.7}$$

Following discussion above, if we carried out the experiment in condensed phase as a reference, shift of R_{ea} will be negligible leaving $\Delta (V_{ia} + V_{ea})$ to be dominating factor as shown in Equation 3.7. Hence, in such condition, the XPS spectra shifts under different electrostatic potential. For example, BE will shift toward higher or lower energy when the atom is surrounded by electronegative or electropositive element, respectively. It is known that BE is dependent on the potential energy of the core level. For example, O-CH₂, the carbon BE is shifted to a higher energy as a result of covalently bonded to the oxygen. Oxygen being a high electronegative atom, the electron density in that carbon is being drawn towards the oxygen atoms resulting the electrons in a given orbital level in carbon atoms to be less shielded from the effective nuclear charge resulting in a deeper potential energy (meaning higher BE). Similarly, a higher oxidation state exhibits a higher BE due to extra coulombic interaction between the orbital and the nucleus, compared to the BE of the elemental atom. The sensitivities of XPS toward chemical environment and oxidation state makes XPS an attractive tool to determine the chemical reactions from the BE shifting. From Equation 3.7, it also becomes clear that comparison between the same molecules in the gaseous phase and in condensed phase would show a shift. Noted the experimentally obtained peak can be identified by comparing with online database such as National Institute of Standards and Technology (NIST), which registered a large number of databases for BE corresponding to different chemical environments or oxidation states.

3.4.3 Data Analysis of XPS

PHI 5000 Versa Probe II XPS system stores the raw data in the format of VMS, which only can be opened by XPS analysis software such as Smart Soft, VAMAS Viewer, or Casa XPS for example. In this work, Casa XPS will be used to preview and export the raw data to ASCII form for various post-processing, such as normalization, curve fitting or deconvolution.



Figure 3.8: The preview of survey scan for sample ITO PEDOT: PSS using Casa XPS.

A complete set of XPS data always comes with a survey scan and several narrow scans. First of all, the survey scan is previewed with Casa XPS to check whether the elements shown as expected. The XPS measurement will be repeated at another spot/sample or increase the number of scans in case expected peak not shown, or presence of unknown peak. Figure 3.8 shows the preview of survey scan for sample ITO/PEDOT:PSS using Casa XPS. All the photoelectron and Auger electron peaks can be identified and displayed on top of the spectrum as shown in Figure 3.8. If the survey scan is promising, all the survey scans and narrow scans are batch converted to ASCII format using Casa XPS, so the post processing can be carried out by OriginPro, a graphing software.

In this thesis, the XPS measurement involved organic materials with abundant of carbon element. Thus, the C-C (and C-H) bonding in organic layer will be served as reference energy, corresponding to 284.8 eV. For each sample, all the spectra (including survey and wide scan) will be shifted for similar magnitude according to its alignment of C1s peak of C-C bonding.

3.5 Near Edge X-Ray Absorption Fine Structure (NEXAFS) Spectroscopy

NEXAFS, also known as X-ray absorption near edge structure (XANES), is one of the features of X-ray Absorption Spectroscopy (XAS). NEXAFS spectroscopy is very sensitive to environment of surrounding atoms, such as coordination geometry, oxidation states, molecular orbitals or band structure. XAS spectrum separates into two regions, namely NEXAFS and EXAFS (Extended X-ray Absorption Fine Structure), corresponding to energy range before the absorption edge, from edge to 50 eV above the edge, and 50 eV -1000 eV above the edge, respectively. NEXAFS spectra contains three features, including pre-edge, absorption edge and XANES. Figure 3.9 shows a normalized Cu K-edge XAS spectrum of copper foil, to illustrate the region of pre-edge, XANES and EXAFS (Gaur 2013).



Figure 3.9: The normalized Cu K-edge spectrum for copper foil measured at ELETTRA synchrotron light source in Italy. The caption indicates the pre-edge, XANES and EXAFS feature (Gaur *et al.*, 2013).

3.5.1 Principle of X-ray Absorption Spectroscopy (XAS)

XAS measured the absorption over a range of photon energies where absorption of the photon depended on the atomic PCS. Hence, the XAS spectra are closely related to the atomic PCS. Figure 3.10 compared the (a) PCS of the nitrogen and (b) normalized nitrogen K-edge spectra for sample PVK in this work. Both spectra show a sharp edge around photon energy of 400 eV, corresponding to the BE of N1s, as seen by the sudden increase of photoabsorption when the photon energy exceeds the BE of nitrogen in Kshell. Overall, the XAS spectra agree well with theoretically calculation of PCS, with intensity decreasing with photon energy.



Figure 3.10: (a) Photoionization cross sections for Nitrogen (Thompson, 2001) (b) XAS spectra of nitrogen K-edge for sample PVK



Figure 3.11: Attenuation coefficient for various interactions between iron and X-ray over different x-ray energies (data generated from (NIST, 2020))

Figure 3.11 shows the attenuation coefficient for different interactions of matter (iron) with x-ray leading to the attenuation of x-ray, including photoelectric absorption, coherent scattering, incoherent as well as pair production (NIST, 2020). Photoelectric absorption is the process where a photon is absorbed by an electron, overcoming the BE and emitted as photoelectron. Scattering occurs where incoming photon deflected off its straight path in many directions. Coherent scattering refers to scattering where energy of photon is conversed, while the energy of photon is not conversed during incoherent scattering because part of the energy is transferred to the electron. There are two types of coherent scattering, namely Rayleigh and Thomson scattering. Rayleigh scattering occurs when the energy of photon is absorbed by electron clouds of the atom (bounded state) as a quantum and reemitted in, while in Thomson scattering the photon energy is absorbed by single unbounded electron and reemitted when deexcitation. For both coherent scattering, the scattered photon has the same energy with the incident photon, but the direction of momentum is changed (noted that the magnitude of momentum still conserved) due to the remittance of electron cloud (or electron) in random directions. However, the Rayleigh scattering is a function of photon wavelength while Thomson scattering is independent of wavelength, even both are coherent scattering. The incoherent scattering also known as Compton scattering, which happened when light interacts with charged particles only such as electron. During Compton scattering, the incident photon losses some of the energy to electron during collision, resulted in longer wavelength of scattered photon and a recoiling electron after collision. Pair production occurred when photon energy is higher than 1.02 MeV, where the photon energy can covert to electron-positron pair according to Einstein's equation with E and m refer to photon energy and mass of electron-positron pair, respectively (Equation 3.8). Beside energy constrain, pair production only can occur near electron or nucleus to satisfy

conservation of momentum (where electron or nucleus can recoil to conserve the momentum).

$$E = mc^2 \tag{3.8}$$

Notice that for photoelectric absorption domain the attenuation coefficient for Xray energy below 10 keV as in Figure 3.11. The incoherent scattering and pair production will be domain for photon energy 100 keV to 10 MeV, and above 10 MeV respectively. Considered the x-ray source for beamline 3.2 is below 1 keV, the fundamental of XAS will be discussed as below, based on photoelectric absorption.

Figure 3.12 (a) shows the process of photoelectric absorption, where the x-ray is absorbed by core level electron and ejected as photoelectron, leaving an empty electronic level (a core hole) in the atoms. The core hole is highly unstable and has very short lifetime (~1 fs) by emitting (b) Auger electron or (c) fluorescence photon. The principle of Auger electron has been discussed in chapter 3.2.2. The photon is emitted (Fluorescence) with energy equivalent to the energy difference between two orbitals involved, which has the energy characteristic of the atom. This technique using X-ray fluorescence as chemical or elemental fingerprint analysis is call X-ray Fluorescence.



Figure 3.12: (a) Photoelectric absorption happens when X-ray photon excite the electron in core level as photoelectron. Two different routes for the excited core hole to relax including (b) Auger electron where an electron was promoted to vacuum or (c) Fluorescence was emitted when a higher-level core level electron replace the core hole.

The XAS measurement involved measuring the physical quantity that changes during photoelectric absorption, Auger electron or fluorescence. Figure 3.13 shows three different approaches commonly used to measure absorption, such as (a) transmission of x-ray, (c) total electron yield (TEY) and (c) TFY. The transmission mode of x-ray is based on Beer-Lambert Law. The absorption spectra can be measured directly from absorption coefficient, μ using Equation 3.9, with *I* and *I*₀, referring to intensity of X-ray before incident and after passing through the sample with thickness *d*, respectively. The total fluorescent yield (TFY) is the measurement of x-ray absorption based on the fluorescent yield (TFY) is the measurement of x-ray absorption based on the fluorescent yield, which is direct proportional to the x-ray absorption. The x-ray absorption also can be indirect measurement of by TEY, by measuring the current flow toward sample to compensate the electron deficiency, due to primary Auger Electron as well as scattered secondary electrons before Auger emission leaves the sample.

$$I(d) = I_0 e^{-\mu d} \tag{3.9}$$



Figure 3.13: Three different approaches to measure absorption including (a) transmission of x-ray, (b) total electron yield by monitoring the compensation current due to the loss of Auger electrons, and (c) total fluorescence yield by recording the emitted fluorescence

X-ray has absorption length up to micron while electron have mean free path of up to 5 nm, as shown in Figure B. Thus, the transmission mode and TFY which measure the transmitted x-ray and emitted x-ray fluorescence, respectively have bulk sensitively up to a few microns. Although transmission of X-ray has better signal/noise ratio compare to TFY, beamline 3.2a does not come with transmission mode, due to the high cross sections of soft x-ray that required for extremely thin homogeneous samples (Turchini *et* *al.*, 1995). Meanwhile, due to the limited mean free path of emitted electron, TEY mode has the advances of highly surface sensitive. Similar to XPS, TEY mode probed the top 10 nm from the surface.

Both Auger electron and fluorescence will compete with each other as the route to de-excited the core hole. The probability of Auger electron increases when energy difference between excited atom and after Auger emission decreases, which low atomic number (Z) atom will have a higher Auger electron yield compared to high Z-atom. At the meantime, the rate of fluorescent yield is proportional to third power of energy difference between the upper and lower level, thus high Z-atom tend to release absorbed x-ray energy via fluorescence. Figure G compares the Auger and fluorescent yield for atomic number less than 110. For organic element such as carbon, nitrogen and oxygen, the core hole is mostly decay via Auger electron with lifetime in the order of femtosecond (10^{-15} s) (Puglisi, 2017).

3.5.2 Principle of NEXAFS

As discussed in introduction at section 3.4, XAS spectrum can be divided to two regimes consisting of NEXAFS and EXAFS. Both X-ray fine structures are resulted from the scattering of photoelectron with neighboring atoms. Although both NEXAFS and EXAFS result from X-ray absorption, but they have different physical meanings due to different wavenumbers (KE) of the photoelectron. NEXAFS is sensitive to oxidation state and coordination chemistry of the absorbing atom, while the EXAFS is sensitive to the distances, coordination number, and species of the neighbors of the absorbing atom.

Figure H shows the regime of NEXAFS and EXAFS. Noted that NEXFS assigned to the near edge region (contains pre-edge, edge and XANES) as shown in the inset while EXAFS referred to extended region (50 - 1000 eV above the edge). The oscillation feature in XANES and EXAFS regions are caused by the constructive and destructive interference of x-ray due to the wave behavior of photoelectron scattering around with neighboring atoms as shown in the top diagram of Figure H.

The absorption edge with NEXAFS abruptly rising when the x-ray energy matches with the BE of the core level as the photon has enough energy to excite the core electron to continuum (above vacuum level). Noted that the absorption edge is a function of BE of core level, which serves as a fingerprint to identify the elements. As previously discussed in section 3.3.2, higher oxidation state increased the BE of core level electron, thus shifting the absorption edge to a higher photo energy. Figure I (a) showed the blue shift of Cr K-edge when chromium oxidation state increased from 0 to 6+.

The pre-edge located below the absorption edge, resulted from the transition between core level and unoccupied state (such as from orbital 1s to 2p), which lower energy compared its BE. In order words, NEXAFS reveals both occupied as well as unoccupied states (in comparison, XPS can only probes occupied states). Hence, pre-edge can be used to deduce useful information from unoccupied state such as local geometry around absorbing atoms, bonding characteristic and band structure. For example, transitions from 1s to 3d is forbidden due to dipole selection rule (allowed transition must have change in total orbital angular momentum, $\Delta l = \pm 1$). However, there is intense preedge peak corresponding to transition from Cr1s to Cr3d from Figure I (a). This observation can be explained with the dramatically increased p-d hybridization when centro-symmetry is broken (such as tetrahedral), allowing the transition of 1s to 3d to occur via electric quadrupole transition. Figure I (b) showed the transition from occupied to unoccupied state for different graphene oxide, for example $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ (Dey *et al.*, 2018).

The XANES region (from edge to 50 eV) and EXAFS region (from 50 eV to 1000 eV) basically form a smooth spline line beyond absorption edge, represents the atomic absorption of bare atom as shown in Figure I. However, a close observation will notice

sinusoidal alike feature oscillating around smooth spline line, which denoted as fine structure, where the name NEXAFS and EXAFS come from. The fine structure can be explained by the interference between the outgoing and back-scattering of photoelectron. When the x-ray energy, hv higher than the BE of core level, a photoelectron will be ejected with KE as described by Equation 3.1. According to de-Broglie equation (Equation 3.10), the de Broglie wavelength of electron, λ is inverse proportion to square root of KE where *h* is the Plank's constant, *p* and *m* are momentum and mass of the electron, respectively. The higher photon energy to the right of the absorption edge, the higher KE of the ejected photoelectron, thus the shorter the wavelength exhibited by the photoelectron. The electron with wavelength equal to λ propagates from photon-absorbed atom to neighboring atom and back-scattering with similar wavelength to the absorbed atom. If the scattered electron can return to the absorbing electron, it will fill up the occupied state and reduce the absorption of photon (since there is no state for core level electron to fill).

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m(KE)}} \tag{3.10}$$

The top diagram in Figure H shows the peaks of out-going waves (blue solid line) and back-scattered waves (blue dash line) between two atoms with interatomic distance R. Noticed that the de Broglie wavelength becomes shorter such as $\lambda = R/3$, R/3.5 and R/4 when KE of photoelectron getting higher. Constructive or destructive interference happened when the interatomic distance R is the n multiple or (n+1/2) multiple of λ , respectively as Equation 3.11 and Equation 3.12. When destructive interference happened, the outgoing and back-scattered wave are completely out of phase, thus all the occupied states had been filled and no core level electron can be excited, resulted in the minimum absorbance. The continue changing of constructive and destructive interference when photon energy increased modulate the photoexcitation cross-section in the XANES and EXAFS, resulted in the fine structure in XAS.

$$\lambda = n\lambda$$
, $n = 1, 2, 3, 4...$ (3.11)

$$\lambda = \left(n + \frac{1}{2}\right)\lambda, n = 0, 1, 2, 3, 4....$$
(3.12)

Since the fine structure is originated from the scattering from neighboring atoms, hence XANES and EXAFS revealed information regarding distribution of surrounding atom such as bond distance, number and type of neighboring atom. Literature showed that the frequency of the oscillation is related to distance from neighbors while amplitude of the oscillation are function of number and type of neighbors (Gaur *et al.*, 2013; Mastelaro & Zanotto, 2018). The different between XANES and EXAFS related to their mean free paths of photoelectron due to the different KE. XANES referred to fine structure produced between absorption edge and 50 eV higher than the edge, the corresponding photoelectron emitted has a longer mean free path (0.5 - 10 nm) due to its low KE as shown in Figure B (b), thus multi scattering become very significant. Meanwhile, the mean free path of photoelectron for EXAFS region (50 eV to 1000 eV) is shorter than XANES, around 0.5 nm to 2 nm, where single scattering is domain. Figure 3.14 shows the multiple scattering and single scattering events happened in XANES and EXAFS.



Figure 3.14: Illustration photoelectron pathway for multiple scattering in XANES (left) and single scattering in EXAFS.

There is no equation to express XANES due to the complication of multiple scattering. Meanwhile, the fine structure of EXAFS can be representing by an EXAFS

formula, which contain parameter such as distance of neighboring atoms, coordination number of neighbor atom and disorder in neighboring distance. The EXAFS spectra will be post-processed such as background substrate and normalized as shown in Figure 3.9 before analysis.

3.5.3 The XAS System

XAS measurement is performed by measuring the change of absorption over range of X-ray energy. Since XAS requires the tunable and intense x-ray beams, the measurement always performed at synchrotron facilities. The XAS measurement in this work was carried out at beamline 3.2a even SLRI has 3 dedicated XAS beamlines including beamline 2.2: Time-resolved XAS (TRXAS), beamline 5.2: XAS and beamline 8: XAS. All the aforementioned dedicated XAS beamlines come with high photon energy, which varies between 1250 – 12700 keV covering the absorption edge for element with atomic number (Z) equal or higher than 12 (Mg with Z=12 has K-edge of 1300 eV), however not suitable to analyse organic samples which mainly composed of carbon, nitrogen and oxygen. The dedicated XAS beamline above use beryllium window at the end station to allow XAS to be measured at atmosphere pressure also significantly block the low energy X-ray (which is prerequisites for XAS measurement on low-Z elements such as C, N and O).

Beamline 3.2a is the only beamline equipped with soft x-ray (photon energy between 124 eV to 1040 eV) in SLRI, thus becomes the only candidate for XAS measurement in this research, which is based on OSC. Indeed, the setup of XAS in beamline 3.2a is almost identical to UPS system, as discussed in section 3.2.2. However, there are two distinct differences for XAS mode compared to UPS mode. First, UPS incident a fixed photon energy on sample while XAS varying the photon energy. Secondly, UPS records the count of photoelectron with different KEs, while XAS records the absorption of the x-ray. Typically, three methods are commonly used for measuring the absorption of x-ray including monitor the change of transmission, TFY or TEY. In beamline 3.2, the absorption of soft x-ray can be measured via both TFY and TEY modes, by photodiode and picoammeter, respectively. The sample was transferred to XAS chamber (similar chamber of UPS/XPS) under ultra-high vacuum of 10^{-9} mbar. The measurement started by varying the photon energy between 124 eV – 1040 eV with interval of 0.1 eV using the monochromator. The TFY and TEY were recorded with incident angle of 90°. Figure 3.15 shows the schematic diagram of XAS measurement in beamline 3.2a. Noted there are differences compared with Figure 3.3 (UPS system) in term of the range of photon energy as well as the sensors used here are photodiode or pico-ammeter instead of the electron analyser.



Figure 3.15: Schematic diagram of XAS measurement system in beamline 3.2a

3.5.4 Data Analysis of NEXAFS

The NEXAFS measurement in beamline 3.2a is carried out via TEY and TFY mode. The TEY mode is surface sensitive down to 10 nm from surface, while TFY is bulk sensitive down to few microns below the surface. During measurement, the in-house LabVIEW program will change the photon energy by adjusted the undulator gap, VLSPG

Monochromator and slit. Synchrotron radiation in SLRI is operating in decay mode, where the electron beam current stored in storage beam (I_e) will decay during operation resulted from the collision with air particle. The intensity of x-ray beam was recorded by measuring the photoelectron current (I_p) of gold mesh, located right before NEXAFS chamber. I_p can normalize the TEY and TFY data from the variation due to the decay x-ray beam intensity over time. Both TEY and TFY was measured simultaneously by pico-ammeter and photodiodes as secondary electron-induced current (I_s) and fluorescent-induced current (I_p). All the collected information displayed in real-time via the LabVIEW window and automatically exported as ASCII format after each measurement. Figure 3.16 shows an example of NEXAFS raw file for sample 30nm PVK, where photon energy, I_e , I_p , I_s , I_f and undulator gap are tabulated. The normalized TEY and TFY data divided with I_p are recorded as I_s/I_p and I_f/I_p as shown.

Photo Ionization Scan								
Date :	14/9/18							
Measured Time: 11:17:25 AM	-	12:32:59 PM						
Select Photon Energy :	1200 lines/mm							
Photon Energy	le	lp	ls	ls\lp	lf	lf/lp	GAP	
Scan :	1							
390	108.113776	4.71E-10	1.44E-09	3.064707	-2.58E-10	-0.547188	34.465	
390.1	108.077139	4.69E-10	1.39E-09	2.966001	-2.57E-10	-0.548309	34.465	
390.2	108.037001	4.67E-10	1.36E-09	2.909295	-2.58E-10	-0.5517	34.470001	
390.3	107.998962	4.70E-10	1.35E-09	2.871891	-2.56E-10	-0.545165	34.4725	
390.4	107.96188	4.68E-10	1.34E-09	2.850114	-2.60E-10	-0.554437	34.4925	
390.5	107.923734	4.69E-10	1.33E-09	2.827378	-2.57E-10	-0.548268	34.494999	
390.6	107.888735	4.68E-10	1.32E-09	2.813013	-2.56E-10	-0.546504	34.502499	
390.7	107.853296	4.69E-10	1.31E-09	2.801012	-2.59E-10	-0.551997	34.505001	
390.8	107.81855	4.67E-10	1.30E-09	2.792374	-2.53E-10	-0.543219	34.512501	
390.9	107.778545	4.69E-10	1.30E-09	2.781822	-2.57E-10	-0.548805	34.517502	
391	107.740556	4.70E-10	1.30E-09	2.7772	-2.57E-10	-0.546211	34.5275	
391.1	107.702492	4.68E-10	1.30E-09	2.76847	-2.55E-10	-0.545665	34.535	
391.2	107.664853	4.67E-10	1.29E-09	2.765521	-2.57E-10	-0.549587	34.540001	
391.3	107.625666	4.67E-10	1.29E-09	2.75932	-2.55E-10	-0.545758	34.547501	
391.4	107.594611	4.65E-10	1.28E-09	2.757758	-2.57E-10	-0.55211	34.549999	

Figure 3.16: Part of the NEXAFS raw data for PVK sample. The scanning range of Nitrogen K-edge started from 390 eV to 430 eV.

The raw file was exported to OriginPro software for post processing such as normalization, background subtraction or curve-fitting before analysis. Figure 3.17 was

plotted according to the raw data shown in Figure 3.17, to compare the different between TEY and TFY for 30 nm PVK. The absorption edge for nitrogen K-edge is located between 402 – 406 eV, associated to the IE of N1s. The sharp spectral features in the energy range between 398 to 405 eV reflect the transition between 1s to π^* , while the broader spectral features at higher energies, more than 405 eV reflect 1s to σ^* transitions (Leinweber *et al.*, 2007; Vall-Ilosera *et al.*, 2008). The π^* and σ^* refer to the antibonding molecular orbital formed when two atomic orbitals overlapping to form a sigma bonding and Pi bonding respectively.



Figure 3.17: NEXAFS spectra for sample 30nm PVK spin coated on ITO. The Nitrogen K-edge measured by two different approaches, TEY and TFY.

The TFY spectra is noisier than TEY for carbon-based organic material, explained by the probability of fluorescence process is less than Auger electron emission for low Zatom as discussed in previous section. However, one can observe that the absorption curve obtained via TEY and TFY modes are identical, implying similar chemical environment for both surface (top 10 nm) and bulk (the 30 nm). This result implied the molecule arranged uniformly along the thickness. The different sensitivity over surface and bulk via TEY and TFY, respectively will be extremely helpful to verify the phase segregation in thin film samples.

3.6 Grazing Incidence X-ray Diffraction (GIXRD) Measurement

GIXRD studies crystallization structure of thin film (< 100 nm) by incident X-ray with very small incident angle, less than 1°. GIXRD technique was first demonstrated by Marra *et al.* to study the crystalline surface. During the measurement, the incident X-ray angle is fixed while the intensity is measured as a function of scattering angle (Marra *et al.*, 1979). GIXRD is an extremely surface sensitivity technique, which can be used to probe the phase, strain or stress presented at the surface as well as depth profiling.

3.6.1 Principle of X-ray Diffraction (XRD)

XRD is a common technique to identify the structure of crystalline materials. XRD principle is based on the wave behavior of X-ray, where wave will be diffracted (bending of wave around obstacles) when a structure with size similar order to the incident x-ray wavelength. When monochromatic X-ray incident on the crystal structure, the regularly spaced atoms in crystal lattice diffracts the X-ray light, analogous to the diffraction of visible light by diffraction grating. Each atom acted as the diffracting center and emitted a secondary wave, the diffracted X-ray that are in phase and out of phase will be constructive and destructive interfered, respectively. The XRD signal can be described mathematically by Bragg's Law (Equation 3.13) for constructive interference, where *d* is the lattice spacing (separation between atomic planes), θ is the X-ray incidence and exit angle, *n* is positive integer (denoted as n-th order) and λ is the wavelength of X-ray. Figure 3.18 (a) shows the geometry derivation of Bragg's law, with two monochromatic X-rays incident on different atomic planes. Noted that the bottom ray travels extra distance (path difference) $2d \sin \theta$ compared the top ray. When the path difference is equal to multiple integer of wavelength, λ , both top and bottom rays are in phase and thus constructive interfered, producing a diffraction beam. For the diffracted angle that fulfilled the Bragg's law, all atoms from various correctly oriented planes will undergo constructive interference, producing an intense and sharp diffraction pattern.

$$2d \sin \theta = n\lambda, \ n = 1, 2, 3, 4 \dots$$
 (3.13)

From Equation 3.13, one can notice that for constant λ and order of diffraction, the reflected angle, θ is getting bigger when the lattice spacing, d is getting smaller. This translated to a greater separation between interference patterns on the screen. This agrees well to the diffraction of light with diffraction grating where smaller slits always produced wider diffraction pattern and vice-versa.



Figure 3.18: (a) Sketch of geometry derivation of Bragg law. The black circle represents the atoms in the crystal and the grey arrows indicate the X-ray beam. θ is the X-ray incidence and exit angle while d is the distance between the reflecting plane. The bottom ray travels further than the top ray for path difference of 2dsin θ . Constructive interference occurs when the path difference equal to integer of λ . (b) Vectorial description of constructive interference, k, k' and q are represented by wavevector of X-ray before and after diffraction and scattering vector respectively.

Figure 3.18 (b) shows the vector diagram when constructive interference, \mathbf{k} and $\mathbf{k'}$ represent the wavevector of X-ray before and after diffraction, respectively while \mathbf{q} represents the scattering vector. Both \mathbf{k} and $\mathbf{k'}$ have similar magnitude $|\mathbf{k}| = |\mathbf{k'}| = 2\pi/\lambda$ because the X-ray is diffracted elastically. Scattering vector, \mathbf{q} shows the change of wavevector during the diffraction which has a magnitude of $2\pi/d$, also known as

reciprocal lattice vector. Scattering vector always is the bisector of the angle between incident and diffraction angle. q value is commonly use in XRD. q value can be expressed in term of θ and λ as shown in Equation 3.14 below by considering the first order diffraction (n=1) in Bragg's law.

$$q = \frac{2\pi}{d} = \frac{4\pi}{\lambda} \sin\theta \tag{3.14}$$

Crystalline materials show a long-range order with periodic arrangement of atoms. The crystal structure is described by unit cell, the smallest repeating unit that have the full symmetry of crystal. Miller index are used to describe the plane or direction in unit cell. (hkl) (h,k,l) and [hkl] are notation to represent the plane, point and direction, respectively. The plane notation (hkl) can be obtained by identifying the plane intercepts at x, y, z axes, and taking the reciprocal of the plane intercept. The direction [hkl] is defined as the direction perpendicular to plane (hkl). Figure J (a) shows various plane in cubic crystal defined with Miller index and (b) demonstrate on how to define plane and direction according to Miller index.

Conventional XRD using symmetrical Bragg Brentano configuration (theta/2theta) as shown in Figure K, where the X-ray is emitted from X-ray tube, incident on the sample with at an angle, θ and which then diffracted from the sample to detector. The diffracted angle, 2θ is defined as angle between incident and diffracted beam. Noted the scattering vector q, which falls on the bisector of incident and diffracted angle, is always perpendicular to sample's surface for Bragg Brentano configuration. Bragg Brentano configuration is exactly similar to the geometry derivation of Bragg equation as shown in Figure 3.18. Thus, the obtained result satisfies the simple relationship as in Bragg equation, making the data analysis simple and straight forward. Typically, the X-ray tube is fixed in Bragg Brentano configuration, while sample holder and detector are rotated with detector moving twice the angular displacement compared to sample holder to satisfy theta/2theta configuration.

