NANYANG
TECHNOLOGICAL
UNIVERSITY

**CHARGE INJECTION AND DOPING ZONE ENGINEERING OF
LIGHT-EMITTING ELECTROCHEMICAL CELLS FOR
SPORTS PERFORMANCE MONITORING**

CHEE JIANZHI, KENJI

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2017

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A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2017

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

04/1/2017

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Date

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Chee Jianzhi, Kenji

Abstract

This thesis first explains the need for light emitting markers as an inexpensive means of biomechanical motion analysis. With analysis of the current sports analysis landscape, flexible organic lighting devices based on conjugated emissive polymers with low turn-on voltage and colour tunability will be deemed as a wearable light marker for different sports and weather conditions. Light-emitting electrochemical cell (LEEC) in comparison to organic light-emitting diodes possesses a combination of advantages. It consists of an active layer blend of conjugated polymer, ion transporter and salt sandwiched between two electrodes that offer simple single layer solution processability, independent of electrode work function and optimized carrier injection due to doped regions based on electrochemical doping of organic polymers. Electrolytes within the active layer of LEEC determines the performance of the active layer. Salt and ion conductors are the constituents of the electrolyte and especially the p doped regions having higher conductivity and larger doped area point toward a dominant character of the anion. Bis(trifluoromethylsulfonyl)imide (TFSI⁻) anion due to its low binding energy, high number of resonance states, high ionic conductivity on the order of 10^{-4} S cm⁻¹ provides efficient doping, lowered turn-on voltages and enhanced maximal brightness of the device (~ 100 cd/m²). Li⁺ and BMIM⁺ cations have been used to revalidate this concept with coherent findings. Complexation between TFSI⁻ anion and polymer was confirmed via X-ray Photoelectron Spectroscopy with strong correlations in Photoluminescence (PL) and Absorption (Abs) studies. Based on this, we have revealed a novel mechanism which explains recombination zone centering in the active layer that enhances brightness and lowers the turn-on voltage. Facile quantum dot (QD) incorporation into this active layer has effected Förster Resonance Energy Transfer facilitating voltage induced wavelength tuning to harness the properties of the QD. Further lowering of turn-on voltage is observed with enhanced brightness and turn-on voltage dependence on the spectral integral overlap between the donor PL and acceptor Abs spectra. Flexible LEEC testing in ambient reveals the device dependence on the mechanical properties of the transparent conductive electrodes and stable operating voltages of such devices.

Acknowledgements

This journey is full of ups and downs. “For example, the journey from Kamakura to Kyoto takes twelve days. If you travel for eleven but stop with only one day remaining, how can you admire the moon over the capital?” *The Writings of Nichiren Daishonin* p. 1027. Staring with a vow and ending with a promise. I’ve experienced a plethora of feelings and thoughts through and through; learnt and analyze many aspects of my life and those around me throughout these few years.

In the past 4.5 years, it was a journey where each walked their own paths before ending up at the same objective. In every struggle, I was met with encouraging words or a helping hand. The encouragement I received made me realize that I could do it myself with my own bare hands; I couldn’t even have seen the light at the end of the tunnel was it not for them. I would like to take this opportunity to give my sincere appreciation to all the people who have helped me one way or another and guided me to where I am today.

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Last but not least, I dedicate this work to my mentor Dr. Daisaku Ikeda, who has given me eternal guidance in my life and has shown me how to live as a true human being.

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Figure 5.1 Chemical structure of (a) repeat unit of PFN-DOF polymer and (b) ionic structure of BMIM⁺ TFSI⁻ ionic liquid. [60] Reused with permission from [60] and adapted from <http://www.sigmaaldrich.com/catalog/product/aldrich/711713?lang=en®ion=SG>.

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Figure A.1 Nyquist Plots of (a) LiX (X = TFSI⁻, CF₃SO₃⁻ and PF₆⁻) and (b) of BMIM X (X = TFSI⁻ and PF₆⁻).

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Figure A.3 Diluted Photoluminescence of 2.4 ml (1 × 10⁻⁶ M; based on PFN-DOF repeat unit) showing the photoluminescence intensity increase of PFN-DOF:IL with ex-situ additions of BMIM TFSI ionic liquid. Photoluminescence experimental details are described in chapter 5.

Figure A.4 XPS Survey scan of PFN-DOF polymer.

Figure A.5 XPS High resolution spectra for (a) C 1s, (b) N 1s and (c) O 1 s of PFN-DOF polymer.

Figure A.6 XPS Survey spectra of BMIM⁺ TFSI⁻ ionic liquid.

Figure A.7 XPS High resolution spectra for (a) C 1s, (b) F 1s (c) N 1 s, (d) O 1s and (e) S 2p of BMIM⁺ TFSI⁻ ionic liquid.

Figure A.8 XPS Survey spectra of active layer containing (PFN-DOF:IL = 10:8.85) mass ratio.

Figure A.9 XPS High resolution spectra for (a) C 1s, (b) F 1s and (c) O 1s of active layer containing (PFN-DOF:IL = 10:8.85) mass ratio.

Figure A.10 PFN-DOF:IL = 10:8.85 EL spectra from (a-f) 6 V to 16 V.

Figure A.11 QD-LEECs showing wavelength tuning with respect to voltage increase based on different PL emissive QD: (a-c) 520 nm, (d-f) 580 nm and (g-i) 620 nm. (j-l) shows the respective CIE plots of the QD devices showing a change of coordinates with different applied bias.

Abbreviations

OLED	Organic Light-Emitting Diode
LEEC	Light-Emitting Electrochemical Cell
QD	Quantum Dot
PPV	Poly(p-phenylene vinylene)
PFO	Poly(9,9-dioctylfluorene)
ITO	Indium-doped Tin Oxide
PET	Polyethylene Terephthalate
MEH-PPV	Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]
PFN-DOF	Poly[(9,9-bis(3'-(N,N -dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)]
TFSI	Bis(trifluoromethylsulfonyl)imide
IL	Ionic Liquid
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
PLED	Polymer Light-Emitting Diode
SMOLED	Small-Molecule Light-Emitting Diode
TCE	Transparent Conductive Electrode
PUA	Poly(urethane acrylate)
AgNW	Silver Nanowires
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
ETPTA	Ethoxylated trimethylolpropane triacrylate
LiCF ₃ SO ₃	Lithium trifluoromethanesulfonate
SY	Superyellow light-emitting polymer
AnE-PVstat	anthracene-containing poly(p-phenylene-ethynylene)-alt-poly(p-phenylene-vinylene) (PPE-PPV) derivative with a statistical distribution of linear octyloxy and branched 2-ethylhexyloxy side groups
PU	Poly(urethane)
PVA	Poly(vinyl alcohol)
CNT	Carbon Nanotube

ZnO	Zinc Oxide
MoO ₃	Molybdenum Trioxide
TiO _x	Titanium Oxide
TADF	Thermally Activated Delayed Fluorescence
BP	Bisphenazine
CF ₃ SO ₃ ⁻	Trifluoromethanesulfonate
THA-TFSI	Tetrahexylammonium-bis(trifluoromethyl)sulfonylimide
PF ₆ ⁻	Hexafluorophosphate
MATS	Methyltriethylammonium Trifluoromethanesulfonate
PS	Polystyrene
TPD	-N,N'-diphenyl-N,N'-bis(4-n-butylphenyl)-(1,1'-biphenyl)-4,4'-diamine
PFCB	Perfluorocyclobutane
VB-TCTA	4,4',4''-tris(N-carbazolyl) triphenylamine bis(vinylbenzylether)
PMMA	Poly(methyl methacrylate)
TBAPF ₆	Tetrabutylammonium hexafluorophosphate
PIL	Poly(vinyl-ethylimidazolium bistrifluoromethanesulfonimide)
EQE	External Quantum Efficiency
F8BT	Poly(9,9-dioctylfluorene-alt-benzothiadiazole)
AFM	Atomic Force Microscopy
CT	Charge Transfer
PEO-DMA	Poly(ethylene glycol) Dimethacrylate Ether
PEO-DME	Poly(ethylene glycol) Dimethyl Ether
DOTCI	3,3'-diethyl-2,2'-oxathiacarbocyanineiodide
CdSe	Cadmium Selenide
CdTe	Cadmium Telluride
InP	Indium Phosphide
CuInS ₂	Copper Indium Sulphide
CuInSe ₂	Copper Indium Selenide
AgInS ₂	Silver Indium Sulphide
InGaN	Indium Gallium Nitride
QLED	Quantum Dot Light-Emitting Diode

ETL	Electron Transport Layer
HTL	Hole Transport Layer
ZnS	Zinc Sulphide
ZnCuInS	Zinc Copper Indium Sulphide
CRI	Colour Rendering Index (CRI)
Poly-TPD	Poly(4-butylphenyl-diphenyl-amine)
ATOAS	Alkyltrioctylamine allylsulfonate
-COOH	Carboxylic Functional Group
FWHM	Full-Width Half Maximum
BMIM ⁺	1-Butyl-3-methylimidazolium
CIE	Commission Internationale de L'eclairage
PL	Photoluminescence
Abs	Absorbance
UV-Vis-NIR	Ultraviolet-Visible-Near Infrared
XPS	X-ray Photoelectron Spectroscopy
B.E.	Binding Energy
DSC	Differential Scanning Calorimetry
CV	Cyclic Voltammetry
EIS	Electrochemical Impedance Spectroscopy
SEM	Scanning Electron Microscopy
PTFE	Polytetrafluoroethylene
<i>V_{on}</i>	Turn-on Voltage
<i>E_g</i>	Band Gap
<i>e</i>	Electron charge
LCE	Luminous current efficiency
HF	Hydrogen Fluoride
DFT	Density functional theory
mDSC	Modulated Differential Scanning Calorimetry
LiF	Lithium Fluoride
LCD	Liquid Crystal Display

PFOPV	Poly[(9,9-dioctyl-2,7-divinylene)fluorenylene]-alt-co-[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene]
4-MBA	4-mercaptobenzoic acid
NMR	Nuclear Magnetic Resonance Spectroscopy
BVIM ⁺	1-Butyl-3-vinylimidazolium
TMPE	Trimethylolpropane ethoxylate
KTFSI	Potassium Bis(trifluoromethanesulfonyl)imide
PVDF	Poly(vinylidene fluoride)
DMSO	Dimethyl sulfoxide
BF ₄ ⁻	Tetrafluoroborate
TOPO	Trioctylphosphine oxide
PVK	Poly(9-vinylcarbazole)
R.T.	Room Temperature

Chapter 1

Introduction

Current trends in biomechanical analysis require long processing times and expensive setups for sports performance monitoring. In recent development, red LEDs have since been used as an alternative inexpensive portable technology in the analysis of swimming performance. Organic Light-Emitting Diodes (OLEDs) and Light-Emitting Electrochemical Cells (LEECs) of low voltage requirements are of interests for low form factor lighting components when integrated with sportswear. Wavelength tunable lighting devices are also of importance for a fully universal sports performance analytical system and safety applications. In this chapter, we discuss the rationale behind the research work in this thesis and give a panoramic view of the potential impact on the derived insights. The thesis overview and hypothesis are summarized. The key idea in this thesis is to develop LEECs with low turn-on voltages LEEC and colour tunability to enable wearable electronic applications such as sports suit for sports performance monitoring.

1.1 Potential Applications of Wearable Lighting Technology

Wearable Technology has come a long way since the invention of wristwatches in the 19th century to the google glass and smartwatches of the 21st century, sailing along the great tide of technological advances. One basic human requirement in this realm of wearable technology is light, something we cannot live without. Combining light and wearables is seen as one of the main driving force towards wearable displays. Wearable lighting has found its way onto human interface such as wearable lights for safety purposes towards lights for runners and cyclists during low light conditions. Phototrope top designed by Schoeller Textiles is a wearable illuminated top enhancing the runner safety of the wearer and the experience of running at night by making the runner feel more comfortable in a dark environment (Figure 1.1a). Moreover, Philips has developed a lower back pain relief product, PulseRelief which aims to use low powered blue LEDs to induce one's body to release Nitric Oxide which increases blood flow, thus encouraging the natural healing process of the body (Figure 1.1b). Light therapy is also an avenue for developments whereby UV-free blue wavelengths can cure persistent skin problems (psoriasis or eczema) that so far medical science have yet to tackle the root of the problem. [1-3] On a lighter note, wearable light-emitting diodes (LEDs) have been touted used in a Bluetooth enabled LED display where by it video streams graphics as a form of visual communication and advertisement. (Figure 1.1c) Organic based light-emitting diodes such as the conventional Organic Light-Emitting Diode (OLED) and Light-emitting electrochemical Cells (LEEC) can easily find its way to wrangle the position of LEDs on the top of the wearable lighting food chain due to many of its advantages which include: (1) large surface area lighting for scalability; (2) almost 100% theoretical efficiency reducing losses through heat, reducing power consumption and uncomfortable heating for the wearer; (3) wider viewing angles which are easy on the eye; and (4) thinner devices with small form factor, easily mountable on skin or clothing alike.

Biomechanical motion analysis is one of the backbones in the sports industry. [4] Its main purpose is to identify optimal techniques for enhancing performance of sportsmen, optimizing wearability of sports gear or treating or prevention of injuries. [5,6]

Figure 1.1 (a) Phototrope top for runner's safety in dark environments [<http://www.paulinevandongen.nl>]; (b) Philips's PulseRelief low powered blue LED reducing pain and enhancing natural healing [<https://www.90yearsofdesign.philips.com/>] and (c) Fos wearable Bluetooth LED display to be mounted onto clothing or bags [<https://www.kickstarter.com>]

Current biomechanical motion analysis setups (Figure 1.2a) require motion capture systems. These systems can be classified into two categories and a few sub-categories. The first are non-optical and optical systems. Non-optical systems encompass inertial, mechanical, magnetic, and passive markers. Non-optical systems although do not require complex computer vision technology has a trade-off compared to optical systems. They generally require wearable suits which restrict movement with multiple modular sensors which track rotational, acceleration and flexion changes based on potentiometers, accelerometers, gyroscopes and magnetometers (Figure 1.2b). These setups are portable as the data can be programmed to synchronize wirelessly to an analytical setup. However, these suits are cumbersome and naturally add weight which would not give an accurate representation of the athletes' performance. Moreover, it necessitates extensive post processing to piece different types of data together for an accurate characterization.

Optical techniques (Figure 1.2c-d) such as passive optical systems require ball-like reflective markers which reflect infra-red lights mounted on cameras and active optical marker system utilizes pulsed-LEDs which can emit light or infra-red and captured by a video camera with sophisticated algorithms which can plot each position in a 3D landscape to identify their relative positions. Although having less bulky suits, existing optical motion tracking systems requires the analyses to be done in special environments

with accurate and stable motion tracking cameras and force platforms, subjected to only certain types of ground based sports such as cricket, football, and athletics (Figure 1.2e).

Figure 1.2 (a) Xsens Inertial Motion Capture Suit [www.xsens.com]; (b) Mechanical motion capture suit [www.metamotion.com]; (c) Body suit fitted with retro-reflective passive markers [www.steam3.com], (d) active optical marker (LED) systems [http://lis3353.wikispaces.com] and (e) complicated camera setups for optical systems [www.moves.com]

Recently, water based sports such as swimming; an inexpensive marker system was developed for the analysis of swimmers' performance. [7-9] In that study, the markers utilized wearable red LEDs manufactured on a flexible circuit board which was easily distinguishable using a normal underwater camera (e.g. GoPro Hero 3) with image processing algorithms. The use of green-blue LEDs might not give a good contrast with respect to underwater conditions. This was a relatively cheap and semi-automated system where the movements were real-time and reducing the need for manual frame-by-frame analysis. However, a low profile lighting device would be advantageous to prevent induced drag during tests for a better representation of athletes' performance. Competing technology such as the QUALISYS performance tracking system (Figure 1.3a) requires the swimmer to don spherical markers which come with induced drag coupled with underwater motion cameras to track swimming movements. To overcome some of this

passive drag during the performance analyses, bi-adhesive black markers were introduced.[10-12] However, this method required a well-trained operator around 27 man hours to complete one tracking test. Therefore, only with the availability of such automatic image processing software could the technology be of significant advantage. Other systems require expensive video tracking camera such as that of ORCA (Figure 1.3b), similar to that reported by Shinichiro *et. al.*[13] to be submerged in the water, supported on a railing above water to capture the swimmer's real-time stroke analysis during the test.

Figure 1.3 (a) Qualisys and (b) ORCA swim tracker devices.

To develop a universal lighting device for use in different sports, albeit land or water based, specific tunable wavelengths are necessary to produce different colour contrasts. In most practical applications in the field of analysis, the colours which provide the best contrasts in daylight are yellow-black. [14] Green-yellow wavelengths are best detected by human vision in day light conditions, but in different light conditions, orange-red wavelengths become more prominent due to different wavelength sensitivity of our eyes. [15, 16] Consequently, development of a wearable organic based lighting device suited for different sporting environments require wavelength tuning.

In the past few years, there has been much buzz around wearable technology and its explosive growth patterns for the next few years with the demand in flexible and stretchable wearable displays expecting to reach \$20 billion by 2023. [17] The percentage

of these wearable devices will encompass close to 90% of all wearable displays by then. [18] A report by IHS Technology and Transparency Market Research [19, 20] showed that fitness and wellness performance tracking devices were in demand with important factors such as comfort, smart and efficient monitoring tools having a high impact on technology purchase and adoption. This leads us to conclude that the future looks bright for such wearable displays, especially those which have a plethora of metrics tracking. In light of this boom in wearable technology there exists a demand in flexible and wearable lighting devices for the application in sports performance analysis. In the realm of competitive sports, instead of conventional rigid and inflexible substrate based LEDs, OLEDs will render a strong advantage due to a few factors. OLEDs have seen its adoption in large and complex surface area lighting as seen in Andreas *et. al.* fabricated by spray coating in ambient air conditions. [21] Chromophore material engineering also leads to higher efficiency compared to LEDs which would mean that surface temperature would not be too uncomfortable for wearable applications. Moreover, it has wider viewing angles where detection of such markers would be easily distinguished by cameras placed at considerable distances. Lastly, totally transparent wearable OLEDs are already possible due to its intrinsically flexible active layer. [22] Therefore, fabrication of flexible organic based lighting devices is highly desirable for such wearable applications.

State of the art of these OLEDs include a free-standing, extremely thin, flexible and collapsible (radii of curvature $<10\text{ }\mu\text{m}$) red light emitting OLED with high brightness ($\sim 100\text{ cd/m}^2$). [23] Recently, Pei's group showed stretchable and foldable lighting displays with up to 120% strain applied. [21] Further efforts have been geared towards more flexibility and higher stretchability, but, the perennial question remains, "how much stretching and flexing does a wearable device require?" For example, wrist worn electronics require a minimum bending radius of $\sim 25\text{ mm}$ and electronics planted on human fingernails range from ~ 13 to $\sim 5\text{ mm}$. [25, 26] This is because human body has its own underlying limitations. As such, flexibility and stretchability is important, but it does not call for ultra-flexibility and ultra-stretching for wearable devices. Powering such wearable technologies require flexible or stretchable power sources like that in the case of flexible batteries with DC output. [27] This would naturally suit OLEDs and LEDs as

due to its rectifying behaviour. However, to power the devices for a substantial amount of time would naturally require lightweight high capacity batteries with high power output current densities that are not yet fully commercially available. *Thus, it is imperative to develop organic based lighting devices that have low turn-on voltages to reduce the need for bulky and rigid batteries.*

Light-emitting electrochemical cells technology was first discovered by Heeger's group as an alternative to OLED (Figure 1.4a). [28] In its mechanism lies a way to optimize charge injection due to in-situ electrochemical doping offered by the salt ions in the active layer. Moreover, due to this advantage, performances of these devices are electrode work function independent and air-stable electrodes can be deposited, enhancing device lifetime. Spin coating of the single active layer (Figure 1.4b) is also a cost effective and facile way of device fabrication compared to multilayer vacuum deposition of conventional OLEDs. Therefore, LEECs prove advantageous and is highly favoured over OLED and LEECs were chosen to be studied in this thesis.

Figure 1.4 (a) Multilayer OLEDs fabricated using vacuum evaporation. [29] (b) All-organic LEEC device with single spin coated active layer showing the constituents of the active layer. [30] Reused with permission from [30].

LEEC active material is versatile as many light-emitting species could be employed, such as small molecules, emissive conjugated polymers, and ionic transition metal complexes (iTMCs). iTMCs have shown to have high luminous efficiencies due to its phosphorescent emitting mechanism. However its use of heavy metal complexes, coupled with the cost of rare earth metals are not favoured when the device only has a moderate lifetime. [31] Small molecules LEECs are not commercially available thus requiring

complex synthesis procedures and it has poor solubility in common solvents. [32-34] Amongst all candidates, emissive conjugated polymers would be an intuitive choice due to its chemical versatility, inherent flexibility and relative cost. Moreover PLEECs have been intensively studied by Edman and Kemerink's groups, which unraveled the electrochemical side reactions, operation mechanisms and effects of constituent optimization, correlated with theoretical simulations. [35-40] Highest brightness reported so far for Polymer based LEECs was $>10,000 \text{ cd/m}^2$ via changing the polymer electrolyte, paving the way for relatively easy performances tunings. [41, 42] Therefore, in this dissertation, conjugated polymers would be the main investigated active layer for LEEC device fabrications.

1.2 Objectives and Scope

This thesis aims at exploring ways to reduce the turn-on voltages required for light emission of organic based active materials and to achieve voltage induced emission wavelength tunability. In order to reduce the turn-on voltages of the devices, we first optimize the electrolyte with different mass ratios and salts to achieve high ionic conductivity. Contribution of enhanced charge injection by anions with different resonance states is elucidated. A new mechanism for brightness enhancement and centering the recombination zone via complexation of polymer and ionic liquid is proposed. Further reduction of turn-on voltages with voltage induced wavelength tuning upon quantum dot (QD) inclusion via Förster Resonance Energy Transfer (FRET) mechanism is realized.

1.3 Hypothesis

In the dissertation, poly(p-phenylene vinylene) (PPV) and poly(9,9-dioctylfluorene) (PFO) derivative based devices have been used to study the effects of electrolyte and ionic liquid with QD incorporation to realize different ways to reduce voltage requirements of devices. Charge injection and doped regions in the active layer affects the performances

of devices. To elucidate the contribution of salt selection, complexation and flexible device performances, the hypothesis is classified into 3 aspects:

Hypothesis 1

It is hypothesized that due to a larger doped area and better conductivity of the p-doped region, performance of LEEC devices are dominated by anion doping compared to cation doping. Enhancement of ionic conductivity in polymer electrolyte can be achieved by judicious choice of anions which allow higher doping level of ions into conjugated polymer and lower the turn-on voltage.

Hypothesis 2

It is hypothesized that ion pinning due to polymer-ionic liquid complexation reduces the eventual p-type doping concentration and shifts the recombination zone of LEECs towards the centre of the active layer thickness. Addition of QD into the polymer active layer serves to enhance emissions, lower the turn-on voltages and promote voltage induced wavelength tuning.

Hypothesis 3

It is hypothesized that active layer LEECs can be fabricated on flexible ITO/PET without electrode work function tuning to realize potential wearable light emitting device with bending capabilities. Stable operational voltage range can be identified by current density measurements and the degradation mechanisms can be identified.

