Interface Engineering and Molecular Conformation Control for Solution Processed Optoelectronic Devices

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Abstract

Solution processable semiconductors offer a promising route to flexible, low-cost and scalable optoelectronic devices. Device performance is critically dependent on both the material interfaces present within, as well as active layer molecular conformation. In this thesis, the effects of interface engineering and molecular conformation control are investigated within the context of two contemporary technologies; polymer light emitting diodes (PLEDs) and perovskite solar cells (PSCs).

Firstly, the role of the conjugated backbone structure of conjugated polyelectrolytes (CPEs) when used as the electron injection layer in PLEDs is investigated. By using a combination of optical, electrical and Kelvin probe microscopy measurements, it is found that the interface between the CPE and light emitting polymer and the interface between the CPE and metal cathode determine both the efficiency and luminance turn-on time of the PLED, allowing general molecular design rules of CPEs to be deduced. Additionally, a novel organic-inorganic hybrid composite material comprised of a CPE and zinc oxide (ZnO) nanoparticles is examined as an electron injection material in inverted hybrid PLEDs. By optimising the ratio of the ZnO:CPE, it is found that this material has great potential as a solution processed electron injection layer in inverted hybrid light emitting diodes.

Next, a novel approach to achieve deep-blue, high-efficiency PLEDs via a simple molecular level conformation change of an emissive conjugated polymer is discussed. Rigid β-phase segments are introduced into a 95% fluorene-5% arylamine copolymer emissive layer, creating intramolecular type II heterointerfaces. The conformational change alters the nature of the dominant luminescence from a broad, charge transfer like emission to a significantly blue-shifted and highly vibronically structured excitonic emission. As a consequence, a significant improvement in the Commission International de L’Eclairage (x, y) coordinates is observed from (0.149, 0.175) to (0.145, 0.123) while maintaining high efficiency (3.60 cd/A, 2.44 lm/W) and improved stability. This approach is further extended to fluorene-benzothiadiazole copolymers.

Finally, the effect of varying the halide composition of mixed halide (bromide-iodide) lead-based perovskite materials on solar cell performance is investigated using a combination of Kelvin probe, air photoemission spectroscopy, surface photovoltage and absorption/emission measurements. It is found that using 25:75 Br:I ratio gives optimum solar cell performance by
(i) passivating defect states within the perovskite, (ii) increasing the optical band gap which increases open circuit voltage and (iii) stabilising the perovskite such that no halide phase segregation occurs.

Collectively, these works highlight the critical role material interfaces play in the operation of solution processed optoelectronic devices and how, by suitable interface engineering strategies, device performance can be fully optimised.
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Declaration of Originality

Except where specific reference is made to the work of others, the work contained in this thesis is original and has not been submitted either wholly or in part to satisfy degree requirements at this or any other university.

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Climate change driven by rising greenhouse gas emissions, particularly carbon dioxide (CO$_2$), is regarded as one of the major scientific and economic challenges of the 21st century.$^{[1]}$ To reduce CO$_2$ emissions, there is a need to develop energy efficient lighting and display technologies such as low power consumption light emitting diodes, as well as producing energy from clean and renewable technologies such as photovoltaics.

Organic light emitting diodes (OLEDs) are LEDs based on the use of organic materials as the emitter (either small molecules or polymers) and offer a route to highly efficient and low-cost display and lighting appliances.$^{[2,3]}$ OLEDs offer several advantages over traditional display technologies; they are self-emissive, can be fabricated on lightweight flexible substrates and emit a range of different colours. This is more energy efficient than current flat panel LED technology that requires a bright backlight with colour filters to produce the required colour. The self-emissive property of OLEDs leads to improved colour contrast, deeper blacks and a better viewing angle. OLEDs also have the potential to be solution processed, allowing for cheaper manufacturing methods such as roll-to-roll printing could be used to produce low cost, large area display and lighting products.

Whilst currently OLEDs are commonly found in mobile phone displays, the technology is still to make significant inroads into the large area display market due to the prohibitive cost vacuum-evaporation deposition of small molecules. Thus, there is still scope to improve the efficiency and stability of solution processed polymer based light emitting diodes (PLEDs) to lower the cost of OLED production.$^{[4]}$ Three of the chapters of this thesis are concerned with understanding material interfaces within solution processed PLEDs and how they can be used to improve both efficiency, colour emission and lifetime device characteristics.

Perovskite solar cells are photovoltaic devices that employ hybrid organic-inorganic lead halide perovskite materials as the active layer. Since 2012, perovskite based photovoltaic devices have shown a rapid increase in performance from 3% to over 20% in just a few years of research.$^{[5]}$ Perovskite materials can be solution processed to produce high quality crystalline films which offer the potential for low cost, high throughput manufacture of solar cell devices. Despite the rapid progress in the performance of perovskite solar cells, issues remain with device stability and hysteresis effects. Understanding the physical processes occurring within the perovskite is key to further progress in this area. The final results chapter of this thesis concerns how altering
both the composition and interfaces within perovskite layers can impact the behaviour and photovoltaic performance of these devices.

The results presented in this thesis focus on the themes of interface engineering and molecular conformational control to achieve highly efficiency solution processed optoelectronic devices. Polymer light emitting diodes typically have a device structure of several organic layers, thus providing a good context to examine how organic/organic interfaces affect optoelectronic device performance. The conformation of the polymer light emitter can also be controlled, allowing the effect of molecular conformation on device performance to be investigated. Conversely, perovskite solar cells provide a good opportunity to investigate organic/inorganic interfaces and their role on device performance since they use organic charge transport layers and a hybrid organic-inorganic active layer.

Chapter 2 presents a brief overview of the theoretical background describing the optoelectronic properties of conjugated polymers, as well as a discussion of the various material hetero-interfaces found in semiconductor devices. Also examined are the physical processes underpinning the operation of OLEDs and photovoltaics. An introduction to perovskite semiconductors is also included along with a brief review of current perovskite research.

Chapter 3 describes the experimental methods used in this thesis. Both sample preparation and the techniques used to characterise samples are described, along with a detailed explanation of air photoemission spectroscopy (APS), Kelvin probe microscopy and surface photovoltage spectroscopy (SPV).

Chapter 4 explores the use of conjugated polyelectrolytes (CPEs) as solution processed electron injection layers for use in PLEDs. Here, the effect of varying the \( \pi \)-conjugated backbone of the CPE on the device performance of PLEDs containing three different light emitting layers is examined. It is found that the structure of the CPE used determines (i) the current and luminance turn-on times and (ii) the device efficiency of the PLEDs depending on the light emitting polymer (LEP) used. Here, the organic-organic CPE/LEP interface is closely examined. From this, design rules are suggested to synthesise an ‘ideal’ CPE that can be universally used with all light emitting layers to produce high efficiency and fast (< 10 µs) turn-on times. Also investigated are zinc oxide (ZnO):CPE nanocomposite materials as solution processed electron injection materials in inverted hybrid light emitting diodes.

Chapter 5 considers how altering the conformation of fluorene copolymers can enhance the device characteristics of deep-blue PLEDs. Planar, rigid \( \beta \)-phase segments are introduced to a
series of sky-blue emitting x\% fluorene: (100-x)\% arylamine copolymer which induces a blue shift in the electroluminescent emission, improving both the colour purity and stability of the OLEDs. This chapter concerns itself with the detailed analysis of photophysics and device characteristics of the \( \beta \)-phase fluorene:arylamine polymers. The concept is further extended in Chapter 6 to a series of fluorene:benzothiadiazole copolymers for use in polymer LEDs. The concept of how molecular conformational control can affect the device properties of PLEDs is investigated here, as well as the intra and inter-molecular quantum well-like interfaces created.

Chapter 7 investigates a series of mixed halide perovskite layers using Kelvin probe, ambient pressure photoemission spectroscopy and surface photovoltage techniques. Here, a detailed energy level map of each perovskite material is presented along with the photovoltaic behaviour whilst in contact with hole and electron transport layers. These behaviours are then related to the solar cell device performance of each perovskite. Here, we examine the role of the organic/inorganic charge transport layer/perovskite interface on photovoltaic device performance and conclude the optimum composition of the mixed halide perovskite.

Chapter 8 summarises the main findings contained in this thesis and suggests further work to be undertaken.
Chapter 2: Background Theory

2.1 Organic Semiconductors

2.1.1 Electronic Structure of Organic Semiconductors

Organic semiconductors refer to a class of carbon-based molecular or polymeric materials that contain π-conjugated structures which consist of alternating single and double carbon-carbon bonds. These structures arise due to the ground state electronic structure of carbon, which is 1s^22s^22p^2 with a vacant 2p_z orbital (Figure 2.1 (a)). When forming chemical bonds, an electron from the 2s orbital is promoted into the vacant 2p_z orbital (Figure 2.1 (b)). From here, the 2p orbitals may hybridise with the 2s orbital; the degree of hybridisation determines the type of chemical bonds carbon may form. In the case of organic semiconductors, only the 2p_x and 2p_y orbitals hybridise with the 2s orbital, creating three hybrid sp^2 orbitals and one unhybridised 2p_z orbital that lies slightly higher in energy (Figure 2.1(c)).

![Figure 2.1: Schematic representation of (a) electronic structure of carbon. (b) Promotion of electron from 2s orbital into empty 2p_z orbital. (c) sp^2 hybridisation of carbon.](image)

The sp^2 hybridised orbitals can then form covalent bonds by sharing their unpaired electrons with another atom. These are termed σ bonds, and they all lie in the same plane. In ethene, each carbon forms three σ bonds, one with another sp^2 hybridised orbital in the other carbon atom, and two more with the 1s orbital in hydrogen atoms. The remaining 2p_z orbitals from adjacent carbon atoms then overlap with each other forming a π bond that is perpendicular to the plane of the σ bonds (see Figure 2.2 (a)), with the electron density lying above and below the molecular axis. Together the σ bond and π bond form a double bond between the carbon atoms.
The overlapping p\textsubscript{z} orbitals can form either \pi-bonding (lower energy) or \pi*-antibonding (higher energy) molecular orbitals depending on if they overlap in-phase or out-of-phase.

Extending this picture to a chain of \textit{n} carbon atoms, the overlapping p\textsubscript{z} orbitals between \textit{n} sp\textsuperscript{2} hybridised carbon atoms will result in \textit{n} molecular orbitals. As each p\textsubscript{z} orbital contains one electron, half (\textit{n}/2) of the molecular orbitals formed will be (in the ground state) doubly occupied \pi-bonding orbitals, whilst the other half will be unoccupied \pi*-antibonding orbitals, all of which are delocalised over the entire chain. As more carbon atoms are added to the molecule, the increasing number of \pi and \pi* orbitals form a quasi-continuous band structure as illustrated in Figure 2.2(b), analogous to the valence and conduction bands of inorganic semiconductors. The \pi bonding orbital highest in energy is known as the highest occupied molecular orbital (HOMO), whilst the \pi* antibonding orbital lowest in energy is termed the lowest unoccupied molecular orbital (LUMO). The energy difference between them is known as the energy gap (E\textsubscript{g}), which is typically 1.5-3.0 eV in organic semiconductors.\textsuperscript{[6]} This allows for absorption and emission of light in the visible range, giving rise to a wide range of optoelectronic applications. The energy gap can be modified by extending the conjugation length (the energy gap is inversely proportional to conjugation length) up to a certain limit.\textsuperscript{[7]} The optoelectronic properties (such as altering energy gap) of organic semiconductors can be further tuned by modification of the chemical structure, which is especially valuable for light emitting or photovoltaic applications.\textsuperscript{[8–10]}

The origin of the energy gap within organic semiconductors is due to Peierl’s distortion.\textsuperscript{[11]} Here, the real structure of an organic semiconductor consists of alternating single and double carbon-carbon bonds rather than a non-dimerised chain that consists of equidistant C-C spacing. This doubles the length of the semiconductor unit cell thus halving the width of the first Brillouin zone. An energy gap then occurs that separates the two bands within the first Brillouin zone producing semiconducting properties. The filled electronic states within the HOMO are pulled down in energy whilst the unfilled states are pushed up, lowering the overall energy of the system.\textsuperscript{[11]}
Figure 2.2: (a) Schematic diagram of an ethene molecule (C$_2$H$_4$) showing σ bonding (shaded blue) and π bonding (shaded red) between the two carbon atoms. (b) shows a schematic energy level diagram of π bonding and π* antibonding orbitals in a carbon chain for N = 1, 2, 4 and n number of carbon atoms long.

2.1.2 Excitations in Organic Semiconductors

2.1.2.1 Neutral Excitations

Excited states in organic semiconductors come in two varieties - neutral and charged. Neutral excited states may be formed by optical excitation consisting of the promotion of an electron from the HOMO to the LUMO via absorption of a photon whose energy is larger than the optical band gap of organic semiconductor. The vacancy left by the electron creates a positively charged hole which is Coulombically bound to the electron, creating a quasi-particle known as an exciton (see Figure 2.3). The type of excitons formed in organic semiconductors are very different to those formed in inorganic semiconductors; the low dielectric constant of organic materials ($\varepsilon_r \approx 2 - 4$) results in tightly bound hole-electron pairs with binding energies ($E_b$) of 0.1 – 1 eV with electronic wavefunctions that are often localised on a single molecule.$^{[12]}$ These are known as a Frenkel type excitons. Mott-Wannier type excitons (typically found in inorganic semiconductors) are by contrast delocalised, with low binding energies ($< 50$ meV) due to the larger dielectric constant effectively screening the Coulomb attraction between the hole and
The localised nature of Frenkel excitons in organic semiconductors leads to strong electron-phonon coupling and thus a rearrangement of the molecular geometry. This often leads to a planarisation of the polymer chain. This has a stabilising effect on the system, shifting the HOMO and LUMO into the energy gap (see Figure 2.3).

![Energy level diagram showing ground state (S₀), singlet exciton (S₁), hole polaron (P⁺) and electron polaron (P⁻) excited states in an organic semiconductor.](image)

**Figure 2.3:** Energy level diagram showing ground state (S₀), singlet exciton (S₁), hole polaron (P⁺) and electron polaron (P⁻) excited states in an organic semiconductor.

So far, only excited states localised to one molecule or chain have been discussed. However, excited states may be delocalised over two chains, with a hole on one molecule and an electron on another. An intermolecular excitation whereby the wavefunction is spread over two of the same molecular species is termed an *excimer*, whilst an excitation spread over two different molecular species is termed an *exciplex*. Intermolecular excitations such as exciplexes have “charge-transfer” character, whereby their absorption and emission properties are red-shifted (lower in energy) compared to excitons, and have longer radiative decay times. This stems from the greater spatial separation of the hole and exciton and hence smaller Coulomb attraction. It is also possible to form charge-transfer type intramolecular excitons; these often arise in copolymers consisting of electron rich (donor type) units and electron poor (acceptor type) units which have the effect of localising the HOMO or LUMO to a particular unit. This again results in a red-shift in exciton energy and longer radiative decay lifetimes.

Neutral excited states in organic semiconductors can also be formed via electrical excitation. Here, electrons and holes can be injected into the organic semiconductor from appropriately chosen electrodes under application of a bias. The injected charges will then move through the bulk until they are in sufficient proximity to form exciton under Coulombic attraction. A key
difference of excitons formed under electrical excitation is that both singlet and triplet type excitons may be formed. The electronic spin of a hole or electron can be $+\frac{1}{2}$ (↑) or $-\frac{1}{2}$ (↓), therefore the total spin number of an exciton can be 0 (in the case of a singlet) or 1 (in the case of a triplet). A singlet exciton can only be formed if both charges have opposite spin and combine out of phase, giving a singlet spin wavefunction of:

$$|\varphi\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$  \hspace{1cm} 2.1

Conservation of spin forbids optical excitation of triplet excitons from the ground state; therefore, only singlet excitons can be generated via photoexcitation. Triplet excitons can be formed if the charges have both the same spin, or if they have opposite spins but combine in phase, giving three possible wavefunctions of:

$$|\varphi\rangle = \frac{1}{\sqrt{2}}(|\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle)$$  \hspace{1cm} 2.2

Thus, if the orientation of spins of injected charges is random, the ratio of singlets to triplets formed electrically is 1:3.

2.1.2.2 Charged Excitations

Charged excitations can be formed in organic semiconductors by addition of an electron to the LUMO or removal of an electron from the HOMO (see Figure 2.3). This can occur by electrical injection from an electrode, chemical doping or separation of an exciton into charges. As mentioned earlier, there is strong electron-phonon coupling in organic semiconductors upon excitation. Therefore, following the creation of a charged excitation there is a distortion in the molecular lattice configuration to minimise its potential energy. This results in the HOMO and LUMO shifting into within the optical energy gap. The resulting charge plus molecular deformation (lattice distortion) is known as a polaron.\textsuperscript{[20]} Further chemical doping can result in molecules with two charges where two electrons are or added, resulting in excitations termed bi-polarons. The strong localisation of polarons removed to a molecule usually results in low charge carrier mobilities within organic semiconductors, though organic semiconductors with significant $\pi-\pi^*$ stacking can achieve mobilities up to 10 cm$^2$/Vs.\textsuperscript{[21-23]}
2.1.3 Optoelectronic Processes in Organic Semiconductors

2.1.3.1 Absorption

As previously discussed, absorption is a process whereby an electron in the HOMO of an organic semiconductor can be excited into the LUMO via absorption of a photon, creating an exciton (strongly bound hole-electron pair). As excited states in organic semiconductors are accompanied by a relaxation of the molecular lattice, the energy associated with optical processes is usually smaller than $E_g$. This is often termed the optical gap ($E_{op}$) and is given by:

$$E_{op} = E_g - E_b$$

Where $E_b$ is the binding energy of the exciton. The lowest energy absorption is from the electronic ground state $S_0$ to the first excited state $S_1$. Within each electronic state are vibrational energy levels ($\nu_n$). When an electronic transition takes place, transitions to excited vibrational energy levels may also occur as shown in Figure 2.4(a).

![Figure 2.4](image)

**Figure 2.4:** Diagram (a) shows the ground state $S_0$ and first excited state $S_1$ with the first four vibrational energy levels. Example absorption transitions are represented with a vertical arrow from the vibronic ground state of $S_0$ to the $\nu_0$, $\nu_1$, $\nu_2$ and $\nu_3$ vibronic energy levels of $S_1$. Diagram (b) shows an example ideal absorption spectrum with vibronic transitions clearly resolved. Figure partly adapted from ref. [24].

As the electronic transition occurs on a timescale much faster ($\sim 10^{-15}$ s) than nuclear rearrangement ($\sim 10^{-13}$ s), we can use the Franck-Condon principle (which makes use of the
Born-Oppenheimer approximation) to treat the nuclear co-ordinates as stationary before and immediately after the transition are the same.\footnote{24} The electronic transitions can thus be represented as vertical lines in Figure 2.4(a). The strength of a particular transition is given by the Franck-Condon factor, which is square of the overlap integral between the initial and final vibrational states $|\langle \chi_i | \chi_f \rangle |^2$. In theory, transitions between initial and final vibrational states give rise to absorption spectra with well-resolved vibronic peaks (see Figure 2.4(b)). Whilst this is often observed in small molecules, it is rarely seen in the absorption spectra of conjugated polymers. This is because conjugated polymers have a Gaussian distribution of electronic states which arises due to a variety of conjugation lengths present from the naturally disordered structure of the polymer. Thus, many different optical gaps are present within a conjugated polymer leading to broad, featureless absorption spectra.

\textit{2.1.3.2 Emission}

The reverse process of absorption is emission, whereby an electron occupying an excited state decays back to ground state, emitting a photon as it does so. In organic semiconductors, after an electronic transition to a particular vibronic state, the exciton undergoes a relaxation back to the lowest vibrational state in a process known as \textit{internal conversion}. Following this, the exciton will diffuse to neighbouring sites of lower energy before undergoing emission from the lowest energy site within the exciton diffusion length\footnote{25} (typically \(~10\) nm in conjugated polymers).\footnote{26–28} Therefore, as emission occurs only from the lowest energy sites within a conjugated polymer film the emission spectra are lower in energy than the absorption spectra\footnote{29} and tend to display a well resolved vibronic progression, as shown in Figure 2.5.
Singlet excitons decay back to the ground state via a process called fluorescence, and this occurs on a timescale of $10^{-10} - 10^{-9}$ s.\cite{30} Radiative decay of triplet excitons to ground state is normally forbidden in conjugated polymers due to conservation of spin, however this may occur in organic materials containing a heavy metal atom that can induce spin-orbit coupling.\cite{31–33} Here, triplet excitons can decay to ground state via a process called phosphorescence which occurs on a timescale of $10^{-6} - 10^{-3}$ s.\cite{30} Singlet excitons may also be converted to triplet excitons via intersystem crossing; as this involves a change in spin quantum number this usually only occurs in the presence of a heavy metal atom. Excitons can also decay to the ground state via non-radiative processes such as coupling to vibrational modes, aggregation caused quenching and chemical defects.\cite{34} A summary of these optoelectronic processes is shown in the Jablonski diagram in Figure 2.6.

**Figure 2.5:** Example of a typical absorption and emission spectrum in a conjugated polymer film.
Figure 2.6: Jablonski diagram showing absorption (S<sub>0</sub>-S<sub>1</sub>), fluorescence (S<sub>1</sub>-S<sub>0</sub>) and phosphorescence (T<sub>1</sub>-S<sub>0</sub>). Non-radiative vibrational relaxation between S<sub>0</sub>-S<sub>1</sub> is also shown. Only the first singlet and triplet excited states are shown; transitions to higher levels of each are possible. Adapted and redrawn from ref. [30].

2.1.4 Excitations in Homopolymers and Copolymers

The nature of the absorption and emission spectra can vary greatly depending on the type of polymer being studied. Poly(9,9-di-octylfluorene) (PFO) is a well-known example of a homopolymer, which consists of only one type of repeat unit. It is a blue-emitting polymer that can form a number of different phases in a solid state thin film depending on the processing conditions; an amorphous, disordered phase known as the glassy phase<sup>[35–37]</sup>, a crystalline phase<sup>[35,37–39]</sup> and an extended, low energy, planar phase known as the β-phase.<sup>[29,35,37,40–43]</sup> These phase of PFO influences the absorption and emission spectra of the film as shown below in Figure 2.7.

A glassy phase film is usually produced by spin coating at an elevated (~100 ºC) temperature before rapidly quenching, whilst a crystalline film is produced by annealing at ~200 ºC before slowly cooling back to room temperature. There are numerous processing methods by which to induce β-phase chain segments, with reported methods including (i) thermal cycling,<sup>[44–46]</sup> (ii) Langmuir-Blodgett film formation and transfer,<sup>[47]</sup> (iii) deposition of films from mixed
solvent,\textsuperscript{[41]} solvent/additive\textsuperscript{[48]} and high boiling point solvent\textsuperscript{[49]} solutions, (iv) post-deposition film exposure to solvent vapours,\textsuperscript{[46]} and (v) dipping in/flooding with solvent.\textsuperscript{[41,50]}

![Absorption and emission spectra for thin films of different phases of PFO](image)

**Figure 2.7:** Absorption and emission spectra for thin films of different phases of PFO. Figure adapted from reference \textsuperscript{[39]}. Common in all absorption spectra is the main $\pi-\pi^*$ absorption band located at $\sim385$ nm. This peak is slightly broader in the crystalline phase film. The PL for the glassy and crystalline films shows a vibronic progression common in $\pi-\pi^*$ like excitonic emission, with the 0-0, 0-1 and 0-2 emission bands located at 420 nm, 455 nm and 480 nm respectively. Interestingly, the $\beta$-phase film appeared in the vapour treated film (Figure 2.7 (d)) shows an additional absorption peak at $\sim433$ nm, indicative of the lower energy, extended conjugation, planar conformation of the polymer chain. The PL emission shows a red shift in emission, with the 0-0, 0-1 and 0-2 vibronic peaks located at $\sim437$, 470 and 500 nm respectively. This shows very efficient energy transfer to the low energy $\beta$-phase segments before undergoing emission.\textsuperscript{[49,51]} PFO is an excellent example of how molecular conformation control can alter the optoelectronic properties of polymers. This idea is further explored in Chapter 5.