The Bragg Brentano configuration is commonly used in X-ray powder diffraction, the random arrangement of polycrystalline mean there must be a small percentage of crystallites that properly oriented to diffraction. Indeed, the obtained result is the integration signal from few ten thousand of random oriented crystals, where every diffraction peak actually contributed from small fraction of correctly oriented crystals. Figure L shows the XRD measurement for a polycrystalline sample, the XRD peak is labelled with corresponding plane that produces the constructive interference. The lower part of the figure showed the random arrangement of a large number of crystals implying that there are statistically equal number of crystals that will be diffracted for every plane. The directional vector [100], [110] and [200] indicate the scattering vector for the corresponding diffracted plane, which always perpendicular to sample surface for Bragg Brentano configuration.

The Bragg Brentano configuration is not suitable for characterization of OSC thin film. Firstly, the signals from the substrate are more intense than thin film, due to the long absorption length, μ^{I} (632 µm for carbon under Cu k α radiation as shown in Table 3.2) relative to thickness of the film. Table 3.2 tabulates the atomic mass, density, linear attenuation coefficient (μ) and absorption length (μ^{I}) for different elements and structures type for Cu k α radiation (8.04 keV). Moreover, the analysis depth varied with θ when sweeping theta/2theta, since the analysis depth, *z* is function of θ and μ as shown in Equation 3.15.

To resolve the issues above, the conventional XRD is modified so that the X-ray is grazing incidence on sample with fixed small angle, namely GIXRD, which will be further discussed in next section.

$$z = \frac{\sin\theta}{2\mu} \tag{3.15}$$

Element	Atomic mass (u)	Modification	Structure type	Density, $ ho$ (g cm ⁻³)	μ (mm ⁻¹)	<i>μ</i> ^{−1} (μm)
С	12.01	Diamond	Diamond	3.51	1.58	632
		Graphite	Graphite	2.25	1.01	985
Si	28.086	c-Si	Diamond	2.32	14.8	67.7
Zn	65.38	Cubic ZnS	Sphalerite	4.10	31.7	31.6
S	32.064	Hexagonal ZnS	Wurtzite	3.98	30.8	32.5
Se	78.96	Cubic ZnSe	Sphalerite	5.42	43.9	22.8
		Hexagonal ZnSe	Wurtzite	5.39	43.7	22.9

Table 3.2: Atomic Mass, density, linear attenuation coefficient (μ) and absorption length (μ^{-1}) of selected element and structure type when radiated by Cu k α (Birkholz, 2005).

3.6.2 Principle of GIXRD

GIXRD is one of the XRD technique with extreme surface sensitivity with X-rays impinges on the sample surface with a constant small incident angle, θ_i . Typical GIXRD detector will scan the 2φ (parallel to the sample surface plane, namely in plane angle) at fixed diffracted angle, θ_f . Some GIXRD, especially synchrotron based light source uses a 2-dimensional (2D) detector which can capture both in plane (xy plane) and out of plane (z plane) at once. Figure 3.19 shows the geometry of GIXRD, where k_i and k_f are the wavevector of incident and diffracted X-ray beam. Noted that the scattering vector (q) is not parallel to the normal (n) of the sample surface (where q is parallel to n in Bragg Brentano configuration). The q_{xy} , q_z represented the horizontal (in plane) and vertical (out of plane) scattering vectors, respectively.

Unlike XPS, the high energy x-ray used in XRD interacts weakly with the materials. The X-ray absorption length of Cu k α (8.04 keV) ranges from 10 μ m to 1mm as shown in Table 3.2. In fact, the refractive index of most materials in x-ray region is slightly less than 1. Therefore, X-ray will exhibit external total reflection at sample surface when the incident angle is less than the critical angle, typically between 0.05° to 0.5° dependent on the material and X-ray energy. The evanescent X-ray will probe the top fraction of the thin film (a few nm) when the incident angle is equal to critical angle

hence is can be extremely surface sensitive. The incident angle is always slightly above critical angle during GIXRD measurement.



Figure 3.19: Geometry of GIXRD measurement. k_i and k_f are wavevectors of incident and diffracted X-ray beam. θ_I , θ_f , 2φ are incident angle, diffracted angle, in plane scanning angle respectively. The normal of the sample and scattering vectors are labeled as *n* and *q*, respectively.

The surface sensitive of GIXRD are resulted from the small incident angle θ_i , which can be explained by pure geometry. Considered X-ray incident on a sample thinner than the absorption length of the X-ray as in Figure 3.20. The large incident angle in (a) can penetrate both the thin film and the substrate, thus the analysis depth, *Z* including both the thin film and substrate, hence a large portion of XRD signals are originated from substrate rather than thin film. By applying small angle as shown in Figure 3.20 (b), all the incident X-rays are absorbed by thin film, and the analysis depth are constrained in thin film, suppressing the background signal from substrate.



Figure 3.20: Different analysis depth (z) when x-ray incident on thin film with (a) large and (b) small incident angle (θ_i). The x-ray spot size getting bigger with reduced θ_i .

Since GIXRD measurement is done with constant incident angle, the analysis depth is fixed throughout the experiment, which is suitable for analysis of thin film samples. Besides, one can also vary the incident angle to change the analysis depth, to perform a depth profile analysis over multilayer thin film. Besides, the small incident angle will reduce the x-ray damage since the X-ray is spread over larger area, shown by the larger X-ray spot size in Figure 3.20.

However, conducting GIXRD experiment on organic thin film is challenging due to the reasons below. The first concern is the scattering factor of different atoms. Higher atomic number contains higher number of electrons, showing a strong ability to X-ray scattering. Organic material, which most of the scattering centers are carbon has low atomic number and low density resulted in poor scattering factor, hence the having low X-ray peak intensity compared to inorganic material. Besides, the highly spatial disorder nature of organic materials, such as polymer sample often correlated to weak diffraction intensity too.

There are few approaches, such as modify the geometry of GIXRD, increasing data integration time, or using a brighter X-ray to resolve issues above. Geometry modification such as moving the detector closer to the sample can increase the diffraction intensity. However, standalone GIXRD system typically not bright enough for organic samples thinner than 100 nm even after geometry modification. Therefore, synchrotron light source with high photon flux and strong beam collimation are necessary for GIXRD measurement on organic thin film. By using synchrotron light source, the bright X-ray able to produce sharp diffraction peak for organic material with shorter acquisition time. 1D detector (linear detector) in lab-grade GIXRD captured the diffraction pattern by continuously changing the out-of-plane scattering angle 2θ (or the in-plane scattering angle 2φ), taking times up to hour. Synchrotron based GIXRD usually comes with 2-dimensinal (2D) detector mounted along the direction of the incoming X-ray and does

not move during measurement. The 2D detector can capture more information at shorter time in the expense of data resolution. However, data resolution is not critical for organic material, as its disorder resulted in broad diffraction peak compared to inorganic. The 2D detector captures a big portion of diffraction pattern (consisted of the in plane and out of plane) in few seconds.

Figure M illustrates diffraction pattern from OPV device captured by 2D detector (Turak *et al.*, 2010). The 2D diffraction pattern includes the diffraction due to the lattice planes parallel and perpendicular to sample surface, are indicated by q_{xy} and q_z in diffraction patterns. Besides, one can also study the diffraction from lattice planes tilted from the surface normal direction by looking at the intensity for vector laid between q_{xy} and q_z . As a comparison, the conventional 1D detector only measures the diffraction along q_{xy} (when sweeping along 2φ), which is the subset of data taken by 2D detector.

2D detector is superior to 1D detector in term of analysis the orientation of the crystalline domains and identify the existence of macrostrain. Figure N shows the correlation between the diffraction pattern with the orientation of crystalline domain. The diffraction pattern will appear as a ring for randomly oriented polycrystalline as shown in (a). The randomly orientated and highly oriented crystalline domains will appear as arc and dot, respectively, as shown in (b) and (c). There will be no any special features for amorphous material. Furthermore, the stretched or shifted dot or ring in diffraction pattern correlated to the macrostrain (the strain induced when bigger ion substitute the smaller one in lattice parameters), which will shifts the diffraction peak position (Chattot *et al.*, 2018).

3.6.3 The GIXRD System

The GIXRD measurement was carried out at Beamline BL7.2W:MX, in SLRI, Nakhon Ratchasima to fulfil the requirement of high brightness of X-ray and high precision control of small (angle). The XRD in LDMRC, Department of Physics, UM unable to study the molecular arrangement of organic thin film in this research due to the limited brightness and comes with Bragg Brentano configuration only.

BL7.2W:MX is designed for Macromolecular Crystallography (MX), which commonly used to study the 3-dimensional (3D) structure of macromolecules such as proteins, ligands and enzyme. However, the setup of MX is suitable to perform GIXRD technique too. The light source of BL7.2W:MX is based on Synchrotron, similar to UPS as discussed in section 3.2.1. The X-ray is produced by passing electron beam through a 6.5 Tesla superconducting wavelength shifter (SWLS). SWLS blue shifts the X-ray wavelength, so the peak of photon flux is shifted towards a higher X-ray energy compared to just using a conventional bending magnet. SWLS in BL7.2W:MX produces an X-ray with the highest photon flux at 8 keV, with photon flux in the order of 10¹⁰ between 7 keV to 18 keV, which is more than sufficient for GIXRD. The brightness of the synchrotron light source typically ranges from 100 to 1000 brighter than the lab-grade Xray source (Helliwell, 1998), which means data collection is 100-1000 times shorter too.

The optical layout of BL7.2W:MX is as depicted in Figure 3.21. The synchrotron radiation passes through various optics such as cylindrical collimating mirror (CM), double-crystal monochromator (DCM) and a toroidal focusing mirror (FM) to select the desired wavelength and focus the hard X- ray beam before incidents onto the sample at the end station. The beam size is reduced to 20 μ m in order to obtain a small beam area on the sample for GIXRD measurements.

Both sample holder and detector are mounted onto the MarDTB Goniometer system (Marresearch GmbH, Norderstedt, Germany), capable in adjusting the incident angle between 0-360 ° with accuracy of 0.002 °. The distance between the detector and the sample can be changed from 45 mm to 390 mm and the detector can rotate around the sample up to 30 °, facilitating the diffraction measurement. The diffraction pattern will be recorded using a Mar165 CCD 2D detector system (Rayonix LLC, Evanston, Illinois,

USA), which can record 2048 x 2048 pixel images in readout time of 5 seconds. The diffraction pattern will be outputted in mccd format, which can be further analysed using SAXSIT or FIT2D, developed by, SLRI or European Synchrotron Radiation Facility (ESRF), respectively.



Figure 3.21: The layout of BL7.2W:MX beamline, X-ray will pass through various optics such as cylindrical collimating mirror (CM), double-crystal monochromator (DCM) and a toroidal focusing mirror (FM) to obtain a focused hard X-ray beam. The inset shows the magnified 2D detector and goniometer at the end-station.

3.6.4 Data Analysis of GIXRD

The diffraction pattern obtained by 2D detector are stored in graphical format (mccd file extension), with file size about 8 MB for each measurement. The mccd file recorded the photon count for each pixel and readily be postprocessed by image processing software such as FIT2D or SAXSIT, by displaying the diffraction pattern as false-colour image.



Figure 3.22: Diffraction pattern of (a) sample ITO/30nm PVK and (b) standard sample 4-Bromo Benzoic acid. The q_{xy} and q_z represent the scattering vector for in plane and out of plane, respectively.

The 2D diffraction pattern can be analyzed qualitatively (by identifying the present state, such as amorphous, polycrystalline, or single crystal nature) or quantitatively (by identifying the diffraction peak, full-width half maximum (FWHM) and others). The qualitative analysis is quite straight forward, by observing the intensity distribution of the diffraction pattern. As previous discussed, upon radiation of monochromatic beam, a single crystal with preferred orientation will appear as dots while an amorphous sample shows no feature on a 2D detector. Meanwhile, a full concentric Debye ring as shown in Figure 3.22 indicating the sample comes with tiny crystals in all orientations, implying that the sample has a perfect polycrystalline texture. Figure 3.22 shows the greyscale image diffraction pattern generated by FIT2D for (a) sample ITO/30nm PVK and (b) standard sample 4-Bromo Benzoic acid by mapping photon counts linearly as shown in the scale bar. Noted that the diffraction pattern for (a) sample ITO/30nm PVK only contains top half of the full circle while (b) standard sample shows full circles, because the ITO substrate will block most of the x-ray that scattered below

the plane xy as shown in Figure M. Besides, the center in diffraction pattern always shows zero intensity due to the beam stopper, to protect the detector from intense primary x-ray damage that has not undergone diffraction. The uniform distribution between scattering vector q_{xy} and q_z qualitatively suggested that the PVK sample shows random orientation as in polycrystalline. However, one cannot confirm the uniform ring is originated from PVK thin film or ITO substrate before quantitative analysis.

Generally, the quantitative analysis of GIXRD can be divided into three stages: calibration, conversion of 2D pattern into 1D pattern and Gaussian fitting for diffraction peak. Firstly, calibration was performed by taking diffraction pattern of a standard sample (4-Bromo Benzoic acid in this research). GIXRD analysis software such as SAXSIT can accurately determine the sample-detector distance and center of 2D images by calibration with the input incident X-ray wavelength, pixel size and other parameters. The 2D diffraction patterns can convert to 1D intensity profiles after obtaining the corrected sample-detector distance, by dividing the circular pattern to the desired sector, often referred to as 'caking' due to the similarity to cutting cake to slice before integration. Meanwhile, the symmetry of diffraction pattern (as seen from the concentric rings) of polycrystalline samples makes the conversion relatively easy, by performing circular averaging. The circular averaging algorithm in SAXSIT program can obtain 1D scattering profile as a function of 2theta or q.

3.7 Device Fabrication

All OSC devices including OLEDs required functional layer encapsulate between contact (anode and cathode) in order to be tested. In this research, ITO coated glass substrate is chosen due to the electric conductivity, optical transparency as well as its high work function, a prerequisite condition for anode of OLEDs devices.

The pre-patterned ITO coated glass is custom made by Luminescence Technology Corp., Taiwan as shown in Figure 3.23. ITO with thickness of 140 nm was first deposited on 1.1 mm x 15 mm x 20 mm glass to fulfil our specification of $9\sim15 \Omega$ /sq sheet resistance and >84 % transparency (at 550 nm). The ITO coated glass was then patterning (etching) according to dimension as shown in Figure 3.23 (a). The pre-patterned ITO has six pixels as illustrated in Figure 3.23 (b).



Figure 3.23: The (a) top and (b) isometric view of pre-patterned ITO substrate. The ITO coated was patterning on glass according to dimension as labelled in (a).

A small quantity of contamination on the surface of ITO can significantly altered the work function as well as barrier height between the organic layer and the anode. ITO substrates need to be thoroughly cleaned in order to fabricate device with consistent electrical and optical performance. All pre-patterned ITO glass substrates were ultrasonically sonicated in deionized (DI) water, acetone, isopropyl alcohol and DI water again for 10 min to dissolve all the contamination such as metal cation, organic substance. Afterward, the ITO glass substrate was purged with purified nitrogen and keep inside oven for more than 2 hours to remove all the moisture.

For device fabrication, all materials were purchased and used as received without further purification. PEDOT:PSS solution (CleviosTM PVP AI4083) was purchased from Heraeus. PVK (average Mw = 1100000), Ba(acac)₂ and 2,2,3,3-Tetrafluoro-1-Propanol 98% were bought from Sigma-Aldrich. 1,3-bis[(4-tert-butylphenyl)-1,3,4oxidiazolyl]phenylene (OXD-7), 2,7-bis(diphenylphosphoryl)-9,9'- spirobi[fluorene] (SPPO13), tris[2-(4-n-hexylphenyl)quinoline]]iridium(III) (Hex-Ir(phq)₃), *fac* tris(2phenylpyridine) iridium (Ir(ppy)₃, [bis(4,6-difluorophenyl) pyridinato-N,C²]picolinate iridium(III) (FIrpic), TcTa were purchased from Luminescence Technology (Taiwan). All the solutions were filtered by 0.45-µm poly(tetrafluoroethylene) filters before use unless otherwise stated.



Figure 3.24: The schematic diagram shows the fabrication steps for OLEDs. (a) Spin coating HTL on substrate, (b) spin coating active layer(s) on top of HTL, (c) vacuum depositing of EIL and Al contact on top of active layer with shadow mask, (d) Encapsulation of OLEDs with cover glass.

The OLEDs fabrication involved a few physical processes such as spin coating, vacuum deposition and encapsulation as shown in Figure 3.24. Before device fabrication, the ITO coated substrate was treated with 35 W forward power oxygen plasma for 5 min using a parallel plate etcher (POLARON PT7170) as shown in Figure 3.25 (a). Oxygen plasma treatment can remove the organic contaminant and increase the work function of ITO. Besides, the oxygen radical produced during the oxygen plasma will react with

surface chemical group, enhancing the surface wettability of ITO (Naseem *et al.*, 2003) which is crucial for next stage, spin coating the HTL.



Figure 3.25: The (a) Parallel plate etcher (Polaron PT7170) and (b) spin coater (WS-650-23nppm, Laurell Technologies) inside clean room. All the fabrication process involve organic material are conducting in the (c) glove box (Mikrouna super 1500), well equipped with UV curing system, hot plate, spin coater and PVD.

After the oxygen plasma treatment, the OLEDs fabrication started immediately

by spin coating PEDOT:PSS Al4083, the HTL with spin coater (model WS-650-23nppm,
Laurell Technologies) as shown in Figure 3.25 (b). The substrate was placed on the vacuum chuck and PEDOT:PSS solution was dropped on top of the substrate, the centripetal force spreads the PEDOT:PSS over the substrate during spin coating, forming a uniform 40nm PEDOT:PSS thin film with recipe of 1500 rpm for 30s. PEDOT:PSS has a high hole mobility and work function (around $\sim 5.0 \text{ eV}$) effectively reducing the hole injection barrier with subsequent layer. The substrate was swabbed with cotton buds that dipped in an appropriate solvent to rub away unwanted spin-coated materials at the top and side ITO (exclude the six pixels) to facilitate contact with aluminum contact. The substrate was then annealed at 120 °C for 10 min on the hot plate inside a nitrogen filled glovebox as shown in Figure 3.25 (c).

Subsequently, the active layers, also known as EML was spin coated on top of PEDOT:PSS in a glove box to prevent the degradation due to the oxidation of oxygen or moisture. The substrate was swabbed with cotton buds before annealed with 100° C for 15 min. Afterwards, 1 nm of CsF, the EIL and Al (100 nm) contact were thermally evaporated through shadow mask at base pressure of 4.2x 10⁻⁴ Pa by physical vapour deposition (PVD) system installed inside the glove box. Finally, the device was encapsulated with a cover glass by curing the UV curable epoxy with UV curing system to protect the active layer from degradation due to moisture and oxygen during the measurement.

3.8 Current Density- Voltage- Luminance (JVL) Measurement

Current Density- Voltage- Luminance (JVL) system is designed in order to characterize the performance (efficiency) of OLEDs. JVL system measures the current and voltage of the OLEDs as well as records the light output simultaneously.

Figure 3.26 (a) shows Keithley 2612B system source meter unit (SMU) with high resolution up to 100fA and capable to measure current and voltage up to 10A and 200V, respectively. The brightness (luminescence) and colour coordinate (CIE coordinate) was measured by Konica Minolta CS-200 chromameter as shown in Figure 3.26 (b). Both source meter and chromameter was coupling with an in-house developed software, named "LIV test system" as shown in Figure 3.26 (c). Figure 3.26 (d) showed the fabricated OLED device, where all the six pixels (anode) and cathode were installed with connection legs before mounting on the sample stages with x, y, z translator. The chromameter and sample stage were fitted to a black box to ensure a fully dark environment for luminescence measurement.



Figure 3.26: The Current Density- Voltage- Luminance (JVL) system comes with (a) Keithley 2612B system source meter, (b) Konica Minolta CS-200 Chromameter, (c) "LIV test system", an in-house developed software and (d) an OLED device mounted on a sample stage with x, y, z translator.

The schematic diagram for the setup of JVL system was depicted in Figure 3.27. The x, y, z translator was manipulated until the pixel of interest was focus on the chromameter by checking on the camera window as shown in the right down application in Figure 3.26 (c). The JVL measurement of OLEDs involved two wires resistance measurement, where two wires connected to cathode and anode (pixel of interest) to the SMU via banana plug connector located at the wall of black box. The start voltage, stop voltage, voltage step size, current compliance and file name are predefined in "LIV test system" before measurement. The measurement initiated by pressing "start" at "LIV test system". The current, brightness and CIE coordinate for the corresponding voltage will be automatically saved to an ASCII file as predefined file name.





The current density (mA/cm²), current efficiency (cd/A) and power efficiency (lm/V) can be extracted from the output of JVL measurement with Equation 2.17, Equation 2.18 and Equation 3.16.

$$Current Density, J = \frac{Current I}{Area of Pixel, A}$$
(3.16)

3.9 Other Measurement

Synchrotron based measurement such as UPS, XPS, NEXAFS and GIXRD are very powerful technique to understand the electronic structure of valance and core energy level, oxidation state or crystallization of matters. However, such measurement can only be performed with synchrotron facilities, which only available at Thailand and Singapore for South East Asia. The access of synchrotron required submitting a proposal 3-5 months before the measurement and subjected to approval, where a measurement usually can be carried out half a year after the idea commenced.

There are numerous laboratory instruments available in LDMRC, department of physics, allowing researchers to test hypothesis in the early stage of research, before further validate the hypothesis with synchrotron facilities. The UV-Vis-IR spectroscopy and EL spectroscopy are available in LDMRC to study the absorption spectra from infrared to ultraviolet range as well as emission spectrum of OLEDs, respectively. The pH meter and surface profiler are helpful to measure the acidity or basic of solution and thickness of thin film accurately. The AFM measurement was outsourced to Quasi-S Technoloy Sdn. Bhd in Universiti Kebangsaan Malaysia (UKM) to probe the surface roughness with resolution in the order of 0.1 nm.

3.9.1 UV-Vis Measurement

UV-Vis spectroscopy also known as absorption spectroscopy. Both UV-Vis spectroscopy and XAS are absorption technique but different in term of photon energy, where UV-Vis using UV and visible light while XAS using X-ray as light source. Commercial UV-Vis spectroscopy usually cover wavelength starting from 200 nm until infrared region because most of the commercial solvent has "cut-off" wavelength at 200 nm, where the solvent start to absorb light below "cut-off" wavelength. Besides, oxygen and moisture in air tend to absorb radiation strongly for wavelength below 160 nm too.

The photon energy used in UV-Vis corresponding to molecular electronic transition for organic material, charge transfer transition or d-d orbital transition in transition metal. UV-Vis is extremely powerful to study conjugated organic compounds since the photon energy (UV and Visible) cover most of the electronic transition. There are 4 possibility of electronic transitions in OSC including $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, and $n \rightarrow \pi^*$ as shown in Figure O below. The sigma (σ) and sigma star (σ^*) are bonding and antibonding orbital form when atomic orbitals overlapping in end-to-end fashion. The pi (π) and pi star (π^*) are bonding and antibonding orbital created when atomic orbitals overlapping by side-to-side fashion. A nonbonding orbital (n) referred to lone pairs (electrons that are not shared with another atom).

The $\sigma \rightarrow \sigma^*$ transition always required photon with wavelength less than 200 nm, which is below the wavelength offered by typical UV-Vis spectroscopy. Most of the absorption spectroscopy are based on $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, and $n \rightarrow \pi^*$ transition, which the absorption peak fall in region of 200- 700 nm. From electronic transition level described in Figure O, one may expect the absorption spectrum of a molecule will show a few sharp lines, at wavelength where the photon energy matches the electronic transition. However, the absorption peak always appears as continuously band instead of sharp lines, due to the superposition of vibrational and rotational transitions with electronic transition as well as energetic disorder nature of OSCs.

UV-Vis spectroscopy is very sensitive to function group, conjugation as well as type of solvent. Figure P shows the wavelength of maximum absorbance (λ_{max}) peak for electronic transitions in some simple organic molecules. The transition from $\sigma \rightarrow \sigma^*$ can take place at different wavelengths depending on function group as shown in ethane and methanol. The increasing conjugation tends to red shift the absorption peak as shown in wavelength increasing in the order of ethane, 1,3-pentadiene and 1,3,5-hexatriene due to increasing number of molecular orbitals bringing the HOMO and LUMO closer together. The unique λ_{max} can serve as fingerprint to identify the molecular structure. Moreover, the polarity of solvent will shift the absorption peak too. For example, the peak due to transition $n \rightarrow \pi^*$ will be blue-shifted with increasing solvent polarity due to the lower energy of n-orbital arise from solvation of lone pair.

When light strike an object, it can be absorbed, transmitted, scattered, reflected, refracted or even fluorescence. During UV-Vis measurement, the scattering, reflection and refraction are minimized by referencing to a blank substrate (for solid) or solvent (for solution). By carefully chosen a sample to minimize the fluorescence, only absorption and transmission play the role in UV-Vis spectroscopy. The absorbance (*A*), percentage transmittance (%*T*) are related by the Beer-Lambert law as Equation 3.17 and Equation 3.18 below, where ε , C, *l* represents the molar extinction coefficient, molar concentration and path length, respectively.

$$\%T = \frac{Intensity of transmisted light,I}{Intensity of incident light,I_0} \times 100$$
(3.17)

$$A = \log \frac{I_0}{I} = \log \frac{100}{\%T} = \varepsilon Cl$$
(3.18)

Figure 3.28 (a) shows the LAMBDA[™] 750 UV/Vis/NIR spectrophotometer from PerkinElmer, which was used to measure absorption spectra in this research. The lambda 750 comes with Deuterium lamp and Tungsten-halogen lamp as a light source for wavelength 190-370 nm and 320-3300 nm respectively, covering measurement ranges between 190-3300 nm. Lambda 750 is designed with double beams, double monochromators to allow real time referencing, by measuring the transmittance over sample and reference simultaneously. Figure 3.28 (b) shows the measuring interface of UV Winlab software by Lambda 750, where the start and stop wavelength, data interval, integration time and other parameters can be setting here.

The sample was prepared by spin coated/ drop casted on quartz substrate due to its capability to transmit UV compared to glass. The UV-Vis was switched on 20 min earlier before the measurement to stabilize the lamp. After configuring all the necessary parameters in UV Winlab software, the measurement begins with 100 %*T* correction, named "Autozero" by scanning without any sample. Once the "Autozero" completed, put the blank quartz and sample in reference and sample compartment, respectively and start the measurement as prompted by the software. The absorption spectra will be exported to CSV format after completed measurement for all the samples. The raw data can be further processing with Microsoft excel or OriginPro.



Figure 3.28: (a) LAMBDATM 750 UV/Vis/NIR spectrophotometer (b) The UV Winlab software interface for transmission measurement.

3.9.2 Electroluminescent (EL) Measurement

An OLED emitting light in the response of electric current, known as EL. The emitting colour of PhOLEDs depend on the wavelength of colour dopant in EML. For example, white PhOLEDs can be obtained by mixing three primary colours: red, green and blue (RGB) dopants or mixing two complementary colours such as blue/orange dopants.

The white PhOLEDs in this research were fabricated by mixing Hex-Ir(phq)₃, Ir(ppy)₃ and FIrpic as RGB dopants with ratio 1:0.1:10 with respect to the host. The quality of light sources are benchmarked by measuring the CCT. CCT quantified the colour temperature of white light sources with scale between 2200 K to 6500 K, where low and high CCT imply warm (yellowish) and cool (bluish) colour temperatures.

