Active Channel Field-Effect Transistors: towards high performance light-emitting transistors

Kristen Ann Tandy
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School of Mathematics and Physics
Abstract

This thesis describes the study of the development and device physics of organic field-effect transistors and organic light-emitting field-effect transistors. Using chemical and physical properties of organic semiconductors such as light emission, multi-functional devices, or “Active Channel Field-Effect Transistors” can be created. This thesis first describes the creation of basic ambipolar FETs before building on this knowledge to develop ambipolar as well as hole-dominated light emitting field-effect transistors.

Ambipolar FETs using a diketopyrrolopyrrole-based copolymer were first investigated in this thesis. When gold electrodes were used, the devices could transport only holes. The charge injection was altered by changing the contacts to aluminium. The devices then were able to conduct both electrons and holes with maximum electron and hole mobilities of order $10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ and $10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ respectively.

Light-emitting field-effect transistors were first studied using the model emissive polymer Super Yellow. Charge injection was studied by altering the electron-injecting contact. Materials used included the low work function metals Ca, Ba and Sm, the inorganic salt Cs$_2$CO$_3$ and the organic material TPBi. Ambipolar devices were created using a neat Super Yellow layer. Electron and hole mobilities in these devices were both of the order of $10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$. The maximum external quantum efficiency was $1.2 \pm 0.2 \%$ with a Sm electron-injecting contact, however this occurred at a brightness of less than 1 cd m$^{-2}$. A maximum brightness of $43 \pm 9$ cd m$^{-2}$ was obtained using a Cs$_2$CO$_3$-Ag electron-injecting contact in electron accumulation mode. At this brightness, the external quantum efficiency was $0.19 \pm 0.04 \%$.

Unipolar devices were also fabricated by adding high mobility charge transport layer of PBTTT underneath the Super Yellow. Since PBTTT had a hole mobility that was orders of magnitude greater than the charge carrier mobilities of Super Yellow, charges were transported in the PBTTT, and recombined within the Super Yellow layer. Super Yellow acted as an emissive layer only. Using this bilayer device architecture, a maximum brightness of $100 \pm 4$ cd m$^{-2}$ was obtained with a Ca electron-injecting contact. An external quantum efficiency of $0.04 \pm 0.01 \%$ was achieved at the maximum brightness.

In order to improve the external quantum efficiency of LEFETs, phosphorescent materials were chosen for use as the emissive layer. A co-evaporated layer of the iridium complex Ir(ppy)$_3$ in a host of CBP was initially used in the devices. Charge injection was studied by using either a Ba or a TPBi/Ba electron-injecting contact.
Devices were first fabricated using PBTTT as a hole-dominated charge transport layer. Using a TPBi/Ba electron-injecting contact, the maximum brightness achieved was 200 ± 40 cd m$^{-2}$ with an external quantum efficiency of 0.18 ± 0.01 % at the maximum brightness. Devices were then fabricated using a charge transport layer of DPP-DTT to create ambipolar devices. Electron and hole mobilities in these devices were both of order $10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$. The maximum external quantum efficiency was 0.4 ± 0.2 % at the maximum brightness of 500 ± 200 cd m$^{-2}$ in hole accumulation mode using an electron-injecting contact of TPBi/Ba.

In order to avoid using a co-deposited emissive layer, a solution-processed iridium-cored dendrimer layer that could be deposited without a host material was used. Like in the previous work, a charge transport layer of PBTTT was deposited underneath the emissive layer. Charge injection in the devices was altered using a change in the device geometry. Non-planar source and drain contacts were used, where one contact was deposited directly on top of the charge transport layer and the other contact on top of the emissive layer. Planar contacts were also used as control devices. There was clear evidence for transport of both holes and electrons when planar contacts were used, with light emission occurring at both contacts.

The maximum mobility, brightness and external quantum efficiency was achieved using the non-planar contact geometry. Holes could be directly injected into the charge transport layer, rather than via the emissive layer. The hole mobility in these devices was $3.5 \times 10^{-3} \pm 6 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$. The maximum brightness was 140 ± 50 cd m$^{-2}$ with an external quantum efficiency of 0.11 ± 0.02 % at the maximum brightness.

This thesis describes work on the study of charge injection into organic field-effect transistors by changing either the material used for the electron-injecting contact, or by changing the device geometry. This was achieved in devices that were either dominated by holes, or showed evidence of both electron and hole transport within the device. By changing the charge injection into the device, it was possible to improve the charge carrier mobilities, the brightness or the external quantum efficiency. Improving one or more of these things brings light emitting transistors towards becoming a viable technology.
Declaration by author

This thesis is composed of my original work, and contains no material previously published or written by another person except where due reference has been made in the text. I have clearly stated the contribution by others to jointly-authored works that I have included in my thesis.

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Publications during candidature

**Peer-reviewed journal articles**


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**Publications included in this thesis**


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<tr>
<td>Dr Yuliang Zhang</td>
<td>Designed solar cell experiments (90%)</td>
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<td>Dr N Venkatramaiah</td>
<td>Density functional theory calculations (100%)</td>
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<td>Dr Muhsen Aljada</td>
<td>Designed and fabricated shadow masks for field effect transistor experiments (100%)</td>
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My contribution to this publication was incorporated into the thesis as Chapter 3. I fabricated and characterised the field-effect transistors as well as some of the characterisation of the polymer (collection of the absorption spectra in solid-state and solution and collection of the NMR spectra).


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This publication was incorporated as Chapter 4 of the thesis.
Contributions by others to the thesis

Chapter 2
The Super Yellow OLED used for the calibration of the photomultiplier tube was fabricated and characterised by Dr Soniya Yambem. The measurements for the photomultiplier tube calibration were performed with the aid of Dr Soniya Yambem and Dr Mujeeb Ullah.

Chapter 3
The polymer used for device fabrication was synthesised at the Solid State and Structural Chemistry Unit, Indian Institute of Science in Bangalore by Dr Gitish Dutta and Prof. Satish Patil. Determinations of molecular weight and polydispersity index, as well as the X-ray Diffraction and Differential Scanning Calorimetry measurements were performed by Dr Gitish Dutta.

The photoelectron spectroscopy in air (PESA) measurements of the ionization potential were performed by Dr Scott Watkins at CSIRO in Clayton, Melbourne. Films for the PESA measurements were prepared by me at COPE and then sent to CSIRO.

The silicon dioxide substrates were prepared by Dr Muhsen Aljada by growing the silicon dioxide on top of silicon substrates. Dr Aljada also prepared the Au bottom gate. The shadow masks used were designed and prepared by Dr Aljada using deep reactive ion etching. Atomic Force Microscopy of the polymer film was performed with the assistance of Dr Aljada.

Chapter 4
Dr Mujeeb Ullah fabricated the single layer Super Yellow devices with Sm electron-injecting contacts. Dr Ullah also designed the asymmetric shadow masks. The solid state photoluminescence quantum yield of Super Yellow was measured by Dr Soniya Yambem.

The ellipsometry measurements were performed by Dr Paul Shaw using films that were prepared by me.

Chapter 5
The DPP-DTT polymer was synthesised and characterised by Dr Jun Li from the Institute of Materials Research and Engineering, Singapore.
Chapter 6
The ellipsometry measurements and curve fitting for the dendrimer and PBTIT were performed by Dr Ravi Chandra Raju Nagiri on films that I prepared. The electroluminescence measurements were performed with the help of Dr Mujeeb Ullah.

Statement of parts of the thesis submitted to qualify for the award of another degree

None.
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Transistor, light-emitting, ambipolar, charge injection, organic, diketopyrrolopyrrole

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\section*{2.1 The LEFET characterisation setup at COPE. \textbf{a)} A schematic showing the position of the photomultiplier tube over the probe station to measure the light output of the device. The distance from the photomultiplier tube to the probe station was fixed. The probes and the photomultiplier tube (pmt) were connected electrically to the Agilent B1500A Semiconductor Analyser that was positioned outside the glove box. The photomultiplier tube was also connected to an external power supply inside the glove box. \textbf{b)} Photograph of the FET characterisation setup inside the clean room.}

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<tr>
<td>α</td>
<td>inverse localisation radius</td>
</tr>
<tr>
<td>A</td>
<td>projected area</td>
</tr>
<tr>
<td>(A_{\text{emission}})</td>
<td>area of emission</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>ANFF</td>
<td>Australian National Fabrication Facility</td>
</tr>
<tr>
<td>C</td>
<td>capacitance</td>
</tr>
<tr>
<td>c</td>
<td>speed of light</td>
</tr>
<tr>
<td>CBP</td>
<td>4,4’-bis(N-carbazolyl)-1,1-biphenyl</td>
</tr>
<tr>
<td>CIE</td>
<td>The International Commission for Illumination (Commission Internationale de l’Eclairage)</td>
</tr>
<tr>
<td>cd</td>
<td>candela</td>
</tr>
<tr>
<td>COPE</td>
<td>Centre for Organic Photonics &amp; Electronics</td>
</tr>
<tr>
<td>Cs₂CO₃</td>
<td>caesium carbonate</td>
</tr>
<tr>
<td>(\Delta\varepsilon_{ij})</td>
<td>energy difference between sites (i) and (j)</td>
</tr>
<tr>
<td>DPP</td>
<td>diketopyrrolopyrrole</td>
</tr>
<tr>
<td>DPP-DTT</td>
<td>diketopyrrolopyrrole-dithienothiophene based polymer</td>
</tr>
<tr>
<td>(e^-)</td>
<td>electron</td>
</tr>
<tr>
<td>EA</td>
<td>Electron affinity</td>
</tr>
<tr>
<td>(\varepsilon_F)</td>
<td>Fermi energy</td>
</tr>
<tr>
<td>(\varepsilon_i)</td>
<td>energy of site (i)</td>
</tr>
<tr>
<td>(E)</td>
<td>Energy</td>
</tr>
<tr>
<td>EQE</td>
<td>External Quantum Efficiency</td>
</tr>
<tr>
<td>F8BT</td>
<td>poly(9,9-di-n-octyl-fluorene-alt-benzothiadiazole)</td>
</tr>
<tr>
<td>FET</td>
<td>Field-effect transistor</td>
</tr>
<tr>
<td>(g(\varepsilon_F))</td>
<td>density of states at the Fermi energy</td>
</tr>
<tr>
<td>(\hbar)</td>
<td>reduced Planck’s constant where (\hbar = h/2\pi)</td>
</tr>
<tr>
<td>HMDS</td>
<td>hexamethyldisilazane</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>(I)</td>
<td>intensity</td>
</tr>
<tr>
<td>IE</td>
<td>Ionization energy</td>
</tr>
<tr>
<td>(I_{\text{DS}})</td>
<td>Source-drain current</td>
</tr>
<tr>
<td>(I_n)</td>
<td>intensity of light emitted normal to the surface</td>
</tr>
<tr>
<td>(\text{Ir(ppy)}_3)</td>
<td>\text{fac-tris-(2-phenylpyridine)iridium}</td>
</tr>
<tr>
<td>(J_0)</td>
<td>electron transfer integral between hopping sites</td>
</tr>
<tr>
<td>(k_b)</td>
<td>Boltzmann’s constant</td>
</tr>
<tr>
<td>(\lambda)</td>
<td>wavelength</td>
</tr>
<tr>
<td>(\lambda_{\text{reorg}})</td>
<td>reorganisation energy</td>
</tr>
<tr>
<td>L</td>
<td>Channel length</td>
</tr>
<tr>
<td>(L_0)</td>
<td>flux per unit solid angle of light leaving the device in the forward direction (brightness)</td>
</tr>
<tr>
<td>LED</td>
<td>light-emitting diode</td>
</tr>
<tr>
<td>LEFET</td>
<td>Light emitting field-effect transistor</td>
</tr>
<tr>
<td>(lm)</td>
<td>lumens</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>(\mu)</td>
<td>mobility</td>
</tr>
<tr>
<td>(\mu_{\text{electron}})</td>
<td>electron mobility</td>
</tr>
<tr>
<td>(\mu_{\text{hole}})</td>
<td>hole mobility</td>
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</table>
A particular molecular state

The ground state ion of $M$ that has lost an electron

Molecule $M$ with an added electron

Molybdenum oxide/silver/Molybdenum oxide stack

number average molecular weight

molybdenum oxide

Metal-oxide-semiconductor field-effect transistor

weight average molecular weight

photonic frequency

"attempt to hop rate" of a charge carrier or the phonon

vibrational frequency

hopping rate between sites $i$ and $j$

number of photons or refractive index depending on the context

organic field-effect transistor

organic light-emitting diode

ON/OFF ratio in electron accumulation ($n$-type) mode

ON/OFF ratio in hole accumulation ($p$-type) mode

octatrichlorosilane

fraction of electrons and holes that recombine and form excitons

(the recombination efficiency)

fraction of photons that can escape from a LEFET

luminous flux

photoluminescence quantum yield in the solid state

is the proportion of excitons allowed to recombine radiatively

due to spin statistics

optical power

spectral power density

poly(2,5-bis(3-alkylthiophene-2-yl)thieno[3,2-b]thiophene)

polydispersity index

photoelectron spectroscopy in air

photoluminescence quantum yield

poly(methyl methacrylate)

photomultiplier tube

spectral colour density

poly[3,6-dithieno[3,2-b]thiophen-2-yl]-2,5-bis(2-octyldodecyl)pyrrrolo[3,4-c]pyrrrole-1,4-dione-5',5''-diyl-alt-4,8-bis(dodecyloxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl

charge of an electron $(1.602 \times 10^{-19} \text{ C})$

physical separation between site $i$ and site $j$

conductivity

Source contact

Self consistent field

Silicon nitride

Silicon dioxide

Super Yellow

angle

temperature

Threshold voltage in electron accumulation ($n$-type) mode

Threshold voltage in hole accumulation ($p$-type) mode

1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene

eye response curve (photopic luminosity function)

source-drain voltage
$V_G$  
\hspace{1cm} \text{gate voltage}

$V_t$  
\hspace{1cm} \text{Threshold voltage}

$W$  
\hspace{1cm} \text{Channel width}

$X$  
\hspace{1cm} \text{tristimulus x value}

$\bar{x}(\lambda)$  
\hspace{1cm} \text{colour matching function representing red light}

$Y$  
\hspace{1cm} \text{tristimulus y value}

$\bar{y}(\lambda)$  
\hspace{1cm} \text{colour matching function representing green light}

$Z$  
\hspace{1cm} \text{tristimulus z value}

$\bar{z}(\lambda)$  
\hspace{1cm} \text{colour matching function representing blue light}
Chapter 1

Introduction

1.1 Motivation

Organic electronics and optoelectronics are viewed as key next generation high-technologies, with organic semiconductors offering a promising route towards creating light weight, flexible and portable devices. Organic semiconductors have so far been used in devices such as solar cells, light emitting diodes (LEDs), sensors and transistors. Field Effect Transistors (FETs) are three electrode devices in which an applied field is used to “switch on” a conducting pathway within a thin semiconducting channel. Historically, transistors have been important in the technological development of devices ranging from radios to smartphones. Properties of organic semiconductors such as light emission can be used to create multi-functional “Active Channel Field Effect Transistors”. These devices are able to do more than just switch on or off, creating new possibilities for new future technologies. In particular, Light Emitting Field-Effect Transistors (LEFETs) combine the emission properties of an organic light emitting diode (OLED) with the switching properties of a transistor. LEFETs are promising for applications in areas such as displays, sensors or for use as the first organic injection laser.

The first reported LEFET was based on the emissive semiconductor tetracene in 2003 [1]. The semiconductor was vacuum-deposited and operated in $p$-type mode only. Since that time, developments have been made to improve the brightness and/or the efficiency of the devices. High mobility polymers [2] or single crystals [3] were used to improve emission characteristics. The device architecture was altered to reflect more of the light out of the device [4]. Devices which can operate at a low applied voltage have also been demonstrated [5]. However, there is little research into the charge injection, charge transport and recombination within LEFETs. This could help to improve device performance to bring LEFETs towards commercial applications.
Ambipolar LEFETs, which are able to transport both electrons and holes within the semiconductor channel, have the potential to emit light with a higher efficiency than devices that can only transport one type of charge carrier. This is because the concentration and accumulation of both charges can be controlled so that electrons and holes can recombine with the maximum efficiency. However, the efficiency at high brightness of ambipolar LEFETs is often low, which is not useful for display applications. Ways to improve the brightness whilst maintaining high efficiency together with the optimization of charge carrier injection are needed to create high performance devices. These considerations have motivated the work that is described in this thesis.

1.2 Properties of organic semiconductors

1.2.1 Organic materials as semiconductors

Conductivity in organic materials occurs because of the existence of hybridized orbitals in the bonding configuration of carbon atoms. In the $sp^2p_z$ configuration, there are three in-plane sigma orbitals on the backbone – two bonded to neighbouring carbons on either side of the carbon chain, and one to a hydrogen atom. The electrons in these three sigma orbitals form covalent bonds to the other two carbon atoms and the hydrogen atom. The fourth electron is not bonded, and resides in the $p_z$ orbital, or the $\pi$ orbital (see Figure 1.1). The electron may delocalise along the carbon chain, and is able to move between atoms and along the molecule. When the molecule becomes large, it is possible for the $\pi$-orbitals to delocalise over greater distances within the molecule, and hence there is more efficient charge transport along the carbon chain [6].

![Figure 1.1](image)

**Figure 1.1.** Schematic of carbon atoms in the bonding configuration $sp^2p_z$. The central carbon atom is bonded to neighbouring carbon atoms in the polymer chain and to a single hydrogen atom. The fourth electron resides in the $p_z$ orbital ($\pi$ orbital) that is out of the plane of the other bonds. This orbital is able to delocalise across the chain, allowing the electrons to move (Figure design based on Reference [6]).

Conjugated organic materials, with alternating single and double bond structures, allow
more effective delocalisation of the $\pi$-orbitals. The $\pi$-orbitals make up the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The HOMO and the LUMO are hybridised molecular orbitals that arise from a linear combination of atomic orbitals. For efficient $p$-type charge transport, it is desirable for the HOMO to be delocalised across the molecule, and for there to be overlap of the HOMO between adjacent molecules. Similarly, for efficient $n$-type charge transport, it is desirable for the LUMO to be delocalised across the molecule.

1.2.2 Charge transport in organic semiconductors

In general, the conductivity of a material is dependent on the charge carrier mobility, $\mu$, charge carrier density, $n$, in the form

$$\sigma = \mu n q$$

(1.1)

where $\sigma$ is the conductivity and $q$ is the charge on an electron. An improvement in either the mobility or charge carrier density can increase the conductivity of the material.

There is no universal model for charge transport in organic semiconductors. Some organic materials show evidence of band transport, like ordered inorganic semiconductors, however most organic semiconductors are regarded to have some degree of disorder in the solid state. It is generally agreed that charge transport occurs by hopping, with the density of states often assumed to have a Gaussian distribution since there is disorder in the system [7] (see Figure 1.2). The charge carrier mobility is dependent on the hopping rate. Some models involve hopping mainly in localized states, however there are also models that include charge carrier conduction in extended states as well as localized states. Some of the relevant models will be described here, however it should be noted that a complete discussion of charge transport in organic semiconductors is longer than can be contained in this thesis.

![Figure 1.2](image)

Figure 1.2. The density of states for organic semiconductors is typically assumed to have a Gaussian distribution with respect to energy. This arises from the disorder in the system.
Simple hopping models consider hops between sites that are nearest neighbours in space, as shown in Figure 1.3 [6]. Charge carriers occupy one site at a time, and hop from site-to-site with a rate that is determined by the spatial separation of the sites and energy difference between the states involved in the hop [8]. In this case, the $\pi$ electronic structure of conjugated organic semiconductors can be treated in a tight-binding approximation where each hop is independent of prior hops [7].

![Energy vs Position](image)

**Figure 1.3.** Nearest neighbour hopping. Charges may hop between sites that are nearest neighbours only. Hops are independent of previous hops.

The Miller-Abrahams model is a low temperature model for the hopping of charge carriers. Charge carriers hop between sites $i$ and $j$ via a phonon-assisted tunnelling mechanism [9]. It is valid for weak electron-phonon coupling. In this model, the physical separation of the two sites, $r_{ij}$, causes an exponential decrease in the transfer rate between hopping sites [8]. The hopping rate, $v_{ij}$, between site $i$ with energy $\varepsilon_i$ and site $j$ with energy $\varepsilon_j$ is given by

$$v_{ij} = v_0 \exp\left(-2\alpha|r_{ij}|\right) \left\{ \begin{array}{ll} \exp\left(-\frac{(\varepsilon_i - \varepsilon_j)}{k_BT}\right) & \text{for} \quad \varepsilon_j > \varepsilon_i, \\ 1 & \text{else} \end{array} \right.$$  \hspace{1cm} (1.2)

where $v_0$ is the “attempt to hop” rate (taken to be the phonon vibrational frequency), $T$ is the temperature and $\alpha$ is the inverse localisation radius. Boltzmann’s constant is given by $k_b$ [9]. Each electronic hop is accompanied by either the absorption or emission of a phonon to account for the energy difference between sites $i$ and $j$. This means that hops upwards in energy require a particular phonon state to be populated since a phonon must be absorbed, and are therefore temperature dependent [8]. Downward hops, which result in the emission of a phonon, are temperature independent.

Mott’s Variable Range Hopping model takes into account hops that are further away than just nearest neighbours. For efficient hopping to occur, a hop must occur to a final state that is not occupied [9]. If there is enough thermal energy in the system, there is the possibility that charge
carriers may hop to a range of states within a narrow energy band around the Fermi energy, $\varepsilon_F$ [8]. This is further demonstrated in Figure 1.4.

**Figure 1.4.** Variable Range Hopping. Charges may hop to sites that are further away than nearest neighbour sites depending on the thermal energy of the system. Hopping occurs around the Fermi energy, $\varepsilon_F$.

If it can be assumed that the density of states is approximately constant in the energy band where hopping takes place (valid at low temperatures) [8],

$$v_{ij} \approx v_0 e^{-\left(\frac{T_0}{T}\right)^{1/4}}$$

(1.3)

$T_0$ is a characteristic temperature given by

$$T_0 = \frac{512}{9\pi \ k_B g(\varepsilon_F)}$$

(1.4)

where $g(\varepsilon_F)$ is the density of states around the Fermi energy, $\varepsilon_F$ [8]. The constant, $\frac{512}{9\pi}$, is dependent on approximations made during the derivation of the above expression.

When strong electron-phonon coupling is considered, there is an alteration of the local lattice configuration to achieve the minimum energy of the system. The electron coupled with the lattice distortion is a quasi-particle known as a polaron [7]. Once a favourable molecular configuration is reached, charges may hop from one site to another [9]. The hopping rate therefore includes a component for the energy required to reorganise the molecule to a favourable configuration, as well as the energy difference between hopping sites $i$ and $j$. The hopping rate between sites can be written as

$$v_{ij} = \frac{|J_0|^2}{\hbar} \sqrt{\frac{\pi}{\lambda_{\text{reorg}} k_B T}} e^{-\frac{2\alpha r_{ij}}{\lambda_{\text{reorg}} k_B T}} e^{-\frac{(\Delta \varepsilon_{ij} + \lambda_{\text{reorg}})^2}{4\lambda_{\text{reorg}} k_B T}},$$

(1.5)

where $J_0$ is the electron transfer integral, $\lambda_{\text{reorg}}$ is the reorganisation energy and $\Delta \varepsilon_{ij} = \varepsilon_j - \varepsilon_i$ and is the energy difference between sites $i$ and $j$ [8]. Planck’s constant is given by $\hbar$. This model assumes that transport occurs in the high temperature regime.
The multiple trapping and release model is a temperature dependent model which considers conduction in extended states as well as in localised states. Charges are able to move in a region of extended, delocalised states in a mechanism similar to band transport in organic semiconductors. Conduction takes place in the delocalised states until the charge is trapped in a localised state. Charges may be thermally excited from the localised states to once again be transported in delocalised states [8]. Since the charge carriers must be thermally released, transfer rates between sites are greater at high temperatures. This model is typically applicable for more ordered crystalline or semi-crystalline materials [10]. It is not suitable for materials in which all charge transport takes place in localised states.

1.2.3 Luminescence and electroluminescence

Many organic materials are luminescent, which means that they can release energy from a higher energy excited state radiatively. When a photon is absorbed, the molecule is promoted from the ground state to an electronic singlet excited state. Usually the molecule will then release some energy non-radiatively to relax to the lowest vibrational level of the electronic excited state. If the molecule is able to emit the remaining energy radiatively from a singlet state, this process is known as fluorescence [11] (see Figure 1.5).

In some systems, following the excitation to a singlet state, intersystem crossing may take place to a triplet excited state. This is a non-radiative transition between states of different spin multiplicity. The probability of intersystem crossing is increased when a molecule contains a heavy atom since the spin-orbit coupling is large [11]. Emission of radiation from a triplet state is known as phosphorescence (see Figure 1.5). Radiative decay to the ground state is spin-forbidden since the ground state is a singlet state, and so triplet excited states are typically long-lived. Typical phosphorescence lifetimes are milliseconds to seconds compared to tens of nanoseconds for fluorescence lifetimes [12].

If electrons and holes are directly injected into a luminescent organic material using electrical contacts, the charges may recombine to emit light. This process is known as electroluminescence [7]. Electroluminescence is a two-step process in organic materials. Since organic materials have a low dielectric constant the electrons and holes first form an exciton, a Coulomb-bound electron-hole pair. This exciton may subsequently recombine to emit light.

Electroluminescence was first observed in an organic material under the application of a DC field by Pope, Kallmann and Magnante in 1963 [13]. This was observed for a single crystal of anthracene at an applied voltage of at least 400 V. Recombination of the charge carriers produced an electroluminescence spectrum that matched the photoluminescence spectrum of anthracene, suggesting that the luminescence was from the bulk in the anthracene layer.
According to spin-statistics, singlet and triplet excitons form in a ratio of 1:3 \([14, 15]\) (see Figure 1.5). This means that in a fluorescent material, where radiative emission can only occur from singlet states, only a \(\frac{1}{4}\) of the excitons that are formed are able to contribute to the luminescence. However, in a phosphorescent material, where radiative emission is possible from triplet excited states, a greater proportion of excitons that are formed will contribute to the luminescence.

![Figure 1.5. Fluorescent and phosphorescent decay.](image)

**Figure 1.5.** Fluorescent and phosphorescent decay. When a photon is absorbed, promoting the molecule to a singlet excited state \((S_1)\). Vibrational relaxation to the lowest vibrational level of the electronic excited state may then occur. Energy may be released radiatively from the singlet state, and the molecule relaxes to the ground state \((S_0)\). This process is known as fluorescence. Alternatively, intersystem crossing may take place to a lower energy triplet excited state \((T_1)\). Emission from the triplet excited state is known as phosphorescence. Singlet and triplet states are also given in Dirac notation with the associated spin multiplicity.