1.4 Dissertation Overview

The thesis focuses on lowering turn-on voltage of organic based active layer devices via emissive material selection, salt selection, quantum dot introduction and proposes the mechanisms of such. The role of each constituent in the active layer are systematically analysed where ion transport is optimized, followed by anion selection facilitating turn-on voltage reduction with enhanced charge injection via fabrication of light-emitting electrochemical cells with electrolyte of high ionic conductivities. Next, it focuses on

engineering the recombination zone through complexation and voltage induced emission wavelength tuning with QD incorporation. Lastly, this thesis provides insights on active layer integration with flexible transparent conductors to realize a potential wearable lighting device. The research overview is summarized as follows:

Chapter 1: Introduction and motivation of the research. Research objectives and scope along with hypothesis is presented.

Chapter 2: Literature review about the conjugated polymers, general light emission mechanisms, LEEC doped regions and propagation, recombination zone engineering and QD-LEEC. This chapter discusses the recent developments on the understanding of LEEC doping dynamics and supports the investigated scope of the thesis.

Chapter 3: This chapter presents the rationale for material selections for LEEC fabrication. Then, principles behind different characterization techniques such as optical, structural and electrical are introduced to understand the mechanisms during LEEC operation. Finally, the experimental and characterization flow was discussed.

Chapter 4: Anions selection for low turn-on voltage in LEEC. In this chapter, lowered turn-on voltage in poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) LEEC due to poly(ethylene oxide) PEO optimization and salt anion selections based on resonance states and the resultant binding energies are reported. Working mechanism on the device performance enhancement is discussed and correlated with solid state film characterization techniques.

Chapter 5: Anion-polymer complexation in wavelength tunable QD-LEEC based on Poly[(9,9-bis(3'-(N,N -dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN-DOF). In this chapter, mechanism of brightness enhancement due to centered recombination zone is proposed. Changes to wavelength emission and device operation due to QD addition into active layer are reported.

Chapter 6: Superyellow based LEECs and QD-LEECs are fabricated on flexible ITO/PET substrates, stable operating voltages are identified, bending tests were carried out and the device performance was characterized in ambient environment. Degradation mechanisms of flexible LEECs are also discussed.

Chapter 7: Summary and future works. In this chapter, results are summarized and future works focusing on direct evidence of proposed mechanisms are provided.

1.5 Findings and Outcomes

In this dissertation, different methods to reduce device turn-on voltage are discussed. A new mechanism for recombination zone is proposed. The summary of the scientific contributions of the thesis are as follows:

1. LEEC devices show that high brightness devices are more dependent on the type of anions due to its doping efficiency, regardless of cation; indicating the dominating influence of the p-doped region. Salts with larger anion require lower dissociation energy allowing for ease of doping and increased light emission at low current densities. Melting points of polymer electrolytes also play a part. Larger electrochemical stabilities of electrolyte is observed with employment of Bis(trifluoromethylsulfonyl)imide (TFSI-) anion.
2. Addition of ionic liquid (IL) into PFN-DOF reduces the green band emission and enhances the photoluminescence (PL) intensity via reduction of aggregation and interchain interactions. The PFN-DOF:IL blends show reduction of turn-on voltages and enhanced brightness due to centered recombination zone. Förster Resonance Energy Transfer mechanism was confirmed with the fabrication of QD-LEECs. PFN-DOF:QD:IL blends further reduced the lower turn-on voltages due to enhanced electron injection. Turn-on voltages of the blends were QD dependent due to spectral integral overlap.

3. Flexible LEEC characterizations showed that the bending performance and degradation mechanisms depend on the mechanical properties of the transparent conducting electrodes that created local variation in sheet resistances and reduced the device performance. Stable operating voltages are determined to reduce unwanted electrochemical side reactions.

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Chapter 2

Literature Review

Organic light-emitting diodes (OLEDs) have been steadily research and developed ever since ground-breaking findings started in 1990s. In this chapter, various mechanisms and up-to-date research will be presented and discussed. OLEDs will be briefly introduced along its state of the art flexible devices. Challenges in OLED and opportunities in light-emitting electrochemical cells (LEECs) will be presented as an alternative technology due to its inherent optoelectronic properties and simple fabrication. Emissive conjugated polymers and other materials making up the LEEC active layer blends will be reviewed along with its in-situ electrochemical doped regions and implications of such. Recombination zone shifting will be shown as an approach for improving device lifetime and efficiency. Quantum dot technology will be introduced and its hybridization with conjugated polymers will be discussed, followed by discussion of challenges with respect to recent research.

2.1 Introduction to Organic Materials

Organic solids generally consist of N, C, S, O based covalent bonded materials with weak van der Waals interactive forces holding them together. It can either exist as crystals, semi-crystalline or amorphous structures. Organic solids are classified into saturated and conjugated systems. Saturated compounds have localized σ electrons between neighbouring atoms and can only respond to high frequencies in the ultraviolet spectrum. Thus, it does not absorb visible light and have properties that are similar to insulators like glass. Conjugated molecules have alternating double and single bonds. In these materials, sp^2 hybridization is formed in the C atoms which results in three sp^2 orbitals (s , p_x , p_y orbitals and forming σ bonds with adjacent atoms) and one p_z orbital (forming π bond with an adjacent p_z orbital). The σ bonds are coplanar with each other at an angle of 120° and strongly localized. The p_z orbitals are perpendicular to the σ bond plane. Two p_z orbitals of adjacent carbon atoms form the relatively weak π bond where electrons are delocalized and move relatively free in the molecule. These conjugated molecules with π bond forms discrete energy levels where π and π^* orbitals form the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), similar to valence and conduction band in inorganic semiconductors. These π electrons are less tightly bounded than that in saturated molecules. In conjugated polymers, electrons are highly delocalized along the polymeric chain and form a one-dimensional electronic system.

The energy gap between HOMO and LUMO energies of the molecules becomes smaller with increasing conjugation, allowing absorption and fluorescence in visible light spectrum. This decrease in energy band gap reduces to a minimum of around 10-15 repeat units. [1] This is based on quantum confinement principles where spreading of the π electron wave function leads to reduction in energy. Moreover, these conjugated polymers have electronic transport properties via interchain hopping mechanisms and intrachain delocalized π -electrons which offer semiconducting properties. Most of the time, HOMO and LUMO levels are determined by the π -bonds and optical transitions correspond to these π - π^* transitions. Thus, these conjugated systems are of interest due

to its light-emitting properties. Conjugated polymers along with its diverse properties have also found its way into different sectors such as sensors [2], actuators [3], photodetectors [4] and electrochromic devices [5]. There are two varieties of organic semiconductors: conjugated polymers and low molecular weight materials called small molecules. They make up the sub-categories of OLED into polymer light-emitting diode (PLED) and small-molecule light emitting diode (SMOLED) respectively and they can be used interchangeably. Light-emitting electrochemical cells (LEEC) which will be discussed later also fall into the same category as OLEDs as the active layer is still an organic layer. Small molecules have the ease of purification and synthesis but fabrication via vacuum processing is the biggest cost challenge. However, conjugated polymers have relatively more flexibility in chemical tailoring with inherent mechanical flexibility. Its fabrication mainly revolves around low-cost wet techniques such as spray coating [6], ink-jet printing [7], spin coating [8] and bar-coating [9]. In this thesis, the focus has been placed on conjugated polymers.

2.1.1 Conjugated Polymers as OLEDs

Organic solids first discovered by A. Bernanose *et. al.* in 1950s have paved the way for research in organic electroluminescence powered by alternating voltages. [10] Direct current powered organic crystals were then discovered by M. Pope *et. al.* in 1963. [11] The first reported OLED emission mechanism based on carrier recombination was proposed by W. Helfrich and W. G. Schneider. [12] Insufficient research during the early days produced poor purity organic materials with primitive sample preparation techniques thus requiring large potentials of >100 V. Renewed attention of organic electroluminescence in 1980s was only brought on by the advent of vacuum processing techniques of small molecule Alq₃, helmed by C. W. Tang and S. A. VanSlyke. [13] Shortly afterwards in 1990, a Cambridge based research team reported the first PLED with poly(p-phenylene vinylene) PPV as the active layer. [14, 15] Since then, enhancements in PLED luminance efficiency, colour properties, device lifetimes and new synthetic routes have developed, albeit lab scale, with operational performances in competition with small-molecule organic light-emitting diode (SMOLED). One of the

reasons why PLEDs are attracting much interest is the low intrinsic material costs and ease of fabrication. Moreover, compared to inorganic molecules, polymers do not need highly crystalline structures to achieve adequate optoelectronic properties. Nonetheless, upscaling of PLEDs as commercially viable replacements of conventional OLEDs still face a number of hurdles. Luminance efficiency and lifetime are still inherent problems faced by the industry. One such factor to highlight is the inherent p-type nature of conjugated polymers creating an imbalance of carrier injection (h^+ mobility $\gg$ e^- mobility), limited by electron injection which affects recombination efficiencies. In addition, to realize devices with superior efficiency, it requires low work function cathodes for electron injection which are easily oxidized unless properly encapsulated (seen in Figure 2.1). [16]

Figure 2.1 OLED dark spot growth mechanisms due to a) water vapour and b) oxygen atmosphere. Both mechanism proceeds with delamination of metal cathode due to oxidation or H_2 bubble formation due to H_2O reduction at cathode. [16] Reused with permission from [16].

Rapid progresses in PLEDs have led to active layers emitting colours which cover the whole visible spectrum, achieved by polymers, copolymers and derivatives of such. Of all the PLED materials, poly(p-phenylene vinylene) (PPVs) and poly(9,9-dioctylfluorene) (PFO)s are heavily researched due to their solution processability and solubility in common solvents, good hole transport, high PL and EL efficiency. [17-19] In this thesis, PPV and PFOs will be studied and used as the emissive active layer and will be discussed in the materials selection of Chapter 3.

2.1.2 State of the Art Wearable of Organic Based Lighting Devices

Stretchable and flexible OLEDs come under the umbrella category of wearable OLEDs. With respect to wearable devices, flexibility is the most important feature. In the 1990s, a fully flexible solution processable OLED on poly(ethylene terephthalate) (PET) substrate was fabricated with an EQE of 1%. [20] Since then, with advances in vacuum technology, substrate chemistry, multilayer processing, advances in active layer processing and fabrication, it has brought this technology one step closer to commercialization. Currently vacuum technology of SMOLED is the most common way of achieving this, due to its high yield, conformal deposition and good optoelectronic properties. However, the cost of processing is one future consideration towards mass adaption. More often than not, mechanical flexibility of plastic substrates is the most attractive way to develop these OLEDs and it hinges on the development of transparent conductive electrodes (TCE). Recently, Pei's group has reported an elastomeric PLEC device based on new elastomeric TCE. [21] Rod coating of silver nanowires (AgNW) with a length-to-diameter ~ 500 formed a percolating network. Subsequently, a poly(urethane acrylate) (PUA) matrix was poured over and UV cured. This embedded the AgNW into a rubbery elastic substrate which bonded well with the dimethacrylate homopolymer, having a sheet resistance of $< 20 \Omega \text{ sq}^{-1}$. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) was spin coated on the TCE to prevent solvent attack from the active layer deposition. An optimized light-emitting electrochemical active layer blend consisting of partially curable ion-transporter ethoxylated trimethylolpropane triacrylate (ETPTA), lithium trifluoromethanesulfonate (LiTf), polyethylene oxide (PEO), superyellow light-emitting polymer (SY) was spin coated onto the PEDOT:PSS layer forming a highly electroluminescent, stretchable active layer. This is because Superyellow polymer, with its high molecular weight, along with PEO and ETPTA are all stretchable constituents. After which, hot pressing of the dual polymer layer structure with another AgNW/PUA TCE at 90°C formed the full device as illustrated in Figure 2.2a. This PLEC device can accommodate stretching strains to 120%, foldability around a $400 \mu\text{m}$ thick cardboard without exhibiting extensive degradation (seen in Figure 2.2b-d). Flexible dot-matrix displays were also demonstrated comprising

of 3×3 pixels with 1 mm^2 device area per pixel (seen in Figure 2.2b) Maximum device brightness was around 2000 cd/m^2 with EQE of $\sim 4\%$ an active area of $\sim 21 \text{ mm}^2$ as shown in the current density-voltage-brightness curve in Figure 2.2e)

Figure 2.2 (a) Device fabrication steps of the wearable PLECs. (b) Images showing the stretchability and foldability of large area PLEC device and dot matrix devices. (c) Luminous efficiency versus strain application of PLEC under 12 V bias. (d) Luminous efficiency versus Luminance of the device. (e) Current density-voltage-luminance characteristics of the PLEC. [21] Reused with permission from [21].

It is ubiquitous that for a flexible device, it is important that the substrate should be able to withstand < 1 mm bending radius. Ultrathin ($2\ \mu\text{m}$), free-standing PLEDs were fabricated by White *et. al.* on ultrathin $1.4\ \mu\text{m}$ thick PET foils which allowed bending radius of $\sim 10\ \mu\text{m}$, applicable for electronic skin devices. [22] These devices were made up of flexible ultrathin PET substrate, PEDOT:PSS layer, nanometer thickness active layer of an anthracene-containing poly(p-phenylene-ethynylene)-alt-poly(p-phenylene-vinylene) (PPE-PPV) derivative with a statistical distribution of linear octyloxy and branched 2-ethylhexyloxy side groups (AnE-PVstat) and LiF/Al as the electron injection cathode as illustrated in Figure 2.3a. Ultra-flexibility comes with collapsible characteristics which are appropriate for devices on human joints such as the knee and elbow which regularly wrinkles, crumples and twists. These devices demonstrated such properties as illustrated in Figure 2.3b-c.

Figure 2.3 (a) Schematic of the ultrathin PLED. (b) Pictures of PLED under twisting and collapsing tests. (c) Compressive tests of PLED after it was applied to a pre-strained elastomer. Further analyses shows that it can withstand bending radius of $30\text{-}10\ \mu\text{m}$. [22] Reused with permission from [22].

Fabric based electronics are also gaining attention due to its light weight and high flexibility. Moreover, integration of devices onto universal fabrics is the most facile way of wearable electronics fabrication. Kim *et. al.* reported a soft fabric based flexible OLED fabricated on woven polyester fibers. [23] For such substrates with high roughness values, it is pertinent that the planarization steps are done to reduce the roughness. Poly(urethane) PU and poly(vinyl alcohol) PVA layers (combined thickness of around 50 μm) were used before successive thermal evaporation steps of the multilayer structure as illustrated in figure 2.4a. In this study, thermal evaporation was crucial as a conformal deposition allows a device to be fabricated on a relatively rough substrate, even after planarization. The devices showed reliable flexibility when it was wrapped around a finger (seen in Figure 2.4b). Under flexing tests of 1000 cycles and bending radii of 5 mm, no significant changes to the optoelectronic performances could be observed (seen in Figure 2.4c). Such devices retained the mechanical characteristics of the bare fabrics with high brightness values of up to 6000 cd/m^2 .

Figure 2.4 (a) Schematic of the multilayered OLED fabricated on soft fabric substrate. (b) OLED flexibility testing when wrapped around a finger. (c) Luminous current efficiency when the device underwent 1000 bending cycles of 5 mm bending radii. [23] Reused with permission from [23].

Figure 2.5 (a) Schematic of the fiber based LEEC device with single free standing device (top left inset) and when woven into a wearable device (top right inset). (b) SEM side view image of the fiber shaped LEEC showing the different layers. (c) Current density-voltage-luminance graph of the device. (d) Stability of luminance upon bending tests. (e) Electroluminescence spectra showing colour tunability of a co-assembled two fiber devices upon brightness ratio control of each fiber. [24] Reused with permission from [24].

By integrating the OLEDs onto a fiber shaped substrate, Zhang *et. al.* has demonstrated that it can potentially be woven into smart light emitting textiles with colour tunability (seen in Figure 2.5a inset). [24] Metal wires were dip coated into zinc oxide (ZnO) precursor which underwent thermal annealing to form ZnO nanocrystals as the electron transport layer. This modified metal wire was then dip coated into LEEC blends to create a thickness independent emissive layer before wrapping of aligned carbon nanotube (CNT) sheets to form the electrode via van der Waals bonds (seen in Figure 2.5a). In this study, SEM images showed sequential layers of metal wire/LEEC/CNT which allowed this device to light up as a free standing fiber as illustrated in Figure 2.5b. Turn on voltages of 5.6 V with peak brightness values of 609 cd/m² at 13 V were reported (seen in

Figure 2.5c). Moreover, flexing tests showed brightness values maintained at around 90% even after 100 cycles bending test at a radii of 6 mm (seen in Figure 2.5d). Interwoven fabrics of different emissive polymers showed colour tunability via brightness control of each fiber device (seen in Figure 2.5e).

2.2 Challenges in OLEDs and Opportunities in LEECs

Performance of PLED is largely determined by a delicate interplay between various properties of each layer. Factors such as thermal stability, oxidation susceptibility, charge carrier mobilities, thickness of each layer affects the overall performance and luminance of the device. Most importantly, efficient charge carrier recombination requires optimization of charge injection from charge transport layers or electrodes.

In PLEDs, for superior electron injection due to high LUMO levels of around 2 eV requires low work function cathodes such as Ca or Ba. This limits the usability of OLEDs in outdoor environments unless properly encapsulated with a thin film barrier film made up of multilayers of inorganic materials which are largely rigid and inflexible. Reported air stable devices used charge transport layer such as ZnO [25-27], MoO₃ [28] and TiO_x [29] as the barrier layer to prevent oxygen ingress. Only with the additional metal oxide layers can air stable electrodes such as Ag or Al be used as the electron barrier heights are also reduced. PLEDs consisting of p-type polymers have reported much higher hole mobilities than electron mobilities. [30-32] This mobility difference directly affects the charge recombination profile and thereby the outcoupling efficiency. [33, 34] Thus, there is a need for materials that have both adequate electron and hole injection into the active layer to enhance the charge recombination and exciton formation in the device.

Active layer thickness is also an issue where resistivity would increase for a thick active layer thus requiring a higher driving voltage. To circumvent this, researchers have enlisted the need of vacuum deposition in order to ensure precise thickness control. Ideally, towards commercialization of OLEDs, simple fabrication and cost reduction of processing is required.

During the progress of OLED research in the 1990s came with the advent of LEEC technology revolutionized by Heeger's group. [35] The most important impact of this research was the optimized charge carrier injection into the active layer with in-situ electrochemical doping forming p- and n- doped regions. Moreover, it was reported to have advantages of electrode work function independence, luminance performance insensitive to active layer thickness, single active layer fabrication and device performance independent of direction of applied bias. This would be crucial in the fabrication of a simple, efficient, cost effective, relatively air stable device.

2.3 Introduction and Mechanism of Light-Emitting Electrochemical Cells

LEECs promise a combination of advantages compared to performance of multilayer OLEDs with ease of fabrication. LEECs consist of a single active layer made up of blend of different chemicals. According to the idealized model proposed by Pei *et. al.* [36] (the mechanism as illustrated in Figure 2.6a-c), the blend of conjugated polymer and a solid electrolyte upon application of a bias voltage greater than the polymer's band gap causes the polymer to be symmetrically p-doped at the anode and n-doped at the cathode.

Due to the limited doping degree of the conjugated polymer, further doping occurs and these doped regions grow towards the middle of the active layer. Holes and electron simultaneously propagate and recombine which counters the doping propagation. Equilibrium of these two process creates a dynamic p-i-n junction. Where i is characteristic of an intrinsically undoped polymer and this is where the electron and holes recombine to form excitons which radiatively decay and emit light. This undoped state of polymer is also conducive for exciton formation as luminance is readily quenched if there is slight doping. The resulting charges migrate from polymer chain to polymer chain under the applied electric field. When these oppositely charged carriers meet in the undoped region on one chromophore, (e.g. a small segment of the conjugated polymer consisting of i.e. 10-15 monomers) it exhibits strong electrostatic (coulombic) attraction forming singlet exciton or triplet excitons in the ratio of 1:3. These excitons represent a localized excited electronic state of the chromophore which can either radiatively decay

promptly (in the order of 10^{-9} - 10^{-7} seconds) through fluorescence or through phosphorescence which in most conjugated polymers (seen in Figure 2.7), decay non-radiatively where the relaxation mechanisms follow the Jablonski diagram (explained in Chapter 3).

Figure 2.6 (a) Device schematic and constituents of the active layer blend with materials PPV as the light emitting conjugated polymer, PEO as the ion-transporting polymer and LiCF₃SO₃ as the salt that will dissociate to form the doped regions. (b) After application of an external bias ($V > E_g/e$), electric double layers are formed at the polymer/electrode interface and electrons and holes are injected into the material. (c) These charges will electrostatically attract compensating ions which establish p- and n- doped regions, propagating towards each other forming a graded p-i-n dynamic junction. The doped regions would facilitate electron and hole injection due to high conductivity of the doped region and under columbic capture form excitons which emit light as it radiatively decays. [36] Reused with permission from [36].

Figure 2.7 Electrons and holes from radical anions and cations which form singlet excitons on conjugated segments which decay through fluorescence and phosphorescence.

LEEC mechanism was conceived based on electrochemical doping of conjugated polymers. Moreover, this mechanism has been reported for a host of conjugated polymers and other active materials such as ionic transitional metal complexes and small organic molecules. However, for most conjugated polymers, singlet excitons are generated which limits the theoretical efficiency to 25%. This system reduced the need for multilayered structures along with high efficiency and low turn-on voltages.

2.3.1 Electrochemical Doping of Conjugated Polymers

Many applications of conjugated polymers such as electrochromics, batteries and electrocatalysis depend on its electrochemical properties. From a cyclic voltammetry test, it is possible to determine the onset oxidation and onset reduction which relate directly to the p-doping and n- doping potentials respectively. It is especially significant in the realm of optoelectronics of conjugated polymers as it defines the HOMO and LUMO levels of the polymer. For an example of a cyclic voltammetry characterization of an electroluminescent conjugated polymer substituted polythiophene as illustrated in Figure 2.8. [37] The p-doping ϕ'_p and n-doping ϕ'_n onsets are determined to be 0.83 V and -1.80 V respectively. Band gaps are estimated from the difference between these values where $\Delta\phi' = \phi'_p - \phi'_n$ and ($E_g = e\Delta\phi' = 2.63 \text{ eV}$). HOMO and LUMO energy levels are calculated from this onset potentials with $E_{LUMO} = -e(\phi'_n + 4.4)$ and $E_{HOMO} = -e(\phi'_p + 4.4)$. In that work, the electrode potential of the Ag/AgCl reference electrode was calibrated to be -0.019 V vs SCE. Thus, the values are shifted accordingly giving HOMO and LUMO energies of -5.04 eV and -2.41 eV respectively. Upon doping of conjugated polymers in LEEC, they will form doped regions which increases the local conductivity by 5 to 10 orders of magnitude. This occurs due to formation of additional mid-gap energy levels in the band gap that is partially filled and thus electrically conducting, with charge transport primarily through hopping. [38, 39] At the polymer/anode, conjugated polymer chains are oxidized by removing electrons and counter anions are doped into the oxidized chains to maintain electroneutrality. The

opposite happens at the polymer/cathode interface where the polymer is reduced by injecting electrons to the chains with counter cations doping into the reduced polymer.

Figure 2.8 Cyclic voltammetry characterization of substituted polythiophene with polymer repeating structure shown in the inset. [37] Reused with permission from [37].