CCT calculation required the input of spectral power density (SPD), also known as EL spectra. LDMRC equipped with Ocean Optics HR4000CG-UV-NIR Spectrometer, capable to measure spectral ranging from 200 nm to 1100 nm, The HR4000CG spectrometer communicated with computer by USB interface as shown in Figure 3.29. The light emitted from OLEDs was transmitted to spectrometer by coupling with optical fiber branded QF600-1-SR, with fiber diameter of 600 µm and high transmittance for wavelength between 400 nm and 900 nm. Figure 3.29 (b) shows the interface of Oceanview, the dedicated software for HR4000CG spectrometer to acquire the EL spectra. The spectrum data can be stored as excel spreadsheet format (.csv) before further processed by graphing software (OriginPro in this work) or used for CCT calculation via "ColorCalculator" software, developed by OSRAM.





3.9.3 pH measurement

The pH scale is used to measure the acidity or alkaline in qualitative term, by described the hydrogen ion concentration, $[H^+]$ in the solution with logarithmic expression as in Equation 3.19. The neutral solution has equal amount of hydrogen ion and hydroxide ion, expressed as $[H^+] = [OH^-] = 10^{-7}$ M, hence has pH of 7.0 at room

temperature. An acidic solution has a pH lower than 7 while a basic solution has pH higher than 7.

$$pH = -\log[H^+] \tag{3.19}$$

There are two common pH measurement methods in laboratory, by direct measurement using a pH meter, or indirect determination by OH⁻ titration. Direct pH measurement is simple, intuition, non-destructive and able to measure a small volume of solution compared to OH⁻ titration. In this work, direct pH measurement was conducted with pH meter branded Mettler ToledoTM FiveEasyTM F20 pH/mV as shown in Figure 3.30.



Figure 3.30: The pH measurement conducted using Mettler Toledo[™] FiveEasy[™] F20 pH/mV.

Prior to pH measurement, the pH meter was calibrated with three standard buffer solutions with pH 4.01, pH 7.00 and pH 9.21 to obtain the calibration slope higher than 95 % and offset lesser than ± 20 mV for accurate measurement. Noted both calibration and measurement must be conducted with solution temperature of 25 °C as pH is sensitive to the temperature change. During measurement, the tip of calibrated electrode must fully

immerse in the solution and reading was taken after the displaying stop blinking (when the signal is stabilized). The electrode must be rinsed with deionized (DI) water before the subsequent measurement.

3.9.4 Surface Profiler

The film thickness is often vitally important parameter in device fabrication or thin film characterization. The thickness of charge transport layer and EML in OLEDs need to be optimized for better efficiency. Besides, calculation of extinction coefficient for absorption spectra of thin film required the input of film thickness as well.



Figure 3.31: (a) The KLA Tencor P-6 Surface Profiler in LDMRC (b) The schematic shows the operating principle of contact surface profiler. The double arrow dashed line indicated the close loop feedback between force compensation modules with pivot. The single arrow dashed line indicated the open loop feedback of stylus height to LVDC sensor.

Figure 3.31 (a) shows the KLA Tencor P-6 Surface Profiler in LDMRC. The P-6 is a contact profiler, where a 5 µm of diamond stylus tips with 60° cones angle contacted the sample surface with specific constant force while scanning laterally across the sample. The measuring mechanism in P-6 surface profiler is shown in Figure 3.31 (b) which consists of 4 main components, including stylus, pivot, force compensation module and linear variable differential capacitor (LVDC) sensor. The low inertia (mass) pivot connected the stylus to topography sensor and force compensation module. The stylus contacts the surface with constant force, realized by close loop feedback of force

compensation module. The LVDC sensor detected the vertical movement of stylus by converted the capacitance change to topography signal.



Figure 3.32: (a) "Profiler" window shows the top view of the sample, the blue arrow is drawn to select the measurement location. (b) The "Analysis" window shows the surface topography with the left panel reported the step height of the desire feature.

The thin film sample was scratched with tips of tweezers to form groove, in order for the stylus to measure the thickness. After loading the sample, the sample surface can be viewed by the high-resolution camera shown in "Profiler" window as in Figure 3.32 (a). The scan recipe for soft material (such as polymer) was chosen before measurement with applied force of 1 μ g and scan speed of 10 μ m/s. The measurement location is chosen by drawing a blue arrow over the desire feature, such as the scratched groove in Figure 3.32 (a). The "Analysis" window in Figure 3.32 (b) displays surface topography along the chosen scan path in Figure 3.32 (a). The left panel reported the step height of the groove as 1017.5 A, implied the film has the thickness of 102 nm.

3.9.5 Atomic Force Microscopy (AFM)

The AFM measurement in this research was carried out with NT-MDT NTEGRA-Prima system by Quasi-S Technoloy Sdn. Bhd in Universiti Kebangsaan Malaysia (UKM). AFM visualize the surface morphology by using a tip attached to the end of cantilever, with position-sensitive photodiode or capacitive sensor to measure the deflection of tip on the sample surface. NTEGRA-Prima offers three different modes for AFM measurement, such as contact mode, semi-contact (tapping) mode and non-contact mode.

The working principle of contact mode is similar to the surface profiler, where the tips applied a continuously force normal to the sample surface. Contact mode provides high resolutivation in the frictional and adhesion force can damage the surface topology and resulted in distorted image. The semi-contact mode or tapping mode operated by oscillation the tips vertically with its resonance frequency. The oscillation amplitude increased when the tip passes through depressed surface and vice versa. Tapping mode obtained the surface topology from the change of oscillation amplitude, suitable for soft material that easily damaged by contact mode. The non-contact mode measures the surface roughness by detecting the attractive Van-Der-Walls force between tips and surface, which is non-destructive method but suffering from poor resolution due to the weak Van-Der-Walls force.

CHAPTER 4: PROBING EFFICIENCY OF EXTRA WARM WHITE ORGANIC LIGHT EMITTING DIODE USING SYNCHROTRON TECHNIQUES

4.1 Introduction

In this research, two widely-used carbazole based HTMs, PVK and TcTa were blended as host, intends to improve the device performance of warm white phosphorescent OLEDs (PhOLEDs). Warm white light contains relatively low level of blue lights in whole spectra, has the advantages of improving sleeping quality. Literatures showed that blue lights component in the white light can suppress melatonin production, affecting natural circadian rhythms and resulted in insomnia (Kozaki *et al.*, 2008; Sato *et al.*, 2005; Shechter *et al.*, 2018).

TcTa has hole mobility of 1.5×10^{-4} cm²V⁻¹s⁻¹ (L. Xiao *et al.*, 2011), which is two order higher than PVK (2×10^{-6} cm²V⁻¹s⁻¹) (Lan *et al.*, 2019; Talik, Woon, & Yap, 2016). The non-conjugated backbone limited the hole mobility of PVK (Liang *et al.*, 2017), since its hole transport is limited to intrachain π - π stacking mechanism (Xie *et al.*, 2008). A number of researchers blended a higher hole mobility TcTa with PVK to improve hole transport in PhOLEDs (Lee *et al.*, 2010; Song *et al.*, 2011; Talik, Woon, & Yap, 2016; Yun *et al.*, 2017) and quantum dot LED (M. D. Ho *et al.*, 2013) to achieve better device efficiency.

Noted that the efficiency of OLEDs may be related to frontier energy level of host and dopant (Cui *et al.*, 2013; Lee *et al.*, 2010), triplet energy (Lee *et al.*, 2010; Zhu *et al.*, 2015), carrier injection and transport (Krucaite & Grigalevicius, 2019; L. Xiao *et al.*, 2011; Xing *et al.*, 2012), molecular conformation (Hamilton *et al.*, 2018; Marcato & Shih, 2019), host to guest energy transfer (Krucaite & Grigalevicius, 2019), just to name a few. The machine learning approach to design blue PhOLEDs by Janai *et al.* correlated the efficiency of blue OLEDs with various parameters revealed triplet energy of ETL and host, as well as HOMO and thickness of EML significantly contributed to the efficiency (Janai *et al.*, 2018). Lee *et al.* blended 7 wt % of TcTa to PVK increased the current efficiency in white PhOLEDs from 15 cd/A to 20 cd/A which the author attributed it to the triplet energy confinement, higher hole mobility and HOMO/LUMO level of TcTa (Lee *et al.*, 2010). However, debates remain what actually attribute to the increase of efficiency.

The extra warm white PhOLEDs here was realized by doping three primary colour phosphorescent emitters, i. e. Hex-Ir(phq)₃, Ir(ppy)₃ and FIpic for red, green and sky-blue colour, respectively. The phosphors ratio in PhOLEDs needs to be correctly optimized in order to emit warm white light without reducing the device efficiency.

The fabricated HOD showed the hole current increased almost triple for PVK:TcTa (60:40) compared to pristine PVK. However, the white PhOLEDs with PVK:TcTa (60:40) only showed only slightly improved current efficiency (7% higher) as compared to pristine PVK. Here, synchrotron techniques such as UPS, GIXRD and NEXAFS measurement were carried out to probe the interfacial dipole and disorder of different blends ratio of PVK:TcTa to investigate the reasons behind the limited improvement of efficiency.

4.2 Experimental Methods

4.2.1 Material

The pre-patterned ITO coated glass substrates were ultrasonically cleaned using DI water, acetone, isopropyl alcohol and DI water again for 10 min, followed by oxygen plasma treatment for 5 min. All materials were purchased and used as received without further purification. TcTa, OXD-7, SPPO13, Hex-Ir(phq)₃, Ir(ppy)₃ and FIrpic were purchased from Luminescence Technology (Taiwan). PVK (average Mw = 1100000) and 2,2,3,3-Tetrafluoro-1-propanol purchased from Sigma-Aldrich. PEDOT:PSS (Clevios P VP Al 4083) was purchased from H.C. Starck. The molecular structure of the OSCs used in this work are illustrated in Figure 4.1.



Figure 4.1: The molecular structure of the OSCs used in this research.

4.2.2 PhOLEDs and Hole only Devices (HODs)

The device structure used in PhOLED was ITO/ PEDOT:PSS/ PVK:TcTa:OXD-7:Hex-Ir(phq)3:Ir(ppy)3:FIrpic (100-X:X:30:1:0.1:10) (30 nm)/ SPPO13 (50 nm)/ CsF (1nm)/ Al (100 nm). ITO/PEDOT:PSS/ PVK:TcTa (100-X:X)/Au (50nm) device was used as the HOD. Figure 4.2 shows the work function of ITO, PEDOT:PSS, CsF/Al, Au and the LUMO and HOMO for PVK, TcTa , OXD-7, Hex-Ir(phq)3, Ir(ppy)3, FIrpic and SPPO13 used in HOD and PhOLEDs in this works. Noted that these frontier orbital energy levels were constructed without considering the vacuum level shift at the interface. Different blending weight ratios of PVK:TcTa (X:100-X) were prepared and spin coated on PEDOT:PSS, a well-known hole injection layer (HIL). 50nm SPPO13 was prepared by dissolving in 2,2,3,3-Tetrafluoro-1-propanol and spin coated on the emissive layer, acted as ETL. The electrode CsF/Al and Au were thermally evaporated through shadow mask at base pressure of 4.2 x 10^{-4} Pa. The fabricated devices were then encapsulated in an N₂ environment using cover glasses and UV curable epoxy as adhesive. Current density (J), voltage (V) and luminance (L) were characterized using a Konica Minolta CS-200 coupled with Keithley 2612B System Sourcemeter. The thickness of all solutionprocessed films were measured using a profilometer (P-6 KLA-Tencor). The emission spectra were captured by Ocean Optic HR4000CG-UV-NIR coupling with fiber optic QF600-1-SR. The photovoltaic measurement was obtained using Newport 67005 under illumination of simulated AM1.5 light source at 100 mW/cm².



Figure 4.2: The vertical line indicates the work function for ITO (X. Deng *et al.*, 2014), PEDOT:PSS (L. Hu, Song, Yin, Su, *et al.*, 2020), CsF/Al (Huang *et al.*, 2015; X.-F. Peng *et al.*, 2017) and Au (Whitcher *et al.*, 2013). The value above and below the box indicate the LUMO and HOMO, respectively for PVK (Liaptsis & Meerholz, 2013), TcTa (S. Wu *et al.*, 2016), OXD-7 (S.-W. Liu *et al.*, 2013), Hex-Ir(phq)₃ (Hasan *et al.*, 2017), Ir(ppy)₃ (Mesta *et al.*, 2013), FIrpic (Z. Liu *et al.*, 2010) and SPPO13 (X. Wang *et al.*, 2017).

4.2.3 UPS, NEXAFS and GIXRD

Different ratios of 30nm thick PVK:TcTa (X:100-X) was spin coated on the bare ITO for UPS, NEXAFAS and GIXRD measurements. The work functions and HOMO levels of the materials were probed using UPS at the soft X-ray undulator beamline BL3.2Ua in the SLRI, Thailand. The samples were measured in a vacuum chamber under the base pressure of 1x 10⁻⁹ mbar, and subjected to UV radiation with a photon energy of 39.5 eV and a pass energy of 81.9 eV. NEXAFS spectroscopy was also performed at BL3.2Ua in SLRI. Nitrogen K-edge absorption spectra were measured in the TEY and TFY modes by scanning photon energy by tuning undulator gap and angle of grating simultaneously. TEY was collected from the sample drain current, and TFY on the multichannel plate detector. The photon energy of the beamline is calibrated in the $C1s \rightarrow \pi^*$ transition in the graphite. The base pressure of analysis chamber is $2x10^{-10}$ mbar and the energy resolution is about 0.4 eV on nitrogen K-edge. The soft X-ray is incident on sample at 70° in the s-polarized configuration. The GIXRD measurements were carried out using the beamline BL7.2W:MX at SLRI, Thailand, with energy of 12.658 keV using Mar165 CCD detector system. The sample holder and the detector are mounted on a MarDTB Goniometer system. The samples were tilted/rotated to adjust the angle of incidence to an angle of 0.1-0.3 °. FIT2D 12 was employed for the analysis.

4.2.4 UV-Vis and AFM

A PerkinElmer Lambda 750 UV-Vis-NIR was used to measure the material absorbance of the spin-coated PVK:TcTa on quartz substrates. The surface morphology of the spin-coated films were carried out via AFM (NT-MDT NTEGRA-Prima) operating at tapping mode.

4.3 **Results and Discussion**

4.3.1 Colour Temperature Tuning for Extra Warm White PhOLEDs

The fabricated of extra warm white PhOLEDs started with tuning the colour temperature by fabricating the device with different ratios of red, green, blue dopants. The CCT usually is related to human's visual comfort, glare, and brightness perception (Boyce, 2014). The colour of device fabricated were determined by comparing the colour coordinate with CIE 1931 (x, y) chromaticity diagram. The device structures used for colour temperature tuning are ITO/PEDOT:PSS/30nm PVK:OXD-7:Hex-Ir(phq)₃:Ir(ppy)₃:FIrpic (100:30:1:X:Y) /50nm SPPO13/CsF/Al. The PVK, a HTM and OXD-7, an electron transport materials (ETMs) are blended together with ratio of 100:30 as the host of EML to facilitate hole-electron charge balance. The SPPO13 has swallow LUMO (2.91 eV) and deep HOMO (6.56 eV) served as an EIL and hole blocking layer,

to confine the exciton in the EML. Hex-Ir(phq)₃, Ir(ppy)₃, FIrpic are chosen as RGB dopants respectively. Noted that FIrpic is chosen in this work because it emits greenishblue, generally yield a warm white in RGB based white PhOLEDs (C.-H. Chang *et al.*, 2010).

For tuning the colour temperature, a set of structural identical OLEDs device with the weight ratio of Hex-Ir(phq)₃ was maintained at 1 % relative to PVK was fabricated, with different weight ratios of Ir(ppy)₃ and FIrpic. The FIrpic ratio was varied for 10 %, 15 % and 20 % while the Ir(ppy)₃ ratio was varied between 0.1 %, 0.2 % and 0.5 %. Noted that the blue phosphor has the high triplet energy, 2.62 eV (Shih *et al.*, 2007; J. Wang *et al.*, 2015) compared to Ir(ppy)₃ (2.4 eV) (Baldo & Forrest, 2000; Miao *et al.*, 2015; Sudhakar *et al.*, 2003) or Hex-Ir(phq)₃ (2.11 eV, refer to Figure Q in Appendix Q), which the energy can be transferred only from FIrpic to Ir(ppy)₃ or Hex-Ir(phq)₃ but not the other way round. The ratio of FIrpic of 10 % and above can ensure the efficient blue component in white PhOLEDs. Meanwhile, the green dopant, Ir(ppy)₃ varied slightly (less than 1 %) in order to fine tune the colour temperature of OLEDs.

Table 4.1 and Figure 4.3 show the colour coordinates and the transition of colour coordinate on CIE 1931 chromaticity diagram for OLEDs with different phosphor ratios. The chromaticity diagram was overlaid with a curve line, named Planckian locus, draw along with perpendicular isothermal line to correlate the colour emitted with the temperature of an incandescent black body. The CCT of the light source can be determined by looking at the intersected isothermal line with colour coordinate. RGB scheme with ratio 1:0.1:10 showed the colour temperature around 2500 K, which is the warmest colour among all configurations. Adding Ir(ppy)₃ shift the colour coordinate toward green region, away from Planckian locus. Increasing FIrpic however do not show consistent change, probably due to concentration quenching with increased FIrpic concentration as reported by Lei *et. al.* (Lei *et al.*, 2011). Subsequently, all the PhOLEDs

were doped with Hex-Ir(phq)₃, Ir(ppy)₃, FIrpic phosphorescent dopant with weight ratio 1:0.1:10 to realize the warm white colour emission.



Figure 4.3: The CIE coordinate of different phosphorescent dopant ratios when 1000 cd/m² overlay with chromaticity diagram. The R, G, and B are acronym for Red (Hex-Ir(phq)₃), Green (Ir(ppy)₃) and Blue (FIrpic) respectively. The black arc inside the diagram represents the Planckian locus of an incandescent black body with the label CCT perpendicular to the locus.

Ratio of Hex-Ir(phq)3:Ir(ppy)3:FIrpic	CIE Colour coordinate (x, y)
1:0.1:10	0.4847, 0.4319
1:0.1:15	0.4648, 0.4294
1:0.1:20	0.4686, 0.4297
1:0.2:10	0.4425, 0.4362
1:0.2:15	0.4454, 0.4404
1:0.2:20	0.4156, 0.4299
1:0.5:10	0.3754, 0.4447
1:0.5:15	0.3800, 0.4428
1:0.5:20	0.4429, 0.4668

Table 4.1: The CIE coordinate of different phosphorescent dopant ratios when brightness is 1000 cd/m^2 .

4.3.2 Effect of Blending TcTa to PVK on Efficiency of PhOLEDs

Afterward, the effect of blending TcTa in PVK host was investigated with the optimized RGB scheme of 1:0.1:10. Three PhOLEDs with different PVK:TcTa ratios were fabricated in order to find the correlation between the ratio of TcTa and PhOLEDs performance. The pristine PVK, PVK:TcTa (90:10) and PVK:TcTa (60:40) were chosen as host in this research. Noted that spin coating thin films with TcTa concentration higher than 50% will exhibit poor film morphology which has adverse effect on performance of PhOLEDs, due to the strong molecular aggregation of TcTa (Talik 2016).

Figure 4.4 (a) and (b) show the brightness-voltage (L-V) and current densityvoltage (J-V) characteristic of different device configurations, respectively. The maximum brightness increased from 4363 cd/m² to 9570 cd/m² when ratio TcTa increased from 0 % to 40 %. Both PVK and PVK:TcTa (90:10) showed similar turn-on voltage, V_{turn-on} (1 cd/m²) at 4 V, while V_{turn-on} for PVK:TcTa (60:40) decreased to 3.8 V. The reduction of V_{turn-on} may attribute to the HOMO level of TcTa (5.8 eV) located between PEDOT:PSS (5.1 eV) and PVK (5.9 eV), which effectively reduces the hole injection barrier between anode and EML (Yeoh *et al.*, 2013). The current density of PVK:TcTa (90:10) and PVK:TcTa (60:40) are 52 mA/cm² and 98 mA/cm² when applied bias of 8V respectively, which are almost the double and triple compared to pristine PVK (27 mA/cm²). The similar J-V trend had been observed in previous work (Talik, Woon, & Yap, 2016). The increasing current density after blended with TcTa may contributed by the better charge balance, since the hole mobility in TcTa is 1.5×10^{-4} cm²V⁻¹s⁻¹ (L. Xiao *et al.*, 2011), which is far higher than PVK (1.98×10^{-6} cm²V⁻¹s⁻¹) (Talik, Woon, & Yap, 2016). However, Talik *et. al.* reported doping TcTa to PVK host decreasing the hole mobility at low concentration of TcTa (<20 %), due to the shallow trap created by TcTa (Talik, Woon, & Yap, 2016). Thus, the higher current density might not be explained by the higher hole mobility of TcTa compared to PVK. Further investigation on hole-only device (HOD), UPS and AFM may explain the increment of current density by looking at the hole current, vacuum level shift and morphology upon blending TcTa.



Figure 4.4: (a) J-V, (b) L-V, (c) current efficiency and (d) power efficiency of white PhOLEDs with different device structures.

Device	V _{turn on} (V)	$\frac{L}{(cd/m^2)}$	$\eta_L^{a, [b]}$ (cd/A)	$\eta_p^{a, [b]}$ (lm/W)	CIE(x, y) ^b
РVК	4.0	4363	19.0[18.9]	10.1[9.6]	(0.497,0.418)
PVK:TcTa (90:10)	4.0	8324	20.2[19.7]	12.3[11.0]	(0.477,0.418)
PVK:TcTa (60:40)	3.8	9570	20.4 [20.4]	13.9[11.8]	(0.483,0.416)

Table 4.2: Performance of devices with different TcTa ratios.

^a Maximum value of the device

^bValues when brightness is 1000 cd/m²

Figure 4.4 (c) and (d) show the current efficiency (η_L) and power efficiency (η_p) versus brightness of different device configurations. The efficiency of the PhOLED is improved by blending TcTa into PVK in the white PhOLED. Compared to the control/reference, doping 10 % TcTa to PVK improves the efficiency from 9.6 lm/W (18.9 cd/A) to 11.0 lm/W (19.7 cd/A) at 1000 cd/m². Further increasing the concentration of TcTa to 40 % improves the efficiency to 11.8 lm/W (20.4 cd/A) at 1000 cd/m². The maximum power efficiency of the device occurred in the region between 200 cd/m² and 800 cd/m², increasing in the order of 0 %, 10 % and 40 % TcTa with 10.1 lm/W, 12.3 lm/W and 13.9 lm/W respectively.

Highlights	Maximum	CIE	Source
	Efficiency	coordinate	
	_	and CCT	
PVK:TcTa blended host doped with	20.4 cd/A,	(0.48,0.42),	This work
red, green, blue iridium complex	13.9 lm/W	2440 K	
Blue fluorescent doped with	5.68 cd/A,	(0.41, 0.34)	(Yoon <i>et al.</i> ,
synthesized orange red TADF	3.93 lm/W		2019)
Synthesized blue TADF and orange	17.3 cd/A,	(0.41, 0.41)	(X. Liao <i>et al.</i> ,
iridium complex as co-dopant	6.8 lm/W		2018)
Synthesized white polymer with	25.0 cd/A,	(0.41, 0.43)	(Y. Wang et al.,
TADF pendant	11.2 lm/W		2017)
Synthesized white polymer with	23.0 cd/A,	(0.37, 0.38)	(C. Li et al., 2017)
TADF pendant	32.8 lm/W		
Synthesized Cu(I) complexes as	12.8 cd/A,	(0.44, 0.47),	(X. Yang et al.,
emitter	5.9 lm/W	3524 K	2017)
Synthesized orange-red iridium	25.6 cd/A,	(0.45, 0.41)	(YL. Deng et al.,
complex with FIrpic	15.3 lm/W		2016)
Ambipolar host with red, green, blue	66.5 cd/A	(0.50, 0.44)	(Jou et al., 2012)
iridium complex	38.8 lm/W	2320 K	

 Table 4.3: Performance of recently published solution processable warm white OLEDs.

Table 4.2 summarizes the performance of different device structures. Noted that the fabricated warm white PhOLEDs have comparable performance to other recent works as shown in Table 4.3. All the three devices showed a CIE colour coordinate around (0.48, 0.42) at 1000 cd/m², corresponding to the extra warm white light emission, since all the devices adapted the RGB scheme of 1:0.1:10 as optimized. Overall, PVK:TcTa (60:40) showed 23 % (7 %) higher in power efficiency (current efficiency) compared to control at 1000 cd/m². The efficiency increase is small considering that the increase in charge balance (current density) upon blending the TcTa into PVK.

4.3.3 Correlated Colour Temperature (CCT) of PhOLEDs with PVK:TcTa Host

The single emissive PhOLEDs fabricated with different percentage of TcTa showed CIE coordinate around (0.48, 0.42), corresponding to extra warm white colour. A stable CCT is obtained even at different brightness enabling the dimming of lighting without complex circuit. Figure 4.5 shows the shift of CIE coordinate with the increment of brightness. When the brightness increases, the CIE coordinates transverse along the Planckian locus with CCT shifting from a warmer to cooler white. Planckian locus is the colour locus of an incandescent black body as the temperature changes. Blending TcTa doesn't change the CCT at 1000 cd/m² at significant level. The CCT for PVK:TcTa with ratios of (100:0), (90:10) and (60:40) at 1000 cd/m² are 2350 K, 2510 K and 2440 K respectively. The CCT is highly dependent on the concentration and doping ratio of phosphorescent emitters. Since the concentration and ratio are maintained to be constant, the second factor that could affect is the shift of zone of recombination(Tyagi et al., 2013). This happens when there is a change of electron and hole mobilities and currents. Since the EML is 30 nm, the zone of recombination is confined within this narrow 30 nm resulting in almost constant CCT. Furthermore, the deviation of CIE coordinate from Planckian locus is small (~0.02 at 1000 cd/m²) an important requirement for a white OLED. The CCT for device PVK:TcTa (60:40) transverses from 2360 K to 2620 K along

the Planckian locus when the brightness increases from 100 cd/m² to 9500 cd/m². The inset of the Figure 4.5 shows the EL of the PVK:TcTa (60:40) at 1000 cd/m². The highest and second highest peaks correspond to the emission from Hex-Ir(phq)₃ and FIrpic, respectively. The green emission is not noticeable due to the trace amount of Ir(ppy)₃ doped in order to tune the spectrum near to the Planckian locus.



Figure 4.5: The shift of CIE coordinates along the Planckian locus for different device structures. The inset is the normalized spectrum of EL at a brightness of 1000 cd/m² for PVK:TcTa (60:40).

4.3.4 Hole only Device (HODs)

The HODs, ITO/PEDOT:PSS/ PVK:TcTa (X:100-X)/Au were fabricated to study the hole injection of PVK:TcTa blend. The fundamental process behind HODs is only hole injection is allowed from the contacts (PEDOT:PSS and Au) into the semiconductor film (PVK:TcTa). To inject holes, the contact must injecting the carrier to the HOMO of organic semiconductor. Without consider interfacial dipole (which can be obtained by UPS measurement later), the energy barrier for hole injection in HODs is estimated around 0.7-0.8 eV based on Figure 4.1. The injected electron in HODs is negligible due to the high barrier (~3.0 eV) between work function of electrode and LUMO of PVK:TcTa.



Figure 4.6: Current density versus electric field of HODs for different PVK-TcTa blending ratios.

Figure 4.6 shows the hole current density increased with percentage of TcTa. The hole current density from 0.212 mAcm⁻² (pristine PVK) to 11.6 mAcm⁻² (pristine TcTa) at 10⁶ V/cm. The almost two order magnitude higher of hole current density for pristine TcTa compared to PVK may result from the hole mobility in TcTa is 1.5×10^{-4} cm²V⁻¹s⁻¹ (L. Xiao *et al.*, 2011), which is far higher than PVK (1.98×10^{-6} cm²V⁻¹s⁻¹) (Talik, Woon, & Yap, 2016). However, the current density increased slowly with electric field when TcTa increases from 0% to 40%. At blending ratio of 30:70 (PVK:TcTa), the current increases at least an order magnitude higher compared to pristine PVK. The non-linear increasing of hole current in the PVK:TcTa blend may be related to reduced energy barrier, formation of percolation network, which will be further discussed after conducting UPS measurement and AFM.