### 1.3 Organic Field-Effect Transistors

Field-effect transistors use an applied electric field to switch between the OFF and ON states. Field Effect transistors are typically 3 electrode devices, with source, drain and gate electrodes. The source and drain electrodes are connected electrically to the semiconductor film, with the gate electrode separated from the semiconductor by a dielectric layer. Commonly used geometries include the bottom gate top contact geometry (see **Figure 1.6a**) in which the top contacts can be deposited on top of the semiconductor layer by thermal vacuum evaporation or by
sputter coating. Bottom gate bottom contact geometries (see Figure 1.6b) are also used to allow patterning of the electrodes prior to the deposition of the semiconductor layer. The dielectric layer can be deposited on top of the semiconductor instead, resulting in geometries such as a top gate bottom contact geometry (see Figure 1.6c) or a top gate top contact (see Figure 1.6d). Bottom contact geometries are often used to avoid damaging the organic semiconductor layer, which can occur when contacts are deposited on top at high temperatures.

![Diagram of FET device geometries](image)

**Figure 1.6.** Commonly used FET device geometries with semiconductor and dielectric layers and source (S), drain (D) and gate electrodes: **a)** bottom gate top contact; **b)** bottom gate bottom contact; **c)** top gate bottom contact geometry and **d)** top gate top contact.

### 1.3.1 Device operation

OFETs are usually operated in what is known as *accumulation mode* where charges are accumulated at the semiconductor/dielectric interface in order to switch the device ON. This is because most organic semiconductors are intrinsically undoped, as opposed to inorganic semiconductors that are intentionally doped [6].

FET operation using an n-type semiconductor is demonstrated in **Figure 1.7a**. Electrons are injected into the semiconductor layer by the source electrode with the application of a voltage between the source and drain electrodes, $V_{DS}$. Application of a positive gate voltage ($V_G$) will build up a capacitance in the dielectric layer. Due to the applied field, electrons accumulate at the interface between the semiconductor and dielectric layers. This causes an increase in the charge carrier density at the interface between the semiconductor and dielectric, which leads to the increase in the conductivity of the channel (see Equation 1.1). The increase in conductivity will result in an
increase in the measured current between the source and drain electrodes and the formation of a conducting channel.

**Figure 1.7.** Field-effect transistor operation and device characteristics: a) device operation for an n-type transistor. Electrons are injected at the source electrode. When a positive gate electrode is applied, a capacitance builds up in the dielectric layer. The dielectric becomes polarised and electrons are accumulated at the interface. This increases the charge carrier density within the semiconductor channel and the transistor turns ON; b) output characteristics where the source-drain voltage is varied as a function of gate voltage steps, with clear linear (low $V_{DS}$) and saturation (large $V_{DS}$) regimes; c) transfer characteristics for a device in the saturation regime, where the gate voltage is varied at constant source-drain voltage.

When the $V_{DS}$ is much smaller than the applied gate voltage ($V_{DS} \ll V_G$), the channel acts like a resistor, and the drain current, $I_{DS}$, is proportional to $V_{DS}$. This is known as the linear region of operation [16]. In the linear region,

$$I_{DS} = \frac{W}{L} \mu C \left[ (V_G - V_t) V_{DS} - \frac{V_{DS}^2}{2} \right].$$ (1.6)
where $I_{DS}$ is the source-drain current, $W$ and $L$ are the length and width of the transistor channel respectively and $C$ is the capacitance of the dielectric layer. The threshold voltage, $V_t$, is the minimum voltage that must be applied to turn the device ON.

As the drain voltage increases, the charge carrier density becomes non-uniform across the channel, and the current becomes non-linear. When $V_{DS} > V_G - V_t$, a region depleted of charge is formed near the drain contact, and the density of mobile carriers in the region is small. This is known as the “pinch off” [6]. Beyond this drain bias, the current remains independent of the applied drain voltage. This is the saturation region of device operation [16]. In the saturation region,

$$I_{DS} = \frac{W \mu C}{L} (V_G - V_t)^2. \quad (1.7)$$

The operating principle is the same for a $p$-type FET, however the source-drain voltage is negative in order to inject holes at the source, and the applied gate voltage is also negative to allow holes to accumulate at the semiconductor-dielectric interface.

There are two ways to operate a FET. The drain voltage can be varied with the gate voltage kept constant. $V_G$ can then be increased in steps. These are the output characteristics. When the gate voltage is varied as function of constant drain voltage, these are the transfer characteristics. An example of both the output and transfer characteristics are shown in Figure 1.7b and 1.7c respectively. The linear regime and saturation regime of transistor operation can be clearly seen in the output characteristics.

### 1.3.2 Charge carrier injection

The process of ionization, where an electron, $e^-$, is removed from a molecule, $M$ can be written as [7]

$$M \rightarrow M^+ + e^-,$$

where $M^+$ represents the ground state ion. The energy required for a molecule to undergo this process is the ionization energy, $IE$, is the difference in energy between the total energy of $M^+$ and $M$ [17].

Similarly, a molecule may undergo the process of electron capture or electron attachment according to [7]

$$M + e^- \rightarrow M^-,$$

where $M^-$ corresponds to the molecule with an added electron. The energy difference between the states $M^-$ and $M$, or the energy required to add an electron to the system is the electron affinity, $EA$ [7]. According to Koopmans’ theorem, the negative of the orbital energy of the occupied Hartree-Fock molecular orbitals is the ionization energy from that particular state [18]. This means that the first ionization energy is approximately the negative of the energy of the highest occupied molecular orbital (HOMO).
Excited state energies can be calculated using self consistent field (SCF) calculations. According to the \( \Delta \text{SCF} \) method, separate calculations are performed for each excited state produced by the removal of an electron from an orbital. The ionization energies are calculated through the energy differences between the excited state energies and the neutral molecule. Using these calculations, the energy of each particular state is minimized, resulting in a stable state. Physically, once an electron is removed, the remaining electronic charge will be reorganized to form a stable state. This energy minimization process is not included in Koopmans’ theorem, and so \( \Delta \text{SCF} \) calculations will give a lower ionization energy [18]. Koopmans’ theorem assumes that there is no variation to the orbital energies once an electron is removed. This is often known as the “frozen orbital” assumption [17]. This is not necessarily a good assumption because the potential that the orbitals experience is changed when an electron is added or removed [18].

Electron correlations are also not taken into account in Koopmans’ theorem [18], however interactions between electrons are quite important for organic molecules. Also, Koopmans’ theorem describes a system in vacuum. When trying to describe a real physical system, the ionization energy and the electron affinity depend on the environment under investigation [19].

Despite these issues, it is still common in parts of the field to use the terms HOMO and IE interchangeably, and also to equate the EA with the lowest unoccupied molecular orbital (LUMO). This is not correct. It should be noted that while the IE and EA are physical values that are experimentally observable, the HOMO and LUMO are not and cannot be measured [17]. Furthermore, the EA is defined through adding electrons to the system but by definition the LUMO is unoccupied. When electrons are added to the system, the orbital is no longer unoccupied and it is a different system under investigation. Keeping all of these issues in mind, the terms IE and EA will be used to describe the injection of holes and electrons respectively into a device.

If the Fermi level of the metal electrode is sufficiently close to the IE of the semiconductor in the presence of an applied electric field, holes may be injected into the device [6]. Conversely, electrons may be injected when the Fermi level of the electrode is sufficiently close to the EA of the semiconductor.

When there is no applied field, all of the energy levels are flat. When a gate voltage is applied, there is a build-up of capacitance within the dielectric of the device and there is an applied field in the organic semiconductor. In the presence of an applied field, the IE and EA bend towards the Fermi level of the metal, which aids charge carrier injection [6] (see Figure 1.8). A greater applied field will increase the bending of the energy levels, which means that it is easier to inject charges into the device. It is important to not only understand the electronics of the organic semiconductor but also to select appropriate electrode metals for efficient charge carrier injection.
Figure 1.8. Demonstration of band bending at the interface between a metal and an organic semiconductor. At zero applied field, the energy levels are flat with respect to each other. When there is an applied field, the energy levels of the IE and EA bend towards the Fermi level of the metal. This enables more efficient charge carrier injection into the organic semiconductor.

1.3.3 Leakage current

There is more than one possible source of leakage current in OFETs. Leakage current can be between the source-drain electrodes when the transistor is not biased by the gate voltage. This is the OFF current, which can be dependent on applied voltages. Gate leakage current is the current that flows between the gate and source electrodes. This can also have a significant effect on device operation. Ideally, the leakage current should be as low as possible in order to maximise the FET switching capability and the ON/OFF ratio [10].

1.3.4 Contact resistance

The total resistance in a FET is the sum of the resistance from the channel and resistance at the contacts. As discussed in Section 1.3.2, appropriate contacts should be chosen so that efficient charge carrier injection can be obtained. This minimises the resistance at the contacts that is independent of channel length, and further decreases with increasing gate voltage [6]. An “ohmic contact” is a contact that has a resistance low enough to be neglected compared to the channel resistance [10]. Large contact resistances lead to errors in mobility measurements. A large channel resistance will cause a change in the voltage distribution across the channel so that the Equation 1.2 and 1.3 can no longer be used as an appropriate model [6].

1.3.5 Hysteresis and bias stress

Devices may also suffer from hysteresis or bias stress effects. Hysteresis effects are short-term, reversible effects which occur during device operation and lead to a looping in the measured
device characteristics [10]. For example, if a polymer dielectric has a slow polarisability is used it will take time to charge. This will have effects on the device characteristics after multiple tests. Charges may also become trapped in trap states, as previously discussed in Section 1.2.2. If this occurs, the charge trapping may also contribute to the hysteresis of the device characteristics.

Bias stress effects are generally more long term than hysteresis effects. The effects do not saturate and may continue until the device is rendered useless [10]. These effects are often caused by continuous stressing of the device by testing.

1.3.6 Ambipolar and unipolar devices

Unipolar transistors primarily transport only one charge carrier during device operation. Ambipolar devices may transport both electrons and holes [20]. Several different approaches have been used to create ambipolar organic field-effect transistors. Different organic semiconductors may be used to transport electrons and holes. This was achieved using a layered structure, where the $p$- and $n$-type organic materials are sequentially deposited. For example, this approach was adopted for devices fabricated using poly(3-hexylthiophene)/[6,6] C$_{61}$ butyric acid methyl ester bilayer structure deposited from solution [21] as well as for a multi-layered device structure using vacuum deposited thiophene derivatives as the $p$-type material and fullerenes as the $n$-type [22, 23]. Blend structures, using either co-evaporated films of $p$- and $n$-type materials [24, 25] or mixtures deposited from solution [26] have also been used to create ambipolar OFETs.

Alternatively, ambipolar transistors can also be fabricated using one organic semiconductor in the active channel. This was more easily achieved using organic semiconductors that have a narrow optical gap because typically a high work function metal can be used to inject both holes and electrons into the IE and EA of the semiconductor [26–31]. More recently, ambipolar FETs with hole mobilities of order 10 cm$^2$ V$^{-1}$ s$^{-1}$ and an electron mobility of ~1 cm$^2$ V$^{-1}$ s$^{-1}$ were reported for devices that used an organic semiconductor based on a polymer incorporating diketopyrrolopyrrole in the transistor channel [31]. Key considerations towards creating devices that are ambipolar is to choose organic semiconductors with measurable electron and hole mobilities, and to select a device architecture with appropriate contacts to inject both electrons and holes.

1.4 Light-Emitting Field-Effect Transistors

Light-emitting field-effect transistors (LEFETs) are devices that combine the switching properties of a transistor with the light emission capability of an OLED in a single device. In order for a LEFET to emit light, both electrons and holes must be able to be injected into the emissive
The injected charges meet to form an exciton. If the exciton can decay radiatively, light can be emitted from the device.

LEFETs have potential for applications in active matrix displays [32], sensors, and have also been suggested as a possible route towards creating the first organic injection laser [6]. This is because LEFETs can sustain higher current densities than OLEDs without breaking down. Furthermore, the emission can be spatially removed from the metal electrodes, which can help prevent losses in light output [33, 34].

Device parameters of interest include the brightness of the device and the external quantum efficiency (EQE). The EQE is the ratio of the emitted photons out of the device to charge carriers injected into the device. Ideally, devices will have both a high brightness and a high EQE. This is a challenge in a LEFET geometry since materials with a high photoluminescence yield often have a low field-effect mobility. Conversely, many high mobility materials have good absorption properties but a low photoluminescence yield. A high mobility can help improve the device brightness since charges move through the organic semiconductor faster to recombine.

Both unipolar and ambipolar LEFETs can be created depending upon the relative electron and hole mobilities of the organic semiconductor and the choice of device architecture. The device operation of both unipolar and ambipolar devices is described in the following sections.

1.4.1 Unipolar LEFET device operation

For unipolar LEFETs, transport is either hole- or electron-dominated. Only one type of charge carrier is accumulated within the channel even though both electrons and holes must be injected for light to be emitted. Unipolar LEFETs can have a single layer, where the charge transport and recombination occur within the same layer, or can be comprised of multiple layers, where charge transport and recombination occur within separate layers. For a hole-dominated device with a single organic semiconductor layer, holes are injected into the device and are transported through the transistor channel. Electrons are injected, but remain close to the electrode since there is poor electron transport through the semiconductor channel. Recombination and emission will therefore occur close to the electron-injecting electrode (see Figure 1.9). The emission zone will be stationary during device operation since the charge transport is always dominated by holes. Operation in an electron-dominated device is the same except electrons are accumulated within the channel, and the polarity of the gate voltage is positive instead of negative.

The first reported LEFET was a tetracene-based single layer unipolar device that operated in hole-accumulation mode [1]. The intensity of the light emitted from the device was dependent on the applied voltage. As the source-drain voltage was increased, more charges were injected into the device. If there are a larger number of charge carriers available to recombine, the intensity of the
light will increase as the applied bias increases. Tetracene was subsequently used in a few reports as the emissive material in early reported unipolar LEFETs [35, 36], including a report of devices fabricated on flexible substrates [37].

Unipolar LEFETs have been reported using symmetric electrodes [38–40] or asymmetric electrodes with metals of differing work function to inject electrons and holes into the device [36, 41, 42]. When symmetric, high work function electrodes are used, electron injection was proposed to occur via a tunnelling mechanism [35]. At high gate voltages, electrons are injected at the EA of the organic semiconductor when the voltage drop at the metal-semiconductor interface is large enough that a distortion of the IE and EA levels takes place.

Unipolar LEFETs can also be constructed using multiple layers [2, 43]. In these devices, a high mobility charge transport layer is usually used with a low mobility emissive layer. For example, for a p-type device, holes are injected into the charge transport layer via the emissive layer. Holes are accumulated within this layer and are transported towards the electron-injecting contact, where they are able to recombine with the electrons injected directly into the emissive layer (see Figure 1.10). Using these devices, the charge transport and light emission functions are performed by separate layers, which allows devices to be constructed with both a high current and a high brightness. The emission zone will be stationary in these devices since usually only one charge carrier moves through the underlying layer and will always recombine close to one of the contacts.
Figure 1.10. Unipolar LEFET device operation with a high mobility hole transport layer. Charge transport and emissive functions are decoupled, with separate charge transport and emissive layers. Charge carriers are injected into the charge transport layer via the emissive layer and are accumulated within the charge transport layer when a negative gate voltage is applied. Holes are transported from the source (S) towards the drain (D) contacts and recombine with electrons injected directly into the emissive layer at the drain contact.

1.4.2 Ambipolar LEFET device operation

For ambipolar LEFETs, both electrons and holes can be transported in the channel, depending on the polarity of the applied voltages [8]. Ambipolar LEFETs may be made up of devices that have asymmetric electrodes using a high work function and low work function electrode (see Figure 1.11). Like the unipolar case, both electron and hole injection is also possible in some cases using a high work function electrode only.

An example of the electrical and optical transfer characteristics for an ambipolar LEFET can be found in Figure 1.11a. There are distinct electron-dominated and hole-dominated regimes, with a cross-over regime, often called the ‘ambipolar regime’. These regimes will now be explained in more detail for the case of a single layer ambipolar LEFET.

Large positive $V_G$

When the $V_G$ is large and positive, the charge transport is dominated by electrons, with electrons accumulating within the transistor channel at the semiconductor/dielectric interface (see Figure 1.11b). Holes are injected into the device and remain close to the hole-injecting contact. Holes will not move far from the hole-injecting contact since the applied field will accumulate electrons at the interface. Electrons may recombine with holes in the vicinity of the hole-injecting contact [44] to emit light. The brightness of the light is at a maximum since the current is high (see Figure 1.11a) [6].

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Figure 1.11. The device operation of single layer ambipolar LEFETs: a) An example of the electrical and optical transfer characteristics for an ambipolar LEFET; b) Device operation with a large positive $V_G$. This causes mainly electrons to accumulate within the transistor channel and the light emission occurs closest to the high work function (WF) hole-injecting electrode; c) Device operation with a $V_G$ close to zero. The hole accumulation increases and so the hole density is able to extend towards the middle of the channel. The charges recombine close to the middle of the transistor channel and away from the electrodes; d) Device operation with a large negative $V_G$. This causes mainly holes to accumulate in the transistor channel and light emission occurs closest to the low work function (WF) electron-injecting contact.
$V_G$ close to zero (small $V_G$)

As the gate voltage becomes closer to zero, the electron accumulation within the channel decreases, and the electron density no longer extends across the whole channel. At the same time, since the gate voltage is less positive, and moving in the negative direction, holes are better able to accumulate, and the density of holes begins to build up and extend further into the channel. The electron and hole currents begin to become more balanced. When hole currents and electron currents are exactly balanced, light emission will occur in the middle of the transistor channel (see Figure 1.11c). The brightness here is low since the current in this region is also low [6].

Large negative $V_G$

When the gate voltage is at a large negative bias, mainly holes accumulate within the channel, with the density extending across the transistor channel towards the electron-injecting contact. Electrons are injected into the device and remain close to the electron-injecting contact (see Figure 1.11d). The emission zone will be close to the electron injecting contact [44].

The first reported ambipolar light emitting devices were either bilayer heterostructure devices made up of two layers of $p$-and-$n$-type materials [45] or a mixed layer of $p$-and-$n$-type materials [24]. Light emission was observed, however there was no report on the brightness or the position of the emission zone in the devices.

Ambipolar LEFETs were then reported using a single layer of organic semiconductor as the channel material [46–48]. In all three of these reports, the emission zone could be moved through the channel with a change in the applied gate voltage. An EQE of $\sim 0.75$ % was obtained using poly(9,9-di-n-octyl-fluorene-alt-benzothiadiazole (F8BT) as the semiconductor material, however this was obtained close to low brightness [48].

1.4.3 Improvement of LEFET performance

Both evaporated [49–53] and solution processed [2, 42, 54–56] organic semiconductors have been used as emissive layers. There are also LEFETs based on carbon nanotubes [57, 58], however these devices emitted light in the infrared and were not useful for display or lighting applications. However, carbon nanotubes have been dispersed in a solution processed polymer layer. These devices emitted light in the visible spectrum and the addition of carbon nanotubes was shown to increase the maximum light intensity from the device [59].
Several approaches have been used to improve either the brightness or the EQE in LEFETs. Both are important for LEFET applications. Ideally, the brightness from the device will be produced with high efficiency. In order to improve the brightness of the devices, high currents are needed. To achieve this, high mobility materials have been used. This can be used in conjunction with multi-layer stacks of materials where the transport of electrons and holes occurs in a separate charge transport layer to the emissive layer. High mobility materials such as single crystals which are more ordered have also been used.

The EQE is a function of several different terms and is more difficult to fully optimise. The EQE is a function of terms involving the charge carrier recombination, as well as the emission properties of the organic semiconductor. The EQE is given by [6]

\[ EQE = \phi_{\text{escape}} \times \phi_{\text{capture}} \times \phi_{\text{spin}} \times \phi_{\text{PLQY}}, \]  

(1.8)

where \( \phi_{\text{escape}} \) is the fraction of photons that can escape from the device (there are losses due to total internal reflection at each interface), \( \phi_{\text{capture}} \) is the fraction of electrons and holes that recombine and form excitons (the recombination efficiency), \( \phi_{\text{spin}} \) is the proportion of excitons allowed to recombine radiatively due to spin statistics and \( \phi_{\text{PLQY}} \) is the photoluminescence quantum yield (PLQY) in the solid state. An improvement in the EQE comes from an improvement in one of these parameters. By changing the device geometry, the outcoupling of the light could be increased to maximise \( \phi_{\text{escape}} \). If the rate of charge carrier recombination improved, \( \phi_{\text{capture}} \) would be increase. The proportion of excitons that are able to recombine due to spin statistics in a particular material is fixed. However, if a material in which triplet excitons can decay radiatively was used, this could improve the EQE since triplet excitons and singlet excitons form in a ratio of 3:1 (see Section 1.2.3). The emissive layer also needs to have a high photoluminescence quantum yield to emit light more efficiently.

All of these approaches to improve the brightness or the EQE have been used in LEFET research so far. A summary of some of the approaches will be described in the following sections. Unlike most established device architectures such as solar cells or light emitting diodes, there is no standard way to report LEFET device characteristics. As a consequence, it can be difficult to draw comparisons between different groups and compare device results.

1.4.3.1 Single Crystal LEFETs

Single crystal organic semiconductors have several advantages for applications in LEFETs. They are thermally stable and have typically high charge carrier mobilities (> 0.1 cm² V⁻¹ s⁻¹) since they have an ordered structure in the solid state [60], which can help to maximise the brightness. Some single crystals have been reported to have high photoluminescence quantum yields of up to ~90% [61]. This is desirable for LEFET applications in order to maximise the light out of the device.
and to improve the EQE (see Equation 1.8). However, LEFETs based on single crystals can be difficult to fabricate since the crystals are difficult to grow and need to be laminated to the dielectric layer or to the substrate to create transistors. Nevertheless, there have been several reports incorporating single crystals in LEFET devices. Most reports of single crystal FETs have been ambipolar, with the position of the emission zone dependent on applied bias [3, 60–65]. Unipolar hole dominated devices have also been reported [66, 67].

A range of EQEs have been reported for single crystal LEFETs. The lowest reported EQE was around 0.03 % for a device based on a rubrene single crystal [62]. A high EQE of ~ 1 % was reported for an ambipolar single crystal LEFET by Sawabe et. al. [65]. This was achieved by etching the crystals to confine the current to a small area. However, the EQE dropped at higher current densities, similar to the roll-off in efficiency that has previously been reported in OLEDs [68]. The brightness increased as the current density increased. The brightness of single crystal LEFETs has mostly been reported in arbitrary units, which means that it is impossible to compare the reports.

Single crystal LEFETs also display waveguiding effects that alter the direction that light is emitted from the device. More of the light is propagated through the bulk of the crystal in the direction parallel to the gate dielectric rather than in the vertical direction, resulting in strong light emission from the edge of the crystals [3, 61, 65]. Waveguiding effects have also been used to tune the colour of the emission [69] in single crystal LEFETs.

1.4.3.2 Phosphorescent LEFETs

As discussed in Section 1.2.3, in a phosphorescent material, more of the excitons that are formed are able to decay radiatively than in a fluorescent material. This has the potential to increase the EQE of the device.

To date, there have been limited reports on the use of phosphorescent materials in LEFETs. The earliest report incorporates an evaporated blend of fac-tris(2-phenylpyridine)iridium (8 wt%): N,N’-dicarbazolyl-4,4’-biphenyl (Ir(ppy)_3 [8 % wt]:CBP) as the emissive layer into the device [32]. The reported brightness was quite high at close to 1000 cd m$^{-2}$, however the EQE was not reported. Solution processed devices using a green-emitting iridium-cored dendrimer as the emissive layer with a PBTTT charge transport layer were also reported. Both the brightness and the EQE of the devices increased when the dendrimer was mixed with a CBP charge transporting host. Brightnesses for these devices were between 500 – 1000 cd m$^{-2}$, with the maximum EQE of 0.45 % recorded at the maximum brightness [70]. A similar EQE was more recently reported for evaporated phosphorescent LEFETs based on the red emitter tris-(8-hydroxyquinoline)aluminium (Alq_3) in a host of platinum-octaethyl-porphyrin (PtOEP) [71]. The maximum EQE of 0.6 % was reported using a solution processed blue emitting semiconductor layer, F8, in combination with a
phosphorescent iridium complex that was allowed to diffuse through the semiconductor layer [72]. The maximum EQE occurred where the source-drain current was low, and so the low brightness was likely to be low.

1.4.3.3 Multi-layer LEFETs

LEFETs with multiple semiconductor layers have been used to try to improve the charge transport in the device, which can increase the brightness. One or more high mobility semiconductor layers are used in tandem with the emissive layer. Both bilayer and trilayer device architectures have been used in LEFET devices. A schematic showing the bilayer and trilayer device architecture is given in Figure 1.12. The emissive polymer Super Yellow was used in combination with a charge transporting layer of poly(2,5-bis(3-alkylthiophene-2-yl)thieno[3,2-b]thiophene) (PBTTT) to obtain a maximum brightness of 2500 cd m$^{-2}$ [2]. This was orders of magnitude higher than the brightness reported for devices with Super Yellow alone as the semiconductor and emissive layer [42]. The maximum EQE of 0.15 % of the Super Yellow/PBTTT bilayer devices [2] was lower than the maximum EQE obtained for single layer Super Yellow devices [42]. The bilayer devices operated in $p$-type mode only, whereas the single layer devices were ambipolar. The lower EQE in the bilayer devices was most probably is due to the imbalance of charge carriers within the device, which can result in a low recombination efficiency. Bilayer devices were also reported using single crystals [66, 67] and evaporated materials [73, 74].

![Figure 1.12. Schematic of a) bilayer and b) trilayer LEFET device architectures with source (S), drain (D) and gate electrodes. In the bilayer device architecture, a charge transport layer is typically used underneath the emissive layer. The emissive layer is sandwiched between a charge transport layer and either a second charge transport layer or a charge injection layer in the trilayer architecture.](image-url)
A conjugated polyelectrolyte layer was used to improve the electron injection into bilayer Super Yellow/PBTTT devices [54, 75]. The polyelectrolyte layer was spin-coated on top of the emissive layer. High work function electrodes could be used instead of the asymmetric electrodes with a low work function metal used in other reports. This simplified device fabrication over previously reported devices since low work function metals were not needed [2]. Further improvements to this device architecture were made using an ordered polymer charge transport layer with a higher mobility than PBTTT as the charge transporting polymer [76]. In this case, the gate dielectric was structured using directional rubbing. This resulted in an increase in the mobility of the charge transporting polymer, poly(3,6-di-alkylthieno[3,2-b]thiophene-co-bithiophene) in the direction of the rubbing. A maximum brightness of ~ 5000 cd m$^{-2}$ was reported using these techniques with an EQE of ~0.13 % at the maximum brightness.

Tri-layer LEFETs have also been reported using $n$-type and $p$-type charge transporting materials to sandwich an emissive layer [43]. Electrons and holes were transported in separate layers and recombined in the emissive layer in between. Device performance was dependent on whether the $n$-type or $p$-type layer is closest to the top electrodes. The maximum EQE was 5 %, which is ~ 2 orders of magnitude higher than the maximum EQE of the equivalent OLED device using the same materials. However, the maximum EQE in the LEFET was achieved at the minimum of the source-drain current, where the brightness is likely to be low. The brightness of the devices at the maximum EQE was not reported.