2.3.2 LEEC Device Structures and Active Material Selections

LEEC devices have two configurations that serve different objectives. The sandwich cell as illustrated in Figure 2.9a is the most common for characterizing the luminance and device performance matrices which is similar to that found in OLEDs. This device architecture consists of the transparent conductive electrode, PEDOT:PSS as the hole injection/transport layer (it improved the hole injection into the HOMO of the material to enable the doping process and reduced possibility of current leakage), the active layer and a metal electrode such as Al. On the other hand, planar LEEC devices (seen in Figure 2.9b) contain no hole injection/transport layer and is essentially a spin coated active layer with two evaporated metal electrodes, with an interelectrode gap of around 100 μm to more than 1 cm. [40, 41] Due to the nature of LEECs whereby operation can also be achieved with thick active layers, planar LEECs are widely accepted as an scaled up

version of a sandwich cell structure. Thus, the objective of planar LEECs is for direct observation of electrochemistry of the device operation dynamics such as the kinetics of doping propagation, recombination zone engineering, charge injection, doping properties of salts and the mechanism of LEECs. [41-46]

LEEC active layer blends comprises of three basic constituents: 1) light-emitting organic materials; (2) ion transporting polymer; and (3) salt, whereby (2) and (3) is the electrolyte, which has significant influence on the device performance. [47, 48] In this thesis, we will focus on conjugated polymers as the light-emitting materials. However, this LEEC concept has already been universally applied into different organic and inorganic-organic emitters. Some studied examples include traditional phosphorescent compounds such as Ruthenium(II) and Iridium(III) based ionic transitional metal complexes [49-55], fluorescent small molecules [56-59] and recently reported small molecules based on Thermally Activated Delayed Fluorescence (TADF) [60] which has promised to have very high EQE, derived from TADF OLED emitters by Adachi's group. [61] Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), superyellow (SY) are the most commonly used fluorescent emitters as conjugated polymers due to their good hole transport, solubility in common solvents, film forming properties and good electroluminescence efficiency. In all cases, whether an organic material can be used as a light emitting conjugated polymer depends on its HOMO and LUMO position as well as the charge transport properties. Most organic materials can be tuned via functional side group additions or modifications which change its optoelectronic properties and band gaps. [37] This method is also extended to ionic transition metal complex (iTMC) whereby Iridium complexes were synthesized with imidazole-type ancillary ligands that blue-shifted with conjugation length allowing for fabrication of white LEECs. [62] Moreover, the polymer weight-average molecular weight has an effect on film forming properties, chain packing, viscosity, luminous efficiency, emission spectra and frequency of hopping sites during charge transport. [63-66]

Figure 2.9 Device architectures of (a) sandwich cell configuration and (b) planar LEEC configuration with both schematics showing different doped regions of p-, n- and undoped conjugated polymer.

2.3.3 Optoelectronic Properties of Conjugated Poly(fluorene) Derivatives

Polyfluorene (PFO) (seen in Figure 2.10) and its derivatives have received much attention due to their processability, high photoluminescence efficiency and good hole

transporting properties. [67] Its chemical and thermal stabilities of PFO have been proven far superior to PPVs and along with its characteristic blue-green emission, found its application in white OLEDs. Moreover, derivatives of PFO such as poly(9,9-dioctylfluorene) has shown different phase morphologies (α & β) with different photophysical properties. [68] In addition, PFO with its blue-emissive EL spectra can be mixed with acceptors to offer wavelength emission tuning. [69, 70] Alternating fluorene/carbazole copolymers showed extended conjugation which improved stable blue emissions up to 350 cd/m^2 , with similar EL spectra compared with pristine PFO devices. HOMO energy levels were also raised by 0.3 eV to enhance hole injection due to carbazole incorporation.

Figure 2.10 Repeat unit of Polyfluorene polymer where R denotes the side group.

Due to its chemical versatility, Wang *et. al.* incorporated symmetrical and asymmetrical pyrazine rings in bisphenazine (BP) via Suzuki polymerization which tailored the electron injection properties by lowering the LUMO levels. [71, 72] The devices surpassed PFO homopolymer OLED performances showing a maximum brightness of $\sim 1500 \text{ cd/m}^2$ and maximal luminous current efficiency of $\sim 10.1 \text{ cd/A}$. [72] However, the most apparent downside of PFO is the emergence of green defect bands which dominate the spectrum during degradation, changing its colour purity. Its origin has been deliberated between ketone defects [73], unwanted crosslinking due to radical formation [74], aggregation formation [75] or excimer formation which cause energy losses [76]. Recently, conjugated polyelectrolytes based on PFO bearing polar terminal tertiary amine groups, poly[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) which can create dipoles and enhance OLED efficiency. [77]

These polyelectrolytes can also work as electron injection/transport layers for photovoltaic applications. [78, 79]

2.3.4 Optoelectronic Properties of Conjugated Poly(p-phenylene vinylene) Derivatives

Currently, simple single layer pristine Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) devices (ITO/MEH-PPV/Al) have very low external quantum efficiencies of 0.0005% to 0.01% [15], 1% [20] and 0.001% [80]. This is due to MEH-PPV forming chain aggregations in the thin film which partially quench the excitons and diminish the photoluminescence (PL) quantum efficiencies. [81] Chain aggregations also increase interchain interactions leading to ineffective energy transfer and it has also been known to decay non-radiatively. [82] MEH-PPV also faces poor air stability under operation due to oxidative reactions that disrupt charge transfer along the conjugated bonds. [83]

Efforts to enhance radiative efficiencies of conjugated polymers-OLEDs such as MEH-PPV have been attributed to the suppression of interchain interactions [84], effective energy transfer due to enhanced structural stability of polymer chain and reduced self-absorption by using additives such as insulating polystyrene [82], blending with quantum dots [85] or using appropriate solvents during the fabrication steps [86]. Another method is through the proper selection of electrode, but, it did not show significant enhancement. [87] Other MEH-PPV devices include those utilizing DNA as electron injection and hole blocking to achieve performances comparable to those using a Ba electrode. [88] MEH-PPV was incorporated with a Cyano group that increased the electron affinity showing better fluorescent quantum yields. [89, 90] Having to enhance MEH-PPV devices require synergistic material selections along with structural modifications to have appropriate morphology of electroluminescent polymer and efficient exciton generation.

2.3.5 Electrolyte

Electrolytes are fundamental in the performance of LEEC and usually comprises of a salt such as Lithium trifluoromethanesulfonate LiCF_3SO_3 and poly(ethylene oxide) PEO. A suitable electrolyte possesses high ionic conductivity coupled with large electrochemical stability windows extending over the p- and n- doping onset potentials of the conjugated polymer it is admixed with. The electrolytes used in LEEC devices include ionic liquids [91], Li salts dissolved in high molecular weight PEO [36], polymerizable ion-pair monomers [92] and ion transporters with curable side groups [43, 93]. Salts within the electrolyte also play a part in the doping dynamics. Commonly used cations and anions are Li^+ , K^+ , trifluoromethanesulfonate (CF_3SO_3^-) and bis(trifluoromethane)sulfonamide (TFSI) due to its processability, thermal properties, doping properties and ionic conductivities. [94-97]

Phase miscibility between the conjugated polymer and electrolyte also play a clear role, which will be further elaborated later. Recently, Edman's group introduced trimethylolpropane ethoxylate (TMPE) as a substitute for PEO. [98] It was reported that it enhanced the electrochemical stability window by 0.2 V more than the conventional LiCF_3SO_3 :PEO electrolyte and the strong coordination of Li^+ cations with low molecular weight TMPE ($M_w \sim 450$) allows the drifting of ion transporter during operation leaving the undoped region devoid of electrolyte species which is parasitic causing detrimental side reactions. [47, 99]

Frozen junction LEECs based on glass temperature, T_g of electrolyte and/or curable side groups have also been used to immobilizing the counterion and electrochemical doping distribution in the film in order to construct a stable p-i-n junction. Moreover it can create a fixed built-in potential within the film, changing the LEEC from a bias independent to one which has rectifying behaviour along with faster turn-on times similar to that of inorganic LEDs.

PEO based electrolytes are commonly used in LEEC but not a perfect ion-transporting material. This electrolyte system was presumably adapted from solid-state Li batteries. [100] PEO can complex with lithium salts, with strong Li^+ solvating ability. The proposed ion transport mechanism in PEO demonstrated that Li^+ ions are coordinated by ether oxygen on the PEO chain. The simultaneous breaking and forming of Li-O bonds causes ion transport by intrachain or interchain hopping as illustrated in Figure 2.11a-b. One issue with PEO based electrolytes is that it is semicrystalline and has a tendency to crystallize at room temperature which impedes ion mobility that requires an amorphous phase. This limits the practical application of high melting point PEO based electrolytes. By heating the PEO above its melting point, enhances ionic mobility and turn-on time of the devices due to increased ionic conductivity. [45, 101] Joule heating effects tested in a PLED at 400 mA/cm^2 would have temperatures up to $60\text{--}80^\circ\text{C}$ can also cause this rise in temperature that would aid in increasing ionic conductivities. [102] Crystallization in PEO based electrolytes creating microscopic domains were also suggested to be the leading cause in LEEC luminance reduction due to light scattering effects. [103] Alternatives to tackle this inherent thermal property of PEO was the selection of TFSI^- anion over the conventional CF_3SO_3^- anion which reduced the crystallization by 1.5-3 times to around 45°C . [94]

Figure 2.11 Mechanism of ion transport in PEO-LiX systems. (a) Intrachain hopping and (b) interchain hopping. [104] Reused with permission from [104].

PEO based electrolytes have been discussed where alkali metal salts are dissolved within. However, there are some setbacks to these electrolytes such as phase separation between electrolyte and the conjugated polymer, small electrochemical stability window and limited ion mobilities at room temperature. The introduction of ionic liquids comes with advantageous properties such as high ionic conductivity at room temperature, low

melting point, chemically and electrochemically stable within a large electrochemical stability range and dissociation to supply cations and anions. Moreover, addition of ionic liquid into the conjugated polymer reduces the amount of constituents and probable phase separation effects.

Ionic liquids that have been studied include tetrahexylammonium-bis(trifluoromethyl)sulfonylimide (THA-TFSI) [105] with cations such as imidazolium and anions such as PF_6 , BF_4 . [91] Shao *et. al.* [106] mixed an organic ionic liquid, methyltrioctylammonium trifluoromethanesulfonate (MATS) in LEEC that resulted in good phase miscibility with conjugated polymer in frozen-junction devices achieving a single phase thermodynamically stable system with brightness of $>10000 \text{ cd/m}^2$. He also proposed that insertion of crosslinked layers polystyrene (PS)-N,N'-diphenyl-N,N'-bis(4-n-butylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD)-perfluorocyclobutane (PFCB) (PS-TPD-PFCB) or 4,4',4''-tris(N-carbazoly) triphenylamine bis(vinylbenzylether) (VB-TCTA) eliminated the electrochemical side reactions at the anodic interfaces and acted as electron blocking layers at high voltages, by separating the light emitting layer and PEDOT:PSS, enhancing device lifetime. [107]

2.3.6 Structure-Performance Relationships in LEECs

Phase separation between hydrophilic electrolyte and hydrophobic light emitting conjugated polymers is one major device failure mechanism. It was hypothesized that the ionic conductivity of polymer electrolyte such as poly(methyl methacrylate) (PMMA) - Tetrabutylammonium hexafluorophosphate (TBAPF_6) was molecular weight dependent as it altered its rheological properties and ionic conductivity. [108] This research showed that a Mw of 350,000 showed the most homogeneous bi-continuous structure thus having higher effective active area (seen in Figure 2.12a-d) and best performance (seen in Figure 2.12e-f) in terms of turn-on voltage and maximum brightness of $>2,000 \text{ cd/m}^2$.

Polymer ionic liquid blends poly(vinyl-ehtylimidazolium bistrifluoromethansulfonimide) (PIL) with conjugated polymer (seen in Figure 2.13a) have also been used to enhance

phase miscibility [Figure 2.13c(a-c)] leading to increase the external quantum efficiency (EQE) and maximum brightness (seen in Figure 2.13b) but mass ratios have to be optimized such that the active layer film is not too soft for evaporation. It was mixed with poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT) yellow light emissive conjugated polymer with atomic force microscopy (AFM) characterization showing bi-continuous structure with no significant increase in root-mean-square roughness values (seen in Figure 2.13c). [109]

Figure 2.12 Optical fluorescence microscopy of LEEC active layer based on PMMA based electrolytes, operated at a device current density of $\sim 15 \text{ mA/cm}^2$. PMMA M_w : (a) 3500; (b) 120,000; (c) 350,000 and (d) 996,000. (e) Current density-voltage performance of the device with legend in the inset. (f) Luminance-voltage performance of the device following the legend in (e) with inset of the device picture while turned on. [108] Reused with permission from [108].

Figure 2.13 (a) Chemical structure of the luminescent polymer F8BT and of the polymer ionic liquid poly(vinyl-ethylimidazolium bistrifluoromethanesulfonimide) (b) Current density-voltage-luminance characteristics of the device. (PIL:F8BT mass ratio) Inset shows the EQE-voltage performances where 0% PIL (solid line), 25% PIL (dotted line) and 50% PIL dashed line. (c) AFM topography images of the active layer films with different PIL mass ratios. (c-a) pure F8BT films with $R_{\text{RMS}} = 1.4$ nm; (c-b) 25% PIL with $R_{\text{RMS}} = 5$ nm and (c-c) 50% PIL with $R_{\text{RMS}} = 15$ nm. [109] Reused with permission from [109].

2.3.7 Doped regions in LEECs

Observation of LEEC mechanism in sandwich devices poses a challenge with current characterization techniques. So far in recent literature, Janelle M. Leger's group is the only research team that has been able to characterize sandwich devices showing the depth profiles of cations. [110, 111] Due to possible relaxation of ions back to its equilibrium state, the characterizations cannot be done with long delay between sample preparation and testing. Moreover, for an accurate representation of the doped regions, fixed or frozen junction LEEC devices are required to immobilize the cations prior to characterization, which limits the electrolyte choice and almost removes the ability to characterize the more commonly adopted dynamic junction LEECs. Thus, Planar LEECs which are 'scaled up' versions of sandwich LEECs are used to study the operational mechanism. Active layer thickness of planar LEECs can range from hundreds of microns

to centimeter thick as discussed earlier and it is purported that this mechanism has thickness independent device turn-on characteristics. It can be argued that performance of the device is thickness dependent as shown by Li *et. al.*. [112] However, with the assumption that the underlying fundamental operation mechanism holds true for sandwich and planar devices, planar LEECs is currently the most pragmatic characterization. [113]

Currently, it is reported that the p-doping area of light-emitting electrochemical cells are much larger than that of the n-doping which suggests the limited n-doping capability of cations. [40, 114] It is also said that the emissive layer is near the cathode for conventional LEECs (seen in Figure 2.14 a-c). [42]

Figure 2.14 (a) Schematic of doped regions and potential drop in an operational planar LEEC. (b) Steady state operation of a planar LEEC with Au electrodes on each side with a $120\text{ }\mu\text{m}$ interelectrode gap with a bias of 5 V . (c) Steady state operation of the same device when bias is -5 V . The recombination zone consistently shifts nearer the cathode. [42] Reused with permission from [42].

A recent study by Rodovsky *et. al.* discussed the electron injection from high work-function metals into the active material LUMO is much poorer compared to the hole injection into the HOMO of the active material. Thus, this affects the doping fronts and eventual emission zone of the device. [46, 115] Consequently, another study proposed that electrochemical side reactions thermodynamically dominate at low applied bias, creating a thin degradation layer at the active material/cathode interface. At higher

voltages, n-doping is kinetically preferred since it is simply not energetically accessible at lower biases. This would at least partially block the electron injection and cause lesser n-type doping. [116] Direct probing of p- and n- doped regions (seen in Figure 2.15a) shows that the conductivity of the p-doped region is of 2 orders of magnitude higher than the n-doped region (seen in Figure 2.15b). [40] It showed that the junction is graded with highest conductivity nearest to the electrode and decreases towards the undoped conjugated polymer layer.

Figure 2.15 (a) Device schematic of a Planar LEEC configuration with defined doped regions of arbitrary thickness. (b) The probe position and current values of the p- and n- doped regions implying the conductivities of each region. [40] Reused with permission from [40].

2.3.8 Self-absorption Effects in LEECs

Planar LEECs also offer insight into the self-absorption mechanisms present during operation with doped regions exhibiting high exciton quenching at low voltages and doped region thicknesses. A sharp reduction in photoluminescence was observed for doping densities between 10^{18} and 10^{19} cm^{-3} , due to polaron-induced exciton quenching mechanism by Förster Resonance Energy Transfer (FRET) and charge transfer (CT). [113, 117] In practical cases, a sandwich device is used and thus the doped regions which are exciton quenching regions although apparent, cannot be discarded as it aids the

charge injection process and is deemed to be technological trade-off. A study conducted by Kaihovirta *et. al.* [103] shows the quantitative effects of doping-induced self-absorption in LEECs as a function of active material thickness and doping concentration, also seen in iTMC LEECs. [118, 119] It supported earlier claims that the quenching mechanisms are due to the overlap between the emission of the exciton and absorption of the doped conjugated polymer. Moreover, it was found that the self-absorption loss at EL peak wavelength was 10% and 70% for 100 nm and 1 μm thick active layer suggesting that thinner devices have better inherent out-coupling efficiency as illustrated in Figure 2.16a. Practical devices fabricated with a reflective cathode were used and the light out-coupling pathways illustrated in Figure 2.16b.

With reference from earlier studies that the p-doped region is much thicker and more conductive than the n-doped region, we can expect that self-absorption effects of practical devices mainly arise from the p-doped region quenching. To reduce the quenching effects albeit to a small degree would require recombination zone engineering to create a centered emission zone.

Figure 2.16 (a) Doping-induced self-absorption of sandwich LEEC device due to overlap between electroluminescence spectra of active material and doped conjugated polymer. (b) Schematic representation of possible quenching sites of light from an LEEC with (1) light out-coupled through p-doped region and (2) depicts light that is emitted from the undoped region, reflected by the cathode and then passing through p-doped region, essentially also passing through the n-doped region twice. [103] Reused with permission from [103].

2.3.9 Recombination Zone Engineering

In an ideal case, centered emission zone in LEECs is preferred due to possible degradation mechanisms such as metal-induced exciton quenching [120-122], doping-induced short-circuit formation [123] and self-absorption effects. In a recent paper by Stephan van Reenen *et. al.*, it was discussed that there was a fundamental tradeoff between emission intensity and efficiency in LEECs, suggesting that the application of LEECs should be sought in high brightness low cost devices rather than high efficiency due to the downsides that LEEC technology possesses. [124] There are various ways to engineer and shift the recombination zone to the center of the active layer. Shin *et. al.* discussed the shifting of recombination zone in dynamic junction LEECs via cation selection between (Li^+ , K^+ and Rb^+). This altered the n-type doping concentration per repeat unit of MEH-PPV due to a general reduced electron delocalization length ($\propto$ of cation) requiring a higher concentration of doping in the n-doped region thereafter centering the recombination zone (seen in Figure 2.17). Table 2.1 summarizes the calculated doping concentration of the n-doped region and ionic conductivity comparisons leading to faster turn-on dynamics. [97] Other cations such as Na^+ , Cs^+ have also been studied. [125] Frozen junction LEECs is also another alternative means of recombination zone engineering. Currently, dynamic junction LEEC suffers degradation due to over oxidation or over reduction in the p-doped regions due to mobile cations under high applied bias. Fixed junction LEECs promise faster turn-on times, controls ion distribution preventing over doping, enhanced lifetime and direct characterization of already-doped sandwich LEECs. Other properties such as rectification behaviour would be useful in display technology and formation of built-in-potential within the active layer opens up the possibility of dual function devices as LEECs and photovoltaic cells. Yu *et. al.* stabilized the dynamic p-i-n junction using short chain PEO end-capped with methacrylate (poly(ethylene glycol) dimethacrylate ether) (PEO-DMA) via crosslinking due to electrolyte exposure to inherent joule heating and light emission compared to poly(ethylene glycol) dimethyl ether (PEO-DME) as illustrated in Figure 2.18a-e. [43] It was reported that the junction was fixed after 72s of device operation and it enhanced luminance, efficiency and device operation upon cycling (seen in Figure 2.18f-h). Tang *et.*

al. [126] localized the recombination zone using a trilayer LEEC device. A thin (5-10 nm) porous, hydrophilic zwitterionic conjugated polymer intermediate layer was sandwiched between two hydrophobic LEEC active layers in which n-doped and p-doped regions are similar, with a thin localized recombination zone between the active layer and intermediate layer. The electroluminescence spectra exhibited a bimolecular exciplex character, different from that shown in pristine zwitterionic conjugated polymer and conjugated polymer matrix. However, this research is still in its early stages of development. Carrier trapping has been shown as another way of recombination zone engineering. A study conducted by Su's group [127] that optimized the addition of a hole trapping molecule 3,3'-diethyl-2,2'-oxathiacarbocyanineiodide (DOTCI) into iTMC LEEC active layer which tailored the carrier mobilities. This controlled the doping propagation and eventual size of the doped region creating a more centered recombination zone with high EQE of $\sim 12.75\%$.

Figure 2.17 Planar LEECs at steady-state operation at 360K after 400s showing the different cations selection shifting the recombination zone. (a) Li⁺ cation; (b) K⁺ cation and (c) Rb⁺ cation. [97] Reused with permission from [97].

Table 2.1 Calculated n-type doping concentration for $X = \text{Li}^+$, K^+ and Rb^+ and comparison of ionic conductivity of electrolyte (PEO-LiX) using different cations. [97]

X = Li^+ vs K^+ vs Rb^+ calculated n-type doping concentration / MEH-PPV unit XCF_3SO_3 salt systems during operation at $T=360\text{K}$	
Li^+	~ 1 dopant/repeat unit
K^+	~ 0.2 dopant/repeat unit
Rb^+	~ 0.4 dopant/repeat unit
$\sigma(\text{X}=\text{K}) > \sigma(\text{X}=\text{Rb}) > \sigma(\text{X}=\text{Li})$

Figure 2.18 (a) Repeat unit of the PEO-DME showing stable methyl end groups. (b) Repeat unit of PEO-DMA showing methacrylate functional groups at both ends with can undergo curing. (c) Planar LEEC device operation using PEO-DME based electrolyte showing the movement of the dynamic recombination zone. (d) Planar LEEC device operation using PEO-DMA based electrolyte which showed stable doping fronts and a frozen junction device. (e) Sandwich device based on PEO-DMA. (f) Cycling performance showing superior luminance of PEO-DMA based electrolyte. (g) Luminance-voltage device characteristics compared between PEO-DMA, PEO-DME and PEO based electrolytes. (h) Luminous efficiency-luminance characteristic. [43] Reused with permission from [43].