Blending of TcTa into PVK results in increased in hole current which could be beneficial for OLEDs, where the hole current/transport is a limiting factor, in particular for PVK which has a low hole mobility. It is well known that mixing two semiconducting materials may result in variation of band bending and vacuum level shift at interface (Whitcher, Wong, *et al.*, 2016), structural conformation (Rivnay *et al.*, 2012), phase segregation (Kang *et al.*, 2008; Shin *et al.*, 2013; Z. Zhang *et al.*, 2020), just to name a few, which may impact the device performance. In this work, UPS, GIXRD, NEXAFS, UV-Vis and AFM will serve as characterization tool to further understand the effect of blending PVK with TcTa, which may explain the marginal improvement in current efficiency.

4.3.5 Photovoltaic Response

A photovoltaic experiment was performed to measure the open circuit voltage (V_{oc}) of the devices, by illuminating the devices under AM1.5 light source at 100 mW/cm². Since all the devices have identical structure except for their ratios of TcTa, the change of V_{oc} corresponds to the reduction in the hole-injection barrier (X. Xiao *et al.*, 2020). As shown in Figure 4.7, the V_{oc} is barely 0.025 V without TcTa and increased from 0.100 V to 0.225 V when the concentration of TcTa is increased from 10 % to 40 %. Referring to Figure 4.2, since the HOMO level of TcTa (5.8 eV) is between PEDOT:PSS (5.1 eV) and PVK (5.9 eV), easier hole injection from PEDOT:PSS to TcTa is expected compared to PVK. Therefore, TcTa should provide an easier route for holes to be injected from PEDOT:PSS to EML compared to PVK. Using photovoltaic experiment, the increased V_{oc} clearly corresponds to the improved hole injection through doping of TcTa. However, photovoltaic response measurement is unable to provide a full picture of energy-level alignment. Despite a small difference (0.1 V) between the HOMO levels of TcTa and PVK, the increased efficiency and change of V_{oc} are large. Doping of TcTa into PVK might affect the degree of vacuum level shift between PEDOT:PSS and EML. In order to

verify this hypothesis, we carried out the UPS analysis to clearly visualize the energy level alignment between anode and EML with different PVK:TcTa ratios on top of PEDOT:PSS.



Figure 4.7: Photovoltaic response of white PhOLEDs with different device structures.

4.3.6 UPS

UPS is used to experimentally determine the electronic structure of the outermost valence, corresponding to the HOMO for organic material as well as vacuum level at the interface. To investigate the HOMO and vacuum level of blending TcTa with PVK, 11 samples with different ratio of PVK:TcTa (100-X:X, x=0, 10, 20, 30.... 90, 100) were measured by UPS. The LECO and HECO of PEDOT:PSS and different blending ratios of PVK:TcTa are labelled in Figure 4.8.



Figure 4.8: (a) HECO and (b) LECO of UPS spectra for PEDOT:PSS and different blending ratios of PVK:TcTa.

The LECO onsets decreases from 1.86 eV (0% TcTa) to 1.62 eV (100% TcTa) indicating reduction of hole energy barrier with increasing TcTa content as shown in Figure 4.9 (a). The hole injection barrier (Δ_h) measured here takes into account of the shift of LECO onset due to the misalignment of vacuum level between PEDOT:PSS and PVK:TcTa, named as interfacial dipole (Δ). The vacuum levels (E_{VAC}) of PVK:TcTa and PEDOT:PSS are obtained by minus the HECO onset from photon energy (39.5 eV). Figure 4.10 shows the interfacial diagram to illustrate the change of LECO onset, hole injection barrier, vacuum level and interfacial dipole between PVK:TcTa are not aligned at same height indicating there are vacuum shift across the interface due to the presence of interfacial dipole.



Figure 4.9: (a) LECO onset of PVK:TcTa blends and (b) interfacial dipole between PEDOT:PSS and PVK:TcTa blends as a function of TcTa ratio.



Figure 4.10: Interfacial diagram of PEDOT:PSS/PVK:TcTa (100-X). The vacuum level (E_{VAC}), Fermi level (E_F) and HOMO onset (LECO onset) was represented by black, blue and red solid horizontal line, respectively. The black dashed line indicated the change of interfacial dipole (Δ) while the red dashed line shows the decreasing HOMO onset with increasing percentage of TcTa. The hole injection barrier (Δ_h) can be measure from the energy difference between PEDOT:PSS Fermi level and HOMO onset, as the blue dashed line.

The interfacial dipole of PEDOT:PSS/PVK:TcTa interface is shown in Figure 4.9 (b). For all PEDOT:PSS/PVK:TcTa interface, all the vacuum level dipoles are pointing away from PVK:TcTa. Blending TcTa to PVK reduced the interfacial dipole from 0.4 eV to 0.2 eV when TcTa content is increased from 0 % to 70 %. However, further increasing the TcTa to 100 % increased the interfacial dipole to 0.49 eV. The mechanism that governed the magnitude of the interfacial dipole can be contributed by various factors such as charge transfer (Crispin *et al.*, 2002), permanent dipole (Yanagisawa *et al.*, 2008), Pauli push-back (Vázquez *et al.*, 2007), image charge (Van Reenen *et al.*, 2014) and just to name a few . Even through carbazole has a strong dipole moment, due to the highly disorder and amorphous nature of the thin film and molecular symmetry of TcTa, the contribution of interfacial dipole from the molecular dipole moment from carbazole moieties in PVK or TcTa is negligible. The HOMO levels of PVK and TcTa obtained from the UPS are 6.26 eV and 5.93 eV respectively. The HOMO level of the TcTa is shallower as it has a larger conjugation as the HOMO electron clouds are distributed to both triphenylamine and carbazole moieties.

Besides, by taking into account of the vacuums level shift between PEDOT:PSS and PVK, blending PVK with 40 % TcTa slightly reduced the hole injection barrier ~0.1 eV compared with pristine PVK. Such a reduction unable to explain the one order magnitude of increase of hole current in HOD device when 40% TcTa.



Figure 4.11: UPS Spectra of PVK:TcTa (50:50) along with the comparison of pristine PVK and TcTa.

A closer look at the LECO reveals the occupied state, also known as DOS of different TcTa ratios are closer related to PVK rather than TcTa. The UPS results of PVK:TcTa (100-X:X) are expected to be proportional to the DOS contributed by both PVK and TcTa according the mass ratio. Figure 4.11 shows the overlay for UPS signals of pristine PVK, TcTa and PVK:TcTa at a ratio of 50:50 with the shifted LECO such that the onset of LECO for all samples are the same for clarity. The difference between UPS signals of TcTa and PVK is the peak located at around 4.3 eV corresponding to the excitation of the triphenylamine moiety in TcTa. Noted that the UPS spectrum of PVK:TcTa (50:50) correlates strongly with pristine PVK rather than proportional to the summation their component of PVK and TcTa. This behavior is seen up to the ratio of 20:80 (PVK:TcTa) as shown in Figure 4.12.



Figure 4.12: UPS spectra for samples with different ratios of PVK:TcTa. The LECO of samples were aligned for comparison. The signature of TcTa located at BE of 4.3 eV, corresponding to the excitation of the triphenylamine moiety was highlighted by circle.

UPS is surface sensitive technique due to the short mean free path of photoelectron, where only top 3-10 nm on the surface are probed. One of the possibilities is that, there might be vertical phase segregation whereby the PVK tends to agglomerate at the top surface. The hypothesis can be verified by measuring NEXAFS on Nitrogen absorption edge (N1s) since PVK and TcTa contain carbazole moieties having different percentage of nitrogen atoms, as well as the different surrounding chemical environment, as NEXAFS is very sensitive to species of neighboring atom.

4.3.7 NEXAFS

In order to verify the vertical phase segregation, NEXAFS was carried out on nitrogen K-edge. Nitrogen K-edge absorption spectra are measured in both the TEY and TFY modes. TEY in NEXAFS is surface-sensitive since the photoelectrons and inelastically secondary electrons are collected with their escape depth of up to 2 nm -10 nm below the surface while TFY can probe up to 50 nm below the surface. Comparing the difference between TEY and TFY would enable us to affirm the presence of vertical phase segregation. The absorption edge of N1s, located at lower energy of 400.5 eV assigned to the transition from N1s to π^* (N1s $\rightarrow \pi^*$) (Kanunnikova *et al.*, 2017) while the broad spectra feature at higher energy (>405 eV) are resulted from the N1s $\rightarrow \sigma^*$ transition (Latham et al., 2017; Leinweber et al., 2007). Figure 4.13 shows the (a) TFY and (b) TEY of nitrogen K-edge for different PVK:TcTa blending ratios, after background subtracting and energy calibrated with absorption edge. The N1s $\rightarrow \sigma^*$ transition around 410 eV redshifted from 411.4 eV to 409 eV with the increasing % TcTa. The similar NEXAFS profile of TFY and TEY of nitrogen K-edge for various PVK:TcTa ratios implied no vertical phase segregation after blending TcTa to PVK. Hence, the similarity of UPS between PVK:TcTa up a ratio of 20:80 with pristine PVK cannot be explained by vertical phase segregation since there is none.



Figure 4.13: (a) TFY and (b) TEY of Nitrogen K-edge for different PVK-TcTa blending ratios.

4.3.8 GIXRD

As shown by the UPS measurement, blending TcTa to PVK barely reduce the hole injection barrier from 1.9 eV to 1.6 eV. Such a marginally reduction ~0.3 eV cannot explain the increased hole current (up to 1 order magnitude) in HOD device when blended with TcTa, as discussed in section 4.3.4. Even TcTa has almost 2 order magnitude of hole mobility higher than PVK, however, hole transport in PVK:TcTa blend occurs by hopping between adjacent carbazole moieties (Ha *et al.*, 2016; Shaheen *et al.*, 1999), and such hopping is typically limited to a maximum distance of 5–10 Å. If TcTa dispersed evenly in PVK:TcTa blend, the hole migration may take place by hopping between PVK and TcTa, where the hole transfer rate will be bottlenecked by the lower hole mobility of PVK.

Hence, TcTa might crystallize in PVK:TcTa blend, which the highly orientated face to face stacking of TcTa can lead to high mobility of TcTa as reported (Xing *et al.*, 2013). Besides, there might be phase segregation (not vertical phase segregation) that creates percolation networks that enable fast charge transport along the TcTa. Here, the crystallinity and phase segregation of the polymer blend were inspected by GIXRD and AFM, respectively.

The GIXRD measurements were carried out for spin coated pristine PVK, PVK:TcTa (60:40) and pristine TcTa film on ITO substrate with incident angle of 0.1 °-0.3 ° to understand the molecular arrangement in thin film. The GIXRD can measure the crystallization in thin film due to the highly surface sensitivity resulted from the small incident. A highly order arrangement of molecular structure (crystallization) will result in diffraction pattern on 2D detector and vice versa.

Figure 4.14 (a-c) shows the 2D diffraction patterns for PVK, PVK:TcTa (60:40) and TcTa. PVK and TcTa do not show any significant diffraction peak, indicate no preferential arrangement of molecules in PVK and TcTa. Even though PVK:TcTa (60:40)

showed two diffraction rings, but it may contribute by the ITO substrate. In such a case, quantitative analysis is required to reveal the origin of the diffraction pattern. GIXRD was performed with 4-Bromo Benzoic acid as standard sample to accurately calibrate the sample-detector distance in SAXSIT program. The 2D diffraction pattern was then post processing to 1D diffraction intensity by circular integration over Cu 2theta angle, followed by normalization as shown in Figure 4.15. Figure 4.15 confirmed the two diffraction rings at 31 ° and 36 ° observed in PVK:TcTa (60:40) corresponding to the ITO substrate along (222) and (400) plane, respectively. Hence, solution processable PVK, PVK:TcTa (60:40) and TcTa do not show any preferential orientation. Xing *et al.* reported vacuum deposited TcTa shows more orientation and high crystallization compared to spin coated film (Xing 2013). The GIXRD results show the TcTa arrangement in the blend is highly disorder, excluding the possibility of high hole current density induced by the π - π stacking of the highly oriented TcTa molecules.



Figure 4.14: The 2D diffraction patterns for (a) Pristine PVK, (b) PVK:TcTa (60:40) and (c) Pristine TcTa.


Figure 4.15: Diffraction intensity of GIXRD for (a) pristine PVK, (b) PVK:TcTa (60:40) and (c) pristine TcTa thin films. The peaks at 31 ° and 36 ° correspond to the plane (222) and (400) for ITO, respectively.

4.3.9 AFM

GIXRD measurement confirmed the random arrangement of TcTa in PVK blend. Here, AFM was used to test the hypothesis of the existence of percolation network among TcTa due to the phase segregation (not vertical phase segregation). This type of phase segregation is the separation of molecules into macroscopic regions of different compositions while maintaining the disorder nature of each component within the percolation networks. AFM has been widely used to validate such a phase segregation in heterogeneous thin film by semi contacting (tapping) mode.

Figure 4.16 shows the phase contrast images of pristine PVK (a) and (b-d) PVK:TcTa blend with ratios of (80:20), (50:50) and (30:70). As expected, PVK shows no phase contrast while PVK:TcTa (80:20) shows an increased phase contrast as indicated in Figure 4.16 (a) and (b) respectively. Blending with 50 % and 70 % TcTa show increased phase contrast as shown in figure (c) and (d). The phase shift between driver

and oscillating tip are modulated by surface properties such as elasticity, viscosity or friction. PVK (a polymer) showing distinct different of surface properties compared to the TcTa (a small molecule). Since the phase image is sensitive to the variation in composition, such phase contrast is a good illustration of phase segregation. Rani et al and Lu et al. works suggested percolation model, where the random resistor network connect each molecular site, forming percolative network in polymer matrix for the charge carrier to transport via variable range hopping(N. Lu *et al.*, 2015; Rani *et al.*, 2017). The phase segregation may form percolation pathways through TcTa, explaining the trend of HOD device.



Figure 4.16: Phase images of thin film obtained from (a) pristine PVK and (b-d) PVK:TcTa blends with ratios of (80:20), (50:50) and (30:70).

Note that bare PVK film coated on the PEDOT:PSS has the largest roughness of root mean square ($R_{\rm rms}$) of 1.53 nm with average roughness ($R_{\rm a}$) of 1.20 nm. Doping TcTa into

PVK improves the uniformity of the film with R_{rms} of 1.12 nm and R_a of 0.88 nm for PVK :TcTa ratio of 30:70 (Figure 4.17 and Table 4.4).



Figure 4.17: Surface roughness for thin film obtained from (a) pristine PVK and (bd) PVK:TcTa blend with ratio (80:20), (50:50) and (30:70).

Table 4.4: Average roughness (R_a) and root mean square roughness (R_{rms}) for PVK:TcTa with ratios (100:0), (80:20), (50:50) and (30:70) measured by AFM.

PVK:TcTa	100:0	80:20	50:50	30:70
R _a (nm)	1.20	1.06	0.92	0.88
R _{rms} (nm)	1.53	1.34	1.17	1.12

4.3.10 UV-Vis Measurement for Different Blending Ratio of PVK:TcTa

The AFM results implied high hole mobility TcTa (compared PVK) may form interconnected network, facilities the hole transport, as indicated by the noticeable phase segregation in PVK:TcTa blend. However, the efficiency of PhOLEDs with PVK:TcTa only improves slightly even with the improved charge carrier balance. By coupling the UPS result with density function theory and molecular dynamic simulation, Woon *et. al.* suggested blending TcTa in PVK may compactify the PVK polymer as shown by the face to face stacking (Lewis *et al.*, 2012) of carbazole moieties in Figure 4.18, which resulted in the PVK dimers (K. L. Woon *et al.*, 2019). PVK dimers reduced the triplet energy of PVK host from 2.88 eV to 2.46 eV (Jankus & Monkman, 2011), increasing the triplet traps that quench the high triplet blue phosphorescent dopant, such as FIrpic (triplet energy : 2.62eV) in this work, limited the efficiency of PhOLEDs.



Figure 4.18: The compactified PVK pentamer in PVK:TcTa (50:50) and their corresponding HOMO (K. L. Woon *et al.*, 2019)

The absorption of the ultraviolet (UV) and visible light ranges in OSCs always arises from electronic excitation between molecular orbital, in particular, transition between HOMO and LUMO. Therefore UV-Vis absorption can be used to experimentally determine the HOMO-LUMO gap. Increasing the number of conjugations in the system always increasing the delocalization of electron density, leading to smaller HOMO-LUMO gap and resulted in redshift of absorption peak (or edge) in UV-Vis spectra. If carbazole moieties tend to stack in face to face orientation, the increased π - π interactions between carbazole moieties in PVK is expected to red-shift the onset of absorption band (H. Liu *et al.*, 2015). UV-Vis spectra for sample of PVK:TcTa (100-X:X, X=0, 10, 20...100) spin coated on quartz substrate were measured as shown in Figure 4.19.



Figure 4.19: Absorption spectra for different PVK-TcTa blending ratios.

Assuming there is little change of the absorption curve of TcTa as obtained in pristine TcTa, the absorption curves contributed solely by the PVK can extract from the composite by deducting out the TcTa absorption curves by weight ratio. The on-set of absorption increases from 356.2 nm to 360.0 nm for pristine PVK and 20:80 PVK:TcTa respectively as shown in Figure 4.20. The onset of absorption is obtained from the intersection of the baseline extending from 450 nm to ~ 360 nm and the slope of the first peaks. The PVK signal was unable to extracted from PVK:TcTa (10:90) due to the low signal to noise ratio. The increase of on-set (red-shift) of absorption edge agrees with the increased densification of PVK, as suggested by the molecular dynamic simulation result (K. L. Woon *et al.*, 2019).



Figure 4.20: Absorption spectra of PVK extracted from different PVK:TcTa blending ratios along with the selected baseline. The vertical line indicated the absorption onset of pristine PVK.

Jankus and Monkman (2011) demonstrated the triplet energy of dimer in PVK is merely 2.1 eV, potentially to quench the emission from blue dopants (Jankus & Monkman, 2011). It is worth noting that blending TcTa into PVK gives only marginal improvement in current efficiency, because the increase in charge balance (as shown in HOD) is superseded by the increase of dimer quenchers. However, due to lower hole injection barrier and better charge balance with higher TcTa content, the driving voltage is reduced, giving a higher power efficiency.

Since PVK is increasingly compactified when more TcTa is added, it may subtly change the density of thin films which translates into increased electron density. As the wave functions of the conductor and the molecule next to it overlaps, due to Pauli exclusion principle, the increased electron density tails at thin films pushed deeper back the electron tails of the conductor (Bauert *et al.*, 2011). This charge rearrangement, called "Pauli push-back" effect may explain the reduction of the surface dipole with increasing

TcTa up to 70 % in Figure 4.8 (b). The reduced PVK content in the PVK:TcTa blend may explain the trend of surface dipole getting higher when TcTa above 80 %.

4.4 Summary

Mixing three primary colour dopants, Hex-Ir(phq)₃, Ir(ppy)₃ and FIrpic in a 1:0.1:10 ratio in PVK host realized an extra warm white PhOLEDs with colour temperature around 2500 K. Adding 40 % TcTa into PVK does not significantly change the colour temperature but improve the current efficiency of PhOLEDs to 20.4 cd/A, which is 7 % higher compared to pristine PVK device. The one order magnitude higher of hole current after blending 40% TcTa cannot be explained neither by the ~0.1 eV reduction of hole injection barrier as shown in UPS nor crystallisation of TcTa since the GIXRD showed TcTa molecule randomly arrange in the blend. The NEXAFS confirmed there is no vertical segregation in PVK:TcTa film. However, the significant phase segregation with higher TcTa ratio was shown in AFM. The hole may be hopping along the percolation path of disorder TcTa explaining the increased hole current when in composite. Lastly, the UV-Vis is used to verify the compactification of PVK resulted in face to face stacking of carbazole moieties as the on-set of absorption of PVK is redshifted. The reduction of energy barrier with addition of TcTa reduced the driving voltage but the increased number of carbazole dimers limited the increase in current efficiency. In future, care must be taken when mixing small molecule and polymer so that compactification of the polymer doesn't result in increased of quenching sites.

CHAPTER 5: WORK FUNCTION MODIFICATION OF PEDOT:PSS BY MIXING WITH BARIUM ACETYLACETONATE

5.1 Introduction

PEDOT:PSS is a conducting polymer ionomer widely used in various electronic devices such as OLEDs (Shufen Chen *et al.*, 2018; K. L. Woon *et al.*, 2019), supercapacitors (Y. Liu *et al.*, 2015), OFETs (S. H. Kim *et al.*, 2017), OPVs (Howells *et al.*, 2018; Whitcher *et al.*, 2014) and many more due to its superior electronic and ionic conductivities, morphology, stability and solution processability. The high conductivity and smooth morphology of PEDOT:PSS rely on the electrostatically of attached PEDOT and PSS ring (Kanwat & Jang, 2016). PEDOT:PSS consists of the insulating negatively charged poly(styrenesulfonate) (PSS) counter-balanced by the positively charged PEDOT. The maximum oxidation of PEDOT is one charge per three monomer units, with the hole polaron delocalized over the three monomers forming a quinoid structure (D. Kim & Zozoulenko, 2019) counter-balanced by the electron located at the sulfonate side group. The weakly interacting ionomers resulted in an expanded coil conformation forming a colloidal dispersion in water.

In recent years, much effort has been concentrated in deepening the work function of the PEDOT:PSS. Several attempts have been carried out such as the use of metal oxide as dopants in PEDOT:PSS (Kanwat & Jang, 2016), surface treatment with alkyl alcohol (Lenze *et al.*, 2015) and addition of Nafion (Mauger *et al.*, 2014; Yeoh *et al.*, 2014) are found to deepen the work function up to 6 eV. Lowering the work function of PEDOT:PSS seems to be less successful. PEDOT:PSS modified with polyethylenimine can only reduce the work function to 4.0 eV (Z. Li, Qin, *et al.*, 2015; Y. Zhang *et al.*, 2015). Hence, efforts have been concentrated on solution processable sodium bicarbonate (Long & Noh, 2018), polymer zwitterion (Ruscello *et al.*, 2017), lithium phenolate complexes (Zhao *et al.*, 2019) and ruthenium acetylacetonate (W. Chen *et al.*, 2017) which are deposited below the aluminum electrode. The increase in the electron injection ability is found to be the result of formation of interfacial dipole between the conductive electrode which lowers the vacuum level of the semiconducting layer (W. Liu *et al.*, 2016; C.-H. Wu *et al.*, 2016). Recent efforts such as the use of self-compensated multivalent anions electron donors (C. G. Tang *et al.*, 2019) is promising as the effective work function of silver can be reduced to as low as 2.4 eV.

The search of solution processable low work function cathode is highly desirable as it can open up the potential of fabricating organic electronic devices without the use of high vacuum system for cathode deposition hence significantly reduces the cost of production. In this research, the Clevios[™] PEDOT:PSS Al4083 was mixed with Ba(acac)₂ in the hope of n-doping the PEDOT:PSS. UPS reveals the work function can be reduced as low as 3.6 eV. XPS suggests that the polystyrene sulfonic acids (PSSH) are being deprotonated, lowering the BE of O1s resulting in the formation of barium polystyrene sulfonate (Ba-PSS). The lowering of work function of PEDOT:PSS are resulted from the formation of interfacial dipole by Ba-PSS.

5.2 Experimental Methods

5.2.1 Material

Figure 5.1 shows the chemical structure of the materials used. PEDOT:PSS solution (Clevios[™] PVP AI4083) was purchased from Heraeus. SPPO13 was purchased from Luminescence Technology (Taiwan). Ba(acac)₂ and 2,2,3,3-Tetrafluoro-1-Propanol 98% were bought from Sigma-Aldrich. All materials were purchased and used as received without further purification.



Figure 5.1: Chemical structure of PEDOT:PSS, SPPO13 and Ba(acac)₂.

5.2.2 Device Fabrication

Different blending ratios of PEDOT:PSS:Ba(acac)₂ (1:X) with X= 0.2, 0.5, 1 and 5 were prepared by adding 3 mg, 7.5 mg, 15 mg and 75 mg of Ba(acac)₂ to 1 g of PEDOT:PSS solution respectively. Pristine Ba(acac)₂ solution was prepared by adding 15 mg of Ba(acac)₂ to 1 g of DI water. SPPO13 solution was prepared by dissolving 25 mg of SPPO13 to 1 ml of 2,2,3,3-Tetrafluoro-1-Propanol. All the solutions were filtered by 0.45-µm poly(tetrafluoroethylene) filter before use unless otherwise stated. Electron only device (EOD) has a device structure of ITO/ PEDOT:PSS:Ba(acac)₂ (1:X)/ SPPO13 (100 nm)/ CsF (1nm) / Al (100 nm). All the ITO coated glass substrates were ultrasonically cleaned using DI water, acetone, isopropyl alcohol and DI water again for 10 min, followed by oxygen plasma treatment for 5 min. Pristine PEDOT:PSS was spin-coated on pre-patterned ITO with spin speed of 500 rpm, 1000 rpm, 1500 rpm and 2000 rpm each 10 s. PEDOT:PSS:Ba(acac)₂ (1:X) samples were prepared by firstly spin coating PEDOT:PSS as buffer layer with similar recipe as pristine, before dispensing PEDOT:PSS:Ba(acac)₂ (1:X) solutions on top of first layer at 30 s at 2000 rpm. The fabricated devices were then annealed in glovebox with 120 °C for 10 min. For EOD, the

SPPO13 solution was subsequently spin-coated on top of PEDOT:PSS:Ba(acac)₂ (1:X) and annealed with 100 °C for 15 min. Finally, CsF (1 nm) and Al (100 nm) were thermally evaporated through shadow mask at base pressure of 4.2x10⁻⁴ Pa. The current density (J), voltage (V) of the devices were characterized with Keithley 2612B System Sourcemeter. The thickness of all solution-processed films was measured using a profilometer (P-6 KLA-Tencor).

5.2.3 UPS and XPS

The work functions of the PEDOT:PSS:Ba(acac)₂ (1:X) were probed using UPS at the soft X-ray undulator beamline BL3.2Ua at the SLRI in Thailand. The samples were measured in a vacuum chamber under the base pressure of 1×10^{-9} mbar, and subject to UV radiation with a photon energy of 39.5 eV and a pass energy of 10 eV. The chemical compositions of the spin-coated films were investigated using the PHI5000 Versa Probe II XPS system at the SUT-NANOTEC-SLRI joint research facility at SLRI in Thailand. The XPS spectra were collected using Al K α (1486.6 eV) radiation, under the base pressure of 1x 10⁻⁹ mbar.

5.2.4 AFM, UV-Vis and pH measurement

The surface morphology of the spin-coated films were measured using AFM (NT-MDT NTEG RA-Prima) operating at tapping mode. A Perkin Elmer PE750 Lambda UV– Vis–NIR was used to measure the material absorbance of the drop-casted and spin-coated PEDOT:PSS:Ba(acac)₂ (1:X) and Ba(acac)₂ thin films on quartz substrates. The pH of the PEDOT:PSS:Ba(acac)₂ (1:X) solution was measured using Mettler ToledoTM FiveEasyTM F20 pH/mV under atmospheric pressure and ambient temperature. Calibration was performed with buffer solution of pH 4.01, pH 7 and pH 9.21 before pH measurement.

5.3 Results and Discussion

5.3.1 pH Measurement

Four different mass ratio of PEDOT:PSS:Ba(acac)₂ solutions were prepared by mixed Ba(acac)₂ into 1ml of PEDOT:PSS. The prepared solutions were stirred for 10 min to obtain a homogenous mixture as shown in Figure 5.2.



Figure 5.2: The outlook of (a) pristine PEDOT:PSS and (b-e) PEDOT:PSS:Ba(acac)₂ (1:0.2), (1:0.5), (1:1) and (1:5) solutions, followed by the (f) pristine Ba(acac)₂ solution upon mixing and stirring.