**1.4.3.4 New LEFET device architectures**

New device architectures have also been developed to improve the EQE. One approach was to spatially control the charge carrier concentration in order to control the recombination and the electroluminescence from the device. This was achieved using a split-gate device architecture [77] as shown in Figure 1.13a. A bottom gate top contact device architecture was adopted using a single layer of F8BT as the emissive semiconductor layer, and a silicon dioxide (SiO$_2$) dielectric passivated with a thin layer of PMMA. Two bottom gates were used with a 4 µm gap between. A polyelectrolyte dielectric was used between the gap to compensate for the drop in electric field in this area. A drop in the electric field could affect the charge accumulation within the device. The two different gates were independently biased to control the electron and hole concentrations within the device. This resulted in a maximum EQE of ~ 1.5 % at the maximum brightness of the device. This was an improvement of the EQE at the maximum brightness over devices previously reported using F8BT and a single gate [48, 56, 78, 79].
Figure 1.13. Schematic of different LEFET device architectures reported in literature: a) The split-gate device architecture [77]. Different voltages were applied to each gate to independently control electron and hole concentrations; b) mirror structure [4]. The bottom silver gate was made very thick to reflect more of the light out of the bottom of the device; c) optoelectronic gate dielectric [80]. The dielectric was made up of layers of alternating SiO$_2$ and silicon nitride (SiN$_x$). The stack was designed to reflect more of the light out at the emission peak of the emissive polymer; d) An example of grating structure which was incorporated into the LEFET design [34]. A grating structure was patterned underneath the semiconductor layer to increase the out-coupling of the light.
In order to increase the out-coupling of light from the device, and improve the EQE, a mirror structure was incorporated into top gate bottom contact devices [4] (see Figure 1.13b). The top gate was a thick layer of silver that was designed to reflect more of the light out of the bottom of the device. The addition of the highly reflective top gate caused optical cavity effects in the device, and so the PMMA thickness was optimized using optical simulations to maximise the out-coupling of the light. This resulted in a maximum EQE of 8 % at almost one third of the maximum brightness of the device.

The out-coupling of light from LEFETs was increased by using an ‘optoelectronic gate dielectric’, which was a layered structure of dielectrics with different refractive indices [80], demonstrated in Figure 1.13c. The silicon nitride/silicon dioxide stacks were designed to increase the reflectivity at the emission peak of the emissive layer. The light was redirected in the forward direction, which increased the amount of light collected from the device to improve both the brightness and EQE. The EQE increased by almost five times compared to the control device. Alternatively, the out-coupling of the light was increased using a grating structure underneath the semiconductor layer to reflect light to the forward direction and to minimise losses from the light traveling parallel to the substrate [34] (see for example Figure 1.13d). This structure also incorporated a rib waveguide structure to help guide the light.

1.4.3.5 Vertical LEFETs

A change in the LEFET device geometry has been explored using what is known as “vertical” LEFETs. In this geometry, the source and drain contacts are positioned vertically relative to each other instead of horizontally as in the standard FET device architecture. In the vertical LEFETs reported by Nakamura et. al., the device was essentially an OLED on top of a pentacene-based transistor in parallel to switch the OLED on [32]. The gate electrode was also positioned vertically relative to the source and drain electrodes. The device was able to achieve high brightnesses of > 1000 cd m⁻².

The geometry reported by McCarthy et. al. had the gate electrode positioned laterally compared to the vertically positioned source and drain electrodes [5]. Aluminium oxide was used to create devices that could be switched ON at a low operating voltage, making the use of LEFETs in a commercial active matrix display a viable option. Although brightnesses of hundreds of cd m⁻² were reported, there was no mention of the EQE.
1.5 Aims of this thesis

Although there have been many reports of LEFETs in literature, there are still areas of research that have received little attention. Whilst there have been some investigations into charge injection in LEFETs, extensive and controlled studies have not been undertaken. More efficient charge carrier injection of both electrons and holes could result in more efficient recombination of charges. This would improve the EQE. There is also the potential to improve the brightness with more efficient charge carrier injection since there would be a larger number of charges available to recombine. Creating ambipolar devices will result in more balanced electron and hole currents. This has the potential to improve the recombination efficiency, and hence the EQE. Furthermore, if ambipolar LEFETs can be made using high mobility materials, a high brightness could be achieved with a high EQE. The aims of this thesis are therefore twofold:

1. To develop an understanding of charge injection or extraction and charge transport in LEFET devices

2. To investigate the use of ambipolar FETs in creating high brightness and high efficiency LEFET devices.

Chapter 2 will outline the main fabrication and characterisation techniques for both standard OFETs and LEFETs used throughout this thesis. Chapter 3 describes work on the investigation of charge injection using a previously unreported diketopyrrolopyrrole co-polymer. This family of materials have had high mobilities reported in literature, and are interesting for use as a bipolar charge transporting material in LEFETs. Charge injection is further investigated in the context of both ambipolar and unipolar LEFETs based on the emissive polymer Super Yellow with the results described in Chapter 4. This was the first time that an extensive and systematic study of charge injection in LEFETs was performed. A possible way to improve device efficiency is to use phosphorescent materials. A study of the charge injection into phosphorescent LEFET devices using evaporated phosphorescent materials as the emissive layer is presented in Chapter 5. Unipolar devices were created using a high mobility hole-transporting polymer, with ambipolar devices fabricated using a diketopyrrolopyrrole co-polymer as the charge transport layer. The thesis culminates in Chapter 6, which describes work on solution processed ambipolar phosphorescent LEFETs. This work brings together techniques and principles presented in previous chapters of the thesis.
Chapter 2
Experimental methods and device characterisation

2.1 Introduction

In this chapter, a brief overview of the experimental techniques used to fabricate organic field-effect transistors for this thesis will be given. This includes the cleaning of the substrates and the deposition of the films and the electrodes. The electrical characterisation for standard FETs will then be described. Following a brief overview of the standards for the description of light and colour, details of the optical characterisation that was undertaken for light emitting FETs will then be given. Details specific to each experiment will also be given in subsequent chapters.

2.2 Device fabrication and testing

All device fabrication and testing was undertaken in a Class 1000 clean room using the facilities available at the Centre for Organic Photonics and Electronics (COPE). Some of the equipment used was provided and maintained by the Queensland node of the Australian National Fabrication Facility (ANFF), which is partly hosted by COPE.

2.2.1 Substrate preparation and cleaning

Silicon dioxide (SiO$_2$) substrates were made by thermally growing the SiO$_2$ on silicon substrates in house. Silicon nitride (SiNx) substrates were all purchased from Silicon Quest International. Substrate cleaning involved the repeated ultra-sonication in more than one solvent. The substrates were first rinsed in acetone and then cleaned by ultra-sonication in acetone for 20 mins. The substrates were then washed in 2-propanol and then ultra-sonicated in 2-propanol for 20 mins. Substrates were dried under a stream of nitrogen.

It has been shown that when surface of the dielectric was free from hydroxyl groups, the electron mobility of the material increased [81]. Passivating the surface in this way is thought to remove electron traps. This important since the charge transport in a FET occurs at the interface
between the semiconductor and dielectric. In this case, the removal of electron traps was responsible for the improved electron mobility. Passivation layers were used throughout all of the experiments in this thesis.

Following substrate cleaning, substrates were transferred to a nitrogen-filled glove box (O$_2$ < 0.1 ppm, H$_2$O < 0.1 ppm) for the deposition of the passivation layer and all subsequent layers. For each new material, several different passivation layers, including poly(methyl methacrylate) (PMMA), octyltrichlorosilane (OTS) and hexamethyldisilazane (HMDS), were initially trialled. In most cases, devices that had a thin PMMA layer close to 100 nm had higher field-effect mobilities and ON/OFF ratios compared with the other passivation layers. This may be because PMMA was better able to promote better film quality, a smooth dielectric/semiconductor interface and better self-organisation of the polymers in the solid state. Two different molecular weights were used. The low molecular weight polymer (15 000 g mol$^{-1}$) was used in Chapter 3 and Chapter 4. The high molecular weight polymer (120 000 g mol$^{-1}$) was used in Chapter 5 and Chapter 6. The PMMA layer was deposited from a solution in either toluene or propyl acetate at speeds from 1500 – 3000 rpm for 60 s. The PMMA-coated substrates were then heated on the hot plate at 100 – 150 °C.

When a thin PMMA layer was used to passivate the SiO$_2$ surface, the total capacitance of the PMMA/SiO$_2$ dielectric was calculated by adding the series capacitance of the oxide layer and PMMA layer. The capacitance of the PMMA layer was calculated using a literature value for the dielectric constant ($k \approx 3.4$) [82] and the measured thickness of the PMMA film.

### 2.2.2 Thin film deposition

If the organic active layers were able to be solution processed, films were deposited by spin-coating at speeds between 1000 and 4000 rpm. In cases where the materials were not able to be deposited from solution, organic layers were deposited using thermal evaporation under vacuum at $1 - 4 \times 10^{-6}$ mbar.

### 2.2.3 Deposition of contacts

Electrical source and drain contacts were deposited using shadow masks to define the electrode structures. The silicon shadow masks used in Chapter 3 were prepared in house using deep reactive ion etching [83]. Using this technique, channel lengths as small as 4 µm can be produced. For the silicon masks used in this thesis, the length of the channel varied from 40 – 150 µm with widths that were between 10 and 40 mm.

Alternatively, shadow masks were made from steel using laser cutting for the device fabrication in Chapters 4, 5 and 6 of this thesis. These masks had channel lengths that were between 70 and 120 µm with a channel width of 16 mm.
Contacts were then deposited through the shadow masks by thermal evaporation under vacuum at $1 - 4 \times 10^{-6}$ mbar.

### 2.2.4 Film thickness determination

Film thicknesses were determined by recording the average step height between the film and the substrate using a Dektak 150 profilometer. At least 5 measurements were taken across the substrate, which were then averaged to find the film thickness. When materials were deposited by thermal evaporation, film thicknesses were measured using a Quartz Crystal Monitor during evaporation. Film thicknesses were then verified using the Dektak 150 profilometer.

### 2.2.5 Material Characterisation

#### 2.2.5.1 Energy level estimation

To estimate the energy of the IE for materials that were not previously characterised, photoelectron spectroscopy in air (PESA) measurements were performed to measure the ionization potential. The measurement is performed by scanning across a range of incident wavelengths of light and measuring the number of counts produced when the electrons are removed from the material. Measurements were performed using a Riken Keiki AC-2 spectrometer using a power intensity of 5 nW.

Note that the optical gap corresponds to the energy of the lowest electronic transition accessible via the absorption of a photon. This is often used as an approximation of the difference between the IE and EA (see **Section 1.3.2**). However, when a photon is absorbed, the electron and hole are still bound by Coulomb attraction. The energy gap between the ionization potential and electron affinity is for separated charges. The difference between the optical gap and the true electronic gap is therefore the binding energy of the electron and hole [84]. The binding energy at room temperature is often small (on the order of a few meV), and can sometimes be neglected [84]. This means that the optical gap is often used as an approximation of the electronic gap, though it should be stressed that this is only an approximation and the two are not strictly the same. The optical gap was added to the IE to estimate the EA. An estimate of the optical gap can be found from the intersection of the scaled absorption and solid-state photoluminescence spectra plotted in energy [12].

#### 2.2.5.2 Photoluminescence quantum yield

When an organic material absorbs a photon, an energetically excited state is formed. This excited state must decay, either radiatively or non-radiatively, to the ground state. The photoluminescence quantum yield (PLQY) is a ratio of the number of photons absorbed to the number emitted. Measurements were performed according to standard literature procedures [85]
using an integrating sphere. The sample was continuously purged with flowing nitrogen and was excited at 325 nm using an IK Series He-Cd laser (Kimmon). Measurements were performed on films of different thicknesses. Different film thicknesses ranging from ~50 nm to ~300 nm were used to better estimate the average and associated errors. Averages were taken over at least 6 readings.

2.2.6 Device testing

Electrical characterization of the devices was performed using an Agilent B1500A Semiconductor Analyser and an SA-6 Semi-Automatic Probe Station (see Figure 2.1 and Figure 2.2). In addition to standard electrical FET characterisation, the light output from the devices was measured during operation. A calibrated photomultiplier tube (Hamamatsu H10721-20) was positioned directly over the device in order to record the light output from the device, as shown in Figure 2.2. The source-drain current of the transistor and photocurrent from the pmt were recorded to determine the electrical and optical device characteristics, as described below in Section 2.3 and 2.5 respectively. Calibration of the brightness of the devices was performed with the aid of a Konica Minolta LS100 luminance metre.

2.3 Standard Field-Effect Transistor characterisation

OFETs are modelled using standard MOSFET (metal-oxide-semiconductor field effect transistor) equations, which were originally developed for inorganic devices [10]. The equations were derived by taking into account the applied fields within the device. The model does not take into account any microstructural details and is therefore considered to be applicable to organic as well as inorganic systems. Important device parameters of interest include the charge carrier mobility, \( \mu \), the ON/OFF ratio and threshold voltage, \( V_t \), which is the minimum gate voltage that must be applied to switch the device ON.

For an n-type device operating in the linear regime, where \( V_{DS} < V_G - V_t \) [10],

\[
I_{DS} = \frac{W}{L} \mu C \left[ (V_G - V_t)V_{DS} - \frac{V_{DS}^2}{2} \right].
\]  

(2.1)

where \( I_{DS} \) is the source-drain current, \( W \) and \( L \) are the length and width of the transistor channel respectively and \( C \) is the capacitance of the dielectric layer. In the saturation regime, where \( V_{DS} \geq V_G - V_t \) [10],

\[
I_{DS} = \frac{W}{L} \frac{\mu C}{2} (V_G - V_t)^2.
\]  

(2.2)
Figure 2.1. The LEFET characterisation setup at COPE. a) A schematic showing the position of the photomultiplier tube over the probe station to measure the light output of the device. The distance from the photomultiplier tube to the probe station was fixed. The probes and the photomultiplier tube (pmt) were connected electrically to the Agilent B1500A Semiconductor Analyser that was positioned outside the glove box. The photomultiplier tube was also connected to an external power supply inside the glove box. b) Photograph of the FET characterisation setup inside the clean room.
Figure 2.2. Close-up of LEFET characterisation setup within the glove box. a) The optical microscope was positioned directly over the device to record images of the devices in operation. There were three probes that were individually controlled and were connected electrically to the device on the stage. b) The position of the photomultiplier tube directly over the device. The photomultiplier tube was calibrated at one height, which was kept constant for all measurements.

These equations are the same for p-type devices, with sign differences to take into account the opposite polarity of the applied voltages. In this thesis, the mobility was estimated from the transfer characteristics in the saturation regime. If the threshold voltage is small, the mobility is given by

$$\mu = \frac{2L}{WC} \left( \sqrt{\frac{I_{DS}}{V_G}} \right)^2$$

in the saturation regime [10]. The threshold voltage was determined by finding the x intercept of a $\sqrt{I_{DS}}$ vs $V_G$ plot.

The ON/OFF ratio is a measure of the switching capability of the FET. In addition to the electrical properties of the semiconductor, the ON/OFF ratio is partially determined by the purity of the semiconductor and any leakage current between the gate and source electrodes [6]. The ON/OFF ratio is the ratio between the maximum current measured when the device is switched on (the “ON current”) and the minimum current (the “OFF current”) at constant $V_{DS}$.

For all experiments in this thesis, averages for the device characteristics are taken for between 5 and 10 devices. Errors quoted are standard deviations from the mean.
2.4 Standardised Measurements for light emission and colour

For light-emitting transistors, calculation of the electrical characteristics is not sufficient to evaluate device performance. In addition to analysing the standard FET device parameters as mentioned in Section 2.3, the brightness and the external quantum efficiency (EQE) of the devices must also be determined. However, before this can be done, some important quantities and characteristics of light emission must be defined.

2.4.1 Radiometric and photometric quantities

There is more than one way to characterise light. The first method is to characterise light in terms of physical quantities, for example the number of photons, photon energy, or optical power [86]. These are radiometric units. In contrast, photometric units are used to characterise light and colour in terms of the sensitivity of the human eye [86]. Quantities using both of these units are needed to determine the brightness and EQE. Some of the important photometric quantities for characterising LEFETs will be defined below.

The luminous intensity is the light intensity of an optical source as perceived by the human eye [86] and is measured in units of candelas (cd). It was originally derived from the light intensity emitted by 1 standardised candle. The formal SI definition of a candela is as follows:

The candela is the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency 540 ×10^12 Hz and that has a radiant intensity in that direction of 1/683 watt per steradian [87].

Note that the radiant intensity is measured as a function of the light emitted in a solid angle from the source.

The luminance or brightness of a source is the ratio of the luminous intensity emitted in a certain direction divided by the projected surface area in that direction. The luminance or brightness is therefore measured in cd m⁻². Throughout this thesis, the quantity will be described using the term brightness in order to fully distinguish it from other photometric units.

The luminous flux is the light power from a source perceived by the human eye measured in units of lumens (lm). The lumen is defined as

A monochromatic light source emitting an optical power of 1/683 watt at 555 nm has a luminous flux of 1 lumen (lm) [86].

In order to be able to calculate the number of photons emitted by a LEFET, a conversion factor between the luminous flux (a photometric unit) and the optical power (a radiometric unit) is needed. The luminous flux, ϕ_{lum}, is related to the optical power by [86]

ϕ_{lum} = 683 \frac{lm}{W} \int V(\lambda)P(\lambda) \, d\lambda, \tag{2.4}
where \( P(\lambda) \) is the spectral power density, \( 683 \frac{lm}{W} \) is a normalization factor and \( V(\lambda) \) is the eye response curve, otherwise known as the photopic luminosity function. The International Commission for Illumination (Commission Internationale de l'Eclairage, CIE) introduced the photopic eye sensitivity function, \( V(\lambda) \), for point-like sources where the viewing angle is 2°. The standard is the CIE 1931 \( V(\lambda) \) function (see Figure 2.3). Since 1931, there have been modifications to take into account, for example, the under-estimation of the sensitivity of the human eye in the blue, however the 1931 \( V(\lambda) \) function is still used as the standard. The function demonstrates how well the emitted radiation is detected by the human eye, since the eye does not detect all wavelengths equally. For example, the UV and infrared parts of the spectrum are invisible to the eye, and therefore emission in this region is not useful as a source of illumination. The luminous flux is therefore dependent on the overlap of the eye response curve with the spectrum emitted by the source to describe how the source appears to the human eye.

![Figure 2.3. Normalized CIE 1931 photopic luminosity function or eye response curve \([V(\lambda)]\) as a function of wavelength.](image)

### 2.4.2 Lambertian emission

Lambertian sources are sources in which the radiance and brightness are constant and independent of viewing angle [86]. The radiance is defined as the optical power emitted per steradian per unit surface area of the source. For a Lambertian source, the light intensity, \( I \), in a particular direction given by the angle \( \theta \) from the normal is given by [86]

\[
I = I_n \cos \theta \tag{2.5}
\]

where \( I_n \) is the intensity emitted normal to the reflected surface.
The projected area $A$ visible to an observer positioned at an angle $\theta$ is given by $A \cos \theta$. So the brightness of a source is proportional to

$$\text{brightness} \propto \frac{I_n \cos \theta}{A \cos \theta}$$

$$\text{brightness} \propto \frac{I_n}{A}$$

which is a constant independent of angle $\theta$. In common with most OLEDs where there are no cavity effects present, the LEFETs described in this thesis will be assumed to be Lambertian emitters unless otherwise stated.

### 2.4.3 Colourimetry

The measurement and description of colour was standardised using colour-matching functions and a chromaticity diagram by the CIE. Three colour-matching functions, $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$ which represent red, green and blue light respectively are shown in Figure 2.4. The three-colour matching functions are measured experimentally from the human eye by measuring the relative intensity of red, green and blue light needed to “colour-match” monochromatic light. The three functions reflect the fact that the colour of light can be described using three variables. The three colour-matching functions are dimensionless. The 1931 CIE standard will be used throughout this thesis, not because it is the most accurate standard available, but it is the most widely used.

For a given colour spectral density $P_{\text{spectrum}}(\lambda)$, the degree of each function required to match the colour of the spectrum is given by the overlap of the spectral density with each of the colour-matching functions [86]:

$$X = \int \bar{x}(\lambda) P_{\text{spectrum}}(\lambda) \, d\lambda$$  \hspace{1cm} (2.6)

$$Y = \int \bar{y}(\lambda) P_{\text{spectrum}}(\lambda) \, d\lambda$$  \hspace{1cm} (2.7)

$$Z = \int \bar{z}(\lambda) P_{\text{spectrum}}(\lambda) \, d\lambda$$  \hspace{1cm} (2.8)

where $X$, $Y$ and $Z$ are known as the tristimulus values. These values give the stimulation or power of each of the three primary colours needed to match the colour of $P_{\text{spectrum}}(\lambda)$.

The colour of the light source can also be represented as co-ordinates on a chromaticity diagram. The chromaticity diagram represents the spectrum of colours visible by the human eye. Chromaticity co-ordinates are calculated from the three tristimulus values according to [86]

$$x = \frac{X}{X + Y + Z}$$  \hspace{1cm} (2.9)

$$y = \frac{Y}{X + Y + Z}$$  \hspace{1cm} (2.10)
Figure 2.4. CIE 1931 colour-matching functions $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$ as a function of wavelength. Note that the green colour-matching function, $\bar{y}(\lambda)$, is identical to the eye response curve, $V(\lambda)$.

The $z$ co-ordinate can also be calculated from the tristimulus values. The $z$ co-ordinate can be given by using the values of the $x$ and $y$ co-ordinates already calculated and therefore it gives no further useful information.

$$z = \frac{z}{x + y + z}$$

$$z = 1 - x - y$$

(2.11)

The $x$ and $y$ co-ordinates (commonly referred to as the “CIE co-ordinates”) can then be displayed on a chromaticity diagram (see Figure 2.5). Red colours correspond to large values of $x$, green to large values of $y$ and blue to large values of $z$. Large values of $z$ also correspond to regions in which both $x$ and $y$ are small.

### 2.5 Light Emitting Field-Effect Transistor optical characterisation

#### 2.5.1 Calibration of the system

In order to calculate the brightness of the emission from LEFETs, the photocurrent measured by the photomultiplier tube (pmt) was calibrated using an OLED fabricated using the
organic polymer Super Yellow as the emissive layer. An OLED was used for the calibration as it could more easily be encapsulated so that the brightness could be measured outside the glove box using a luminance metre. The $I-V$ characteristics of the OLED were measured and the brightness was recorded using the luminance metre (Konica Minolta LS100). Once the brightness of the OLED was known at a particular applied voltage, this device could then be used to calibrate the photocurrent from the pmt. The distance from the pmt to the device was fixed, and the pmt current for various OLED brightnesses was measured. The pmt current as a function of the OLED brightness at a particular gain was plotted to calibrate the pmt. The calibration curve for the pmt set at a gain of 0.4 can be found in Figure 2.6. The error in the brightness was estimated from multiple measurements of the OLED brightness with the same applied voltage.

![Chromaticity diagram](image)

**Figure 2.5.** Chromaticity diagram representing the possible colours the human eye can perceive with $x$ and $y$ co-ordinates. Red colours are found for large values of $x$ and green for large values of $y$. Blue colours are found for small values of both $x$ and $y$. The values of $x$ and $y$ are dimensionless.
Figure 2.6. Calibration curve of the photomultiplier tube (pmt) showing the photocurrent response of the pmt at known brightness of a Super Yellow OLED.

The slope of the calibration curve can then be used to find the brightness of a device with known pmt current. For a gain of 0.4, the slope of the calibration is $69.0 \text{ nA/(cd m}^{-2}\text{)}$ and so

$$1 \text{ cd m}^{-2} \approx 69.0 \text{ nA} \quad (2.12)$$

This is for an OLED area of 0.92 mm$^2$. In order to account for the difference in emission area of the LEFET and OLED, this calibration can be adjusted

$$1 \text{ cd m}^{-2} \approx 69.0 \text{ nA} \times \frac{\text{Area}_{\text{emission (LEFET)}}}{\text{Area}_{\text{emission (OLED)}}} \quad (2.13)$$

The conversion between pmt current in nA and brightness in cd m$^{-2}$ is then

$$\text{Brightness (cd m}^{-2}\text{)} = \text{pmt current (nA)} \times \frac{\text{Area}_{\text{emission (OLED)}}}{\text{Area}_{\text{emission (LEFET)}}} \times \frac{1}{69.0 \text{ nA/cd m}^{-2}} \quad (2.14)$$

A digital camera connected to an optical microscope was used to image the device emission area. The image was then analysed by taking an intensity profile across the emission region. The width of the emission zone was then measured by taking 50% of the full width at half maximum of the peak of the emission.

The minimum current measured by the photomultiplier tube (the dark current, or level of noise) is of the order of pA. Depending on the electroluminescence spectrum and light emitting area of the device, this corresponds to a brightness of order $10^{-3} – 10^{-2}$ cd/m$^2$. A brightness of at least 0.1 cd/m$^2$ should be able to be detected above the noise since it is at least one order of
magnitude higher.

### 2.5.2 Calculation of the External Quantum Efficiency

The EQE was calculated according to standard methods used for OLED characterisation [88] and applied to the measurements made for LEFETs. The emission from the device is assumed to be approximately Lambertian, and so the luminous flux per solid angle is dependent on the cosine of the viewing angle. The emission is greatest at an angle perpendicular to the device. The emission from the device was detected perpendicular to the contacts (see Figure 2.7), and integrated over the solid angle of emission to find the total emission. The brightness is independent of angle (see Section 2.4.2).

![Detection of light from between source and drain electrodes in a LEFET](image)

**Figure 2.7.** Detection of light from between source and drain electrodes in a LEFET. Emission from the device was detected at X, perpendicular to the emission. Detection occurred at a fixed distance, a, from the substrate.

The EQE is formally defined as

\[
EQE = \frac{\text{number of photons emitted from the device into free space per second}}{\text{number of electrons injected into the device per second}}. \tag{2.15}
\]

Both the number of photons per second emitted and the number of electrons per second injected must be determined in order to calculate the EQE. The number of photons per second emitted from the device will first be calculated.

The luminous flux, \( \phi_{\text{lum}} \), is the flux leaving the device without being waveguided through the device (for example, via substrate modes). Using geometry, the total flux is given by [88]

\[
\phi_{\text{lum}} = \int_0^{\pi/2} 2\pi L_0 \cos\theta \sin\theta \, d\theta \tag{2.16}
\]

where \( \theta \) is the angle from the normal at which the light is detected and \( L_0 \) is the flux per unit solid angle of light leaving the device in the forward direction. This was the brightness determined from
the calibration of the pmt in Section 2.5.1. Using the trigonometric identity \( \cos \theta \sin \theta = \frac{1}{2} \sin 2\theta \), Equation 2.16 becomes

\[
\phi_{\text{tum}} = \int_0^{\pi/2} 2\pi L_0 \frac{1}{2} \sin 2\theta \, d\theta
\]

\[
\phi_{\text{tum}} = \pi L_0 \left(-\frac{1}{2} \cos 2\theta\right)_0^{\pi/2}
\]

\[
\phi_{\text{tum}} = \pi L_0 \left[ \frac{1}{2} - \left(-\frac{1}{2}\right) \right]
\]

\[
\phi_{\text{tum}} = \pi L_0
\]  \hspace{1cm} (2.17)

If \( L_0 \) is in units of \( \text{cd/m}^2 \), then

\[
\phi_{\text{tum}} = \pi L_0 \times \text{Area}_{\text{emission}}
\]  \hspace{1cm} (2.18)

where \( \text{Area}_{\text{emission}} \) is the area of light emission for \( \phi_{\text{tum}} \) to be in units of lumens (\( \text{lm} \)).