Whilst excitations within homopolymers can be generally characterised by excitonic-like species ($\pi-\pi^*$ transition bands, vibronic PL spectra and fluorescence decay times on the order of $\sim10^{-10}$ s), excitations within copolymers (polymers containing two or more different
monomeric units within the chain) can behave differently. In particular, copolymers with a strong donor-acceptor character such as poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT) can form charge transfer type excitons. In F8BT, this arises due to the large separation in energy between the F8 and the BT units, leading to only a weak interaction that results in LUMO being strongly localised to the BT unit whilst the HOMO is relatively delocalised along the conjugated backbone.\(^{[19]}\) This leads to a greater spatial separation of the hole and electron density within the polymer, and thus a reduction in exciton energy. Figure 2.8 shows the absorption and emission spectra for F8BT.

![Figure 2.8: Absorption and emission spectra of F8BT. Adapted from reference [52].](image)

The inclusion of the BT unit in an otherwise fluorene backbone leads to a new absorption peak appearing at ~460 nm and is termed the charge-transfer (CT) absorption band and is the \(S_0-S_1\) HOMO to LUMO transition. The higher energy excited peak at ~320 nm is the \(S_0-S_9\) transition and is \(\pi-\pi^*\) in character.\(^{[18]}\) The PL spectra shows a relatively broad, featureless emission from the F8BT, with a peak at ~544 nm and shoulder at ~577 nm. This type of emission is also ‘CT’ like emission and can be characterised by its longer-lived fluorescence lifetime of ~2 ns, a factor of ten slower than PFO, as well as its propensity to show a solvatochromic shift.\(^{[18]}\) The Stoke’s shift is significantly larger in F8BT than in PFO due to the larger geometrical relaxation that occurs after excitation. These ideas of charge transfer excitons are visited in further detail in Chapters 5 and 6.

## 2.2 Interfaces in Optoelectronic devices

Different interfaces (organic/organic and organic/inorganic) within organic semiconductor devices play a critical role in determining the optoelectronic properties and device performance
such as organic light emitting diodes and photovoltaic cells. Metal-semiconductor interfaces determine the efficiency of charge injection and charge balance, a requirement for efficient device performance. Organic-organic interfaces within OLED stacks determine the location of recombination zones and are important in the transport or trapping of charges which is essential in forming excitons to undergo radiative recombination. In this section, we review the type of interfaces commonly found in organic semiconducting devices.

2.2.1 Metal-Semiconductor Interfaces

Metal-semiconductor junctions are formed when a metal makes a physical contact with a semiconductor. These junctions can either be rectifying (where the interface forms a Schottky junction) or non-rectifying (in which case an ohmic contact is formed).

2.2.1.1 Rectifying junctions

A Schottky junction is formed for a p-type semiconductor when the workfunction of the metal ($\Phi_m$) is less than the workfunction of the semiconductor ($\Phi_s$), whilst for an n-type semiconductor a Schottky junction is formed if $\Phi_m$ is larger than $\Phi_s$. Figure 2.9 shows the formation of an n-type Schottky junction. Here, electrons will transfer from the semiconductor into the metal forming a positively charged space charge region in the semiconductor near the interface with the metal (represented by band bending in Figure 2.9(b)) and causes Fermi level alignment between the semiconductor and the metal. Under a forward bias, electrons can be injected into the semiconductor subject to overcoming an energetic barrier (known as the Schottky barrier, $\Phi_b$). The barrier height for electron injection is then given as $\Phi_m - \chi$ (where $\chi$ is the electron affinity of the semiconductor). Under reverse bias, this barrier is raised and no current flows.
The width of the space charge region, $w$, is dependent on the carrier densities and the level of doping within the semiconductor. The carrier densities of electrons ($n$) and holes ($p$) can be found respectively by

$$n = n_i \exp \left( \frac{E_f - E_i}{k_b T} \right) \quad p = p_i \exp \left( \frac{E_i - E_f}{k_b T} \right)$$ \hspace{1cm} (2.4)

where $n_i$ and $p_i$ are the intrinsic carrier densities of the electrons and holes, whilst $E_f$ is the Fermi level and $E_i$ is the intrinsic Fermi energy level of the semiconductor (the energy that lies exactly in the middle of the energy gap). When the space charge region is formed, the densities of charge carriers change and induce a potential profile $\varphi(x) = E_f - E_i(x)$ where $x$ is the direction perpendicular to the semiconductor surface. By differentiating this twice, we can find the charge density ($\rho(x)$) at a particular location as

$$\frac{d^2 \varphi}{dx^2} = -\frac{\rho(x)}{\varepsilon}$$ \hspace{1cm} (2.5)

The charge density is also given as the sum of the charge carrier densities ($p$ and $-n$) and the donor and acceptor dopant concentration ($N_D$ and $-N_A$)

$$\rho(x) = e(N_D - N_A + p - n)$$ \hspace{1cm} (2.6)

The built-in potential, $V_{bi}$, within the semiconductor can then be found by solving equation 2.6 to give

$$V_{bi} = -\frac{eN_D w^2}{2\varepsilon\varepsilon_0}$$ \hspace{1cm} (2.7)
which can then be rearranged to give the width of the depletion region

\[ w = \sqrt{\frac{2e\varepsilon_0V_{bi}}{eN_D}} \]  

where \( e \) is the elemental charge, \( \varepsilon \) is the relative permittivity of the material, and \( \varepsilon_0 \) is the permittivity of free space.

The above describes an ideal metal-semiconductor junction, however in real cases, vacuum level alignment at the metal-semiconductor interface does not occur. In inorganic semiconductors, this is due to a high density of surface or defect states present within the forbidden gap of the semiconductor caused by dangling bonds. As a result, the majority carriers fill the defect states creating a space charge region that effectively screens the influence of the metal and forms a dipole. The Fermi level is then pinned to the defect state level.\(^{[53]}\)

In the case of metal-organic semiconductor junction, the above picture applies in the case that the organic film contains residual impurities. These impurities effectively ‘dope’ the semiconductor and free charge carriers are present within the film, as has been observed in the case of thermally evaporated \( \text{C}_{60} \) fullerene. Here, the bulk Fermi level of the bulk \( \text{C}_{60} \) was observed in ~500 nm thick films.\(^{[54]}\)

However, well purified organic semiconductors are generally intrinsic semiconductors. In this case, there is negligibly small band bending in the semiconductor due to the lack of charge carriers within the organic layer. The large Schottky barrier prevents transfer of charges from the metal into the organic material, thus no charge transfer occurs across the interface. In this case, the value of the semiconductor Fermi level assumes the value of the metal Fermi level.\(^{[55]}\)

### 2.2.1.2 Non-rectifying junctions

An ohmic metal-semiconductor junction is formed for p-type semiconductors when \( \Phi_m > \Phi_s \), and for n-type semiconductors when \( \Phi_m < \Phi_s \). Here, the majority charge carrier can transfer from the metal to the semiconductor to further enhance the charge carrier density at this interface. An example of an n-type ohmic contact is shown in Figure 2.10 whereby electrons are transferred from the metal to the n-type semiconductor, further increasing the n-type charge carrier density and showing Fermi level alignment. The current density should increase linearly with voltage for ideal ohmic contacts in both directions.
In organic semiconductors, an ohmic contact is formed when the workfunction of the metal is greater than the ionisation potential of the organic material for a p-type contact or the metal workfunction is less than the electron affinity of the organic material for an n-type contact. In the p-type case (Figure 2.11), there is a spontaneous transfer of electrons from the HOMO of the organic material to form hole polarons.\(^{30}\) As discussed in section 2.1.2.2, the hole polarons occupy an energetic state known as the hole polaron level whereby the HOMO shifts into the energy gap of the organic semiconductor due to the lattice relaxation. This is different from the Fermi level of the semiconductor which is the theoretical energy level at which there is a 50% probability of being occupied by an electron. As this transfer takes places, the number of positively charged molecules increases and the metal substrate becomes increasingly negatively charged, forming an interfacial dipole. The Fermi level of the metal is then pinned to the hole polaron level rather than the Fermi level of the semiconductor. This interfacial dipole shifts the vacuum level downward by an amount \(\Delta = \Phi_m - E^+_p\) where \(E^+_p\) is the energy of the hole polaron. \(^{56-58}\) The organic semiconductor is effectively doped in the interfacial region near the metal contact.\(^{56-58}\) This model is known as the integer charge transfer model in organic semiconductors, however this model does not hold true universally for all cases of ohmic injection.\(^{58}\)

Similarly, for the n-type case, electrons spontaneously transfer from the metal to the LUMO of the organic semiconductor until the Fermi level is pinned to the electron polaron energy level. Here, the interfacial dipole will be negative and thus the vacuum level of the semiconductor will lie higher in energy than that of the semiconductor.

Figure 2.10: Schematic energy level diagram of a metal and n-type semiconductor ohmic junction (a) before contact and (b) after contact.
Ohmic contacts are important in organic semiconductor devices; organic light emitting diodes require balanced charge injection from each contact to achieve high efficiencies, whilst organic photovoltaics rely on ohmic contacts to effectively extract charges from within the bulk of a photoactive layer.

### 2.2.2 Semiconductor-Semiconductor Interfaces

Semiconductor heterojunctions play a critical role in the performance of organic optoelectronic devices. Semiconductor heterojunctions are classified by the alignment of the valence band (HOMO) and conduction band (LUMO) at the interface.

A schematic energy level diagram of type I and type II semiconductor interfaces is shown in Figure 2.12. A type I heterojunction is formed when the LUMO of semiconductor 2 (SC2) lies deeper in energy than SC1, whilst the HOMO of SC2 lies at a shallower energy level than that of SC1, i.e. the band gap of SC2 ‘straddles’ that of SC1. A type II heterojunction is formed when both the HOMO and LUMO of SC2 lie deeper in energy than SC1, forming a ‘staggered’ energy level profile across the interface.\[^{59}\]
Figure 2.12: Schematic energy level diagrams showing HOMO (or valence band) and LUMO (or conduction band) in (a) a type I heterojunction and (b) a type II heterojunction.

At a type I semiconductor interface, excitons created in SC1 would undergo preferential energy transfer to SC2 as it has a smaller energy gap. However, excitons created in SC2 will most likely decay (radiatively or non-radiatively) as energy transfer from SC2 to SC1 would only be possible if the exciton has enough thermal energy to overcome the difference in the energy gap between the two semiconductors ($\Delta E \sim kT$). These interfaces are important when designing OLED devices to confine excitons within the emissive layer (i.e. the materials either side of the emissive layer should have larger energy gaps).\[60\]

Figure 2.12(b) shows the energy level diagram of a type II heterojunction. It is possible energy transfer can still occur across this interface, however if the LUMO or HOMO energy offset, $\Delta E$, is larger than the exciton binding energy ($0.2 - 1.0 \text{ eV}$)\[12\] then charge transfer may occur across this interface. For example, the electron of a photoexcited exciton on SC1 (electron donor) will be transferred to SC2 (electron acceptor). This forms a hole polaron on SC1 and an electron polaron on SC2. These charges then form a charge transfer state (or exciplex) across the interface that could decay, or dissociate and form free charges through the system.\[61,62\] This latter case is of particular importance in organic photovoltaics, and much effort has gone into selecting materials to form type II heterojunctions that efficiently form free charges.\[63\] Type II heterojunctions can be made use of in OLEDs, whereby electrons and holes are trapped at the interface to form exciplex states. These are generally undesirable as exciplex emission is red-shifted compared to exciton emission,\[64\] however bulk excitons may be regenerated at these interfaces if the energies of the bulk exciton and exciplex are comparable, as is the case in F8BT and TFB heterojunctions.\[65\]
2.3 Organic Light Emitting Diodes

Organic light emitting diodes (OLEDs) are considered to be one of the most promising applications of organic semiconductors, with many commercial lighting and display products now based on the technology. The basic premise of OLEDs is the production of light under an applied bias with the active layer of the material being organic. The production of luminescence in response to an electrical current is known as *electroluminescence*.

Electroluminescence in organic materials was first observed in single crystals of anthracene in the 1960s.\[^{[66]}\] However, the high voltages of ~400 V required to produce electroluminescence meant no practical application was found. In 1987, the first thin film OLED was fabricated by Tang and Van Slyke, consisting an aromatic diamine hole transport layer and an 8-hydroxyquinoline aluminium (Alq3) emissive layer sandwiched between a semi-transparent anode of indium tin oxide (ITO) and a magnesium-silver alloy cathode.\[^{[2]}\] This OLED represented a major step forward, with visible luminescence from voltages as low as 3 V. Small molecule based OLEDs are the dominant type of available commercial OLEDs, however their fabrication is based on batch processed, vacuum evaporated deposition making cheaper, solution processed OLEDs desirable. In this respect, OLEDs based on polymers (polymer light emitting diodes or PLEDs) provide a route to low cost, solution processed light emitting devices. The first PLED was reported in 1990 by Burroughes et al. consisting of a single active layer of poly(p-phenylene vinylene) with an ITO anode and aluminium cathode and achieved efficiencies of 0.05%.\[^{[3]}\] Most modern PLEDs now consist of multi-layer architectures including polymeric hole injection layers, a hole transporting/electron blocking interlayer and a low workfunction metal electron injection layer. A typical example of conventional PLED architecture is shown below in **Figure 2.13**. Also explored in this thesis are hybrid organic-inorganic light emitting diodes (HyLEDs) which use an inverted structure whereby the ITO acts as a cathode rather than an anode with metal oxides such as zinc oxide acting as an electron injecting layer and molybdenum oxide used as a hole injecting layer.\[^{[67]}\]
The external quantum efficiency of a PLED, $\eta_{\text{EQE}}$, is defined as the ratio of the number of emitted photons to the number of injected electrons, however it can also be expressed as the product of several efficiency terms shown below in equation 2.9$^{[68]}$.

$$\eta_{\text{EQE}} = \gamma \cdot \eta_s \cdot \eta_{\text{PL}} \cdot \eta_{\text{ext}}$$ \hspace{1cm} 2.9

Here, $\gamma$ is the exciton formation efficiency i.e. the ratio of the number of excitons formed to the number of injected electrons. This number would be unity if every injected electron combines with a hole to form an exciton. The second term, $\eta_s$, is the ratio of singlet excitons formed to the total number of excitons formed, whilst the third term, $\eta_{\text{PL}}$, is the fraction of singlet excitons formed within the LEP material that radiatively decay. This not only depends on the photoluminescence quantum yield (PLQY) of the material, but also takes into account quenching effects by metal electrodes. The final term, $\eta_{\text{ext}}$, is the outcoupling efficiency of the device. This is the fraction of photons emitted by the LEP that escape the device. This number depends on the orientation of the emitting dipoles within the LEP, the refractive indices of materials within the device and the location of the recombination zone.

### 2.3.1 Operating Processes of Organic Light Emitting Diodes

The operational mechanism of an OLED involves four fundamental processes to produce light in response to a current:

1. Injection of charge carriers at their respective electrodes.
2. Transportation of charges through the bulk of the device into the emissive layer.
3. Formation of exciton from charge carriers by Coulombic attraction.
4. Radiative recombination of the exciton to form a photon of light.
These processes are represented schematically in Figure 2.14.

![Figure 2.14: Schematic energy level diagram showing the electroluminescence processes of an OLED under forward bias.](image)

2.3.1.1 Charge Injection

Organic semiconductors are typically intrinsic and thus have a low density of free charge carriers, thus charge injection is a critical process in OLEDs to introduce charge carriers into the system. As discussed in section 2.2.1, the metal-semiconductor interface plays an important role in charge injection for organic semiconductors. One factor in choosing materials for use as cathodes in OLEDs are the workfunctions ($\Phi_A$ for the anode and $\Phi_C$ for the cathode) to minimise charge injection barriers ($\Phi_b = \Phi_C - E_{LUMO}$ for electrons and $\Phi_b = E_{LUMO} - \Phi_A$ for holes) and form an ohmic contact. Balanced hole and electron charge injection is desirable in OLEDs to improve device efficiency.

Charge injection occurs from a metal into an organic semiconductor via two main processes; thermionic emission and Fowler-Nordheim tunnelling (Figure 2.15).\textsuperscript{[69,70]} Thermionic emission is the injection of charge carriers over an energetic barrier due to thermal excitation of the charge carriers and dominates at high temperatures. Fowler-Nordheim tunnelling is quantum tunnelling of the electrons from the metal into the organic semiconductor through a triangular barrier. As electric field increases, the band bending (slope) of the semiconductor increases, decreasing the width of the triangular barrier and hence increasing the current. This type of injection dominates at large applied electric fields.
Figure 2.15: Schematic energy level diagram showing electron injection via (a) thermionic emission and (b) Fowler-Nordheim tunnelling.

Semi-transparent ITO acts as the anode, whilst poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS), a water soluble mixture of two polymers is used as a hole injection layer. PEDOT:PSS is known for being a transparent, highly conductive polymer with a high workfunction (~5.1 eV) that allows hole injection into a wide variety of materials. An interlayer such as poly(9,9-dioctylfluorene-alt-N-(4-sec-butylphenyl)-diphenylamine) (TFB) is commonly deposited between the PEDOT:PSS and light emitting polymer (LEP) to help improve the efficiency and lifetime of the device. The acidic nature of PEDOT:PSS can cause degradation of the LEP and thus a thin interlayer (10-15 nm) is helpful in preventing this.

Low workfunction metals such as barium, or more commonly calcium, are often chosen as electron injection materials. However, their high reactivity results in poor stability in air. More desirable alternatives include using solution processed conjugated polyelectrolytes as electron injection layers, or air stable solution processed metal oxides. This is further explored in Chapter 4.

2.3.1.2 Charge Transport

Injected charges must be transported to the recombination zone where exciton formation can take place. The parameter that determines the ease of charge transport through a semiconductor is given by the charge mobility, $\mu$, and is given by:

$$\mu = \frac{v_d}{E} \quad (2.10)$$
Where $v_d$ is the drift velocity of the charge carriers and $E$ is the applied electric field. As previously discussed, excited states in organic semiconductors such as polarons are localised within single molecules. Due to this, charge transport in organic semiconductors takes place via a thermally activated inter molecular tunnelling process known as ‘hopping’. This is in stark contrast to charge transport in inorganic crystalline solids where intramolecular band like transport dominates.

Charge transport is highly dependent on both the molecular and energetic disorder of the organic semiconductor. Small molecules and polymers that show lamellar stacking generally display high charge mobilities in the $\pi-\pi$ direction due to enhanced intermolecular overlap of the molecular orbitals. The amorphous nature of PLED materials also means there is Gaussian distribution of the HOMO and LUMO levels, i.e. energetic disorder. This leads to field dependent mobility given by the Poole-Frenkel relationship:

$$\mu = \mu_0 \exp(\sqrt{\beta E}) \quad \text{(2.11)}$$

Where $\beta$ is a temperature dependent constant and $E$ is electric field. Variations in molecular orbital localisation, molecular morphology and/or charge carrier specific traps often lead to organic semiconductors having largely asymmetrical hole and electron mobilities. This can cause problems in PLEDs, especially if one mobility is much higher than the other as this can reduce efficiency and accelerate device degradation with a large density of free charge carriers of only one type. \[70\]

### 2.3.1.3 Exciton Formation

Charge recombination within OLEDs is Langevin type; the recombination of charge carriers is a random process and kinetically bimolecular.\[79,80\] For a hole and electron to recombine, the carriers must be within Coulombic capture radius, $r_c$, which can be found from the condition that electrostatic energy is approximately equal to the thermal energy of the carriers ($kT$), thus:

$$r_c = \frac{q^2}{4\pi\varepsilon kT} \quad \text{(2.12)}$$

where $q$ is the charge of an electron, $T$ is the temperature, $k$ is the Boltzmann constant and $\varepsilon$ is the permittivity. Exciton formation within OLEDs can be increased through several methods. One is by introducing electron or hole blocking layers (i.e. energetic barriers formed by semiconductor heterojunctions) to prevent the dominant charge carriers from crossing through...
Another method is to control the mobility of charges by introducing hole or electron transporting moieties within the LEP. By achieving the correct proportion of units within the polymer, the location of the recombination zone can be tuned within the OLED and exciton formation and hence device efficiency increased. This concept is explored further in Chapter 5.

2.3.1.4 Radiative Decay

Whilst the first three electroluminescence processes (charge injection, charge transport and exciton formation) determine the value of the exciton formation efficiency, \( \gamma \), the radiative decay efficiency of an exciton is determined by the fraction of emissive excitons formed (the fraction of singlet excitons, \( \eta_s \), in light emitting polymers) and the photoluminescence efficiency of the emissive excitons (\( \eta_{PL} \)). The random spin statistics suggests that the fraction of singlet excitons formed in organic semiconductors from electrical excitation is 25%, however spin-dependent exciton formation has been observed in conjugated polymers, with singlet fractions closer to \( \sim 40-50\% \). This has been postulated to be 1-dimensional nature of the polymer chain giving a greater spatial extension and thus giving a longer range attraction.

To increase the fraction of emissive excitons formed further, triplet harvesting is required. One method is to incorporate organic complexes containing a heavy metal atom such as platinum or iridium into the emissive layer of the OLED. The heavy metal atom induces spin-orbit coupling, a consequence of which allows decay of excited triplet states to the ground singlet state \( \text{via} \) phosphorescence. A well-structured OLED incorporating a phosphorescence emitting dopant can achieve internal quantum efficiencies of 100%. A drawback of using phosphorescent emitters is that as the triplet state lies at a lower energy level than the singlet making synthesis of deep-blue emitting phosphorescent host and guest materials difficult.

Triplets can also be harvested in fluorescent emitters by a variety of methods. Fluorescent polymers have been shown to display triplet-triplet annihilation (TTA), a process whereby two triplet excitons can annihilate each other to produce a highly excited singlet state and a ground state singlet. This process is particularly efficient when an excited singlet state, \( S_n \), has twice the energy of the first excited triplet state, \( T_1 \). The process is represented below in equation 2.13.

\[
T_1 + T_1 \rightarrow S_n + S_0
\]  

2.13
The excited singlet state, $S_n$, then undergoes non-radiative decay to the first excited singlet state, $S_1$, before undergoing emission. The singlets generated by TTA can contribute up to $\sim40\%$ of steady state emission.\[86–89\]

Finally, recent progress in fluorescent small molecule emitters have shown a process known as thermally activated delayed fluorescence (TADF) resulting in fluorescent OLEDs with $\sim100\%$ IQE.\[90,91\] Here, the molecule is designed in such a way as to minimise the energy between the ground state singlet and triplet states via spatial separation of the HOMO and LUMO density. This allows reverse intersystem crossing of electrically excited $T_1$ triplets to the $S_1$ state via thermal excitation provided the energy gap between $S_1$ and $T_1$, $\Delta E_{ST} \sim kT$.\[92,93\]

Another important factor to consider when designing materials and device structures for use in OLEDs is the suppression of non-radiative decay channels. Formation of co-facial (or H) aggregates in emissive materials can lead to a phenomenon known as aggregation caused quenching (ACQ) which can greatly reduce the PL efficiency of a material in the solid state.\[94\] To prevent this, often emitters are doped into a host matrix at typically 5-10% loading levels to reduce aggregation, however phase separation or unsuitable hosts may mean this is not always a viable method.\[95\] Alternatively, one can use chemical design to prevent aggregation of emitting species to make them less prone to stacking. Methods such as side chain engineering and altering the cis/trans linkage within polymers can reduce ACQ and improve $\eta_{PL}$.\[96\]

When designing the OLED architecture, it is critical that the recombination zone is near the centre of the stack and kept away from any quenching interfaces such as metallic electrodes. Image charge quenching from such interfaces is a major loss mechanism in OLEDs, and as such the use of organic charge injection layers and interlayers is helpful in preventing this.\[97\] These concepts are explored further in chapter 4.

2.3.2 Characterisation of OLEDs

The human eye exhibits a non-uniform sensitivity to different wavelengths to light in the 400 – 700 nm range. Figure 2.16(a) shows the photopic response function of the eye in light adapted conditions. The eye is most sensitive to light at 555 nm, with sensitivity decreasing sharply as the wavelength nears the UV and near infra-red range. Whilst the external quantum efficiency, $\eta_{eqe}$, can be used to characterise both visible and near infra-red LEDs. However, a
more useful measure of efficiencies for OLEDs that emit in the visible range are based on *photometric* quantities which consider the perceived brightness of emission to the human eye.

![Figure 2.16](image)

**Figure 2.16:** (a) plot showing photopic response curve of the human eye, (b) colour matching functions $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$ and (c) CIE $(x, y)$ chromaticity diagram with white colour point at $(0.33, 0.33)$.

The luminous flux, $\phi$, (luminous energy per unit time) of a visible light source is measured using the lumen (lm) and is defined as a power output of $1/683$ W for a monochromatic source at 555 nm. As many light sources have some directional property (e.g. OLEDs can be modelled as Lambertian emitters), it is useful to define the luminous intensity as the luminous flux per unit of solid angle. This is measured by the candela (cd), which is equal to 1 lumen per steradian. Finally, the perceived brightness of a light source can be measured by the luminance. This is the luminous intensity per unit of a projected source area, and thus has units of cd/m$^2$.