2.4 Quantum Dots and its Applications

Quantum dots (QD) are nanoscale semiconducting (CdSe [128], CdTe [129], InP [130] and recently cadmium-free ternary quantum dots such as CuInS₂ [131], CuInSe₂ [132], AgInS₂ [133] and InGaN [134]) are particles which offer tunable emission spectra with respect to size, small full width half maximum spectra (for non-ternary QDs) towards wider colour gamut, high photoluminescence quantum yield and excellent photostability. It can absorb and emit light within the visible and infrared spectrum. These properties have seen its adaptation into applications such as bioimaging [135], display technology [136, 137], solar cells [138] and memory devices [139]. Surface modification of these inorganic quantum dots such as ligand exchange or core-shell structures allows flexibility for altering its solubility in different chemical environments and interesting photophysical properties. [140, 141]

In the field of optoelectronics, narrow emission spectra and high quantum yield of QD has led to advances in LED technology. [142] By controlling the size of the quantum dots, the bandgaps can be altered and thus change the absorption and emission wavelength. White LED comprising of quantum dots have the capability to revolutionize the lighting industry, replacing conventional incandescent light sources with more energy efficient. In 2010, lighting energy consumption accounts for 20% of all energy usage in the United States. [143] Therefore, quantum dots would be potential for displays and lighting applications. In a recent paper, high luminance of 112,000 cd/m² by Quantum dot light-emitting diodes (QLEDs) has been reported at a driving voltage of 7 V, with a maximum EQE of 12.5%. [144] The current challenge facing inorganic LEDs and QDs alike is the toxicity of heavy metals and high cost of manufacturing. [142] Simplifying fabrication steps and processes is one alternative method to make this technology more competitive. Moreover, the low efficiency of QLEDs due to poor heat sink and imbalanced charge injection is still up for further investigation. To date, colloidal CdSe/ZnS core-shell QD have been most researched due to their high quantum yield and high photostability at room temperature. [145-150] In addition to active layer EL, QDs can also act as down

conversion phosphors in white LEDs utilizing its efficient photoluminescence properties. [151]

2.4.1 Quantum Confinement

Size dependent properties of the QD arise from the quantum confinement effect. This happens when the size of the nanocrystal is reduced much smaller than its own Bohr radius. The Bohr radius is the dimension that describes the spatial extension of the exciton in the semiconductor and this size ranges from 1- 100 nm depending on its chemical makeup. The Bohr radius can be calculated by:

$$a_0 = \frac{\epsilon \hbar^2}{e^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right)$$

Where a_0 is the Bohr radius, ϵ is the dielectric constant of the semiconductor material, $\hbar$ is the reduced Planck's constant, m_e effective mass of electron, m_h effective mass of hole and e is the elementary charge. When the size of the QD is almost equal or lesser than the size of the Bohr radius, this would confine the exciton wavefunction and induce alterations in the density of states and separate the energy levels into discrete bands. As a result, the bandgap of the QD becomes size dependent. The smaller the QD, the bandgap increases to an extent, leading to a blue-shift in its photoluminescence properties.

2.4.2 Mechanism of Light Emission in QDs

Light emission from QDs can happen in four different mechanisms. Firstly, optical excitation is one way where QD can emit light (seen in Figure 2.19a). This is where a QD layer is deposited between an electron transport layer (ETL) and hole transport layer (HTL), with either side emitting a photon equal or larger than the bandgap of the QD. The QD will absorb this energy and emit light corresponding to its own bandgap. ETL and HTL are bounded to the requirement that its absorption spectra should not overlap with the emission of the QD to ensure efficient light out-coupling.

Figure 2.19 QD excitation mechanisms. (a) optical excitation formed by absorption of a photon where its energy is higher than the bandgap of the QD. (b) Direct charge injection where the exciton is formed via charge recombination in the neighbouring charge transport layers. (c) Energy transfer via FRET mechanism from a donor matrix or donor charge transport layer. (d) Ionization of QD via high applied electric fields where tunneling and recombination of charges in QD give rise to emission. [142] Reused with permission from [142].

Secondly, direct charge injection into QDs from injected holes and electrons which are supplied by hole and electron transport layers (seen in Figure 2.19b). This is the main operating mechanism found in LEDs. ETL and HTL selection is crucial in harnessing the excellent optoelectronic properties of QDs by reducing the charge injection barrier via HOMO-LUMO tuning or enhancing the charge mobilities of the transport layer. Thirdly, nonradiative energy transfer between QD and ETL/HTL such as Förster Resonance Energy Transfer (seen in Figure 2.19c).

The QD can be either between the ETL and HTL or reside in the matrix of an emissive conjugated polymer where it should satisfy a few criteria: (1) Donor E_g must be larger than the Acceptor (in this case it is the QD) E_g ; (2) There should be good spectral overlap between the donor photoluminescence and acceptor absorbance spectra; (3) The donor and acceptor intermolecular distance must be less than 10 nm which can be easily tuned

by increasing the concentration of the acceptor molecules. [152] Lastly, ionization of QD via high electric fields (seen in Figure 2.19d) can extract an electron from the valence band of the QD. This free electron will tunnel into another QD and leaving a hole in the first QD. Another electron would tunnel into that QD causing charge recombination. However, this type of emission mechanism does not follow the same device structure as the first three as the QD is sandwiched between two dielectric materials and it eliminates the need for energy band alignment. This method of excitation due to its high electric field requirement and dielectric layers limits the brightness of the devices to $\sim 10^{-3}$ lm/W but is a unique way of characterizing QDs under applied fields. [142]

2.4.3 QD-Conjugated Polymer Blends

Figure 2.20 (a) Structure of the bilayer of 2 monolayer thick red emissive $\text{ZnCuInS}/\text{ZnS}$ core-shell QD and blue-green emissive Poly(4-butylphenyl-diphenyl-amine) (poly-TPD). (b) EL spectra of pristine QDs, pristine poly-TPD and bilayer device. (c) Current density-voltage-luminance characteristics of the device. [155] Reused with permission from [155].

Efficient energy transfer has been observed in CdSe/ZnS and blue light emitting conjugated polymer blend films characterized via time resolved photoluminescence measurements confirming FRET mechanism. [153] Hybrid devices of CdSe/ZnS with poly(p-methyltriphenylamine-b-cysteamine acrylamide) (PTPA-b-CAA) based on hybridization with QD grafted onto the conductive block copolymer showed a low turn-on voltage of 4 V with EQE of $> 1.5\%$. [154] Other than blended films, researches on bilayer configurations of red QD and blue emissive polymer have been conducted, realizing a white hybrid light emitting diode via direct charge injection into the QD and emissive polymer (seen in Figure 2.20a-b). [155] This structure reduces contribution from the FRET mechanism due to the distance between the donor and acceptor and decreases unwanted absorptions. In this study, ZnCuInS/ZnS core-shell QDs improved the colour rendering index (CRI) to 92 due to its inherently larger FWHM compared to cadmium based QDs which is due to optical transitions and impurity levels of ternary core-shell QDs. Maximum brightness values of $\sim 400 \text{ cd/m}^2$ was obtained with EQE of around 0.035% due to inefficient carrier injection into red emitting QD with dominant polymer emission (seen in Figure 2.20c).

2.4.4 QD-LEECs

LEEC mechanism in combination with QD has only been studied by a few groups. [156-158] It combines the optimized charge injection fueled by the p-i-n junction formation and the high PL quantum yields and efficient charge recombination shown in QDs. The first paper was reported by Bader *et. al.* [158] where optimized blending of QD with LEEC active layer and polymerizable ionic liquid alkyltrioctylamine allylsulfonate (ATOAAS) showed colour tuning abilities with different mass ratios of QDs. It proposed that the charge transport in the doped region would circumvent tunneling through the QD and enhance charge transport into the recombination zone where direct charge injection into QD leading to almost pure QD emission (seen in Figure 2.22a-b). Saturated and multi-coloured white emission from QD based LEEC devices were reported by Qian *et. al.* [156] Ligand exchange removed the insulating trioctylphosphine oxide (TOPO) surface ligands and functionalized QD surfaces with carboxylic (-COOH) end groups that

improved charge injection and mobility of charges (seen in Figure 2.21a). Pure QD emission and of similar full-width half maximum (FWHM) compared to PL were observed and mixing of the QD in appropriate ratios allowed fabrication of white QD-LEEC (seen in Figure 2.21b-c).

Figure 2.21 (a) Ligand exchange process. (b) Normalized emission spectra of solution PL and QD-LEEC EL. (c) Above shows the normalized EL spectra of blue, green and red monochrome QD-LEECs and below shows the EL spectrum of white QD-LEECs driven at 10 V with device picture in the inset. [156] Reused with permission from [156].

Figure 2.22 (a) EL spectra of QD-LEEC with different mass ratio of two emissive QDs with peak emission at 576nm and 615nm. (b) CIE coordinates and photos of the aforementioned QD-LEEC. [157] Reused with permission from [157].

Recently, bilayer structure of CdSe/CdS core-shell QD/iTMC ($[\text{Ir}(\text{ppy})_2(\text{pbpy})]^+[\text{PF}_6]^-$) with ionic liquid, 1-Butyl-3-methylimidazolium Hexafluorophosphate ($[\text{BMIM}]^+[\text{PF}_6]^-$) was reported that showed direct charge injection into both iTMC and QD simultaneously

confirmed by time resolved photoluminescence. Voltage induced colour tuning was observed due to preferential charge injection of QD and iTMC at low voltages and only iTMC at high voltages (seen in Figure 2.23a-c). [158]

Figure 2.23 (a) Picture of devices at different voltage. (b) Normalized EL spectra showing wavelength shift upon voltage increase. (c) Commission Internationale de L'eclairage (CIE) coordinates of the different emissions. [158]. Reused with permission from [158].

2.5 PhD Studies in Contest with Literature

In this thesis, we focus on the investigation of mechanisms to reduce turn-on voltages and recombination zone engineering via anion selection and complexation respectively. Within the realm of LEEC research, the question to whether the anion or cation doping is dominant in the performance of conventional LEECs has yet to be investigated as studies have conflicting points of view. Ion mobility and smaller anion size was thought to reduce turn-on voltages [159], but this was conflicted with theoretical simulations that proposed the importance of binding energies of salts to allow ease of dissociation and doping [160]. Thus there is an opportunity to study the anion effects due to the larger and therefore presumably dominating effect of the p-doped region in p-type conjugated

polymers. Furthermore, with respect to recombination zone engineering, research efforts have mostly been one sided, either tackling the p- or n- doped regions individually for each device. One research gap that has not been paid much attention is the polymer complexation behaviour in trapping anions. A similar study showed that carrier trapping can reduce p-doping propagation, centering the recombination zone. However, the possibility of recombination zone engineering brought on by complexation has not been found. In this dissertation, we emphasize on gaining a better understanding between complexation behaviour by tackling the p- and n- doped regions simultaneously and its effects on LEECs. Moreover, single active layer QD-LEECs based on FRET that shows voltage tunable wavelength would be discussed.

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Chapter 3

Experimental Methodology

Characterization of active layer films provides a deeper insight into the mechanisms and complex processes during device operation. This chapter describes the fundamental principles of these characterization techniques. Optical characterizations aid the understanding of the photophysical properties of the active layer films. Structural characterizations such as atomic force microscopy and x-ray photoelectron spectroscopy help to understand the phase morphology and chemical binding energies within the sample to deduce a correlation with experimental device results. Device fabrications and characterizations with detailed experimental flow of the different studies will be introduced.

3.1 Optical Characterization

3.1.1 Photoluminescence

Photophysics of organic materials deals with the processes that occur when light interacts with matter. One such technique is photoluminescence. Photoluminescence occurs when a sample is excited by absorbing photons and relaxes through different mechanisms. Fluorescence and phosphorescence are the two emission mechanisms when an excited molecule relaxes, but both occurs with different time interval with respect to absorption and emission. Moreover, there exists a theoretical statistical probability limit of fluorescence (25%; singlet exciton) and phosphorescence (75%; triplet exciton) of any molecule according to quantum mechanical rules. In conjugated systems, the significance of photoluminescence is that the amount and wavelength of the emitted energy depends on the chromophore (small polymeric segment of 10-15 monomers), the chemical environment and the spacing between the electronic levels of the polymer. This process is described in detail from the Jablonski Energy Diagram (seen in Figure. 3.1).

Figure 3.1 The Jablonski Diagram showing the different mechanisms after excitation of a chromophore and its related mechanisms towards relaxation.

When these conjugated system absorbs a photon ($\approx 10^{-15}$ seconds), the photon is excited to a singlet electronic excited state and relaxes through non-radiative internal conversion and vibrational relaxation on the order of 10^{-14} to 10^{-11} seconds to the first excited singlet state. At this point fluorescence happens on the order of 10^{-9} to 10^{-7} seconds and emits a photon. However, this mechanism is in competition with other less dominant mechanisms such as intersystem crossing, which can cause radiative decay via phosphorescence (10^{-3} to 10^{-2} seconds). Such emission is usually forbidden at room temperature, but is commonly seen in metalorganic systems such as inner transitional metal complexes. [1, 2] There is also a possibility that the molecule can transfer energy back to the singlet state and decays through non-radiative relaxation or delayed fluorescence. In addition, photoluminescence is another way to understand the optoelectronic transitions in the material as seen in Figure 3.2.

Figure 3.2 Fluorescence spectrum with relation to the Jablonski Diagram. In the diagram, the following internal conversions are indicated: $S_{2,4} \rightarrow S_{1,0}$, $S_{2,2} \rightarrow S_{1,0}$, $S_{2,0} \rightarrow S_{1,0}$ and $S_{1,0} \rightarrow S_{0,0}$. The dashed arrows represent non-radiative transitions. Solid arrows purple and blue denotes the absorption spectra. Green and red solid arrows denotes the photoluminescence spectra of fluorescent or phosphorescent moieties and shows a distribution of wavelengths.

In our optical characterization, solid-state and diluted polymer samples were characterized using the Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer ($\lambda_{\text{ex}} = 350\text{nm}$). In the fluorescence spectrophotometer, it measures the wavelength for any given excitation wavelength as shown in Figure 3.3. [3] This excitation wavelength is dependent on the absorbance spectrum of the material which will be addressed later. In photoluminescence spectra of polymers, individual peaks can be related to structural properties of the polymers, which will ultimately affect its performance as an active layer in an organic light-emitting device. [4, 5]

Figure 3.3 (a) The absorbance and photoluminescence spectra of a known material PFN in a diluted solution concentration of 10^{-5} M (based on the polymer repeat unit) with respect to the different solvents they are dissolved in. [3] Reused with permission from [3].

3.1.2 Absorbance

Absorbance spectroscopy deals with the measurement of absorbance of radiation in terms of wavelength or frequency. With relation to the operation of organic light emitting

diodes and light-emitting electrochemical cells, it can determine the wavelength band of absorption that could provide a deep understanding about eventual light out-coupling of the device due to self-absorbance of the active layers and substrates. Moreover, it can be used to determine the spectral integral overlap between two chromophores (donor and acceptor) which is pertinent in systems with Förster Resonance Energy Transfer mechanisms. In Figure 3.3, it shows the absorbance maxima of PFN in both solvents at around 380 nm. This is the absorbance wavelength with maximum intensity. If there is a wavelength source that emits around that region, it satisfies one of the conditions for efficient Forster Energy Resonance Transfer and emits the fluorescence of the acceptor. In Figure 3.4, it explains the parts of standard spectrophotometers which serves to determine the absorbance (Figure 3.4a) and photoluminescence (Figure 3.4(b)). The instruments that were used in this thesis for the measurement of absorbance and photoluminescence were Cary 5000 UV-Vis-NIR Spectrophotometer and Cary Eclipse Fluorescence Spectrophotometer, respectively.

Figure 3.4 (a). UV-Vis-NIR Spectrophotometer. Light is emitted by a source and a prism or grating disperse the light. A desired wavelength λ is selected by the monochromator. The output beam is split into two beams, each with the same magnitude of intensity. The beams are directed towards two cuvettes containing the sample and the reference in which the reference sample only contains the solvent. As the output wavelengths in the beam are altered within a range, the intensities of the corresponding light output from both cuvettes are measured. (b) Photoluminescence spectrophotometer. The 1st monochromator outputs a preset specific wavelength which excites the molecules in the solid or liquid sample. The light emitted from the sample is collected by the 2nd monochromator located at 90 ° with respect to the incident light to

minimize intensity of scattered light reaching the detector. The excitation wavelength is fixed while the 2nd monochromator collects the intensities of the light emitted within a set wavelength range. The fluorescence spectra is shown in Figure 3.2.

The absorbance A_λ at wavelength λ is defined as:

$$A_\lambda = \log[I_0(\lambda)/I(\lambda)]$$

And is equal according to the Lambert-Beer law to:

$$A_\lambda = \epsilon(\lambda)cd$$

Where $\epsilon(\lambda)$ is the extinction coefficient at wavelength λ for the particular molecule, c is the concentration and d the path length of the cuvette, for instance 1 cm.

Fluorescence intensity $I_{\text{fluorescence}}(\lambda)$ is also proportional to:

$$I_{\text{fluorescence}}(\lambda) \propto \epsilon(\lambda)I_0 \phi$$

Where $\epsilon(\lambda)$ is the extinction coefficient at excitation wavelength λ , I_0 is the monochromatic light intensity, and Φ is the quantum yield of fluorescence. This equation is valid for dilute chromophore solutions, in which absorbance of the aromatic compound never exceeds 0.05.

In this thesis, photoluminescence and absorbance characterizations are correlated with the structure and phase morphologies of the active layer. Changes in the photoluminescence can be attributed with charge trapping and polymeric structure interactions. These changes affect the eventual wavelength distribution of the light emission. Absorbance changes such as bathochromic shifts can also be related to extended conjugation of polymer hosts.

3.2 Structural Characterizations

3.2.1 Atomic Force Microscopy

Atomic Force Microscopy is a technique that can investigate a sample's surface characteristics such as topography and phase morphology with resolution of less than 10 nm. [6] In Figure 5, it uses a cantilever with a very sharp tip of a few atoms across (Si_3N_4 or Si) to scan over the sample surface. Its working principle is based on interatomic potentials that are developed between atoms of the tip and atoms on the surface of the sample. When a constant force is applied to the tip and is dragged along the surface, interatomic potentials changes which causes the deflection of the flexible microcantilever. A laser is pointed towards the tip of this cantilever. The deflection of the cantilever also changes the position of the laser which is captured by a positional photo detector. Thus, a topographical image such as surface morphology can be captured in real time. Advancements in laser technologies has allowed atomic level deflections of the cantilever to be detected easily. There are three types of modes. Contact and tapping mode. The different modes are self-explanatory, dependent on the distance between the tip and the sample surface.

Figure 3.5 A schematic of atomic force microscopy.

In contact mode AFM, the working principle is based on the repulsive Van der Waals interactions. The tip is slowly lowered towards the surface of the sample. Because the tip is in contact with the surface, strong repulsive Van der Waals forces causes the cantilever to bend as it passes through its features. If the cantilever exhibits a spring constant lower than that of the surface, it bends and the force on the tip is repulsive. By scanning the cantilever over a predetermined area, the deflection is measured by the position detector. A feedback loop maintains a constant cantilever deflection which produces an accurate topographic AFM image of the surface. This mode is advantageous at fast scanning and for rough samples. However, there is a possibility of contamination of surface and this is somewhat a destructive characterization technique that deforms the samples due to significant force application. Dragging the tip can also cause areas of high stress which can damage the tip as well.

Tapping mode is an intermittent tapping of the tip with the surface. The probe is oscillated at the materials resonant frequency and the tapping occurs when the tip contacts the surface at the bottom of its swing. The oscillation amplitude is usually 20-100nm. It taps the surface lightly with a very short tip-sample time interaction. This interaction will alter the amplitude, resonance frequency and phase angle. Tapping mode is usually used for samples which are easily damaged such as biological samples. Moreover, phase separations can be detected by the viscoelastic dissipated property (chemical-dependent phase) of the surface which is especially important in solid-state films of organic blends. [7] In this work, AFM is used to characterize the LEEC active layer to study the phase morphology between the constituents of the blend due to its tendency to phase separate as a result of the polar nature of the polymer electrolyte and the non-polar character of conjugated polymers [8]. Solubilities of certain components can also give rise to this phase separation [9] being a major issue in polymer electrolytes. Interpenetrating networks of polymer electrolyte and light emitting polymer is expected for better performance LEEC. [10] Thus, it is imperative to study the phase morphology of the active layer blends.

3.2.2 X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) is a characterization technique that provides a quantitative and chemical state information from the surface of the material. It has an analytical depth of 2-5 nm. XPS can reveal the chemical elements and the nature of the chemical bonds due to interactions such as whether it is reduced or oxidized. It can detect a wide range of chemical elements except hydrogen and helium due to the low photoelectron cross sections. It quantifies the elemental composition whereby the element in interest is >0.05 atomic %. To achieve accurate data, it is conducted in an ultrahigh vacuum condition of around 10^{-10} torr.

The principle of XPS analysis is based on the photoemission principle (seen in Figure 3.6). When soft x-rays of sufficient energy (200-2000eV) interact with the surface atoms, it causes the electrons in specific bound states to be excited and it will break the photoelectron away from the nuclear attraction force of that element. The kinetic energy of that electron depends on the photon energy and the binding energy of the electron. By measuring the kinetic energies, the detector will plot the number of photo-ejected electrons versus time (counts/second) versus the binding energy. Each prominent peak in this spectrum corresponds to a specific element in the sample. The relationship between the energies are expressed by:

$$K.E._{XPS} = E_{ph} - \phi_{XPS} - B.E._{XPS}$$

Where $K.E._{XPS}$ is the kinetic energy of the electron emissions departing the sample, E_{ph} is the initiating photon energy, ϕ_{XPS} is the work function of the instrument and $B.E._{XPS}$ is energy difference between the ionized and neutral atoms.

Figure 3.6 The excitation process of the electron during x-ray interaction and the determination of the different energies.

The peak intensities of the XPS spectrums is also a close quantitative estimate of how much of each element is in the sample. More of than not, relative intensities are used to determine the stoichiometry of the sample. Using the spectrum, the peaks are further investigated and undergo deconvolution using curve fitting software such as CasaXPS before the data can be confirmation.

In this thesis, XPS is used to determine the complexation between ionic liquid and the host polymer as seen in Chapter 5 when we consider the effect of the terminal amino groups seen in the polymer as a direct means of interaction characterization, also shown in studies by Martin *et. al.* [11]. An increase in the binding energy will equate to withdrawal of valence electron charge (oxidation) and a decrease in the binding energy will equate to the opposite (reduction). The binding energies of an electron also are dependent on the local chemical and physical environment of the element, such as those in polymer complexations.

The XPS used in this thesis is the PHI Quantera II spectrometer employing a focused monochromated Al K α source ($\hbar\nu = 1486.6$ eV). X-ray power is 1486.6eV, spectrometer was calibrated and charge corrected to C 1s peak at 284.8 eV, spot size diameter was 200 μm , instrument base pressure was $\sim 10^{-7}$ Pa and spectrometer resolution is 0.48 eV. The survey and narrow scan details are: Survey scan: Pass Energy 280eV, 10 sweeps, 1.0 eV/step, 0-1300 eV; Narrow Scan: pass energy 140 eV, 0.25 eV/step, C 1s 30 sweeps 276-296 eV, N 1s 70 sweeps 390-410 eV, O 1s 30 sweeps 521-541 eV, F 1s 30 sweeps 679-699 eV, S 2p 50 Sweeps 155-175 eV.

3.2.3 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is an effective thermal analysis tool to characterize physical properties of an organic material. This method enables determination of: (1) glass transition temperature T_g ; (2) melting transitions; (3) latent

heat of fusion and reactions; (4) percentage crystallinity; (5) specific heat capacity; (6) reaction kinetics; (7) oxidative and thermal stability; (8) rate and degree of curing and (9) blend copolymer analysis. [12]

DSC measures the energy absorbed or released by a sample as it is heated or cooled. When a sample undergoes phase transitions or matter transitions, the amount of heat that flows into it will be compared to a null reference to maintain both at same temperature. Exothermic and endothermic reactions (such as oxidations or reductions) can be detected as heat flow changes. Crystallization, curing and phase transitions also cause a change, easily detected by the shape of the heat flow (J) vs temperature curve (K) as they are characterized by its distinct shape. Enthalpies of transition can be determined by integrating the shape of the curve of the corresponding transition.