A certain degree of precipitation was observed when mixed with Ba(acac)₂, especially the noticeable dark solid adhere to the wall of vial for PEDOT:PSS:Ba(acac)₂ with ratio 1:1 and 1:5. Filtering the mixture at the ratios of 1:1 and 1:5 (with 0.45µm pore filter) separated the precipitation, resulted in a clear solution. Noted the filtered solution of mixture at ratio of 1:0.2 and 1:0.5 remained dark blue, similar to the colour of the pristine PEDOT:PSS.

Precipitation can happen if the concentration of mixture exceeds its solubility (a physical process) or the formation of new substance (a chemical change). PEDOT:PSS is an well-known acidic solution with pH around 1.5-2.5 (S. Chen *et al.*, 2014) due to the presence of SO₃H group in PSS releasing H⁺ to solution. pH measurement appears to be a simply yet effective way to confirm the precipitation is due to physical or chemistry process, as change in pH hints a chemical process involved hydrogen ion (H⁺).



Figure 5.3: pH of PEDOT:PSS:Ba(acac)₂ (1:X) solutions.

Figure 5.3 shows the pH of PEDOT:PSS:Ba(acac)₂. The pH of pristine PEDOT:PSS is 2.15, while the pH of the resulting solutions of PEDOT:PSS to Ba(acac)₂ ratios for 1:0.2 and 1:0.5 are 2.24 and 2.45 respectively. At higher concentration, the pH becomes 5.42 and 8.13 for 1:1 and 1:5 ratios respectively. The change of pH indicates that chemical reactions must have taken place between Ba(acac)₂ and PEDOT:PSS. The Ba(acac)₂ solution (15 mg/ml) has a pH 7.11. Notice that adding 20 % or 50 % of Ba(acac)₂ reduce the acidity significantly or even become slightly alkaline when adding 100 % and 500 % Ba(acac)₂ respectively. Such a resistance in pH change may be related to buffer solution. Buffer solution is solution which resists change in pH when small quantity of acid or alkaline are added to it. PEDOT:PSS contains a weak acid, PSSH and its conjugate base: anion poly(styrenesulfonate) (PSS⁻). In water, the PSSH can exist in equilibrium between PSS⁻ and H⁺ as shown in Equation 5.1, resulted in pH of 2.15. The negative charge PSS⁻ was balanced with hole polarons existing on PEDOT chain as

shown in Figure 5.4, where the hole polaron can are delocalized along the PEDOT chain, responsible for the hole transfer/injection.

$$PSSH \rightleftharpoons PSS^- + H^+ \tag{5.1}$$



Figure 5.4: The electrostatic interaction between hole polaron on PEDOT (PEDOT⁺, as shown at top) with negative charge on PSS chain (PSS⁻, as shown at bottom).

Since the acidity reduces when Ba(acac)² was added, one of the possible mechanism is when the Ba²⁺ are bounded to PSS⁻, more PSSH dissociates into PSS⁻ and H⁺ ions in order to maintain the equilibrium while excess H⁺ ions recombine with acetylacetonate ions to form acetylacetone until most poly(styrenesulfonate) acids are being deprotonated. The deprotonated of PSSH break the electrostatic interaction between PEDOT⁺ and PSS⁻, leading to dedoping of PEDOT, which explain the formation of precipitation. Supposed the mechanism above is true, some/all the PEDOT component will be removed after filtration. Therefore, UV-Vis measurement, UPS and XPS measurement were performed on the filtered solution to verify the suggested hypothesis.

5.3.2 UV-Vis Measurement

The unique optical signature of PEDOT and PSS in UV-Vis can give information about the evolution of their content after mixing with Ba(acac)₂. Figure 5.5 (a) and (b) show the ultraviolet absorption spectroscopic data of drop-casted and spin-coated filtered solutions, respectively. The absorbance peak at 265 nm is assigned to the aromatic transition of single ethylenedioxythiophene monomer in PEDOT (Elshchner *et al.*, 2011) while the normalized absorbance peaks at 195 nm and 225 nm are assigned to transitions from the PSS aromatic rings (Y. H. Kim *et al.*, 2011; Xia *et al.*, 2012; Yemata *et al.*, 2020). It is important to point out that the absorption of PEDOT signal is relatively weak compare to PSS, therefore a set of drop-casted samples were prepared in order to observe the PEDOT:PSS signal as shown in Figure 5.5 (a).

The drop in the intensity of absorbance peak at 265nm with the increasing concentration of Ba(acac)₂ indicates the removal of PEDOT from PEDOT:PSS films. Meanwhile, the peak corresponding to PSS remains clearly seen. This agrees well with suggested mechanism, where the precipitation formed are resulted from the dedoping of PEDOT. Since all the precipitation (dedoped PEDOT) are removed after filtration, the reduced intensity of PEDOT signature hints that more PEDOT is dedoped with the increasing concentration of Ba(acac)₂. In order to gain insights on how Ba(acac)₂ and PEDOT:PSS interact, UPS and XPS measurement were carried out.



Figure 5.5: The ultraviolet absorption spectroscopic data of (a) drop-casted films (b) films formed from spin-coated filtered solution.

5.3.3 UPS

UPS analysis can investigate the work function of the film as well as the density of states of the valence states. The chemical reaction took places when mixed with Ba(acac)₂ may modify the work function, as a number of researchers reported mixing metal oxide (Kanwat & Jang, 2016), Nafion (Mauger *et al.*, 2014; Yeoh *et al.*, 2014), pentacene (H. Kim *et al.*, 2012) to PEDOT:PSS can significantly change the work function. In this section, UPS will study the variation of work function and interaction between PEDOT:PSS and Ba(acac)₂ upon mixing with Ba(acac)₂.



Figure 5.6: HECO from the UPS spectra for pristine PEDOT:PSS, pristine Ba(acac)₂ and PEDOT:PSS:Ba(acac)₂ at different ratios.

Figure 5.6 shows the HECO of UPS spectrum for bare ITO, pristine PEDOT:PSS (Clevios PVP Al4083), pristine Ba(acac)₂ and PEDOT:PSS:Ba(acac)₂ with different ratios. The work function of sample can be obtained by minus the HECO onset with

photon energy, 39.5 eV. Both ITO and PEDOT:PSS have work function of 4.90 eV. Increasing the amount of Ba(acac)² into PEDOT:PSS lowers the work functions to 4.08 eV, 4.16 eV, 3.63 eV and 3.56 eV for the ratios of 1:0.2 , 1:0.5, 1:1 and 1:5 respectively. Note that, Ba(acac)² on top of the ITO has a work function of 4.06 eV while the 1:1 and 1:5 ratios have lower work functions than Ba(acac)². The significant work function reduction of PEDOT:PSS upon mixing Ba(acac)² has a better energy alignment with the LUMO of organic layer which benefit the injection of electron and open up the opportunity to realize a fully solution processable cathode. EOD will be fabricated to compare the electron injection with different ratios of PEDOT:PSS:Ba(acac)² to ETM such as SPPO13.

Figure 5.7 shows the LECO of UPS spectra, which the first peak of each curve shifted to coincide with the rest of the other samples. Notice that the UPS spectra can be approximately divided into two groups as shown. For the ratios at 1:0.2 and 1:0.5, the low energy UPS spectra are very similar to the pristine PEDOT:PSS while at higher ratios (1:1 and 1:5), the differences are obvious compared with pristine Ba(acac)₂. This is in agreement to the fact that the 1:1 and 1:5 filtered solutions are clear while the 1:0.2 and 1:0.5 are not. However, 1:1 and 1:5 are not Ba(acac)₂ solutions, in particular the peak at 18.6 eV for Ba(acac)₂ is absent in all other ratios. This indicates that Ba(acac)₂ is likely to have been disassociated to Ba²⁺ and (acac)⁻ after interacting with PEDOT:PSS. The reduction of acidity of PEDOT:PSS resulted in the dedoping of PEDOT:PSS. In previous studies, mixing sodium poly(styrene sulfonate) (Na-PSS) with barium chloride resulted in an exothermic reaction forming Ba-PSS (Hansch et al., 2018). Here, Ba-PSS might have formed by the Coulombic force between Ba^{2+} and PSS⁻. The dedoping of PEDOT:PSS can inevitably lead to the separation of PEDOT and PSS that could result in precipitation. In order to have better understand on the formation of Ba-PSS, XPS measurement was performed on the similar samples after UPS measurement.



Figure 5.7: LECO of UPS spectra for PEDOT:PSS with different concentrations of Ba(acac)₂.

5.3.4 Electron only Devices (EODs)

Figure 5.8 shows the current-voltage behavior of electron transporting SPPO13 with a device structure of ITO/ PEDOT:PSS:Ba(acac)₂/ SPPO13/ CsF /Al. CsF/ Al is an excellent EIL and electrons are expected to be injected with ease from the CsF/ Al (Wei *et al.*, 2013; Zheng *et al.*, 2012). As pristine PEDOT:PSS is not a perfect electron blocker, injected electron can be recombined in the hole polaron of PEDOT giving rise to current at high forward bias voltage i.e. $\sim 3 \text{ mA/cm}^2$ at 10 V. However, at reverse bias, little current is detected implying that PEDOT:PSS is a poor electron injector as expected. In short, the forward bias indicates the ability for the interface to extract electrons while the reverse-bias indicates its ability to inject electrons. Addition of Ba(acac)₂ for the ratio

of 1:1, the forward bias electron current density is very similar to the EOD published elsewhere (Jeon *et al.*, 2009).



Figure 5.8: The current-voltage behavior of EOD, with structure of ITO/PEDOT:PSS:Ba(acac)₂/SPPO13/CsF/Al.

The enhanced electron current density of PEDOT:PSS with increasing Ba(acac)² content can be explained by the decreasing of electron injection height, along with the reduction of its work function. It is important to align the vacuum level of two materials before determining the electron injection height. UPS measurement was carried out on SPPO13 spin coated on PEDOT:PSS:Ba(acac)² (1:1). The interfacial dipole between PEDOT:PSS:Ba(acac)² at 1:1 ratio and SPPO13 is negligible as both of them show similar HECO as seen in Figure 5.9.



Figure 5.9: UPS spectra show the HECO of PEDOT:PSS:Ba(acac)₂ (1:1) and PEDOT:PSS:Ba(acac)₂ (1:1)/SPPO13.

Figure 5.10 displays the interfacial diagram between PEDOT:PSS:Ba(acac)₂ (1:1) with SPPO13 consider the interfacial dipole is negligible as shown in Figure 5.9. The LUMO and HOMO of SPPO13 obtained from literature are 2.91 eV and 6.56 eV, respectively (X. Wang *et al.*, 2017). The electron injection barrier height (Δ_e) is obtained from the offset between E_F and LUMO of SPPO13. Pristine PEDOT:PSS has high electron injection barrier (Δ_e), up to 1.99 eV, impeding the electron injection resulted in low forward electron current. The reduce of Δ_e up to 0.6-0.7 eV at high concentration of Ba(acac)₂ is in good agreement with the increasing current density showed in the forward bias of EOD.



Figure 5.10: Interfacial diagram of ITO/ PEDOT:PSS:Ba(acac)₂/ SPPO13. The vacuum level (E_{VAC}) of ITO and different ratios of PEDOT:PSS:Ba(acac)₂ were labelled as black horizontal line relative to Fermi level (E_F). The top and bottom of the grey box indicated the LUMO and HOMO of SPPO13, respectively. The electron injection barrier height (Δ_e) corresponding to the offset between E_F and LUMO of SPPO13.

5.3.5 XPS

XPS measurements were carried out in order to elucidate the interactions between

PEDOT:PSS and Ba(acac)₂. By analysis the KE of photoelectron, the XPS can identify

the element composition as well as the chemical states and electronic states in the material.

All the XPS spectra were calibrated with adventitious carbon (C-C hydrocarbon bond) at

284.8 eV.



Figure 5.11: XPS (S2p) spectra for PEDOT:PSS: Ba(aca)₂ at various concentrations.

Figure 5.11 is the S2p core level with two signature broad peaks, assigned to sulphur atom from PEDOT and PSS (Jin Bae *et al.*, 2016). The higher BE (~168 eV) belongs to PSS because of the electronegative oxygen attached to the Sulphur atom in the sulfonate fragment of the PSS. The Sulphur atom from thiophene unit in PEDOT, which is attached to carbon atom has lower BE (~164 eV).



Figure 5.12: Curve fitting of S2p peaks of PEDOT:PSS:Ba(acac)² in order to obtain different ratios of PEDOT to PSS.

All the S2p peaks were deconvoluted with Gaussian fitting function by OriginPro to separate the PEDOT and PSS component as shown in Figure 5.12. A homogeneous mixed PEDOT:PSS Al4083 has a ratio of PEDOT to PSS around 1: 7.5 (Heraeus, 2019). Noted that XPS is a surface sensitive technique, the S2p signature from PEDOT is far weaker with a composition ratio of ~ 1: 8.9 indicating a richer PSS at the top surface in comparison with the homogeneous mixed PEDOT:PSS. At 20% loading, the ratio of PEDOT to PSS does not change while at 50% loading the ratio has changed to 1: 11. At even higher loading of Ba(acac)₂, the S2p peak for PEDOT has reduced significantly with high noise and hence reliable PEDOT to PSS ratio cannot be obtained as shown in Figure 5.12 (d) and (e). The reduction of PEDOT content with high loading of Ba(acac)₂ indicated that the dedoped PEDOT has precipitated and been removed after filtration.

A careful observation on Figure 5.12 showed the S2p peak assigned to PSS are around 168.5 eV for PEDOT:PSS, PEDOT:PSS:Ba(acac)₂ (1:0.2) and (1:0.5), had redshifted to around 168.0 eV with higher loading of Ba(acac)₂. The red shift of PSS signature indicates that that the PSSH was deprotonate to PSS⁻ and H⁺ and subsequently forming the PSS-Ba. The deprotonation resulted in higher electron density in oxygen and its attached Sulphur, slightly increase the shielding of the Sulphur nuclear and redshift the BE of photoelectron.



Figure 5.13: Integration of area of S2p to Ba 4p by curve fitting of the films in order to obtain different ratios of barium and Sulphur.

Since the BE of Ba4p and S2p located between 150 eV and 190 eV, the surface composition of barium and PSS can be measured in a single measurement. The elemental ratio of Sulphur to barium, obtained by integrating the area under S2p and Ba4p, corrected by PCS are 25: 1, 14: 1, 2.6: 1 and 1.8: 1 for PEDOT:PSS:Ba(acac)₂ at the ratios of 1:0.2 1:0.5, 1:1 and 1:5 respectively as seen in Figure 5.13. This might suggest that at higher ratios Ba-PSS may have formed.



Figure 5.14: XPS (O1s) spectra for PEDOT:PSS:Ba(acac)₂ at various concentrations.

Figure 5.14 shows the BE of O1s for the mixtures and the pristine Ba(acac)₂. The broad peak showed by pristine Ba(acac)₂ is contributed by the convolution of negatively charged O-C (lower BE at ~ 529.3 eV) and neutral O=C (~531.5 eV) in acetylacetonate ions. The shift of the BE of O1s toward a lower BE suggested the PSSH fragment $(S(=O)_2-OH)$ are deprotonated to form PSS⁻ and H⁺. The oxygen in PSS⁻ has a lower BE

compared to PSSH due to the increasing electron density that enhanced the nuclear charge shielding. The hydrogen ion combined with acetylacetonate ion as the acidity of the solution reduced, while Ba²⁺ and PSS⁻ attracted to each other by the electrostatic interaction, consistent with the understanding that Ba-PSS has formed.



Figure 5.15: XPS (C1s) spectra for PEDOT:PSS: Ba(aca)₂ at various concentrations.

Figure 5.15 shows the BE of C1s for the mixtures and the pristine Ba(acac)₂. The peak at 284.8 eV corresponds to the C atoms in the PSS and PEDOT, as well as adventitious carbon, which are not bonded to the oxygen. The peak at a higher BE, 286.5 eV corresponds to those C atoms in the PEDOT which are bonded to oxygen atoms. A new peak at 288.3 eV appeared at a higher concentration of Ba(acac)₂, which can be assigned to the C=O bonds in the acetylacetone residuals that are still embedded inside

the thin films. This peak located very close to the peak at ~289 eV is assigned to the C=O and C-O⁻ of the acetylacetone in Ba(acac)₂. Since UPS spectra and XPS spectra (S2p and O1s) indicated that upon mixing of Ba(acac)₂ and PEDOT:PSS, most barium⁺ cations dissociated from the acetylacetonate counter ions and since, acetylacetone is a volatile liquid with a boiling point of 140 °C, one would assume that any remaining acetylacetone will be evaporated in high vacuum (UPS and XPS chambers) and the residual of acetylacetone unlikely to remain yet the detection of its signature at XPS (288.3 eV) indicates not all Ba(acac)₂ are dissociated.

5.3.6 AFM and Surface Profiler

The surface morphology for PEDOT:PSS:Ba(acac)² at different concentrations are shown in Figure 5.16 (a), (b) and (c). The root means square roughness (R_{rms}) are 1.35 nm, 1.29 nm and 10.9 nm for pristine PEDOT:PSS, 1:0.2 and 1:1 ratios respectively. The R_a of pristine PEDOT:PSS is similar to the value reported elsewhere (Su *et al.*, 2012). Blending 20% Ba(acac)² does not significantly change the film morphology. Meanwhile, the high R_a showed by 1:1 ratio reflected the surface roughness of ITO substrate since the film thickness of 1:1 was getting thinner after the precipitation removed by filtration. The surface profiler, ideal for measure the thin film thickness will be used to check the thickness of PEDOT:PSS:Ba(acac)² films subsequently.

It is clear that the morphology has changed from the fibre-like network structure at low concentration of Ba(acac)₂ to compacted elongated sphere and pearl necklace-like appearance. The compactification could be due to the columbic attraction between Ba²⁺ with the negatively charged sulfonate within the same chain or different chains that collapsed the chains (coil-globule transition) (Hansch *et al.*, 2018).



Figure 5.16: Surface morphology for (a) PEDOT:PSS (b) PEDOT:PSS:Ba(acac)₂ at 1:0.2 (c) at 1:1 ratio. Phase image for (d) PEDOT:PSS (e) PEDOT:PSS:Ba(acac)₂ at 1:0.2 (f) at 1:1 ratio.

Figure 5.16 (d-e) show the phase images of PEDOT:PSS:Ba(acac)² with various concentrations. In terms of phase image of PEDOT:PSS, the bright colour is often referred to as PEDOT-rich domains while PSS-rich domains often appear darker (J.-R. Kim *et al.*, 2011; B. Lu *et al.*, 2019). When 20% loading is added into PEDOT:PSS, the surface becomes noticeably darker, possibly an indication of PSS enriched surface as

shown in Figure 5.16 (e). A closer look at the scale of the phase image indicated the smaller phase angle lag for 20% loading (15°) compared pristine PEDOT:PSS (30°), indicated the reduced phase segregation on film surface, resulted from the reduced PEDOT content as the removal of dedoped PEDOT after filtration. Figure 5.16 (f) shows the morphology of PEDOT:PSS:Ba(acac)₂ at 1:1 ratio with the uniform distributed fibrils nature as a background juxtaposed by the appearance of elongated sphere and pearl necklace-like states, suggesting that the PSS is evenly distributed over the film.

The thickness of the resulting thin films are measured by surface profile as shown in Figure 5.17. The film thickness for PEDOT:PSS, at ratios of 1:0.2, 1:0.5 and 1:1 are (84 ± 9) nm, (38 ± 3) nm, (43 ± 2) nm and (7 ± 1) nm respectively. For 1:5 ratio, the thickness of the film is too thin to be measured reliably. The resulting thickness of a spin coated 15 mg/ml Ba(acac)₂ is found to be less than 5 nm.

Since the thickness is less than 10 nm for 1:1 and 1:5 ratios, the charge injection/extraction can be dominated by quantum tunneling. Previously, 1.4 nm thin Al₂O₃ buffer layer was deposited on ITO to manipulate the carrier injection by quantum tunneling (L. Zhou *et al.*, 2013). For thin film with 1:0.2 and 1:0.5 ratios, the thickness of these films are larger than 10 nm. Electron conduction for thicker films can occur through combination of ionic motion, hopping through the barium ions within these layers under applied bias (Chueh *et al.*, 2015).



Figure 5.17: Depth profiling of different films with different concentrations of PEDOT:PSS:Ba(acac)₂ (1:X).

5.3.7 Model of Work Function Modification of PEDOT:PSS:Ba(acac)₂

The wettability of the ITO surface is enhanced after oxygen plasma treatment. Because PSS has a flexible backbone and the Ba^{2+} cations have high degree of freedom in water solution compared with PSS, the Ba^{2+} cations can preferentially reorientate on the ITO surface during the film formation. The barium ions would polarize the ITO to form an electric field (image charge) that opposes the desorption of positive charged ions. From the past literature, similar polarization is reported by researcher on ITO (D. Li *et al.*, 2020) as well as TiO₂ substrate (Dong *et al.*, 2013). Since the ITO is a highly doped n-type semiconductor, the static dielectric constant should be large enough to stabilize the image charge.



Figure 5.18: The mechanism of interfacial dipole formation along with the image charge that moves the vacuum level downward.

The collective of positive Ba²⁺ and negative charge of the ITO surface resulted in the dipole pointed toward ITO, as shown in Figure 5.18. The image charge idea had been applied elsewhere to discuss the charge trapping in OFETs (Duarte & Dodabalapur, 2012). Such a interfacial dipole can shift the vacuum level of PEDOT:PSS:Ba(acac)₂ downward relative to ITO substrate. The existence of interfacial dipole will affect the energy distance between Fermi level and vacuum level, which defines the work function, Φ .



Figure 5.19: Interfacial dipole for PEDOT:PSS, Ba(acac)₂ and PEDOT:PSS:Ba(acac)₂ at different ratios.

In this research, the change of work function is resulted from the formation of interfacial dipole. This is particularly true at the ratios of 1:1 and 1:5. The vacuum levels between ITO and PEDOT:PSS:Ba(acac)₂ at different ratios can be obtained by minus the HECO onset from the UPS spectra onset (Figure 5.6) from the photon energy (39.5 eV). The vacuum levels of ITO and PEDOT:PSS:Ba(acac)₂ at different ratios are not aligned at same height indicated the presence of interfacial dipole. Figure 5.19 shows the interfacial dipole formed by the various ratios of PEDOT:PSS:Ba(acac)₂ on the ITO. The interfacial dipole at the ratios of 1:1 and 1:5 are 1.26 eV and 1.37 eV respectively indicating a downward vacuum shift that lowers the effective work function. This is larger

than the vacuum shift of pristine $Ba(acac)_2 (\sim 0.93 \text{ eV})$ possibly indicating the flexibility of counter ions might be important for reorientation. The vacuum shift for 1:0.2 and 1:0.5 ratios are 0.85 eV and 0.77 eV respectively indicated only part of the PEDOT:PSS had been dedoped to form the Ba-PSS.

5.4 Summary



Figure 5.20: Graphical illustration shows spin coating filtered PEDOT:PSS:Ba(acac)₂ solution on ITO, followed by annealing resulted in low work function resulted from the interfacial dipole induced by the barium cation.

Mixing Ba(acac)² into PEDOT:PSS changes the pH of the solution, suggesting that PSSH has been deprotonated. The formation of precipitation, especially high concentration of Ba(acac)² indicated the PEDOT was dedoped. Furthermore, filtering the mixture resulted in a clear solution after filtration as all the dedoped PEDOT removed. UV-Vis measurement revealed the absence of absorption peak of PEDOT at 263 nm indicating the removal of PEDOT after filtration. By UPS measurement, the HECO shows the work function can be lowered to as low as 3.6 eV for PEDOT:PSS:Ba(acac)² (1:5). Besides, the LECO portion of UPS spectra indicated the formation of Ba-PSS when mixing with Ba(acac)². Moreover, the low work function of PEDOT:PSS:Ba(acac)² enhanced the electron injection and extraction due to the reduced electron injection barrier height, had been demonstrated by the increasing electron current density with Ba(acac)₂ in EOD, by using SPPO13 as an ETL. The deconvolution on S2p peak from XPS showed the reduction of PEDOT content as the dedoping PEDOT had been filtered. Comparison of S2p with Ba4p as well as the redshift in S2p and O1s suggested that the polystyrene sulfonic acids are being ionized to form Ba-PSS. Lastly, the lowering of work function was attributed to the formation of interfacial dipole as large as 1.37 eV at the ITO/Ba-PSS interface, due to the reorientation of Ba²⁺ cations on top of the ITO surface as shown by graphical illustration in Figure 5.20. This finding implies that ionic polymer with barium or caesium as counter cation can be used to lower the effective work function of a surface. Since PSSH is an insulating polymer, future works will involve the use of highly conjugated polymer as an ionomer in order to improve the charge transport.
CHAPTER 6: CONCLUSION AND FUTURE WORKS

6.1 Conclusion

This thesis attempted to investigate the limited improvement over efficiency of OLEDs upon blending PVK to TcTa as well as the reduced work function upon n-doping the PEDOT:PSS with Ba(acac)₂. The probing of interfacial energy level in this works are carried out based on synchrotron measurement, especially UPS. The main results from the investigation will be concluded as below.

Firstly, a high efficiency solution processable extra warm white PhOLEDs was successfully fabricated by mixing three primary colour dopants, Hex-Ir(phq)₃, Ir(ppy)₃ and FIrpic in a 1:0.1:10 ratio, with performance comparable to other recent works as shown in Table 4.3. Blending 60 % PVK with 40 % TcTa was found to increase the hole current up to one order magnitude higher but only marginally improved the efficiency of PhOLEDs to 20.4 cd/A (11.8 lm/W), which is 7 % (23 %) higher compared to pristine PVK in term of current efficiency (power efficiency). The interfacial energy level between PEDOT:PSS/PVK:TcTa blends were measured by UPS and revealed the hole injection barrier is merely ~0.1 eV which cannot explained the increasing hole current in HOD. Even TcTa has two order magnitude higher of hole mobility compared to PVK, GIXRD and NEXAFS excluded the possibility of neither crystallization of TcTa nor vertical segregation. Meanwhile, AFM showed significant phase segregation when high percentage of TcTa, suggested the hopping of hole along percolation path of phase segregated TcTa may explain the increasing hole current. Finally, UV-Vis confirmed the molecular conformation in PVK:TcTa blend, where the red-shifted of the on-set of absorption of PVK suggested compactification of PVK resulted in face to face stacking of carbazole moieties. Blending TcTa to PVK reducing the hole injection barrier as seen

from the increasing of V_o in photovoltaic response, but the increasing number of carbazole dimers limited the increase in current efficiency.

Besides, this research successfully demonstrated that mixing Ba(acac)₂ can ndope and significantly lowering the work function of PEDOT:PSS, which applicable as EIL or even cathode for fully solution processable OSC devices. The increasing pH of the solution and formation of precipitation when mixing Ba(acac)₂ indicated poly(styrenesulfonate) acid has been deprotonated and PEDOT was dedoped. Filtering the solution will remove the dedoped PEDOT, as seen by the absence of absorption peak of PEDOT at 263 nm in UV-Vis measurement. The UPS measurement revealed the ndoped PEDOT:PSS work function as low as 3.6 eV as well as the formation of Ba-PSS Ba(acac)₂. The low when mixing PEDOT:PSS with work function of PEDOT:PSS:Ba(acac)₂ facilitated the electron injection and extraction due to the reduced electron injection barrier height. This was demonstrated by the increasing electron current density with Ba(acac)₂ in EOD, by using SPPO13 as an ETL. After the deconvolution of the S2p peak from XPS, the diminishing S2p peak at ~164 eV (signature of PEDOT) with increasing Ba(acac)₂ content indicated the dedoping PEDOT had been filtered. Besides, comparing S2p and Ba4p and the redshift in S2p and O1s showed the polystyrene sulfonic acids are being ionized to form barium polystyrene sulfonate (Ba-PSS). Lastly, the formation of interfacial dipole as large as 1.37 eV at the ITO/Ba-PSS interface, due to the reorientation of Ba cations on top of the ITO surface may explain the reduction of work function upon surface modification by PEDOT:PSS:Ba(acac)₂. This finding implies that other ionic polymers with barium or caesium as counter cation potentially be used to reduce the effective work function of a surface.