This allows us to define an efficiency known as the *luminous efficiency*, $\eta$, and is defined as the amount of luminance produced by a device per unit of current density and is given in units of cd/A

$$\eta = \frac{\text{luminance (cd/m}^2\text{)}}{\text{current density (A/m}^2\text{)}}$$

2.14
Whilst this efficiency takes into account the current driving the device, it does not take into
take into account the voltage (and hence power) at which this occurs. Power efficiency, $\eta_P$, is more useful
this regard and is defined as the luminous flux in the forward direction per unit of electrical
power and is given in units of lm/W. It is related to luminous efficiency by

\[
\eta_P = \frac{\text{luminous optical power (lm)}}{\text{electrical power (W)}} = \frac{\pi}{V} \eta \tag{2.15}
\]

Finally, to quantify the perceived colour of a particular LED, a system was devised by the
Commission Internationale d'Eclairage (CIE) which allowed the spectrum of a light source to
be linked to the colour perceived to the human eye. Here, colour matching functions, $\bar{x}(\lambda)$, $\bar{y}(\lambda)$
and $\bar{z}(\lambda)$ are defined as the chromatic response of an observer and are shown in Figure 2.16(b).
The overlap of each of these functions with the electroluminescent (EL) spectrum, $I(\lambda)$, of an
OLED gives the tristimulus values of a spectrum:

\[
X = \int I(\lambda) \bar{x}(\lambda) d\lambda \tag{2.16}
\]

\[
Y = \int I(\lambda) \bar{y}(\lambda) d\lambda \tag{2.17}
\]

\[
Z = \int I(\lambda) \bar{z}(\lambda) d\lambda \tag{2.18}
\]

These are then used to calculate the CIE chromaticity co-ordinates $x$ and $y$ by:

\[
x = \frac{X}{X + Y + Z} \tag{2.19}
\]

\[
y = \frac{Y}{X + Y + Z} \tag{2.20}
\]

These co-ordinates can then be plotted on a CIE chromaticity diagram shown in Figure 2.16(c)
which gives a visual representation of the colour of a particular spectrum.

### 2.4 Photovoltaic Devices

Chapter 7 of this thesis focuses on the application of organic-inorganic perovskite materials for
solar cell device applications, thus this section will briefly cover the fundamental photovoltaic
working principles.

Photovoltaic devices broadly work by converting light into electricity via four processes:
1. Absorption of light to form excitons within active layer.
2. Separation of hole and electron into free charges.
3. Charge transport through bulk.
4. Charge extraction into external circuit.

At each process, several loss mechanisms are present than can reduce the efficiency of a given solar cell. This thesis will be mainly exploring loss mechanisms such as charge recombination and charge trapping within perovskite solar cells.

A solar cell is characterised by measuring the current density as a function of applied voltage whilst the device is illuminated under an intensity of 1 sun. Figure 2.17 shows an example J-V curve of a working perovskite solar cell under 1 sun illumination with some key performance parameters highlighted.

![J-V Curve](image)

**Figure 2.17**: Example J-V curve of an operation perovskite solar cell under 1 sun illumination. The maximum power, short circuit current and open circuit voltage values are highlighted on the graph.

The open circuit voltage, $V_{oc}$, is the applied bias at which no current flows within the device, whilst the short circuit current, $J_{sc}$, is the current density measured in the absence of an applied bias. The power output of the cell is product of the voltage and current, thus the maximum power voltage, $V_{MPP}$, and maximum power current density, $J_{MPP}$, are the values at which the
power output of the cell is maximised. The fill factor (FF) is then defined as the product of these two values divided by the product of the open circuit voltage and short circuit current

$$FF = \frac{V_{MPP}J_{MPP}}{V_{oc}J_{sc}}$$  \hspace{1cm} 2.21

and thus, gives a measure of how ‘square’ the current voltage curve is. The power conversion efficiency (PCE) is given by

$$PCE = \frac{J_{sc}V_{oc}FF}{P_i}$$  \hspace{1cm} 2.22

where $P_i$ is the power density of the incident illumination. The $J_{sc}$, $V_{oc}$ and FF parameters are to be maximised to give the largest PCE, and in Chapter 7 the means to do this in a mixed halide perovskite system are considered.

### 2.5 Hybrid Organic-Inorganic Perovskites

In recent years, much research in optoelectronic devices has involved a new class of solution-processable organic-inorganic hybrid semiconductor known as lead-halide perovskites. In only four years, power conversion efficiencies (PCEs) in solar cells based on perovskites have increased from ~3% to over 20% with the bulk of these taking place in 2012-2013.\cite{98-100} The hybrid organic-inorganic perovskite material compositions used typically consist of a lead metal cation (Pb$^{2+}$), with an alkylammonium cation (often CH$_3$NH$_3^+$) and then three halide anions (typically I$^-$, Br$^-$ or Cl$^-$). The crystal structure is shown below in Figure 2.18.
Figure 2.18: Perovskite $\text{CH}_3\text{NH}_3\text{PbX}_3$ crystal structure where typically $X = \text{I}^-$, $\text{Br}^-$ or $\text{Cl}^-$ or mixtures thereof.

Whilst perovskite based semiconductors have only recently the attention of the scientific community, the first report of lead halide semiconductors (with caesium cations) was in fact made in the late 19th century.$^{[101]}$ The crystal structure of perovskite semiconductors was later identified in 1957$^{[102]}$ whilst in 1978, the first hybrid organic-inorganic lead halide perovskite materials were synthesised with a methylammonium cation replacing the caesium.$^{[103]}$ More recently, in 2009, methylammonium lead iodide (MAPI) and methylammonium lead bromide (MAPBr) were successfully used as the light sensitizers in dye-sensitized solar cells, however the use of these materials within a liquid electrolyte lead to modest performances (up to 3.8% PCE) and poor stability.$^{[99]}$

The critical breakthrough for perovskite based solar cells found in 2012 was engineered by replacing the liquid electrolyte with an organic thin film hole transport layer of spiro-OMeTAD and an alumina scaffold to enhance electron transport through the perovskite.$^{[98]}$ This increased PCE efficiencies to 10.9%. Recent works have sought to optimise the device performance, most notably by improving perovskite film quality and reducing crystal defects. Deposition techniques such as sequential solution deposition (whereby lead iodide is first deposited followed by immersion in methylammonium iodide) and dual-source vapour deposition within a vacuum can form dense, uniform films of MAPI.$^{[104,105]}$ Solvent engineering techniques also provide a route to uniform films by spin coating from mixed solvent solutions such as $\gamma$-butyrolactone (GBL) and dimethylsulphoxide (DMSO) before quenching with a non-solvent
such as toluene.\textsuperscript{[106,107]} Additionally, solvent additives such as hypophosphorous acid can aid film formation and reduction of energetic defects.\textsuperscript{[108]} Beyond this, tuning the composition of the perovskite by varying the halide anion by including bromide or chloride ions\textsuperscript{[109,110]}, or by varying the methylammonium cation to formamidinium or caesium provide a route to alter the band gap and energy levels of the perovskite material.\textsuperscript{[111,112]} The culmination of these research efforts have rapidly pushed the PCEs of perovskite solar cells to over 22\%, which places their performance on par with established technologies such as crystalline silicon and CdTe solar cells.\textsuperscript{[113]}

Similar to organic semiconductors, the advantages of hybrid organic-inorganic lead halide perovskites lie in their facile, low-cost solution processing and relatively cheap, abundant precursor materials. Their energy band gap can also be easily tuned, giving a wide range of optoelectronic applications.\textsuperscript{[110]} However, unlike organic semiconductors, the materials properties of perovskites are more like traditional inorganic semiconductors. Their high dielectric constants give rise to low exciton binding energies (~50 meV)\textsuperscript{[114,115]}, possess relatively long excited state decay times (up to ~10^{-6} s)\textsuperscript{[116]} and have long diffusion lengths exceeding 1 \textmu m\textsuperscript{[116,117]}. This allows photogenerated excitons to easily dissociate into charges without the need for a type II heterojunction, and accounts for the high PCE observed in perovskite solar cells.

Routes to higher efficiency perovskite solar cells now relies on understanding the physics behind the perovskite and developing hole and electron transport materials. Interfaces are a key property in perovskite solar cell efficiency. Depositing the perovskite layer on low surface energy materials can result in poor crystal quality and surface coverage, thus it is desirable to deposit the perovskite layer on higher energy (charged) materials such as PEDOT:PSS and CPEs.\textsuperscript{[100]} Interface engineering is also critical in transporting charges to the respective electrodes, energy level matching and high mobility materials are ideal for use in perovskite solar cells to reduce charge recombination and increase power conversion efficiency.\textsuperscript{[100,106,118–120]}

Chapter 7 of this thesis explores how varying the composition of mixed halide iodide-bromide perovskites (with 0\%, 25\%, 50\%, 75\% and 100\% bromide content) affects inverted solar cell device performance using PEDOT:PSS as a hole transport layer and PCBM as an electron transport layer. This study finds that the 25\% Br mixed halide perovskite produces the best performing solar cell device. Previous studies of titanium oxide (TiO_{2}) based mixed halide
perovskite solar cells indicate that low levels of bromide incorporation (20-25%) produce the highest efficiency solar cells by increasing $V_{oc}$ due to the larger energy gap produced when incorporating bromide into the perovskite.\textsuperscript{[110,121,122]} However, further bromide incorporation beyond this causes a loss in efficiency due to a decrease in $J_{sc}$ and possible phase segregation between iodide and bromide regions.\textsuperscript{[123]}

Chapter 7 in particular investigates how altering the mixed halide composition affects device performance based on how incorporating bromide influences the energy levels (HOMO, LUMO and Fermi level) of the perovskite, and also how the interfaces between the perovskite and hole and electron transport materials is changed. To do this, Kelvin probe microscopy, surface photovoltage spectroscopy and air photoemission spectroscopy techniques are used to probe the HOMO and Fermi level (in dark and under illumination). These values can be used to deduce the size and direction of any band bending occurring at each perovskite interface, as well as giving valuable information about how suitable each interlayer is at extracting charge from the perovskite layer, as well as the quality of the perovskite film.\textsuperscript{[124]} This can be particularly valuable in the case of mixed halide perovskite solar cells since previous studies have shown that recombination (and hence device performance) within these devices is based strongly on LUMO offset between the perovskite and PCBM.\textsuperscript{[125]} These measurements, along with optical spectroscopy measurements such as UV-vis absorption and low temperature photoluminescence elucidate the reason why 25% Br is the best performing mixed halide perovskite and the critical role the interfaces between the perovskite and the charge transport layers play in determining device efficiency.
Chapter 3: Experimental Methods

3.1 Sample Preparation

3.1.1 Solutions

Polymer and conjugated polyelectrolyte (CPE) solutions were prepared first by weighing out the dry, solid material using an electronic balance (to an accuracy of ±1 mg) then dissolving in a specified amount of solvent (typically toluene for polymers) or 2-methoxyethanol (CPEs). The solution parameters used for each material are noted in this thesis, however a typical polymer concentration of 10 mg/ml in toluene is used to achieve a 60-70 nm thick thin film. Solutions were left to stir for up to two hours at 60 °C until fully dissolved. CPE solutions were typically prepared at a concentration of 2.5 – 5 mg/ml to give film thicknesses of ~10 nm before filtering through a 0.45 μm PTFE filter. Spectroscopic measurements of dilute polymer solutions were typically performed at 0.1 mg/ml.

Perovskite precursor solutions were prepared by separately weighing the methylammonium halide (either iodide or bromide) and lead halide powders using an electronic balance before transferring to a single vial. A solvent mixture of γ-butyrolactone (GBL) and dimethyl sulfoxide was added in a ratio of 7:3 to reach a concentration of 1 M. Mixed halide solutions of methylammonium lead bromide and methylammonium lead iodide were then produced by blending the individual solutions in the desired ratio.

3.1.2 Thin Film Deposition

For optical characterisation, thin film samples were fabricated via spin coating on 12 x 12 x 1.5 mm sized quartz (spectrosil) substrates. Substrates were first cleaned by successive 10-minute ultrasonic baths in acetone and isopropanol (IPA) before undergoing oxygen plasma treatment for 3 minutes at 80 W using an Emitech K1050X. Solutions were then spin coated at a speed of 1000 rpm or higher for between 30 – 60 s to produce uniform films.

3.1.3 Light Emitting Diode Fabrication

Light emitting diodes were prepared on indium-tin oxide (ITO) patterned glass substrates. The ITO (150 nm thick) substrates were cleaned for 15 minutes each in a sequence of ultrasonic
baths using acetone, isopropanol and detergent (Hellmanex III, 2% by volume in deionised (DI) water). The substrates were then rinsed in DI water before being dried on a hotplate at 115 °C for 10 minutes. This was followed by oxygen plasma ashing in an Emitech K1050X at 80 W for 3 minutes. For conventional PLEDs, a 35nm thickness film of PEDOT:PSS (Clevios P VP) was deposited as hole injecting layer by spin-coating at 3000 rpm and annealing in air for 15min at 135 °C to drive off residual water. This was followed by spin-coating (at 1000 rpm for 30 s) a 15 nm thickness electron-blocking poly(9,9-diocetylfluorene-alt-N-(4-sec-butylphenyl)-diphenylamine) (TFB) interlayer from a 2 mg/ml toluene solution, and then baking in nitrogen at 180 °C for one hour to facilitate cross linking and rendering the layer insoluble.[73] A 60 - 70 nm light emitting polymer (LEP) layer is then deposited via spin coating. For PLED devices containing a CPE electron injection layer (EIL), a 10 nm CPE layer would then be deposited via spin coating at 3000 rpm for 60 s. Finally, an MBraun thermal evaporator was used to deposit the top cathode comprising calcium (25 nm) and aluminium (100 nm). For PLEDs containing a CPE EIL, only a 100 nm layer of aluminium was deposited. A shadow mask was used to give six pixels of size 4.5 mm².

For inverted hybrid organic-inorganic light emitting diodes, instead of a PEDOT:PSS hole injecting layer, an EIL of zinc oxide (ZnO) was deposited via sol-gel method onto cleaned ITO substrates.[126] Here, zinc acetate dihydrate and ethanolamine were dissolved into 2-methoxyethanol and made up to 0.5 M solutions. The solution was then ultrasonicated until fully dissolved before being spin coated at 500 rpm for 12 s (wetting step) then 2000 rpm for 30 s. Substrates were then annealed at 450 °C for one hour to form ~ 70 nm thick ZnO thin films. Following this, the LEP was deposited before thermal evaporation of molybdenum oxide powder (MoO₃ – 10 nm) and gold (100 nm).

Single carrier diodes were fabricated using the same methods as LEDs but using different electrode materials to block injection of a particular carrier type. For hole-only devices the device structure used was ITO/PEDOT:PSS/Active layer/MoO₃/Au. For electron-only devices, the device structure used was ITO/ZnO/Active layer/Ca/Al.

Perovskite solar cells were fabricated in an ITO/PEDOT:PSS/Perovskite/PCBM/Ca/Al architecture. After PEDOT:PSS deposition, samples were transferred to a nitrogen filled glove box. Perovskite layers were deposited via spin coating from the precursor solution (described in section 3.1.1) at 3000 rpm for 90 s. After 60 s, 250 µl of toluene was dropped onto the substrate to induce perovskite crystallisation.[127] The samples were then annealed at 100 °C
for 15 minutes before a 40 nm thick layer of PCBM was deposited via spin coating from a 20 mg/ml toluene solution at 2500 rpm for 60 s. A Ca/Al cathode was then evaporated as described above.

3.2 Sample Characterisation

3.2.1 Device Characterisation

PLEDs were characterised at room temperature in a sealed sample chamber under nitrogen, using a computer-controlled Keithley Source Measure unit to apply a bias voltage to the chosen pixel (each substrate accommodated 6 PLED pixels) and to measure the resultant current. A Minolta LS100 spot luminance meter measured the corresponding pixel luminance. The source meter was connected and controlled through a PC with a programme written in LabVIEW. The electroluminescence spectra were recorded using an Ocean Optics USB 2000 CCD spectrometer equipped with a fibre light collection bundle. Accelerated lifetime testing was measured under room temperature in a sealed sample chamber under nitrogen, using a computer-controlled Keithley Source Measure unit to apply a bias voltage to the chosen pixel (each substrate accommodated 6 PLED pixels) and to measure the resultant current. A Minolta LS100 spot luminance meter measured the corresponding pixel luminance.

For electroluminescent transient techniques, the PLED sample was held in the same brass chamber under nitrogen in an airtight seal. The chamber was then connected to a HP 3325B pulse generator which applied a square wave voltage pulse to the device of varying voltages (between 5-9V), with a 1 Hz frequency. The electroluminescent emission from the PLED device was then captured using a Thor Labs PDA36A-EC photodiode. The output from the photodiode, pulse generator and current from the device was measured using a Tektronix DPO2014B digital phosphor oscilloscope and then recorded using Tektronix own software on PC. The average of up to 50 measurements were used to determine the EL transient characteristics of a particular device to lower the noise. The signals were recorded at various time scales from 100 ns to 1 s so the evolution of the EL signal could be accurately resolved over the 0.5 s voltage pulse.

Once the EL transient signal was recorded, time constants could then be extracted. The time constants recorded were the delay time, \( t_d \), and the rise time, \( t_r \) (**Figure 3.1**). The delay time represents the time taken for the for the holes and electrons to meet inside the device and form
excitons, whilst rise time represents the time taken for the minority carrier density to saturate in the recombination zone.\textsuperscript{[128]}

\textbf{Figure 3.1}: Plot showing applied pulse voltage (black) and EL intensity (blue) as a function of time. The distance between the rising edge of the voltage pulse and the rise of the EL signal (shown clearly in inset) represent the delay time, $t_d$, whilst the intersection of the tangent of the rising edge of the EL pulse to the saturation level of the EL represents the rise time, $t_r$. Figure adapted from [129].

Solar cell performance was characterised by measuring the current density-voltage values using a Keithley 2400 source measurement unit. The photocurrent was measured under AM1.5 illumination using a Newport Thermo Oriel 91192 1000W Solar Simulator.

\subsection*{3.2.2 UV-vis Absorption Spectroscopy}

Ultraviolet-visible (UV-vis) absorption spectra were collected using a Shimadzu UV-2550 UV-visible spectrophotometer. The instrument records the transmitted intensity ($T$), however this is converted to an absorbance ($A$) via the Beer-Lambert law

$$A = - \log_{10} \left( \frac{T}{T_0} \right)$$ \hspace{1cm} \text{(3.1)}

where $T_0$ is the transmittance of a blank quartz substrate. Absorbance does not account for any reflection or scattering which could introduce artefacts into the measurement. All spectra were baselined and normalised.

\subsection*{3.2.3 Photoluminescence Spectroscopy and PLQY}

Steady state photoluminescence (PL) spectra were recorded in reflection geometry using a Jobin Yvon Horiba Fluoromax-3 spectrofluorometer. The excitation source used was a 150 W
xenon arc lamp which is passed through a monochromator to excite samples at a specified wavelength $\lambda_{\text{ex}}$ (usually chosen to coincide with the maximum absorption of a sample). The sample fluorescence is then passed through a second monochromator before being collected by a R928P photomultiplier tube. The recorded spectra are first baselined then multiplied by a reference correction file.

For photoluminescence quantum yield (PLQY) measurements, the Fluoromax-3 is equipped with a diffusely reflecting integrating sphere. To determine the PLQY of a sample, three measurements are required with identical experimental parameters (e.g. integration time, excitation wavelength). Firstly, a measurement is taken of the empty sphere (Figure 3.2(a)), followed by a measurement of the sample inside the sphere but outside the path of the excitation beam (Figure 3.2(b)) to correct for self-absorption from the sample. Finally, a measurement is taken whilst the sample is directly in the path of the excitation beam (Figure 3.2(c)).

![Experimental configuration of the integrating sphere setup for PLQY measurements](image)

**Figure 3.2**: Experimental configuration of the integrating sphere setup for PLQY measurements showing (a) measurement of empty sphere, (b) measurement of sample outside beam path and (c) measurement of sample directly in beam path. (d) shows recorded example recorded spectra of empty sphere (black), indirect excitation (red) and direct excitation (blue) with the left panel showing the excitation beam and right showing the sample PL. Sample PL is multiplied by 100 for clarity. Adapted and redrawn from ref. [130].
An example of the three scans is shown in Figure 3.2(d). The PLQY for a given sample can be calculated using the method outlined by DeMello et al.\textsuperscript{[130]} The integrated area under the laser peak is given as $L_A$, $L_B$ and $L_C$ for experimental configuration (a), (b) and (c) respectively. This represents the amount of unabsorbed photons in each experiment, therefore experiments (b) and (c) have progressively smaller laser peaks as more photons are absorbed. From these values, an absorption coefficient, $A$, can be calculated as (see ref.\textsuperscript{[130]} for more information)

$$A = \left(1 - \frac{L_C}{L_B}\right). \quad 3.2$$

The integrated area under the emission spectra represent the number of emitted photons in experiments (b) and (c) and are given as $P_B$ and $P_C$. The PLQY can then be calculated by

$$\eta_{PL} = \frac{P_C - (1 - A)P_B}{L_A A}. \quad 3.3$$

### 3.2.4 Time Resolved Photoluminescence Spectroscopy

Time-correlated single photon counting (TCSPC) spectroscopy is a time dependent PL technique used to measure excited state lifetime in semiconductors. Here, a sample is excited via a pulsed monochromatic light source (in this case a diode laser) and sample emission is passed through a monochromator before being collected at a particular wavelength, $\lambda_{em}$, by a photomultiplier tube detector (PMT).

The TCSPC electronics can be thought of as a stopwatch with two inputs. The pulsed laser diode source acts as a START trigger signal which is sent to a time-to-amplitude converter (TAC). This initiates a linear voltage ramp. Once the PMT detects a photon from the sample PL then a STOP signal is sent to the TAC which stops the voltage ramp. The time between the START and STOP signals is represented by an increase of a memory value in that particular time bin in a histogram. Over millions of cycles, an accurate histogram of counts vs channels represents PL intensity vs time. It is important that intensity is kept low to prevent “photon pile-up” where more than one photon is detected from the sample per excitation pulse.

The PL intensity decays in an exponential fashion over time. Many samples are multi-exponential if more than type of excitonic species is present. For this reason, the PL intensity, $I$, is fitted with the following function

$$I = \sum_i A_i \exp(-t/\tau_i) \quad 3.4$$
with enough exponentials used to achieve a reasonable $\chi^2$ goodness-of-fit value. The value $\tau_i$ is the time decay constant of a particular exponential, and $A_i$ is the relative amplitude of the exponential, with $\sum_i A_i = 1$. The average lifetime of a sample, $\tau_{av}$, is found by

$$\tau_{av} = \sum_i A_i \tau_i. \quad \text{(3.5)}$$

Finally, the radiative and non-radiative decay constants, $k_r$ and $k_{nr}$ respectively, can be found if the PLQY is known from

$$\eta_{PL} = \frac{k_r}{k_r + k_{nr}}. \quad \text{(3.6)}$$

In this work, time-resolved photoluminescence decay measurements used an IBH fluorescence lifetime spectrometer operating in time-correlated single photon counting (TCSPC) mode. The excitation source was a 404 nm pulsed LED operating at 1 MHz rep-rate with a pulse temporal width of 200 ps. IBH Datamax software was used to deconvolve the instrument response function from the data and to fit multi-exponential decay functions.

### 3.2.5 Low Temperature PL Measurements

Samples were inside a helium filled gas cooled closed-cycle cryostat, with spectra recorded at 20 K increments between 10 – 290 K. The cryostat temperature was held constant via for 5 minutes prior to each measurement, enabling the sample to reach thermal equilibrium. The excitation wavelength was 400 nm, produced using a monochromated supercontinuum light source (intensity of 0.13 mW). Emitted light was collected perpendicular to excitation and focused into a 100 $\mu$m diameter optical fibre. An Andor SR-163 spectrometer was then used to disperse the emitted light onto a CCD (Andor i-Dus), with the signal averaged over 100 accumulations of 0.1 s exposure to enhance the signal noise ratio. A dark background was subtracted from all spectra before correcting with a calibration file derived from a known light source to account for detector response. No changes aside from temperature were made to the optical configuration between measurements.