In this thesis, TA Instruments DSC 2920 under N₂ gas flow condition is used to characterize the thermal properties of the sample. It determines the melting points of electrolytes to identify the melting point maximum and enthalpies of transition. This is especially important in polymer electrolytes when it is heated close to its melting point, ionic conductivities increase. Joule heating due to large current densities during LEEC device performance can effect this temperature increase leading to enhanced doping and better performing device. Studies using DSC as a means to investigate ion-transport properties of polymer electrolytes have also been utilized by Edman *et. al.* [13]

3.3 Electrical Characterization

3.3.1 Cyclic Voltammetry and Electrochemical Impedance Spectroscopy

Cyclic Voltammetry (CV) is a technique to characterize a film's electrochemical properties. This is performed via voltage cycling of the organic film on a working electrode and measuring the resultant current. The fundamental process of doping in organic semiconductors can be most directly explored by using this technique. This allows the characterization of electrochemical stability windows, HOMO-LUMO levels

and studies the doped regions of LEEC operation. The components of this setup include a working electrode, a counter electrode and a reference electrode submerged in an electrolyte. For the purpose of characterizing polymer samples, experiments should be done in an inert atmosphere or bubbled with inert gas. The reference electrode, whose electrochemical potential is known, is used to measure the potential at the working electrode. The counter electrode, usually Pt metal is an inert conductor used to complete the circuit. The material is spin coated or drop casted onto the working electrode, usually Au where potential between working and reference is cycled from small to a large electrochemical potential range. Ions suspended in the electrolyte will dope the organic polymer and it will show an increase in current due to its doped nature. It is also possible to calculate the approximate HOMO-LUMO levels using the doping onset potentials which were discussed in chapter 2. In this thesis, the CV technique is used to approximate the enhancement in electrochemical stability window in accordance to studies done by Edman's group (scan rate = 25 mV/s). [14, 15]

Electrochemical Impedance Spectroscopy (EIS) is conducted on solid state electrolyte films to measure its ionic conductivity. It applies an sinusoidal AC potential onto the sample from two electrodes which sandwich the sample measuring the impedance and phase shift of the current. The Nyquist impedance plot is generated (Z' vs Z'' plot) and is used to determine the appropriate equivalent circuit. It will aid in the estimation of ion transport properties. [16] CV and EIS measurements were conducted on Solatron 1470E.

3.4 Device Fabrication

3.4.1 Spin Coating

Spin coating is a film formation technique for use in organic research due to its ability to form relatively thin films (<100 nm) and high uniformity with low surface roughness. It generally involves application of a thin film via appropriate syringe filtration pore size and medium. We have employed static dispensing spin coating as opposed to dynamic dispensing. Static dispense would allow better coverage for solutions of high

concentration and viscosity while spinning at lower speeds such as ≤ 1000 rpm. However, the downside is that it requires much more ink per substrate during film formation compared to dynamic dispense.

Figure 3.7 Typical spin coating thickness versus spin speed. Image taken from www.ossila.com.

For the case in this thesis, high boiling point (>373 K) and low vapour pressure solvents are used to prevent instantaneous evaporation during application of ink before spin coating. Moreover, spin coating is done in an inert environment such as that of an argon glovebox (<0.1 ppm H_2O ; <0.1 ppm O_2) with inert pressures higher than that of atmospheric pressures, reducing evaporation of solvents. After spin coating, devices are checked through change of colour as it can easily mean a variation of 5nm in height. It is important to note that although there are numerous ways to characterize a film's thickness and roughness, microscopy techniques such as AFM, Scanning Electron Microscopy (SEM), optical or ellipsometry. These techniques might not be suitable in cases where the organic film is susceptible to photo-oxidation, forming carbonyl bonds and disrupting the conjugated nature of the film and affect eventual device performance. [17] Spin coating allows easy control of film thickness and it is proportional to the inverse of the spin squared.

$$t \propto \frac{1}{\sqrt{w}}$$

Where t is the thickness and w is the angular velocity (related to spin speed). Increasing speed of rotation would give a thinner film such as an example in Figure 3.7.

Thickness measurements were performed using a step profilometer (Alpha-step 200, Tencor Instruments) to determine the eventual dried film thickness of the active layer.

3.4.2 Experimental Flow

First, master solutions of different organic solutions were prepared. For conventional organic light-emitting diode fabrication, organic polymers were used as purchased and dissolved in appropriate solvents and stirred under heating at 323 K. For light-emitting electrochemical cells, constituent salts were dried in an oven at 373 K to remove residual moisture. Emissive polymer, ion-transporting polymer and salts were dissolved in appropriate solvents to form master solutions. Blended solutions were formed by mixing aliquots from master solutions to form appropriate mass ratios. Blended solutions were then spin coated on cleaned and plasma treated ITO glass (83% transmittance and $10 \Omega/\square$) via static dispense from syringe filtration (Polytetrafluoroethylene, PTFE, $0.45 \mu\text{m}$ pore size).

Drying of the wet films after spin coating was done at 333 K. All film fabrications were conducted in an inert argon atmosphere. Appropriate spin speeds were used to form the desired thickness. Al cathode deposition via thermal resistance evaporation from bulk source materials was done with a deposition rate of $0.1 \text{ \AA/s}$ to achieve a thickness of $\sim 150 \text{ nm}$. For performance characterization, solid state films of similar fabrication history are used due to limitations for mechanism investigations during device operation. Device schematics of LEECs on ITO and on ITO/PET are shown in Figure 3.8.

Figure 3.8 Device schematic and constituents for the (a) LEECs based on ITO seen in Chapter 4 and 5. (b) Flexible LEECs in Chapter 6. Both are encapsulated with UV-curable epoxy. Devices based on ITO have a cover glass on top of the epoxy and devices based on flexible ITO/PET have another layer of PET on top of the epoxy.

3.5 Device Optoelectronic Characterization

Current densities vs voltage vs brightness measurements were done using a two terminal device configuration and performed with a computer controlled Kiethley Semiconductor Characterization system (4200-SCS) coupled with a spectrophotometer (Konica Minolta Chroma Meter, CS-200). The spectrophotometer measured the luminance and CIE coordinates of the device light output. Wavelength spectra of the light output was measured using a spectrometer (Acton SP-2356) and thermoelectric-cooled CCD (Princeton PIXIS:100) utilizing a 7-core optice fibre cable coupled onto the monochromator. The CCD was cooled to <200 K before measurements were done. The shutter speed was 100 ms/frame.

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Chapter 4

Anion Selection for Low Turn-on Voltage

Performances of light-emitting electrochemical cells are defined by its electrolyte properties. Optimizing the constituents of the electrolyte containing cations, anions and ion-transporting matrix is crucial to provide the desired mechanism for high brightness and low turn-on voltage. With limited n-type doping in conventional conjugated polymer light-emitting electrochemical cells, it is hypothesized that anion doping is critical. In this chapter, poly(ethylene oxide)-lithium salt electrolyte systems have been investigated to determine the influence of anions on the LEEC performances. Ionic conductivities of $\sim 10^{-4} \text{ S cm}^{-1}$ have been obtained with TFSI based electrolytes. Device characterizations based on different anions have been considered. Active layers of similar processing history was characterized using photoluminescence, atomic force microscopy and modulated differential scanning calorimetry to give a systematic investigation on the film structures and its correlations with device operating mechanisms. Lastly, to further validate the dominance of the anion, ionic liquid cation was used in similar device configurations and coherent findings were achieved.

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4.1 Rationale

In LEEC operation, it consistently shows a larger area and better conductivity of the p-doped region, it is hypothesized that performance of light-emitting electrochemical devices are predominantly based on anion doping compared to cation doping. Recently, it was proposed that binding energy of ions is a better indicator of turn-on dynamics due to salt dissolution during initial operation. [1] TFSI⁻, CF₃SO₃⁻ and PF₆⁻ anions have differing anion volume which relates to its binding energies. Moreover, these anions have differing resonance states which are hypothesized to directly affect charge transport along PEO chains. Enhanced ionic conductivity of polymer electrolyte based on different salt anions will allow higher doping level of ions into conjugated polymer which lowers turn-on voltage. Studies have shown the superior stability of TFSI against hydrolysis and enhancement of the electrochemical stability window of the electrolyte with increased ionic conductivity. [2-4] Hence, it is hypothesized that TFSI⁻ anion based PEO electrolytes offer enhanced LEEC device performances, lower turn-on voltages (defined as the onset voltage at which brightness is 1 cd/m²) and enhances the electrochemical stability window of the device.

4.2 Introduction and Motivation

Since the discovery of polymer light-emitting diodes (PLEDs) in 1990, organic light-emitting diodes (OLEDs) have already been realized in a multitude of everyday electronic devices ranging from wearable technology to displays and future lighting applications due to many benefits over conventional lighting technology. Driving factors such as high efficiency, low material utilization rates, poor scalability and high capital cost have pushed OLED manufacturing towards its limits. For example, high efficiency and low driving voltages of OLED require multilayer processing to provide a staircase gradient with respect to charge barrier heights. Efforts to tackle this problem have led to the emergence of polymer light-emitting electrochemical cells (PLEECs) first reported by Pei *et. al.* [5], potentially simplifying fabrication and enhancing device performance.

A LEEC device for display purposes require a sandwich configuration consisting of a few chemicals blended together and spin coated in between two conducting substrates. In the said active layer, it requires an emissive conjugated polymer and an electrolyte system consisting of a salt and an ion-transporting polymer. The active layer is then deposited via spin coating. Moreover, the active layer thickness is relatively larger than most OLEDs, making fabrication possible with low-cost processing wet chemical methods such as screen-printing, inkjet printing and spray coating. With the active layer being the only important layer, its optimization is critical for good performance matrices such as lifetime, brightness and turn-on voltages.

The selection of electrolyte system and its material-weight optimizations are of utmost concern because of the impact on device physics leading to enhanced performance. [6, 7] However, there is currently limited understanding on its mechanisms, albeit with some inference from simulations or studies from planar light-emitting electrochemical cells. Planar Light-Emitting Electrochemical Cells are essentially LEECs with large active layer thicknesses of around 100 μm to more than 1cm. Its wide interelectrode gap allows direct observation of mechanism and operation and they have been fabricated to study the effects of electrolytes [8-15], salts [16-22], annealing temperature [23-25] and electrodes [26-28]. One of these observations is that the emission zone is never ideally centered with consistent inclination towards the cathode. This enhances the probability of doping-induced short circuits [29] and metal-induced exciton quenching [30, 30] which leads to short device lifetime. This also suggests that there is limited n-doping capability of cations. [32] Limited n-doping of cations can also be a leading effect of electrode work-function and HOMO-LUMO charge injection barriers or thin oxidized barriers of Al_2O_3 [28] that affects electron injection. [33]

Direct imaging and probing tests on p-doped regions showed current values which were two orders of magnitude higher than that of n-doped regions. [34] This leads us to ponder on the effect of cation and anion on electrochemical doping as there seems to be limited n-type doping. Emissive conjugated polymers have been used widely in OLED or LEEC systems. Such p-type semiconducting polymers offer good hole transport and its HOMO

energy levels are close to that of conventional ITO. Thus, it is naturally expected that hole injection barrier is lower and it easily attracts the compensating anion resulting in a larger p-type region. Salts in the LEEC (PEO-Salt) electrolyte systems studied include cations such as Li^+ , K^+ , Rb^+ ; anions of interest include TFSI⁻ and CF_3SO_3^- . [16] It is clear that ionic conductivity and probable phase miscibility of the electrolyte affects the device characteristics in terms of turn-on duration, doping propagation and overall brightness of the device. LEEC operational simulations [1] also provided a deeper understanding of salt selection where it was proposed that size of anion/cation does not play a dominant role but rather a lesser salt dissociation energy allows for ease of transport and eventual doping.

In this chapter, we present a systematic study on the salt selection of the electrolyte and its effects on the electrolyte ionic conductivity, electrochemical stability window and doping, correlating it with the device performance in terms of brightness and turn-on voltages. We report results based on sandwiched LEECs active layers containing Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), Poly(ethylene oxide) (PEO) and LiX salt, [X = Bis(trifluoromethylsulfonyl)imide (TFSI), Hexafluorophosphate (PF_6^-)] in comparison with an optimized active layer reference devices based on the typical lithium trifluoromethanesulfonate (LiCF_3SO_3) salts. After which, to revalidate the effect of the anion, the Li^+ ion was replaced with BMIM⁺ ionic liquid cation and its effect on device performance characterized. We reveal that TFSI⁻ anion blend delivers high ionic conductivity and resulting in a lower turn-on voltage and higher device brightness, related to the enhancement in anion doping.

4.3 Experimental Section

4.3.1 Chemicals Used

1,2-dichlorobenzene (99%) was purchased from Alfa Aesar. Lithium Bis(trifluoromethanesulfonyl)imide (LiTFSI) (>98%) was purchased from Tokyo Chemical Industry. Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-

PPV) ($M_n = 40,000-70,000$), lithium trifluoromethanesulfonate (LiCF_3SO_3) (96%), poly(ethylene oxide) ($M_n = 5 \times 10^6 \text{ g mol}^{-1}$), anhydrous inhibitor-free tetrahydrofuran (THF) ($\geq 99\%$), ACS reagent grade cyclohexanone ($\geq 99\%$), 1-Butyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)imide (BMIM TFSI) ($\geq 98\%$) and Lithium hexafluorophosphate (LiPF_6) (98%), were purchased from Sigma-Aldrich. 1-Butyl-3-methylimidazolium hexafluorophosphate (BMIM PF_6) (99%) was purchased from International Laboratory, USA.

4.3.2 Device Fabrication

Lithium salts were left to dry overnight in the glovebox at 100°C to remove residual moisture. Chemicals were dissolved into respective solvents at a concentration of 10mg/ml: MEH-PPV in 1,2-dichlorobenzene, salts and ionic liquid in tetrahydrofuran and PEO in cyclohexanone. All of these solutions were left to stir overnight on a magnetic hot plate at 50°C . Small aliquots of the master solutions were mixed in appropriate ratios and left to stir overnight at the same temperature. Etching of the indium tin oxide (ITO) / glass substrates (83% transmittance and sheet resistance of $10 \Omega/\square$) was done in Aqua Regia in the volume ratio of (HCl (37 % weight in water): HNO_3 (69 % weight in water): H_2O (deionized) = 3:1:1) under a hot plate at 60°C in a fumehood for 2mins to create electrodes of 5mm width. The proceeding 4 step substrate cleaning procedure was done in ultrasonic treatments: 1) Soap water; 2) deionized water; 3) acetone; 4) isopropanol. Plasma treatment was done on the substrate to remove organic residue and to form a hydrophilic surface. Spin coating of the blended solutions was done on the ITO with a spin speed recipe (5 sec; 300 rpm and 60 sec; 800 rpm) which resulted in a film thickness of $\sim 200 \text{ nm}$, characterized by a step profilometer (Alpha-step 200, Tencor Instruments). The active layer was dried under a hot plate at $T = 323 \text{ K}$ overnight. Al electrodes were deposited by thermal evaporation at pressure $< 6 \times 10^{-4} \text{ Pa}$ (rate = $0.2 \text{ \AA/s}$) to achieve a thickness of around 150 nm and a cross bar device area of 15 mm^2 .

4.3.3 Device Performance Characterizations

Optoelectronic characterizations of the LEEC devices were done using a Keithley Semiconductor Characterization System (4200-SCS) which was linked with a spectrophotometer (Konica Minolta Chroma Meter, CS-200). Priming of device was done at 4 V, 1 mA compliance for 5 mins before characterization. Device fabrications and characterizations were done in an Argon filled glovebox ($O_2 < 0.1$ ppm; $H_2O < 0.1$ ppm). During characterization, devices were tested with a voltage step profile of 0.2 V/step with the 100 ms off and 10 s shown in the pulse wave in Figure 4.1. The LEEC shows negligible hysteresis with the short off-time and each measurement was taken only after current densities were stable after a fixed duration of 1 min. The fast-doping relaxation due to self-heating and bias removal in planar LEEC studies [35, 36] was not observable or apparent in our sandwich configuration. In addition, pulsed sweep step voltage bias applied immediately after device priming. The time lapse between pre-charging and device measurement was not significant with each device being scanned in the same procedure, under similar conditions.

Figure 4.1 A segmented view of the voltage step sweep pulse 0.2V/step increments used during current density-voltage-luminance device tests (0.099 Hz; 10 sec on/100 ms off). [37] Reused with permission from [37].

4.3.4 Characterizations of Solid-State Films and Electrolytes

Electrochemical impedance spectrum (EIS) tests were conducted on Solatron 1470E and the ionic conductivities were determined from Nyquist plots of the different electrolytes. Modulated Differential Scanning Calorimetry (mDSC) was carried out in a TA Instruments DSC 2920 under N₂ flow gas condition and thermograph data was analyzed from TA Instruments Universal Analysis 2000. The film was spin coated, heated and dried at the same conditions as the LEEC fabrication and heated at a rate of 10 °C/min from 25-250 °C. Phase morphology was conducted using an Atomic Force Microscopy (AFM) setup (NTEGRA AFM). Photoluminescence (PL) spectra of the active layer was collected using a Shimadzu RF5301 Spectrometer. Cyclic Voltammetry tests were conducted on Solatron 1470E with Au working electrode coated with a thin film of MEH-PPV, Pt plate was used as the counter and a Ag wire was used as the quasi-reference electrode with calibrations against Fc/Fc⁺ redox couple after each measurement. The electrolyte solution was 0.1 M LiX (X = CF₃SO₃⁻ & TFSI⁻) + 2 M PEO (M_n = 400) in CH₃CN. Scans were done at 25 mV/s in an Ar environment in accordance to similar characterizations conducted by L. Edman *et.al.* [33]

4.4 Results and Discussion

4.4.1 PEO-LiX Electrolyte Optimization

Conventional LEEC active layers were fabricated using the commonly used salt LiCF₃SO₃. The PEO/Li⁺ mass ratios were varied (10, 30, 60) which were 1:0.085:0.03, 1:0.25:0.03 and 1:0.50:0.03 respectively for (MEH-PPV:PEO:LiX). From Figure 4.2a, it shows the current density-voltage-luminance graphs. The device which showed the maximum brightness with lowest turn-on voltage was the device with PEO/Li⁺ ratio of 30. A high PEO content such as that of PEO/Li⁺ ratio of 60 would result in increased resistance in the active layer and enhanced phase separation between the emissive conjugated polymer and the electrolyte. Too low a PEO content (PEO/Li⁺ ratio of 10) reduces the amounts of ion transportation pathways and maintains a higher degree of

crystallinity [37], leading to higher T_g whereas amorphous regions are more suitable for ion transport. From Figure 4.2a, it is evident that a PEO/Li⁺ ratio of 60 shows lower current density owing to increased resistance compared to the samples of lower ratios. The luminous current efficiencies (LCE) of the different PEO-LiCF₃SO₃ molar ratios (with respect to PEO repeat unit) against voltage is defined as the absolute brightness per Ampere. The optimal LCE at mid voltages is the device with PEO/Li⁺ ~ 30. Moreover, it provided the highest ionic conductivity value (seen in Table 4.1). This was supported with studies concluding that a PEO/Li⁺ ratio of > 15 would exhibit high ionic conductivity with enhanced ion transport. [38, 39] With this optimized electrolyte ratio of PEO/Li⁺ ~ 30, it was assumed that all the ions participated in the electrochemical doping process. Substituting the LiCF₃SO₃ with other anions such as PF₆⁻ and TFSI⁻ was carried out to study its effects and evaluate device performance. In Table 4.1, the PEO-LiTFSI based electrolytes exhibited similar ionic conductivities with PEO-LiCF₃SO₃ at a ratio of ~30 and PF₆ based electrolytes showed the lowest.

Table 4.1 Calculated ionic conductivities of the different electrolytes used in this study, derived from Nyquist plots in Appendix Figure A.1a-b

Salt/Ionic Liquid	Ionic Conductivity (S cm ⁻¹)
Li CF ₃ SO ₃ (PEO/Li ⁺ ratio ~ 10)	5.23×10^{-5}
Li CF ₃ SO ₃ (PEO/Li ⁺ ratio ~ 30)	1.29×10^{-4}
Li CF ₃ SO ₃ (PEO/Li ⁺ ratio ~ 60)	7.64×10^{-5}
Li TFSI (PEO/Li ⁺ ratio ~ 30)	1.05×10^{-4}
Li PF ₆ (PEO/Li ⁺ ratio ~ 30)	4.68×10^{-5}
BMIM TFSI (PEO/Li ⁺ ratio ~ 30)	1.22×10^{-4}
BMIM PF ₆ (PEO/Li ⁺ ratio ~ 30)	5.29×10^{-5}

Figure 4.2 (a) Current density-voltage-luminance graphs of the LEEC devices based on the optimization of the PEO/Li⁺ ratios of the LiCF₃SO₃ salt. (b) Luminous current efficiencies of the optoelectronic characterizations. [37] Reused with permission from [37].

4.4.2 Active Layer Optoelectronic and Structural Characterizations

Figure 4.3 (a) Photoluminescence spectra of active films of pristine MEH-PPV, LiTFSI and LiCF₃SO₃ based active layer. Atomic Force Microscopy phase morphologies of (b) LiTFSI (c) LiCF₃SO₃ and (d) LiPF₆ based active layer with PEO/Li⁺ ratio of ~ 30. [37] Reused with permission from [37].

As illustrated in Figure 4.3a, PL spectra of different active layers based on the respective anions TFSI⁻, CF₃SO₃⁻ and pristine MEH-PPV thin film was collected (PF₆⁻ based active layers was not shown). All the films showed similar dual peaks arising from intra and interchain excitons. The single excited state species (intrachain excitons) appear at ~ 590 nm and the interchain excitons which has a characteristic shoulder tailing at ~ 630 nm. [40-42] The PL spectra is an observable manifestation of polymer morphology and can be correlated to the AFM phase morphology of the active layer seen in Figures 4.3b-d. In the active layer containing MEH-PPV and LiTFSI based electrolyte, we can see a smaller red shift in intrachain exciton peak compared to LiCF₃SO₃. LiCF₃SO₃ has larger domain

sizes and phase angle deviations compared to LiTFSI polymer blend (comparing Figure 4.3b and 4.3c). This enhanced phase separation of LiCF₃SO₃ electrolytes with MEH-PPV led to charge pinning and surface states creating intermediate energy bands within the bandgap of MEH-PPV with vibrational relaxation pathways, thus, losing excitation energy. [43] Moreover, the reduced PL intensity at the LiTFSI interchain exciton wavelength meant a lower packing degree of MEH-PPV due to better phase miscibility. [44] All these points to improved dual phase polymer blend formations of PEO-LiTFSI electrolytes and the conjugated polymer. However, for the LiPF₆ based active layer, although it has similar PL spectra with LiTFSI sample, the LiPF₆ sample does not exhibit a bi-continuous structure in the AFM phase image seen in Figure 4.3d owing to limited salt dissociation and low ionic conductivities (Table 4.1).

4.4.3 Device Performances of PEO-LiX based LEECs

Active layers based on different anions were fabricated into a fully operational LEEC device. Optoelectronic characterizations (Figure 4.4a) indicated that TFSI⁻ based LEEC devices showed the lowest turn-on voltages of around 2.4 V. This value (V_{on}) is approximately equal to E_g/e (E_g is the band gap of MEH-PPV and e is the electronic charge constant), showing improved electrochemical doping and charge recombination. This was much lower compared to PF₆⁻ based LEEC devices and can be associated with the ionic conductivity values on the order of 10⁻⁴ S cm⁻¹ exhibited by TFSI⁻ and CF₃SO₃⁻ based LEEC devices. The consequences of low ionic conductivity (5 × 10⁻⁵ S cm⁻¹) of other anions are the reduced electrochemical doping with low redox currents and inferior turn-on dynamics during p-i-n doped region establishment.