The total optical power, \( P \), emitted by a light source is given by an integration over all wavelengths is

\[
P = \int P(\lambda) \, d\lambda.
\]  \hspace{1cm} (2.19)

This is found by integrating over the normalized electroluminescence spectrum collected from the device since the area under the curve is the same.

Using the previously presented expression for \( \phi_{\text{tum}} \) in Equation 2.4 and Equation 2.19, the ratio between the luminous flux and optical power is

\[
\frac{\phi_{\text{tum}}}{P} = 683 \frac{\text{lm}}{\text{W}} \frac{\int \nu(\lambda)p(\lambda) \, d\lambda}{\int P(\lambda) \, d\lambda}.
\]  \hspace{1cm} (2.20)

Using Equation 2.18, the optical power, \( P \), is given by

\[
P = \frac{\pi L_0}{683 \text{lm} \int \nu(\lambda)p(\lambda) \, d\lambda}.
\]  \hspace{1cm} (2.21)

The optical power is used to find the number of photons emitted by the device. The energy, \( E \), of \( n \) photons is

\[
E = nh\nu
\]

where \( h \) is Plank’s constant and \( \nu \) is the frequency of the photons. This can be re-written in terms of wavelength as follows

\[
E = \frac{nhc}{\lambda}
\]  \hspace{1cm} (2.22)

where \( \lambda \) is the wavelength and \( c \) is the speed of light.

Instead of a single wavelength of light being emitted by the device, there is actually a spectrum of wavelengths. For a recorded electroluminescence spectrum, the average wavelength, \( \lambda_{\text{av}} \), is

\[
\lambda_{\text{av}} = \int \frac{E(\lambda) \lambda \, d\lambda}{E(\lambda) \, d\lambda}
\]  \hspace{1cm} (2.23)
where $E(\lambda)$ is the recorded electroluminescence spectrum from an operational device.

The number of photons is then given by substituting **Equation 2.23** into **Equation 2.22** and rearranging for $n$ to give

$$n = \int \frac{E(\lambda) d\lambda}{E(\lambda)} \times \frac{1}{hc} \times E.$$  \hspace{1cm} (2.24)

The number of photons per second, $N$, is then

$$N = \int \frac{E(\lambda) d\lambda}{E(\lambda)} \times \frac{1}{hc} \times P$$ \hspace{1cm} (2.25)

using the optical power calculated using **Equation 2.21**.

The number of electrons per second carried through the device, $e$, can be found by dividing the measured source-drain current by the charge of one electron, $q$:

$$e = \frac{I_{DS}}{q}$$ \hspace{1cm} (2.26)

$$e = \frac{I_{DS}}{1.602 \times 10^{-19} C}.$$ 

The EQE can then be found by dividing the number of photons per second which escape from the device, $N$, by number of electrons per second through the device, $e$ to give

$$\text{EQE} = \frac{N}{e}.$$ \hspace{1cm} (2.27)

### 2.5.3 Calculation of CIE coordinates

The $x$ and $y$ CIE coordinates are calculated for the devices based on the methods described above in **Section 2.4.3** using the electroluminescence emission spectrum of operational LEFET devices. The $x$ and $y$ co-ordinates is reported for devices with a given emissive layer.
Chapter 3

Ambipolar Field-effect Transistors using a diketopyrrolopyrrole-based polymer

3.1 Introduction

In this chapter, device fabrication and characterization is described for a previously unreported diketopyrrolopyrrole-based polymer. The device performance was tuned by altering the work function of the metal used for the source and drain contacts. Devices that were fabricated using Au top contacts operated in p-type mode. When the contacts were changed from Au to Al, the devices exhibited ambipolar behaviour with clear hole accumulation (p-type) and electron accumulation (n-type) regimes. Ambipolar devices are particularly important for logic circuit applications, and the fabrication of organic inverters made from a single active layer. Furthermore, an understanding in the fabrication and characterization of ambipolar FETs aids the fabrication and characterization of ambipolar light-emitting transistors.

3.2 Material design and structure

3.2.1 DPP polymers

Diketopyrrolopyrrole (DPP) based narrow optical gap polymers have been used extensively in high mobility field-effect transistors [29, 31, 89, 90, 91]. Donor-acceptor type polymers using DPP as an electron acceptor in conjunction with an electron donor have been used to create both ambipolar [28, 30, 90, 92–94] and unipolar [29, 91, 95] FETs. Reported hole mobilities have mainly been in the range of ~ 0.01 to 1.5 cm$^2$ V$^{-1}$ s$^{-1}$. The highest reported mobilities have been close to 10 cm$^2$ V$^{-1}$ s$^{-1}$ for polymers containing a DPP subunit [31, 89, 96]. These are among the highest mobilities reported so far for a solution-processed polymer FET.

The main approach to the design of DPP-based polymers is to have the DPP moiety flanked by two thiophenes, giving a base building unit of thiophene-DPP-thiophene [29, 31, 90–92, 95–97]. Variations in the polymer structure have focused on linking the moieties between the thiophene-
DPP-thiophene units and have included dithienothiophenes [95], naphthalene [91], seleno- and thiophenes [29], and benzothiadiazoles [92]. Apart from the thiophene-DPP-thiophene, reports in which the thiophene units are replaced by thienothiophenes to give a base unit of thienothiophene-DPP-thienothiophene are limited [30].

Given the promising DPP results previously reported, a DPP polymer with thienothiophene subunits was investigated for applications in ambipolar FETs. By changing the work function of the metal used for the contacts, charge carrier injection could be studied.

### 3.2.2 Structure of the DPP-based copolymer

The DPP polymer was a new thienothiophene-DPP-thienothiophene based polymer, poly(3,6-dithieno[3,2-b]thiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4-dione-5',5''-dihydro-4H-[1,2-b:4,5-b']dithiophene-2,6-diy1 (PTTDPP-BDT) (see Figure 3.1). Gel Permeation Chromatography was used to determine the molecular weight of the polymer and it was found that $M_n = 4.4 \times 10^4$ g mol$^{-1}$ and $M_w = 2.3 \times 10^4$ g mol$^{-1}$ with a polydispersity index of 5.4 (against polystyrene standards). This polymer was incorporated into bottom gate top contact FETs to investigate its charge transport properties.

![Chemical structure of the diketopyrrolopyrrole-based copolymer, PTTDPP-BDT.](image)

**Figure 3.1.** Chemical structure of the diketopyrrolopyrrole-based copolymer, PTTDPP-BDT. PTTDPP-BDT is based on a diketopyrrolopyrrole subunit flanked by thienothiophenes with a benzodithiophene subunit.

### 3.3 Experimental

#### 3.3.1 Material characterization

The UV-visible absorption spectra in solution and solid-state were recorded with a Varian Cary 5000 spectrometer. The absorption spectrum in solution was recorded in chloroform (99.9%, anhydrous) with a concentration of $2 \times 10^{-3}$ mg mL$^{-1}$ using 1 cm path length quartz cuvettes. The solid-state spectrum was recorded from a thin film that was spin-coated on a quartz substrate. The film was spin-coated hot at 100 °C from a ~ 4 mg mL$^{-1}$ solution at 1500 rpm for 60 s. The film was
~ 34 ± 5 nm thick, measured using a Dektak profilometer. The film thickness was determined from an average of 5 measurements taken across the film with the error given by the standard deviation.

Photoelectron spectroscopy in air (PESA) measurements were performed to obtain the ionization potential of the polymer and to help estimate the energy of the IE. The films were formed by spin-coating from a ~ 9 mg mL$^{-1}$ solution in chlorobenzene (99.9 %, anhydrous) at 1500 rpm for 60 s on glass to form a ~ 60 ± 10 nm thick film. PESA measurements were performed using a Riken Keiki AC-2 spectrometer using a power intensity of 5 nW.

3.3.2 Device fabrication

PTTDPP-BDT-based devices were fabricated using symmetric Al or Au contacts on SiO$_2$ substrates. The SiO$_2$ layer (350 nm thick) was thermally grown on a heavily $n$-doped silicon wafer in house (using facilities at the Australian National Fabrication Facility, Queensland Node). The bottom layer of SiO$_2$ was removed using a hydrogen fluoride treatment and evaporated Au on the bottom to act as a bottom gate. The SiO$_2$ substrates were cleaned as described in Chapter 2 and either left bare, or passivated with a thin layer of poly(methyl methacrylate) (PMMA). The PMMA layer was formed by spin-coating from a 10 mg mL$^{-1}$ solution in toluene (99.8%, anhydrous) at 3000 rpm for 60 s to give a final thickness of 40 ± 5 nm. The polymer films were formed by spin-coating a ~ 9 mg mL$^{-1}$ solution in chlorobenzene (> 99.9 %, anhydrous) at 1500 rpm for 60 s. The solutions were heated to 60 °C for several hours prior to spin-coating and were spin-coated hot at 100 °C to ensure the material was completely dissolved. The polymer did not fully dissolve at low temperatures and so had to be spin-coated at 100 °C to achieve a high quality film.

There was no difference in device performance by subsequent annealing at temperatures up to 250 °C. This result indicated that the optimum structure was achieved through the cooling of the hot solution during the spin-coating process.

Top Au or Al contacts were deposited by thermal evaporation under vacuum. 30 nm of Au or Al were deposited at a rate of 0.3 – 0.4 Å s$^{-1}$ to complete the devices.

For the devices where a thin PMMA layer was used to passivate the SiO$_2$ surface, the total capacitance of the PMMA/SiO$_2$ dielectric was calculated by adding the series capacitance of the oxide layer and PMMA layer. The capacitance of the PMMA layer was calculated using a literature value for the dielectric constant ($k \approx 3.4$) [82] and the measured thickness of the PMMA film. Device characteristics were calculated as described in Chapter 2.
3.4 PTTDPP-BDT properties

3.4.1 Absorption spectra

The UV-visible absorption spectrum of the polymer was measured both in solution and in the solid-state (see Figure 3.2). The film extinction coefficient was calculated using the thickness of the film, which was 34 nm. The solution and solid-state spectra had the similar features, with the maximum of the absorption at 776 nm. The absorption edge occurred at ~ 880 nm in thin film and at 840 nm in solution. The optical gap would be in the range from the absorption edge to the absorption maximum and would be between 1.4 eV and 1.6 eV. Since this polymer had a narrow optical gap, it was a candidate for the development of ambipolar devices.

![Figure 3.2. Film extinction coefficient and solution absorbance of PTTDPP-BDT. The solution absorbance was measured at a concentration of 2 × 10^{-3} mg mL^{-1} in chloroform. The solid-state spectrum was measured from a ~ 34 nm thick film on quartz.](image)

3.4.2 Thermal properties

Characterization of the thermal properties of PTTDPP-BDT was undertaken using Differential Scanning Calorimetry (DSC) (see Figure 3.3). Differential Scanning Calorimetry (DSC) was performed on a Mettler DSC-1 instrument at a rate of 10 °C/min under N₂. DSC analysis showed that the polymer had an endothermic transition near the decomposition temperature. A transition was observed at ~ 332 °C in the heating cycle and was assigned to the
melting of the polymer. The corresponding transition from the melt to the solid state was seen at 315 °C. No glass transition was observed.

Figure 3.3. Heat flow versus Temperature scan of PTTDPP-BDT

3.4.3 Thin film XRD

The structure of the polymer films was studied using X-ray diffraction (XRD). The X-ray diffraction pattern of a PTTDPP-BDT drop cast thin film is shown in Figure 3.4. The diffraction peak at a 2θ value of 4.1° corresponds to a d-spacing of 21.4 Å, which represents the interlayer spacing between two adjacent polymer chains. The diffraction peak at a 2θ value of 25.3° with d-spacing of 3.51 Å corresponds to π-π stacking interactions. Such close packing strongly suggests that the polymer was able to adopt a planar conformation in the solid-state.
Figure 3.4. Thin film XRD pattern of PTTDPP-BDT on an octyltrichlorosilane treated Si/SiO$_2$ substrate.

3.4.4 AFM imaging of the polymer film
Atomic Force Microscopy (AFM) was used to observe the morphology of the surface of the film. There was very little structure of the film surface, with variation in the film thickness of less than 10 nm (see Figure 3.5.).

Figure 3.5. AFM image of PTTDPP-BDT film surface.
3.4.5 Energy level estimation

The ionization potential of the polymer in thin film was determined to be 5.0 eV. In the cases where the EA cannot be directly determined, it is general practice to add the optical gap from the solid-state measurements to the ionization potential. The optical gap is usually determined from the intersection of the scaled absorption and solid-state photoluminescence spectra [12]. However, in common with many materials with a narrow optical gap, the PTTDPP-BDT was not sufficiently fluorescent in the solid-state to collect a reliable photoluminescence spectrum. An estimate of the optical gap for this polymer was therefore determined as the range from the onset of absorption to the first absorption peak, yielding 1.4 – 1.6 eV. This gave a range of the EA from 3.4 – 3.6 eV.

An energy level diagram showing the IE and EA of PTTDPP-BDT relative to the work function of the contacts used in this chapter is shown in Figure 3.6. Given the value of the IE, Au (work function 5.1 eV [98]) should be suitable for use as an appropriate contact for hole transport in the devices. However, the work function of Au was at least 1.6 eV away from the estimated EA, which means that there may not be efficient injection of electrons. The work function of Al is only approximately 0.8 eV away from the EA of PTTDPP-BDT, and there should therefore be more efficient electron injection when Al is used.

3.5 Bottom gate top contact devices using PTTDPP-BDT

The device architectures used for the PTTDPP-BDT devices are shown in Figure 3.7. All devices were fabricated in a bottom gate top contact device geometry using SiO$_2$ as a dielectric layer. The devices with Au contacts were fabricated with either bare SiO$_2$ (Figure 3.7a) or SiO$_2$ passivated with a layer of PMMA (Figure 3.7b). The devices with Al contacts were fabricated on SiO$_2$ passivated with PMMA (Figure 3.7c).

3.5.1 PTTDPP-BDT devices with Au top contacts on bare SiO$_2$

Most of the materials in the DPP family are narrow optical gap polymers. High work function contacts such as Au have been previously used to inject both electrons and holes to create ambipolar DPP-based devices [28, 92–94, 97]. With this in mind, and given that Au should be able to inject holes into the device (see Figure 3.6), Au was first selected as a contact for the PTTDPP-BDT devices. Output and transfer curves for the PTTDPP-BDT devices with Au contacts can be found in Figure 3.8. When Au was used as the source and drain contacts, with the polymer deposited directly onto the SiO$_2$ dielectric (see Figure 3.7a), only hole-transport was possible through the channel, creating unipolar devices. No electron mobility could be determined. In this
device configuration the hole-mobility was of order $10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ (see Table 3.1). Device results in $p$-type mode are given in Table 3.1 with the hole mobility ($\mu_{\text{hole}}$), the threshold voltage (Threshold voltage$_{\text{hole}}$) and the ON/OFF ratio (ON/OFF$_{\text{hole}}$).

![Energy level diagram showing the estimated IE and EA of PTTDPP-BDT with the work functions of Au and Al.](image)

**Figure 3.6.** Energy level diagram showing the estimated IE and EA of PTTDPP-BDT with the work functions of Au and Al. The work functions of the metals were taken from literature [98]. Au should provide efficient hole injection since the work function of Au and the IE of PTTDPP-BDT are only 0.2 eV apart. The work function of Al is 0.8 eV away from the EA of PTTDPP-BDT (compared with 1.6 eV for Au) and so more efficient electron injection would be expected with Al contacts.

![Configuration of the devices fabricated using PTTDPP-BDT: a) device architecture using Au source-drain contacts and a bare SiO$_2$ substrate; b) device architecture using Au source-drain contacts and with the SiO$_2$ surface modified with a PMMA layer; c) device architecture using Al source-drain contacts with the SiO$_2$ surface modified with a PMMA layer.](image)

**Figure 3.7.** Configuration of the devices fabricated using PTTDPP-BDT: a) device architecture using Au source-drain contacts and a bare SiO$_2$ substrate; b) device architecture using Au source-drain contacts and with the SiO$_2$ surface modified with a PMMA layer; c) device architecture using Al source-drain contacts with the SiO$_2$ surface modified with a PMMA layer.
Figure 3.8. Representative output and transfer characteristics for a device fabricated with Au top contacts on a bare SiO$_2$ substrate using a PTTDPP-BDT channel: a) output characteristics with the gate voltage varied between 0 and −100 V in 20 V steps; b) transfer characteristics measured using a constant $V_{DS}$ of −80 V. The characteristics were obtained on a device that had a channel length of 100 µm and a width of 40 mm.

3.5.2 PTTDPP-BDT devices with Au top contacts on PMMA/SiO$_2$

In an attempt to improve the electron transport in the device, the SiO$_2$ surface was passivated with a thin PMMA layer (see Figure 3.7b) to remove electron traps at the semiconductor-dielectric interface. This has been reported to improve the electron transport through the semiconductor channel [81]. Output and transfer characteristics for the devices can be found in Figure 3.9. The devices still operated only in the $p$-type mode. An electron mobility was too small to be determined. This suggested that the work function of Au was at least 1.6 eV away from the EA of PTTDPP-BDT and so there was not efficient electron injection. The addition of the PMMA layer increased the hole mobility by almost an order of magnitude to $1.0 \times 10^{-3} \pm 2 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$. The PMMA surface could have promoted better PTTDPP-BDT film quality, resulting in lower roughness. This could also have lead to a smoother dielectric/semiconductor interface. A lower surface roughness of the gate dielectric has been previously shown to result in an increased mobility [99]. The smooth interface is essential to reduce the scattering of carriers in the channel. The PMMA layer could also have promoted better self-organisation of the crystalline domains of the PTTDPP-DTT in the solid state. Self-organisation effectively decreases the barrier for hopping between the crystalline domains.
Figure 3.9. Representative output and transfer characteristics for a PTTDPP-BDT device fabricated with Au top contacts on a PMMA modified SiO$_2$ substrate: a) output characteristics with the gate voltage varied between 0 and $-100$ V in 20 V steps; b) transfer characteristics measured using a constant $V_{DS}$ of $-80$ V. The characteristics were obtained on a device that had a channel length of 120 µm and a width of 20 mm.

Table 3.1. Field-effect transistor performance of PTTDPP-BDT with different device architectures. All reported values were averaged over at least 6 devices. The errors reported are the calculated standard deviations of the results.

<table>
<thead>
<tr>
<th></th>
<th>Au contacts with SiO$_2$</th>
<th>Au contacts with PMMA/SiO$_2$</th>
<th>Al contacts with PMMA/SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{hole}}$</td>
<td>$2.5 \times 10^{-4} \pm 9 \times 10^{-5}$</td>
<td>$1.0 \times 10^{-3} \pm 2 \times 10^{-4}$</td>
<td>$9 \times 10^{-4} \pm 6 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\mu_{\text{electron}}$</td>
<td>-</td>
<td>-</td>
<td>$8 \times 10^{-5} \pm 2 \times 10^{-5}$</td>
</tr>
<tr>
<td>Threshold voltage$_{\text{hole}}$ (V)</td>
<td>$-5 \pm 3$</td>
<td>$-4 \pm 2$</td>
<td>$-38 \pm 7$</td>
</tr>
<tr>
<td>ON/OFF$_{\text{hole}}$</td>
<td>$2 \times 10^2 \pm 1 \times 10^2$</td>
<td>$1.3 \times 10^2 \pm 2 \times 10^4$</td>
<td>$3 \times 10^4 \pm 1 \times 10^4$</td>
</tr>
<tr>
<td>Threshold voltage$_{\text{electron}}$ (V)</td>
<td>-</td>
<td>-</td>
<td>$-11 \pm 4$</td>
</tr>
<tr>
<td>ON/OFF$_{\text{electron}}$</td>
<td>-</td>
<td>-</td>
<td>$2.0 \times 10^2 \pm 1.0 \times 10^4$</td>
</tr>
</tbody>
</table>
3.5.3 Devices with Al top contacts on PMMA/SiO$_2$

By changing the source and drain contacts to Al in combination with a PMMA passivation layer, ambipolar devices were created. Clear hole-dominated and electron-dominated regimes were present in the output and transfer characteristics (see Figure 3.10). Output characteristics for a device operating in the $p$-type and $n$-type modes can be found in Figures 3.10a and 3.10b, respectively.

![Figure 3.10](image)

**Figure 3.10.** Device characteristics for a typical ambipolar PTTDPP-BDT based OFET with Al contacts: a) output characteristics in $p$-type mode (where the gate voltage was varied from 0 to $-100$ V in 20 V steps); b) output characteristics in $n$-type mode (where the gate voltage was varied from 0 to $+100$ V in 20 V steps); c) transfer characteristics with a constant $V_{DS}$ of $-100$ V. The characteristics were obtained on a device with a channel length of 100 µm and a width of 20 mm.

Transfer characteristics are shown in Figure 3.10c. The reason that these devices were ambipolar was due to the lower work function of Al compared to Au (4.4 eV compared to 5.1 eV, respectively [see Figure 3.6]). This allowed improved charge carrier injection of electrons into the device, since the work function of Al was only 0.8 eV away from the estimated EA of the polymer. At low applied gate voltages, the output characteristics were similar to a diode, due to the buildup
of both $p$-type and $n$-type regions within the device $[100]$ (see Figures 3.10a and 3.10b). The charge transport in the device was still clearly dominated by holes, with an average hole mobility of $9 \times 10^{-4} \pm 6 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$. The average electron mobility was an order of magnitude lower at $8 \times 10^{-5} \pm 2 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$ (see Table 3.1). The electron mobility ($\mu_{\text{electron}}$), threshold voltage in $n$-type mode (Threshold voltage$_{\text{electron}}$) and the ON/OFF ratio in $n$-type mode (ON/OFF$_{\text{electron}}$) are given in Table 3.1 along with the device parameters in $p$-type mode.

3.6 Conclusion

When OFET devices were fabricated using Au contacts on either bare SiO$_2$ or SiO$_2$ modified with PMMA, unipolar devices were created, with only hole-transport was evident in the device characteristics. On bare SiO$_2$ substrates, the hole mobility was $2.5 \times 10^{-4} \pm 9 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$. When a thin PMMA interlayer was added to the SiO$_2$, the hole mobility increased by almost an order of magnitude to $1.0 \times 10^{-3} \pm 2 \times 10^{-4}$ V$^{-1}$ s$^{-1}$.

Ambipolar devices were created by tuning the work function of the top contacts. When the contacts were changed from Au to Al, there was more efficient electron injection into the device due to the lower work function of Al compared to Au. Efficient injection of holes was still possible, with similar hole mobilities measured with Au and Al contacts. Average charge carrier mobilities were close to $10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ for holes and $10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$ for electrons.

In this chapter, the charge transport of the devices was tuned by the choice of the metal used for the source and drain contacts. Here, ambipolar charge transport was only achieved for devices with Al contacts. Al allowed charge carrier injection of both electrons and holes, which was not possible in device configurations with Au contacts. This demonstrates that the electrode choice is an important consideration for the fabrication of ambipolar devices. The choice of electrode material or charge injection layer in the context of ambipolar light-emitting FETs is further explored in Chapter 4: Charge injection layers in Light Emitting Field-Effect Transistors.
Chapter 4

Charge injection layers in Light-Emitting Field-Effect Transistors

4.1 Introduction

Little investigation has been undertaken into the systematic improvement of charge carrier injection in LEFETs. More efficient injection of either electrons or holes has the potential to lead to a better balance of electrons and holes within the device, which could improve the external quantum efficiency (EQE). If a greater number of electrons and holes are able to recombine, this could also improve the device brightness. This chapter describes the effect of changing the charge carrier injection layer in fluorescent LEFETs.

To investigate charge injection in LEFETs, devices were fabricated using the model emissive fluorescent polymer Super Yellow. Both single layer and bilayer device configurations were used. In the single layer configuration, only Super Yellow was employed as the semiconducting channel. Super Yellow was used in conjunction with a high mobility PBTTT charge transport layer in the bilayer configuration. All devices were fabricated using molybdenum oxide with a gold cap to inject holes, with a variation in the electron-injecting electrode. Materials used as the electron-injecting layer included low work function metals, inorganic salts and organic layers. The Super Yellow only devices were ambipolar with clear electron- and hole-dominated regimes. PBTTT is a hole-dominated organic semiconductor with a hole mobility that is orders of magnitude higher than either the electron or hole mobilities in the neat Super Yellow films. This meant that the majority of the charge transport in the device was the conduction of holes through the PBTTT layer. Holes were then able to recombine within the Super Yellow layer to emit light. An understanding of how to effectively control charge injection into unipolar and ambipolar devices aids to improve the brightness and EQE in LEFETs.
4.2 Deposition of asymmetric source-drain electrodes

Charge carrier injection is an important device parameter that needs to be optimised in LEFETs in order to obtain the maximum possible brightness and EQE. In some cases, it is possible to construct ambipolar light emitting devices using simple device fabrication methods with symmetric high work function source-drain electrodes (such as Au) [48, 55]. However, this fabrication method is not universal for all emissive organic semiconductors, especially when considering those that have a wide optical gap. In order to obtain efficient injection of both electrons and holes into a single layer of organic semiconductor, asymmetric high and low work function metal electrodes must be used. It is also difficult both in terms of fabrication and reproducibility to form asymmetric source and drain contacts in a planar transistor geometry. There have been limited reports investigating the effect of the electrode on the emission properties in LEFETs [49, 50, 73, 101]. Extensive and systematic studies of charge injection in LEFETs have not been previously reported.

To create ambipolar LEFETs, often asymmetric source and drain contacts must be used. In order to investigate charge injection a way to deposit asymmetric contacts easily and reproducibly needed to be developed. A number of different methods have been used with varying degrees of success [36, 41, 102, 103]. One possible method is to use shadow masks and sequentially deposit two different metals. The same mask is shifted laterally after the first evaporation, but before the second evaporation is performed [102, 103]. Interdigitated electrode structures have also been created using sequential evaporations with this method [36]. However, it is difficult to align and move the shadow mask between metal evaporations consistently. Even with the aid of an optical microscope [103], the mechanical alignment is difficult to achieve in a reproducible fashion.

Lithography has also been employed to achieve a more reproducible alignment of the asymmetric source-drain contacts in bottom contact device architectures with a solution processed polymer active layer [41]. However, this technique is limited to bottom contact architectures and electrodes that have sufficient stability to survive the subsequent solution processing steps. Low work function electrodes such as calcium, or multi-layer stacks involving organic materials cannot be easily used in the bottom contact geometry when solution processed active layers are employed.