### 3.2.6 Atomic Force Microscopy

Characterisation of sample surface morphology was carried out using atomic force microscopy (AFM). Images were obtained using a Park NX10 atomic force microscope operating in non-contact mode.
3.2.7 Cyclic Voltammetry

For measurement of electronic energy levels of polymers, cyclic voltammetry (CV) measurements were performed. Films were prepared by spin coating onto ITO substrates that acted as the working electrode in a traditional three-electrode setup. A platinum wire was used as the auxiliary electrode and Ag/Ag$^{+}$ as reference electrode. The measurements (scan rate 100 mV/s) were carried out using a 0.1M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) acetonitrile solution for both oxidation and reduction, and recorded using an Autolab PGSTAT101 instrument. For the CV measurements in acetonitrile, the glassware was dried at 100 °C and the cell purged with argon during the measurement to prevent oxygen contamination.

The measurement was calibrated by collecting a CV scan for ferrocene, with its known ionisation potential of 4.8 eV. The corresponding half wave potential ($E_{1/2}$) for Fe/Fe$^+$ was measured to be 0.40 eV in our setup, yielding:

\[ E_{\text{HOMO}} = (E_{\text{ox}} + 4.40 \text{ eV}) \] \hspace{1cm} \text{3.7}
\[ E_{\text{LUMO}} = (E_{\text{red}} + 4.40 \text{ eV}) \] \hspace{1cm} \text{3.8}

where $E_{\text{ox}}$ and $E_{\text{red}}$ are the onset voltages for oxidation and reduction respectively.

3.3 Ambient-Pressure Photoemission Spectroscopy System

The characterisation of mixed-halide perovskite semiconductors has been carried out using a system known as the ambient-pressure photoemission spectroscopy system (APS-04) which has three distinct measurement modes: scanning kelvin probe microscopy (SKPM), surface photovoltage spectroscopy (SPS) and ambient-pressure photoemission spectroscopy (APS). In all three measurements, the same tip is used as a current collector. A diagram of the setup is shown below in Figure 3.3.
Figure 3.3: Schematic diagram of the APS-04 system showing deuterium UV-lamp and monochromator (3.0-7.0 eV) used for APS measurement, quartz-tungsten-halogen (QTH) visible lamp and monochromator (400-1000 nm) used for SPS measurement and Faraday cage containing mounted Kelvin probe mounted on 3-axis stage for scanning capability. Figure adapted from [131].

3.3.1 Scanning Kelvin Probe Microscopy

The scanning kelvin probe microscope (SKPM) is a tool to measure the difference in workfunction, $\Delta \phi$, between a vibrating metallic reference tip and a metal or semiconducting sample. If the metallic tip and sample have dissimilar workfunctions (Figure 3.4(a) for metal samples and (d) for semiconductor samples), a charge will flow from the lower workfunction material to the higher upon electrical contact (Figure 3.4(b) for metals and (e) for semiconductors) resulting in negatively charged high workfunction and positively charged low workfunction surfaces. The potential difference that now exists between them is known as the contact potential difference, $V_c$, and results in an electric field between the samples. Traditional Kelvin probes operate by applying a backing voltage, $V_b$, which is adjusted until a zero or null value is reached.[132] In this case, the flat band condition is restored and the contact potential difference can be determined as $V_b = -V_c$ (Figure 3.4(c) for metals and (f) for semiconductors).
Figure 3.4: Schematic energy level diagrams of the metallic Kelvin probe tip of workfunction $\phi_{KP}$ and a dissimilar metal sample of workfunction $\phi_M$ or semiconductor of $\phi_S$. (a) and (d) show samples not in contact with Kelvin probe, (b) and (e) show samples after electrical contact and (c), (f) show samples with backing voltage applied equal to the contact potential difference.

Such a method is however rather sensitive to noise as the Kelvin probe signal diminishes as $V_b$ approaches $V_c$. The APS-04 Kelvin probe system utilises an ‘off-null’ detection to obtain far more accurate values of $V_c$ to within 1-3 meV. Since the Kelvin probe tip is vibrated above the sample with an angular frequency of $\omega$, a time varying capacitance, $C(t)$, is produced between the tip and the sample which can be represented by:

$$C(t) = \varepsilon_0 \varepsilon_r A / d(t)$$ \hspace{1cm} (3.9)

where $\varepsilon_0$ and $\varepsilon_r$ are the permittivity of free space and the relative permittivity respectively, $A$ is the surface area of the Kelvin probe tip and $d(t)$ is the time varying distance between the Kelvin probe time and sample. The distance between the tip and the sample can be represented as:

$$d(t) = d_0 + d_1 \sin \omega t$$ \hspace{1cm} (3.10)

where $d_0$ is the average distance between tip and sample and $d_1$ is the amplitude of the tip motion, thus substituting into equation 3.9, the capacitance can be represented as:
\[ C(t) = \frac{C_0}{1 + n \sin \omega t} \]  

Here, \( C_0 \) is the average capacitance and \( n \) is the distance modulation index \( (n = d_1/d_0) \). Whilst a backing potential, \( V_b \), is being applied, the instantaneous surface charge located on the Kelvin probe tip is given by \( Q_s = (V_c + V_b)C \). Thus, the tip output current, \( I(t) \), is given as:

\[ I(t) = \frac{dQ_s}{dt} = \frac{d}{dt}(V_b + V_c).C \]  

which solving for peak-to-peak voltage output \( (V_{pp}) \) gives:

\[ V_{pp} = (V_c + V_b).C_0. R_f. \omega. n. \sin \omega t \]  

where \( R_f \) is circuit feedback resistance and \( G \) is amplifier gain. Since equation 3.13 shows \( V_{pp} \) as linear with respect to \( V_b \), a plot of \( V_{pp} \) vs. \( V_b \) will show a straight line intersecting the \( V_b \) axis where \( V_b = -V_c \). Thus, we can measure \( V_{pp} \) at two values (in our case +7 and -7 V) and interpolate the value at which \( V_b = \pm V_c \) [133,134]

This technique is used to measure the Fermi energy level of mixed halide perovskites on ITO and PEDOT:PSS in Chapter 7. The contact potential difference \( (V_c) \) measured by the Kelvin probe is converted to a Fermi level (or workfunction) reading by adding \( V_c \) to the tip workfunction. The tip workfunction is calibrated using a known reference of HoPG (4.65 eV).[135]

### 3.3.2 Surface Photovoltage Spectroscopy

Surface photovoltage spectroscopy (SPS) is well-known contactless method to characterise changes in the surface of a semiconductor induced by photogenerated charges. The technique can reveal information about the nature of bulk, surface and interface properties in semiconductors such as defect/trap states, charge carrier lifetimes and internal electric fields. Being contactless, it can be used to probe semiconductor stacks layer-by-layer rather than requiring a complete device as is the case for transient photovoltage (TPV) techniques.

The surface of inorganic semiconductor thin films often contains surface-localised states caused by dangling bonds (termination of crystal lattice thus surface atoms have no upper atom to bind to), a change in chemical bonding configuration at the surface to minimise energy or by impurities adsorbed on the surface of the semiconductor.[136] These states cause a space
charge region to form at the surface of the semiconductor, as shown in Figure 3.5(a) for a p-type semiconductor.

**Figure 3.5**: Schematic energy level diagram showing a p-type semiconductor with a surface space charge region where (a) no illumination present, (b) SPV generated under super band gap illumination and (c) saturation of SPV under intense illumination.

When light above the energy gap of the material illuminates the semiconductor, the resultant photogenerated charge carriers cause a redistribution of charge at the surface of the semiconductor. In the example shown in Figure 3.5(b), the bands are bent downwards due to depletion of electrons, thus photoelectrons generated in the bulk are transferred to the surface which reduces band bending. The change in surface potential is then defined as the surface photovoltage (SPV), i.e., $V_{SPV} = V_s (\text{light}) - V_s (\text{dark})$. At high illumination intensities, the SPV can become saturated (Figure 3.5(c)) whereby the surface band bending becomes completely flattened. Surface photovoltage spectroscopy (SPS) reveals the dependence of the generated SPV on wavelength and can give information about the variation in the absorption spectra of the semiconductor (at energies about the band gap) or information about defect state transitions within the semiconductor (at energies below band gap).

Whilst the above discussion concerns surface states only, the SPV can be influenced by buried interfaces within the sample, especially in samples containing only a thin semiconductor layer. As discussed in Chapter 2, space charge regions can be generated between metal-semiconductor or semiconductor-semiconductor junctions. In the case of semiconductors with low intrinsic charges, this space charge region can extend through the bulk of the sample, thus photogenerated charge carriers could be swept to the surface based on internal electric fields generated at buried interfaces. Thus, surface photovoltage spectroscopy is sensitive to both surface and buried interfacial states.$^{[137]}$
The APS-04 is equipped with a 150 W Quartz-Tungsten-Halogen (QTH) lamp with a tuneable monochromator that allows the sample to be illuminated with white light or variable wavelength between 400-1000 nm. SPV is detected by the Kelvin probe by adding an additional backing voltage \( V_{SPV} \) to achieve flat band conditions. Measurements can be performed in DC mode (modulated by Kelvin probe tip vibration) or AC mode (modulated via optical chopper). This technique is used to measure the Fermi level of mixed halide perovskites under illumination to determine the band bending within the samples in Chapter 7. The SPV can be measured by altering the intensity of illumination and also by measuring the temporal response of the SPV in response to an illumination. An example of both of these types of measurement is shown below in Figure 3.6.

![Figure 3.6: Example of SPV measurement of perovskite material. (a) shows the variation in SPV with white light illumination intensity and (b) shows temporal response of SPV to 200 W/m^2 intensity white light. Left panel is just after light is turned on and right panel is just after light is turned off.](image)

3.3.3 Ambient-Pressure Photoemission Spectroscopy

Whilst Kelvin probe microscopy can prove a measurement of metal workfunctions relative to a metallic tip, ambient-pressure photoemission spectroscopy (APS) provides a direct way of measuring workfunction (for metals) or valence band/HOMO (for semiconductors). APS has direct advantages over traditional ultra-violet photoelectron spectroscopy (UPS) in that no vacuum is required to measure samples and only a low energy excitation source is used (unlike UPS where >20 eV lasers are used), minimising damage to samples. A schematic energy band diagram of the APS system is shown below in Figure 3.7.
The APS system comprises of a deuterium UV lamp source with a grating monochromator which allows for incident light of energy $3.0 - 7.0$ eV. The UV photons incident on the sample are adsorbed onto the surface, and provided the energy of the incident photons, $E_{ph}$, is larger than the workfunction (for metals) or valence band/HOMO (for semiconductors), electrons are emitted from the surface of the sample. After exciting the sample, and electron cloud is formed $1 - 3$ µm from the surface where they undergo inelastic scattering by atmospheric molecules ($N_2$, $O_2$, $H_2O$). The molecules are then ionised by the photoejected electrons to produce $N_2^-$ and $O_2^-$ ions. The Kelvin probe tip is positively biased, thus the ions drift towards the tip where the ion current is recorded as a function of incident photon energy. Above the threshold energy, the ion current increases proportionally to $(E_{ph} - \phi_M)^{1/2}$ for metals and $(E_{ph} - E_{VB})^{1/3}$ for semiconductors, thus a straight line can be fitted to square or cube root plot of the ion photocurrent against energy. The intersect of the straight line and baseline (where no current is detected) will give the value of workfunction (or valence band for semiconductors). An example is shown below in Figure 3.8.

A relative indication of the trap density of states can be found by integrating the area between the photoemission spectra, baseline and extrapolated straight line fit (blue shaded area in Figure 3.8). The photoemission here is emission from trapped sub band gap electrons and can give an indication of the amount of defects within a semiconductor.
Figure 3.8: Example of photoemission spectra for a mixed halide perovskite sample. The HOMO can be found by extrapolating the linear part of the spectra (blue dashed line) to the baseline of the spectra (orange dashed line). The shaded area indicates trap density of states (TDoS).

This technique is used to measure the HOMO of the mixed halide perovskites in Chapter 7.
Chapter 4: Solution Processed Electron Injection Layers in Polymer Light Emitting Diodes

The work contained in this chapter was carried out in collaboration with Minwon Suh, Jim Bailey and Kyungmok Kim and is in preparation for publication. Kyungmok Kim and Minwon Suh synthesised the conjugated polyelectrolyte materials and zinc oxide nanoparticles. Minwon Suh further aided in recording the atomic force microscopy images.

4.1 Influence of Conjugated Polyelectrolyte Molecular Structure on Electron Injection in Polymer Light Emitting Diodes

4.1.1 Introduction

Conjugated polyelectrolytes (CPEs) are a class of polymers chiefly characterised by a delocalised π-conjugated backbone with tethered pendant ionic groups. The ionic functionality allows CPEs to be dissolved in alcohol- or water-based polar solvents and makes them particularly attractive for use in multilayer organic optoelectronic devices on account of the resulting ‘orthogonality’ to typical organic solvent deposited active layer materials and allowing the realisation of all-printable devices\(^{[75,139,140]}\).

Recently, CPEs have found use as interlayer materials in organic optoelectronic devices.\(^{[75]}\) In particular, thin CPE electron injection layers (EILs) have been found to greatly enhance electron injection from high workfunction electrodes into polymer light-emitting diodes (PLEDs) and improve device efficiency.\(^{[139–146]}\) This allows CPEs to replace traditional low workfunction metals that are both less stable and less environmentally friendly.\(^{[140]}\) The precise mechanism for the enhanced electron injection in CPE based PLEDs is still unclear. One common suggestion is that the mobile counterions in the CPE film undergo long range redistribution under application of a bias which causes an enhancement of the electric field in the device\(^{[144]}\). Another is that the ions in the CPE form a dipole near the CPE/metal interface due to macromolecular reorientation, which lowers the potential barrier and allows for enhanced charge carrier injection\(^{[147]}\). The electric dipole from the ions induces a dipole in the
metal cathode which reduces the cathode workfunction with respect to the vacuum level and allows for easier electron injection. The amount at which the workfunction of the cathode is reduced should be directly related to the strength of the dipole moments induced by the ions of the CPE. CPE interfacial layers have also been used to improve the device performance of organic photovoltaics (OPVs) and organic field effect transistors (OFETs). CPEs can also function as the active layers in light emitting electrochemical cells (LECs) and biosensors.

One of the drawbacks of using CPEs as EILs in PLEDs is rearrangement of the counterions following application of an electric field across the device as this can significantly increase the response times in PLEDs to a few seconds, which is too slow for display purposes where fast switching is required. Previous literature has focused on modifying the size and structure of the counterions, whereby large ions (such as tetrakis(1-imidazolyl)borate (BIm₄) anions) are exchanged for smaller halide ions (such as F⁻ ions) can improve device response due to improved chain packing and faster movement of ions, however response times remain too long. Other methods to improve device response include synthesis of zwitterionic CPEs where both cation and anion groups are tethered to the conjugated backbone. These devices show fast turn-on times of ~10 μs. Thermal treatment and pre-biasing was found to improve response times from 46 s to 200 μs via ‘locking’ of ions.

Modification of the conjugated backbone structure of CPEs remains underexplored. Recently, Suh et al. demonstrated fast responding (<10 μs) and highly efficient PLEDs based on poly(9,9-di-n-octylfluorene-alt-benzothiadiazole) (F8BT) with CPEs containing mobile counterions by inserting benzothiadiazole (BT) units into the otherwise fluorene based conjugated backbone of a CPE. This reduced the electron injection barrier at the F8BT/CPE interface and improved device performance. Interestingly, previous attempts to use CPEs incorporating BT units have led to drastically reduced device performance in non F8BT-based PLEDs, the reason of which is poorly understood.

This chapter reports the effects of varying the π-conjugated structure on electroluminescence (EL) turn-on time and device performance (luminous and luminous power efficiency) are rationalised by examining the CPE/cathode interface and the light emitting polymer (LEP)/CPE interface. Here, we examine the device performance of PLEDs containing three different LEPs; F8BT, an F8BT-TFB random copolymer and MEH-PPV. These LEPs were chosen due to the variation in (i) optical band gap, (ii) HOMO/LUMO level position and (iii)
charge transport properties. This allows the key factors that determine PLED device performance to be identified. For each LEP, a wide band gap, polyfluorene-based CPE and an F8BT based CPE are compared as electron injection layers. By identifying the critical factors that determine EL turn on time and device performance, design rules for a universal CPE that provides both ‘fast’ turn-on times and good device performance are suggested.

4.1.2 Materials Characterisation

In this chapter, PLEDs are fabricated with two different CPE structures (one based on a polyfluorene backbone, the other based on an F8BT backbone) in combination with three different LEP structures. In each case, the PLED is optimised by the inclusion of a thin layer of poly(9,9-dioctylfluorene-co-N-(4-butylphenyl)-diphenylamine) (TFB).

4.1.2.1 Light Emitting Polymers

For each CPE material, three different LEPs are compared. The π-conjugated structure of the LEP causes several factors to change, most importantly in this study (i) the band gap of the polymer, (ii) the position of the HOMO and LUMO levels and (iii) the relative hole and electron mobilities. By altering (i) and (ii), the type of heterojunction formed at the CPE/LEP interface can be modified; the effect of this on device performance will be investigated in this chapter. The relative hole and electron mobilities then determine the location of the recombination zone (RZ) within the LEP device. The chemical structure and energy levels are shown below in Table 4.1.
Table 4.1: Light emitting polymer chemical structures and their hole and electron mobilities.

<table>
<thead>
<tr>
<th>Material</th>
<th>Structure</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>Charge Mobilities (cm²/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F8BT</td>
<td><img src="image" alt="F8BT Structure" /></td>
<td>5.9[160]</td>
<td>3.5[160]</td>
<td>μₑ &gt; μₕ[161,162] (electron dominated)</td>
</tr>
<tr>
<td>F8BT-TFB</td>
<td><img src="image" alt="F8BT-TFB Structure" /></td>
<td>5.5[163]</td>
<td>3.4[163]</td>
<td>μₑ ≈ μₕ[163] (balanced)</td>
</tr>
<tr>
<td>MEH-PPV</td>
<td><img src="image" alt="MEH-PPV Structure" /></td>
<td>5.1[144]</td>
<td>3.0[144]</td>
<td>μₑ &lt; μₕ[32] (hole dominated)</td>
</tr>
</tbody>
</table>

The first LEP examined is F8BT which has a relatively deep HOMO and LUMO (5.9 and 3.5 eV respectively)[160] and a comparatively high electron mobility (also known as electron transporting or n-type polymer), with a measured electron mobility, μₑ, of up to $4.8 \times 10^{-3}$ cm²/Vs[161], whilst the hole mobility, μₕ, of the polymer is has been measured to be in the range of $10^{-8}$-$10^{-6}$ cm²/Vs[162]. This leads to an RZ that is close to the anode at the LEP/interlayer (IL) interface[60]. The optical energy gap of F8BT is 2.4 eV. The UV-vis absorption and PL spectra of F8BT are shown in Figure 4.1. As previously discussed, the localisation of the LUMO on the BT unit causes a ‘charge-transfer’ state to form which is the origin of the low energy absorption band at ~460 nm. The PL similarly shows a broad, featureless emission characteristic of charge transfer states[18].
Secondly, a random copolymer made up of F8BT and TFB units which is referred to as F8BT-TFB copolymer. The TFB contains electron-donating amine moieties which have the effect of shifting the HOMO energy towards vacuum by ~0.4 eV. The LUMO is localised on the BT unit – thus there is little shift in the LUMO energy compared to F8BT. The HOMO electron density however is mostly localised to the arylamine unit. As can be observed from Figure 4.1(a), the optical band gap is slightly blue-shifted for F8BT-TFB compared to F8BT due to the reduction in conjugation length. The PL emission (Figure 4.1(b)) shows only F8BT-like emission due to fast intra molecular energy transfer from TFB units to F8BT units, with a slightly red-shifted emission due to the enhanced charge transfer character. Additionally, the hole and electron currents become more balanced due to the hole transporting nature of the TFB unit. This has the effect of broadening the RZ through the device.

The final polymer which is utilised as an LEP is poly(2’-methoxy-5-2’-ethylhexyloxy)-1,4-pheylenevinylene) (MEH-PPV), which is a red-orange emitting polymer with relatively shallow energy levels of 5.1 and 3.0 eV for the HOMO and LUMO respectively. The UV-vis absorption spectrum (Figure 4.1(a)) shows a broad absorption band at ~490 nm, whilst the PL spectrum (Figure 4.1(b)) shows a vibronic progression with the S1-S0 0-0 transition at ~570 nm. The relative strength of the vibronic peaks are strongly dependent on the morphology of the MEH-PPV layer. As with most PPVs, it is a strongly hole dominated polymer due to the presence of deep electron traps limiting electron transport. This has the effect of shifting the RZ close to the cathode at the LEP/CPE interface. This shift allows the role the LEP/CPE interface plays in device performance to be closely probed.
4.1.2.2 Conjugated polyelectrolytes

The CPE materials used in this study are (poly[(9,9-bis(8″-(3″-methyl-1″-imidazolium)octyl)-2,7-fluorene)-alt-2,7-(9,9-di-octylfluorene)] dibromide (F8im-Br)) – a wide band gap CPE based on polyfluorene and the other based on a fluorene-benzothiadiazole copolymer (poly[(9,9-bis(8″-(3″-methyl-1″-imidazolium)octyl)-2,7-fluorene)-alt-(benzo(2,1,3)thiadiazol-4,8-diyl) dibromide) (F8imBT-Br)). The chemical structures are shown in Figure 4.2. The addition of the imidazolium and bromide groups allow the polymers to be soluble in polar solvents such as 2-methoxyethanol. Including the BT unit varies both the energy gap and LUMO position of the CPE; this allows us to vary the type of interface formed at the LEP/CPE interface (either type I or type II heterojunction).

Figure 4.2: Chemical structures of F8im-Br and F8imBT-Br.

The normalised thin film UV-vis absorption spectra for both F8im-Br and F8imBT-Br are shown below in Figure 4.3.
Figure 4.3: Thin film (20 nm) UV-vis absorption spectra for F8im-Br and F8imBT-Br.

The F8im-Br absorption spectra shows only one broad absorption peak centred at ~404 nm and represents a $\pi$-$\pi^*$ HOMO-LUMO transition with both the HOMO and LUMO delocalised over the fluorene units. The absorption peak represents a red-shift of ~20 nm from the neutral form of F8im-Br (PFO – see chapter 5), possibly indicating the fluorene chains adopt a more planar conformation compared to PFO.

The F8imBT-Br shows a similar absorption profile to F8BT (see Figure 4.1(a)) with a low energy absorption peak centred at ~463 nm, relating to the charge-transfer absorption band that arises from localisation of the LUMO on the BT unit. The higher energy absorption peak centred at ~330 nm relates to transitions from the HOMO to higher energy LUMOs that are delocalised across the polymer chain. In F8imBT-Br, the ratio of the low energy absorption intensity ($I_{463}$) to the high energy absorption intensity ($I_{330}$) is 0.82 – lower than for F8BT (1.03). This indicates the ions could disrupt the degree of localisation of the LUMO on the BT unit, weakening the dipole oscillation strength of the transition.\textsuperscript{[169,170]}

To find the HOMO energy level of the F8im-Br and F8imBT-Br CPEs, air photoemission spectroscopy (APS) measurements were taken and the data shown below in Figure 4.4.
By extrapolating the linear fit of the cube root of the photoemission to baseline, we find the HOMO energy level for F8imBT-Br to be 5.73 ± 0.05 eV, whilst the HOMO of F8im-Br is 5.58 ± 0.05 eV. These values are slightly shallower compared to the commonly accepted HOMO values of F8BT (5.9 eV) and PFO (5.8 eV). By adding the band gap of F8imBT-Br and F8im-Br (2.36 and 2.88 eV respectively) we can find the LUMO of each material to approximately be 3.37 and 2.70 eV. This is summarised in Table 4.2.