Anions with large charge delocalization such as TFSI⁻ have relatively lower binding energies with its cation and allow easier salt dissociation resulting in high ionic conductivities. The TFSI⁻ anion has five resonance states compared to CF₃SO₃⁻ (4 resonance states) and PF₆⁻ (one) as seen in Figure 4.5a-c. [45] This allows facile ionic transport with PEO chains and subsequently effective doping and faster turn-on. These anions also differ in size which promotes dissociation of the larger anion (PF₆⁻ = 73.0 Å³;

$\text{CF}_3\text{SO}_3^- = 86.9 \text{ \AA}^3$; $\text{TFSI}^- = 163 \text{ \AA}^3$). [46] This agrees with the turn-on dynamics dependence on binding energies proposed by Stephan *et. al.* [1]

Figure 4.4 (a) Current density-voltage-luminance graphs of LEEC devices based on PEO/LiX ratio ~ 30 where ($X = \text{TFSI}^-$, CF_3SO_3^- and PF_6^-). (b) Luminous current efficiency characterizations showing a low voltage regime in blue and mid to high voltages above 3.2 V. [37] Reused with permission from [37].

In Figure 4.4a, CF_3SO_3^- based devices show a small turn-on voltage difference of ~ 0.3 V compared to TFSI^- due to its similar ionic conductivities and owing to the anticipated lower binding energy of LiTFSI salts compared to LiCF_3SO_3 supported by the aforementioned larger anion volume. Moreover, LiCF_3SO_3 based LEEC devices exhibiting higher current ($10\text{--}600\text{ mA/cm}^2$) that would normally enhance joule heating and bring the device close to the T_g of the electrolyte (400 mA/cm^2 would result in device temperatures of $60\text{--}80\text{ }^\circ\text{C}$) which increases ionic conductivity. [47-49] However, it did not match up to the LiTFSI based LEEC device and sped up the thermodynamically favoured unwanted side reactions or induce micro-shorts. [21, 29, 50] Steady and linear increase of current density led up to its eventual device degradation. In Figure 4.4b, at the low voltages of $2.0\text{--}3.2$ V, high LCE point towards efficient doping of TFSI^- into MEH-PPV. Above 3.2 V, LiCF_3SO_3 based LEEC devices showed higher LCE between $3.2\text{--}4.4$ V with device degradation onset above 4.4 V. In the case of LiTFSI based LEEC devices, it showed stability in the high voltages regime (> 4.4 V) due to enhanced electrochemical stability windows with correlation from Figure 4.4a and Figure 4.6. CIE coordinates of devices did not differ during high operation voltage which points to stable colour purity (shown in Figure A.2 and Table A.1)

Low current densities ($\sim 10\text{ mA/cm}^2$) of PF_6^- based LEEC devices is shown in Figure 4.4a. This is in agreement with the finding that LiPF_6 based MEH-PPV LEEC device required high voltages of 30 V but only managing brightness values of 0.2 cd/m^2 . [11] Thus, it might require voltages probably above 10 V for any meaningful light emission values ($\sim 10\text{--}100\text{ cd/m}^2$). In this voltage regime, it is intuitively too large and not within its electrochemical stability windows, leading to over-reduction and over-oxidation of MEH-PPV with unwanted side reactions. This would naturally speed up degradation processes. PF_6^- anion also has a history of lower doping ability in MEH-PPV compared to CF_3SO_3^- anion in a study conducted by Holt *et. al.*, evident from the lower optical contrast of electrochromic experiments along with irreversible doping. [51] LiPF_6 is inherently thermally and environmentally unstable. At slightly elevated temperatures of $60\text{ }^\circ\text{C}$, it decomposes into an insulating compound LiF and produces a gas, which prompts electrode delamination seen in Chapter 2, Figure 2.1. [52-55] Residual water

degradation mechanisms predicted by density functional theory (DFT) calculations include more unwanted by products such as acidic HF gas. [56]

Figure 4.5 Resonance states of different anions (a) TFSI⁻, (b) CF₃SO₃⁻ and (c) PF₆⁻. [37]
Reused with permission from [37].

4.4.4 Electrochemical Stability Window of LEEC Based on PEO-LiX (X = TFSI⁻ and CF₃SO₃⁻)

Figure 4.6 Cyclic voltammetry data of the doping and de-doping process of LiTFSI and LiCF₃SO₃ into thin films of MEH-PPV. [37] Reused with permission from [37].

Figure 4.6 shows the cyclic voltammetry of the two better performing active layers, LiCF₃SO₃ and LiTFSI. The anion doping in the positive potential range effected by TFSI⁻ shows a lower onset potential due to the doping onset at around -0.37 V, compared to -0.13 V by CF₃SO₃⁻ anion. At 1 V, it also shows a thermodynamically favourable over reduction of the electrolyte system containing the CF₃SO₃⁻ anion compared to TFSI⁻ anion. This shows the stability of TFSI⁻ in the positive potential range. In the negative potential range of TFSI⁻ based LEEC device, it follows an obvious reversible n-doping behaviour before over reduction potentials whereas CF₃SO₃⁻ based LEEC devices would naturally show over reduction before n-type doping of MEH-PPV, giving it lesser electrochemical stability. This results support the behaviour seen in Figure 4.4a where the TFSI⁻ based LEEC device does not show apparent degradation from 4.4 V to 5 V.

To understand the thermal behavior of the polymer blends with different types of salt, modulated differential scanning calorimetry (mDSC) was performed on the as prepared films with the same processing history.

4.4.5 Thermal Properties of Active Films

Figure 4.7 Non reversible heat flow modulated DSC thermographs of active films based on different anions (a) LiTFSI, (b) LiCF₃SO₃ and (c) LiPF₆. [37] Reused with permission from [37].

Figure 4.7a-c shows the melting points collected by mDSC studies of the PEO-LiX based electrolytes as the amorphous nature of MEH-PPV would not produce an observable melting peak. Lower latent enthalpy of melting of 14.16 J/g and lower melting point is observed for LiTFSI based active layers. This further strengthens the hypothesis that LiTFSI leads to lower energy requirements for p-i-n junction formation. Early anion studies by L. Edman *et. al.* showed that PEO₁₀-LiTFSI electrolytes have a lower melting point of around 41-47 °C compared to PEO₁₀-LiCF₃SO₃ which is 1.5-3 times higher at 60-120 °C. [18] Figure 4.7c shows the probable degradation of LiPF₆ with two distinct melting peaks. The higher melting point of 166.61 °C was due to the high melting point

of LiF insulator where small amounts might have irreversibly produced giving the active layer small crystalline domains. These minute by products would enhance the destruction of electrolyte and interfaces. The other melting point at 71.54 °C is attributed to the PEO-LiPF₆ electrolyte.

4.4.6 LEEC Device Performance Based on BMIM⁺ Cation

Figure 4.8 Current density and brightness as a function of voltage of LEEC devices based on BMIM⁺ cation with differing anions (TFSI⁻ and PF₆⁻) where brightness and current values were taken after it was stabilized.

To revalidate the effect of the anion, the PEO-Li⁺ based salts were substituted with BMIM ionic liquid based electrolytes due to its chemically and electrochemically stable nature with a large potential range, its high ionic conductivity and nonvolatile nature, and water insensitivity. The same PEO/cation ratio of 30 was maintained. Ionic conductivities were measured and TFSI⁻ based PEO-ionic liquid electrolytes consistently showed high values of $\sim 1 \times 10^{-4} \text{ S cm}^{-1}$ (Table 4.1). On the Figure 4.8, it is evident that the BMIM TFSI ionic liquid based device showed better performance starting from the low to intermediate voltage ranges and this is related to its phase morphology (seen in Figure 4.9a-b). It has much lower turn-on voltages, consistent with behaviour observed in Figure 4.4a. Quantum mechanical calculations also show a larger dissociation energy of PF₆⁻

anion vs TFSI⁻ anion when paired with BMIM⁺ (80.7 vs 76.38 kcal mol⁻¹). [57] This proves the anion dominance in performance matrices of LEEC devices.

Turn-on voltage differences between BMIM TFSI and LiTFSI was ~ 0.2 V due to the small phase miscibility issues of hydrophobic BMIM⁺ and hydrophilic PEO, whereas PEO dissolves large quantities of alkali metal cations easily. Due to this phase miscibility albeit on a small scale, ionic liquid domains would exist and incomplete dissociation of ions from the PEO-ionic liquid matrix would occur. In Figure 4.8, the BMIM TFSI based LEEC device peaked at 4.2 V with brightness values of ~ 100 cd/m². Voltages above 4.4 V degrades the film due to the domains of ionic liquids forming current leakage pathways creating a current density of > 400 mA/cm².

Phase morphology studies (seen in Figure 4.9a-b) also show that the BMIM TFSI ionic liquid showed lesser phase separation compared to BMIM PF₆ and smaller domain radius (< 200 nm vs 300-500 nm) which is critical for LEEC performance during salt dissolution. Moreover, BMIM PF₆ is also known to have phase separation issues with MEH-PPV due to polarity differences. [21]

Figure 4.9 (a) Atomic Force Microscopy phase morphologies of BMIM TFSI based polymer blend with ratio PEO/BMIM⁺ ~ 30 and (b) BMIM PF₆ based polymer blends with PEO/BMIM⁺ ratio of ~ 30 .

4.5 Conclusion and Outlook

In this chapter, the effect of anions and its dominant character in LEEC performance was studied. Optimizations of PEO/Li⁺ ratios were conducted to identify the right balance between phase morphology, ion transport characteristics and resistance. This optimized ratio was extended to different anions. Formation of p-i-n junction in conventional LEECs based on p-type conjugated emissive polymers is dependent on the properties of its anions. It directly affects the LEEC devices and alters its turn-on dynamics, maximal brightness and electrochemical stability potentials. Anions that offer large anion volume, high resonance states and ionic conductivity values deliver the best performance. PEO-LiTFSI based electrolytes offered adequate ionic conductivities of $\sim 10^{-4}$ S cm⁻¹ similar to that of PEO-LiCF₃SO₃. Improved phase miscibility and smaller domain size are observed in the LiTFSI based LEEC active layer. Moreover, photoluminescence spectra shows reduced interchain exciton intensities due to reduced aggregation and phase separation effects. Lesser intraexciton peak shifts of around ~ 5 nm is also observed when compared to LiCF₃SO₃ based active layers due to reduced charge pinning at electrolyte/MEH-PPV interfaces. Device performances were extracted and supported such interpretations. The PEO-LiTFSI based LEEC device showed lower turn-on voltages than conventional PEO-LiCF₃SO₃ based LEEC devices and larger electrochemical stability window that was confirmed with cyclic voltammetry tests. Thermal studies of the active layers showed a reduced latent enthalpy of melting for LiTFSI based active layer confirming the reduced energy required for dissociation and ionic conductivity enhancement due to joule heating. On the other hand, LiPF₆, shows lowered doping ability with resultant poor device brightness due to low ionic conductivity and highly probable formation of unwanted species such as LiF and HF. This hypothesis was extended to other cation types such as BMIM⁺ ionic liquid and similar properties were shown. Quantum mechanical calculations confirmed the lowered binding energies. However, compared to Li⁺ based devices, BMIM TFSI showed slightly less phase miscibility due to its hydrophobic/hydrophilic incompatibilities that acted as short circuit pathways during optoelectronic characterizations at mid voltages that degraded the device.

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Chapter 5

Anion-Polymer Complexation in Wavelength Tunable Quantum Dot Light-Emitting Electrochemical Cells

Recombination zone engineering allows for enhanced LEEC performance along with reduced self-absorption effects, short-circuit and exciton quenching mechanisms. Complexation between ionic liquid and polymer is shown to be another way to tailor the ion concentrations which affects doping propagation and eventual recombination zone. Quantum dots (QD) addition into polymer matrix allows emission characteristics with quantum confinement effects leading to small full-width half maximum of the emission peak and colour purity. In this chapter, complexation behaviour between bis(trifluoromethylsulfonyl)imide (TFSI) anion (from BMIM TFSI ionic liquid) and Poly[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN-DOF) polymer matrix is studied and shown to improve brightness and reduces turn-on voltage. Photophysical studies show the reduction of interchain interactions and enhanced PL due to BMIM TFSI addition. X-Ray Photoelectron Spectroscopy (XPS) studies confirm such complexation behaviour. A new recombination zone engineering mechanism via complexation behaviour is proposed. QD addition into the optimized active layer shows further reduced turn-on voltages and maximal device brightness based on spectral integral overlap with wavelength tuning capabilities.

5.1 Rationale

Towards sport performance monitoring in different environments require specific wavelength tuning based on different colour contrasts. As such, colour changing devices are required. Recently, in LEEC technology, recombination zone engineering via fixed junction devices and dynamic junction centering have been shown to reduce many device performance limiting factors such as self-absorptions and short-circuit formations. Complexation behaviour of anions and polymers showed interesting properties that might allow for such recombination zone shifting properties. Moreover, QD incorporation into the blue light-emitting PFN-DOF moiety might allow wavelength tuning via FRET mechanism. Thus, it is hypothesized that complexation behaviour between ions from the ionic liquid and polymer matrix will reduce the eventual p-doped region, centering the recombination zone. Furthermore, the addition of QD into the polymer:ionic liquid (IL) matrix will allow for enhanced emissions, wavelength tuning and narrow emission linewidths.

5.2 Introduction and Motivation

Light-emitting electrochemical cells have emerged as an alternative lighting technology due to its advantageous properties. Commercially available organic light-emitting diodes have impressed consumers with its drive towards thinner, larger and brighter displays. However, its multilayered vacuum-atmosphere fabrication techniques [1] poses a downside as high cost will hinder its future development. Light-emitting electrochemical cells in contrast will prove as an immediate attractive alternative with studies showing low-cost processing such as ambient large-area slot-die coating, [2] inkjet printing, [3-5] rod and/or blade coating, [6] spray-coating [7, 8] and an exclusively solution-processed organic device [9, 10].

This revolutionary mechanism, first discovered by Pei *et. al.*, [11] overcomes much fabrication and cost issues but its technology has been hindered due to inherent problems such as non-centered recombination zone affecting device lifetime, seen in theoretical

and experimental sandwich and planar light-emitting electrochemical cells. [12-24] Existence of this recombination zone close to the cathode enhances short-circuit probability or reduces lighting efficiency due to doping-induced short circuits, [20] metal-induced exciton quenching, [26, 27] possible limited n-type doping [14, 28], interfacial metal-oxide formation [24] and self-absorption due to neighboring doped regions. [29, 31]

Research towards recombination zone engineering is seemingly divided into a two major groups. Fixed junction light-emitting electrochemical cells and centered dynamic junction light-emitting electrochemical cells. Fixed junction light-emitting electrochemical cells have been studied by employing cross-linkable electrolyte bearing acrylate functional groups [32-34], ion-transport materials with high $T_g \gg$ Room Temperature (R.T.) [35-37], electrochemical polymerization of ionic liquids (ILs) [38] and porous interlayer localizing the recombination zone. [39] Centered dynamic junction light-emitting electrochemical cells revolves around tailoring carrier mobilities with induced traps, [40] n-doped regions having significant electronic conductivity, [41] altering cation-doping concentration using Li^+ , K^+ and Rb^+ [15] and spatial control of emission zone using gate control, [42-44] with much advances only having a one sided approach. However, in conventional active layers in light-emitting electrochemical cell revolves around semiconducting conjugated emissive polymers such as Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), Super-Yellow (SY) and Poly(9,9-dioctylfluorene) (PFO) are p-type with $h^+ \gg e^-$ mobilities, [45-47] due to the ease of design, synthesis and better air stability. Thus, reports of n-type organic materials have so far been of academic interest. This material limitation would lead to the dominance of the p-type doping and larger highly-doped areas, [48, 49] pushing the emission zone closer to the cathode, effects of which were earlier explained.

Ionic liquids have long been incorporated into polymer matrix for the use of light-emitting electrochemical cells. [37, 50-53] Addition of ionic liquid would improve the device performance but in practice, >50% mass ratio would make the films too soft for cathodic thermal evaporation. [52] TFSI based ionic liquids were usually chosen due to

its lower melting point and extensive charge delocalization. However, the structure-performance relationship was not clearly explained in these papers and focused more on the phase separation of the films. Recently, complexation behaviour between polymers and ionic liquids show interesting properties with lowered melting point of polymer electrolytes, [54-57] high complex stability constants forming quasi 'naked' BVIM⁺ cations [58, 59]. Novel electroluminescent conjugated polyelectrolytes derived from polyfluorene were synthesized bearing terminal tertiary amino groups which are electron donating due to electron rich Nitrogen. [60] This could lead to enhanced interactions between ions and polymers, altering its effective dissociation energy and doping propagation in turn-on dynamics of light-emitting electrochemical cells.

Semiconductor quantum dots such as CdSe [61], CdTe [62], InP [63] offer tunable emission spectra with respect to size, small full width half maximum spectra towards wider colour gamut, high photoluminescence (PL) quantum yield. Surface modification of these inorganic quantum dots such as ligand exchange or core-shell structures allows flexibility for altering its solubility in different chemical environments and interesting photophysical properties. [64, 65] However, the band alignment of such quantum dots require multilayered processing or blending into organic host for direct charge excitation or energy transfer mechanisms such as Förster Resonance Energy Transfer (FRET). [66]

In any case, quantum dots already offer a huge potential market with it being implemented in high-end liquid crystal display (LCD) TVs but faces tough competition from OLED TVs nonetheless due to its lower contrast ratio. Device incorporation of two different luminophores such as conjugated polymers and ionic transition-metal complexes show emissive spectra tuning [67] and recently reported bi-layer quantum-dot/inter transition-metal complex devices due to different charge injection barriers require band engineering and restricts the use of different inorganic or organic constituents. [68] Förster Resonance Energy Transfer is also another potentially wavelength tunable excitation method with dual blends in host-guest light-emitting electrochemical cells such as polymer blends, [69] small molecules [70, 71] and combinations of both organic and inter transitional-metal complexes. [72-74]

Combining both quantum dots and organic matrix would naturally harvest the advantageous properties of such. In recent, reports of single layer quantum dot light-emitting electrochemical cells are rare. CdSe/ZnS core-shell QD was admixed with Poly[(9,9-dioctyl-2,7-divinylene-fluorenylene)-alt-co-[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene] (PFOPV) and polymerizable ionic liquid allyltriethylammonium allylsulfonate (ATOAS) [38] to form fixed junction quantum dot light-emitting electrochemical cells. It reported charge quantum dot circumvention in doped areas recombining only in the undoped junction exhibiting voltage-independent dominant quantum dot emission with slight host emission. [75] Pure-quantum dot and white-light emission were fabricated using CdSe/CdS:PVK:BMIM PF₆ as the blended active layers. It proposed that ligand exchange of the insulating triethylphosphine oxide (TOPO) with 4-mercaptobenzoic acid (4-MBA) enhanced the miscibility of quantum dots with ionic liquid, facilitating enhanced charge injection and mobility. Other light-emitting electrochemical devices have also been fabricated utilizing perovskite nanoparticles, albeit with low luminance. [76] Although it is argued that host emission is unwanted in these active layers, it can actually serve as dominant wavelength tuning in circumstances where wavelength changes in the same device is required.

In this chapter, we present a novel mechanism utilizing complexation of ionic liquid anion with host polymer which reduces turn-on voltage and enhances brightness attributed to a centered recombination zone. This system can be further modified with addition of different emissive CdSe/ZnS quantum dots to show voltage dependent wavelength tuning.

5.3 Experimental Section

5.3.1 Chemicals Used

Chlorobenzene (99.8%), ACS reagent grade cyclohexanone ($\geq 99\%$), ionic liquid counterion 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM]⁺

[TFSI]⁻) ($\geq 98\%$) were purchased from Sigma-Aldrich. Indium Tin oxide (ITO)-coated glass substrates ($20 \Omega/\square$), (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate) (PEDOT:PSS) (AI 4083), Hellmanex II cleaning solution, UV-curable epoxy and glass encapsulation cover slides were purchased from Ossila Limited. Core-shell CdSe/ZnS quantum dots powder (520 nm, 580 nm and 620 nm PL quantum dot) were purchased from Ocean Nanotech and used without modifications. Poly[(9,9-bis(3'-(N,N - dimethylamino)propyl)-2,7- fluorene)-alt -2,7-(9,9-dioctylfluorene)] (PFN-DOF) was used as purchased from Luminescence Technology Corp.

5.3.2 Device Fabrication

Master solutions of 10 mg/ml concentrations were prepared: PFN-DOF was dissolved in chlorobenzene and heated to 60 °C. BMIM TFSI and CdSe/ZnS were dissolved in cyclohexanone and chlorobenzene respectively. Blends were formed by mixing the master solutions in appropriate mass ratios and left to stir on a magnetic hot plate overnight at 60 °C. The ITO glass slides were cleaned by a two-step ultrasonic treatments in Hellmanex II and deionized water. The substrates were then treated by a plasma chamber for 2 min to remove any organic residue on the ITO surface and as a hydrophilic treatment due to induced hydroxyl groups. PEDOT:PSS was spin coated on the ITO electrodes: 300 rpm; 5 sec. 4000 rpm; 60 sec to form a thin 50nm hole transport layer as described in chapter 4. After which, active layer blends were spin coated at using a two-step recipe: 300 rpm; 5sec, 800 rpm; 60 sec and dried at 60 °C overnight. The resulting film thickness (~200 nm) was measure by a Profile meter (Alpha-step 200, Tencor Instruments). Al electrodes was deposited by thermal evaporation at $p < 6 \times 10^{-4}$ Pa (rate = $0.2 \text{ \AA/s}$) to achieve a thickness of around 100 nm and a device area of 4.5 mm^2 . Encapsulation was done using a UV-curable epoxy and a glass cover slide under UV irradiation for 15 min. All device fabrication was carried out in an argon filled glovebox ($\text{O}_2 < 0.1 \text{ ppm}$; $\text{H}_2\text{O} < 0.1 \text{ ppm}$).

5.3.3 Device Performance Characterizations

Device optoelectronic measurements were characterized using a computer controlled Keithley Semiconductor Characterization System (4200-SCS) coupled with spectrophotometer (Konica Minolta Chroma Meter, CS-200) and ZIF Test Board (Ossila E221). Systematic device characterization was carried out after initial charging of LEECs at 6 V with 1 mA compliance for 5 mins at room temperature to form an initial p-i-n junction. Electroluminescence of the devices was characterized by a spectrometer, which includes a monochromator (Acton SP-2356) and thermoelectric-cooled CCD (Princeton PIXIS: 100). The thermoelectric-cooled CCD was cooled down to -75 °C when recording the spectra in order to reduce the background noise. The maximum enquiry speed of the CCD is ~10 ms/frame. Characterization of all devices were done in ambient. Current density-voltage-luminance characterization was done at 0.1 V/s from 0-16 V.