This research demonstrated that blending/mixing is a facile approach to align the interfacial energy level. The hole injection barrier in extra warm white PhOLEDs was marginal reduced upon blending PVK with TcTa. Despite one order higher of hole

mobility, the efficiency of PhOLEDs was marginally improved due to the triplet quenching induced by the molecular conformation in PVK:TcTa blend. Secondly, the work function of PEDOT:PSS can be reduced by mixing with Ba(acac)₂. The formation of Ba-PSS explained the significant interfacial dipole upon mixing, which lowered the vacuum level and facilitating better interfacial energy level on cathode side.

6.2 Future Works

Based on the summarized results, some of future works are suggested as below:

- I. Precaution must be taken when mixing small molecule and polymer so that compactification of the polymer doesn't result in increasing quenching sites.
- II. PSSH is an insulating (non-conjugated) polymer with limited mobility, coupling with highly conjugated polymer as an ionomer with Ba(acac)₂ can improve the charge transport.
- III. Combining the extra warm white PhOLEDs with PEDOT:PSS:Ba(acac)₂ as electron injection layer, along with silver paste as cathode may realize the fully solution processable OLEDs, eliminate the expensive and timeconsuming vacuum deposition process.
- IV. The low work function of PEDOT:PSS:Ba(acac)₂ has great potential to serve as the buffer layer in OPVs, as the electrode in n-type OFETs or other OSC devices via high resolution patterning to replace the traditional vacuum deposited aluminum cathode.
- V. The fundamental mechanism of how to avoid or encourage phase separation between small molecule and polymer via molecular design needed to study as this is highly relevant to OPV and OLED

REFERENCES

- Adachi, C., Baldo, M. A., Thompson, M. E., & Forrest, S. R. (2001). Nearly 100% internal phosphorescence efficiency in an organic light-emitting device. *Journal* of Applied Physics, 90(10), 5048-5051.
- Akaike, K., Koch, N., & Oehzelt, M. (2014). Fermi level pinning induced electrostatic fields and band bending at organic heterojunctions. *Applied Physics Letters*, 105(22), Article#223303.
- Akamatu, H., Inokuchi, H., & Matsunaga, Y. (1956). Organic semiconductors with high conductivity. i. complexes between polycyclic aromatic hydrocarbons and halogens. *Bulletin of the Chemical Society of Japan, 29*(2), 213-218.
- Alloway, D. M., Hofmann, M., Smith, D. L., Gruhn, N. E., Graham, A. L., Colorado, R., Wysocki, V. H., Lee, T. R., Lee, P. A., & Armstrong, N. R. (2003). Interface dipoles arising from self-assembled monolayers on gold: UV–Photoemission studies of alkanethiols and partially fluorinated alkanethiols. *The Journal of Physical Chemistry B*, 107(42), 11690-11699.
- Anthopoulos, T. D., Markham, J. P. J., Namdas, E. B., Samuel, I. D. W., Lo, S.-C., & Burn, P. L. (2003). Highly efficient single-layer dendrimer light-emitting diodes with balanced charge transport. *Applied Physics Letters*, 82(26), 4824-4826.
- Atkins, P. W., & De Paula, J. (2006). *Atkins' Physical chemistry*. Oxford; New York: Oxford University Press.
- Bagus, P. S., Hermann, K., & Wöll, C. (2005). The interaction of C6H6 and C6H12 with noble metal surfaces: Electronic level alignment and the origin of the interface dipole. *The Journal of Chemical Physics*, 123(18), Article#184109.
- Baldo, M. A., & Forrest, S. R. (2000). Transient analysis of organic electrophosphorescence: I. Transient analysis of triplet energy transfer. *Physical Review B*, 62(16), 10958-10966.
- Baldo, M. A., O'Brien, D. F., You, Y., Shoustikov, A., Sibley, S., Thompson, M. E., & Forrest, S. R. (1998). Highly efficient phosphorescent emission from organic electroluminescent devices. *Nature*, 395(6698), 151-154.
- Ban, X., Sun, K., Sun, Y., Huang, B., & Jiang, W. (2016). Design of high triplet energy electron transporting material for exciplex-type host: Efficient blue and white phosphorescent OLEDs based on solution processing. Organic Electronics, 33, 9-14.

- Banerjee, D. (2006). X-Ray Diffraction (XRD). Retrieved from https://www.iitk.ac.in/che/pdf/resources/XRD-reading-material.pdf.
- Bässler, H. (1993). Charge transport in disordered organic photoconductors a Monte Carlo simulation study. *Physica Status Solidi (b), 175*(1), 15-56.
- Basurto, J. G., & Burshtein, Z. (1975). Electroluminescence studies in pyrene single crystals. *Molecular Crystals and Liquid Crystals*, 31(3-4), 211-217.
- Bauert, T., Zoppi, L., Koller, G., Garcia, A., Baldridge, K. K., & Ernst, K.-H. (2011). Large induced interface dipole moments without charge transfer: Buckybowls on metal surfaces. *The Journal of Physical Chemistry Letters*, 2(21), 2805-2809.
- Berry, A., & O'Neill, H. S. C. (2004). A XANES determination of the oxidation state of chromium in silicate glasses. *American Mineralogist*, *89*, 790-798.
- Birkholz, M. (2005). Identification of chemical phases. In *Thin Film Analysis by X-Ray Scattering* (pp. 43-84).
- Borse, K., Sharma, R., Gupta, D., & Yella, A. (2019). High-efficiency organic solar cells with solution processable non-fullerene acceptor as an interlayer. *IEEE Journal of Photovoltaics*, 9(5), 1266-1272.
- Boyce, P. R. (2014). Human Factors in Lighting, Third Edition: Taylor & Francis.
- Bredas, J.-L. (2014). Mind the gap! Materials Horizons, 1(1), 17-19.
- Burgelman, M., Minnaert, B., & Grasso, C. (2006). Chapter 2 Device modeling of nanostructured solar cells. In T. Soga (Ed.), *Nanostructured Materials for Solar Energy Conversion* (pp. 45-80). Amsterdam: Elsevier.
- Burroughes, J. H., Bradley, D. D. C., Brown, A. R., Marks, R. N., Mackay, K., Friend, R. H., Burns, P. L., & Holmes, A. B. (1990). Light-emitting diodes based on conjugated polymers. *Nature*, 347(6293), 539-541.
- Cacelli, I., Carravetta, V., Rizzo, A., & Moccia, R. (1992). Calculation of photoionization cross section: an overview. in D. Mukherjee (Ed.), *Applied Many-Body Methods* in Spectroscopy and Electronic Structure (pp. 105-132). Boston, MA: Springer US.
- Chang, C.-H., Tien, K.-C., Chen, C.-C., Lin, M.-S., Cheng, H.-C., Liu, S.-H., Wu, C.-C., Hung, J.-Y., Chiu, Y.-C., & Chi, Y. (2010). Efficient phosphorescent white OLEDs with high color rendering capability. *Organic Electronics*, 11(3), 412-418.

- Chang, J.-F., Sun, B., Breiby, D. W., Nielsen, M. M., Sölling, T. I., Giles, M., McCulloch, I., & Sirringhaus, H. (2004). Enhanced mobility of poly(3-hexylthiophene) transistors by spin-coating from high-boiling-point solvents. *Chemistry of Materials*, 16(23), 4772-4776.
- Chattot, R., Le Bacq, O., Beermann, V., Kühl, S., Herranz, J., Henning, S., Kühn, L., Asset, T., Guétaz, L., Renou, G., Drnec, J., Bordet, P., Pasturel, A., Eychmüller, A., Schmidt, T. J., Strasser, P., Dubau, L., & Maillard, F. (2018). Surface distortion as a unifying concept and descriptor in oxygen reduction reaction electrocatalysis. *Nature Materials*, 17(9), 827-833.
- Chen, S., Song, L., Tao, Z., Shao, X., Huang, Y., Cui, Q., & Guo, X. (2014). Neutral-pH PEDOT:PSS as over-coating layer for stable silver nanowire flexible transparent conductive films. *Organic Electronics*, 15(12), 3654-3659.
- Chen, S., Zhang, Q., Shang, W., Liu, L., Yu, H., Zhang, S., Deng, L., Wang, M., Wang, M., Li, X., Mi, B., & Huang, W. (2018). Interfacial engineering of graphene for highly efficient blue and white organic light-emitting devices. *Scientific Reports*, 8(1), Article#8155.
- Chen, W., Chen, S., Huang, H., Qi, D. C., Gao, X. Y., & Wee, A. T. S. (2008). Molecular orientation dependent interfacial dipole at the F₁₆CuPc / CuPc organic heterojunction interface. *Applied Physics Letters*, 92(6), Article#063308.
- Chen, W., Luo, S., Wan, Z., Feng, X., Liu, X., & He, Z. (2017). Ruthenium acetylacetonate in interface engineering for high performance planar hybrid perovskite solar cells. *Optics Express*, 25, Article#A253.
- Chen, Y., Chen, J., Zhao, Y., & Ma, D. (2012). High efficiency blue phosphorescent organic light-emitting diode based on blend of hole- and electron-transporting materials as a co-host. *Applied Physics Letters*, 100(21), Article#213301.
- Chueh, C.-C., Li, C.-Z., & Jen, A. K. Y. (2015). Recent progress and perspective in solution-processed interfacial materials for efficient and stable polymer and organometal perovskite solar cells. *Energy & Environmental Science*, 8(4), 1160-1189.
- Crispin, X., Geskin, V., Crispin, A., Cornil, J., Lazzaroni, R., Salaneck, W. R., & Brédas, J.-L. (2002). Characterization of the interface dipole at organic/ metal interfaces. *Journal of the American Chemical Society*, 124(27), 8131-8141.
- Cui, L.-S., Liu, Y., Yuan, X.-D., Li, Q., Jiang, Z.-Q., & Liao, L.-S. (2013). Bipolar host materials for high efficiency phosphorescent organic light emitting diodes: tuning the HOMO/LUMO levels without reducing the triplet energy in a linear system. *Journal of Materials Chemistry C*, 1(48), 8177-8185.

- Cusumano, P., Arnone, C., Giambra, M., & Parisi, A. (2020). Donor/Acceptor Heterojunction Organic Solar Cells. *Electronics*, 9, Article#70.
- de Kok, M. M., Buechel, M., Vulto, S. I. E., van de Weijer, P., Meulenkamp, E. A., de Winter, S. H. P. M., Mank, A. J. G., Vorstenbosch, H. J. M., Weijtens, C. H. L., & van Elsbergen, V. (2004). Modification of PEDOT:PSS as hole injection layer in polymer LEDs. *Physica Status Solidi (a), 201*(6), 1342-1359.
- Delgass, W. N., Haller, G. L., Kellerman, R., & Lunsford, J. H. (1979). Chapter 8 X-RAY PHOTOELECTRON SPECTROSCOPY. In W. N. Delgass, G. L. Haller, R. Kellerman, & J. H. Lunsford (Eds.), Spectroscopy in Heterogeneous Catalysis (pp. 267-322): Academic Press.
- Deng, X., Nie, R., Li, A., Wei, H., Zheng, S., Huang, W., Mo, Y., Su, Y., Wang, Q., Li, Y., Tang, J., Xu, J., & Wong, K.-y. (2014). Ultra-Low Work Function Transparent Electrodes Achieved by Naturally Occurring Biomaterials for Organic Optoelectronic Devices. Advanced Materials Interfaces, 1(7), Article#1400215.
- Deng, Y.-L., Cui, L.-S., Liu, Y., Wang, Z.-K., Jiang, Z.-Q., & Liao, L.-S. (2016). Solution-processable iridium phosphors for efficient red and white organic lightemitting diodes with low roll-off. *Journal of Materials Chemistry C, 4*(6), 1250-1256.
- Deniz, A. A., Dahan, M., Grunwell, J. R., Ha, T., Faulhaber, A. E., Chemla, D. S., Weiss, S., & Schultz, P. G. (1999). Single-pair fluorescence resonance energy transfer on freely diffusing molecules: Observation of Förster distance dependence and subpopulations. *Proceedings of the National Academy of Sciences*, 96(7), 3670-3675.
- Dey, A., Krishnamurthy, S., Bowen, J., Nordlund, D., Meyyappan, M., & Gandhiraman, R. P. (2018). Plasma jet printing and in situ reduction of highly acidic graphene oxide. ACS Nano, 12(6), 5473-5481.
- Di, D., Yang, L., Richter, J. M., Meraldi, L., Altamimi, R. M., Alyamani, A. Y., Credgington, D., Musselman, K. P., MacManus-Driscoll, J. L., & Friend, R. H. (2017). Efficient triplet exciton fusion in molecularly doped polymer lightemitting diodes. *Advanced Materials*, 29(13), Article#1605987.
- Domercq, B., Yu, J., Kaafarani*, B. R., Kondo, T., Yoo, S., Haddock, J. N., Barlow, S., Marder, S. R., & Kippelen, B. (2008). A comparative study of charge mobility measurements in a diamine and in a hexaazatrinaphthylene using different techniques. *Molecular Crystals and Liquid Crystals, 481*(1), 80-93.
- Dong, C., Li, X., Zhao, W., Jin, P., & Qi, J. (2013). Theoretical analysis of built-in interfacial electric dipole field in dye-sensitized solar cells. *The Journal of Physical Chemistry C*, 117(18), 9092-9103.

- Duan, L., Hou, L., Lee, T.-W., Qiao, J., Zhang, D., Dong, G., Wang, L., & Qiu, Y. (2010). Solution processable small molecules for organic light-emitting diodes. *Journal* of Materials Chemistry, 20(31), 6392-6407.
- Duarte, D., & Dodabalapur, A. (2012). Investigation of the physics of sensing in organic field effect transistor based sensors. *Journal of Applied Physics*, 111(4), Article#044509.
- Elshchner, A., Kirchmeyer, S., Lovenich, W., Merker, U., & Reuter, K. (2011). PEDOT. principles and applications of an intrinsically conductive polymer. *Boca Raton* (*FL*).
- Endo, A., Ogasawara, M., Takahashi, A., Yokoyama, D., Kato, Y., & Adachi, C. (2009). Thermally activated delayed fluorescence from sn⁴⁺-porphyrin complexes and their application to organic light emitting diodes — a novel mechanism for electroluminescence. *Advanced Materials*, 21(47), 4802-4806.
- Endo, A., Sato, K., Yoshimura, K., Kai, T., Kawada, A., Miyazaki, H., & Adachi, C. (2011). Efficient up-conversion of triplet excitons into a singlet state and its application for organic light emitting diodes. *Applied Physics Letters*, 98(8), Article#083302.
- Facchetti, A. (2013). Polymer donor-polymer acceptor (all-polymer) solar cells. *Materials Today*, 16(4), 123-132.
- Facchetti, A., Yoon, M.-H., Katz, H., & Marks, T. (2003). Materials for n-type organic electronics: synthesis and properties of fluoroarene-thiophene semiconductors (Vol. 5217): SPIE.
- Fadley, C. S. (1973). Theoretical Aspects of X-Ray Photoelectron Spectroscopy, Dordrecht.
- Fahlman, M., Fabiano, S., Gueskine, V., Simon, D., Berggren, M., & Crispin, X. (2019). Interfaces in organic electronics. *Nature Reviews Materials*, 4(10), 627-650.
- Fediai, A., Symalla, F., Friederich, P., & Wenzel, W. (2019). Disorder compensation controls doping efficiency in organic semiconductors. *Nature Communications*, 10(1), Article#4547.
- Forsythe, E. W., Choong, V.-E., Le, T. Q., & Gao, Y. (1999). Interface analysis of naphthyl-substituted benzidine derivative and tris-8-(hydroxyquinoline) aluminum using ultraviolet and x-ray photoemission spectroscopy. *Journal of Vacuum Science & Technology A*, 17(6), 3429-3432.

- Freitas, A. M., Gomes, R. A. M., Ferreira, R. A. M., & Porto, M. P. (2019). Experimental performance of commercial OPV panels tested outdoor. *Renewable Energy*, 135, 1004-1012.
- Gao, Y. (2010). Surface analytical studies of interfaces in organic semiconductor devices. *Materials Science and Engineering: R: Reports, 68*(3), 39-87.
- Gao, Z. Q., Mi, B. X., Xu, G. Z., Wan, Y. Q., Gong, M. L., Cheah, K. W., & Chen, C. H. (2008). An organic p-type dopant with high thermal stability for an organic semiconductor. *Chemical Communications*(1), 117-119.
- Gather, M., & Reineke, S. (2015). Recent advances in light outcoupling from white organic light-emitting diodes. *Journal of Photonics for Energy*, 5(1), Article#057607.
- Gaur, A., Shrivastava, B., & Nigam, H. (2013). X-ray absorption fine structure (XAFS) spectroscopy A Review. *Proceedings of Indian National Science Academy*, 79, 921-966.
- Germs, W. C., Guo, K., Janssen, R. A. J., & Kemerink, M. (2012). Unusual Thermoelectric Behavior Indicating a Hopping to Bandlike Transport Transition in pentacene. *Physical Review Letters*, 109(1), Article#016601.
- Godumala, M., Hwang, J., Kang, H., Jeong, J.-E., Harit, A. K., Cho, M. J., Woo, H. Y., Park, S., & Choi, D. H. (2020). High-performance, solution-processable thermally activated delayed fluorescent organic light-emitting diodes realized via the adjustment of the composition of the organoboron acceptor monomer in copolymer host materials. ACS Applied Materials & Interfaces, 12(31), 35300-35310.
- Gomez, E. D., & Loo, Y.-L. (2010). Engineering the organic semiconductor-electrode interface in polymer solar cells. *Journal of Materials Chemistry*, 20(32), 6604-6611.
- Goswami, S., Matula, A. J., Rath, S. P., Hedström, S., Saha, S., Annamalai, M., Sengupta, D., Patra, A., Ghosh, S., Jani, H., Sarkar, S., Motapothula, M. R., Nijhuis, C. A., Martin, J., Goswami, S., Batista, V. S., & Venkatesan, T. (2017). Robust resistive memory devices using solution-processable metal-coordinated azo aromatics. *Nature Materials*, 16(12), 1216-1224.
- Greiner, M. T., & Lu, Z.-H. (2013). Thin-film metal oxides in organic semiconductor devices: their electronic structures, work functions and interfaces. *NPG Asia Materials*, 5(7), Article#e55-e55.

- Guo, B., Yin, Q., Zhou, J., Li, W., Zhang, K., & Li, Y. (2019). Semiconductive polymerdoped PEDOT with high work function, conductivity, reversible dispersion, and application in organic solar cells. ACS Sustainable Chemistry & Engineering, 7(9), 8206-8214.
- Ha, D.-G., Kim, J.-J., & Baldo, M. A. (2016). Link between hopping models and percolation scaling laws for charge transport in mixtures of small molecules. *AIP Advances*, 6(4), Article#045221.
- Hamilton, I., Chander, N., Cheetham, N. J., Suh, M., Dyson, M., Wang, X., Stavrinou, P. N., Cass, M., Bradley, D. D. C., & Kim, J.-S. (2018). Controlling molecular conformation for highly efficient and stable deep-blue copolymer light-emitting diodes. ACS Applied Materials & Interfaces, 10(13), 11070-11082.
- Hansch, M., Hämisch, B., Schweins, R., Prévost, S., & Huber, K. (2018). Liquid-liquid phase separation in dilute solutions of poly(styrene sulfonate) with multivalent cations: Phase diagrams, chain morphology, and impact of temperature. *The Journal of Chemical Physics*, 148(1), Article#014901.
- Hasan, Z. A., Woon, K. L., Wong, W. S., Ariffin, A., & Chen, S.-A. (2017). Solution processed multilayer red, green and blue phosphorescent organic light emitting diodes using carbazole dendrimer as a host. *Journal of Luminescence*, 183, 150-158.
- Heine, V. (1990). Theory of Surface States. In W. Mönch (Ed.), *Electronic structure of metal-semiconductor contacts* (pp. 83-90). Dordrecht: Springer Netherlands.
- Helander, M. G., Wang, Z., & Lu, Z.-H. (2016). Electrode-organic interface physics. in B. Bhushan (Ed.), *Encyclopedia of Nanotechnology* (pp. 1015-1024). Dordrecht: Springer Netherlands.
- Helfrich, W., & Schneider, W. G. (1965). Recombination radiation in anthracene crystals. *Physical Review Letters*, 14(7), 229-231.
- Helliwell, J. R. (1998). Synchrotron radiation facilities. *Nature Structural Biology*, 5(8), 614-617.
- Heraeus. (2019). *Clevios P VP AI 4083 Heraeus*. Retrieved from: https://www.heraeus.com/media/media/hec/documents_hec/data_sheets_hep/Cle vios_P_VP_AI_4083.pdf
- Hill, I. G., Milliron, D., Schwartz, J., & Kahn, A. (2000). Organic semiconductor interfaces: electronic structure and transport properties. *Applied Surface Science*, *166*(1), 354-362.

- Ho, M. D., Kim, D., Kim, N., Cho, S. M., & Chae, H. (2013). Polymer and small molecule mixture for organic hole transport layers in quantum dot light-emitting diodes. ACS Applied Materials & Interfaces, 5(23), 12369-12374.
- Ho, S., Chen, Y., Liu, S., Peng, C., Zhao, D., & So, F. (2016). Interface effect on efficiency loss in organic light emitting diodes with solution processed emitting layers. *Advanced Materials Interfaces*, 3(19), Article#1600320.
- Höfle, S., Pfaff, M., Do, H., Bernhard, C., Gerthsen, D., Lemmer, U., & Colsmann, A. (2014). Suppressing molecular aggregation in solution processed small molecule organic light emitting diodes. *Organic Electronics*, 15(1), 337-341.
- Hofmann, O. T., Rangger, G. M., & Zojer, E. (2008). Reducing the metal work function beyond pauli pushback: a computational investigation of tetrathiafulvalene and viologen on coinage metal surfaces. *The Journal of Physical Chemistry C,* 112(51), 20357-20365.
- Hopkins, J., Fidanovski, K., Lauto, A., & Mawad, D. (2019). All-organic semiconductors for electrochemical biosensors: an overview of recent progress in material design. *Frontiers in Bioengineering and Biotechnology*, 7(237).
- Horowitz, G. (2015). Validity of the concept of band edge in organic semiconductors. Journal of Applied Physics, 118(11), Article#115502.
- Howells, C. T., Saylan, S., Kim, H., Marbou, K., Aoyama, T., Nakao, A., Uchiyama, M., Samuel, I. D. W., Kim, D.-W., Dahlem, M. S., & André, P. (2018). Influence of perfluorinated ionomer in PEDOT:PSS on the rectification and degradation of organic photovoltaic cells. *Journal of Materials Chemistry A*, 6(33), 16012-16028.
- Hu, L., Song, J., Yin, X., Su, Z., & Li, Z. (2020). Research progress on polymer solar cells based on PEDOT:PSS electrodes. *Polymers*, 12(1), Article#145.
- Hu, Z., Zhong, Z., Zhang, K., Hu, Z., Song, C., Huang, F., Peng, J., Wang, J., & Cao, Y. (2017). Dipole formation at organic/metal interfaces with pre-deposited and postdeposited metal. NPG Asia Materials, 9(5), e379-e379.
- Huang, H., Zhao, F., Liu, L., Zhang, F., Wu, X.-g., Shi, L., Zou, B., Pei, Q., & Zhong, H. (2015). Emulsion synthesis of size-tunable CH₃NH₃PbBr₃ quantum dots: an alternative route toward efficient light-emitting diodes. ACS Applied Materials & Interfaces, 7(51), 28128-28133.
- Hung, L. S., Tang, C. W., & Mason, M. G. (1997). Enhanced electron injection in organic electroluminescence devices using an Al/LiF electrode. *Applied Physics Letters*, 70(2), 152-154.

- Hwang, D. K., Fuentes-Hernandez, C., Berrigan, J. D., Fang, Y., Kim, J., Potscavage, W. J., Cheun, H., Sandhage, K. H., & Kippelen, B. (2012). Solvent and polymer matrix effects on TIPS-pentacene/polymer blend organic field-effect transistors. *Journal of Materials Chemistry*, 22(12), 5531-5537.
- Ishii, H., & Seki, K. (1997). Energy level alignment at organic/metal interfaces studied by UV photoemission: breakdown of traditional assumption of a common vacuum level at the interface. *IEEE Transactions on Electron Devices*, 44(8), 1295-1301.
- Ishii, H., Sugiyama, K., Ito, E., & Seki, K. (1999). Energy level alignment and interfacial electronic structures at organic/metal and organic/organic interfaces. Advanced Materials, 11(8), 605-625.
- Izawa, S., Shintaku, N., & Hiramoto, M. (2018). Effect of band bending and energy level alignment at the donor/acceptor interface on open-circuit voltage in organic solar cells. *The Journal of Physical Chemistry Letters*, 9(11), 2914-2918.
- Janai, M. A. B., Woon, K. L., & Chan, C. S. (2018). Design of efficient blue phosphorescent bottom emitting light emitting diodes by machine learning approach. *Organic Electronics*, 63, 257-266.
- Jankus, V., & Monkman, A. P. (2011). Is Poly(vinylcarbazole) a good host for blue phosphorescent dopants in pleds? dimer formation and their effects on the triplet energy level of poly(n-vinylcarbazole) and poly(n-ethyl-2-vinylcarbazole). Advanced Functional Materials, 21(17), 3350-3356.
- Jeon, S. O., Yook, K. S., Joo, C. W., & Lee, J. Y. (2009). A phosphine oxide derivative as a universal electron transport material for organic light-emitting diodes. *Journal of Materials Chemistry*, 19(33), 5940-5944.
- Jin Bae, E., Hun Kang, Y., Jang, K.-S., & Yun Cho, S. (2016). Enhancement of thermoelectric properties of PEDOT:PSS and tellurium-PEDOT:PSS hybrid composites by simple chemical treatment. *Scientific Reports*, 6(1), Article#18805.
- Jou, J.-H., Hwang, P.-Y., Wang, W.-B., Lin, C.-W., Jou, Y.-C., Chen, Y.-L., Shyue, J.-J., Shen, S.-M., & Chen, S.-Z. (2012). High-efficiency low color temperature organic light emitting diodes with solution-processed emissive layer. Organic Electronics, 13(5), 899-904.
- Jou, J.-H., Sahoo, S., Kumar, S., Yu, H.-H., Fang, P.-H., Singh, M., Krucaite, G., Volyniuk, D., Grazulevicius, J. V., & Grigalevicius, S. (2015). A wet- and dryprocess feasible carbazole type host for highly efficient phosphorescent OLEDs. *Journal of Materials Chemistry C*, 3(47), 12297-12307.