Another method involves an angled evaporation technique where either the substrate [44, 46] or the sources inside the evaporator [48, 104, 105] are positioned at an angle. Optical lithography has also been used to form similar electrode structures [56]. These methods use the overlap of two metals or a metal and metal oxide to form source and drain contacts. Although these techniques offer more reproducible control over the channel length and width, the techniques only allow the electrodes to be comprised of the same materials with differing work functions caused by
the asymmetric contact with the active layer. Again, this severely limits material combinations and options.

To this end, it was important to first design a simple and reproducible method to form asymmetric source and drain contacts. In order to properly study charge injection in these devices, it was also important that this method could not only be applied to metals, but could be used for organic or inorganic charge injection layers, overcoming any material constraints. This chapter details these efforts, first focusing on ambipolar single layer Super Yellow devices, followed by the results using a PBTTT charge transport layer underneath the Super Yellow emissive layer.

4.3 Device design and experimental methods

4.3.1 Device architecture and shadow mask design

Bottom gate top contact devices were fabricated using a custom-made set of steel shadow masks that were made using laser cutting. The complementary shadow masks were used in combination to alternatively evaporate the hole injecting and electron injecting contacts and form interdigitated “finger” structures (see Figure 4.1). The masks were designed such that the “fingers” of shadow mask 1 would alternate with that of shadow mask 2 (see Figures 4.1a and 4.1d). The mask and substrate holder were co-designed so that the two-mask alignment was fixed and reproducible at a scale much less than the critical channel width and length dimensions. Each substrate was diced to a size of 15 mm × 15 mm in order to exactly fit the set of steel shadow masks. Sequential evaporations were performed where the two shadow masks were exchanged between deposition of the source and drain contacts in each case (see Figure 4.1c). Not only did this method deliver interdigitated cathode and anode electrodes, the contacts themselves could be comprised of stacks of more than one material. This allowed thin (nanometre) electron and hole injection layers to be used. Four devices were formed on each substrate, each with a channel width of 16 mm and a channel width of either 70, 100, 120 or 140 µm.

All devices used Super Yellow (SY), a phenyl-substituted poly(p-phenylene vinylene) (PPV) co-polymer as the emissive layer. The device architectures used are shown in Figure 4.2. The devices fabricated used SY as either a single layer (Figure 4.2a), or in a bilayer configuration with a charge transporting layer underneath (see Figure 4.2b). The charge transporting layer in this case was poly(2,5-bis(3-alkylthiophene-2-yl)thieno[3,2-b]thiophene) (PBTTT), which was chosen because of its high hole mobility [106]. The chemical structures for both SY and PBTTT are illustrated in Figure 4.2c. A silicon nitride (SiNx) dielectric with a thin poly(methylmethacrylate) (PMMA) passivation layer was used for all devices.
Figure 4.1. Shadow mask and mask holder design: a) schematic of the deposition of asymmetric contacts by shadow masks where the masks were exchanged between sequential depositions; b) shadow masks with the mask holder; c) close up of complementary shadow masks; d) example of a substrate with asymmetric contacts deposited.

A stack of materials was used to create the electron and hole injecting contacts. The hole injecting contact (gold/molybdenum oxide [MoOx-Au]) was kept constant with only the electron injecting contact being varied. The metals chosen for the electron injecting contact were low work function metals Ca and Ba, each with a Ag cap, or Sm alone. Calcium was previously been used in SY-based LEFETs [2, 46], but has not been used in conjunction with a MoOx-Au layer for hole injection. As an alternative to Ca, Ba and Sm were chosen since they have a similar work function [98]. Caesium carbonate (Cs$_2$CO$_3$) was chosen as an alkali/salt injection layer, since it was previously used as an electron-injection layer in SY-based OLEDs [107, 108]. TPBi [1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene] has also been used in OLEDs as an electron transport layer [109], and hence was chosen as an example of an organic electron injection layer. The chemical structure for TPBi is given in Figure 4.2c.
Figure 4.2. Design of the SY LEFETs used in this chapter: a) device architecture for single layer SY devices; b) device architecture for bilayer SY/PBTTT devices; c) chemical structures of Super Yellow, poly(2,5-bis(3-alkythiophene-2-yl)thieno[3,2-b]thiophene) (PBTTT) and 1,3,5-tris(N-phenylbenzimidizol-2-yl)benzene (TPBi).

4.3.2 Experimental

The substrates used were n-doped Si substrates with a 400 nm SiNx dielectric layer grown by low pressure physical vapour deposition technique (LPCVD). The substrates were purchased from Silicon Quest, International, Inc. Substrates were cleaned as previously described in Chapter 2. A PMMA (poly(methylmethacrylate)) (15000 g mol$^{-1}$) solution of concentration 25 mg mL$^{-1}$ in n-propyl acetate ($\geq$ 99.5 %) was spin-coated onto the substrates at 2500 rpm for 30 s. Substrates were then baked on a hot plate at 150 $^\circ$C for 20 mins. The film thicknesses were measured to be 75 ± 7 nm. Super Yellow (PDY-132) and PBTTT were both purchased from Merck and used without further purification. For the SY/PBTTT devices, a PBTTT layer was deposited on top of the PMMA layer by spin-coating a 4 mg mL$^{-1}$ solution in chlorobenzene ($\geq$ 99 %, anhydrous) at 1500 rpm for 45 s and then at 2000 rpm for 15 s. The PBTTT solution was heated to 120 $^\circ$C prior to spin-coating. After spin-coating the PBTTT, the substrates were annealed at 150 $^\circ$C for 25 mins. SY was deposited on top of the PBTTT layer for the bilayer devices, or directly onto the PMMA layer for the single layer devices. SY Films were formed by spin-coating a 7 mg mL$^{-1}$
solution in toluene (> 99.9%, anhydrous) at 2500 rpm for 45 s then at 3000 rpm for 15 s to ensure the films were dry. The substrates were baked on the hot plate at 150 °C for 25 mins.

Devices fabrication was completed with either symmetric Au contacts, or asymmetric contacts using MoOx as a hole injection layer. For the symmetric contacts, ~50 nm Au was deposited by thermal evaporation under vacuum at a rate of ~0.5 Å s⁻¹. For the asymmetric contacts, a ~15 nm thick MoOx layer was evaporated followed by a 50 – 60 nm Au layer for the hole injecting contact. The electron injection layers were either capped with a non-reactive metal (such as Au or Ag) or a layer ~ 100 nm thick was deposited so that any small amount of oxidation at the contact surface would not affect the charge carrier injection into the device. The electron injecting contact was formed by evaporating 60 nm of Ca, 20 nm of Ba or 6 nm of Cs₂CO₃ with a 40 nm Ag cap, a 70 – 80 nm layer of Sm, or a 40 nm layer of TPBi with a 50 nm Au cap.

The capacitance of the PMMA/SiNx dielectric was calculated as described in Chapter 3, Section 3.3.2. The calculations of the optical and electrical FET characteristics were performed as described in Chapter 2. At least 5 devices for each device configuration were measured. Quoted mobilities are the average of all measured devices. The error in the measurements was given by the standard deviation.

**4.4 Super Yellow single layer device results**

Single layer SY devices were initially fabricated using symmetric Au/Au source and drain electrodes to investigate charge injection and transport. The devices were ambipolar, with both p- and n-type behaviour were observed in both the output (Figures 4.3a and 4.3b) and transfer (Figure 4.3c) characteristics. However, there was no light emission from the devices. This is likely due to poor electron injection, since the barrier height from Au to the EA of Super Yellow is ~2.6 eV.

When devices with asymmetric contacts were fabricated using a high work function MoOx-Au stack and a low work function electrode, light emission was observed. Light was emitted along the interdigitated fingers of the contacts and moved from the electron injecting contact to the hole injecting contact with a change in the applied gate voltage (see Figure 4.4). The width of the emission zone remained constant at ~ 4 µm.
Figure 4.3. Transistor characteristics for a SY device with symmetric Au contacts: a) output characteristics when operated in $p$-channel mode where the gate voltage was varied from 0 to $-100$ V in 20 V steps; b) output characteristics in the $n$-channel mode. The gate voltage was varied from 0 to $+100$ V in 20 V steps; c) transfer characteristics with a constant $V_{DS}$ of $-100$ V. The characteristics were obtained on a device with a channel length was 140 µm and the channel width was 16 mm.

The light emission properties were measured from operational devices. The photoluminescence and electroluminescence emission spectra are shown in Figure 4.5. The electroluminescence spectra were measured from the devices at the maximum brightness at $V_G = +100$ V and $V_{DS} = -100$ V. The photoluminescence and emission spectra of the devices did not change significantly with a change in the contacts. The CIE co-ordinates for SY only devices therefore were almost the same with a change in electron-injecting contact. The CIE coordinates were $x = 0.45, y = 0.52$ when Ca was used, $x = 0.43, y = 0.52$ when Cs$_2$CO$_3$-Ag was used and $x = 0.45, y = 0.53$ when Ba was used as an electron-injecting contact.
Figure 4.4. Images of the emission zone from a single layer SY device with Sm used as the electron-injecting electrode. The gate voltage was gradually swept from a positive $V_G$ at a) to a negative $V_G$ at d) and the emission gradually moved from adjacent to the hole injecting electrode (left hand electrode) to the electron injecting electrode (right hand electrode).

Figure 4.5. Normalized photoluminescence and electroluminescence spectra from single layer SY devices with different contacts: a) photoluminescence spectra; b) electroluminescence spectra.

Light emission in these devices occurred because of the improved electron injection into the SY layer from the low work function electrode. The devices were ambipolar, operating in both $p$-and-$n$-type regimes. Representative output characteristics for a device that had a Cs$_2$CO$_3$-Ag electron-injecting contact are shown in Figure 4.6. Electrical transfer characteristics for devices with different electron-injecting contacts with the corresponding brightness and EQE can be found in Figures 4.7a, 4.7b and 4.7c, respectively. Both electron and hole dominated regimes were evident in the transfer characteristics (see Figure 4.4a). Calculated mobilities for both electrons and holes are given in Table 4.1. The devices emitted light in both the electron-dominated and hole-
dominated regimes, as shown in Figure 4.5b. For each electron-injection layer, the maximum brightness occurred when the devices were operated in $n$-type mode (where the $V_G$ was positive). The higher brightness in $n$-type mode over $p$-type mode results from improved electron injection at high positive gate voltages.

Figure 4.6. Output characteristics for a SY device with a Cs$_2$CO$_3$-Ag electron injecting contact: a) $p$-type mode; b) $n$-type mode. The applied gate voltage was varied in 20 V steps from 0 to −80 V ($p$-type mode) or 0 to +100 V ($n$-type mode). The output characteristics were obtained on a device with a channel length of 70 µm and a channel width of 16 mm.

The electron and hole mobilities for each device configuration were equal within error (see Table 4.1) and were comparable to those previously reported for SY LEFETs [46]. There was a shift in threshold voltage by approximately 3 V (taking into account experimental error) in $n$-type mode for devices with Cs$_2$CO$_3$-Ag contacts compared to those with Ca-Ag and Ba-Ag contacts. This indicated a change in the charge carrier injection of the devices, with all other charge transport characteristics remaining the same. The ON/OFF current ratios for the single layer devices were all at least $10^3$. This is two orders of magnitude greater than previously reported ON/OFF ratios of single layer devices with a metal oxide charge injection layer using F8BT [poly (9, 9-diocylfluorene-co-benzothiadiazole)] as the emissive layer (~$10^1$) [4]. The electron and hole mobilities ($\mu_{\text{electron}}$ and $\mu_{\text{hole}}$ respectively), the threshold voltage in $n$-type and $p$-type modes (Threshold voltage$_{\text{electron}}$ and Threshold voltage$_{\text{hole}}$) as well as the ON/OFF ratio in $n$-type and $p$-type modes (ON/OFF$_{\text{electron}}$ and ON/OFF$_{\text{hole}}$) are given in Table 4.1.
Figure 4.7. Device characteristics for light emitting SY devices: a) electrical transfer characteristics; b) corresponding brightness; c) EQE as a function of gate voltage. $V_{DS}$ was kept constant at $-100$ V in all cases. The characteristics were obtained on devices with channel width of 70 µm and length of 16 mm.

The electron injection layer that delivered the maximum brightness was Cs$_2$CO$_3$-Ag with a brightness of $43 \pm 9$ cd m$^{-2}$. This was followed by Ba-Ag and Sm which had maximum brightnesses of $24 \pm 7$ cd m$^{-2}$ and $23 \pm 9$ cd m$^{-2}$ respectively (see Figure 4.7b and Table 4.2). All three of these electron injection layers showed an improvement in maximum brightness over the Ca layer, which has traditionally been used as an electron injecting contact in SY LEFETs [42, 46]. This demonstrated that the choice of electron injection layer is particularly important, not only for the achievement of the maximum brightness, but for the improvement of the EQE.

The EQE was a maximum at a gate voltage of $\sim 25$ V (see Figure 4.7c), where the source-drain current and brightness (see Figure 4.7b) were at minima. When gate voltage is low, the devices are operating in an ambipolar regime where neither electron nor hole transport dominate in the channel. The electron and hole transport becomes more balanced compared to when high gate voltages are applied. The EQE is dependent on the efficiency of recombination, and so as the electron injection improves, the balance between the electrons and holes in the device improves.
The hole injection should stay the same since the same hole-injecting contacts are used, and the same voltages are applied. If a larger number of electrons are available to recombine with the same number of injected holes, the efficiency of recombination increases, which in turn increases the EQE. This is discussed further in Section 4.7. Even though the devices operated with a low brightness, those made with Sm and Ca contacts had higher EQEs than the previously published single layer SY devices [42]. It should be noted that the brightness measured was near the threshold of the capability of the experimental setup at the time these measurements were performed.

The maximum EQE for the Sm contact devices was up to 1.2 ± 0.2 %. This is one of the highest EQEs achieved so far in a single layer LEFET using a fluorescent material. Gwinner et al. reported 8 % EQE from a single layer LEFET at a brightness of ~4000 cd m⁻² [4]. However, this value was obtained by employing an ambipolar material (F8BT) in which electrons and holes were intrinsically balanced when a high work function electrode was used. Furthermore, a high EQE from the F8BT LEFETs originated from an uncommon photo-physical process in which two initially formed triplet excitons interacted to form singlet excitons [4].

Table 4.1. Electrical FET characteristics for SY single layer devices. Averages of at least 5 devices are quoted with standard deviations. Data is independent of channel length.

<table>
<thead>
<tr>
<th>Contact</th>
<th>Ca-Ag</th>
<th>Ba-Ag</th>
<th>Cs₂CO₃-Ag</th>
<th>Sm</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu_{\text{hole}} ) (cm² V⁻¹ s⁻¹)</td>
<td>( 7 \times 10^{-5} \pm 2 \times 10^{-5} )</td>
<td>( 1.0 \times 10^{-4} \pm 0.1 \times 10^{-4} )</td>
<td>( 8 \times 10^{-5} \pm 3 \times 10^{-5} )</td>
<td>( 8 \times 10^{-5} \pm 3 \times 10^{-5} )</td>
</tr>
<tr>
<td>Threshold voltage(_{\text{hole}}) (V)</td>
<td>40 ± 10</td>
<td>31 ± 5</td>
<td>42 ± 5</td>
<td>30 ± 10</td>
</tr>
<tr>
<td>( \mu_{\text{electron}} ) (cm² V⁻¹ s⁻¹)</td>
<td>( 3 \times 10^{-4} \pm 2 \times 10^{-4} )</td>
<td>( 3.0 \times 10^{-4} \pm 0.8 \times 10^{-4} )</td>
<td>( 4.0 \times 10^{-4} \pm 0.9 \times 10^{-4} )</td>
<td>( 5 \times 10^{-4} \pm 2 \times 10^{-4} )</td>
</tr>
<tr>
<td>Threshold voltage(_{\text{electron}}) (V)</td>
<td>(-37 \pm 12)</td>
<td>(-34 \pm 2)</td>
<td>(-27 \pm 4)</td>
<td>(-30 \pm 10)</td>
</tr>
<tr>
<td>ON/OFF(_{\text{hole}})</td>
<td>( 4 \times 10^{3} \pm 3 \times 10^{3} )</td>
<td>( 6 \times 10^{3} \pm 5 \times 10^{3} )</td>
<td>( 2 \times 10^{3} \pm 1 \times 10^{3} )</td>
<td>( 3 \times 10^{3} \pm 2 \times 10^{3} )</td>
</tr>
<tr>
<td>ON/OFF(_{\text{electron}})</td>
<td>( 7 \times 10^{3} \pm 6 \times 10^{3} )</td>
<td>( 8 \times 10^{3} \pm 7 \times 10^{3} )</td>
<td>( 3 \times 10^{3} \pm 2 \times 10^{3} )</td>
<td>( 8 \times 10^{3} \pm 5 \times 10^{3} )</td>
</tr>
<tr>
<td>Maximum current density (A cm⁻²)</td>
<td>7 ± 1</td>
<td>6.4 ± 0.8</td>
<td>9 ± 1</td>
<td>11 ± 6</td>
</tr>
</tbody>
</table>
Table 4.2. Summary of LEFET optical device characteristics for single layer SY devices. Averages were taken for at least 5 devices, with standard deviations given for the associated error. Data is independent of channel length.

<table>
<thead>
<tr>
<th>Contact</th>
<th>Ca-Ag</th>
<th>Ba-Ag</th>
<th>Cs$_2$CO$_3$-Ag</th>
<th>Sm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum EQE (%)</td>
<td>0.6 ± 0.3</td>
<td>0.9 ± 0.3</td>
<td>0.5 ± 0.3</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td>Maximum Brightness (electron accumulation mode) (cd m$^{-2}$)</td>
<td>14 ± 2</td>
<td>24 ± 7</td>
<td>43 ± 9</td>
<td>23 ± 9</td>
</tr>
<tr>
<td>EQE at maximum brightness (electron accumulation mode) (%)</td>
<td>0.15 ± 0.03</td>
<td>0.16 ± 0.02</td>
<td>0.19 ± 0.04</td>
<td>0.14 ± 0.03</td>
</tr>
<tr>
<td>Maximum Brightness (hole accumulation mode) (cd m$^{-2}$)</td>
<td>0.4 ± 0.2</td>
<td>11 ± 8</td>
<td>4.6 ± 0.9</td>
<td>2 ± 1</td>
</tr>
<tr>
<td>EQE at maximum brightness (hole accumulation mode) (%)</td>
<td>0.006 ± 0.002</td>
<td>0.08 ± 0.06</td>
<td>0.035 ± 0.006</td>
<td>0.003 ± 0.001</td>
</tr>
<tr>
<td>Width of recombination zone (µm)</td>
<td>4.1 ± 0.4</td>
<td>5.6 ± 0.9</td>
<td>4.1 ± 0.7</td>
<td>4.0 ± 0.9</td>
</tr>
</tbody>
</table>

The current density for the devices with Cs$_2$CO$_3$-Ag and Sm contacts were the highest in the electron-dominated regime, with 9 ± 1 A cm$^{-2}$ and 11 ± 6 A cm$^{-2}$, respectively (see Table 4.1). The current density was calculated using the maximum current, the channel width (16 mm), and the assumption that the charge density was concentrated in a ~2 nm thick layer (since the charge accumulation region is confined to the first few nanometres at the semiconductor-dielectric interface). The increase in current density with the same applied voltages and gate dielectrics indicates a probable improvement in the electron injection. The maximum brightness occurred at maximum measured current density. At larger gate voltages (particularly at large positive gate voltages), the EQE again increased. This indicated an increase in the hole injection with the application of a positive gate voltage at high fields. It should be noted at the time this work was performed, the existing testing system did not allow for the higher gate voltages typically used to achieve the highest brightnesses reported in the literature.
The stability of the single layer devices containing Cs$_2$CO$_3$ in air was also tested. The devices were removed from the glove box for a few minutes. When the devices were re-tested, it was observed that the Cs$_2$CO$_3$-Ag electrodes had cracked and the devices no longer turned ON. This is likely to be because Cs$_2$CO$_3$ is hygroscopic. The electrodes were probably destroyed after absorbing water from the atmosphere.

### 4.5 Super Yellow/PBTTT bilayer device results

Electrical transfer characteristics for the SY/PBTTT devices are shown in Figure 4.8a, with the corresponding brightness and EQE in Figures 4.8b and 4.8c, respectively. Representative output characteristics for a SY/PBTTT device with a Cs$_2$CO$_3$-Ag electron injecting contact are shown in Figure 4.8d. There was little change in the charge transport and output characteristics with different electron injection layers (see Table 4.3). The holes move through the PBTTT charge transport layer and only pass into the emissive layer to recombine with the electrons, and so it is not surprising that the device characteristics do not change within error. PBTTT is mainly a p-type semiconductor with a maximum hole mobility of $\sim 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [106], which is almost five orders of magnitude higher than the electron and hole mobilities in Super Yellow (See Table 4.1). The PBTTT layer therefore dominates the charge transport within the device, meaning that the Super Yellow layer mainly operates as an emissive layer for the charges to recombine. The mobilities and threshold voltages would therefore be expected to be the same. Light emission occurred close to the electron injecting contact since the devices were hole-dominated. Both the organic and inorganic charge injection layers had comparable device performance to the traditional metallic injection layers (see Figure 4.8 and Table 4.4). The width of the emission zone ($\sim$10 um) did not significantly change with different electron injection layers. In this case, the emission zone was stationary with respect to the applied voltage (Figure 4.9). This is because the movement of charge within the device occurs through the PBTTT charge transport layer and not the Super Yellow emissive layer.

The EQE of Super Yellow/PBTTT devices as a function of gate voltage is given in Figure 4.8c. The EQE reached a maximum of $0.04 \pm 0.01 \%$ for devices fabricated with Ca as the electron injecting contact. There was no saturation of the EQE with gate voltage. The maximum gate voltage that could be applied with our testing equipment at the time of these experiments was limited to $\pm 100 \text{ V}$. If the applied gate voltages were higher, it is expected that a much higher current could be achieved. A greater current density and brightness and therefore EQE would be obtained. The current densities calculated here were lower than those previously reported [2], which explains the lower brightness reported here.
Figure 4.8. Device characteristics for SY/PBTTT devices: a) the electrical transfer characteristics and b) the corresponding brightness for SY/PBTTT devices; c) EQE as a function of gate voltage; d) representative output characteristics for a SY/PBTTT device with a Cs$_2$CO$_3$-Ag electron injecting contact. All characteristics were obtained on with a channel length of 100 µm and a width of 16 mm.

Figure 4.9. Emission from a SY/PBTTT device showing the hole injecting (left) and electron injecting (right) electrodes. The gate voltage was varied from a) $\sim 0 \ V_G$ to c) a large negative $V_G = -100 \ V$). The emission gradually increased in intensity and was stationary throughout device operation. The position of the emission zone remained next to the electron-injecting electrode on the right.
Table 4.3. Electrical FET characteristics for SY/PBTTT bilayer devices. Averages of at least 5 devices are quoted with standard deviations given for the errors. Data is independent of channel length.

<table>
<thead>
<tr>
<th>Contact</th>
<th>Ca-Ag</th>
<th>Ba-Ag</th>
<th>Cs₂CO₃-Ag</th>
<th>Sm</th>
<th>TPBi-Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{hole}}$ (cm² V⁻¹ s⁻¹)</td>
<td>$1.9 \times 10^{-2} \pm 0.2 \times 10^{-2}$</td>
<td>$1.9 \times 10^{-2} \pm 0.3 \times 10^{-2}$</td>
<td>$7 \times 10^{-3} \pm 3 \times 10^{-3}$</td>
<td>$8 \times 10^{-3} \pm 1 \times 10^{-3}$</td>
<td>$1.3 \times 10^{-2} \pm 0.9 \times 10^{-2}$</td>
</tr>
<tr>
<td>Threshold voltage $V_{\text{th}}$ (V)</td>
<td>$-3.2 \pm 0.4$</td>
<td>$-3 \pm 5$</td>
<td>$-5 \pm 4$</td>
<td>$-12 \pm 1$</td>
<td>$47 \pm 6$</td>
</tr>
<tr>
<td>ON/OFF hole</td>
<td>$2.1 \times 10^5 \pm 0.5 \times 10^5$</td>
<td>$1.9 \times 10^5 \pm 0.3 \times 10^5$</td>
<td>$6 \times 10^4 \pm 3 \times 10^4$</td>
<td>$5 \times 10^5 \pm 3 \times 10^4$</td>
<td>$1 \times 10^5 \pm 1 \times 10^4$</td>
</tr>
<tr>
<td>Maximum Current density (kA cm⁻²)</td>
<td>$0.6 \pm 0.1$</td>
<td>$0.6 \pm 0.2$</td>
<td>$0.3 \pm 0.1$</td>
<td>$0.33 \pm 0.05$</td>
<td>$0.8 \pm 0.2$</td>
</tr>
</tbody>
</table>

Table 4.4. LEFET optical characteristics for SY/PBTTT bilayer devices. Averages of at least 5 devices quoted with standard deviations given for the errors. Data is independent of channel length.

<table>
<thead>
<tr>
<th>Contact</th>
<th>Ca-Ag</th>
<th>Ba-Ag</th>
<th>Cs₂CO₃-Ag</th>
<th>Sm</th>
<th>TPBi-Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>EQE at 1 cd m⁻² (%)</td>
<td>$0.015 \pm 0.005$</td>
<td>$0.0011 \pm 0.0007$</td>
<td>$0.006 \pm 0.002$</td>
<td>$0.010 \pm 0.002$</td>
<td>$0.008 \pm 0.006$</td>
</tr>
<tr>
<td>Maximum brightness (cd m⁻²)</td>
<td>$100 \pm 4$</td>
<td>$18 \pm 9$</td>
<td>$40 \pm 30$</td>
<td>$44 \pm 5$</td>
<td>$40 \pm 20$</td>
</tr>
<tr>
<td>EQE at maximum brightness (%)</td>
<td>$0.04 \pm 0.01$</td>
<td>$0.02 \pm 0.01$</td>
<td>$0.02 \pm 0.01$</td>
<td>$0.020 \pm 0.002$</td>
<td>$0.006 \pm 0.005$</td>
</tr>
<tr>
<td>Width of recombination zone (µm)</td>
<td>$15 \pm 3$</td>
<td>$9 \pm 2$</td>
<td>$14 \pm 7$</td>
<td>$10 \pm 5$</td>
<td>$6 \pm 2$</td>
</tr>
</tbody>
</table>
4.6 Operating mechanism

The SY only devices and the SY/PBTTT devices were clearly different in device operation (ambipolar vs unipolar), but the charge transport in the devices also occurred within different layers. A schematic of the operating mechanism for single layer SY devices and bilayer SY/PBTTT devices is given in Figure 4.10. In both cases, electrons were injected from low work function metal, or via the EA of the organic semiconductor in the case of TPBi, into the Super Yellow layer. The source-drain voltage was biased such that holes were injected from the MoOx layer into the Super Yellow. The charge injection is demonstrated using an energy level diagram in Figure 4.10a. Values for the IE and EA of the organic semiconductors, as well as approximate work functions for the metal and inorganic layers were taken from literature (Au, Ca, Ba, Sm, Ag [98]; MoOx [110]; Cs$_2$CO$_3$-Ag [107]; TPBi [111]; PBTTT [70]; SY [46]). These values were measured using different methods and by various groups and so they are not “absolute” and should be taken as a guide for the trends observed. There is a large range in work function for the Cs$_2$CO$_3$-Ag electron-injecting contact since the work function is dependent upon the thickness of the Cs$_2$CO$_3$ and Ag layers.