Table 4.2: Table showing values of HOMO, band gap and calculated LUMO.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>HOMO (eV)</th>
<th>Band Gap (eV)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F8imBT-Br</td>
<td>5.73</td>
<td>2.36</td>
<td>3.37</td>
</tr>
<tr>
<td>F8im-Br</td>
<td>5.58</td>
<td>2.88</td>
<td>2.70</td>
</tr>
</tbody>
</table>

4.1.3 Polymer Light Emitting Diodes

To show the relationship between the conjugated backbone structure of the CPE and device performance, we fabricate and characterise the JVL and efficiency of PLEDs in a conventional architecture of ITO/PEDOT:PSS/TFB/LEP/CPE/Al where the LEP = F8BT, F8BT-TFB or MEH-PPV and CPE = F8im-Br or F8imBT-Br, along with reference calcium EIL devices for each LEP. Single carrier devices for F8BT-TFB and MEH-PPV were also fabricated containing F8im-Br or F8imBT-Br as EIL/hole blocking layers. The PLEDs are characterised further by recording the transient current density and electroluminescent intensity response to a 1 Hz, 5 V pulse. Figure 4.5(a) shows the device structure whilst (b) shows the schematic energy levels for the material set used in the devices.
4.1.3.1 F8BT based PLEDs

Firstly, F8BT PLED devices were tested with F8imBT-Br, F8im-Br or Ca as EILs. Figure 4.6 shows (a) J-V-L and (b) luminous and luminous power efficiencies for F8BT PLEDs with Ca, F8imBT-Br and F8im-Br EILs. The F8imBT-Br and Ca devices show a sharp increase in current density after 1.8 V (reaching 16.7 and 7.1 mA/cm² at 3.0 V) whilst F8im-Br displays a more gradual increase in current density, reaching only 0.60 mA/cm² at 3.0 V. Consistent with this, the luminance turn-on voltages (defined as the voltage at which the luminance exceeds >1cd/m²) are 2.1, 2.0 and 2.6 V for Ca, F8imBT-Br and F8im-Br EIL F8BT devices respectively. This indicates that whilst electron injection into F8BT from F8imBT-Br and Ca is largely ohmic, electron injection from F8im-Br appears injection limited.
Figure 4.6: (a) J-V-L characteristics for F8BT PLEDs with Ca/Al (black), F8imBT-Br/Al (red) and F8im-Br/Al (blue) cathodes. (b) shows extracted luminous (cd/A) and luminous power (lm/W) efficiencies. (c) shows a plot of luminance versus current density and (d) shows the EL spectra of the devices.

At current densities of 100 mA/cm\(^2\), the luminance values reached for the F8imBT-Br and F8im-Br devices are 12,300 cd/m\(^2\) and 9,800 cd/m\(^2\) respectively. This is likely due to the fact the hole and electron currents are more balanced in the F8imBT-Br device due to improved electron injection especially at lower voltages. This is reflected in the peak luminous and luminous power efficiencies which are 13.2 cd/A, 12.0 lm/W for F8imBT-Br and 12.3 cd/A, 8.1 lm/W for F8im-Br. The lower luminance turn-on voltage for F8imBT-Br greatly enhances the luminous power efficiency of the device. The Ca reference device shows a luminance value of only 7,750 cd/m\(^2\) at 100 mA/cm\(^2\). Both CPE devices display greater efficiencies than the Ca device which has maximum luminous and luminous power efficiencies of 7.9 cd/A and 7.0 lm/W. The Ca metal cathode causes quenching of the luminescence, thus displays lower brightness and efficiencies compared to the CPE devices.\(^{171}\) For F8BT, single carrier devices had already been previously fabricated, showing F8imBT-Br had improved electron injection over F8im-Br, whilst both CPEs were good hole blocking materials.\(^{158}\) Figure 4.6(d) shows the normalised EL spectra of each F8BT device measured at 5 V.
The normalised EL spectra of both CPE devices are the same, showing a slightly enhanced high energy peak at ~555 nm with a low energy shoulder at ~570 nm. The Ca device however shows a slight enhancement in the low energy shoulder, and a broader emission width overall. This is due to the removal of the ~10 nm CPE layer, which causes weak microcavity effects within the device structure and hence can cause constructive/destructive interference for certain wavelengths.\cite{172} No emission from the CPE layers was observed.

To investigate the transient properties of the CPE PLEDs, the luminescence ($L(t)$) and current density ($J(t)$) transients were recorded using the set-up described in section 3.2.1. The input signal used was a 1 Hz, 5 V square wave voltage pulse. The $L$ and $J$ transients for the Ca, F8imBT-Br and F8im-Br devices are shown below in Figure 4.7.
Figure 4.7: (a) normalised current density (top panel) and luminance (bottom panel) transients of F8BT PLEDs with Ca, F8imBT-Br and F8im-Br EILs. (b) shows the voltage pulse used to excite the PLED and (c) shows the unnormalised EL transient signals for each device plotted on a semi-log plot.

The reference Ca devices show the typical square wave response for both J(t) and L(t). The F8im-Br device however shows a slow rise for J(t) and L(t) similarly to previously reported CPE EIL PLED devices. Following an initial ~60% rapid increase in J(t) and L(t) the rise time, t_r, of the luminance transient (see section 3.2.1) is found to be on the order of ~10^5 μs, which is too slow for display applications. The slow rise in J(t) and L(t) can be attributed to mobile ion re-arrangement within the CPE upon application of the electric field to optimise the dipole position created by the ions and hence lower the electron injection barrier at the LEP/Al interface. By contrast, the F8imBT-Br J(t) and L(t) transients show a fast rise time, t_r, of 4.9 μs, with a minor decay in both the L and J signals of ~10%. This decrease is not a result...
of degradation as the signal recovers to its original height in the second voltage pulse. EL transient data of F8BT/F8imBT-Br device taken at 5, 7 and 9 V is shown below in Figure 4.8.

![EL transient data](image)

**Figure 4.8:** Normalised luminance transient of F8BT/F8imBT-Br devices taken at 5, 7 and 9 V, 1 Hz square wave voltage pulses.

Very little change appears to occur when increasing the voltage amplitude from 5 to 9 V. This indicates that there is no increase in EL signal decay (or no irreversible degradation) with voltage for the F8BT/F8imBT-Br device, showing this CPE/LEP is an excellent combination for a high efficiency device. This decay in EL signal could be related to the movement of ions within the CPE layer. To investigate if the F8imBT-Br can be used as a universal CPE for different LEPs, devices using an F8BT-TFB and MEH-PPV LEP were fabricated.

The L(t) and J(t) transients are reminiscent of those found in light emitting electrochemical cells (LECs)\(^{173–175}\). In the case of F8im-Br, both the current density and luminance rise over a time period of \(10^1\) s. Just after the turn-on time (~\(10^6\) s), the PLED operation is dominated by the electron injection barrier from Al to F8im-Br. However, movement of the negative Br\(^-\) ions towards the LEP/CPE interface creates an n-doped region, whilst near the Al/CPE interface, a p-doped region may be induced. This movement of ions occurs over a timescale of \(0.1 - 1\) s. This thins the electron injection barrier and allows enhanced electron injection into the device. In LECs however, this process occurs on a timescale of hours given the much thicker layer (>100 nm) compared to CPE injection layers (<10 nm).\(^{173–175}\)

In summary, F8BT PLEDs have been fabricated with two different CPEs, one based on a PFO backbone (F8im-Br) and one based on F8BT (F8imBT-Br). Whilst both CPE PLEDs showed improved efficiencies compared to the standard Ca PLED, the F8imBT-Br PLED displayed the highest efficiencies (13.2 cd/A, 12.0 lm/W) and a fast (4.9 \(\mu\)s) luminance turn-on time. This is in contrast to F8im-Br device which showed both lower efficiencies (12.3 cd/A, 8.1 lm/W)
and slower turn-on times (~$10^5$ μs). These results show similar values to previously published F8BT devices.\cite{158}

### 4.1.3.2 F8BT-TFB Copolymer PLED Devices

Secondly, F8BT-TFB PLED devices were tested with F8imBT-Br, F8im-Br or Ca as EILs. **Figure 4.9(a)** below shows the J-V-L characteristics of the F8BT-TFB PLEDs containing Ca, F8imBT-Br and F8im-Br EILs, whilst (b) shows the corresponding luminous and luminous power efficiencies.

**Figure 4.9:** (a) J-V-L characteristics for F8BT-TFB PLEDs with Ca/Al (black), F8imBT-Br/Al (red) and F8im-Br/Al (blue) cathodes. (b) shows extracted luminous (cd/A) and luminous power (lm/W) efficiencies. (c) shows a plot of luminance versus current density and (d) shows the EL spectra of the devices.

Both Ca and F8imBT-Br EILs show sharp luminance turn-on voltage at 2.1 V, whilst the F8im-Br CPE has a larger turn on at 2.6 V. As previously shown, Ca forms an ohmic electron injecting contact with F8BT\cite{72} and the correspondence in turn-on voltage thus indicates that electron injection into the F8BT-TFB LEP is also ohmic for both the Ca/Al and F8imBT-Br/Al electrodes, whilst for F8im-Br/Al it is injection barrier limited. Above threshold at 3.0 V, the current density values for Ca, F8imBT-Br and F8im-Br EIL PLEDs are 42.2 mA/cm², 11.7 mA/cm² and 2.6 mA/cm² respectively. The higher current density through the Ca EIL is
attributed to a larger hole leakage current, which is reduced in the CPE-containing devices due to their hole blocking properties.\cite{158} This is consistent with the lower reverse bias current and forward bias current below turn-on (see Figure 4.9(a)) for the CPE containing F8BT-TFB PLEDs. To confirm this, single-carrier devices were fabricated (shown below in Figure 4.10). The electron only devices were fabricated in an ITO/ZnO/F8BT-TFB/CPE/Al structure, whilst the hole only device were fabricated in an ITO/PEDOT:PSS/F8BT-TFB/CPE/Au structure.

![Figure 4.10: J-V measurements for (a) electron only and (b) hole only single carrier F8BT-TFB devices containing no CPE (black), F8imBT-Br (red) and F8im-Br (blue).](image)

The electron current density in electron-only devices is 3.5 times greater for F8imBT-Br than F8im-Br at 4 V forward bias, indicating that the former CPE affords greater electron injection. By contrast, the hole-only devices showed that at 4 V forward bias, the hole current was reduced by a factor of 11 for the F8imBT-Br device relative to Au only devices and by a factor of 75 for F8im-Br hole-only devices (again relative to Au only device) indicating that F8im-Br is even more hole blocking than F8imBT-Br. Given that the hole current is greater than the electron current in the F8BT-TFB devices and the hole blocking nature of the CPEs, it can be
assumed that the recombination zone is located near the LEP/CPE interface in these CPE devices.

At 100 mA/cm$^2$, the F8im-Br F8BT-TFB device produces a luminance of 2180 cd/m$^2$, which is 4.6 times greater than F8imBT-Br device which only shows a corresponding luminance of 480 cd/m$^2$. This gives rise to a greater maximum luminous efficiency of 2.8 cd/A and maximum luminous power efficiency of 1.4 lm/W for F8im-Br F8BT-TFB devices. Interestingly, the current efficiency increases between 2.6 V to 9 V for F8im-Br device, whilst the maximum luminous efficiency for F8imBT-Br is at 3.8 V, but remains relatively constant over the whole voltage range shown (see Figure 4.10(b)) with a maximum of 0.5 cd/A. This indicates that there is better initial charge balance inside the F8imBT-Br PLEDs whereas, in the case of F8im-Br devices, the charge balance increases with voltage due to barrier-limited electron injection. The Ca reference devices are, in turn, like the F8imBT-Br PLEDs, showing good initial charge balance with a luminous efficiency peaked at 1.1 cd/A at 3.8 V that varies relatively little across the 2.4-10 V range and a maximum luminous power efficiency of 1.2 lm/W.

The higher luminous efficiency for F8im-Br than Ca/Al EIL devices can in part be explained by reduced exciton quenching at metal cathode. The Ca/Al cathode is reported to efficiently quench the excitons formed in the LEP layer$^{[171]}$, so by moving the recombination zone away from a metal interface in F8im-Br PLEDs this quenching is expected to be reduced. However, despite the superior electron injection (and hence charge balance) of the F8imBT-Br device, the F8imBT-Br device performance is worse than both the F8im-Br and Ca devices. This indicates that an additional quenching pathway is introduced that quenches more strongly than the metal cathode interfaces. It is possible then that the F8imBT-Br layer itself causes quenching of the luminescence in the F8BT-TFB layer.

Figure 4.9(d) shows the EL spectra of the three device types. Both CPE containing devices show a broad charge-transfer like emission centred at 560 nm, consistent with F8BT-TFB PL spectrum shown in Figure 4.1(b). This indicates that in both device types the EL emission comes predominantly from the LEP layer. In the Ca EIL reference devices, the EL emission is slightly blue shifted, having the same overall spectral shape but peaked at 550 nm; a shift that is most likely due to weak microcavity effects induced by a metal cathode.$^{[176,177]}$

To investigate further the effect of the CPE layer on F8BT-TFB PLED device performance, normalised current density ($J(t)$) and luminance ($L(t)$) transient response curves were measured using again using a constant square wave, 5 V amplitude, 1 Hz repetition rate pulses; these are
shown in Figure 4.11 (a) with the input voltage wave shown in Figure 4.11(b). The L(t) and J(t) signals for the Ca reference device follows closely the square wave voltage input signal. The F8im-Br device shows an initial rapid rise in L(t) and J(t) signals of ~10μs, followed by a more gradual rise of ~0.25 s, typical of CPEs containing mobile ions\cite{5,30}. This is clearly observed in a semi-log plot of the luminance in Figure 4.11 (c). The F8imBT-Br device shows, however, a different L(t) and J(t) response. The latter follows closely the square wave potential with a fast (~10 μs) rise, as seen in the previous F8BT LEP PLED case. The L(t) transient, in contrast, reaches an initial peak after ~100 μs and then decays by 42% over the 0.5 s pulse duration. Since the decay in L(t) for reference F8BT LEP PLEDs with F8imBT-Br/Al as cathode (where the recombination zone is near the anode\cite{73}) is much less, this suggests that the substantial decay here is due to interactions at the LEP/CPE interface. As sequential L(t) response curves are the same (comparing the two transients in Figure 4.11(a) bottom panel), this decay is not due to irreversible degradation.
Additional electroluminescence transients were taken for F8BT-TFB/F8imBT-Br devices for 1 Hz square wave pulses different driving voltages, from 5-8 V and are shown below in Figure 4.12. The data shows an increase that the decay in the EL signal is larger when a larger driving voltage is used. For example, the decay in EL is ~42% when driven at 5 V over the course of 0.5 s, however when driven at 8 V, the reduction in EL signal increases to ~55%, indicating as the relative quenching of the F8BT-TFB luminescence by the F8imBT-Br increases with driving voltage. This could be due to a shift in recombination zone towards the cathode, causing more excitons to be formed near the F8imBT-Br layer and hence a larger fraction is quenched.
over the course of the 0.5 s signal. The shift in recombination zone is likely to be brought about by increased imbalance in the hole and electron currents with increased voltage.

![Figure 4.12: Normalised electroluminescence transients for F8BT-TFB/F8imBT-Br device with 5-8 V, 1 Hz square wave driving potentials.](image)

4.1.3.3 MEH-PPV PLED Devices

To investigate further the effect the energy levels of the LEP and CPE have on device performance, devices were fabricated using MEH-PPV as an LEP layer with F8im-Br, F8imBT-Br and Ca as EILs. MEH-PPV is known to be a strong hole transporting polymer with poor electron transport\(^{[70,165,179]}\), with energy levels of 2.9 eV LUMO and 5.1 eV HOMO\(^{[179]}\) giving an energy gap of 2.2 eV (smaller than F8BT). This will result in the formation of a type II heterojunction at the MEH-PPV/F8imBT-Br interface, and a type I heterojunction at the MEH-PPV/F8im-Br interface. The strong hole transporting nature of MEH-PPV means that the recombination zone will lie close to the MEH-PPV/CPE interface.\(^{[144]}\) Figure 4.13 shows the J-V-L and luminous/luminous power efficiencies of the MEH-PPV devices with Ca, F8imBT-Br and F8im-Br EILs.
Figure 4.13: (a) J-V-L characteristics for MEH-PPV PLEDs with Ca/Al (black), F8imBT-Br/Al (red) and F8im-Br/Al (blue) cathodes. (b) shows extracted luminous (cd/A) and luminous power (lm/W) efficiencies. (c) shows a plot of luminance versus current density and (d) shows the EL spectra of the devices.

Figure 4.13(a) shows the J-V-L characteristics of the MEH-PPV PLEDs. The turn-on voltage for the F8imBT-Br device is 2.5 V whilst for F8im-Br it is 2.6 V. The reference Ca device has a turn-on voltage of 2.4 V. Above the current turn-on threshold, 3.0 V, the current densities for the Ca, F8imBT-Br and F8im-Br EIL devices are 4.05, 14.15 and 1.12 mA/cm², respectively. As observed in the F8BT and F8BT-TFB devices, this indicates that the F8imBT-Br EIL facilitates good electron injection whilst the F8im-Br devices are injection limited. This suggests that the limiting step for electron injection for all devices is from the aluminium cathode into the CPE since the F8im-Br has a shallower LUMO (2.8 eV) than F8imBT-Br (3.4 eV). As for the F8BT-TFB LEP devices above, we also studied single carrier device structures for MEH-PPV PLEDs. Figure 4.13(a) reports data for electron-only devices confirming that F8imBT-Br delivers efficient electron injection into MEH-PPV. Here, the current density at 4 V is six times greater than for F8im-Br devices. Figure 4.13(b) also shows that both F8imBT-Br and F8im-Br have good hole blocking properties due to the offset in their HOMO energies (5.7 and 5.6 eV respectively) relative to MEH-PPV (5.0 eV). Previous poor performance in PPV based devices with an F8BT based CPE has been explained by poor electron injection.
from the CPE into the PPV. Based on this data, this would not appear to be the case in our devices since the electron injection from F8imBT into MEH-PPV appears very efficient.

The MEH-PPV/F8im-Br and MEH-PPV/Ca PLEDs show a rapid increase in luminance after turn-on (see Figure 4.14(a)), reaching 306.5 cd/m² and 261.3 cd/m² at 100 mA/cm² respectively. In contrast, there is a much slower luminance increase for the F8imBT-Br EIL device, reaching only 4.94 cd/m² at 100 mA/cm², 62 times less than for the F8im-Br EIL device. This stark contrast in performance is further emphasised by the EL efficiencies. MEH-PPV/F8im-Br PLEDs have a maximum luminous efficiency of 0.44 cd/A at 7.6 V and a maximum luminous power efficiency of 0.22 lm/W at 5.8 V whilst the F8imBT-Br EIL devices give a maximum luminous efficiency of 0.006 cd/A at 8.8 V and a maximum luminous power efficiency of 0.003 lm/W at 4.0 V. This indicates an increase in active quenching by the F8imBT-Br EIL in MEH-PPV LEP devices relative to F8BT-TFB LEP PLEDs. The F8im-Br
EIL devices are also superior to the MEH-PPV/Ca reference devices, which had a maximum luminous efficiency of 0.39 cd/A and a maximum power efficiency of 0.15 lm/W, supporting the generic benefit of CPE EILs in reducing exciton quenching at the metal electrode interface.

Figure 4.15: (a) Normalised EL spectra for MEH-PPV PLED devices with Ca (black), F8imBT-Br (red) and F8im-Br (blue) EILs and (b) normalised PL spectra for MEH-PPV (black), F8imBT-Br (red) and MEH-PPV/F8imBT-Br bilayer (blue).

**Figure 4.15(a)** shows the peak normalised EL spectra of the MEH-PPV PLEDs with Ca, F8im-Br and F8imBT-Br EILs. The Ca device spectrum displays a main peak at 581 nm and a strong secondary peak at 618 nm, with a FWHM of 100 nm whilst the F8im-Br EL shows a main peak at 581 nm but a much weaker shoulder at 618 nm and an overall narrower emission with a FWHM of 81 nm. Prior literature has reported that the relative intensity of the second peak is sensitive to changes in microstructure and associated interchain interactions. The F8imBT-Br EIL device EL spectrum has an emission onset at shorter wavelength (505 nm), with the main peak blue-shifted to 575 nm and a FWHM of 98 nm. The blue shift of this spectrum indicates the presence of emission from the F8imBT-Br CPE EIL as well as from MEH-PPV and comparison of the PL spectra of MEH-PPV, F8imBT-Br and MEH-PPV/F8imBT-Br bilayer structures (Figure 4.15(b)) support this whereby emission < 530 nm is clearly from the F8imBT-Br. Voltage dependent EL measurements (Figure 4.16) also show that increasing the voltage increases the relative amount of F8imBT-Br emission present in spectra. This will clearly be undesirable for PLED device efficiency since (i) the ions within the CPE will further quench luminance and (ii) there will be an increase in exciton quenching from the Al cathode due to the closer proximity of the excitons.
The time dependent measurements were next performed on the MEH-PPV PLEDs using square wave, 8 V amplitude, 1 Hz repetition rate, electrical pulses. Figures 4.17(a) and (b) show the J(t) and L(t) responses, respectively, for MEH-PPV LEP / Ca, F8im-Br and F8imBT-Br EIL devices. Whilst the L(t) transients for the Ca and F8im-Br devices relatively closely follow their J(t) transients, the F8imBT-Br transients are markedly different. In the latter case J(t) quickly rises and plateaus (in similar vein to J(t) for Ca devices), whereas L(t) rapidly peaks and then falls, yielding a 65% reduction in signal over the pulse duration. As above, this decay does not seem to be associated with a permanent degradation (compare sequential transients in Figure 4.17). Similarly to the previous F8BT and F8BT-TFB devices, the L(t) and J(t) transients show rapid turn-on times for the F8imBT-Br devices (of ~10 µs). Despite the optical band gap of F8imBT-Br now being larger than that of the LEP, the reduction in luminance (and hence device efficiency) is much more pronounced than in the F8BT-TFB case.
In considering the origin of the reduction in EL signal we note that there is expected to be an accumulation of holes at the LEP/CPE EIL interface due to the ≈ 0.6 eV HOMO offset between MEH-PPV and F8imBT-Br. An excess of holes can lead to quenching of light emission from the MEH-PPV LEP\textsuperscript{182} but the HOMO offset is similar for the F8im-Br EIL for which a negligible L(t) decay is observed. Hole-accumulation is unlikely then to be the primary cause. Accumulation of holes combined with trapping of electrons within the F8imBT-Br EIL (evidenced by the CPE emission) may lead to exciton formation within the CPE layer following hole tunnelling. As voltage is increased, F8imBT-Br emission also appears to increase which would support hole tunnelling from the MEH-PPV into the F8imBT-Br layer.
The ionic moieties in CPEs are known to quench luminescence\textsuperscript{[170]} and would be expected to lead to a consequent drop in luminous efficiency for these devices. As with the F8BT and F8BT-TFB devices, additional luminance transient measurements were taken for MEH-PPV/F8imBT-Br devices for driving voltages between 5-9 V (Figure 4.18 (a)). As for the F8BT-TFB case, there is an increase in the decay of the EL transient with increasing voltage, from $\sim$45\% at 5 V to $\sim$70\% at 9 V. This correlates with the increase in F8imBT-Br emission shown in the EL spectra (Figure 4.16). The likely cause of the decay in luminance then is an increase in quenching due to hole tunnelling from the MEH-PPV into the F8imBT-Br layer. This suggests that the formation of a type II heterojunction at the MEH-PPV/F8imBT-Br interface is the primary cause of quenching within the device. The MEH-PPV/F8im-Br interface is of type I type, hence does not cause quenching (Figure 4.18 (b)).

\begin{figure}
\centering
\includegraphics[width=\textwidth]{image}
\caption{(a) Normalised electroluminescence transients for MEH-PPV/F8imBT-Br device with 5-8 V, 1 Hz square wave driving potentials. (b) Schematic energy level diagram showing type I heterojunction of MEH-PPV/F8im-Br and type II heterojunction of MEH-PPV/F8imBT-Br.}
\end{figure}
A summary of the device performance is shown below in Table 4.3.

### Table 4.3: Performance parameters for F8BT, F8BT-TFB and MEH-PPV LEP PLEDs with F8imBT-Br and F8im-Br EILs with results for equivalent Ca cathode devices for comparison.