- Jung, M., & Lee, J. Y. (2020). Exciplex hosts for blue phosphorescent organic lightemitting diodes. *Journal of Information Display*, 21(1), 11-18.
- Kahn, A. (2016). Fermi level, work function and vacuum level. *Materials Horizons, 3*(1), 7-10.
- Kallmann, H., & Pope, M. (1960). Bulk conductivity in organic crystals. *Nature*, 186(4718), 31-33.
- Kampas, F. J., & Gouterman, M. (1977). Porphyrin films. electroluminescence of octaethylporphin. *Chemical Physics Letters*, 48(2), 233-236.
- Kaneto, K., Yoshino, K., Kao, K.-c., & Inuishi, Y. (1974). Electroluminescence in polyethylene terephthalate. *Japanese Journal of Applied Physics*, 13(6), 1023-1024.
- Kang, J., Shin, N., Jang, D. Y., Prabhu, V. M., & Yoon, D. Y. (2008). Structure and properties of small molecule–polymer blend semiconductors for organic thin film transistors. *Journal of the American Chemical Society*, 130(37), 12273-12275.
- Kanunnikova, O. M., Aksenova, V. V., Karban, O. V., Muhgalin, V. V., Senkovski, B. V., & Ladjanov, V. I. (2017). Mechanical activation effect on structure, physicochemical, and biological properties of potassium/magnesium orotates. *IOP Conference Series: Materials Science and Engineering, 283*, Article#012004.
- Kanwat, A., & Jang, J. (2016). High work function with reduced phase separation of PSS in metal oxide modified PEDOT:PSS interlayers for organic photovoltaics. *RSC Advances*, 6(115), 114800-114807.
- Karki, A., Wetzelaer, G.-J. A. H., Reddy, G. N. M., Nádaždy, V., Seifrid, M., Schauer, F., Bazan, G. C., Chmelka, B. F., Blom, P. W. M., & Nguyen, T.-Q. (2019). Unifying energetic disorder from charge transport and band bending in organic semiconductors. *Advanced Functional Materials*, 29(20), Article#1901109.
- Kawabata, T., & Ohno, Y. (2013). Optical measurements of OLED panels for lighting applications. *Journal of Modern Optics*, 60(14), 1176-1186.
- Kido, J., Hongawa, K., Okuyama, K., & Nagai, K. (1994). White light-emitting organic electroluminescent devices using the poly(N-vinylcarbazole) emitter layer doped with three fluorescent dyes. *Applied Physics Letters*, 64(7), 815-817.
- Kim, C., Bonnassieux, Y., & Horowitz, G. (2014). Compact DC modeling of organic field-effect transistors: review and perspectives. *IEEE Transactions on Electron Devices*, 61(2), 278-287.

- Kim, D., & Zozoulenko, I. (2019). Why is pristine PEDOT oxidized to 33%? a density functional theory study of oxidative polymerization mechanism. *The Journal of Physical Chemistry B*, 123(24), 5160-5167.
- Kim, H., Lee, J., Ok, S., & Choe, Y. (2012). Effects of pentacene-doped PEDOT:PSS as a hole-conducting layer on the performance characteristics of polymer photovoltaic cells. *Nanoscale Research Letters*, 7(1), Article#5.
- Kim, J.-R., Jung, J. H., Shin, W. S., So, W.-W., & Moon, S.-J. (2011). Efficient TCOfree organic solar cells with modified poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) anodes. *Journal of Nanoscience and Nanotechnology*, 11(1), 326-330.
- Kim, J.-S., & Murphy, C. (2011). Organic-organic Semiconductor interfaces for molecular electronic devices, optoelectronic devices and properties. Retrieved from: https://www.intechopen.com/books/optoelectronic-devices-andproperties/organic-organic-semiconductor-interfaces-for-molecular-electronicdevices
- Kim, S. H., Kim, J., Nam, S., Lee, H. S., Lee, S. W., & Jang, J. (2017). Tuning the work function of printed polymer electrodes by introducing a fluorinated polymer to enhance the operational stability in bottom-contact organic field-effect transistors. ACS Applied Materials & Interfaces, 9(14), 12637-12646.
- Kim, Y.-H., Han, T.-H., Cho, H., Min, S.-Y., Lee, C.-L., & Lee, T.-W. (2014). Polyethylene imine as an ideal interlayer for highly efficient inverted polymer light-emitting diodes. *Advanced Functional Materials*, 24(24), 3808-3814.
- Kim, Y. H., Sachse, C., Machala, M. L., May, C., Müller-Meskamp, L., & Leo, K. (2011). Highly conductive PEDOT:PSS electrode with optimized solvent and thermal post-treatment for ITO-free organic solar cells. *Advanced Functional Materials*, 21(6), 1076-1081.
- Knupfer, M. (2003). Exciton binding energies in organic semiconductors. *Applied Physics A*, 77(5), 623-626.
- Knupfer, M., & Paasch, G. (2005). Origin of the interface dipole at interfaces between undoped organic semiconductors and metals. *Journal of Vacuum Science & Technology A*, 23(4), 1072-1077.
- Köhler, A., & Bässler, H. (2009). Triplet states in organic semiconductors. *Materials* Science and Engineering: R: Reports, 66(4), 71-109.
- Kohn, W., Becke, A. D., & Parr, R. G. (1996). Density functional theory of electronic structure. *The Journal of Physical Chemistry*, 100(31), 12974-12980.

- Koopmans, T. (1934). Über die zuordnung von wellenfunktionen und eigenwerten zu den einzelnen elektronen eines atoms. *Physica*, *1*(1), 104-113.
- Kozaki, T., Koga, S., Toda, N., Noguchi, H., & Yasukouchi, A. (2008). Effects of short wavelength control in polychromatic light sources on nocturnal melatonin secretion. *Neuroscience Letters*, 439(3), 256-259.
- Krucaite, G., & Grigalevicius, S. (2019). A review on low-molar-mass carbazole- based derivatives for organic light emitting diodes. *Synthetic Metals*, 247, 90-108.
- Kumar, M., & Pereira, L. (2020). Mixed-host systems with a simple device structure for efficient solution-processed organic light-emitting diodes of a red-orange TADF emitter. ACS Omega, 5(5), 2196-2204.
- Kunkel, T., Daly, S., Miller, S., & Froehlich, J. (2016). Chapter 15 Perceptual design for high dynamic range systems. In F. Dufaux, P. Le Callet, R. K. Mantiuk, & M. Mrak (Eds.), *High Dynamic Range Video* (pp. 391-430): Academic Press.
- Kwon, J. H., Jeon, W. S., & Park, T. J. (2009). 23.4: Invited paper: ideal host-dopant system for highly efficient phosphorescent OLEDs. SID Symposium Digest of Technical Papers, 40(1), 317-320.
- Lan, L., Liu, B., Tao, H., Zou, J., Jiang, C., Xu, M., Wang, L., Peng, J., & Cao, Y. (2019). Preparation of efficient quantum dot light-emitting diodes by balancing charge injection and sensitizing emitting layer with phosphorescent dye. *Journal of Materials Chemistry C*, 7(19), 5755-5763.
- Latham, K. G., Simone, M. I., Dose, W. M., Allen, J. A., & Donne, S. W. (2017). Synchrotron based NEXAFS study on nitrogen doped hydrothermal carbon: Insights into surface functionalities and formation mechanisms. *Carbon, 114*, 566-578.
- Lee, D.-H., Liu, Y.-P., Lee, K.-H., Chae, H., & Cho, S. M. (2010). Effect of hole transporting materials in phosphorescent white polymer light-emitting diodes. *Organic Electronics*, 11(3), 427-433.
- Lei, X., Yu, J., & Jiang, Y. (2011). Influence of doping concentrations in white organic light-emitting diodes based on phosphorescent iridium complexes. *Energy Procedia*, 12, 620-624.
- Leinweber, P., Kruse, J., Walley, F. L., Gillespie, A., Eckhardt, K.-U., Blyth, R. I. R., & Regier, T. (2007). Nitrogen K-edge XANES – an overview of reference compounds used to identify `unknown' organic nitrogen in environmental samples. *Journal of Synchrotron Radiation*, 14(6), 500-511.

- Lenze, M. R., Kronenberg, N. M., Würthner, F., & Meerholz, K. (2015). In-situ modification of PEDOT:PSS work function using alkyl alcohols as secondary processing solvents and their impact on merocyanine based bulk heterojunction solar cells. Organic Electronics, 21, 171-176.
- Lewis, M., Bagwill, C., Hardebeck, L. K. E., & Wireduaah, S. (2012). THE USE OF HAMMETT CONSTANTS TO UNDERSTAND THE NON-COVALENT BINDING OF AROMATICS. Computational and Structural Biotechnology Journal, 1(1), Article#e201204004.
- Li, C., Nobuyasu, R. S., Wang, Y., Dias, F. B., Ren, Z., Bryce, M. R., & Yan, S. (2017). Solution-processable thermally activated delayed fluorescence white OLEDs based on dual-emission polymers with tunable emission colors and aggregationenhanced emission properties. *Advanced Optical Materials*, 5(20), Article#1700435.
- Li, D., Ruan, L., Sun, J., Wu, C., Yan, Z., Lin, J., & Yan, Q. (2020). Facile growth of aluminum oxide thin film by chemical liquid deposition and its application in devices. *Nanotechnology Reviews*, 9(1), 876-885.
- Li, P., Ingram, G., Lee, J.-J., Zhao, Y., & Lu, Z.-H. (2019). Energy disorder and energy level alignment between host and dopant in organic semiconductors. *Communications Physics*, 2(1), Article#2.
- Li, W., Shuai, Z., & Geng, H. (2018). Theoretical insights into molecular blending on charge transport properties in organic semiconductors based on quantum nuclear tunneling model. *Journal of Photonics for Energy*, 8(3), Article#032204.
- Li, Z., Gadipelli, S., Yang, Y., He, G., Guo, J., Li, J., Lu, Y., Howard, C. A., Brett, D. J. L., Parkin, I. P., Li, F., & Guo, Z. (2019). Exceptional supercapacitor performance from optimized oxidation of graphene-oxide. *Energy Storage Materials*, 17, 12-21.
- Li, Z., Liang, Y., Zhong, Z., Qian, J., Liang, G., Zhao, K., Shi, H., Zhong, S., Yin, Y., & Tian, W. (2015). A low-work-function, high-conductivity PEDOT:PSS electrode for organic solar cells with a simple structure. *Synthetic Metals*, *210*, 363-366.
- Li, Z., Qin, F., Liu, T., Ge, R., Meng, W., Tong, J., Xiong, S., & Zhou, Y. (2015). Optical properties and conductivity of PEDOT:PSS films treated by polyethylenimine solution for organic solar cells. *Organic Electronics*, *21*, 144-148.
- Liang, J., Ying, L., Yang, W., Peng, J., & Cao, Y. (2017). Improved efficiency of blue polymer light-emitting diodes using a hole transport material. *Journal of Materials Chemistry C*, 5(21), 5096-5101.

- Liao, J., Si, H., Zhang, X., & Lin, S. (2019). Functional sensing interfaces of PEDOT:PSS organic electrochemical transistors for chemical and biological sensors: A Mini Review. Sensors (Basel, Switzerland), 19(2), Article#218.
- Liao, X., Yang, X., Cheng, J., Li, Y., Meng, X., Li, J., Pei, Q., & Li, L. (2018). Solutionprocessed warm white organic light-emitting diodes based on a blue thermally activated delayed fluorescence dendrimer. *ChemPlusChem*, 83(4), 274-278.
- Liaptsis, G., & Meerholz, K. (2013). Crosslinkable TAPC-based hole-transport materials for solution-processed organic light-emitting diodes with reduced efficiency rolloff. Advanced Functional Materials, 23(3), 359-365.
- Liu, C., Huang, K., Park, W.-T., Li, M., Yang, T., Liu, X., Liang, L., Minari, T., & Noh, Y.-Y. (2017). A unified understanding of charge transport in organic semiconductors: the importance of attenuated delocalization for the carriers. *Materials Horizons*, 4(4), 608-618.
- Liu, H., Nichols, V. M., Shen, L., Jahansouz, S., Chen, Y., Hanson, K. M., Bardeen, C. J., & Li, X. (2015). Synthesis and photophysical properties of a "face-to-face" stacked tetracene dimer. *Physical Chemistry Chemical Physics*, 17(9), 6523-6531.
- Liu, S.-L. (2016). Relations between photoionization cross sections and photon radius.
- Liu, S.-W., Chang, Y.-T., Lee, C.-C., Yuan, C.-H., Liu, L.-A., Chen, Y.-S., Lin, C.-F., Wu, C.-I., & Chen, C.-T. (2013). Single-layer blue electrophosphorescent organic light-emitting diodes based on small-molecule mixed hosts: comparison between the solution and vacuum fabrication processes. *Japanese Journal of Applied Physics*, 52(1R), Article#012101.
- Liu, W., Liang, T., Chen, Q., Yu, Z., Zhang, Y., Liu, Y., Fu, W., Tang, F., Chen, L., & Chen, H. (2016). Solution-processed 8-hydroquinolatolithium as effective cathode interlayer for high-performance polymer solar cells. ACS Applied Materials & Interfaces, 8(14), 9254-9261.
- Liu, Y., Weng, B., Razal, J. M., Xu, Q., Zhao, C., Hou, Y., Seyedin, S., Jalili, R., Wallace, G. G., & Chen, J. (2015). High-performance flexible all-solid-state supercapacitor from large free-standing graphene-PEDOT/PSS films. *Scientific Reports*, 5(1), Article#17045.
- Liu, Z., Helander, M. G., Wang, Z., & Lu, Z. (2010). Band alignment at anode/organic interfaces for highly efficient simplified blue-emitting organic light-emitting diodes. *The Journal of Physical Chemistry C*, 114(39), 16746-16749.

- Long, D. X., & Noh, Y.-Y. (2018). Baking soda: an ultra-cheap and air stable electron injection layer for organic electronic devices. *Journal of Materials Chemistry C*, 6(47), 12871-12878.
- Lu, B., Yuk, H., Lin, S., Jian, N., Qu, K., Xu, J., & Zhao, X. (2019). Pure PEDOT:PSS hydrogels. *Nature Communications*, 10(1), Article#1043.
- Lu, N., Li, L., & Liu, M. (2015). Universal carrier thermoelectric-transport model based on percolation theory in organic semiconductors. *Physical Review B*, 91(19), Article#195205.
- Lu, S.-Y., Mukhopadhyay, S., Froese, R., & Zimmerman, P. M. (2018). Virtual screening of hole transport, electron transport, and host layers for effective OLED design. *Journal of Chemical Information and Modeling*, *58*(12), 2440-2449.
- Marcato, T., & Shih, C.-J. (2019). Molecular orientation effects in organic light-emitting diodes. *Helvetica Chimica Acta*, 102(5), Article#e1900048.
- Marcus, R. A. (1965). On the theory of electron-transfer reactions. VI. unified treatment for homogeneous and electrode reactions. *The Journal of Chemical Physics*, 43(2), 679-701.
- MarketResearchFuture®. (2020). Global organic Semiconductor Market Research report. Retrieved from https://www.marketresearchfuture.com/reports/organicsemiconductor-market-8069.
- Marra, W. C., Eisenberger, P., & Cho, A. Y. (1979). X-ray total-external-reflection– Bragg diffraction: A structural study of the GaAs-Al interface. *Journal of Applied Physics*, 50(11), 6927-6933.
- Martínez, J. I., Abad, E., González, C., Ortega, J., & Flores, F. (2012). Theoretical characterization of the TTF/Au (111) interface: STM imaging, band alignment and charging energy. *Organic Electronics*, 13(3), 399-408.
- Martins, T., Ribeiro, A., Souza, G., Cordeiro, D., Silva, R., Colmati, F., Lima, R. B., Aguiar, L., Carvalho, L., Reis, R., & Santos, W. (2018). New materials to solve energy issues through photochemical and photophysical processes: The Kinetics Involved.
- Mastelaro, V. R., & Zanotto, E. D. (2018). X-ray Absorption fine structure (XAFS) studies of oxide glasses—a 45-year overview. *Materials*, 11(2), Article#204.
- Mauger, S. A., Li, J., Özmen, Ö. T., Yang, A. Y., Friedrich, S., Rail, M. D., Berben, L. A., & Moulé, A. J. (2014). High work-function hole transport layers by self-

assembly using a fluorinated additive. Journal of Materials Chemistry C, 2(1), 115-123.

- Mesta, M., Carvelli, M., de Vries, R. J., van Eersel, H., van der Holst, J. J. M., Schober, M., Furno, M., Lüssem, B., Leo, K., Loebl, P., Coehoorn, R., & Bobbert, P. A. (2013). Molecular-scale simulation of electroluminescence in a multilayer white organic light-emitting diode. *Nature Materials*, 12(7), 652-658.
- Miao, Y., Du, X., Wang, H., Liu, H., Jia, H., Xu, B., Hao, Y., Liu, X., Li, W., & Huang, W. (2015). Simplified phosphorescent organic light-emitting devices using heavy doping with an Ir complex as an emitter. *RSC Advances*, 5(6), 4261-4265.
- Milad, R., Shi, J., Aguirre, A., Cardone, A., Milián-Medina, B., Farinola, G. M., Abderrabba, M., & Gierschner, J. (2016). Effective conjugation in conjugated polymers with strongly twisted backbones: a case study on fluorinated MEHPPV. *Journal of Materials Chemistry C*, 4(28), 6900-6906.
- Miller, A., & Abrahams, E. (1960). Impurity conduction at low concentrations. *Physical Review*, 120(3), 745-755.
- Min, Y., Dou, C., Tian, H., Geng, Y., Liu, J., & Wang, L. (2018). n-Type azaacenes containing B←N units. Angewandte Chemie International Edition, 57(7), 2000-2004.
- Modest, M. F. (2003). Chapter 1 fundamentals of thermal radiation. In M. F. Modest (Ed.), *Radiative Heat Transfer (Second Edition)* (pp. 1-29). Burlington: Academic Press.
- Mott, N. F. (1969). Conduction in non-crystalline materials. *The Philosophical Magazine:* A Journal of Theoretical Experimental and Applied Physics, 19(160), 835-852.
- Mott, N. F. (1939). The theory of crystal rectifiers. *Proceedings of the Royal Society of* London. Series A. Mathematical and Physical Sciences, 171(944), 27-38.
- Naik, P. A. (2017). X-ray spectroscopy, theory. In J. C. Lindon, G. E. Tranter, & D. W. Koppenaal (Eds.), *Encyclopedia of Spectroscopy and Spectrometry (Third Edition)* (pp. 725-734). Oxford: Academic Press.
- Nakamura, S. (2015). Background story of the invention of efficient blue InGaN light emitting diodes (Nobel Lecture). *Annalen der Physik*, 527(5-6), 335-349.
- Narayan, K., Varadharajaperumal, S., Mohan Rao, G., Manoj Varma, M., & Srinivas, T. (2013). Effect of thickness variation of hole injection and hole blocking layers on

the performance of fluorescent green organic light emitting diodes. Current Applied Physics, 13(1), 18-25.

- Naseem, A., Olliff, C. J., Martini, L. G., & Lloyd, A. W. (2003). Effects of oxygen plasma treatment on the surface wettability and dissolution of furosemide compacts. *Journal of Pharmacy and Pharmacology*, 55(11), 1473-1478.
- Navamani, K., & Senthilkumar, K. (2017). Effect of dynamic disorder on charge transport in organic molecules. arXiv:1705.05648 [cond-mat.soft], arXiv:1705.05648 [cond-mat.soft].
- Negi, S., Mittal, P., & Kumar, B. (2018). Impact of different layers on performance of OLED. *Microsystem Technologies*, 24(12), 4981-4989.
- NIST. (2020). X-Ray form factor, attenuation, and scattering tables. Retrieved from https://physics.nist.gov/PhysRefData/FFast/html/form.html.
- Oehzelt, M., Akaike, K., Koch, N., & Heimel, G. (2015). Energy-level alignment at organic heterointerfaces. *Science Advances*, 1(10), Article#e1501127.
- Oehzelt, M., Koch, N., & Heimel, G. (2014). Organic semiconductor density of states controls the energy level alignment at electrode interfaces. *Nature Communications*, 5(1), Article#4174.
- Olaya-Castro, A., & Scholes, G. D. (2011). Energy transfer from Förster–Dexter theory to quantum coherent light-harvesting. *International Reviews in Physical Chemistry*, 30(1), 49-77.
- Otero, R., Vázquez de Parga, A. L., & Gallego, J. M. (2017). Electronic, structural and chemical effects of charge-transfer at organic/inorganic interfaces. *Surface Science Reports*, 72(3), 105-145.
- Palmberg, P. W., & Industries, P. E. (1972). Handbook of auger electron spectroscopy: a reference book of standard data for identification and interpretation of auger electron spectroscopy data: Physical Electronics Industries.
- Park, Y., Soon Choi, K., & Young Kim, S. (2012). Graphene oxide/PEDOT:PSS and reduced graphene oxide/PEDOT:PSS hole extraction layers in organic photovoltaic cells. *physica status solidi (a)*, 209(7), 1363-1368.
- Pascarelli, S. (2016). X-Ray absorption spectroscopy: fundamentals and simple model of EXAFS (PowerPoint slides). Retrieved from http://www.esrf.eu/files/live/sites/www/files/events/conferences/2017/User_Mee ting_2017/Part%20I%20.pdf.

- Pauley, S. M. (2004). Lighting for the human circadian clock: recent research indicates that lighting has become a public health issue. *Medical Hypotheses, 63*(4), 588-596.
- Peljo, P., Manzanares, J. A., & Girault, H. H. (2016). Contact potentials, fermi level equilibration, and surface charging. *Langmuir*, 32(23), 5765-5775.
- Peng, X., Hu, L., Qin, F., Zhou, Y., & Chu, P. K. (2018). Low work function surface modifiers for solution-processed electronics: a review. *Advanced Materials Interfaces*, 5(10), Article#1701404.
- Peng, X.-F., Wu, X.-Y., Ji, X.-X., Ren, J., Wang, Q., Li, G.-Q., & Yang, X.-H. (2017). Modified conducting polymer hole injection layer for high-efficiency perovskite light-emitting devices: enhanced hole injection and reduced luminescence quenching. *The Journal of Physical Chemistry Letters*, 8(19), 4691-4697.
- Pode, R. (2020). Organic light emitting diode devices: An energy efficient solid state lighting for applications. *Renewable and Sustainable Energy Reviews*, 133, Article#110043.
- Pope, M., Kallmann, H. P., & Magnante, P. (1963). Electroluminescence in organic crystals. *The Journal of Chemical Physics*, 38(8), 2042-2043.
- Pople, J. A., Head-Gordon, M., & Raghavachari, K. (1987). Quadratic configuration interaction. A general technique for determining electron correlation energies. *The Journal of Chemical Physics*, 87(10), 5968-5975.

Puglisi, A. (2017). Ab-initio study of x-ray spectroscopy of molecular ions.

- Quinn, J. T. E., Zhu, J., Li, X., Wang, J., & Li, Y. (2017). Recent progress in the development of n-type organic semiconductors for organic field effect transistors. *Journal of Materials Chemistry C*, 5(34), 8654-8681.
- Rani, V., Sharma, A., Kumar, P., Singh, B., & Ghosh, S. (2017). Charge transport mechanism in copper phthalocyanine thin films with and without traps. *RSC Advances*, 7(86), 54911-54919.
- Reineke, S., Lindner, F., Schwartz, G., Seidler, N., Walzer, K., Lüssem, B., & Leo, K. (2009). White organic light-emitting diodes with fluorescent tube efficiency. *Nature*, 459(7244), 234-238.
- Reiser, P., Benneckendorf, F. S., Barf, M.-M., Müller, L., Bäuerle, R., Hillebrandt, S., Beck, S., Lovrincic, R., Mankel, E., Freudenberg, J., Jänsch, D., Kowalsky, W., Pucci, A., Jaegermann, W., Bunz, U. H. F., & Müllen, K. (2019). n-Type doping

of organic semiconductors: immobilization via covalent anchoring. *Chemistry of Materials*, 31(11), 4213-4221.

- Rivnay, J., Mannsfeld, S. C. B., Miller, C. E., Salleo, A., & Toney, M. F. (2012). Quantitative determination of organic semiconductor microstructure from the molecular to device scale. *Chemical Reviews*, 112(10), 5488-5519.
- Roberts, G. G., McGinnity, M., Barlow, W. A., & Vincett, P. S. (1979). Electroluminescence, photoluminescence and electroabsorption of a lightly substituted anthracene langmuir film. *Solid State Communications*, 32(8), 683-686.
- Ruscello, M., Stolz, S., Gonzalez Arellano, D. L., Ullrich, F., Hillebrandt, S., Mankel, E., Pucci, A., Kowalsky, W., Emrick, T., Briseno, A. L., & Hernandez-Sosa, G. (2017). Electron injection and interfacial trap passivation in solution-processed organic light-emitting diodes using a polymer zwitterion interlayer. Organic Electronics, 50, 384-388.
- Sano, M., Pope, M., & Kallmann, H. (1965). Electroluminescence and band gap in anthracene. *The Journal of Chemical Physics*, 43(8), 2920-2921.
- Sato, M., Sakaguchi, T., & Morita, T. (2005). The effects of exposure in the morning to light of different color temperatures on the behavior of core temperature and melatonin secretion in humans. *Biological Rhythm Research*, 36(4), 287-292.
- Sauer, M., Hofkens, J., & Enderlein, J. (2011). Handbook of fluorescence spectroscopy and imaging: from single molecules to ensembles. *Handbook of Fluorescence Spectroscopy and Imaging: From Single Molecules to Ensembles*.
- Schmechel, R. (2002). Gaussian disorder model for high carrier densities: Theoretical aspects and application to experiments. *Physical Review B*, 66(23), Article#235206.
- Schulte, F. K. (1977). On the theory of the work function. Zeitschrift für Physik B Condensed Matter, 27(4), 303-307.
- Scofield, J. H. (1976). Hartree-Slater subshell photoionization cross-sections at 1254 and 1487 eV. Journal of Electron Spectroscopy and Related Phenomena, 8(2), 129-137.
- Seah, M. P., & Dench, W. A. (1979). Quantitative electron spectroscopy of surfaces: A standard data base for electron inelastic mean free paths in solids. *Surface and Interface Analysis*, 1(1), 2-11.

- Segal, M., Baldo, M. A., Holmes, R. J., Forrest, S. R., & Soos, Z. G. (2003). Excitonic singlet-triplet ratios in molecular and polymeric organic materials. *Physical Review B*, 68(7), Article#075211.
- Seki, K., Tani, T., & Ishii, H. (1996). Electronic structures of organic-inorganic interfaces studied by UV photoemission. *Thin Solid Films*, 273(1), 20-26.
- Shaheen, S. E., Kippelen, B., Peyghambarian, N., Wang, J.-F., Anderson, J. D., Mash, E. A., Lee, P. A., Armstrong, N. R., & Kawabe, Y. (1999). Energy and charge transfer in organic light-emitting diodes: A soluble quinacridone study. *Journal of Applied Physics*, 85(11), 7939-7945.
- Shechter, A., Kim, E. W., St-Onge, M.-P., & Westwood, A. J. (2018). Blocking nocturnal blue light for insomnia: A randomized controlled trial. *Journal of Psychiatric Research*, 96, 196-202.
- Shih, P.-I., Chien, C.-H., Chuang, C.-Y., Shu, C.-F., Yang, C.-H., Chen, J.-H., & Chi, Y. (2007). Novel host material for highly efficient blue phosphorescent OLEDs. *Journal of Materials Chemistry*, 17(17), 1692-1698.
- Shin, N., Kang, J., Richter, L. J., Prabhu, V. M., Kline, R. J., Fischer, D. A., DeLongchamp, D. M., Toney, M. F., Satija, S. K., Gundlach, D. J., Purushothaman, B., Anthony, J. E., & Yoon, D. Y. (2013). Vertically segregated structure and properties of small molecule–polymer blend semiconductors for organic thin-film transistors. *Advanced Functional Materials*, 23(3), 366-376.
- Shirakawa, H., Louis, E. J., MacDiarmid, A. G., Chiang, C. K., & Heeger, A. J. (1977). Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, (CH). *Journal of the Chemical Society, Chemical Communications*(16), 578-580.
- Singh, M., Jou, J.-H., Sahoo, S., S. S, S., He, Z.-K., Krucaite, G., Grigalevicius, S., & Wang, C.-W. (2018). High light-quality OLEDs with a wet-processed single emissive layer. *Scientific Reports*, 8(1), Article#7133.
- Sohn, S., & Han, Y. S. (2011). Transparent conductive oxide (TCO) films for organic light emissive devices (OLEDs).
- Song, M., Park, J. S., Nam, K.-S., Yoon, M., Yoon, H. W., Kim, A. J., Kim, Y. I., Gal, Y.-S., Lee, J. W., & Jin, S.-H. (2011). Synthesis and electrophosphorescent properties of iridium complexes based on phenylpyridine-based main ligand for organic light-emitting diodes. *Journal of Crystal Growth*, 326(1), 103-108.
- Songsiriritthigul, P., Kjornrattanawanich, B., Tong-on, A., & Nakajima, H. (2007). Design of the first undulator beamline for the Siam Photon Laboratory. *Nuclear*

Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, 582(1), 100-102.