In the case of the single layer devices, the charge transport had to occur within the Super Yellow layer. The distribution of the charges was strongly dependent on the bias applied by the gate voltage. Exciton formation occurred in the SY where the electrons and holes combined, and excitons were able to decay radiatively to the ground state with the emission of a photon. The position of the recombination zone was dependent on the applied gate voltage, which controlled the accumulation of charge within the device. This changed the spatial distribution of the emission zone (see Figure 4.10b).

In order to improve the EQE, the efficiency of recombination must improve. Since the hole mobility in SY is higher than the electron mobility, all devices were prepared with the same MoOx-Au hole injection contact to keep the hole injection the same. There was a variation in the electron injection layer to try to improve the electron injection into the device to improve the concentration of electrons. If the concentration of electrons within the device increased with the same concentration of holes, a greater number of holes have the potential to recombine with an electron. This would increase the recombination efficiency, which would in turn increase the EQE. The device results show that by changing the work function of the electron injecting contact, the EQE increased. This is consistent with a higher concentration of electrons injected at the EA of the SY layer.
Figure 4.10. Energy level diagram and operational mechanisms of SY-based LEFETs. Devices were fabricated with a MoOx/Au hole injecting contact and a corresponding low work function (WF) electron-injecting contact: a) energy level diagram; b) operational mechanism for SY only LEFETs. Both charges were transported in the channel, producing light where the electrons and holes recombined. The position of the emission zone was controlled by the applied gate voltage; c) Operational mechanism for SY/PBTTT LEFETs. Holes were transported in the PBTTT layer and recombined with electrons in the vicinity of the electron-injecting contact. The emission zone was stationary with an applied gate voltage since recombination only occurred next to the electron-injecting contact.
It is expected that the Ca, Ba and Sm based electron-injecting contacts would have similar device performance in the single layer SY devices since they have similar work functions (Figure 4.10a). This is indeed what was observed. The devices with Ba and Sm contacts had a small increase in brightness over Ca. The work function of Ba and Sm is 0.3 eV away from the EA of SY, compared to Ca, which is 0.5 eV away. It is possible that there was an improvement in the electron injection when Ba and Sm were used since they are 0.2 eV closer to the EA of SY than Ca.

A schematic showing the operating mechanism for the SY/PBTTT LEFETs is shown in Figure 4.10c. Under negative gate bias, holes are injected from the MoOx/Au electrode to the PBTTT layer via the IE of the SY layer. Holes are transported in the semiconductor channel through the PBTTT layer. The holes recombine with electrons in the SY emissive layer in the vicinity of the drain electrode. Charges may be injected into, or recombine in the SY layer, however the charge transport occurs through the PBTTT layer. The SY layer mainly acts as an emissive layer on top of the PBTTT semiconducting channel. Charge transport in the devices was largely dominated by holes since the hole mobility of PBTTT is orders of magnitude larger than that of SY with mobilities of up to ~ 1 cm² V⁻¹ s⁻¹ [106] compared with ~ 10⁻⁴ cm² V⁻¹ s⁻¹ measured in the neat SY films.

The maximum current density and brightness for the SY/PBTTT devices were all the same within error. This would be expected when considering the operating mechanism of the devices. Most of the physics in the SY/PBTTT devices is controlled by holes, not electrons, so it would be expected that these devices would be more sensitive to a change in the hole injecting contact rather than the electron injecting contact.

4.7 Recombination Efficiency

In LEFETs, electrons and holes are injected from opposite source-drain electrodes and the charges moved across the channel under the influence of the electric field. Some of the charges recombine, forming singlet state and triplet state excitons. Based on spin statistics, the ratio of singlet to triplet exciton formation upon recombination would be 1:3. The efficiency of light emission is given by the following equation [6]:

$$EQE = \phi_{\text{escape}} \times \phi_{\text{capture}} \times \phi_{\text{spin}} \times \phi_{\text{PLOY}} ,$$  \hspace{1cm} (4.1)

where the EQE is dependent on $\phi_{\text{escape}}$, which is the percentage of photons that can escape from the device (there are losses due to total internal reflections), $\phi_{\text{capture}}$ is the fraction of electrons and holes that recombine and form excitons (recombination efficiency), $\phi_{\text{spin}}$ is the proportion of excitons allowed to recombine radiatively due to spin statistics (in this case, SY is a singlet emitter
and so $\phi_{\text{spin}} = 0.25$) and $\phi_{\text{PLQY}}$ is the photoluminescence quantum yield (PLQY) in the solid state. The percentage of photons that can escape, $\phi_{\text{escape}}$, is approximately $1/2n^2$ where $n$ is the refractive index [88]. SY is birefringent, which made measurements of the refractive index by ellipsometry difficult. A refractive index range of 1.8 and 2.1 was used, which is consistent with literature reports for the refractive index of other PPV derivatives [112]. This resulted in a range of possible recombination efficiencies for the devices (see Table 4.5).

Films were prepared in identical conditions to the devices for photoluminescence quantum yield (PLQY) measurements (see Chapter 2). The PLQY of the SY film was $\sim 68\%$.

The recombination efficiency for single layer SY devices is presented in Table 4.5. The estimated recombination efficiency for the SY only devices at the maximum EQE varied between $18 - 45\%$ for a refractive index of 1.8, and $25 - 60\%$ for a refractive index of 2.1. The greatest recombination efficiency was obtained for devices with the Sm electron-injecting contact with an efficiency of $45 - 60\%$.

**Table 4.5.** Recombination efficiencies for single layer SY devices with different electron-injecting contacts.

<table>
<thead>
<tr>
<th>Contact</th>
<th>Ca-Ag</th>
<th>Ba-Ag</th>
<th>Cs$_2$CO$_3$-Ag</th>
<th>Sm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recombination</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>efficiency at maximum EQE (%)</td>
<td>24 – 32</td>
<td>34 – 45</td>
<td>18 – 25</td>
<td>45 – 60</td>
</tr>
<tr>
<td>Recombination</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>efficiency at maximum brightness (electron accumulation mode) (%)</td>
<td>4 – 6</td>
<td>6 – 8</td>
<td>7 – 9</td>
<td>5 – 7</td>
</tr>
</tbody>
</table>

The recombination efficiency for bilayer SY/PBTTT devices is presented in Table 4.6. The recombination efficiencies of bilayer LEFETs were much lower than the single layer LEFETs. The maximum recombination efficiency of $1\%$ was obtained when a Ca-Ag electron-injecting contact was used. Several factors may contribute to the lower recombination efficiency. Excitons may be quenched near the metal electrode since the recombination zone of the light emission is in close proximity to the electron-injecting contact. This issue has been previously reported in OLEDs [113]. It is also possible that holes will be transported towards the drain contacts without recombination with the electrons in the SY layer.
Table 4.6. Recombination efficiencies for SY/PBTTT devices with different electron-injecting contacts.

<table>
<thead>
<tr>
<th>Contact</th>
<th>Ca-Ag</th>
<th>Ba-Ag</th>
<th>Cs$_2$CO$_3$-Ag</th>
<th>Sm</th>
<th>TPBi-Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recombination</td>
<td>1–2</td>
<td>0.08–0.11</td>
<td>0.9–1.3</td>
<td>0.8–1.0</td>
<td>0.07–0.1</td>
</tr>
<tr>
<td>efficiency at</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>maximum</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>brightness (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.8 Conclusion

It was possible to tune the LEFET device performance using different charge injection layers underneath the contacts. The inorganic Cs$_2$CO$_3$ electron-injection layer in the single SY layer devices had a greater maximum brightness than the other electron-injecting layers used. Using the SY/PBTTT device architecture, it was demonstrated that an organic electron-injecting layer such as TPBI could be used directly under the contacts as an electron-injecting layer. A major limiting factor for the devices was the recombination efficiency. A recombination efficiency of 45 % and 1 % from single and bilayer LEFETs respectively was obtained by tuning the electron-injection layer, albeit in the former case at low brightness. However, even at ~40 cd m$^{-2}$, the recombination efficiency was still 5–10 % for the single layer devices.

In summary, simultaneous improvement in the light emission and switching properties of LEFETs was achieved by tuning the charge carrier injection in the devices. A maximum EQE of 1.2 ± 0.2 % with an ON/OFF ratio greater than 10$^3$ and a low threshold voltage (< 30 V) was obtained for single layer devices. At the highest brightness (43 ± 9 cd m$^{-2}$), the EQE was 0.19 ± 0.04 % for devices with a Cs$_2$CO$_3$-Ag electron-injection layer. For bilayer devices with Ca electron-injecting contacts, the EQE reached a maximum of 0.04 ± 0.01 % with an ON/OFF ratio ~10$^5$, and a threshold voltage of less than 3 V. Even though a higher brightness was achieved using the bilayer SY/PBTTT devices, the devices were unipolar and dominated by holes, resulting in a lower EQE than the single layer devices.

In order to further improve the bilayer device performance, a high mobility ambipolar charge transport layer could be used to improve the balance of electrons and holes within the device, which has the potential to improve the EQE. Furthermore, a phosphorescent material could be used instead of a fluorescent material to attempt to harvest more photons out of the device, since triplet excitons can decay radiatively in a phosphorescent material. The use of charge injection in an
attempt to improve the brightness and EQE in both unipolar and ambipolar phosphorescent LEFETs is further investigated in Chapter 5: Charge injection in phosphorescent LEFETs.
Chapter 5

Evaporated Phosphorescent LEFETs

5.1 Introduction

Phosphorescence is the process in which radiative emission results from the relaxation of triplet excited states [11], as opposed to fluorescence where radiative emission occurs from singlet states only. As discussed in Chapter 1, Section 1.2.3, excitons form in a singlet:triplet ratio of 1:3, which means that theoretically 75% of excitons do not contribute to the emission in fluorescent materials. If phosphorescent materials were used to harvest the triplet excitons as well as the singlet excitons, it is theoretically possible for 100% of the excitons formed to decay radiatively [114].

Phosphorescent materials have been used in OLEDs to try to increase the device efficiency since the EQE is dependent on the singlet-triplet ratio [6] (see Section 1.4.3). To maximise the device performance, evaporated phosphorescent small molecules are blended in a “guest-host” system. Solid-state interactions between the molecules lead to dimer, excimer or aggregate formation, resulting in the quenching of the luminescence [7] known as “concentration quenching”. A semiconducting host material dispersed amongst the phosphorescent guest can be used to avoid this problem [114]. The phosphorescent emitter fac-tris-(2-phenylpyridine)iridium (Ir(ppy)₃) in a host of 4,4’-bis(N-carbazolyl)-1,1-biphenyl (CBP) has been used as an emissive layer in OLEDs to form green emitting devices [114–116]. Blends of Ir(ppy)₃ and CBP have also been used in conjunction with other emissive layers to form white emitting devices [117]. Despite the widespread use of phosphorescent emissive layers in OLEDs, there have only been a limited number of reports in the literature on LEFETs [5, 32, 70–72].

The work described in Chapter 4 showed that a high EQE could be obtained using single layer ambipolar LEFETs. The maximum EQE occurred at a low brightness, which is a significant drawback for display applications. Moreover, the bilayer SY/PBTTT devices suffered from a low EQE due to the imbalance of the charge carrier concentrations of accumulated holes and injected electrons. Using a phosphorescent emissive layer instead of a fluorescent layer could help to improve the low EQE in the bilayer device configuration. In addition, if a high mobility bipolar
charge transport layer able to conduct both electrons and holes was used, the balance of charge carriers within the device could be improved. This could further improve the EQE.

In this chapter, devices in which the Ir(ppy)$_3$:CBP blend is used as a model phosphorescent emissive layer are described. This study was undertaken to further understand charge injection, charge transport within the devices and recombination in phosphorescent LEFETs. Charge injection was studied using an organic layer as part of the electron-injecting contact in an attempt to improve the EQE and brightness. Ambipolar devices in a bilayer configuration are reported, incorporating the diketopyrrolopyrrole moiety introduced in Chapter 3 as part of the polymer used as the charge transport layer. Ambipolar devices in a bilayer configuration have the potential to achieve a high EQE due to the balance of electrons and holes, which could improve the efficiency of recombination. If the semiconductor materials had a high charge carrier mobility, there is also to the potential to achieve a high brightness in these devices.

5.2 Device design and experimental methods

5.2.1 Device architecture

The devices described in this chapter used a bilayer devices architecture with Ir(ppy)$_3$:CBP as an emissive layer in conjunction with a high mobility charge transport layer (Figure 5.1). Devices were also constructed using a layer of Ir(ppy)$_3$:CBP alone in the channel, however these devices did not turn ON in either $p$-type or $n$-type modes, suggesting that the mobility of electrons and holes within the Ir(ppy)$_3$:CBP layer was very low. Deposition of a high mobility charge transport layer under the active layer was required to increase the conductivity of the transistor channel.

Two different charge transport layers were used. PBTTT (see Figure 5.1c) was used as a hole transport layer, since it was previously used successfully in LEFETs in conjunction with SY as described in Chapter 4. A bipolar charge transport material based on a diketopyrrolopyrrole polymer (DPP-DTT) [31] (see Figure 1c) was used to try to increase the transport of both electrons and holes within the device. DPP-DTT was previously reported to have high electron and hole mobilities of at least 1 cm$^2$ V$^{-1}$ s$^{-1}$ in a transistor configuration [31]. The EQE is dependent on the efficiency of recombination. The recombination efficiency improves as the electrons and holes become balanced in the device. If this could be achieved at high currents, a high EQE at a high brightness could possibly be obtained. DPP-DTT as a charge transport layer could be one possible route towards achieving this. Devices were fabricated using Ba as an electron-injecting contact, as well as using a layer of TPBi (1,3,5-tris(N-phenylbenzimidizol-2-yl)benzene) (see Figure 5.1c) underneath the Ba layer to try to improve the charge carrier injection (see Figures 5.1a and 5.1b).
Figure 5.1. Device architecture and chemical structures for Ir(ppy)$_3$:CBP devices: a) device architecture using Ba as an electron-injecting contact; b) device architecture using TPBi/Ba as an electron-injecting contact; c) chemical structures of the organic materials used in this chapter: poly(2,5-bis(3-alkylthiophene-2-yl)thieno[3,2-b]thiophene) (PBT TT), diketopyrrolopyrrole-dithienothiophene polymer (DPP-DTT), fac-tris-(2-phenylpyridine)iridium (Ir(ppy)$_3$), 4,4’-bis(N-carbazolyl)-1,1-biphenyl (CBP) and 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBi).

5.2.2 Experimental

SiNx substrates were cleaned as described in Chapter 2, Section 2.2.1 and transferred into a nitrogen-filled glove box (H$_2$O < 0.1 ppm, O$_2$ < 0.1 ppm). A passivation layer of PMMA (120 000 g mol$^{-1}$) was spin-coated from a 30 mg mL$^{-1}$ solution in propyl acetate at 2000 rpm for 45 s then at 3000 rpm for 15 s and left to bake on a hot plate for 25 – 30 mins at 150 °C. The final
film thickness was 100 ± 10 nm. A charge transport layer of either PBTTT or DPP-DTT was spin-coated on top. PBTTT was deposited from a 4 mg mL$^{-1}$ solution in chlorobenzene (99.9 %, anhydrous) that was heated to 120 °C at 1500 rpm for 45 s, then at 2000 rpm for 15 s to form a film of 60 ± 20 nm. DPP-DTT ($M_n = 125 \, 600 \, \text{g} \, \text{mol}^{-1}$, $M_w = 349 \, 000 \, \text{g} \, \text{mol}^{-1}$, PDI = 2.8) was deposited from a 2 mg mL$^{-1}$ solution (7 % by volume chloroform (99 %, anhydrous) in 1,2-dichlorobenzene (99.9 %, anhydrous)). The DPP-DTT solution was heated at ~ 60 °C for 30 mins while stirring to ensure the organic material was dissolved. The hot plate was then switched off with the solution was left on the hot plate as it cooled. DPP-DTT was spin-coated at 1000 rpm for 45 s, then at 1500 rpm for 15 s. The final DPP-DTT film thickness was 80 ± 10 nm. After deposition of the charge transport layer, the substrates were annealed at 150 °C for 25 – 30 mins.

An emissive layer composed of a blend of Ir(ppy)$_3$ and CBP (Ir(ppy)$_3$:CBP) was co-evaporated on top of the charge transport layer. The deposition rates of Ir(ppy)$_3$ and CBP were independently controlled with quartz crystal monitors during evaporation. The film thicknesses were calibrated using a Dektak profilometer. The deposition rate for Ir(ppy)$_3$ was kept at 0.02 – 0.03 Å s$^{-1}$ and at 0.44 – 0.46 Å s$^{-1}$ for the CBP to result in a ratio of 6 – 7 wt % Ir(ppy)$_3$ in CBP. A blend ratio of 6 – 8 wt % was shown to be the optimal blend ratio [118]. The final thickness of the emissive layer was 68 ± 2 nm.

Asymmetric source and drain contacts were deposited by vacuum evaporation, as described in Chapter 4, using two complementary shadow masks. An 8 nm thick molybdenum oxide (MoOx) layer was deposited followed by a 30 nm thick Au layer from the same source within the evaporator without breaking vacuum, to act as the hole-injecting contact. The shadow masks were then exchanged to evaporate either Ba alone or a TPBi/Ba layer as the electron-injecting contact. The final thickness of the TPBi was 40 ± 5 nm. A 30 nm Ba electrode was either evaporated on top of the TPBi or directly onto the charge transport layer as the electron-injecting contact. The TPBi/Ba contact was deposited from different sources within the evaporator without breaking the vacuum.

The capacitance of the PMMA/SiNx dielectric was calculated as described in Chapter 3, Section 3.3.2. The calculations of the optical and electrical FET characteristics were performed as described in Chapter 2. At least 5 devices for each device configuration were measured. Quoted mobilities are the average of all measured devices. The error in the measurements was given by the standard deviation.
5.3 Device results using PBTTT as a charge transport layer

5.3.1 Ba as the electron-injecting contact

All devices fabricated using Ir(ppy)$_3$:CBP as the emissive layer emitted light in the green region of the spectrum (see Figure 5.2) with CIE co-ordinates $x = 0.27$, $y = 0.65$. There was little difference between the photoluminescence and electroluminescence spectra (see Figure 5.2a). Green light was emitted along the edges of the fingers of the contacts (see Figure 5.2b) on the electron-injecting contact. Green light was emitted along the edges of the fingers of the contacts (see Figure 5.2b) on the electron-injecting contact.

Figure 5.2. Emission characteristics of Ir(ppy)$_3$:CBP devices: a) photoluminescence (PL) and electroluminescence (EL) spectra of the Ir(ppy)$_3$:CBP devices with a PBTTT charge transport layer with Ba contacts; b) optical micrograph of an Ir(ppy)$_3$:CBP device with a PBTTT charge transport layer with $V_G = V_{DS} = -100$V.

The devices fabricated using Ba as the electron-injecting contact operated in hole accumulation mode since the charge transport was dominated by the underlying PBTTT layer. Electrical and optical output and transfer characteristics are given in Figures 5.3a and 5.3b, respectively. The average hole mobility ($\mu_{\text{hole}}$) was $1.27 \times 10^{-2} \pm 4 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ (see Table 5.1). The ON/OFF ratio was of the order of $10^4$.

The brightness of the devices increased as the current increased (see Figure 5.3b). The maximum brightness was $60 \pm 20$ cd m$^{-2}$. The emission zone was spatially fixed throughout device operation and was positioned adjacent to the electron-injecting contact. There was little variation in the EQE throughout device operation (see Figure 5.3c). This indicated that the rate of recombination of electrons and holes remained the same, since the singlet-triplet ratio, the photoluminescence quantum yield and the percentage of photons escaping from the device should be constant as a function of gate voltage. The recombination efficiency is the only parameter that
can vary (see Equation 1.8). The average EQE at the maximum brightness was 0.069 ± 0.008 \%.
This was a marginal improvement over the best SY/PBTTT devices fabricated in Chapter 4.

![Figure 5.3](image)

**Figure 5.3.** Device characteristics for a representative Ir(ppy)$_3$:CBP device using a PBTTT charge transport layer and Ba as an electron-injecting contact: a) optical and electrical output characteristics, where $V_G$ was varied from 0 to −200 V in 50 V steps; b) optical and electrical transfer characteristics with a constant $V_{DS}$ of −150 V; c) external quantum efficiency (EQE) as a function of $V_G$ with a constant $V_{DS}$ of −150 V. The characteristics were obtained on a device with a channel length of 70 µm and a channel width of 16 mm.

### 5.3.2 TPBi/Ba as the electron-injecting contact

A layer of TPBi was inserted underneath the Ba contact to try to improve the electron carrier injection. The output and transfer curves are for an Ir(ppy)$_3$:CBP/PBTTT device with a TPBi/Ba electron-injecting contact are given in Figures 5.4a and 5.4b, respectively. The EQE is given in Figure 5.4c as a function of the gate voltage. The charge transport within the channel was dominated by holes. The average hole mobility was $4 \times 10^{-3} \pm 1 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$. The ON/OFF ratio remained the same at $\sim 10^4$. There was also no change in the threshold voltage, within error (see Table 5.1).
Figure 5.4. Device characteristics for a representative Ir(ppy)$_3$:CBP device using a PBT TT charge transport layer and TPBi/Ba as an electron injecting contact: a) optical and electrical output characteristics, where $V_G$ was varied from 0 to $-100$ V in 20 V steps; b) optical and electrical transfer characteristics with a constant $V_{DS}$ of $-150$ V; c) EQE as a function of $V_G$ with a constant $V_{DS}$ of $-150$V. The characteristics were obtained on a device with a channel length of 120 µm and a channel width of 16 mm.

The emission zone was spatially invariant throughout device operation and remained adjacent to the electron-injecting contact. The maximum brightness with the TPBi/Ba contact had an average of $200 \pm 40$ cd m$^{-2}$, which was more than three times the brightness obtained with a Ba electron-injecting contact. The average EQE at the maximum brightness was $0.18 \pm 0.01 \%$.

A small amount of light was emitted at positive gate voltages (see Figure 5.4b). The light was emitted adjacent to the hole-injecting contact only. The EQE in this region also increased because the amount of light emitted from the device increased more rapidly than the source-drain current (see Figure 5.4b). The EQE remained flat throughout the remainder of the device operation, between 0 and $-150$ V.
Table 5.1. Optical and electrical device characteristics for Ir(ppy)$_3$:CBP/PBTTT devices with either Ba or TPBi/Ba contacts. Averages and standard deviations were taken from at least 5 devices.

<table>
<thead>
<tr>
<th></th>
<th>Ba</th>
<th>TPBi/Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu$ hole (cm$^2$ V$^{-1}$ s$^{-1}$)</td>
<td>$1.27 \times 10^{-2} \pm 4 \times 10^{-4}$</td>
<td>$4 \times 10^{-3} \pm 1 \times 10^{-3}$</td>
</tr>
<tr>
<td>Threshold voltage (V)</td>
<td>$17 \pm 8$</td>
<td>$21 \pm 2$</td>
</tr>
<tr>
<td>ON/OFF</td>
<td>$2 \times 10^4 \pm 1 \times 10^4$</td>
<td>$1.1 \times 10^4 \pm 7 \times 10^3$</td>
</tr>
<tr>
<td>Maximum brightness (cd m$^{-2}$)</td>
<td>$60 \pm 20$</td>
<td>$200 \pm 40$</td>
</tr>
<tr>
<td>EQE at maximum brightness (%)</td>
<td>$0.069 \pm 0.008$</td>
<td>$0.18 \pm 0.01$</td>
</tr>
<tr>
<td>Width of emission zone (µm)</td>
<td>$25 \pm 5$</td>
<td>$21 \pm 5$</td>
</tr>
</tbody>
</table>

5.3.3 Discussion

For light to be emitted, both electrons and holes must be able to be injected into the device. Holes were injected from the MoOx layer into the PBTTT charge transport layer via the IE of Ir(ppy)$_3$:CBP. Electrons were directly injected from Ba at the EA of Ir(ppy)$_3$:CBP, or injected via the EA of TPBi. This is demonstrated using an energy level diagram in Figure 5.5a. Values for the IEs and EAs of Ir(ppy)$_3$ in CBP [114], PBTTT [70] and TPBi [111] and for approximate the work functions of Au [98], MoOx [110] and Ba [98] were taken from literature.

The hole mobility within the devices varied between $10^{-3} \sim 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$. Since transistors fabricated using Ir(ppy)$_3$:CBP layer alone in the transistor channel did not turn ON, the mobility through the Ir(ppy)$_3$:CBP layer was too low to measure. This means that it is more likely that the Ir(ppy)$_3$:CBP layer functions as an emissive layer only for the charges to recombine, with the PBTTT layer performing the main charge transport functions within the device. With the application of a negative gate voltage, holes were accumulated within the PBTTT layer and were transported through the transistor channel. Electrons and holes were able to recombine in the vicinity of the electron-injecting contact to emit light within the Ir(ppy)$_3$:CBP layer (see Figure 5.5b).
Figure 5.5. Energy level diagram and operating mechanism of Ir(ppy)$_3$:CBP/PBTTT devices: a) energy level diagram showing the approximate IE and EA of the organic materials and work functions of the metals and metal oxides used. Electrons were injected from Ba or via the EA of TPBi into the Ir(ppy)$_3$:CBP layer. Holes were injected from the MoOx into the PBTTT layer via the IE of the Ir(ppy)$_3$:CBP layer; b) schematic of the device operation. Electrons were mainly accumulated in the vicinity of the electron-injecting contact. Holes accumulated and were transported through the PBTTT layer towards the electron-injecting contact. Electrons and holes could recombine in the vicinity of the electron-injecting contact to emit light.
An increase in the brightness and the EQE was seen when TPBi was used between the Ba and Ir(ppy)$_3$:CBP layers. The brightness of the device could be improved if there were more electrons available for recombination with holes to produce a greater number of photons. This suggests that the TPBi layer improved the electron injection into the device. The EQE also increased because a greater proportion of holes injected were able to recombine with electrons to emit light.

When positive gate voltages were applied, a small amount of light appeared adjacent to the hole-injecting contact. This means that electrons must be transported through the device from the electron-injecting contact towards the hole-injecting contact to recombine in this region. Devices fabricated using a layer of Ir(ppy)$_3$:CBP alone did not turn ON, and so it would be unlikely that the Ir(ppy)$_3$:CBP layer transported a significant amount of charge. This would mean that electrons may be able to travel through the PBT TT layer instead. This means that the PBT TT layer acts to transport the charges through the device, with the Ir(ppy)$_3$:CBP acting as an emissive layer only.