<table>
<thead>
<tr>
<th>Light Emitting Polymer</th>
<th>Cathode</th>
<th>Turn-on Voltage (V)(^a)</th>
<th>Luminance (cd/m(^2))(^b)</th>
<th>Peak Luminous Efficiency (cd/A)</th>
<th>Peak Power Efficiency (lm/W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F8BT</td>
<td>Ca/Al</td>
<td>2.1</td>
<td>7,450</td>
<td>7.9 @ 4.0 V</td>
<td>7.0 @ 3.2 V</td>
</tr>
<tr>
<td></td>
<td>F8imBT-Br/Al</td>
<td>2.0</td>
<td>13,388</td>
<td>13.2 @ 4.2 V</td>
<td>12.0 @ 3.0 V</td>
</tr>
<tr>
<td></td>
<td>F8im-Br/Al</td>
<td>2.4</td>
<td>11,088</td>
<td>12.3 @ 5.8 V</td>
<td>8.1 @ 3.6 V</td>
</tr>
<tr>
<td>F8BT-TFB</td>
<td>Ca/Al</td>
<td>2.1</td>
<td>1,091</td>
<td>1.1 @ 3.4 V</td>
<td>1.2 @ 2.6 V</td>
</tr>
<tr>
<td></td>
<td>F8imBT-Br/Al</td>
<td>2.1</td>
<td>443</td>
<td>0.5 @ 4.2 V</td>
<td>0.5 @ 2.4 V</td>
</tr>
<tr>
<td></td>
<td>F8im-Br/Al</td>
<td>2.6</td>
<td>2,056</td>
<td>2.5 @ 9.0 V</td>
<td>1.4 @ 3.4 V</td>
</tr>
<tr>
<td>MEH-PPV</td>
<td>Ca/Al</td>
<td>2.4</td>
<td>261.3</td>
<td>0.39 @ 9.0 V</td>
<td>0.15 @ 7.4 V</td>
</tr>
<tr>
<td></td>
<td>F8imBT-Br/Al</td>
<td>2.5</td>
<td>4.94</td>
<td>0.006 @ 8.8 V</td>
<td>0.003 @ 4.0 V</td>
</tr>
<tr>
<td></td>
<td>F8im-Br/Al</td>
<td>2.6</td>
<td>306.5</td>
<td>0.44 @ 7.6 V</td>
<td>0.22 @ 5.8 V</td>
</tr>
</tbody>
</table>

\(^a\) – Voltage required to produce 0.1 cd/m\(^2\) luminance  
\(^b\) – Luminance values taken at 100 mA/cm\(^2\)

#### 4.1.4 Discussion

The difference in F8imBT-Br and F8im-Br device performance across F8BT, F8BT-TFB and MEH-PPV active layer devices can be explained by a combination of the energy level alignment at the LEP/CPE interface and the location of the recombination zone. As previously discussed, F8BT is an n-type copolymer meaning the electron mobility (and hence electron transport) is larger than the hole mobility.\(^{[161,162]}\) This means that the recombination zone of the F8BT PLED will be located at the TFB/F8BT interface rather than the F8BT/CPE interface,\(^{[73]}\) meaning that the effect of any quenching processes that occur near the CPE interface are likely to be significantly reduced. In the case of F8BT and F8imBT-Br however, due to the well aligned energy levels of the two materials no significant quenching is expected to occur.

On the other hand, MEH-PPV is a p-type polymer with very strong hole transport, meaning the recombination zone of MEH-PPV PLED is located near the MEH-PPV/CPE interface.\(^{[144]}\) This means that the interface formed of the MEH-PPV and either F8im-Br and F8imBT-Br needs to be carefully considered. **Figure 4.19** below shows the interfaces formed between MEH-PPV
and F8im-Br (a-c) and MEH-PPV and F8imBT-Br (d-f) as they would be in a PLED device under forward bias.

**Figure 4.19**: Schematic energy level diagrams of MEH-PPV and F8im-Br (a-c) or F8imBT-Br (d-f) under forward bias in a PLED device. (a) and (d) show the interface formed without taking into account ions or hole accumulation. (b) and (e) show with ion redistribution and (c) and (f) take into account hole accumulation.

**Figure 4.19 (a) and (d)** shows the energy level interfaces formed between MEH-PPV and F8im-Br or F8imBT-Br under forward bias without taking into account ion redistribution or hole accumulation, showing a type I heterojunction formed in the case of F8im-Br and type II for F8imBT-Br. **Figures 4.19 (b) and (e)** show the effect of taking the ionic redistribution into
account. Under applied bias, the ionic groups within the CPE will undergo re-arrangement forming an n-type region near the LEP/CPE interface and a p-type region near the CPE/Al interface\footnote{144,183} (similar to the aforementioned case of LECs\cite{173-175}). This causes the voltage to drop only across the ionic regions leaving an intrinsic type region in the middle of the CPE and large band bending to occur at the interfaces of the CPE. Finally, hole accumulation in the MEH-PPV at the MEH-PPV/CPE interface causes the electric field to be screened within the MEH-PPV thus the electric field drops only across the MEH-PPV/CPE and CPE/Al interfaces.

Due to the heterojunctions formed in each case, the F8im-Br device allows the injected electrons to pass freely into the MEH-PPV whereby excitons are formed and radiatively decay. The type I heterojunction formed means the excitons formed in the MEH-PPV do not pass back into the F8im-Br where they are quenched. In the case of F8imBT-Br however, due to the type II heterojunction, non-emissive exciplexes may be formed between the MEH-PPV and F8imBT-Br, resulting in the low luminance and efficiency observed. Some holes tunnel from the MEH-PPV into the F8imBT-Br layer as observed in the EL emission (Figure 4.16) however as the ionic moieties in CPEs are known to quench luminescence\footnote{170}, this too would lead to a consequent drop in luminous efficiency for these devices.

4.1.5 Quantification of Electron Injection Barriers

The Kelvin probe is an effective tool for probing the vacuum level shift at the metal/CPE interface, i.e. how much the workfunction of the Al cathode is shifted by the ionic dipoles of the CPE.\footnote{74,184} To identify the factors yielding fast turn on for F8imBT-Br based CPE devices, kelvin probe measurements were taken for bare Al, Al/F8imBT-Br (10 nm) and Al/F8im-Br (10 nm) samples (Figure 4.20 below).
Figure 4.20: Workfunction measurements of Al, Al/F8im-Br and Al/F8imBT-Br samples.

The workfunction of the bare aluminium was found to be 3.88 eV, similar to the values reported (measured by the Kelvin probe technique in air) in the literature.\textsuperscript{[184]} The workfunction of the Al/F8im-Br sample was measured as 3.41 eV, a reduction in workfunction of 0.47 eV compared to Al. The Al/F8imBT-Br workfunction was measured as 3.50 eV, a reduction of 0.38 eV. Since the LUMO of F8imBT-Br is 3.37 eV, this allows ohmic electron injection to occur from Al to F8imBT-Br (Figure 4.21 (a)) as the barrier to electron injection is then only \(~0.1\) eV. The electron injection from Al to F8im-Br however remains barrier limited (Figure 4.21 (b)). The higher lying LUMO of F8im-Br (2.70 eV) means the electron injection barrier is much larger at \(~0.7\) eV.

![Figure 4.21](image)

Figure 4.21: Schematic energy level diagram showing vacuum energy level shift in (a) Al/F8imBT-Br and (b) Al/F8im-Br. The expected barrier heights ($\phi_b$) are \(~0.1\) eV for Al/F8imBT-Br and \(~0.7\) eV for Al/F8im-Br.

Since electron injection from Al into F8imBT-Br is already ohmic, the re-arrangement of counterions in F8imBT-Br layer upon application of an electric field does not modify the
charge injection properties of the F8imBT-Br containing PLED. Thus, no delayed component of the EL transient is observed in F8imBT-Br PLEDs. By contrast, the electron injection from Al into F8im-Br is injection limited. In an F8im-Br PLED device, the ionic dipoles will align with the electric field to orient themselves perpendicular to the Al cathode. This will modify the workfunction of the Al and further reduce the electron injection barrier from Al into F8im-Br – thus the electron injection in this case does depend on the movement of ions and hence in all F8im-Br devices, a delayed component in the EL and J transients are observed due to rearrangement of the ionic dipoles enhancing electron injection.[185]

4.1.6 Summary

This study reveals new insights into how conjugated polyelectrolytes function as PLED EILs by comparing the performance of two CPE EILs (F8imBT-Br and F8im-Br) with different π-conjugated backbones. Using F8BT as an LEP, F8imBT-Br EIL devices gave the most efficient devices (13.2 cd/A, 12.0 lm/W peak values) compared to F8im-Br (12.3 cd/A, 8.1 lm/W peak values) and Ca (7.9 cd/A, 7.0 lm/W peak values). In this case, the F8imBT-Br EIL luminance transient showed a fast turn on (~10 μs) with only a small (~5%) decay whilst the F8im-Br CPE device shows a slow rise in EL and J signal of ~10^5 μs. Kelvin probe measurements show that this is due deeper LUMO of F8imBT-Br allowing ohmic electron injection into F8imBT-Br from Al.

When using a random F8BT-TFB copolymer as the LEP, the F8imBT-Br CPE PLED device yields lower device efficiency (0.5 cd/A, 0.5 lm/W peak values) than both the F8im-Br CPE (2.8 cd/A, 1.4 lm/W) and Ca (1.1 cd/A, 1.2 lm/W). The transient L(t) response for the F8imBT-Br devices shows a 42% decay in EL over the course of a 0.5 s, 5.0 V square wave pulse whereas no such decay was observed for the corresponding F8im-Br and Ca devices. On changing the LEP to MEH-PPV, an even greater difference in performance is seen. The MEH-PPV/F8imBT-Br PLEDs show drastically reduced peak device efficiencies (0.006 cd/A, 0.003 lm/W) compared to MEH-PPV/F8im-Br PLEDs (0.44 cd/A, 0.22 lm/W) and MEH-PPPV/Ca PLEDs (0.38 cd/A, 0.14 lm/W).

EL transient measurements reveal quenching of the LEP luminescence by F8imBT-Br, possibly due to formation of type II heterojunctions as well as quenching due to ions. This is likely the primary reason for the poor device performance of MEH-PPV and F8BT-TFB based F8imBT-Br PLEDs, as the quenching effect is exacerbated by the location of the recombination.
zone being close to the LEP/CPE interface. This is especially true of the MEH-PPV device, where some F8imBT-Br emission is observed.

Important considerations emerge from these deductions that impact on the design of CPE electron injection materials for PLEDs. The LUMO level of the CPE is responsible for current density and luminance response times of the PLED; the LUMO needs to be deep enough so that ohmic injection is achieved from Al. This is achieved in the case of F8imBT-Br but not for F8im-Br. However, the interface between the LEP and the CPE plays a key role in the device efficiency. The energy gap of the LEP appears not to have an effect on device performance, however the position of the HOMO and LUMO levels do; if a type II heterojunction is formed (as is the case with F8BT-TFB and MEH-PPV with F8imBT-Br) then device performance is drastically reduced compared to if a type I heterojunction is formed. If the LEP has strong hole transporting characteristics (and weak electron transport c.f. MEH-PPV) and the CPE forms a type II heterojunction then the device performance will likely be further reduced as the recombination zone will sit close to the quenching CPE interface. Thus, achieve both fast PLED response times and high device efficiency for all LEPs, the CPE should be designed in a way that it has a deep enough LUMO to provide ohmic electron injection from Al, but shallow enough (and with a wide enough band gap) to form type I heterojunctions with a wide range of LEPs.

4.2 Organic-Inorganic Hybrid Composites as an Electron Injection Layer in Highly Efficient Polymer Light Emitting Diodes

4.2.1 Introduction

Organic-inorganic hybrid light emitting diodes (HyLEDs) have been proposed as a possible solution by making use of air stable metal oxides as charge injection layers which can shield the active layers from oxygen and moisture and thus increase device lifetime without the need for encapsulation\textsuperscript{[186]}. Typically, HyLEDs are fabricated in an inverted architecture with an n-type metal oxide used as an EIL on top of indium tin oxide (ITO) which forms a semi-transparent cathode\textsuperscript{[67,187]}, and a high workfunction top anode. Zinc oxide (ZnO) is a promising candidate due to its solution processability, high transparency and tuneable morphology.
However, drawbacks to using ZnO include the deep conduction band value of 4.2 eV causing a significant electron injection barrier between the zinc oxide and light emitting polymer (LEP) which can significantly limit device performance. To overcome this, thin interfacial layers such as conjugated polyelectrolytes (CPEs) can be used to improve electron injection. However, using CPEs can itself have drawbacks due to long current and electroluminescence (EL) turn-on times on the order of seconds making them unsuitable for display applications. Additionally, the high temperatures (up to 450 °C) used in the fabrication of ZnO layers mean that it is unsuitable to be used in fabricating flexible LEDs. Solutions of colloidal ZnO nanoparticles (NPs) fabricated at room temperature have been used as an alternative EIL in HyLEDs to fabricate flexible devices, though issues remain with poor surface coverage when deposited on ITO due to agglomeration of particles requiring multiple depositions to achieve good performance.

Recently, Kim et al. have demonstrated a composite CPE:ZnO hybridised nanoparticle (NP) material that shows excellent electron injection properties and high performance in conventionally structured PLEDs, showing efficiencies of 11.7 cd/A and 8.6 lm/W with a yellow PPV light emitting polymer. The layer comprised of ZnO NPs blended with an alkoxy side-chain tethered polyfluorene CPE, poly[(9,9-bis((8-(3-methyl-1-imidazolium)octyl)-2,7-fluorene)-alt-(9,9-bis(2-(2-methoxyethoxy)ethyl)-fluorene)] dibromide (F8imFO4-Br). Both the alkoxy side-chains and bromide ions of F8imFO4-Br have been shown to passivate the surface defects of the ZnO NPs by forming coordination bonds with Zn$^{2+}$ ions, and hence allow a uniform blend of CPE and ZnO NP. As CPE contains ionic groups, it is miscible in the same solvent as the ZnO NPs, allowing the blend to be solution processed as well as reducing the electron injection barrier for improved LED performance. As the material can be solution processed as a single layer without need for an annealing step it has great potential as an EIL for high performance flexible HyLEDs.

Here, a novel application of CPE:ZnO hybridised nanoparticles is demonstrated whereby they can be used as an efficient electron injection layer in high performing green emitting F8BT inverted structure LEDs. The composition of the CPE:ZnO composite layer optimised to achieve the best device efficiency. We compare the device characteristics of the CPE:ZnO blend F8BT HyLED device with three other EILs: compact ZnO, ZnO nanoparticles only and a compact ZnO/CPE bilayer. From this, we deduce the CPE:ZnO blend offers several advantages over existing EILs, namely (i) fast (7.12 μs) EL turn-on times compared to using a ZnO/CPE bilayer, (ii) single layer deposition with no high temperature anneal required and (iii)
smoother film surface morphology and improved film quality compared to ZnO NP only layers, leading to higher device efficiencies.

4.2.2 Results and Discussion

To assess the suitability of the CPE:ZnO NP hybrid composite materials as an EIL in an inverted structure HyLEDs were fabricated with CPE:ZnO NP composites as the EILs at different CPE concentrations of 0 (ZnO NP only), 2.25, 4.5 and 9 wt% in an ITO/CPE:ZnO/F8BT/MoO$_3$/Au structure. The average size (diameter) of the bare ZnO NPs are 5.5 nm, whilst the average size of the hybridised CPE:ZnO NP composites are 13.4 nm. Later, we also compare the best performing CPE:ZnO device to a compact ZnO/F8imFO$_4$ bilayer. Figure 4.22(a) shows the device configuration of the inverted HyLEDs with CPE:ZnO as the EIL, and Figure 4.22(b) shows the corresponding energy level diagram. Figure 4.22(c) shows the structure of the CPE:ZnO NPs.

**Figure 4.22:** (a) Schematic view of an inverted HyLED device structure comprising of ITO/CPE:ZnO (30 nm)/F8BT (75 nm)/MoO$_3$ (5 nm)/Au (100 nm). (b) corresponding energy level diagram (in eV). (c) Schematic illustration of CPE:ZnO structure.
Figure 4.23: (a) current density and luminance against voltage (J-V-L) and (b) luminous and luminous power efficiencies for HyLEDs containing CPE(x wt%):ZnO NP EIL layers where x = 0, 2.25, 4.5 and 9 wt%.

Figure 4.23(a) shows the current density-voltage-luminance (J-V-L) characteristics of the CPE:ZnO EIL F8BT HyLEDs with different concentrations of CPE. The ZnO NP only device shows the lowest luminance turn-on voltage (defined as voltage required for >1 cd/m² luminance) of 2.0 V. The low turn-on voltages for ZnO only devices have previously been explained by the preferential injection of holes through MoO₃ into the F8BT, causing hole accumulation at the F8BT/ZnO interface. This in turn generates an internal electric field at the F8BT/ZnO interface and aids the injection of electrons. As the loading of CPE increases, the turn-on voltage increases to 2.2 V for 2.25wt% CPE and to 2.4 V for 4.5 and 9wt% CPE.

The ZnO NP only EIL device shows an initial rapid increase in luminance above the turn-on voltage between 2 - 4 V, however both the current density and luminance begin to saturate more quickly than the CPE:ZnO devices, eventually reaching a luminance of L = 2,257 cd/m² at 10 V. This results in relatively low maximum luminous efficiency (LE) and luminous power efficiency (PE) of LEₘₐₓ = 0.34 cd/A at 4.4 V and 0.30 lm/W at 3.2 V. By contrast, the CPE:ZnO hybrid NP EILs show much larger increase in luminance above turn-on, with the devices reaching luminance levels of L = 19,260 cd/m² for (2.25%)CPE:ZnO, L = 27,780 cd/m² for (4.5%)CPE:ZnO and L = 46,760 cd/m² for (9.0 wt%)CPE:ZnO hybrid NP EIL layers at 10 V.
V. This translates into improved maximum device efficiencies of $\text{LE}_{\text{max}} = 1.14$, $2.49$ and $4.06$ cd/A and $\text{PE}_{\text{max}} = 0.62$, $2.15$ and $3.27$ lm/W for CPE concentrations of $2.25$, $4.5$ and $9$wt% respectively. This passivation reduces the luminescence quenching of the F8BT from the ZnO NPs, indicating that the increased CPE content will increase the passivation and hence device performance. However, it is noted that increasing the loading of CPE beyond $9$wt% would highly likely result in poorer performance due to quenching from the mobile ions within CPE as has been observed previously.\textsuperscript{194}

The origin of this improvement in device efficiency is likely to be twofold. Firstly, the CPE acts as a stabiliser for the ZnO NPs in solution, preventing aggregation of the ZnO NPs.\textsuperscript{194} Previous studies have indicated pristine solution-processed ZnO NP layers can form rough layers with non-uniform surface coverage due to particle aggregation.\textsuperscript{195,196} To test this, the surface morphologies of the layers were investigated by atomic force microscopy (AFM). Figure 4.24 shows the 2D surface morphologies of the ZnO NP and CPE:ZnO composite layers with CPE concentrations of $2.25$, $4.5$ and $9$wt% respectively. The root mean square (rms) roughness values for each layer are shown below in Table 4.4.

Table 4.4: Table showing RMS roughness values of CPE(xwt%):ZnO NPs layers, where x = 0, 2.25, 4.5 and 9 wt%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>RMS Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO NP</td>
<td>7.4</td>
</tr>
<tr>
<td>CPE(2.25wt%):ZnO NPs</td>
<td>5.9</td>
</tr>
<tr>
<td>CPE(4.5wt%):ZnO NPs</td>
<td>5.1</td>
</tr>
<tr>
<td>CPE(9wt%):ZnO NPs</td>
<td>3.1</td>
</tr>
</tbody>
</table>
Figure 4.24: Atomic force microscopy topology images of (a) Pristine ZnO NP, (b) CPE(2.25wt%):ZnO NPs, (c) CPE(4.5wt%):ZnO NPs and (d) CPE(9wt%):ZnO NP layers deposited on ITO.

The pristine ZnO NP layer exhibited a high surface roughness with a root mean square (rms) value of 7.4 nm. The addition of 2.25wt% CPE helped to reduce the roughness and improve the surface morphology, with a rms roughness value of 5.9 nm, whilst 4.5 and 9wt% concentration of CPE helped reduce the roughness further down to 4.1 and 3.1 nm respectively. The 9wt%CPE:ZnO layer thus showed a smooth, dense NP layer. This helps to reduce film defects and increase coverage, facilitating good electron injection and hole blocking in the EIL, which is key to device performance. Indeed, this can be observed from the large leakage current of the ZnO NP only device, which exhibits a two order of magnitude larger current density below turn-on, which can be attributed to the high surface roughness of the film reducing the effectiveness of the EIL in blocking holes, causing poor device performance.
Secondly, Kelvin Probe measurements obtained from pristine ZnO NP samples and CPE(xwt%):ZnO NP samples (Figure 4.25) show the workfunction of the layer decreases as the CPE concentration of the EIL increases. The workfunction of the pristine ZnO NP layer deposited on ITO is 4.73 eV, whilst adding CPE at concentrations of 2.25, 4.5 and 9 wt% shifts the workfunction to values of 4.63, 4.37 and 4.22 eV respectively, leading to a reduction in workfunction of 0.51 eV. This shift in workfunction corresponds to a vacuum level shift allowing for easier electron injection from ZnO into F8BT.\textsuperscript{[149,184,198]} This is due to interfacial dipoles formed between the CPE and the ZnO NPs due to coordinate bonding from the bromide ions and the oxygen atoms in F8imFO\textsubscript{4-}Br to the Zn\textsuperscript{2+} ions in the ZnO NPs.\textsuperscript{[194]} This is illustrated in Figure 4.26.
Figure 4.26: Schematic energy level diagram of the charge injection processes in pristine ZnO NP HyLEDs (left) and composite CPE:ZnO NP HyLEDs (right). The CPE component of CPE:ZnO HyLEDs induces a vacuum level shift.

One key advantage of inducing a vacuum level shift in this manner is that the mobile ions present in the CPE (the bromide ions) are now fixed due to the coordination bonding with ZnO NP. Early HyLEDs containing CPEs used a bilayer of compact zinc oxide (c-ZnO) and CPE deposited on top to aid electron injection via modification of the workfunction of the ZnO layer due to the formation of dipoles at the ZnO/CPE interface.\(^{(188,189,199)}\) The bromide ions are attracted to the ZnO layer whilst repelled by the hydrophobic F8BT layer, forming a negative dipole that shifts the energy levels of the ZnO closer to vacuum.\(^{(188,189,199)}\) As mentioned, c-ZnO/CPE bilayers are undesirable in HyLEDs due to high processing temperatures required for ZnO layer (making it unsuitable for flexible substrates) and long current and electroluminescence turn-on times. To test the performance of best performing 9wt% CPE:ZnO NP blend EIL, c-ZnO and c-ZnO/CPE bilayer EIL F8BT HyLEDs were fabricated. Figure 4.27 compares the J-V-L and efficiency characteristics of devices containing c-ZnO, c-ZnO/F8imFO\(_4\) bilayer and CPE(9wt%):ZnO NP blend layer as the EIL.
Figure 4.27: (a) current density and luminance against voltage (J-V-L) and (b) luminous and luminous power efficiencies for HyLEDs containing pristine c-ZnO, c-ZnO/CPE bilayer and CPE(9wt%):ZnO NP composite EIL layers. (c) Normalised current density (J) and electroluminescence (EL) with accompanying voltage excitation pulse for HyLEDs with different EILs. (d) Magnified plot of normalised current and EL transients.

Similarly to the ZnO NP only device, the c-ZnO device shows a low turn-on voltage of 2.0 V, however shows a slightly higher luminance at 10 V of $L = 6,453 \text{ cd/m}^2$, with maximum efficiencies of $L_{\text{E max}} = 0.52 \text{ cd/A}$ and $P_{\text{E max}} = 0.32 \text{ lm/W}$. Depositing a layer of F8imFO$_4$ CPE on c-ZnO layer to form a ZnO/CPE bilayer EIL increases the luminance produced by the device, with a luminance of 36,900 cd/m$^2$ at 10V. This is likely due to the bromide-Zn and oxygen-Zn coordination bonding passivating the ZnO NPs and reducing quenching from ZnO defects.$^{194,200,201}$ The maximum efficiencies of the bilayer device is $L_{\text{E max}} = 3.8 \text{ cd/A}$ and $P_{\text{E max}} = 3.0 \text{ lm/W}$, showing slightly lower performance than the CPE(9wt%):ZnO NP devices.