- Sotthewes, K., van Bremen, R., Dollekamp, E., Boulogne, T., Nowakowski, K., Kas, D., Zandvliet, H. J. W., & Bampoulis, P. (2019). Universal Fermi-level pinning in transition-metal dichalcogenides. *The Journal of Physical Chemistry C*, 123(9), 5411-5420.
- Srinivasan, V., Spence, D. W., Pandi-Perumal, S. R., Trakht, I., Esquifino, A. I., Cardinali, D. P., & Maestroni, G. J. (2008). Melatonin, environmental light, and breast cancer. *Breast Cancer Research and Treatment*, 108(3), 339-350.
- Starr, D. E., Favaro, M., Abdi, F. F., Bluhm, H., Crumlin, E. J., & van de Krol, R. (2017). Combined soft and hard X-ray ambient pressure photoelectron spectroscopy studies of semiconductor/electrolyte interfaces. *Journal of Electron Spectroscopy* and Related Phenomena, 221, 106-115.
- Su, Z., Wang, L., Li, Y., Zhao, H., Chu, B., & Li, W. (2012). Ultraviolet-ozone-treated PEDOT:PSS as anode buffer layer for organic solar cells. *Nanoscale Research Letters*, 7(1), Article#465.
- Sudhakar, M., Djurovich, P. I., Hogen-Esch, T. E., & Thompson, M. E. (2003). Phosphorescence quenching by conjugated polymers. *Journal of the American Chemical Society*, 125(26), 7796-7797.
- Talik, N. A., Woon, K. L., & Yap, B. K. (2016). Effect of mixed hole transporting host on the mobility, Gaussian density of states and efficiencies of a heterojunction phosphorescent organic light emitting diode. *Journal of Physics D: Applied Physics, 49*(15), Article#155103.
- Talik, N. A., Woon, K. L., Yap, B. K., Wong, W. S., Whitcher, T. J., Chanlek, N., Nakajima, H., Saisopa, T., & Songsiriritthigul, P. (2016). Highly efficient processable molybdenum trioxide as a hole blocking interlayer for super-yellow organic light emitting diode. *Journal of Physics D: Applied Physics, 49*(39), Article#395105.
- Tanaka, Y., Kanai, K., Ouchi, Y., & Seki, K. (2009). Role of interfacial dipole layer for energy-level alignment at organic/metal interfaces. *Organic Electronics*, 10(5), 990-993.
- Tang, C. G., Syafiqah, M. N., Koh, Q.-M., Zhao, C., Zaini, J., Seah, Q.-J., Cass, M. J., Humphries, M. J., Grizzi, I., Burroughes, J. H., Png, R.-Q., Chua, L.-L., & Ho, P. K. H. (2019). Multivalent anions as universal latent electron donors. *Nature*, 573(7775), 519-525.

- Tang, C. W., & VanSlyke, S. A. (1987). Organic electroluminescent diodes. Applied Physics Letters, 51(12), 913-915.
- Tang, J. X., Lee, C. S., & Lee, S. T. (2007). Electronic structures of organic/organic heterojunctions: From vacuum level alignment to Fermi level pinning. *Journal of Applied Physics*, 101(6), Article#064504.
- Tauc, J. (1968). Optical properties and electronic structure of amorphous Ge and Si. *Materials Research Bulletin, 3*(1), 37-46.
- Tessler, N., Preezant, Y., Rappaport, N., & Roichman, Y. (2009). Charge transport in disordered organic materials and its relevance to thin-film devices: a tutorial review. *Advanced Materials*, 21(27), 2741-2761.
- Thompson, A. C. (2001). *X-ray data booklet*: Lawrence Berkeley National Laboratory, University of California.
- Trifunovic, M., Sberna, P. M., Shimoda, T., & Ishihara, R. (2017). Solution-based polycrystalline silicon transistors produced on a paper substrate. *npj Flexible Electronics*, 1(1), Article#12.
- Turak, A., Hanisch, J., Barrena, E., Welzel, U., Widmaier, F., Ahlswede, E., & Dosch, H. (2010). Systematic analysis of processing parameters on the ordering and performance of working poly(3-hexyl-thiophene):[6,6]-phenyl C61-butyric acid methyl ester solar cells. *Journal of Renewable and Sustainable Energy*, 2(5), Article#053103.
- Turchini, S., Delaunay, R., Lagarde, P., Vogel, J., & Sacchi, M. (1995). Soft X-ray absorption spectroscopy in transmission mode: Ce M4,5 edges. *Journal of Electron Spectroscopy and Related Phenomena*, 71(1), 31-37.
- Tyagi, P., Srivastava, R., Kumar, A., Tuli, S., & Kamalasanan, M. N. (2013). Study of shifting of recombination zone in multi-emissive layer organic light emitting devices and its effect on color stability. *Journal of Luminescence*, *136*, 249-254.
- Uoyama, H., Goushi, K., Shizu, K., Nomura, H., & Adachi, C. (2012). Highly efficient organic light-emitting diodes from delayed fluorescence. *Nature*, 492(7428), 234-238.
- Vall-llosera, G., Gao, B., Kivimäki, A., Coreno, M., Ruiz, J. Á., Simone, M. d., Ågren, H., & Rachlew, E. (2008). The C 1s and N 1s near edge x-ray absorption fine structure spectra of five azabenzenes in the gas phase. *The Journal of Chemical Physics*, 128(4), 044316.

- Van Dyck, C., Geskin, V., & Cornil, J. (2014). Fermi level pinning and orbital polarization effects in molecular junctions: the role of metal induced gap states. *Advanced Functional Materials*, 24(39), 6154-6165.
- Van Reenen, S., Kouijzer, S., Janssen, R. A. J., Wienk, M. M., & Kemerink, M. (2014). Origin of work function modification by ionic and amine-based interface layers. *Advanced Materials Interfaces*, 1(8), Article#1400189.
- Vázquez, H., Dappe, Y. J., Ortega, J., & Flores, F. (2007). Energy level alignment at metal/organic semiconductor interfaces: "Pillow" effect, induced density of interface states, and charge neutrality level. *The Journal of Chemical Physics*, 126(14), Article#144703.
- Vegiraju, S., Huang, D.-Y., Priyanka, P., Li, Y.-S., Luo, X.-L., Hong, S.-H., Ni, J.-S., Tung, S.-H., Wang, C.-L., Lien, W.-C., Yau, S. L., Liu, C.-L., & Chen, M.-C. (2017). High performance solution-processable tetrathienoacene (TTAR) based small molecules for organic field effect transistors (OFETs). *Chemical Communications*, 53(43), 5898-5901.
- Venkateshvaran, D., Nikolka, M., Sadhanala, A., Lemaur, V., Zelazny, M., Kepa, M., Hurhangee, M., Kronemeijer, A. J., Pecunia, V., Nasrallah, I., Romanov, I., Broch, K., McCulloch, I., Emin, D., Olivier, Y., Cornil, J., Beljonne, D., & Sirringhaus, H. (2014). Approaching disorder-free transport in high-mobility conjugated polymers. *Nature*, 515(7527), 384-388.
- Vincett, P. S., Barlow, W. A., Hann, R. A., & Roberts, G. G. (1982). Electrical conduction and low voltage blue electroluminescence in vacuum-deposited organic films. *Thin Solid Films*, 94(2), 171-183.
- Wagner, C. D., Davis, L. E., Zeller, M. V., Taylor, J. A., Raymond, R. H., & Gale, L. H. (1981). Empirical atomic sensitivity factors for quantitative analysis by electron spectroscopy for chemical analysis. *Surface and Interface Analysis*, 3(5), 211-225.
- Wandelt, K., & Hulse, J. E. (1984). Xenon adsorption on palladium. I. The homogeneous (110), (100), and (111) surfaces. *The Journal of Chemical Physics*, 80(3), 1340-1352.
- Wang, D.-C., Zhang, C., Zeng, P., Zhou, W.-J., Ma, L., Wang, H.-T., Zhou, Z.-Q., Hu, F., Zhang, S.-Y., Lu, M., & Wu, X. (2018). An all-silicon laser based on silicon nanocrystals with high optical gains. *Science Bulletin*, 63(2), 75-77.
- Wang, J., Zhang, H., Ji, W., Zhang, H., & Zhu, F. (2015). Origin of efficiency roll-off for FIrpic based blue organic light-emitting diodes and implications on phosphorescent molecule design. *Japanese Journal of Applied Physics*, 54(10), Article#101601.

- Wang, X., Liu, L., Zhu, S., Peng, J., & Li, L. (2017). Preparation of exciplex-based fluorescent organic nanoparticles and their application in cell imaging. *RSC Advances*, 7(65), 40842-40848.
- Wang, Y., Zhu, Y., Xie, G., Zhan, H., Yang, C., & Cheng, Y. (2017). Bright white electroluminescence from a single polymer containing a thermally activated delayed fluorescence unit and a solution-processed orange OLED approaching 20% external quantum efficiency. *Journal of Materials Chemistry C*, 5(41), 10715-10720.
- Wei, H.-X., Ou, Q.-D., Zhang, Z., Li, J., Li, Y.-Q., Lee, S.-T., & Tang, J.-X. (2013). The role of cesium fluoride as an n-type dopant on electron transport layer in organic light-emitting diodes. Organic Electronics, 14(3), 839-844.
- Whitcher, T. J., Talik, N. A., Woon, K., Chanlek, N., Nakajima, H., Saisopa, T., & Songsiriritthigul, P. (2014). Determination of energy levels at the interface between O2 plasma treated ITO/P3HT : PCBM and PEDOT : PSS/P3HT : PCBM using angular-resolved x-ray and ultraviolet photoelectron spectroscopy. *Journal* of Physics D: Applied Physics, 47(5), Article#055109.
- Whitcher, T. J., Wong, W. S., Talik, A. N., Woon, K. L., Chanlek, N., Nakajima, H., Saisopa, T., & Songsiriritthigul, P. (2016). Electrostatic model of the energybending within organic semiconductors: experiment and simulation. *Journal of Physics: Condensed Matter, 28*(36), Article#365002.
- Whitcher, T. J., Woon, K. L., Wong, W. S., Chanlek, N., Nakajima, H., Saisopa, T., & Songsiriritthigul, P. (2016). Interfacial behavior of resistive switching in ITO– PVK–Al WORM memory devices. *Journal of Physics D: Applied Physics, 49*(7), Article#075104.
- Whitcher, T. J., Yeoh, K. H., Ng, Y. B. C., Talik, N. A., Chua, C. L., Woon, K. L., Chanlek, N., Nakajima, H., Saisopa, T., Songsiriritthigul, P., Oswald, S., & Yap, B. K. (2013). Enhancement of the work function of indium tin oxide by surface modification using caesium fluoride. *Journal of Physics D: Applied Physics*, 46(47), Article#475102.
- Witte, G., Lukas, S., Bagus, P. S., & Wöll, C. (2005). Vacuum level alignment at organic/metal junctions: "Cushion" effect and the interface dipole. *Applied Physics Letters*, 87(26), Article#263502.
- Wittmer, M., & Zschokke-Gränacher, I. (1975). Exciton-charge carrier interactions in the electroluminescence of crystalline anthracene. *The Journal of Chemical Physics*, 63(10), 4187-4194.

- Woon, K. L., Hasan, Z. A., Ong, B. K., Ariffin, A., Griniene, R., Grigalevicius, S., & Chen, S.-A. (2015). Triplet states and energy back transfer of carbazole derivatives. *RSC Advances*, 5(74), 59960-59969.
- Woon, K. L., Wong, W. S., Chanlek, N., Nakajima, H., Tunmee, S., Songsiriritthigul, C., Lee, V. S., & Songsiriritthigul, P. (2019). Conformational distortion in solution processable PVK:TcTa blends and the effect on extra warm white organic phosphorescent light emitting diodes. *Organic Electronics*, 74, 1-6.
- Wu, C.-H., Tsai, K.-W., Huang, W.-J., Wu, C.-Y., Chen, T.-Y., Guo, T.-F., Hsu, Y.-J., & Wen, T.-C. (2016). Amide-functionalized small molecules as solution-processed electron injection layers in highly efficient polymer light-emitting diodes. *Advanced Materials Interfaces*, 3(6), Article#1500621.
- Wu, Q.-H. (2013). Progress in modification of indium-tin oxide/organic interfaces for organic light-emitting diodes. *Critical Reviews in Solid State and Materials Sciences*, 38(4), 318-352.
- Wu, S., Han, S., Zheng, Y., Zheng, H., Liu, N., Wang, L., Cao, Y., & Wang, J. (2011). pH-neutral PEDOT:PSS as hole injection layer in polymer light emitting diodes. *Organic Electronics*, 12(3), 504-508.
- Wu, S., Li, S., Sun, Q., Huang, C., & Fung, M.-K. (2016). Highly efficient white organic light-emitting diodes with ultrathin emissive layers and a spacer-free structure. *Scientific Reports*, 6(1), Article#25821.
- Xia, Y., Sun, K., & Ouyang, J. (2012). Highly conductive poly(3,4ethylenedioxythiophene):poly(styrene sulfonate) films treated with an amphiphilic fluoro compound as the transparent electrode of polymer solar cells. *Energy & Environmental Science*, 5(1), 5325-5332.
- Xiang, H.-Y., Li, Y.-Q., Meng, S.-S., Lee, C.-S., Chen, L.-S., & Tang, J.-X. (2018). Extremely efficient transparent flexible organic light-emitting diodes with nanostructured composite electrodes. *Advanced Optical Materials*, 6(21), Article#1800831.
- Xiao, L., Chen, Z., Qu, B., Luo, J., Kong, S., Gong, Q., & Kido, J. (2011). Recent progresses on materials for electrophosphorescent organic light-emitting devices. *Advanced Materials*, 23(8), 926-952.
- Xiao, X., Wang, K., Ye, T., Cai, R., Ren, Z., Wu, D., Qu, X., Sun, J., Ding, S., Sun, X. W., & Choy, W. C. H. (2020). Enhanced hole injection assisted by electric dipoles for efficient perovskite light-emitting diodes. *Communications Materials*, 1(1), Article#81.

- Xie, L.-H., Ling, Q.-D., Hou, X.-Y., & Huang, W. (2008). An effective friedel–crafts postfunctionalization of poly(n-vinylcarbazole) to tune carrier transportation of supramolecular organic semiconductors based on π -stacked polymers for nonvolatile flash memory cell. *Journal of the American Chemical Society*, 130(7), 2120-2121.
- Xin, X. K. (1986). An indirect measurement of energy gap for silicon and germanium. Solid-State Electronics, 29(9), 845-847.
- Xing, X., Zhang, L., Liu, R., Li, S., Qu, B., Chen, Z., Sun, W., Xiao, L., & Gong, Q. (2012). A deep-blue emitter with electron transporting property to improve charge balance for organic light-emitting device. ACS Applied Materials & Interfaces, 4(6), 2877-2880.
- Xing, X., Zhong, L., Zhang, L., Chen, Z., Qu, B., Chen, E., Xiao, L., & Gong, Q. (2013). Essential differences of organic films at the molecular level via vacuum deposition and solution processes for organic light-emitting diodes. *The Journal* of *Physical Chemistry C*, 117(48), 25405-25408.
- Xu, X., Xiao, T., Gu, X., Yang, X., Kershaw, S. V., Zhao, N., Xu, J., & Miao, Q. (2015). Solution-processed ambipolar organic thin-film transistors by blending p- and ntype semiconductors: solid solution versus microphase separation. ACS Applied Materials & Interfaces, 7(51), 28019-28026.
- Yanagisawa, S., Lee, K., & Morikawa, Y. (2008). First-principles theoretical study of Alq3 / Al interfaces: Origin of the interfacial dipole. *The Journal of Chemical Physics*, 128(24), Article#244704.
- Yang, J., Zhao, Z., Wang, S., Guo, Y., & Liu, Y. (2018). Insight into high-performance conjugated polymers for organic field-effect transistors. *Chem*, 4(12), 2748-2785.
- Yang, J.-P., Shang, L.-T., Bussolotti, F., Cheng, L.-W., Wang, W.-Q., Zeng, X.-H., Kera, S., Li, Y.-Q., Tang, J.-X., & Ueno, N. (2017). Fermi-level pinning appears upon weak electrode-organic contact without gap states: A universal phenomenon. *Organic Electronics*, 48, 172-178.
- Yang, X., Yan, X., Guo, H., Liu, B., Zhao, J., Zhou, G., Wu, Y., Wu, Z., & Wong, W.-Y. (2017). Charged dinuclear Cu(I) complexes for solution-processed single-emitter warm white organic light-emitting devices. *Dyes and Pigments*, 143, 151-164.
- Yang, Y., Liu, C., Ding, Y., Arain, Z., Wang, S., Liu, X., Hayat, T., Alsaedi, A., & Dai, S. (2019). Eliminating charge accumulation via interfacial dipole for efficient and stable perovskite solar cells. ACS Applied Materials & Interfaces, 11(38), 34964-34972.

- Yang, Z., Xu, B., He, J., Xue, L., Guo, Q., Xia, H., & Tian, W. (2009). Solutionprocessable and thermal-stable triphenylamine-based dendrimers with truxene cores as hole-transporting materials for organic light-emitting devices. Organic Electronics, 10(5), 954-959.
- Yemata, T. A., Zheng, Y., Kyaw, A. K. K., Wang, X., Song, J., Chin, W. S., & Xu, J. (2020). Modulation of the doping level of PEDOT:PSS film by treatment with hydrazine to improve the Seebeck coefficient. *RSC Advances*, 10(3), 1786-1792.
- Yeoh, K. H., Ng, C. Y. B., Chua, C. L., Azrina Talik, N., & Woon, K. L. (2013). High power efficiency solution-processed double-layer blue phosphorescent organic light-emitting diode by controlling charge transport at the emissive layer and heterojunction. *physica status solidi (RRL) – Rapid Research Letters*, 7(6), 421-424.
- Yeoh, K. H., Talik, N. A., Whitcher, T. J., Ng, C. Y. B., & Woon, K. L. (2014). The efficiency enhancement of single-layer solution-processed blue phosphorescent organic light emitting diodes by hole injection layer modification. *Journal of Physics D: Applied Physics*, 47(20), Article#205103.
- Yersin, H. (2004). Triplet Emitters for OLED Applications. Mechanisms of exciton trapping and control of emission properties. In *Transition Metal and Rare Earth Compounds: Excited States, Transitions, Interactions III* (pp. 1-26). Berlin, Heidelberg: Springer Berlin Heidelberg.
- Yoon, J., Choi, S., Jeong, C. H., Kim, S. K., Lee, H., Kim, Y., Kwon, J. H., Park, S., Cho, M. J., & Choi, D. H. (2019). Solution-processed white organic light-emitting diodes with blue fluorescent and orange-red thermally activated delayed fluorescent dendritic luminogens. *Dyes and Pigments*, 170, Article#107650.
- Yoshikawa, K., Kawasaki, H., Yoshida, W., Irie, T., Konishi, K., Nakano, K., Uto, T., Adachi, D., Kanematsu, M., Uzu, H., & Yamamoto, K. (2017). Silicon heterojunction solar cell with interdigitated back contacts for a photoconversion efficiency over 26%. *Nature Energy*, 2(5), Article#17032.
- Youn, W., Lee, J., Xu, M., Singh, R., & So, F. (2015). Corrugated sapphire substrates for organic light-emitting diode light extraction. ACS Applied Materials & Interfaces, 7(17), 8974-8978.
- Yun, S.-J., Jeon, J., Jin, S.-H., Kang, S. K., & Kim, Y.-I. (2017). Synthesis, structure, and OLEDs application of cyclometalated iridium(iii) complexes utilizing substituted 2-phenylpyridine. *Bulletin of the Korean Chemical Society*, 38(7), 788-794.

Zangwill, A. (1988). Physics at Surfaces. Cambridge: Cambridge University Press.

- Zhang, S., Kumar, P., Nouas, A. S., Fontaine, L., Tang, H., & Cicoira, F. (2015). Solventinduced changes in PEDOT:PSS films for organic electrochemical transistors. *APL Materials*, 3(1), Article#014911.
- Zhang, T., Liang, Y., Cheng, J., & Li, J. (2013). A CBP derivative as bipolar host for performance enhancement in phosphorescent organic light-emitting diodes. *Journal of Materials Chemistry C*, 1(4), 757-764.
- Zhang, Y., Chen, L., Hu, X., Zhang, L., & Chen, Y. (2015). Low work-function poly(3,4ethylenedioxylenethiophene): poly(styrene sulfonate) as electron-transport layer for high-efficient and stable polymer solar cells. *Scientific Reports*, 5(1), Article#12839.
- Zhang, Z., He, Z., Bi, S., & Asare-Yeboah, K. (2020). Phase segregation controlled semiconductor crystallization for organic thin film transistors. *Journal of Science: Advanced Materials and Devices*, 5(2), 151-163.
- Zhao, Z. Q., You, S., Huang, J., Yuan, L., Xiao, Z. Y., Cao, Y., Cheng, N., Hu, L., Liu, J. F., & Yu, B. H. (2019). Molecular modulator for stable inverted planar perovskite solar cells with efficiency enhanced by interface engineering. *Journal* of Materials Chemistry C, 7(31), 9735-9742.
- Zheng, R., Huang, W., Xu, W., & Cao, Y. (2012). Effect of CsF buffer layer on chargecarrier mobility in organic light-emitting diodes based on a polyfluorene copolymers by admittance spectroscopy. *Synthetic Metals*, 162(21), 1919-1922.
- Zhong, S., Zhong, J. Q., Mao, H. Y., Zhang, J. L., Lin, J. D., & Chen, W. (2012). The role of gap states in the energy level alignment at the organic-organic heterojunction interfaces. *Physical Chemistry Chemical Physics*, 14(41), 14127-14141.
- Zhou, K., Dong, H., Zhang, H.-l., & Hu, W. (2014). High performance n-type and ambipolar small organic semiconductors for organic thin film transistors. *Physical Chemistry Chemical Physics*, 16(41), 22448-22457.
- Zhou, L., Zhuang, J. Y., Tongay, S., Su, W. M., & Cui, Z. (2013). Performance improvement of organic light emitting diode with aluminum oxide buffer layer for anode modification. *Journal of Applied Physics*, 114(7), Article#074506.
- Zhou, Y., Fuentes-Hernandez, C., Shim, J., Meyer, J., Giordano, A. J., Li, H., Winget, P., Papadopoulos, T., Cheun, H., Kim, J., Fenoll, M., Dindar, A., Haske, W., Najafabadi, E., Khan, T. M., Sojoudi, H., Barlow, S., Graham, S., Brédas, J.-L., Marder, S. R., Kahn, A., & Kippelen, B. (2012). A universal method to produce low-work function electrodes for organic electronics. *Science*, 336(6079), 327-332.

- Zhu, L., Wu, Z., Chen, J., & Ma, D. (2015). Reduced efficiency roll-off in allphosphorescent white organic light-emitting diodes with an external quantum efficiency of over 20%. *Journal of Materials Chemistry C*, 3(14), 3304-3310.
- Zojer, E., Taucher, T. C., & Hofmann, O. T. (2019). The impact of dipolar layers on the electronic properties of organic/inorganic hybrid interfaces. *Advanced Materials Interfaces*, *6*(14), Article#1900581.
- Zou, S.-J., Shen, Y., Xie, F.-M., Chen, J.-D., Li, Y.-Q., & Tang, J.-X. (2020). Recent advances in organic light-emitting diodes: toward smart lighting and displays. *Materials Chemistry Frontiers*, 4(3), 788-820.

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LIST OF PUBLICATIONS AND PAPERS PRESENTED

List of publications

- Woon, K. L., Wong, W. S., Chanlek, N., Nakajima, H., Tunmee, S., Songsiriritthigul, C., Lee, V. S., & Songsiriritthigul, P. (2019). Conformational distortion in solution processable PVK:TcTa blends and the effect on extra warm white organic phosphorescent light emitting diodes. *Organic Electronics*, 74, 1-6.
- Woon, K. L., Wong, W. S., Chanlek, N., Nakajima, H., Tunmee, S., Lee, V. S., Ariffin, A., & Songsiriritthigul, P. (2020). Work function modification of PEDOT:PSS by mixing with barium acetylacetonate. *RSC Advances*, 10(30), 17673-17680.

The following papers finished during this period are either overlap or the subjects are outside the scope of this thesis.

- Whitcher, T. J., Wong, W. S., Talik, A. N., Woon, K. L., Chanlek, N., Nakajima, H., Saisopa, T., & Songsiriritthigul, P. (2016a). Electrostatic model of the energybending within organic semiconductors: experiment and simulation. *Journal of Physics: Condensed Matter*, 28(36), 365002.
- Whitcher, T. J., Woon, K. L., Wong, W. S., Chanlek, N., Nakajima, H., Saisopa, T., & Songsiriritthigul, P. (2016). Interfacial behavior of resistive switching in ITO-PVK-Al WORM memory devices. *Journal of Physics D: Applied Physics*, 49(7), 075104.
- Whitcher, T. J., Wong, W. S., Talik, A. N., Woon, K. L., Chanlek, N., Nakajima, H., Saisopa, T., & Songsiriritthigul, P. (2016b). Investigation into the Gaussian density of states widths of organic semiconductors. *Journal of Physics D: Applied Physics*, 49(32), 325106.
- Talik, N. A., Woon, K. L., Yap, B. K., Wong, W. S., Whitcher, T. J., Chanlek, N., Nakajima, H., Saisopa, T., & Songsiriritthigul, P. (2016). Highly efficient processable molybdenum trioxide as a hole blocking interlayer for super-yellow organic light emitting diode. *Journal of Physics D: Applied Physics*, 49(39), 395105.
- Hasan, Z. A., Woon, K. L., Wong, W. S., Ariffin, A., & Chen, S.-A. (2017). Solution processed multilayer red, green and blue phosphorescent organic light emitting diodes using carbazole dendrimer as a host. *Journal of Luminescence*, 183, 150-158.
- Whitcher, T. J., Wong, W. S., Talik, A. N., Woon, K. L., Rusydi, A., Chanlek, N., Nakajima, H., Saisopa, T., & Songsiriritthigul, P. (2018). Energy level alignment of blended organic semiconductors and electrodes at the interface. *Current Applied Physics*, 18(9), 982-992.

- Lee, H. L., Woon, K. L., Tan, S., Wong, W. S., Ariffin, A., Chanlek, N., Nakajima, H., Saisopa, T., & Songsiriritthigul, P. (2019). Structural, chemical and electronic differences between bare and nitrogen-doped carbon nanoparticles. *Carbon Letters*, 29(3), 255-262.
- Kumar, P., Woon, K. L., Wong, W. S., Mohamed Saheed, M. S., & Burhanudin, Z. A. (2019). Hybrid film of single-layer graphene and carbon nanotube as transparent conductive electrode for organic light emitting diode. *Synthetic Metals*, 257, 116186.
- Hamood Al-Masoodi, A. H., Goh, B. T., Farhanah Binti Nazarudin, N. F., Mohd Sarjidan, M. A., Wong, W. S., & Binti Abd Majid, W. H. (2020). Efficiency enhancement in blue phosphorescent organic light emitting diode with silver nanoparticles prepared by plasma-assisted hot-filament evaporation as an external light-extraction layer. *Materials Chemistry and Physics*, 256, 123618.

Papers Presented

1. Wong, W. S., & Woon, K. L. (2016). *Efficient Extra Warm White All Solution Processable Phosphorescent Organic Light Emitting Diode*. Paper presented at the National Physics Conference 2016, Hotel Pullman Kuala Lumpur, Bangsar, 59200 Kuala Lumpur, MALAYSIA.