5.3.4 Characterizations of Solid-State Films and Electrolytes

Solid-state active layers were prepared in the same conditions to that used in the eventual device. Solid-state and liquid PL spectra were characterized by Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer ($\lambda_{\text{ex}} = 350 \text{ nm}$). Solid-state and liquid absorbance (Abs) spectra of were characterized by Agilent Technologies Cary 5000 UV-Vis-NIR. X-ray Photoelectron Spectroscopy (XPS) spectra were recorded using a PHI Quantera II spectrometer employing a focused monochromated Al K α source ($h\nu = 1486.6 \text{ eV}$). X-ray power is 1486.6 eV, spectrometer was calibrated and charge corrected to C 1s peak at 284.8 eV, spot size diameter was 200 μm , instrument base pressure was $\sim 10^{-7} \text{ Pa}$ and spectrometer resolution is 0.48 eV. The survey and narrow scan details are: Survey scan: Pass Energy 280eV, 10 sweeps, 1.0 eV/step, 0-1300 eV; Narrow Scan: pass energy 140 eV, 0.25 eV/step, C 1s 30 sweeps 276-296 eV, N 1s 70 sweeps 390-410 eV, O 1s 30 sweeps 521-541 eV, F 1s 30 sweeps 679-699 eV, S 2p 50 Sweeps 155-175 eV. The software used for curve-fitting was CasaXPS version 2.3.1PR1.1. All peaks were fitted using a Shirley background and Voigt line shapes (Gaussian 73%, Lorentzians 27%). Full width at half maximum (FWHM) constrains of ~ 1.6 were applied to all

spectra. [77] Residual standard deviation of all spectra was <3.5%. Spectral integral overlap calculations were made using a/e version 2.2 UV-Vis-IR Spectral Software with MATLAB Compiler Runtime version 8.3 (R2014a, Win64-bit).

5.4 Results and Discussion

5.4.1 Photophysical Properties of Ionic Liquid-Polymer Active Layer

The LEEC active layers were fabricated based on blends of PFN-DOF and BMIM TFSI ionic liquid (chemical structure seen in Figure 5.1). Optimization of the blend with various mass ratios (PFN-DOF:BMIM TFSI = 10:2.95, 10:5.9 and 10:8.85) were done with thin film photophysical characterizations done. In Figure 5.2a, it is observed that there was an overall PL intensity increase with increasing IL concentration. This correlates well with the PL of the diluted solution (1×10^{-6} M; based on PFN-DOF repeat unit) (seen in Figure A.3) where single molecule chains interaction with BMIM TFSI showed PL intensity increases. This shows the PL intensity dependence with ex-situ BMIM TFSI addition due to increased π conjugated associations. [78] In addition, IL does show small photoluminescence intensities around 425 nm (seen in Figure A.3) supported with optical studies by Paul *et. al.*. [79]

PFN-DOF:IL PL as illustrated in Figure 5.2a; trend A, showed small spectral red-shifts of ~2 nm of the 0-1 vibronic transitions. Vibronic transitions are the energy relaxation pathways of excitons where 0-1 correlates to lowest energy state of the first singlet state to the first excited state of the ground state ($S_{1,0} \rightarrow S_{0,1}$) thereby giving a lower energy wavelength. [80] These small spectral red-shifts are due to exciton energy losses due to charge trapping mechanisms. [81]

In the inset of Figure 5.2a, it shows the normalized PL intensities of the same graph. The graphs are normalized to the intensities of the first blue peak at 425 nm, ascribed to the 0-0 vibronic transitions of PFN-DOF due to the Polyfluorene backbone. [60] It is evident that there is an increase in blue colour purity with respect to the PL due to decreasing

trends of the lower wavelength emission (trend B and C). This also signals the suppression of unwanted broadband green emissions. [82] This effect is attributed to higher solubility of polymer chain with BMIM TFSI interacting with single or a few chains of PFN-DOF thereby reducing its self-aggregation and reducing interchain interactions. [83, 84] The absorbance spectrum provides support to this observation. In Figure 5.2b, it shows the absorbance spectrum of the optimization blends of the active layers. There is a red shift in the absorption maxima from 387 nm to 401 nm with increasing IL concentration. This bathochromic shift of 14 nm shows the extended conjugation of polymer host and lesser aggregation leading to enhanced electron delocalization along polymer chains. [80, 85, 86] Photophysical investigations have pointed to a strong interaction between these two constituents. Without excessive heating treatments and catalysts used in the blend preparation, we investigate the possible complexations between these two molecules.

5.4.2 XPS Complexation Characterizations

XPS study of the PFN-DOF:IL blends was carried out to investigate the interactions between the two constituents. The survey scans and high resolution XPS spectra of PFN-DOF, BMIM and the blended active layer are shown in the appendix labelled as Figure A.4;A.5, Figure A.6; A.7 and Figure A.8;A.9 respectively. The survey scans show different peaks related to the different elements at their respective binding energies (BE). Detailed scans of the different elemental compositions are shown as the high resolution spectra. All deconvolutions of peaks and fitting was done using CasaXPS software. In these figures 5.3a-b, the peaks have been fitted with residual errors of <1%. In Figure 5.3a, the N (1s) of the blended active layer thin film is fitted to well-distinct components. N (1s) is splitted into four peaks: (1) The spectra in blue represents the N located on the BMIM^+ ring where it has a relatively larger intensity due to charge delocalization of the aromatic ring thus having two positive N atoms [87]; (2) The spectra in pink represents the N on the anion of TFSI^- and it can also be identified to the tertiary amino N belonging to PFN-DOF, thus not having a 1:1.9 concentration ratio between the nitrogen atoms in the IL [87]; (3) The spectra in green represents an oxidation of the tertiary amine

with a new peak at ~ 403 eV [88] which is ascribed to atmospheric oxidation due to transient ambient exposure and (4) The red spectra identified by the large chemical shift of tertiary amine peaks of more than 0.6 eV, larger than the resolution of the XPS instrument. This shows the oxidative state of the tertiary amine on the PFN-DOF polymer. The tertiary amine underwent positive BE shift with respect to the spectra shown in Figure A.5b. In Figure 5.3b shows the S (2p) fitted into 6 different peaks: (1) The spectra in blue and pink is fitted into doublet peaks S $2p_{3/2}$ and S $2p_{1/2}$ with a respective area constraint ratio of 1:0.511 and a positional constraint of (χ : $\chi + 1.16$ eV; where χ is the position of S $2p_{3/2}$) [89]; (2) The spectra in green and red are fitted to peaks which represent the TFSI⁻ extent of charge delocalization which can happen over the S-N-S moiety [90] or even the O=S=O moieties [49]; (3) The appearance of these two peaks of lower BE (164 eV and 162 eV) is attributed to reduction of S leading to S-N interactions between the TFSI⁻ anion and the terminal tertiary amine groups of the PFN-DOF.

Figure 5.1 Chemical structure of (a) repeat unit of PFN-DOF polymer and (b) ionic structure of BMIM⁺ TFSI⁻ ionic liquid. [60] Reused with permission from [60] and adapted from <http://www.sigmaaldrich.com/catalog/product/aldrich/711713?lang=en®ion=SG>.

Figure 5.2 (a) Photoluminescence and (b) Absorbance spectra of the blends with different mass ratios. The inset in (a) shows the photoluminescence of the active layer with normalized intensities. The different arrows shown in (a) shows the different trends observed upon BMIM TFSI ionic liquid addition.

Figure 5.3 High resolution spectra with fitted peaks of the blended active layer (PFN-DOF:IL = 10:8.85) (a) N 1s and (b) S 2p. The different coloured spectrums represents the different fitted peaks described as an inset in the picture. In (b) it shows the different reductions of the different elements of TFSI due to large charge delocalization.

5.4.3 Device Performance Characterizations

Active layers based on different IL concentrations were fabricated into a fully operational LEEC device. Optoelectronic characterizations (Figure 5.4) showed that with addition of IL up to a mass ratio of 10:8.85. It is important to note that any higher amount of ionic liquid would enhance the ionic conductivity of the film; however, due to its low melting temperature of $-3\text{ }^{\circ}\text{C}$ [91], the additional ionic liquid worsen its film-forming properties and became too soft for thermal deposition of cathode. In cases where film-forming is poor, it would lead to appearance of small holes ideal for short circuit formations, thicker layers are required to circumvent this which results in higher driving voltages. In this present case, IL addition to an extent can reduce the T_m of the active film which enhances ionic conductivity due to joule heating during post p-i-n junction formation. [92, 93] It will result in enhanced doping and increased electron and hole injection. The active layer with the highest IL concentration lowered the turn-on voltages to $\sim 13.5\text{ V}$ and exhibited maximum brightness of $\sim 20\text{ cd/m}^2$. This notably high turn-on voltage was due to the lack of ion conductors (seen in chapter 4) which would enhance ion transport but phase separation effects with large domains would ensue. To explain for the enhancement of brightness and lowered turn-on voltage, a novel mechanism is proposed that incorporates complexation behaviour observed due to XPS characterizations.

Figure 5.4 Current density-voltage-luminance characteristics of the LEEC devices based on PFN-DOF:IL blends with mass ratios indicated in the graph.

5.4.4 Complexation Mechanism

In the aforementioned blends of mass ratio PFN-DOF:IL = 10:8.85, it is shown to have better device performance matrices. In this case, complexation behaviour between TFSI⁻ anions and PFN-DOF functional groups due to strong interactions that promotes oxidation and reductions of the amine group of PFN-DOF and reductions in the Sulphur of TFSI⁻ respectively, resulting in TFSI⁻ anion pinning into the PFN-DOF matrix as shown in Figure 5.5. The tertiary amine groups functionalized on the PFN-DOF main chain has two lone pairs of electrons which can facilitate this complexation. Moreover, the complexation has reduced self-aggregation and interchain interactions, extending the conjugation of the polymer. In a recent paper by Amajjahe *et. al.*, BVIM TFSI was blended with β -Cyclodextrin forming complexations that were confirmed via Nuclear Magnetic Resonance Spectroscopy (NMR) and microcalorimetric measurements. [58, 59] The stability of such complexation was only perturbed at elevated temperatures of ~ 70 °C. Furthermore, it created quasi “naked” BVIM⁺ cations.

Figure 5.5 Schematic describing PFN-DOF:IL complexation. (a) Shows the PFN-DOF polymer structure with increased interchain interactions. (b) Depicts the ingress of BMIM TFSI ionic liquid where TFSI pinning in the PFN-DOF matrix reduces interchain interactions.

With correlation to our study, we propose that this complexation created a relatively higher concentration of freely moving BMIM^+ cations. This anion pinning leads to lesser anion concentration. As such, existence of anion trapping sites along with its lowered concentration leads to impedance of ion transport and reduced overall p-doping regions due to slower p-doping propagation rates. This would lead to eventual centering of a dynamic junction LEEC. In addition, the low current densities $< 10 \text{ mA/cm}^2$ would not sufficiently increase device temperatures to reverse the effects of the complexations. Such an effect of recombination zone engineering (seen in Figure 5.6) would naturally reduce the probability of short circuits, self-absorption effects and optimize device efficiencies as described earlier. With respect to recombination zone shifting studies conducted by Shin *et. al.*, BMIM^+ cation doping would be larger than monovalent cations such as Rb^+ and K^+ . [15] An enhanced electron delocalization due to the aromatic rings in BMIM^+ would require lesser n-type doping concentration per polymer repeat unit that leads to thicker n-type doped regions, further shifting the recombination zone closer to anode.

Figure 5.6 Schematic of recombination zone engineering brought on by anion-polymer complexation. (a) Electric double layer formation depicted by grey regions which are formed at the active layer/metal interfaces. (b) P-doping propagation rates are reduced much slower than conventional LEEC active blend systems. With relatively higher BMIM^+ concentrations, it is expected to have similar if not slightly higher doping propagation rate which leads to larger n-doped regions.

5.4.5 QD Incorporation into Active Layer Blend

For a QD-LEEC device to be fabricated, different sizes of CdSe/ZnS quantum dots were added into the active layer. The CdSe/ZnS was characterized by its PL emissions: 520 nm, 580 nm and 620 nm). In Figure 5.7, PL and the absorption (Abs) measurements of the PFN and QD were conducted to verify the possibility of FRET mechanism between polymer donor and QD acceptor. For efficient FRET mechanism to occur, the donor (PFN-DOF) E_g must be higher than the acceptor (QD) E_g . The second criterion is that there must be sufficient overlap between donor PL and acceptor Abs such that sufficient energy can be transferred without significant energy loss. Lastly, the distance between host and guest must be $<100 \text{ \AA}$. For the last criteria to be satisfied, it is imperative to increase the concentration of the acceptor to reduce the intermolecular distance, but, excess QD concentration causes strong aggregation induced non covalent interactions in the active layer due to noncovalent that leads to decrease in luminance and efficiency. These emission quenching mechanisms have been attributed to electronic coupling and exciton energy transfer. [94-98] Relevant studies on QD-LEECs used a polymer:QD ratio of 10:8 in which we have also showed reduced donor emission in thin film PL seen in Figure 5.8 (QD used was CdSe/ZnS with emission PL of 620nm). [75, 99] Thus, we have used this mass ratio for the relevant and subsequent QD-LEEC devices. Förster [100] in 1959 showed that the efficiency of FRET process depended on the equation:

$$E_{FRET} = \frac{R_0^6}{R_0^6 + r^6}$$

Where R_0 is the Förster radius (the distance at which the efficiency of energy transfer is 50%) and r is the distance between the donor and acceptor pair. The Förster radius depends on the fluorescence quantum yield of the donor in absence of the acceptor f_d , the refractive index of the solution η , the dipole angular orientation of each molecule K^2 and the spectral overlap integral of the donor-acceptor pair J and is given by the equation:

$$R_0(\text{\AA}) = 9.78 \times 10^3 (\eta^{-4} \cdot f_d \cdot J \cdot K^2)^{\frac{1}{6}} \text{\AA}$$

The spectral integral overlap J is given as:

$$J(M^{-1}cm^{-1}nm^4) = \frac{\int \epsilon(\lambda)f(\lambda)\lambda^4 d\lambda}{\int f(\lambda) d\lambda}$$

For simplification, we have assumed that the quantum yield f_d and extinction coefficient $\epsilon(\lambda)$, index of refraction η , orientation between fluorophores K^2 and donor-acceptor intermolecular distance r to be the same. Thus, we have used spectral integral overlap as the determinant for efficient FRET efficiency. Spectral integral overlap calculations were done using UV-Vis-IR Spectral Software based on the PL and spectra of the PFN-DOF:IL and different Abs spectrums of core-shell QD sizes with the results as follows:

Table 5.1 Spectral integral overlap calculations of the different QDs

CdSe/ZnS QD PL emission	Spectral Integral Overlap
520 nm	1.275 E ¹⁰ nm ⁴ /M cm
580 nm	2.169 E ¹⁰ nm ⁴ /M cm
620 nm	1.978 E ¹⁰ nm ⁴ /M cm

From Table 5.1, it is evident that CdSe/ZnS having a PL emission of 580 nm is expected to exhibit efficient FRET due to good spectral overlap. [101] In Figure 5.9a-c, solution PL was collected from ex-situ addition of 50 μ l aliquots of 5 mg/ml QD solution into 5 mg/ml PFN-DOF concentrations. Different QDs were used and it was confirmed that the emission of PFN-DOF donor was decreased with increasing concentration of QDs along with enhanced QD PL intensities. [102] One might point to the obvious red-shift of the polymer from thin film PL studies in Figure 5.2a. This is due to concentration dependent solution aggregation formation [103], which did not significantly impede the exhibition of FRET mechanism.

Figure 5.7 Overlapping of PFN-DOF:IL spectra with absorption spectra of CdSe/ZnS quantum dots to confirm the probability of Förster Resonance Energy Transfer mechanism.

Figure 5.8 PFN-DOF:QD (CdSe/ZnS; PL emission = 620 nm) optimization showing FRET mechanism in thin film PL. 10:8 mass ratio of polymer matrix to QD was used in chapter 6, similar to that seen in as reported QD-LEECs. [75, 99]

Figure 5.9 Confirmation of FRET via addition of small aliquots (50 μ L) of QD showing the decrease of PFN-DOF PL and increase of QD PL.

5.4.6 QD-LEECs Device Performance Characterizations and Wavelength Tuning

In Figure 5.10, it shows the different QD-LEECs based on different sizes of core-shell CdSe/ZnS and with differing amounts of IL. In general, it shows the enhanced electron injection efficiency of all devices when compared to PFN:IL devices in Figure 5.4. QD addition shows a dominant effect on the turn-on voltages. This is due to the existence of QDs near the cathodes that enhances the localized electron injection efficiency as ZnS shells inherently possess high electron mobilities of $\sim 250 \text{ cm}^2/\text{V} \cdot \text{s}$ whereas Polyfluorene are on the order of $10^{-5} - 10^{-3} \text{ cm}^2/\text{V} \cdot \text{s}$. [104] At low voltages, the turn-on voltages are QD dependent (based on PL QD emission, the turn-on voltage trend was $580 \text{ nm} < 615 \text{ nm} < 520 \text{ nm}$) giving respective values of 4.5 V, 5.5 V and 6.2 V albeit with small QD emission intensity at 6 V. This shows that the spectral overlap integral determines the turn-on voltage with the assumption that each QD has the same thickness of ZnS where we have assumed quantum yields to be the same (ZnS shell thickness affects QD

emission properties and quantum yield). [105] Therefore, it shows that there is no direct charge injection mechanism from cathode to QD and its emission is solely based on FRET. Moreover, it also determines the maximum brightness values and the current density trends.

Figure 5.10 Current density-voltage-luminance graphs of QD-LEECs. It shows the corresponding QD-LEECs based on three types of CdSe/ZnS having different PL emissions: 520 nm, 580 nm and 620 nm with mass ratios of (PFN-DOF:IL:QD = x:y:z).

For the devices having a PFN-DOF:IL:QD ratio of (10:5.9:8) is shown merely for turn-on voltage comparison and would not be discussed due to its lower performance matrices shown earlier. In Figure A.10, FWHM increment of the EL spectrum broadening is due to Polyfluorene backbone defect emissions formed upon higher potential bias which causes red-shifts in the dominant EL peak. For the devices having a PFN-DOF:IL:QD ratios of (10:8.85:8), at higher voltage and current densities, with correlation to Figure A.10: (1) For the devices containing 520 nm PL emission QDs (Device A2), it is expected that PFN-DOF will have degraded blue wavelengths due to higher current densities leading to lower energy photons absorbed by the QD, limiting its brightness. With correlation to Figure 5.7a, we can also see that the absorbance of this QD does not extend above 550

nm. (2) For the devices containing 580 nm PL emission QD (Device B2), it will still absorb more energy due to a higher absorption at 480 nm and 520 nm, which are expected to be emitted by the PFN-DOF:IL donor due to defect emissions usually seen in Polyfluorene derivatives. [106, 107] The device continues to increase in brightness even after 16 V showing brightness values of $\sim 40 \text{ cd/m}^2$. However, other devices using different QDs appear to taper off in its brightness after reaching a maximum brightness value. (3) For the devices containing 620 nm PL emission QD (Device C2), based on Figure 5.7c, it shows low absorptions within the range of 480–520 nm. Thus, it will not increase in brightness at high voltage ranges. The device shows maximum brightness at 14 V before tapering off. Moreover, the current density values of $\sim 250\text{--}300 \text{ mA/cm}^2$ might have induced significant joule heating and reversing the PFN-DOF:IL complexation as described earlier. Wavelength tunability was also observed for the QD-LEEC. This is the first voltage-induced emission wavelength tunable device reported so far in literature. Figures in A.11 describes the different EL spectra and CIE plots with voltage changes. Table 5.2 depicts the different colour emission of the devices upon increasing applied bias.

Table 5.2 Device pictures based on different QDs and different applied voltages showing wavelength tuning. (Mass ratio of PFN-DOF:IL:QD = 10:8.85:8)

Voltage/Device	A2	B2	C2
8 V
12 V
16 V

5.5 Conclusion and Outlook

In this chapter, we have shown that the addition of IL into PFN-DOF reduces aggregation, interchain interactions and lowers the green emission intensity in PL studies. XPS studies showed the existence of a positive chemical shift in the B.E. of tertiary amine belonging to PFN-DOF polymer chain and the lower BE peaks emerging in the S 2p XPS high resolution spectra confirm the strong interactions between TFSI⁻ and PFN-DOF. A mechanism based on this complexation between anion and polymer host was proposed which is expected to enhance the device performance via recombination zone shifting due to anion trapping as well as cation selection. This led to reduced turn-on voltages and enhanced maximum brightness values. Addition of core-shell CdSe/ZnS QDs into the PFN-DOF:IL matrix confirmed an efficient FRET mechanism with QD emission which dominated the turn-on voltages, and governed by the spectral integral overlaps. Moreover, it reduced the turn-on voltages by a significant amount due to localized electron injection from cathode to QD. Wavelength tuning due to enhanced FRET at higher voltages was presented.

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Chapter 6

Flexible LEEC Testing and Degradation Mechanisms

In this chapter, flexible LEEC devices are fabricated and tested in ambient with respect to bending tests to realize potential wearable applications. Slight degradation of device performances occurred when bent to a radius of 5 mm due to the exponential increase in the resistance of the ITO/PET substrates around the critical bending radii. Lastly, a flexible QD-LEEC device is shown to be driven at 10 V with white light emission confirmed via EL spectra and CIE plot. Degradation mechanisms are also discussed.

6.1 Introduction and Motivation

Flexible devices have long been a requirement in wearable applications as a means of safety or for ease and comfortable technological monitoring applications such as that seen in biomechanical motion analysis. LEEC offers simple fabrication, optimized charge injection and cathode requirements insensitive to work-function. Thus, simple and high brightness devices can be incorporated when LEECs are fabricated on flexible transparent conducting electrodes (TCEs). In this chapter, we have fabricated and tested superyellow LEECs due to the inherent high contrast ratio (of yellow light emission on black background) suitable in low light ambient environments which would facilitate ease of detection via inexpensive video cameras. Before, during and after flexing, the current density-voltage-luminance graphs are presented. In this chapter, QD-LEECs on flexible TCE based on active layer (from Chapter 5) are also fabricated and characterization of the device performance was carried out. Degradation mechanism will be discussed.

6.2 Experimental Section

6.2.1 Chemicals Used

Superyellow (SY) emissive polymer was purchased from Merck. Trimethylolpropane ethoxylate (TMPE) ($M_n \sim 450$), Potassium Bis(trifluoromethanesulfonyl)imide (KTFSI), Poly(vinylidene fluoride) (PVDF) ($M_w \sim 534,000$) and Dimethyl sulfoxide (DMSO Molecular Biology grade $\geq 99.9\%$) were purchased from Sigma Aldrich. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) (Al 4083), Hellmanex II cleaning solution, UV-curable epoxy was purchased from Ossila Limited. Indium doped Tin Oxide (ITO)/Polyethylene Terephthalate (PET) flexible transparent conductive substrates were purchased from Latech Scientific Supplies Pte. Ltd. (Transmittance 75-85%, $150 \Omega/\square$). Leitsilber 200 Silver Paint was purchased from Ted Pella Inc. Methyl Ethyl Ketone was purchased from J. T. Baker.

6.2.2 Flexible Device Fabrication

Master solutions of 7.5 mg/ml concentrations were prepared: SY, KTFSI and TMPE were dissolved in cyclohexanone and left on a magnetic hot plate to stir overnight at 60 °C. Blend solutions were created by mixing the master solutions to satisfy a mass ratio of (SY:TMPE:KTFSI = 1:0.1:0.062). It was left to stir on a magnetic hot plate overnight at 60 °C. ITO/PET finger electrodes were fabricated via etching of the ITO/PET substrates in Aqua Regia in the volume ratio of (HCl (37 % weight in water):HNO₃ (69 % weight in water):H₂O (deionized) = 3:1:1) under a hot plate at 60 °C in a fume hood for 2 mins to create electrodes of 5 mm width. PEDOT:PSS was spin coated on the ITO/PET substrates to form a hole injection layer of 50 nm. Active layer was spin coated (300 rpm; 5 sec, 2000 rpm; 60 sec) on the PEDOT:PSS to form a thickness of ~ 100 nm. Al cathode thermal evaporation ($p < 6 \times 10^{-4}$; rate = 0.2 Å/s) was done on the active layer to form a thickness of 100 nm cathode made up of Al/Au as a protection layer for Al during transient atmospheric events and a device area of 15 mm². Encapsulation was done using a UV-curable epoxy and a glass cover slide under UV irradiation for 15 min. All device fabrication was carried out in an argon filled glovebox (O₂ < 0.1 ppm; H₂O < 0.1 ppm). Silver paint was applied on the ITO electrodes to act as a contact point for the anode.