Figure 4.27(c) shows the normalised transient response curves for current density (J) and electroluminescent intensity (EL) to a 5 V amplitude 1 Hz repetition rate square wave voltage.
pulses. The current density response of the c-ZnO and ZnO NP devices follow the voltage input signal, whilst the EL trace shows an approximately square wave response, with a minor signal drop (~3%) over the course of the 0.5 s pulse. For the ZnO/F8imFO4 bilayer devices, both the J and EL signals show an initial rapid rise up to ~75% of the final intensity, followed by a slower rise in intensity with a time constant of ~0.2 s. This slow rise in J and EL intensity has previously been observed for CPE devices due to rearrangement of the mobile ions under an applied electric field. Interestingly, the CPE(9wt%):ZnO NP composite device shows the same J and EL transient response as the c-ZnO device despite containing mobile bromide ions from the F8imFO4-Br. The EL and J traces show fast (7.12 µs) rise times. On the other hand, the bilayer device, shows much longer rise times of 0.4 s, unsuitable for display applications. This indicates that in the CPE(9wt%):ZnO NP composite device the mobile bromide ions are now ‘locked’ due to the coordinate bonds the bromide ions form with the ZnO nanoparticles. Similar reductions in rise times were observed in CPEs where thermal treatment under an applied bias allowed the ions to become locked. This shows a further advantage to using the CPE:ZnO NP composite layer as an efficient EIL over the bilayer as the long rise time induced by rearrangement of mobile ions is eliminated. A summary of the device characteristics is shown below in Table 4.5.

**Table 4.5**: Summary of HyLED devices fabricated with pristine ZnO NP, CPE:ZnO NP and ZnO/CPE bilayer EIL layers.

<table>
<thead>
<tr>
<th>EIL</th>
<th>Turn-on (V)</th>
<th>Max. Luminance (cd/m²)</th>
<th>LE$_{\text{max}}$ (cd/A) (@ bias)</th>
<th>PE$_{\text{max}}$ (lm/W) (@ bias)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO NP</td>
<td>2.0</td>
<td>2,257</td>
<td>0.34 (@ 4.4 V)</td>
<td>0.30 (@ 3.2 V)</td>
</tr>
<tr>
<td>CPE(2.25%):ZnO composite</td>
<td>2.2</td>
<td>19,260</td>
<td>1.14 (@ 7.8 V)</td>
<td>0.62 (@ 4.0 V)</td>
</tr>
<tr>
<td>CPE(4.5%):ZnO composite</td>
<td>2.4</td>
<td>27,780</td>
<td>2.49 (@ 5.4 V)</td>
<td>2.15 (@ 3.2 V)</td>
</tr>
<tr>
<td>CPE(9%):ZnO composite</td>
<td>2.4</td>
<td>46,760</td>
<td>4.10 (@ 6.4 V)</td>
<td>3.27 (@ 3.2 V)</td>
</tr>
<tr>
<td>c-ZnO</td>
<td>2.0</td>
<td>6,453</td>
<td>0.52 (@ 7.4 V)</td>
<td>0.32 (@ 4.0 V)</td>
</tr>
<tr>
<td>c-ZnO/CPE bilayer</td>
<td>2.4</td>
<td>36,900</td>
<td>3.82 (@ 7.0 V)</td>
<td>2.96 (@ 3.6 V)</td>
</tr>
</tbody>
</table>
4.2.3 Summary

We have demonstrated a novel use of CPE-hybridised ZnO NPs as an electron injection layer in inverted HyLEDs. We found that 9wt% CPE:ZnO was the optimum fraction of CPE to give best device performance in inverted HyLEDs, due to an improvement in film topology with increasing CPE content, and an increase in vacuum level shift allowing for improved electron injection. The 9wt% CPE:ZnO EIL Hyped device also displayed improved device characteristics compared to a ZnO/CPE bilayer, with both improved device efficiencies and fast turn-on times of ~7.12 µs due to the ‘locked’ nature of the ions within the blend layer.

Importantly, these results show that high performance in HyLEDs can be achieved using a simplified device architecture and facile fabrication process. The CPE:ZnO films can be formed from a one-step solution processed deposition under ambient conditions with no annealing step, making them ideal for high throughput manufacture of flexible HyLEDs. This could be extended to other flexible optoelectronic devices such as organic photovoltaics.

4.3 Conclusion

In this chapter, firstly the effect of varying the π-conjugated backbone structure of CPE (F8im-Br and F8imBT-Br) as electron injection layers in three different PLED devices with different active layers (F8BT, an F8BT-TFB copolymer and MEH-PPV) was studied.

For F8BT devices, F8imBT-Br EIL devices produced the best performing devices with luminous and luminous power efficiencies of 13.2 cd/A and 12.0 lm/W. By contrast, the F8im-Br EIL showed peak luminous efficiencies of 12.3 cd/A and 8.1 lm/W. Both CPE devices however were more efficient than the reference Ca device (7.2 cd/A, 7.0 lm/W) due to a reduction in image-charge induced quenching from the metal cathode. The F8imBT-Br device showed faster luminance and current turn-on times (<10 µs) compared to the F8im-Br device (which showed ~10^5 µs turn-on times). This is due to the reduction in LUMO of the F8imBT-Br to allow for ohmic electron injection from Al into the F8imBT-Br as the energetic barrier is reduced to 0.1 eV. By contrast, the higher lying LUMO of F8im-Br means electron injection from Al is barrier limited due to a larger energy barrier of 0.7 eV.

When using an F8BT-TFB random copolymer or MEH-PPV as the LEP however, the device performance of F8imBT-Br devices drastically decreases. For F8BT-TFB devices, the peak luminous efficiencies of F8imBT-Br devices are 0.5 cd/A, 0.5 lm/W, lower than the
corresponding F8im-Br and Ca devices (2.8 cd/A, 1.4 lm/W and 1.1 cd/A, 1.2 lm/W respectively). MEH-PPV/F8imBT-Br PLEDs show drastically reduced peak device efficiencies (0.006 cd/A, 0.003 lm/W) compared to MEH-PPV/F8im-Br PLEDs (0.44 cd/A, 0.22 lm/W) and MEH-PPPv/Ca PLEDs (0.38 cd/A, 0.14 lm/W). The origin for this reduction in efficiency is an increase in LEP exciton quenching due to the F8imBT-Br. This is confirmed by EL transient measurements showing decay of ~42% at 5 V over 0.5 s; this decay increases with voltage. The increase in quenching is likely due to formation of a type II heterojunction at the LEP/F8imBT-Br interface (when F8BT-TFB and MEH-PPV are used as the LEPs). This quenching is not observed in F8im-Br devices since this CPE forms a type I heterojunction with the LEPs.

This study raises important considerations when designing CPEs for use as electron injection layers in PLEDs. Careful chemical design must be considered so as to (i) position the LUMO deep enough to allow for ohmic electron injection from an Al cathode and hence allow for ‘fast’ (µs) luminance turn-on times and (ii) make sure the LUMO is not so deep as to form a type II heterojunction with the LEP to reduce exciton quenching and hence increase device efficiency.

The second part of this chapter explores using CPE-hybridised ZnO NPs as an EIL in PLEDs with an inverted architecture. The EIL was optimised with respect to the composition of the layer – here 9wt% CPE was found to be the optimum composition to achieve high device efficiencies of 4.1 cd/A and 3.27 lm/W. This was due to improved film quality and an increase in vacuum level shift allowing for improved electron injection. The CPE:ZnO hybrid NP devices showed fast luminance turn-on times of ~7.12 µs due to the ‘locked’ nature of the ions within the blend layer.

Importantly, these results show that superior performance in HyLEDs can be achieved using a simplified device architecture and facile fabrication process. The CPE:ZnO films can be formed from a one-step solution processed deposition under ambient conditions with no annealing step, making them ideal for high throughput manufacture of flexible HyLEDs. This could be extended to other flexible optoelectronic devices such as organic photovoltaics.
Chapter 5: Controlling Molecular Conformation of Fluorene-Amine Copolymers for Highly-Efficient Deep-Blue Light Emitting Diodes

The work contained in this section 5.3 of this chapter was carried out in collaboration with Nathan Chander, Nathan Cheetham and Matthew Dyson and has been published in ACS Applied Materials & Interfaces in 2018 (https://pubs.acs.org/doi/abs/10.1021/acsami.8b00243). Further permissions related to this material should be directed to ACS. Nathan Chander aided in initial conceptualisation. Nathan Cheetham provided additional samples and optical spectroscopy measurements of the 80F8:20BSP copolymer. Matthew Dyson aided in performing low temperature photoluminescence measurements.

5.1 Introduction

Since the discovery of electroluminescence from conjugated polymers in 1989,[3] there has been significant interest in solution processable PLEDs as potential candidates for low cost, energy efficient display and lighting applications. Tremendous efforts have been made to develop deep-blue (usually defined by the electroluminescence (EL) emission having CIE \((x, y)\) coordinates both \(\leq 0.15\))[203] light emitting polymers (LEPs) for use in high-luminance and high-efficiency PLED displays,[204–206] with this requirement essential to achieving the colour gamut needed for high quality display applications. An additional commercialisation challenge is the limited stability of blue fluorescent LEPs,[207] for which the operational device lifetime is relatively short compared to red and green phosphorescence-based polymer emitters; the latter have encapsulated lifetimes of over 100,000 hours.[208] In this chapter, the fabrication of highly efficient, deep-blue and stable PLEDs is demonstrated via a simple conformation change in the conjugated backbone of fluorene-arylamine copolymers. A further application of this conformational change is shown using a series of fluorene-benzothiadiazole copolymers.

Conjugated polymers based on fluorene backbones have been extensively studied as blue OLED emission materials on account of both (i) their wide optical gaps, e.g. \(~3.0\) eV for PFO,[209] that are favourable for deep-blue emission and (ii) their high photoluminescence (PL) quantum yields, e.g. up to 50-60% for glassy phase poly(9,9-di-octylfluorene) (PFO).[210,211] They can, however, suffer from poor operational and colour stability arising from fluorenone
defects, giving rise to ‘green band’ excimer emission at 535 nm. \[^{212-214}\] PFO is an especially well-studied member of the fluorene-homopolymer family and can be prepared with a number of distinct microstructures \[^{35,37}\], namely the glassy-, \[^{35-37}\] crystalline-, \[^{35,37-39}\] liquid-crystalline (LC) \[^{37,45,46,215}\] and chain-segment-extended $\beta$-phases. \[^{29,35,37,40-43}\] The $\beta$-phase has an increased backbone planarity within a fraction of chain segments, with the corresponding torsion angle between adjacent fluorene units $\approx 180^\circ$, resulting in the octyl substituent groups for neighbouring monomers lying on opposite sides of the chain. In contrast, the glassy phase is a disordered phase with a broad distribution of torsion angles between monomers. \[^{35-37}\] The different phases can be identified using both optical absorption and PL spectroscopy measurements. \[^{29,35,43,46,49,51}\]

The $\beta$-phase has attracted much attention due to the action of its extended chain segments as a ‘self-dopant’ \[^{45}\] within an otherwise glassy matrix. These segments constitute the most ordered, lowest energy states and trigger an efficient energy transfer from the surrounding high energy state glassy segments. \[^{35,40,45,49,51}\] The $\beta$-phase chain segments have been shown to act as charge carrier-trapping and exciton formation sites, with the extension in conjugation length reducing the optical gap of PFO by some 0.3 eV. \[^{20,24,27,29-32}\] As a consequence, $\beta$-phase PFO PLEDs have been reported with a nearly two-fold increase in luminous efficiency from 1.0 cd/A to 1.9 cd/A compared to their glassy counterparts. \[^{48,50}\]

The $\beta$-phase of PFO has promise in the field of solid state lasing and nanopatterning, where $\beta$-phase microstructure films have demonstrated amplified spontaneous emission with low threshold energies and high optical gain, thereby demonstrating a route towards electrically pumped organic lasers. \[^{219-221}\] Finally, the $\beta$-phase has been demonstrated to form in a variety of other polyfluorene derivatives such as PODP$\Phi$ \[^{222}\] and PF10, \[^{223}\] as well as copolymers containing PFO units. \[^{224,225}\]

Approaches to high efficiency within simple PLED device architectures require that individual layers be optimised to perform more than one function. In contrast to blending materials with different functionality \[^{226}\], covalently linked copolymers combine functionalities in a way that is resistant to phase separation. As a consequence, state of the art polymer LED emission materials are now invariably complex copolymers featuring emission and electron- and hole-transport moieties with optimized fractional compositions and chain architectures. \[^{227-229}\] The main focus of the work in this chapter is on 9,9-dioctylfluorene (F8):butyl-substituted
phenylenediamine (BSP) copolymers (section 5.2) and in particular the 95% F8:5% BSP, or for short 95F8:5BSP, copolymer. The 100F8 homopolymer PFO and a blend of 90% PFO and 10% poly(9,9-diocetylfluorene-alt-bis-N,N’-(4-butylphenyl)-bis-N,N’-phenyl-1,4-phenylenediamine) (PFB) (with a corresponding volume fraction of 95% F8 and 5% BSP units) labelled 90PFO/10PFB are directly compared to investigate both intra- and inter-molecular energy transfer. Further results are presented for 97F8:3BSP, 90F8:10BSP, 80F8:20BSP and 50F8:50BSP (PFB) copolymers.

Incorporation of BSP and other arylamine moieties into an F8 backbone reduces the ionisation potential from -5.8 eV versus vacuum for PFO to -5.09 eV for PFB.\cite{230–232} At low density (5-10%), BSP acts as hole traps and hence exciton formation sites which can increase PLED efficiency beyond that of conventional PFO devices.\cite{233} The associated optical gap remains large\cite{230,234} but because the emission acquires a more charge-transfer-like character with a broadened spectrum it is no longer suitable to address the display requirement for deep-blue luminescence despite the improvement in efficiency.

The work presented in this chapter looks to combine the electrical benefits of arylamine incorporation in an F8 based polymer with a conformational approach to control the spectral properties of high-efficiency, deep-blue PLEDs by inducing the β-phase conformation within long, uninterrupted F8 chain segments of the 95F8:5BSP copolymer. This allows a significant improvement in CIE (x, y) from (0.149, 0.175) to (0.145, 0.123) and yields peak luminous efficiency, $\eta = 3.60 \text{ cd/A}$ (at 146.5 cd/m²) and luminous power efficiency, $\eta_w = 2.44 \text{ lm/W}$ (at 10.8 cd/m²). A detailed study of the photophysics allows the mechanism of the improvement in spectral properties to be elucidated.

5.2 Materials and Methods

5.2.1 Fluorene-Arylamine Copolymers

The (100-x)F8:xBSP copolymers discussed in this chapter were supplied by Cambridge Display Technology Ltd. The fraction of BSP incorporation was varied from x = 0, 3, 5, 10, 20 and 50. The chemical structure of the copolymers is shown in Figure 5.1.
Figure 5.1: Chemical structure of 9,9-dioctylfluorene:butyl substituted phenylenediamine (F8:BSP) copolymers \( (x = 0, 3, 5, 10 \text{ and } 20 \text{ for 100 F8 (PFO) 97F8:3BSP, 95F8:5BSP, 90F8:10BSP, 80F8:20BSP and } x = 0.5 \text{ for 50F8:50BSP or PFB})\).

All \((100-x)\text{F}8:xB\text{BSP}\) polymers were synthesized via Suzuki coupling, with the fraction \(x\) controlled by the monomer composition of the reaction mixture. This comprised 50\% boronic ester disubstituted F8, \((50-x)\%\) bromine disubstituted F8 and \(x\%\) bromine disubstituted BSP. The coupling process links carbon atoms with a boronic ester substituent to carbon atoms with a bromine substituent and thus creates F8-F8 and F8-BSP linkages but not BSP-BSP linkages. The chain formation process is statistical in nature, dependent on BSP monomer concentration. The low fraction of BSP monomer units in the reaction mixture then ensures that the copolymer will contain long sequences of F8 units, interrupted only by sparsely distributed BSP units.

5.2.2 Experimental Methods

Optical spectroscopy was undertaken on ~60 nm thickness PFO homopolymer, F8:BSP copolymer and polymer/polymer blend films spin-coated from toluene solution (10 mg/ml) onto quartz substrates. UV-vis absorption, photoluminescence and TCSPC measurements were carried out as described in Chapter 3.

The PLED device architecture consists of a multilayer stack comprising ITO/PEDOT:PSS/TFB/EML/LiF/Ca/Al. ITO anode structures on glass substrates (size 12 mm x 8 mm) were cleaned for 15 minutes each in a sequence of ultrasonic baths using acetone, isopropanol and detergent (Hellmanex III, 2\% by volume in DI water). This was followed by oxygen plasma ashing in an Emitech K1050X. Next, a 35nm thickness film of PEDOT:PSS (Clevios P VP) was deposited as hole injecting layer by spin-coating at 3000 rpm and annealing in air for 15min at 135 °C. This was followed by spin-coating (at 1000 rpm) a 15 nm thickness electron-blocking TFB interlayer from 2 mg/ml toluene solution, and then baking in nitrogen at 180 °C for one hour. The 95F8:5BSP EML (60 nm thickness) was deposited on top of the TFB interlayer, again by spin coating, at 2500 rpm from a 10 mg/ml toluene solution. For the
90PFO/10PFB blend EML, PFO and PFB toluene solutions were separately prepared and mixed to give the desired weight ratio before spin-coating (2500 rpm) to a thickness of 60 nm. Finally, for PFO EML samples, toluene solutions were spin-coated (2500 rpm) to a thickness of 60 nm. To induce β-phase chain segments in the EMLs, each sample was solvent vapor annealed in a toluene atmosphere at 50 °C for 2 hours. An MBraun thermal evaporator was used to deposit the top cathode comprising a triple layer of LiF (2 nm), calcium (30 nm) and aluminium (100 nm). PLED characterisation was carried out as described in Chapter 3.

5.3 Controlling Molecular Conformation of F8:BSP Copolymers

5.3.1 Electrochemical Determination of HOMO/LUMO Levels

For reference in the discussion of energy transfer processes occurring in the PFO homopolymer, 95F8:5BSP copolymer and 90PFO/10PFB blend films, the HOMO and LUMO levels of PFO, 95F8:5BSP and PFB were determined using cyclic voltammetry (CV). The cyclic voltammograms are shown below in Figure 5.2, whilst the oxidation and reduction potentials together with the HOMO and LUMO energy levels are shown in Table 5.1.
Figure 5.2: Cyclic voltammograms for thin film samples of (a) PFO, (b) 95F8:5BSP and (c) PFB recorded in TBAPF₆ acetonitrile solution.

Table 5.1: Table showing values of oxidation onset energy, reduction onset energy and estimated HOMO and LUMO energies for PFO, 95F8:5BSP and PFB.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>E_{ox} (eV)</th>
<th>E_{red} (eV)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFO</td>
<td>1.40</td>
<td>-2.30</td>
<td>5.80</td>
<td>2.10</td>
</tr>
<tr>
<td>95F8:5BSP</td>
<td>1.09</td>
<td>-2.30</td>
<td>5.49</td>
<td>2.10</td>
</tr>
<tr>
<td>PFB</td>
<td>0.65</td>
<td>-2.40</td>
<td>5.05</td>
<td>2.00</td>
</tr>
</tbody>
</table>

For PFO, the HOMO level was found to be 5.80 eV and the LUMO 2.10 eV, consistent with previous reports.[232] For 95F8:5BSP a small oxidation peak is observed at ~ 0.3 V below the main F8 oxidation peak. This can be assigned to preferential oxidation of BSP moieties confirming HOMO localization at these sites. For PFB, the greater electron density causes a larger shift in the oxidation peaks of the polymer, thus the BSP oxidation peak (HOMO) is measured to be 5.05 eV, again consistent with previous reports.[230] The delocalisation of the
LUMO means it is less affected by the BSP unit, thus it is measured to be 2.10 eV for the 95F8:5BSP copolymer and 2.00 eV for PFB.

5.3.2 Effect of Molecular Conformation Change on Optical Properties

Optical absorption spectra for PFO, 95F8:5BSP copolymer and 90F8/10PFB blend films on spectrosil substrates are shown in Figures 5.3(a), (b), and (c), respectively, before and after solvent treatment to generate F8 \( \beta \)-phase chain segments. The glassy-phase spectra of the 95F8:5BSP copolymer (Figure 5.3(b)) and 90F8/10PFB blend (Figure 5.3(c)) films closely resemble that of PFO with the main \( \pi-\pi^* \) absorption peak located at \( \sim 384 \) nm. After solvent vapor annealing (SVA) with toluene, the characteristic \( \beta \)-phase absorption peak at 433 nm was observed for all three samples, including the copolymer. This confirms that the BSP moieties within the copolymer backbone do not prevent \( \beta \)-phase chain segment formation. The small BSP fraction (5 wt%) ensures that there are sufficiently long F8 segments within which the \( \beta \)-phase can form; oligofluorenes with as few as five 9,9-dioctylfluorene repeat units are reported to show \( \beta \)-phase spectral features.\(^{[235]}\)
Figure 5.3: Peak normalized optical absorption (solid) and PL emission (dashed) spectra for (a) PFO, (b) 95F8:5BSP copolymer and (c) 90PFO/10PFB blend films spin coated on spectrosil substrates. Glassy phase data are shown with black lines whilst β-phase data are shown with red lines. PL emission spectra were excited at λ ex = 385 nm.

The absorption spectra of the homopolymer (PFO), copolymer (95F8:5BSP) and blend (90PFO/10PFB) films can be described as a superposition of the absorption of disordered glassy-phase (broad peak centred at ≈ 385 nm) and well-ordered β-phase (resolved vibronic band with S0-S1 0-0 peak at ≈ 435 nm) chain segments. To estimate the fraction of β-phase chain segments in each film, the appropriate reference ‘purely-glassy’ absorption spectrum (blue dashed line in Figure 5.4) is fitted at 3.55 eV where there is negligible β-phase segment absorption.[40] The normalised glassy spectrum is then subtracted from the film spectrum and the residual corresponds to the β-phase chain segment absorption (red dashed line). The fraction of β-phase segments in the film can then be estimated from the ratio of the integrated
absorption areas after taking into account the enhanced oscillator strength for β-phase segments (a factor of 1.08).

$$\beta\text{-phase fraction (\%)} = \frac{\Delta A}{\Delta A + \{(A_{\text{total}} - \Delta A) \times 1.08\}} \times 100$$

In the examples shown in Figure 5.4 the estimated fraction of β-phase chain segments is 10, 5 and 12%.

![Image](image.png)

**Figure 5.4:** Normalised absorption spectra of homopolymer PFO, copolymer 95F8:5BSP and blend 90PFO/10PFB β-phase films (black solid line). In each case, a ‘purely-glassy’ film spectrum (blue dashed lines) is overlaid. The difference spectra correspond to the β-phase segment absorptions (red).

A higher fraction of β-phase chain segments is formed in films of the PFO homopolymer (10%) and 90PFO/10PFB blend (12%) than of the 95F8:5BSP copolymer (5%). The β-phase fraction in the homopolymer is broadly consistent with previous results in the literature.[40,220] The 50F8:50BSP alternating copolymer (PFB) does not have any extended sequences of F8 units in which the β-phase can form and hence in the blend only the PFO chains support β-phase segments. Bulky BSP moieties disrupt close chain packing, leading to a more disordered glassy microstructure for PFB with no observed crystallization on thermal annealing,[230],[234] therefore it is not surprising that the 95F8:5BSP copolymer has a smaller fraction of β-phase chain segments formed during SVA than PFO. In the case of the blend films, the 10% fraction of PFB chains (with 50% BSP content) will not support β-phase segment formation so one might expect a proportionate reduction in overall β-phase fraction relative to PFO. This is not seen; most likely as a result of an increase in free volume that compensates by facilitating conformation change in the PFO chains.
The PL emission spectra for each of the three film types are shown in Figures 5.3(a), (b) and (c) before and after solvent treatment to generate F8 β-phase chain segments. All spectra were excited at $\lambda_{\text{ex}} = 385$ nm. The glassy homopolymer PFO film spectrum in Figure 5.3(a) is consistent with literature reports, with $S_1-S_0$ 0-0 and 0-1 vibronic peaks at 421 nm and 447 nm, respectively.\textsuperscript{[35,42,43,49,51]} The glassy 95F8:5BSP copolymer film shows a red-shifted, broad, asymmetric (with long wavelength tail), and largely featureless PL spectrum, which is very similar (but slightly red shifted (455 nm peak) and broadened) to that of the PFB component (450 nm peak) in the blend film. The 95F8:5BSP copolymer film spectrum doesn’t reveal an obviously PFO-like (F8-localised) component indicating efficient energy transfer from locally excited F8 excitons to BSP centered excitons.\textsuperscript{[236]}

Despite both having the same volume fraction of F8 and BSP units, the glassy phase 90PFO/10PFB blend film PL spectrum contains emission components from both PFO (evidenced by the shoulder at 425 nm) and PFB (main peak at 450 nm) polymer chains, whereas the 95F8:5BSP copolymer seemingly does not. This indicates that energy transfer from majority F8- to minority BSP-centered sites is less efficient in the blend (PFO to PFB inter-chain transfer) than found in the copolymer (for combined inter- and intra-chain transfer); blend microstructure will clearly also play a role in this.