The highest reported EQE in literature for a green phosphorescent emitter was for a second generation dendrimer with fac-tris(2-phenylpyridyl)iridium(III) complex core, biphenyl-based dendrons and 2-ethylhexyloxy surface groups blended with a CBP charge transport host [68] as the emissive layer with PBT TT as a charge transport layer. In that study, an EQE of 0.45 % was achieved at the maximum brightness using Yb (work function 2.6 eV) as the electron-injecting contact. This is a higher EQE than Ir(ppy)$_3$:CBP devices reported in this chapter. The EA of the TPBi layer could be up to 0.4 eV away from the EA of the Ir(ppy)$_3$:CBP layer. Even though the electron injection was improved with the additional layer of TPBi, the electron injection could still be inefficient with a 0.4 eV difference between the EA of the Ir(ppy)$_3$:CBP and the EA of the TPBi. This could contribute to a lower EQE for these devices than other reported green-emitting phosphorescent LEFETs [68]. The electron injection may not be fully optimised even with the addition of the TPBi layer.

5.4 Device results using DPP-DTT as a charge transport layer

5.4.1 Ba as the electron-injecting contact

Like in the devices which had a PBT TT charge transport layer, Ba was first used as an electron-injecting contact for the Ir(ppy)$_3$:CBP/DPP-DTT devices. The output and transfer characteristics for Ir(ppy)$_3$:CBP devices with a DPP-DTT charge transport layer and Ba as an electron-injecting contact are shown in Figure 5.6. The devices were ambipolar, with clear electron- and hole-dominated regimes. Output characteristics in $p$-type and $n$-type modes are given in Figures 5.6a and 5.6b respectively. In $p$-type and $n$-type modes, the output characteristics
displayed diode-like behaviour. This was observed at low gate (less than ± 20 V) and high source-drain voltages (greater than ± 100 V), where the source-drain current increased rather than fully saturating. Light was emitted in both the electron and hole-accumulation modes. The hole mobility was $6 \times 10^{-3} \pm 3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and the electron mobility was $1.4 \times 10^{-2} \pm 5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The ON/OFF ratio in $p$-type mode ($\text{ON/OFF}_{\text{hole}}$) and in $n$-type mode ($\text{ON/OFF}_{\text{electron}}$) was at least $10^2$. The average threshold voltage for hole accumulation (Threshold voltage$_{\text{hole}}$) was $44 \pm 7 \text{ V}$ and $-59 \pm 8 \text{ V}$ for electron accumulation (Threshold voltage$_{\text{electron}}$) (see Table 5.2).

**Figure 5.6.** Device characteristics for a representative Ir(ppy)$_3$:CBP device using a DPP-DTT charge transport layer and Ba as an electron injecting contact: **a)** optical and electrical output characteristics, where $V_G$ was varied from 0 to $-200 \text{ V}$ in 50 V steps; **b)** optical and electrical output characteristics, where $V_G$ was varied from 0 to $+200 \text{ V}$ in 50 V steps; **c)** optical and electrical transfer characteristics with a constant $V_{DS}$ of $-150 \text{ V}$; **d)** EQE as a function of $V_G$ with a constant $V_{DS}$ of $-150 \text{ V}$. The characteristics were obtained on a device with a channel length of 70 µm and a channel width of 16 mm.

Light was emitted along the interdigitated fingers of the contacts for both the electron-injecting and hole-injecting contacts in both the electron and hole accumulation modes as
shown in Figure 5.7. The width of the emission zone was the same within error for both contacts. The width was $23 \pm 3 \, \mu m$ at the hole-injecting contact and $25 \pm 4 \, \mu m$ at the electron-injecting contact. The average maximum brightness in the hole accumulation mode was $170 \pm 80 \, \text{cd m}^{-2}$, which was the same as the average maximum brightness for the electron accumulation mode within error (see Table 5.2). The EQE at the maximum brightness in the hole accumulation mode was approximately an order of magnitude lower than in electron accumulation mode. The average EQE in the electron accumulation mode was $0.14 \pm 0.04 \%$.

**Figure 5.7.** Light emission of an Ir(ppy)$_3$:CBP/DPP-DTT device with Ba as an electron injecting contact: a) electron accumulation mode at maximum brightness ($V_G \approx +150 \, \text{V}$). Light emission occurred at both the electron- and hole-injecting contacts along the interdigitated fingers of the contacts; b) hole accumulation mode at maximum brightness ($V_G \approx -150 \, \text{V}$).

### 5.4.2 TPBi/Ba as the electron injecting contact

TPBi was then added as an electron-injection layer underneath the Ba contact. Electrical and optical output characteristics in the hole accumulation mode are given in Figure 5.8a with the corresponding output characteristics in the electron accumulation mode in Figure 5.8b. Transfer characteristics are shown in Figure 5.8c. The devices were still ambipolar in operation with mobilities of order $10^{-2} \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}$ for both electrons and holes.

Light emission occurred adjacent to both contacts in both the electron and hole accumulation modes. The light emission was brighter and wider on the electron-injecting contact (see Figure 5.9 and Table 5.2). The emission also spread underneath the electrodes. This is visible in Figure 5.9, where the middle of the electron-injecting contact was not completely dark since some of the light underneath was partially transmitted through the contact. The average maximum
brightness in the hole accumulation mode was $500 \pm 200 \text{ cd m}^{-2}$, which is approximately the same as the maximum brightness in hole accumulation mode with a Ba electron-injecting contact within error (see Table 5.2). The average maximum brightness in the electron accumulation mode was $300 \pm 100 \text{ cd m}^{-2}$, which again was the same as that obtained using a Ba electron-injecting contact within error.

The EQE is given in Figure 5.8d as a function of gate voltage. When the TPBi layer was added, the EQE at maximum brightness increased by an order of magnitude to $0.4 \pm 0.2 \%$ in the hole accumulation mode. The EQE at the maximum brightness in the electron accumulation mode remained the same within error.

**Figure 5.8.** Device characteristics for an Ir(ppy)$_3$:CBP device using a DPP-DTT charge transport layer and TPBi/Ba as an electron injecting contact: **a)** optical and electrical output characteristics, where $V_G$ was varied from 0 to $-200$ V in 50 V steps; **b)** optical and electrical output characteristics, where $V_G$ was varied from 0 to $+200$ V in 50 V steps; **c)** optical and electrical transfer characteristics with a constant $V_{DS}$ of $-150$ V; **d)** EQE as a function of $V_G$ with a constant $V_{DS}$ of $-150$ V. The characteristics were obtained on a device with a channel length of 70 µm and a channel width of 16 mm.
5.4.4 Discussion

When the devices operated in hole accumulation mode ($V_G < 0$), there was an increase in the hole density at the semiconductor/dielectric interface. Holes were injected into the DPP-DTT layer from the MoOx layer via the IE of the Ir(ppy)$_3$:CBP blend. Electrons were injected into the Ir(ppy)$_3$:CBP layer from the Ba electrode. An energy level diagram and the operating mechanism for Ir(ppy)$_3$:CBP/DPP-DTT devices are given in Figure 5.10a. The values for the IE and EA of DPP-DTT [31], Ir(ppy)$_3$ in CBP [114], and TPBi [111] and the approximate the work functions of Au [98], MoOx [110], Cs$_2$CO$_3$-Ag [107] and Ba [98] were taken from literature. Since the electron mobility within the Ir(ppy)$_3$:CBP blend was low, electrons accumulated adjacent to electron-injecting contact. Holes were transported through the DPP-DTT layer towards the electron-injecting contact where they recombined in the vicinity of the electron-injecting contact to emit light. Since the DPP-DTT layer was bipolar, electrons were also mobile within the DPP-DTT layer. Under the applied field between the source and drain electrodes, electrons travelled towards the hole injecting electrode, where they recombined with the holes that were directly injected into the Ir(ppy)$_3$:CBP layer. This created a second emission zone within the device (see Figure 5.10b).
<table>
<thead>
<tr>
<th></th>
<th>Ba</th>
<th>TPBi/Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu^{\text{hole}}$ (cm$^2$ V$^{-1}$ s$^{-1}$)</td>
<td>$6 \times 10^{-3} \pm 3 \times 10^{-3}$</td>
<td>$1.2 \times 10^{-2} \pm 2 \times 10^{-3}$</td>
</tr>
<tr>
<td>Threshold voltage$^{\text{hole}}$ (V)</td>
<td>44 $\pm$ 7</td>
<td>10 $\pm$ 10</td>
</tr>
<tr>
<td>ON/OFF ratio$^{\text{hole}}$</td>
<td>$7 \times 10^2 \pm 4 \times 10^2$</td>
<td>$1.7 \times 10^2 \pm 9 \times 10^1$</td>
</tr>
<tr>
<td>$\mu^{\text{electron}}$ (cm$^2$ V$^{-1}$ s$^{-1}$)</td>
<td>$1.4 \times 10^{-2} \pm 5 \times 10^{-3}$</td>
<td>$5 \times 10^{-2} \pm 2 \times 10^{-2}$</td>
</tr>
<tr>
<td>Threshold voltage$^{\text{electron}}$ (V)</td>
<td>$-59 \pm 8$</td>
<td>$-17 \pm 5$</td>
</tr>
<tr>
<td>ON/OFF ratio$^{\text{electron}}$</td>
<td>$1.2 \times 10^3 \pm 9 \times 10^2$</td>
<td>$4 \times 10^3 \pm 3 \times 10^3$</td>
</tr>
<tr>
<td>Maximum brightness (hole accumulation mode) (cd m$^{-2}$)</td>
<td>170 $\pm$ 80</td>
<td>500 $\pm$ 200</td>
</tr>
<tr>
<td>EQE at maximum brightness (hole accumulation mode) (%)</td>
<td>0.04 $\pm$ 0.01</td>
<td>0.4 $\pm$ 0.2</td>
</tr>
<tr>
<td>Maximum brightness (electron accumulation mode) (cd m$^{-2}$)</td>
<td>200 $\pm$ 100</td>
<td>300 $\pm$ 100</td>
</tr>
<tr>
<td>EQE at maximum brightness (electron accumulation mode) (cd m$^{-2}$)</td>
<td>0.14 $\pm$ 0.04</td>
<td>0.17 $\pm$ 0.07</td>
</tr>
<tr>
<td>Width of emission zone (hole injecting contact) (µm)</td>
<td>23 $\pm$ 3</td>
<td>19 $\pm$ 9</td>
</tr>
<tr>
<td>Width of emission zone (electron injecting contact) (µm)</td>
<td>25 $\pm$ 4</td>
<td>32 $\pm$ 7</td>
</tr>
</tbody>
</table>
Figure 5.10. Energy level diagram and operating mechanism for DPP-DTT devices: a) energy level diagram showing the IE and EA of DPP-DTT, TPBi and Ir(ppy)$_3$ in CBP with the work functions of Au, MoOx, Ba and Cs$_2$CO$_3$-Ag; b) device operation in the hole accumulation mode. Electrons were injected at the EA of the Ir(ppy)$_3$:CBP layer and holes were injected into the DPP-DTT layer via the IE of the Ir(ppy)$_3$:CBP layer. Holes accumulated at the semiconductor/dielectric interface and recombined with the electrons that were injected into the Ir(ppy)$_3$:CBP close to the low work function (WF) contact. Since the device was ambipolar, mobile electrons in the DPP-DTT layer moved towards the MoOx/Au recombined with holes adjacent to the contact; c) device operation in the electron accumulation mode. Electrons accumulated near the semiconductor/dielectric interface and recombined with holes near the MoOx/Au contact. The mobile holes in the DPP-DTT layer recombined with the electrons directly injected into the Ir(ppy)$_3$:CBP emissive layer in the vicinity of the low WF contact.
When the devices operated in electron accumulation mode \( (V_G \gg 0) \) there was an increase in the electron density at the semiconductor/dielectric interface. Electrons were injected into the DPP-DTT layer via the EA of Ir(ppy)$_3$:CBP. Holes were injected into the device from the MoOx layer. Electrons travelled through the DPP-DTT layer towards the hole-injecting electrode to emit light. Mobile holes within the DPP-DTT layer travelled towards the electron-injecting contact and recombined with the electrons that were directly injected into the Ir(ppy)$_3$:CBP layer to emit light in the vicinity of the low work function contact (see Figure 5.10c). The DPP-DTT layer again operated mainly to transport the charges, with recombination and light emission occurring within the low mobility Ir(ppy)$_3$:CBP layer.

At low gate voltages (between 20 and 50 V), neither electrons nor holes were fully accumulated, and neither is dominant within the channel. There was potential to have more balanced electron and hole transport in the device, with recombination of the electrons and holes still adjacent to the contacts. Since the charge transport was more balanced, there was a small increase in the EQE in this region, which was evident in the transfer characteristics.

When the TPBi layer was added, the maximum brightness in hole accumulation mode increased by \( \sim 50 \) cd m$^{-2}$ (when the errors are taken into account). The mobilities, and optical characteristics in electron accumulation mode remained the same within error. The EQE at the maximum brightness in hole accumulation mode also increased by approximately an order of magnitude.

The hole injection should be the same since MoOx/Au contacts were used in both cases. The charge carrier mobilities did not change significantly within error and so the transport of electrons and holes through the device should remain the same. The maximum brightness and EQE in hole accumulation mode could be increased if there was better electron injection from the TPBi/Ba contact directly into the Ir(ppy)$_3$:CBP layer. There would be more efficient recombination in mainly hole accumulation mode and next to the TPBi/Ba contact.

The maximum EQE achieved using a DPP-DTT charge transport layer was greater than that achieved using a PBTTT charge transport layer. DPP-DTT was bipolar, and both electrons and holes could move within that layer with mobilities of order $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The charge transport in the PBTTT layer was dominated by holes, with very little movement of electrons within the device. The increase in the EQE when a DPP-DTT charge transport layer was used is likely due to the better balance of the electron and hole concentrations.

The maximum EQE in hole accumulation mode of $0.4 \pm 0.2 \%$ is comparable to the maximum EQE of $0.45 \%$ for green phosphorescent LEFETs reported in literature. However, a significant amount of light appeared to come from underneath the electron- and hole-injecting
contacts. If more of that light could be extracted out of the device, it would be expected that the EQE would improve since there would be more photons measured coming out of the device for the same number of charges injected in. The use of semi-transparent contacts with appropriate work functions for charge injection into the IE and EA of the Ir(ppy)$_3$:CBP would be one possible way to achieve this.

5.5 Conclusion

In this chapter, results from phosphorescent LEFETs using an Ir(ppy)$_3$:CBP emissive layer were reported. Devices that operated in the hole accumulation mode only were created using a PBTTT charge transport layer. The brightness and EQE were improved by adding a TPBi layer underneath the Ba electrode to improve the electron injection. The maximum brightness was 200 ± 40 cd m$^{-2}$ with an average EQE of 0.18 ± 0.01 % at the maximum brightness.

The device performance was further improved by using the bipolar polymer, DPP-DTT, as the charge transport layer instead of PBTTT. The average maximum brightness for Ir(ppy)$_3$/DPP-DTT devices with a TPBi/Ba electron-injecting contact in the hole accumulation mode was 500 ± 200 cd m$^{-2}$ with an EQE of 0.4 ± 0.2 % at the maximum brightness. The maximum brightness in the electron accumulation mode was 300 ± 100 cd m$^{-2}$ with an EQE of 0.17 ± 0.07 % at the maximum brightness. Similar to the case with the Ir(ppy)$_3$/PBTTT devices, the EQE in the hole accumulation mode for the Ir(ppy)$_3$/DPP-DTT devices was improved with the addition of the TPBi layer.

The EQE and brightness increased when the bipolar material, DPP-DTT, was used. This allowed a better charge carrier balance in the device with a high current. However, the emissive layer in these devices was composed of a co-evaporation of two materials, which increased the complexity of the device fabrication. It would be desirable to use a phosphorescent material that does not require a host material to prevent luminescence quenching. A solution processed phosphorescent dendrimer layer that can be used without a host material as an emissive layer will be used in the devices described in Chapter 5.
Chapter 6

Host free blue phosphorescent dendrimer
Light Emitting Field-Effect transistors

6.1 Introduction

Phosphorescent LEFETs were first described in this thesis in Chapter 5 using an evaporated emissive layer. The Ir(ppy)$_3$:CBP blend was used in tandem with either a PBTTT or DPP-DTT charge transport layer. Even though the emissive layer was phosphorescent, the EQE was still below 1% and not comparable to OLED efficiencies. Furthermore, to reduce concentration quenching of the luminescence, the devices reported in Chapter 5 and in literature [5, 71] required the use of a guest-host blend system. This approach increased the complexity of device fabrication as precise co-deposition of the elements of the blend is challenging. In order to avoid using a co-evaporated emissive layer, solution processable dendrimers were developed for OLED applications as another way to overcome the detrimental luminescence quenching issues in the solid state [119]. This chapter will describe work using a phosphorescent dendrimer that could be deposited without the use of a host material as an emissive layer for LEFET applications.

In order for LEFETs to be realised for full colour display applications, it must be possible to fabricate separate LEFET pixels that emit red, green or blue light. Reports of blue-emitting LEFETs are few with most of the devices using solution-processed fluorene-based fluorescent polymers [54, 56, 59, 120, 121]. A small number of evaporated materials [5, 49, 121] and single crystals [61, 63] have also been used. It has been shown that a maximum EQE of over 0.5% can be achieved for a fluorescent blue-emitting device, however this efficiency occurred when the brightness was only 1 cd m$^{-2}$ [120]. At higher brightnesses (greater than 100 cd m$^{-2}$), blue-emitting LEFETs have generally had lower (less than 0.1%) EQEs [54, 120].

A blue phosphorescent dendrimer previously reported in OLEDs [122] gave a maximum EQE of 3.9%. The reported OLED brightness reached a maximum of 200 cd m$^{-2}$. The dendrimer layer did not require a host material. This removed the need for the complex co-evaporation of two
different organic materials. In this chapter, work is presented on the use of this dendrimer in solution-processed blue phosphorescent LEFETs. Hole-dominated devices were created using PBTTT as a charge transport layer. The charge injection into these devices was tuned using a change in the device geometry to inject holes directly into the charge transport layer instead of via the emissive layer. The operating mechanism will also be discussed.

6.2 Device design and experimental methods

6.2.1 Device architecture

The substrates used had an n-doped Si gate with 400 nm silicon nitride (SiNx) layer. A 150 nm poly(methylenecrylate) (PMMA) layer was spin-coated on top to passivate the surface. Devices were first fabricated using a neat dendrimer layer spin-coated on top of the PMMA layer, however these devices had very low currents (less than 10 pA) and did not turn on. A charge transport layer underneath the PMMA layer was needed to increase the current through the device. PBTTT [poly(2,5-bis(3-alkylthiophene-2-yl)thieno[3,2-b]thiophene)] was again used as a high mobility hole transport layer to create hole-dominated dendrimer LEFETs. The blue phosphorescent dendrimer [122] with the molecular structure shown in Figure 6.1c was deposited on top of the charge transport layer by spin-coating.

Interdigitated source and drain contacts were formed using complementary shadow masks as described in Chapter 4. Either a planar top contact configuration (Figure 6.1a) or a non-planar configuration (Figure 6.1b) were used in this study. In the non-planar contact configuration, one contact was deposited directly on top of the charge transport layer with the dendrimer layer spin-coated on top. The final contact was then deposited on top of the dendrimer layer (Figure 6.1b). The non-planar contact device geometry was previously shown to overcome parasitic contact resistance due to the top emissive layer to harvest a higher device brightness when PBTTT was used as a charge transport layer [120]. This geometry also altered the charge carrier injection as holes could be injected directly into the PBTTT charge transport layer rather than via the dendrimer emissive layer. A thin molybdenum oxide (MoOx) layer with an Au cap was used as an hole-injecting layer. TPBi [1,3,5-tris(N-phenylbenzimidizol-2-yl)benzene] was used as an electron-injecting layer in tandem with the low work function Ba to act as the top contact.
Figure 6.1. The device architectures and chemical structures used in this study: a) device architecture using planar contacts; b) device architecture using non-planar contacts. One contact was deposited prior to spin-coating the emissive layer; c) the chemical structures of the organic compounds used in these devices [poly(2,5-bis(3-alkylthiophene-2-yl)thieno[3,2-b]thiophene) (PBTTT), 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBi) and the blue phosphorescent dendrimer].

6.2.2 Experimental

Substrates were cleaned as described in Chapter 2, Section 2.2.1 and transferred to a nitrogen-filled glove box (H₂O < 0.1ppm, O₂ < 0.1ppm). Poly(methylmethacrylate) (PMMA) (\( \bar{M}_w = 120000 \) g mol\(^{-1} \)) films were spin-coated on top at 2000 rpm for 30 s from a 30 mg mL\(^{-1} \) solution in toluene (99.9 %, anhydrous). These films were then baked on a hot plate at 150 °C for 20 mins, and left to cool. PBTTT films were spin-coated from a 4 mg mL\(^{-1} \) solution in chlorobenzene (99.9 %, anhydrous) at 1500 rpm for 45 s followed by a drying step of 2000 rpm for
15 s. PBTTT was heated to a temperature of 120 °C prior to spin-coating. The PBTTT films were annealed at 150 °C for ~ 25 mins. The film thickness of the PBTTT film was 60 ± 20 nm. Dendrimer films were formed on top of the charge transport layers by spin-coating at 2000 rpm for 60 s from an 18 mg mL⁻¹ solution in toluene (99.9 %, anhydrous).

Source and drain electrodes were formed using two complementary shadow masks as previously described in Chapter 4, Section 4.3. An 8 nm molybdenum oxide layer followed by a layer of 40 nm of Au were thermally evaporated from the same source within the evaporator without breaking the vacuum as the hole-injecting contact. A 40 nm layer of TPBi was thermally evaporated as an electron-injecting layer, followed by a 30 – 40 nm Ba layer without breaking the vacuum. Devices were fabricated using a range of channel lengths (70, 100, 120 and 140 µm) with widths of 16 mm. Devices were characterised as described in Chapter 2.

Solid-state photoluminescence spectra were recorded with a HoribaJobin Yvon Fluoromax-4 spectrofluorometer using an incident wavelength of 325 nm. The neat dendrimer spectrum was recorded in the solid state on a quartz substrate. The film was prepared by spin-coating using the same conditions as the devices to form a film that was 40 ± 10 nm thick. Other films were prepared using the same methods as described above for the devices on SiNx substrates. Top contacts for the photoluminescence measurements were deposited using the same conditions that were used for the devices.

Spectroscopic ellipsometry measurements were performed using a JA Woolman spectroscopic ellipsometer. Measurements on thin films of the dendrimer and PBTTT were prepared on silicon wafers using the same spin-coating conditions used for the devices. Measurements were performed at multiple angles of incidence. The data was fitted to determine the approximate refractive index, \( n \), the extinction coefficient, \( k \), and the complex refractive index \( (n + ik) \). These values were then used in the optical modeling performed in Section 6.6.

The capacitance of the PMMA/SiNx dielectric was calculated as described in Chapter 3, Section 3.3.2. The calculations of the optical and electrical FET characteristics were performed as described in Chapter 2. At least 5 devices were measured for each device configuration. Quoted mobilities are the average of all measured devices. The error in the measurements was given by the standard deviation.

6.3 Device results

6.3.1 Devices with planar contacts

Control devices were fabricated using planar source and drain contacts and with PBTTT as a charge transport layer (see Figure 6.1a). Electrical and optical device characteristics are shown in
Figure 6.2. The devices were dominated by holes and had a mobility (µ-hole) of $1.4 \times 10^{-3} \pm 7 \times 10^{-4} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ and an ON/OFF ratio of the order of $10^5$ (see Table 6.1). The brightness of the devices increased with the source drain current. The brightness reached a maximum of $16 \pm 5 \text{cd m}^{-2}$. The EQE at the maximum brightness was $0.08 \pm 0.02 \%$ (Table 6.1).

Figure 6.2. Device characteristics for a device (length = 70 µm, width = 16mm) fabricated with a PBTTT charge transporting layer and planar source-drain contacts: a) optical and electrical output characteristics where $V_G$ is varied between 0 and $-100 \text{ V}$ in 20 V steps; b) optical and electrical transfer characteristics with $V_{DS} = -150 \text{ V}$; c) EQE and luminous efficiency as a function of gate voltage with a constant $V_{DS}$ of $-150 \text{ V}$.

The light emission was spatially invariant during device operation. Even though the transport was dominated by holes, light emission occurred adjacent to the electron-injecting contact as well as the hole-injecting contact. Below $-75 \text{ V}$, light was emitted next to the electron injecting contact only. As the gate voltage was increased above $-75 \text{ V}$ towards $-150 \text{ V}$, the light gradually appeared next to the hole injecting contact as well. The relative intensity of the emission at each electrode is shown in Figure 6.3. The percentage of the light emission at each contact was found by first integrating under the entire spectrum to find the total area. The integrated area under each emission peak was then divided by the total area of the emission. Most of the light emission was at
the electron-injecting contact. The emission adjacent to the electron injecting contact corresponded to 69 ± 2 \% of the total integrated emission.

![Figure 6.3](image)

**Figure 6.3.** The relative intensity of the light emission at each contact as a function of the distance between the contacts. More of the light intensity was near the electron injecting contact. The integrated area underneath the peak adjacent to the electron injecting contact was 69 ± 2 \%, with 31 ± 1 \% adjacent to the hole injecting contact. The applied gate voltage was −150 V and the source-drain voltage was −150 V.

**Table 6.1** Blue phosphorescent LEFET results using a PBTTT charge transport layer and either a planar or non-planar contact geometry. Averages were taken for at least 5 devices with standard deviations given for the errors.

<table>
<thead>
<tr>
<th></th>
<th>Planar contacts</th>
<th>Non-planar contacts</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu_{\text{hole}} ) (cm(^2) V(^{-1}) s(^{-1}))</td>
<td>(1.4 \times 10^{-3} \pm 7 \times 10^{-4})</td>
<td>(3.5 \times 10^{-3} \pm 6 \times 10^{-4})</td>
</tr>
<tr>
<td>Threshold voltage (V)</td>
<td>7 ± 5</td>
<td>16 ± 5</td>
</tr>
<tr>
<td>ON/OFF ratio</td>
<td>(4 \times 10^{5} \pm 3 \times 10^{5})</td>
<td>(4 \times 10^{5} \pm 2 \times 10^{5})</td>
</tr>
<tr>
<td>Maximum brightness</td>
<td>16 ± 5</td>
<td>140 ± 50</td>
</tr>
<tr>
<td>(cd m(^{-2}))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EQE at maximum brightness (%)</td>
<td>0.08 ± 0.02</td>
<td>0.11 ± 0.02</td>
</tr>
<tr>
<td>Luminance efficiency at maximum brightness (cd A(^{-1}))</td>
<td>0.13 ± 0.03</td>
<td>0.20 ± 0.04</td>
</tr>
<tr>
<td>Width of emission zone (µm)</td>
<td>8 ± 2</td>
<td>11 ± 2</td>
</tr>
</tbody>
</table>
6.3.2 Devices with non-planar contacts

Devices were then fabricated using the non-planar device architecture shown in Figure 6.1b. Electrical and optical device characteristics are shown in Figure 6.4. The hole mobility increased to $3.5 \times 10^{-3} \pm 6 \times 10^{-4}$ cm$^2$ V$^{-1}$s$^{-1}$. The ON/OFF ratio remained at $10^5$.