Flexible QD-LEECs on ITO/PET substrates were fabricated using the active layer constituent mass ratio of (PFN-DOF:IL:QD = 10:8.85:8). The QD used was CdSe/ZnS with a PL of 620 nm. For the ITO/PET based devices, finger electrodes were fabricated via etching of the ITO/PET to create electrodes of 10 mm width as described earlier. Two-step washing was done in similar fashion as described earlier. Spin coating of the PEDOT:PSS and active layers were done in the same method as described earlier. Thermal evaporation was done to form 100 nm thickness cathode made up of Al/Au as a protection layer for Al during transient atmospheric events. Encapsulation with the same UV-curable epoxy with a PET cover was used to form 50 mm² devices.

6.2.3 Device Performance Characterizations

Device optoelectronic measurements were characterized using a computer controlled Keithley Semiconductor Characterization System (4200-SCS) coupled with spectrophotometer (Konica Minolta Chroma Meter, CS-200). Systematic device characterization was carried out after initial charging of LEECs at 6 V with 1 mA compliance for 5 mins at room temperature to form an initial p-i-n junction. Electroluminescence of the devices was characterized by a spectrometer, which includes a monochromator (Acton SP-2356) and thermoelectric-cooled CCD (Princeton PIXIS: 100). The thermoelectric-cooled CCD was cooled down to -75 °C when recording the spectra in order to reduce the background noise. The maximum enquiry speed of the CCD is ~10 ms/frame. Characterization of all devices was done in ambient. Test during flexing were done such that the bending apparatus was tilted such that the spectrophotometer it was perpendicular to the device area. Current density-voltage-luminance device characterization was done with a scan speed of 0.1 V/s from 0-16 V for SY-LEEC and 0-10 V for QD-LEEC.

6.3 Results and Discussion

Contrary to our previous chapters, we have fabricated a LEEC based on superyellow due to its high electroluminescent performance, low turn-on voltages and long lifetime devices reported. The ion-transporter in mention was TMPE which has proved to evacuate the recombination zone during LEEC operation due to its strong coordination with the cation. [1] The salt used was KTFSI in which potassium ion has been a promising candidate for causing recombination zone shifting due to its higher electron delocalization radius than Lithium. [2] TFSI⁻ anion was used as it previously showed ability to lower turn-on voltage due to its lower binding energy and high number of resonance states (as we have found in Chapter 4). Devices were fabricated and their optoelectronic characterization was carried out. In Figure 6.1, it shows the different current density-voltage-luminance tests done on the same device before flexing, during flexing and after flexing. Before Flexing, the maximum brightness of ~ 20 cd/m² can be

achieved. The current density plateau at around 13 V shows the completion of dope region growth. [3] Brightness continues to increase steadily without onset of degradation.

During flexing tests from bending radii of 11.3 – 4.7 mm. Devices were only characterized at the 4.7 mm due to the limit of ITO/PET bending where any smaller value would increase the sheet resistance by a large amount. However, it showed degradation at that value which current densities were reduced by half when compared to the device while flexing. As seen in Figure 6.1 and 6.2, during flexing to the small bending radii of < 5 mm, the device resistance increases exponentially for the ITO/PET electrodes due to micro crack formation in which insufficient charge transfer occurs across the electrode. [4] Other degradation mechanisms would be discussed later. This reduced the current density and brightness during mid voltage range of around 7-15 V. When large voltage was applied across the device, it regained the same brightness and current densities at 16 V. To the best of our knowledge, there has been no characterization of SY based LEEC during flexing. In Figure 6.3, during the flexing test at bending radii of < 5 mm, the device anode and cathode faced tensile and compressive stresses respectively. For metal cathodes to face a compressive stress it would have easily created cracks and puncture into the soft matrix of the active layer which is made up of SY and low molecular weight TMPE. At low voltage 6-15 V, the defects reduced the current densities due to lowered sheet resistances. At higher voltages, these defects enhanced the current densities at higher voltages due to enhanced local electric field concentrations leading to ‘recovered’ current densities and brightness.

After the flexing tests with devices back to its flat state, due to the inherent non-recoverable nature of ITO/PET electrodes, slight degradation of the TCE occurred and further reduced the current densities. Turn-on voltage shifts due to substrate degradation was shifted no more than 2 V. In Figure 6.1, degradation mechanisms after flexing test could arise from a host of issues. Firstly, SY based LEECs are predominantly not air-stable due to its inherent reactivity of constituents. LEECs are made of emissive polymer, (salt and PEO). Residual oxygen and water content due to transient atmospheric events is one cause of degradation during the flexing test conducted in ambient. The degradation is

exacerbated by the exertion of mechanical flexing test; the air-stability is less severe when the devices are tested in flat state. Other form of degradation during tests was due to photo-oxidation leading to carbonyl formations [5, 6] which interrupted the conjugation and reduced conjugation length. However, the dominant degradation was caused by the dark spot formation mechanism where cracks caused oxygen and moisture ingress leading to cathode delamination as proposed by Schaer *et. al.* [7], and which was also observed by Asadpoordavish *et. al.* [8] in similar experiments. This led to reduced current densities of the device. Electroluminescence eventually decreased and further oxidation caused a full device failure. In Figure 6.2, at around 5 mm, cracks and delamination in the UV-curable epoxy can be found during bending owing to the limited flexibility. This allowed oxygen ingress and initiated the photo-oxidation process which reduced the EL intensities of the emissive polymer.

Figure 6.1 Current density-voltage-luminance of the SY-LEEC Flexible device. Three optoelectronic tests were done. Flat is the device characterization at the original state without any stress application. Flexing is the device characterization during flexing with a bending radii of 4.7 mm. After flexing is the device characterization after the bending test in its original flat state.

During further flexing tests, the cured epoxy was delaminated from the device which stripped out the metal contacts and prevented charge injection as well as exposing the active layer to more oxidative processes. It is pertinent to note that flexibility bending radii requirements are very much governed by its application. It is therefore important to develop air-stable and flexible active and encapsulation materials for LEEC. Currently, there are not many commercialized encapsulations with small bending radii which are

required for realization of wearable devices. Thus, the need is there for such materials.

As discussed in Chapter 2 for wearable devices, different parts of the body require different minimum bending radii capability of devices. In Figure 6.4 electroluminescent spectra of the SY-LEEC devices were collected at 10 V, the results are comparable with other SY OLED studies. [9]

Figure 6.2 Photos of flexing of the SY-LEEC device with different bending radii.

Figure 6.3 Device cross section during bending showing the compressive and tensile stresses on the electrode. The Neutral Axis where the stress/strain vanishes is not of concern as the materials are polymeric and not likely to have adverse reactions to stress compared to the electrodes.

Figure 6.4 Electroluminescence spectra of SY at 12 V.

Figure 6.5 (a) Picture of QD-LEEC fabricated on ITO/PET tested without flexing (in flat state). (b-c) Picture of QD-LEEC with slight flexing, red circle denotes small black spots growth after a span of 1 minute. (d) Current density-voltage-luminance graph of the QD-LEEC device (e) EL spectra taken at 10 V bias. (f) CIE plot showing the coordinates at 10 V.

QD-LEECs were also fabricated based on ITO/PET which showed FRET mechanism and white light based on PFN-DOF and QD dual chromophore emissions. Results on a large device area (50 mm²) (Figure 6.5a-c) was shown without flexing and with flexing tests. Device performance characterization is seen in Figure 6.5d with EL spectra and CIE plot in Figure 6.5 e-f. In Figure 6.5b and 6.5c, black spot formation was due to local film inhomogeneity during fabrication of device. The dark spot growth region eventually spurred the device failure as it showed pronounced substrate deformation arising from that area due to enhanced joule heating events. The dark spot was characterized by either high electrolyte concentration and or local thinning of the active layer, seen also in studies conducted by Asadpoordarvish *et. al.* [8], whom also utilized the same UV-curable epoxy. This defect spot suffers higher strain concentration during the flexing test subjected to the device. Due to these two possible mechanisms, it enhanced the local current densities which evolved into high joule heating points leading the device failure.

6.4 Conclusion and Outlook

SY-Flexible LEEC devices have been tested due to its inherent high contrast ratio which is suitable for biomechanical motion analysis in dark ambient environments. The device without applied stress can reach a brightness of $\sim 20 \text{ cd/m}^2$. From the current density-voltage graphs in Figure 6.1, we could see the formation of the p-i-n junction due to the plateau observed at $\sim 13 \text{ V}$. This shows the corresponding voltages where devices should be operated below this value to reduce the probability of electrochemical side reactions for the as mentioned active layer mass ratio. Performances show slight degradation due to bending radius $< 5 \text{ mm}$ whereby resistance of the electrodes increase exponentially, rendering lesser charge transfer into the active layer. With comparison to Liang *et. al.*, the device showed 4 times lower current densities but brightness values were the same order of magnitude. [11] In that study, the substrate was a Silver Nanowire-Polyurethane Acrylate composite electrode which had high flexibility due to the substrate that allowed the device to be folded over a $400 \text{ }\mu\text{m}$ thick cardboard. Furthermore, the study used trimethylolpropane ethoxylate acrylate (ETPTA) that would crosslink upon heat and light to form a frozen junction LEEC. Moreover, subsequent addition of PEO enhanced the mechanical properties of the substrate. Another study used flexible chemically derived graphene/PET as the cathode where bending tests did not show inhomogeneity of light emission although without device characterization during the flexing test. [12] In our device, turn-on voltage shift due to substrate degradation after flexing test was found to be $< 2 \text{ V}$. Optoelectronic tests have been conducted to show its brightness stability measured under bent state. Degradation mechanisms point towards inflexibility of ITO/PET and epoxy which caused sheet resistance changes and ingress of oxygen leading to lowered brightness due to cathode delamination. It is concluded that there is a device performance dependence on the flexibility of the electrode rather than the active layer. Lastly, a flexible QD-LEEC fabricated on ITO/PET showed a white light emission at 10 V without flexing. Further flexing tests showed the device degradation based on joule heating due to dark spot formation.

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Chapter 7

Thesis Conclusion and General Outlook

In this chapter, the novelty and scientific advancements of the thesis are discussed. Anion effects in polymer electrolyte systems have been investigated, with the objective to reduce turn-on voltages of LEECs. Complexation used to tailor the recombination zone shifting is presented as a new mechanism for reducing turn-on voltage and enhancing maximal brightness. This chapter presents a summary in the contributions to LEEC technology accompanied by reflections of the results and general outlooks. Future works based on planar LEEC was proposed.

7.1 Scientific Contribution and Conclusion of this Thesis

This thesis is devoted to addressing charge injection issues faced in conventional p-type polymers in single active layer organic based light-emitting devices. First, HOMO engineering via materials selection has allowed for efficient charge transfer leading to lower driving voltages. Next, salt and ion transporter were added to enhance the electron injection of these materials. In the LEEC operation mechanism, doped region with regards to the anions (which normally play a significant role due to p-type properties of the commonly used emissive polymers) was the primary focus. Anions selection and optimization were used to reduce its turn-on voltage. Finally with careful selection of anions and its desired effects, recombination zone shifting due to anion-polymer complexation creates a relative increase in BMIM⁺ cation concentration. This allows for larger n-doped region stabilizing the recombination zone in the center. Appropriate techniques were used to characterize and analyze the results to form the proposed mechanisms. Achievements and novelty of this thesis are discussed in the following sections.

7.1.1 Anion Selection for Low Turn-on Voltage

This thesis studies the constituents that make up the electrolyte system which has proved to be dominant in LEEC performances. Most studies have pointed to the cations as a way to tune performance. Due to the p-doped region having a better conductivity and a larger area as seen in planar LEECs, it was directed towards its investigation where anions are the ions which make up the p-doped region. New insights and a proposed mechanism with regard to the binding energy and electron delocalization of TFSI⁻ anion have shown to reduce the turn-on voltage to 2.4 V and enhance electrochemical stability window when paired with the Li⁺ cation in PEO matrix. In this thesis, different anions have been used to prove this effect. However, cations should also be considered as a means to strengthen this conclusion. In comparison with thorough literature reviews based on doping zones in LEEC, the novelty in this thesis lies on the elaboration of the resonance states and binding energies on the ions in polymer, which opens a pathway to design new

anions for performance enhancement in LEEC.

7.1.2 Anion-Polymer Complexation for Recombination Zone Engineering and Voltage Induced wavelength Tuning in QD-LEECs

Along with investigation of doping regions is the ability to tune and shift the recombination zone which prove to be detrimental to LEEC stabilities if it is too close to the cathode. In chapter 5, it was highlighted that the advantages of ionic liquid addition enhanced the PL intensities, and reduced interchain interactions implied from PL and Abs investigations. Complexation was confirmed from XPS studies that showed strong interactions between TFSI⁻ and PFN-DOF polymer matrix. Recombination zone shifting mechanism based on anion pinning at low device current densities have been proposed. This work also highlights the need to tackle n- and p-doped regions through proper selection of cations and anions, rather than a normal one sided approach seen in literature. This thesis shows the novelty in the proposed mechanism based on anion pinning that has not been discussed before in relevant literature which is based upon cation doping concentrations or by chemical fixation of the p-i-n junctions of LEEC. Moreover, this thesis is the first to show the emission wavelength tunability based on facile QD incorporation whereby FRET mechanism allows for donor to acceptor energy transfer, allowing the device to harness the emissive properties of the QD. QD in general also reduces turn-on voltage and it proves to be a universal method to determine the turn-on voltage based on spectral integral overlaps as observed in chapter 5. This blend can be fully extended to devices operating at different red wavelengths, if the spectral overlaps allow. However, polymer systems based on terminal tertiary amine groups with better electroluminescent performances can be characterized as the polymer used in this thesis did not have high brightness values. [1]

7.1.3 Flexible LEEC Testing and Degradation Mechanisms

The flexible LEEC testing showed that device performance during flexing was very much dependent on the mechanical properties of the transparent conducting electrodes as micro

crack formation caused local variations in sheet resistances that reduced the current densities and brightness of the devices. The maximum driving voltages were also determined to be 13 V for the flexible LEEC, in order to avoid unwanted electrochemical side reactions.

7.1.4 General Outlook on LEEC technology

In this thesis, approaches such as anion selection and anion-polymer complexation are employed to elucidate the contribution of the electrolyte determining the performance and recombination zone centering efforts towards reducing turn-on voltages and enhancing brightness of LEEC devices. However, there are challenges still present in LEEC that need to be addressed. LEEC technology has come a far way; however, it still has yet to reach the heights and achievements of OLED technology, despite the simple fabrication processes of LEECs.

One persistent problem is the electrochemical stabilities which upon high voltage application, causes over-oxidation or over-reduction leading to undesirable electrochemical side reactions [2], leading Stephan *et. al.* to conclude that here is an inherent tradeoff between emission intensity and device efficiency [3] . This ultimately reduces the device lifetime and efficiency after device usage. One direction that researchers can focus on is to widen the electrochemical stability windows of polymer electrolytes. This reduces the probability of side reactions and degradations, promoting its commercialization. In designing and synthesizing new polymer ion transporters, it would be then possible to create more stable devices in future.

Lastly, it is well documented that light emitting polymer based devices have limited theoretical efficiencies (~25%) due to its light emitting mechanism based on fluorescence, hindering large increments in its brightness. OLEDs have so far reached a maximal brightness at $\sim 100,000 \text{ cd/m}^2$ albeit at pulsed operation [4], whilst the brightest LEEC device could only reach around $14,000 \text{ cd/m}^2$. [5] This potentially prevents LEEC technology from overtaking OLED. Nonetheless, new research towards formulation of

high theoretical efficiency molecules (close to 100%) initiated by Adachi's group [6] based on thermally activated delayed fluorescence can potentially enhance brightness of LEECs much more than it is now. Preliminary works synthesizing new organic emitters based on Adachi's concepts have been conducted by Wong *et. al.* [7] Thus, there is a critical need for synthesis of newer, more efficient organic emitters towards higher brightness devices, which have potential applications in a wide range of industries.

7.2 Future Work

7.2.1 Complexation Behaviour and TFSI⁻ Anion Effects in planar LEECs

The results described in chapter 4 points towards the low turn-on voltage due to the resonance states and low binding energy with cations. Moreover, it was proposed in chapter 5 that anions pinning due to complexation effects leads to recombination zone shifting. It is proposed that planar Light-Emitting Electrochemical Cells (device schematic in Figure 7.1) to be fabricated to support these mechanisms where its effects have been observed based on current density-voltage-luminance studies. This structure has been used mainly to ensure a direct observation on doping dynamics and operational mechanisms. [7, 8] This is with the assumption that planar LEECs work based on the same operating mechanisms as sandwich LEEC devices. In addition, direct thermal investigations on the real-time temperature monitoring during LEEC operation could provide a clearer picture on the effects of joule heating on LEEC performance.

7.2.2 Realization of LEEC on Green Substrates

Current available transparent conductive films have been fabricated on substrates such as polycarbonate [9], polyethylene terephthalate [10-16], glass-fabric reinforced plastic film [17], polyvinyl alcohol [18], poly(tert-butyl acrylate) [19], self-healing polymers [20], polydimethylsiloxane [21-23] and polyurethane acrylate [24]. The biodegradability of such substrates raised some concerns among the community. Recently, nanocellulose based electrodes have stirred the excitement due to its environmentally friendly

properties such as recyclable, biocompatible and degradable nature that are well received. It has reported high mechanical strength [25] due to enhanced fiber interactions with high transparency values and low surface roughness ($R_{\text{RMS}} = 6.3 \text{ nm}$) even when incorporated with Ag nanowires. [26] Preliminary results showing LEEC based on nanocellulose substrate albeit with low performance values show the feasibility of such devices. Along with the low current density values reported in chapter 6 which do not produce significant joule heating, it can be viable substrate for truly low cost flexible light-emitting devices. Our preliminary results can be shown in Figure 7.2, devices (schematic shown in Figure 7.2a) were first planarized by poly(vinylidene fluoride) (PVDF) there after spin coating of the anode consisting of (PEDOT:PSS:DMSO:Zonyl fluorosurfactant) (Figure 7.2b) where zonyl incorporation allows for spin coating onto hydrophobic substrates, reducing the need for plasma treatment that might damage the sensitive organic material based substrate. After which, active layer of PFN-DOF:IL:QD was spin coated with cathode thermal evaporation. Devices (Figure 7.2c) should be tested in a vacuum chamber to minimize atmospheric photo-oxidation mechanisms (Figure 7.2d-e).

Figure 7.1 Device schematic of planar LEEC whereby doped regions and recombination zone

could be observed directly during p-i-n junction formation.

Figure 7.2 Preliminary results and future work for LEEC active layers based on nanocellulose. (a) Schematic of the nanocellulose based device. (b) Picture of the nanocellulose based device with PVDF planarization layer and PEDOT:PSS blend spin coated to form as the anode. (c) Device picture during testing in vacuum chamber cum probe station. (d-e) Pictures showing the device light emission with low brightness when biased at 20 V.

7.2.3 Feasibility Study of Wearable LEECs in Biomechanical Analysis

The device in chapter 6, shows the brightness of flexible device which are well within the requirements for use in low-light environments. It is proposed that wearable LEECs based on flexible conductive substrates would be utilized in place of conventional LEDs for use in biomechanical analysis, using simple video camera detection, as seen in work done by Slawson *et. al.* [27] Wearable LEEC devices are planned to be mounted on the leg joints of human subjects to study its feasibility in such applications. Moreover, it is

important to evaluate the sensitivity of visible wavelengths based on contrast in different lighting environments and weather conditions towards fabrication of different devices for diverse sporting applications.

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Publication List

1. **Kenji Jianzhi Chee**, Pooi See Lee, “Modulated Charge Injection Barrier and Energy-Efficient Organic Light-Emitting Devices Towards Potential Applications in Sports Performance Analysis 1st International Conference in Sports Science & Technology (ICSST), 11-12 Dec 2014, Singapore (oral).
2. **Kenji Jianzhi Chee**, Pooi See Lee, “Light-Emitting Electrochemical Cells with Enhanced Electrochemical Stability and Lowered Turn-On Voltage for Next Generation Displays”, MRS-Spring, 2016, Phoenix, USA (oral).
3. **Kenji Jianzhi Chee**, Vipin Kumar, Cuong Viet Nguyen, Jiangxin Wang and Pooi See Lee, “Polymer Light-Emitting Electrochemical Cell Blends Based on Selection of Lithium Salts, LiX [X = Trifluoromethanesulfonate, Hexafluorophosphate, and Bis(trifluoromethylsulfonyl)imide] with Low Turn-On Voltage”, *Journal of Physical Chemistry C*, **2016**, 120, 11324-11330.
4. Jiangxin Wang, Chaoyi Yan, **Kenji Jianzhi Chee** and Pooi See Lee, “Highly Stretchable and Self-Deformable Alternating Current Electroluminescent Devices”, *Advanced Materials*, **2015**, 27, 2876-2882.

APPENDIX

Figure A.1 Nyquist Plots of (a) LiX ($X = \text{TFSI}^-$, CF_3SO_3^- and PF_6^-) and (b) of BMIM X ($X = \text{TFSI}^-$ and PF_6^-).

Figure A.2 CIE plot showing LiTFSI based LEEC (0.589, 0.410) with the device picture in the inset at a brightness of $\sim 100 \text{ cd/m}^2$.

Table A.1 Commission Internationale de L'eclairage (CIE) coordinates (x,y) at 4.2V. The CIE plots do not differ for devices at adequate brightness. For PF_6 devices, CIE plot deviation is due to much lower brightness values observed.

Salt/Ionic Liquid	X coordinate	Y coordinate
Li CF_3SO_3	0.5874	0.4119
Li TFSI	0.589	0.4104
BMIM TFSI	0.5958	0.4039
Li PF_6	0.6152	0.3751
BMIM PF_6	0.6105	0.383

Figure A.3 Diluted Photoluminescence of 2.4 ml (1×10^{-6} M; based on PFN-DOF repeat unit) showing the photoluminescence intensity increase of PFN-DOF:IL with ex-situ additions of BMIM TFSI ionic liquid. Photoluminescence experimental details are described in chapter 5.

Figure A.4 XPS Survey scan of PFN-DOF polymer.

Figure A.5 XPS High resolution spectra for (a) C 1s, (b) N 1s and (c) O 1s of PFN-DOF polymer.

Figure A.6 XPS Survey spectra of BMIM⁺ TFSI⁻ ionic liquid.

Figure A.7 XPS High resolution spectra for (a) C 1s, (b) F 1s (c) N 1s, (d) O 1s and (e) S 2p of BMIM⁺ TFSI ionic liquid.

Figure A.8 XPS Survey spectra of active layer containing (PFN-DOF:IL = 10:8.85) mass ratio.

Figure A.9 XPS High resolution spectra for (a) C 1s, (b) F 1s and (c) O 1s of active layer containing (PFN-DOF:IL = 10:8.85) mass ratio.

Figure A.10 PFN-DOF:IL = 10:8.85 EL spectra from (a-f) 6 V to 16 V.

Figure A.11 QD-LEECs showing wavelength tuning with respect to voltage increase based on different PL emissive QD: (a-c) 520 nm, (d-f) 580 nm and (g-i) 620 nm. (j-l) shows the respective CIE plots of the QD devices showing a change of coordinates with different applied bias.