**Figure 6.4.** Device characteristics for a LEFET (length = 70 µm, width = 16 mm) with a PBTTT charge transport layer and non-planar contacts: **a)** optical and electrical output characteristics where $V_G$ varied between 0 and −100 V in 20 V steps; **b)** optical and electrical transfer characteristics ($V_{DS} = -150$ V); **c)** external quantum efficiency (EQE) and luminous efficiency as a function of gate voltage ($V_{DS} = -150$ V).

The maximum brightness was an average of $140 \pm 50$ cd m$^{-2}$ (see Table 6.1). This was an improvement of an order of magnitude over the devices that had planar contacts and is comparable to the brightness achieved in the OLEDs previously reported [122]. At the maximum brightness, the EQE reached a local maximum (see Figure 6.4c). In this region, the average EQE was $0.11 \pm 0.02$ % and had a luminance efficiency of $0.20 \pm 0.04$ cd A$^{-1}$. The EQE was comparable to solution-processed green phosphorescent dendrimer LEFETs which had EQEs mainly in the range of 0.1 – 0.5 % [70]. The EQEs for the blue phosphorescent dendrimer LEFETs were significantly higher than the red phosphorescent LEFETs fabricated with solution processing which had a
maximum EQE of $5 \times 10^{-3}\%$ [70]. The emission zone did not move through the channel during device operation, and occurred adjacent to the electron injecting contact only. The width of the emission zone was $11 \pm 2\ \mu m$ at a gate voltage of $-150\ V$ and a source-drain voltage of $-150\ V$.

### 6.4 Emission characteristics

The photoluminescence and electroluminescence emission spectra were measured from the devices to quantify the colour of the light emitted by the device. Photoluminescence and electroluminescence emission spectra are shown in Figure 6.5a for a device with planar contacts.

![Figure 6.5](image)

**Figure 6.5.** Emission characteristics from the blue phosphorescent dendrimer devices: a) photoluminescence (PL) and electroluminescence (EL) emission spectra from a dendrimer/PBTTT device with planar contacts; b) optical micrograph from a working device with a PBTTT charge transport layer, dendrimer active layer and non-planar contacts c) CIE co-ordinates ($x = 0.16$, $y = 0.29$) plotted on a chromaticity diagram.
There were small differences between the photoluminescence and electroluminescence spectra however the position of the two main emission peaks were approximately the same at ~ 430 nm and ~ 500 nm. The electroluminescence emission spectrum corresponds to the CIE co-ordinates $x = 0.16, y = 0.29$. This corresponds to emission in the blue region of the spectrum. Electroluminescence spectra for devices with planar and non-planar contacts behaved similarly.

The solid-state photoluminescence emission spectrum of the neat dendrimer film was measured for comparison with the device photoluminescence and electroluminescence spectra. The measured emission spectra recorded from the LEFETs did not match the photoluminescence emission spectrum of the neat dendrimer film (see Figure 6.6). The dendrimer spectrum had two main peaks at approximately 430 nm and 460 nm, with a shoulder at ~ 500 nm. The CIE co-ordinates of the neat blue dendrimer were previously reported to be $x = 0.16, y = 0.13$ calculated from the photoluminescence spectrum in solution [122], which differs from the LEFET spectrum in terms of the $y$-coordinate. This corresponds to a slight colour change, shifting the emission from a deep blue for the neat dendrimer towards a sky blue for the LEFET (see Figure 6.5).

![Figure 6.6. Comparison of the solid state neat blue dendrimer photoluminescence (PL) spectrum with the electroluminescence (EL) spectrum measured from a dendrimer/PBTTT device with planar contacts. The dendrimer PL spectrum was measured on quartz with a film thickness of 40 nm.](image)

To determine whether optical cavity effect such as interference were occurring in the underlying layers to change the emission spectrum of the devices from that of the neat dendrimer
film, the photoluminescence emission spectrum of the dendrimer was measured on top of a SiNx substrate with layers of PMMA and PBT TT spin-coated on top. The photoluminescence emission spectrum was also recorded with a top contact of MoOx/Au or TPBi/Ba evaporated on top of the dendrimer. The structures used are shown in Figure 6.7a. These structures were used as a proxy for the LEFET device architecture. It is difficult to isolate the effect of each electrode on the resulting photoluminescence spectrum using the LEFET device architecture since the contacts are interdigitated. The diode structures were used instead to determine if it was possible that top contacts could have any effect whatsoever on the emission spectra.

**Figure 6.7.** The photoluminescence emission spectrum of the dendrimer on a stack of PBT TT/PMMA/SiNx/Si with a top contact or alone: a) The structure of the different geometries measured including the dendrimer on PBT TT/PMMA on a SiNx substrate, and the dendrimer on PBT TT/PMMA on SiNx substrates with either a MoOx/Au top contact or TPBi/Ba top contact; b) comparison of the photoluminescence emission spectra of the structures shown in a) with the solid state dendrimer photoluminescence emission spectrum; c) comparison of the LEFET electroluminescence spectrum from a device with planar contacts with the Au/MoOx/dendrimer/PBT TT/PMMA stack and the Ba/TPBi/dendrimer/PBT TT/PMMA stack on SiNx substrates.
The neat dendrimer spectrum and the spectrum of the dendrimer/PBTTT/PMMA stack on a SiNx substrate have the same features, with two main peaks at \( \sim 430 \) nm and \( \sim 460 \) nm and a shoulder at 500 nm (Figure 6.7b). This suggests that the underlying layers alone did not significantly change the dendrimer photoluminescence spectrum. When top contacts of MoOx/Au or TPBi/Ba are added, there were still the two main peaks at \( \sim 430 \) nm and \( \sim 460 \) nm, however there is also a significant peak in the spectrum near 500 nm (Figure 6.7b). This suggests that the addition of contacts affected the emission properties of the device. This peak was in approximately the same position as the second main peak in the LEFET electroluminescence spectrum (see Figure 6.7c).

One possible explanation for these effects is the formation of a weak micro-cavity when the top metal layers are added. Micro-cavity effects in OLEDs can cause an angular dependence of the emission [123]. If there is a strong angular dependence, the emission from the device can no longer be approximated to be Lambertian (see Chapter 2, Section 2.4.2). The photoluminescence spectrum for a blue phosphorescent LEFET with a PBTTT charge transport layer as a function of angle is given in Figure 6.8. The photoluminescence spectrum was measured directly above the substrate (90°), at 45° and at 20°. The photoluminescence spectra at different angles did not match exactly, with a narrowing of the peak at \( \sim 430 \) nm at a 45° angle and a slight blue shift of the peak near 500 nm. These changes would be consistent with the formation of a weak micro-cavity in these devices. However, given that there was minimal change as a function of angle, the integrated spectrum did not change significantly. The blue phosphorescent LEFETs were still approximated as Lambertian. Additionally, the luminance efficiency in cd A\(^{-1}\) will be reported for these devices, since this is taken from the emission in the forward direction, and is not dependent on an integration as a function of angle.

6.5 Operating mechanism

When PBTTT was used as a charge transport layer with planar contacts, light emission occurred on both contacts. The emission was wider and brighter on the electron-injecting contact. Holes were injected into the PBTTT layer via the IE of the dendrimer (see Figure 6.9a). Electrons were injected into the dentrimer layer via the EA of the TPBi. An energy level diagram showing the approximate IE and EA for the dendrimer [122], PBTTT [70] and TPBi [111] layers as well as the work functions of the Au [98], Ba [98] and MoOx [110] is shown in Figure 6.9a. It should be noted that these values were taken from literature and determined using different methods and the diagram should be used as a guide only, rather than representing absolute values.
Figure 6.8. Angular dependence of the photoluminescence emission spectra from a blue phosphorescent dendrimer device with a PBTTT charge transport layer and asymmetric MoOx/Au and TPBi/Ba contacts. There were some small changes to the photoluminescence emission spectra as a function of angle. This would have a minimal effect on the EQE calculations.

When a negative gate voltage was applied, holes were accumulated at the PBTTT/dielectric interface. Holes were transported towards the TPBi/Ba contact, where they were able to recombine with electrons that were injected into the dendrimer layer to emit light.

When planar contacts were used, a second emission zone was also present in the device adjacent to the MoOx/Au contact. This means that there must be some electron transport in the device towards the hole-injecting contact. Electrons within the device travelled towards the MoOx/Au contact under the applied field between source and drain electrodes. These electrons recombined with the holes that were directly injected into the dendrimer layer to form a second emission zone in the device. The second emission zone at the hole injecting contact occurred at a higher gate voltage than the emission adjacent to the electron injecting contact.
Figure 6.9. The energy level diagram and operating mechanism for the blue phosphorescent dendrimer devices: a) energy level diagram; b) operating mechanism with planar contacts with electrons moving mainly in the dendrimer layer and holes moving mainly in the PBTTT layer, resulting in light emission at both contacts; c) operating mechanism with planar contacts with electrons and holes moving in the PBTTT layer, resulting in light emission at both contacts; d) operating mechanism with non-planar contacts. Holes were directly injected into the PBTTT charge transport layer. Holes were transported within the PBTTT layer and recombined with electrons in the dendrimer layer to emit light next to the electron-injecting contact only.
Electron mobilities calculated from the transfer curve using gate voltages between +10 and +50 V were of the order \(10^{-6} - 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\), which is at least two orders of magnitude lower than the hole mobility. The light first appeared at the electron-injecting contact because there is a difference of orders of magnitude between the mobilities. Since the electron mobility was very low in these devices, a higher field was needed to drive electrons towards the hole injecting contact to emit light.

There were two possible ways that electrons could be transported through the device. The first is that electrons were directly injected into and transported through the dendrimer layer. An electron population was able to build up in the top of the dendrimer layer. Electrons recombined with the holes that are also directly injected into the dendrimer layer in the vicinity of the MoOx/Au contact (Figure 6.9b).

However, devices fabricated with a neat dendrimer layer without the PBTTT charge transport layer had very low currents and did not turn on, so it would be unlikely that a significant amount of charges would be travelling through the dendrimer layer. The second possibility would be that the electrons were injected from the dendrimer layer into the PBTTT layer adjacent to the electron-injecting contact and travelled in the PBTTT layer instead. Holes were directly injected into the dendrimer layer from the MoOx/Au contact and formed excitons with electrons passing through the dendrimer layer towards the contact to drain out of the device. The electrons recombined with the holes injected into the device near the MoOx/Au in the dendrimer layer. This resulted in a second emission zone near the hole-injecting contact (Figure 6.9c).

When non-planar contacts were used with a PBTTT charge transport layer, light emission occurred next to the electron-injecting contact only. Holes were directly injected into the PBTTT layer from the MoOx/Au contact. Electrons were injected into the dendrimer layer via the EA of the TPBi at the electron-injecting contact. Holes accumulated within the PBTTT and were transported towards the TPBi/Ba contact. Holes recombined with the electrons in the dendrimer layer to emit light at the TPBi/Ba contact (see Figure 6.9d). When holes were directly injected into the PBTTT charge transport layer, the hole mobility increased, which suggests that holes were transported more efficiency towards the electron-injecting contact. As a result, a greater maximum brightness and EQE was obtained.

There was still a small amount of electron transport evident in the transfer characteristics at positive gate voltages (Figure 6.4b). However, in this case, any electrons transported in the PBTTT layer towards the MoOx/Au contact would not pass through the dendrimer layer to reach the contact and drain out of the device. There could be no recombination with electrons in the dendrimer layer adjacent to the MoOx/Au contact. This resulted in only one emission zone near the TPBi/Ba contact in the devices with non-planar contacts.
6.6 Optical field calculations

To determine whether the differences between the device electroluminescence emission spectrum and the dendrimer emission spectrum were the result of micro-cavity effects in the device, optical field calculations were performed. Even though these structures are not strictly the same as the LEFET structures, the electrode geometry is quite complex and so these calculations would be quite complex using the full LEFET structure. These calculations were designed to determine whether there could be any effects whatsoever using this layer of materials. Calculations were performed in a diode structure. Furthermore, by using the diode structure, the effects could be correlated with the photoluminescence measurements performed in Section 6.4. The program used was developed by van de Lagemaat et al. from the National Renewable Energy Laboratory (NREL) based on the transfer matrix method of Pettersson et al. [124]. This method is a transfer matrix method and is used to determine how reflections at interfaces affect the distribution of the optical electric field inside a device. This can be particularly important in thin film device structures, especially when there is a metal electrode that is highly reflective. In this method, a single wavelength of light is incident on the device structure (see Figure 6.10). Reflection and transmission at each interface is calculated using the complex refractive index obtained from spectroscopic ellipsometry. A plot of the modulus squared of the optical electric field, $|E|^2$, versus position $x$ in the film directly represents the production of excited states at each point and can help to describe the excitation profile in a layered structure [124].

Optical field calculations were performed on the device structures shown in Figure 6.10. Incident wavelengths of either 325 nm or 500 nm were used on the device structure. An incident wavelength of 325 nm was chosen since this was the incident wavelength used for the photoluminescence measurements in Section 6.4. An incident wavelength of 500 nm was used since this is in the region where changes in the photoluminescence emission spectra are seen with the addition of top contacts. The light was incident at 90° relative to the substrate (see Figure 6.10). The Si substrate was much thicker than the other layers (millimetre scale compared to nanometre scale) and so was approximated to be infinite. The optical constants for PMMA, SiNx, Si and Au were taken from literature (PMMA [125], SiNx[126], Si[127], Au[128]). Optical constants for MoOx, PBTTT and the blue dendrimer were determined as described in Section 6.2.2. The film thicknesses used in the calculations were the same as that used in the devices within error.

The optical field calculations are not strictly the same as what occurs in a LEFET, since in the LEFET case, the excitation originates from inside the organic film, rather than being incident on the device-like structure. However, the case where the excitation occurs from the inside of the device is a more complex case, which would require methods such as finite difference time domain
methods to propagate the excitation through all of the layers. This was beyond the scope of this project. The aim of these calculations was to determine if it was at all possible for cavity effects to occur within these devices. This is possible using the calculations described above.

**Figure 6.10.** Setup of diode structure used in optical electric field calculations. Calculations were performed with the light incident directly onto the dendrimer, followed by the underlying layers, or using a MoOx/Au contact on top of the dendrimer layer. Either a wavelength of 325 nm or 500 nm was incident at 90° on the structures.

Firstly, calculations were performed both with and without a top MoOx/Au contact (see Figure 6.10). The results are shown in **Figure 6.11.** The magnitude of the optical field with the addition of the MoOx/Au changes since the MoOx/Au layer can partially attenuate some of the light before it reaches the dendrimer layer. Upon first inspection of the distribution with an incident wavelength of 325 nm, the shape of the optical field and the position of the peaks were the same with and without the top contact (Figure 6.11a). However, upon closer inspection when the y-axis of Figure 6.11a was changed, the position of the peaks in the dendrimer/PBTTT/PMMA/SiNx layers shifts with the addition of the top electrode (Figure 6.11b). This effect was more pronounced with an incident wavelength of 500 nm (Figure 6.11c).
Figure 6.11. The effect of the addition of a MoOx/Au contact on the optical electric field: a) The optical field using an incident wavelength of 325 nm; b) The optical field using an incident wavelength of 325 nm rescaled. There were small shifts in the position of the peak in the film; c) the optical field using an incident wavelength of 500 nm. A shift in the position of the peak within the film can clearly be seen when a MoOx/Au contact is added on top of the active layers.

Further investigations were performed to determine whether changes in the thickness of the layers altered the optical field. Minimal differences in the optical field were seen when the thickness of the Au, MoOx, dendrimer or the PBTTT layers were changed. When the thickness of the SiNx layer was changed, the position of the peaks in the optical electric field shifted as demonstrated in Figure 6.12 for incident wavelengths of 325 nm or 500 nm. Again, on a large scale, there does not seem to be a big difference in the optical field with an incident wavelength of 325 nm. However, when the axis was re-scaled, gradual shifts of the peaks of the optical field in the PMMA and SiNx layers in particular can clearly be seen with a variation in SiNx thickness (Figure 6.12a and Figure 6.12b). When an incident wavelength of 500 nm was used, a shift in the peaks of the optical field can clearly be seen in all of the layers (Figure 6.12c).
Figure 6.12. The effect of a change in the SiNx thickness on the optical electric field: a) The optical field distribution with an incident wavelength of 325 nm; b) the optical field distribution with an incident wavelength of 325 nm rescaled; c) The optical field distribution with an incident wavelength of 500 nm. There was a gradual shift in the position of the peaks in the optical field as the thickness of the SiNx was changed.

The changes in the optical electric field seen with a change in the SiNx thickness is consistent with the presence of weak microcavity effects in the device structure. Since large changes were only seen when there was a change in the SiNx thickness, the microcavity was mainly controlled by the high refractive index SiNx, as well as the transparency of the most reflecting contact. Weak microcavity effects could be responsible for a change in the emission spectra, as previously seen in OLEDs [129–131]. The spatial distribution of the field changed since interference effects within the layers were likely to have affected the emission.
6.7 Conclusion

The LEFETs were fabricated in a bilayer transistor architecture, using a PBTTT charge transport layer underneath a host-free phosphorescent dendrimer emissive layer. These devices were hole-dominated. When planar contacts were used, there was clear evidence for electron transport in addition to hole transport since light emission appeared adjacent to both electron- and hole-injecting contacts. Both the EQE and brightness were improved by using a non-planar contact geometry to directly inject the holes into the charge transport layer. Holes were then directly transported to the electron-injecting contact to recombine with electrons, rather having to first pass through the dendrimer layer. The maximum brightness was $140 \pm 50 \text{ cd m}^{-2}$ with an EQE of $0.11 \pm 0.02 \%$ at the maximum brightness with non-planar contacts. There was also evidence for the presence of weak micro-cavity effects within the devices, demonstrated by the changes in the photoluminescence spectra when contacts were added, and by using optical modeling. Weak micro-cavity effects could be responsible for the shift in the colour of the emission in the devices.

Even though systematic investigations using phosphorescent materials was undertaken, little stability testing was performed. Phosphorescent OLEDs have traditionally required encapsulation from ambient oxygen and humidity to perform well in the long term. Stability testing on these devices should be performed as one of the next steps towards making LEFETs a viable technology.
In this thesis, a body of work on the study of the device physics of LEFETs was described. Concepts such as the effect of altering the charge injection on device performance and the use of ambipolar devices in order to obtain a better balance of electron and hole concentrations were investigated with a view to improve the EQE and brightness from the devices. This is important so that LEFETs can be used in applications such as simplified pixels for displays, as sensors or possibly as injection lasers.

In Chapter 1, a brief summary of some of the charge transport mechanisms in organic semiconductors was described, as well as the luminescence properties of organic materials. The operational mechanisms for standard organic field-effect transistors and for light-emitting field-effect transistors were then discussed. This was followed by a summary of some of the ways that improvements to LEFET performance have been made in literature.

The fabrication and characterisation techniques for the devices reported in this thesis were presented in Chapter 2. One of the early challenges in this project was the characterisation of both electrical and optical characteristics of light emitting transistors. Light emitting transistors had never before been tested at the Centre for Organic Photonics and Electronics. The characterisation setup first had to be designed and then calibrated. The calibration was performed using a light emitting diode as a standard.

The device fabrication and characterisation of ambipolar FETs using a previously unreported diketopyrrolopyrrole-based polymer was described in Chapter 3. This work was undertaken in order to learn more about the device fabrication and device physics of ambipolar FETs. By changing the work function of the contacts, the electron and hole mobilities could be tuned. A maximum electron mobility of order $10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ with a hole mobility of order $10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ was obtained in the device configuration with a PMMA surface passivation layer and Al contacts. This was the first demonstration in this thesis that by tuning the work function, and therefore the charge carrier injection, the relative electron and hole mobilities and device performance could be improved.

These ideas were then applied in the work described in Chapter 4 to tune charge carrier injection in LEFETs. Asymmetric source and drain contacts were needed to efficiently inject both electrons and holes into the devices, and so electron injection could be systematically varied. Shadow masks were designed to allow the deposition of asymmetric electrodes consistently. The masks were designed such that multiple layers could be used as part of the source and drain.

Conclusion and Outlook
contacts. This was not achieved reliably in other reports of devices with asymmetric contacts. Appropriate passivation layers were also required to prevent electron traps at the semiconductor/dielectric interface to improve electron transport in the devices. Both of these considerations were particularly important for the development of ambipolar devices.

This study was undertaken for the ambipolar single layer SY LEFETs as well as the unipolar bilayer SY/PBTTT LEFETs. In the single layer devices, it was shown that when the work function of the electron injection layer was closer to the estimated LUMO of SY, the brightness of the devices and the maximum external quantum efficiency increased. Since there was improved electron injection, there was a larger number of electrons available to recombine with holes, increasing the device brightness. The recombination efficiency increased since there was a better balance of electrons and holes in the device. This, in turn, increased the external quantum efficiency. A maximum EQE of $1.2 \pm 0.2\%$ was achieved for the devices that had a Sm electron-injecting contact, however the maximum EQE was obtained at close to the minimum brightness. The maximum brightness of the single layer devices was $20 - 40$ cd m$^{-2}$ in electron accumulation mode.

The performance of the bilayer devices did not change significantly with a change in the electron injection layer since the device performance was dominated by the underlying PBTTT hole transport layer. The charges were mainly transported through the PBTTT layer, with the top Super Yellow layer acting as an emissive layer. The maximum brightness of the bilayer devices with a Ca electron injecting contact $100 \pm 4$ cd m$^{-2}$ with an external quantum efficiency of $0.04 \pm 0.01\%$ at the maximum brightness.

Chapter 4 described the main approach of the rest of the thesis, where a charge injection layer was used directly underneath one of the electrodes. This approach has similarities to the tri-layer LEFETs [43] first discussed in Section 1.4.3.3 in the Introduction. In both cases, a layer on top of the emissive layer was used to help control the charges that were injected into the emissive layer. In the tri-layer LEFETs, a high mobility layer could be used on top to help charge transport though the device, and aid the charge extraction close to the electrodes. The device performance can also be controlled depending on whether a $p$- or $n$-type semiconductor was used on top of the emissive layer. However, this approach requires a transparent top layer so that the light from the emissive layer can be extracted. This difficulty can be avoided by placing a charge injection layer directly underneath the electrodes so that the emission that occurs in the channel can still be extracted. Also, in the tri-layer devices, the maximum EQE was achieved at the minimum of the source-drain current, where the brightness is likely to be low. It was shown in Chapter 4 that the maximum EQE could occur at the maximum brightness when a charge injection layer was used in combination with a bilayer device architecture. A charge injection layer directly under the
electrodes also allows the charge injection into the emissive layer to be de-coupled from the charge transport through the transistor.

By using a phosphorescent emissive layer, there is the potential to achieve a higher EQE since the triplet excitons formed can decay radiatively. This was applied to the experiments described in Chapter 5 with an evaporated layer of the phosphorescent Ir(ppy)$_3$ in a host of CBP. By applying a charge injection layer of TPBi, the brightness and external quantum efficiency was improved for the devices which used a PBTTT charge transport host. A maximum brightness of $200 \pm 40$ cd m$^{-2}$ with an external quantum efficiency of $0.18 \pm 0.01\%$ was obtained in hole accumulation mode. Ambipolar devices were created using a DPP-DTT charge transport layer underneath the Ir(ppy)$_3$:CBP emissive layer. Using the ambipolar devices, a greater maximum external quantum efficiency of $0.4 \pm 0.2\%$ was achieved in hole accumulation mode. This was due to the better balance of charge carrier concentrations within the device. The maximum external quantum efficiency in these devices were comparable to the highest EQEs reported in literature for a phosphorescent LEFET.

However, the phosphorescent emissive layer of Ir(ppy)$_3$:CBP required a co-deposition of the two organic compounds, which increased the complexity of device fabrication. Chapter 6 describes the development of host free phosphorescent LEFETs. A phosphorescent dendrimer was used as the emissive layer without the requirement for a host to prevent luminescence quenching. The dendrimer was deposited on top of PBTTT, which was used as the charge transport layer. A change in the device geometry was used to alter the charge carrier injection in the device. The use of non-planar top contacts allowed direct injection into the charge transport layer, rather than by first injecting charge into the emissive layer. When PBTTT was used as a charge transport layer, a maximum external quantum efficiency of $0.11 \pm 0.02\%$ was obtained at the maximum brightness $(140 \pm 50$ cd m$^{-2}$) with non-planar contacts. This was a significant improvement in terms of the brightness over the devices fabricated with planar contacts, which had an average maximum brightness of $16 \pm 5$ cd m$^{-2}$. Additionally, the emission spectra of these devices was altered with the addition of top contacts. Photoluminescence measurements and optical modelling were consistent with the presence of weak micro-cavity effects in the devices.

In summary, we have learnt that changing the charge injection in the device can affect the overall LEFET performance. By tuning the injection layers used in devices, the optical properties can be tuned. Secondly, improvements EQE are seen when ambipolar devices are created since electron and hole concentrations can be controlled within the device to achieve a higher efficiency of recombination.

Using what we have learned, several steps towards making LEFETs a viable technology can now be taken. From a device engineering perspective significant advances still need to be made.
before LEFETs can truly be incorporated into displays as a viable alternative to OLEDs. The maximum brightnesses achieved in this work are already above the minimum brightness needed for display applications (of the order of 100 cd m$^{-2}$), so the device brightness is not an issue. As discussed in Chapter 5, light also appears to come from underneath the source and drain contacts. If transparent contacts were used, this would allow more light out of the device at the same current and applied voltage, which would help to improve the EQE.

The operating voltage of LEFETs is high. Even in the bilayer configuration, hundreds of volts are needed to achieve the brightnesses that would be required for display applications. The next priority should be to reduce the high operating voltage. One possible route towards achieving this goal would be to use an alternative gate dielectric. Dielectrics such as aluminium oxide have been shown to be a viable option for low operating voltage OFETs.

The next priority would be to investigate how well a LEFET would respond to the continual stresses that it would be required to withstand. Studies into continual bias stress testing with the application of applied voltages to date have not been reported for LEFETs. This means that it is unknown how suitable these devices could be for a working display.

Very little stability testing has been performed for LEFETs since the technology is still in its infancy. These devices would need to perform well in long term testing if they are to become a viable technology. In order to survive ambient environmental conditions, air-stable electrodes should be considered. If the devices are not able to be fabricated using air-stable components, serious considerations should be given to the appropriate level of encapsulation required so that the devices can survive ambient levels of oxygen and humidity.

Finally, LEFETs could then be incorporated into a working RGB active matrix display to determine the viability of such a device in terms of the ease of device fabrication and to ensure it is possible to create a display reproducibly with a small number of pixel defects.

One other possible application for LEFETs is as an organic injection laser. Threshold current densities for lasing are of the order of kA cm$^{-2}$. LEFETs are easily able to achieve current densities of this magnitude as demonstrated in Chapter 4. This makes LEFETs an attractive option for the development of the first organic injection laser. As yet, injection lasing has not been observed in an organic electronic device and is an open area of research.
References