The excited states responsible for the glassy copolymer PL have been shown to have significant charge transfer (CT) character\textsuperscript{[236]} as observed for PFB and poly(9,9-dioctylfluorene-co-N-(4-butylphenyl)diphenylamine) (TFB).\textsuperscript{[237]} The dilute solution PL spectra of PFO homopolymer, PFB and 95F8:5BSP for solvents of different polarity (toluene, THF and dichlorobenzene) are shown below in Figure 5.5.

![Figure 5.5: PL spectra of PFO, PFB and 95F8:5BSP in dilute Toluene, THF and Dichlorobenzene solutions.](image-url)
The PFO PL shows little change with solvent polarity, whilst for PFB there is a large red shift and broadening with increasing polarity, strongly indicative of CT character. For 95F8:5BSP the emission comprises both vibronically-structured F8 and broadband BSP related contributions with the former experiencing no solvatochromic shift whilst the latter red-shifts and broadens, confirming a coexistence of both bound neutral exciton and CT emission states. The CT character originates from a differential spatial partitioning of the HOMO and LUMO wavefunctions across the BSP and F8 units, leading to a displacement in associated hole and electron charge densities.[236]

The PL spectra are significantly altered by the generation of β-phase chain segments. All three film-types then display well-resolved vibronic structure with a close match of the blend and copolymer PL spectral features to those of PFO; the characteristic β-phase vibronic peaks appear at 437, 465 and 498 nm. However, differences do exist, with the vibronic peaks best resolved for PFO, less so for the blend and least for the copolymer. In addition, the apparent strength of the S1-S0 0-1 and 0-2 vibronic peaks relative to the 0-0 is greater for the 90PFO/10PFB blend than PFO and greatest for the 95F8:5BSP copolymer, consistent with the blend and copolymer spectra comprising a superposition of β-phase PFO-like structured excitonic emission and residual PFB-like broadband CT emission. Separation of the 95F8:5BSP copolymer and 90PFO/10PFB blend spectra in this way (Figure 5.6) reveals that 62% of the copolymer emission is β-phase structured emission whilst 38% is residual PFB-like emission. The 90PFO/10PFB blend shows 82% β-phase emission and 18% residual PFB emission.
Figure 5.6: Deconvolution of PL spectra for 95F8:5BSP copolymer β-phase sample (top panel—open circles) and 90PFO/10PFB blend β-phase sample (bottom panel—open circles). The red dashed line shows residual PFB-like CT emission whilst the blue dashed line shows the vibronic β-phase emission. The solid black line shows the combined sum of residual CT and β-phase emissions. The fractional contribution from each component was deduced by integration (shaded area) over their deconvoluted spectra. For the copolymer, the β-phase fraction accounted for 62% of total emission whilst for the blend, β-phase PFO emission accounted for 82% of the total spectra.

UV-vis absorption and photoluminescence spectroscopy measurements were also taken for 97F8:3BSP, 90F8:10BSP, 80F8:20BSP and 50F8:50BSP (PFB) copolymers which are shown below in Figure 5.7. Here, one can observe that β-phase segment formation still occurs (to a lesser degree) for 90F8:10BSP and (marginally) 80F8:20BSP copolymer films compared to 95F8:5BSP, however 97F8:3BSP unsurprisingly shows a slightly greater amount of β-phase formation. The PFB copolymer shows no evidence of β-phase formation under solvent anneal.
Figure 5.7: UV-vis absorption (left column) and PL spectra (right column) for pre- (black line) and post- (red line) solvent-vapour-annealed copolymer films of 97F8:3BSP ((a) and (b)), 90F8:10BSP ((c) and (d)), 80F8:20BSP ((e) and (f)) and 50F8:50BSP (PFB) ((g) and (h)).
The relative fractions of β-phase segments formed, and β-phase emission is shown below in Table 5.2.

Table 5.2: Estimated β-phase fractions and β-phase PL contributions in film samples of PFO, 97F8:3BSP, 95F8:5BSP, 90PFO/10PFB blend, 90F8:10BSP copolymer, 80F8:20BSP and PFB.

<table>
<thead>
<tr>
<th>Film type</th>
<th>β-phase fraction</th>
<th>β–phase PL contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFO</td>
<td>10% ± 2%</td>
<td>100%</td>
</tr>
<tr>
<td>97F8:3BSP</td>
<td>6% ± 1%</td>
<td>69%</td>
</tr>
<tr>
<td>95F8:5BSP copolymer</td>
<td>5% ± 1%</td>
<td>62%</td>
</tr>
<tr>
<td>90PFO/10PFB blend</td>
<td>12% ± 2%</td>
<td>82%</td>
</tr>
<tr>
<td>90F8:10BSP copolymer</td>
<td>3% ± 1%</td>
<td>46%</td>
</tr>
<tr>
<td>80F8:20BSP</td>
<td>0.2% ± 0.1%</td>
<td>8%</td>
</tr>
<tr>
<td>PFB (50F8:50BSP)</td>
<td>0%</td>
<td>0%</td>
</tr>
</tbody>
</table>

Efficient energy transfer from high energy glassy to low energy β-phase segments in PFO has been extensively studied, with only a few % of β-phase segments needed for dominant β-phase emission.[35,43,49] Intriguingly, similar behavior is observed here with the presence of β-phase segments in the copolymer and blend films leading to a strong promotion of structured vibronic emission. This is despite the fact that as a consequence there is a net increase in mean PL emission energy relative to the glassy film spectra (with dominant CT-like emission); this can be explained by the very small Stokes shift (1 ~ 5nm) for β-phase segments. β-phase PL spectral components are also evident in the SVA 97F8:3BSP, 90F8:10BSP and 80F8:20BSP copolymer films but not for PFB (50F8:50BSP alternating copolymer) (Figure S2). As the fraction of BSP units increases, the fraction of β-phase segments formed after SVA decreases (Table S1), resulting in larger residual fractions of PFB-like emission. Radiative decay times for the competing emissive species are likely to be important in this context.

5.3.3 Excitonic Species within PFO, 95F8:5BSP and 90PFO/10PFB Films

To further characterize the emissive species contributing to the PL spectra, time correlated single photon counting (TCSPC) measurements were used to record PL decay transients under 404 nm excitation and collected at wavelength ranges between 420 – 540 nm to cover the
majority of the emissive spectra for glassy and β-phase samples of PFO, 95F8:5BSP and 90PFO/10PFB blend samples. The transients are shown below in Figure 5.8.

Figure 5.8: Thin film TCSPC decay curves ($\lambda_{ex} = 404$ nm) collected for the glassy- (left column) and β-phase (right column) microstructures of PFO ((a) and (b)), 95F8:5BSP ((c) and (d)) and 90PFO/10PFB ((e) and (f)). The dashed line is the instrument response function (IRF) and the decay curves from top to bottom run from long to short wavelengths (see legends for wavelength values in nm).

A multi-exponential decay model was used to fit each PL transient of the form

$$\sum_i A_i \exp \left(-t/\tau_i \right)$$

The average decay time is found as the weighted sum of the fitted lifetimes

$$\tau_{av} = \sum_i A_i \tau_i$$

The fitted transients taken at 460 nm are shown in Figure 5.9 and Table 5.3.
To aid in the assignment of the photoexcited states, additional TCSPC measurements were taken of dilute toluene solutions of PFO, 95F8:5BSP and PFB as well as a thin film sample of PFB (Figure 5.10).

![Figure 5.9: PL decay transients collected at 460 nm for (a) glassy- and (b) β-phase films of, from top to bottom, 95F8:5BSP copolymer (red), 90PFO/10PFB blend (blue) and PFO homopolymer (black). The measured instrument response function (IRF) is also shown (dashed grey line).](image)

**Table 5.3:** Decay times and percentage amplitudes obtained by fitting the transient PL data presented in Figure 3 to a multi-exponential decay model. The $\chi^2$ values are indicative of the fit-quality. Photoluminescence quantum efficiency (PLQE) values are also included.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\tau_1$ (ns):($A_1$)</th>
<th>$\tau_2$ (ns):($A_2$)</th>
<th>$\tau_3$ (ns):($A_3$)</th>
<th>$\tau_{av}$ (ns)</th>
<th>$\chi^2$</th>
<th>PLQE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFO Glassy</td>
<td>0.314:(97%)</td>
<td>1.34:(3%)</td>
<td>-</td>
<td>0.35</td>
<td>1.21</td>
<td>35 ± 5</td>
</tr>
<tr>
<td>PFO β-phase</td>
<td>0.270:(98%)</td>
<td>1.15:(2%)</td>
<td>-</td>
<td>0.29</td>
<td>1.13</td>
<td>35 ± 5</td>
</tr>
<tr>
<td>95F8:5BSP Glassy</td>
<td>0.580:(43%)</td>
<td>2.18:(45%)</td>
<td>11.9:(12%)</td>
<td>2.66</td>
<td>1.07</td>
<td>45 ± 5</td>
</tr>
<tr>
<td>95F8:5BSP β-phase</td>
<td>0.319:(56%)</td>
<td>1.32:(35%)</td>
<td>7.43:(9%)</td>
<td>1.31</td>
<td>0.89</td>
<td>40 ± 5</td>
</tr>
<tr>
<td>90PFO/10PFB Glassy</td>
<td>0.295:(64%)</td>
<td>1.48:(27%)</td>
<td>8.2:(9%)</td>
<td>1.33</td>
<td>0.92</td>
<td>20 ± 5</td>
</tr>
<tr>
<td>90PFO/10PFB β-phase</td>
<td>0.247:(97%)</td>
<td>1.93:(3%)</td>
<td>-</td>
<td>0.30</td>
<td>1.05</td>
<td>25 ± 5</td>
</tr>
</tbody>
</table>
Figure 5.10: TCSPC decay curves for (a) PFO, (b) 95F8:5BSP and (c) PFB in dilute (0.05 mg/ml) toluene solution. The homopolymer and alternating copolymer show single exponential decays whilst the sparse copolymer has more complex kinetics consistent with its two-component (PFO-like vibronic plus PFB-like CT) PL emission spectrum. (d) shows thin film TCSPC decay curves for PFB.

The glassy PFO films yield a predominantly fast neutral singlet exciton decay with ~ 314 ps time constant, in agreement with decay times reported previously for this microstructure (~300 - 400 ps). A minor (~ 3%) fraction of longer-lived (~1.34 ns) PL is also observed, attributed to inter-chain/segment states, including non-geminate pairs and fluorenone-defect-based excimers (yielding ‘green-band’ emission) (Figure 5.8(a)). Consistent with this assignment, the PFO decay transients for dilute solutions are mono-exponential at all detection wavelengths, with ~ 356 ps decay time (Figure 5.10(a)). For PFO β−phase film samples, the 460 nm decay times reduce marginally to ~270 ps and ~1.15 ns, which (given no PLQE decrease (Table 2)) points to an increase in transition dipole moment, consistent with the known increase in conjugation length.

The PL transients of the 95F8:5BSP copolymer in dilute solution (Figure 5.10(b)) show a bi-exponential decay at shorter wavelengths (420 and 440 nm), attributed to combined PFO-like excitonic emission (with τ₁ ~ 140 ps) and PFB-like CT emission (with τ₂ ~ 1.4 ns). At longer wavelengths, beyond 460 nm, a mono-exponential decay with τ ≈ 1.4 ns is observed, identical to the dilute solution decay for PFB (Figure 5.10(c)). In the case of glassy 95F8:5BSP
copolymers films the overall decay at 460 nm can be described by three components with $\tau_1 \sim 580$ ps (43%), $\tau_2 \sim 2.18$ ns (45%) and $\tau_3 \sim 11.9$ ns (12%), each attributable to CT emission. The average lifetime is then $\tau_{av} \sim 2.66$ ns. These time constants all differ from the solution CT-state decay, consistent with the influence of heterogeneity in solid-state packing and inter-chain/segment interactions, as also reported in previous studies of fluorene-amine copolymers.[236,243,244] The decay times vary substantially with emission wavelength (Figure 5.8(c)), again suggesting a distribution of CT lifetimes within the copolymer. Interestingly, the longest-time constant ($\tau_3 \sim 11.9$ ns) decay is not observed in PFB (50F8:50BSP alternating copolymer) (Figure 5.10(d)) and its observation here then points to a potentially more substantial spatial separation of electron and hole wavefunctions in glassy 95F8:5BSP. One possibility would be inter-chain excitations formed between high electron affinity F8 units in one chain and low ionization potential BSP units in a neighboring chain. However, as no distinct exciplex peak is seen in either PL or EL this remains speculative.

The spectral changes that occur when β-phase chain segments are induced in 95F8:5BSP copolymer films are accompanied by a strong change in 460 nm PL decay dynamics (Figure 5.9 and Table 5.3). Each of the fitted decay times reduces, to $\tau_1 \sim 319$ ps (56%), $\tau_2 \sim 1.32$ ns (35%) and $\tau_3 \sim 7.43$ ns (9%), with a large shift in fractional weighting towards the $\tau_1$ component. The average lifetime correspondingly reduces to $\tau_{av} \sim 1.31$ ns. The majority sub-320 ps decay component is consistent with the spectral dominance of vibronic F8-based emission (Figure 5.9 (b)) whilst the 1.32 and 7.43 ns time constants signal the presence of residual CT emission. As for the glassy case, the decays are slower for longer collection wavelengths (Figure 5.8(d)). However, unlike the situation for PFO and blend films, a modest decrease in PLQE from 45% to 40% was observed when the β-phase was induced in copolymer films (Table 5.3), albeit that the PLQE itself remains relatively high (c.f. 35% for PFO and 25% for the blend). Among possible explanations, fluorenone-centred quenching is plausible but remains unproven.

The 460 nm PL decay transient for glassy 90PFO/10PFB blend films can also be fit to three exponentials, although their relative fractions and decay times, not surprisingly, differ from those of the 95F8:5BSP copolymer (Table 5.3). Excitonic emission from the PFO chains is dominant, with CT-like emission accounting for much smaller fractions than in the copolymer; corresponding decay times are $\tau_1 \sim 295$ ps (64%), $\tau_2 \sim 1.48$ ns (27%) and $\tau_3 \sim 8.2$ ns (9%). As for the copolymer, when emission is collected at longer wavelengths, longer lifetime emissive
species are increasingly important (Figure 5.8(e)). In the blend case, the longest time constant excited states ($\tau_3 \sim 8.2$ ns) have previously been shown to be exciplexes generated between PFO and PFB, with thermally assisted energy transfer to a PFB CT-like exciton.[17] Upon $\beta$-phase induction, the decay becomes almost mono-exponential with excitonic emission from PFO $\beta$-phase chain segments totally dominant; decay times are $\tau_1 \sim 247$ ps (97%) and $\tau_2 \sim 1.93$ ns (3%). The lack of a longer-lived time constant indicates the majority excitons generated on PFO chains no longer form exciplexes with PFB and instead efficiently transfer to $\beta$-phase segments before undergoing radiative decay. As detection wavelength is increased (Figure 5.8(f)), the short-lived decay time remains relatively constant ($\tau \sim 271$-325 ps) until 500 nm, where CT emission increases. The PLQE values for glassy and $\beta$-phase 90PFO/10PFB blends were 20% and 25% respectively, smaller than for both PFO and 95F8:5BSP copolymer films, indicating more substantial non-radiative decay.

5.3.4 Low-Temperature Photoluminescence Measurements

To further probe the nature of the energy transfer in $\beta$-phase 95F8:5BSP films, low temperature measurements were taken of $\beta$-phase PFO, glassy 95F8:5BSP glassy and $\beta$-phase 95F8:5BSP thin films and the spectra are shown below in Figure 5.11(a), (b) and (c) respectively. All samples were excited at $\lambda_{\text{ex}} = 400$ nm and spectra recorded at 20 K intervals between 10-290 K.
Figure 5.11: Photoluminescence spectra ($\lambda_{ex} = 400$ nm) of (a) β-phase PFO, (b) glassy phase 95F8:5BSP and (c) β-phase 95F8:5BSP samples at a temperature range of 10 to 290 K. Arrows show the effect of reducing temperature. Panel (d) shows the β-phase 95F8:5BSP spectra at 10 K and 290 K and (e) shows the deconvolution of the 10 K β-phase 95F8:5BSP spectra into the component β-phase and residual CT emission. Panel (f) shows the percentage fraction of β-phase emission as a function of temperature.

Figure 5.11(a) shows that as the PFO β-phase sample decreases in temperature, the PL spectra red shifts by ~ 5 nm whilst the 0-0 linewidth decreases by some ~35 meV which has been previously linked to increases in β-phase conjugation length and planarity. The 0-1 and 0-2 vibronics show distinctive splitting into at least three peaks as the temperature decreases. This
is due to coupling of the electronic transitions to the vibrational modes of the \( \beta \)-phase at 735, 1281 and 1604 cm\(^{-1} \) which correspond to in-plane fluorene unit deformation, C-C interunit stretch and phenyl-ring quadrant stretch respectively.\(^{[51]} \) The glass 95F8:5BSP copolymer (Figure 5.11(b)) emission reduces in linewidth as temperature decreases, with the spectra resolving into a main high energy peak at ~454 nm with a lower energy shoulder at ~478 nm. This indicates a narrowing of the energetic density of states for the charge transfer (CT) exciton, consistent with previous reports of other polymers.\(^{[28,245]} \) Low temperature \( \beta \)-phase 95F8:5BSP PL measurements (Figure 5.11(c) and (d)) reveal that the spectrum remains a superposition of both vibronic \( \beta \)-phase emission (Figure 5.11 (a)) and CT-like emission from BSP centred states (Figure 5.11(b)) over the whole 10 to 290 K range. Spectral deconvolution reveals that the component spectra are identical to the PFO \( \beta \)-phase and glassy 95F8:5BSP spectra at each temperature, as for example shown at 10 K (Figure 5.11(e)). By integrating the component spectra at each temperature (Figure 5.11(f)) the fraction of \( \beta \)-phase emission decreases with temperature, from ~64% at 290 K to ~32% at 10 K.

5.3.5 Surface Topography

As noted in section 5.3.2, the PL spectra of the 90PFO/10PFB blend film (Figure 5.3(c)) shows residual PFO emission in the form of a shoulder at ~425 nm which is absent in the thin film spectra of the 95F8:5BSP copolymer. This implies some possible phase separation between the PFO and PFB polymers. To confirm this, AFM topography measurements were taken of glassy and \( \beta \)-phase PFO, 95F8:5BSP and 90PFO/10PFB films (Figure 5.12) with the surface roughness of each sample tabulated in Table 5.4.

The PFO and 95F8:5BSP films show largely featureless thin film microstructures (Figure 5.12 (a)-(d)), however there is an increase in roughness once \( \beta \)-phase is induced, consistent with previous reports.\(^{[48,217,246]} \) The 90PFO/10PFB blend films do indeed show phase separation between PFB and PFO chains in the glassy phase (Figure 5.12 (e)), with the image appearing to show ~10 nm raised islands through the film with a roughness of 1.32 nm. The \( \beta \)-phase blend thin film microstructure (Figure 5.12 (f)), however, appears to show ~10 nm sized recesses with a roughness of 1.76 nm. This suggests that whilst BSP units are evenly distributed through the 95F8:5BSP copolymer film, in the blend case the PFB chains are segregated.
Figure 5.12: AFM topography images for glassy phase (left column) and β-phase (right column) microstructures of PFO ((a) and (b)), 95F8:5BSP copolymer ((c) and (d)) and 90PFO/10PFB blend ((e) and (f)) films.
Table 5.4: Root mean square roughness values ($R_q$) for PFO, 95F8:5BSP copolymer and 90PFO/10PFB blend films with glassy- and β-phase microstructures.

<table>
<thead>
<tr>
<th>Film Type</th>
<th>Roughness, $R_q$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFO Glassy</td>
<td>0.349</td>
</tr>
<tr>
<td>PFO β-phase</td>
<td>0.627</td>
</tr>
<tr>
<td>95F8:5BSP Glassy</td>
<td>0.459</td>
</tr>
<tr>
<td>95F8:5BSP β-phase</td>
<td>0.680</td>
</tr>
<tr>
<td>90PFO/10PFB Glassy</td>
<td>1.319</td>
</tr>
<tr>
<td>90PFO/10PFB β-phase</td>
<td>1.763</td>
</tr>
</tbody>
</table>

5.3.6 Display Related PLED Device Characteristics

To test the effect of β-phase segment formation on device performance, PLEDs were fabricated with a conventional bottom-emitting device architecture, comprising glass substrate / indium tin oxide (ITO) anode / poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) hole injection layer / TFB electron blocking interlayer / emission layer (EML) / LiF / Ca / Al cathode. Schematic device and energy level diagrams are shown in Figure 5.13.
Figure 5.13: (a) Device structure of blue PLEDs and (b) corresponding schematic energy level diagram. The polymer energy levels were deduced from CV measurements. The shaded grey area indicates the smaller energy gap for β-phase segments in PFO and 95F8:5BSP, whilst the pale green area indicates the energy gap for BSP units within the 95F8:5BSP copolymer.

Figures 5.14 (a) and (b) compare the current density and luminance vs voltage (J-V-L) characteristics for, respectively, glassy and β-phase PFO homopolymer, 95F8:5BSP copolymer and 90PFO/10PFB blend EML devices. Figures 5.14 (c) and (d) show the corresponding luminance-dependent glassy and β-phase PLED efficiencies $\eta$ (cd/A) and $\eta_w$ (lm/W) and Figures 5.14 (e) and (f) the associated external quantum efficiencies $\eta_{eqe}$ (EQE). Other parameters (turn-on voltage, peak $\eta$, $\eta_w$ and $\eta_{eqe}$) for these devices are collated in Table 5.5 and their electroluminescence (EL) spectra are shown in Figure 5.15 (a).
Figure 5.14: PLED characteristics for glassy (filled symbols, (a), (c) and (e)) and β-phase (open symbols, (b), (d) and (f)) EML film microstructure devices. J-V-L data are plotted in (a) and (b), Luminous (cd/A) and luminous power (lm/W) efficiency data as a function of luminance in (c) and (d) and associated EQE data in (e) and (f). 95F8:5BSP copolymer EML data are plotted as red circles, 90PFO/10PFB blend data as blue triangles and PFO homopolymer data as black squares.
Table 5.5: Summary of best PLED performance for the current study showing turn-on voltages, peak luminous (cd/A), luminous power (lm/W) and external quantum efficiencies (%) and their values at 100 cd/m² and 1000 cd/m², and CIE (x, y) colour coordinates for PFO, 95F8:5BSP copolymer and 90PFO/10PFB blend EML films with both glassy and β-phase microstructures.

<table>
<thead>
<tr>
<th>EML Type</th>
<th>Turn-on Voltage (V)</th>
<th>Luminous efficiency η (cd/A)</th>
<th>Luminous Power efficiency ηₖ (lm/W)</th>
<th>External quantum efficiency ηₑₑₑ (%)</th>
<th>CIE (x,y)</th>
</tr>
</thead>
</table>
|                   |                     | @ 100 cd/m² | @ 1000 cd/m² | @ 100 cd/m² | @ 1000 cd/m² | @ 100 cd/m² | @ 1000 cd/m² | (
|                   |                     | Peak     | Peak       | Peak       | Peak       | Peak       | Peak       | 0, 0)     |
| PFO Glassy        | 4.2                 | 0.43 @   | 0.22 @     | 0.31 @     | 0.26 @     | 0.155, 0.098 |
|                   |                     | 6.8 V    | 5.6 V      | 6.6 V      | 6.6 V      |           |           |           |
|                   |                     | 0.36     | 0.22       | 0.31       | 0.26       |           |           |           |
|                   |                     | 0.43     | 0.19       | 0.31       | 0.31       |           |           |           |
| PFO β-phase       | 4.0                 | 0.70 @   | 0.38 @     | 0.43 @     | 0.30 @     | 0.157, 0.117 |
|                   |                     | 6.2 V    | 5.4 V      | 6.0 V      | 6.0 V      |           |           |           |
|                   |                     | 0.48     | 0.32       | 0.43       | 0.30       |           |           |           |
|                   |                     | 0.69     | 0.37       | 0.43       | 0.43       |           |           |           |
| 90PFO/10PFB Glassy| 3.8                 | 1.52 @   | 0.97 @     | 0.89 @     | 0.86 @     | 0.162, 0.174 |
|                   |                     | 5.6 V    | 4.6 V      | 5.6 V      | 5.6 V      |           |           |           |
|                   |                     | 1.47     | 0.95       | 0.89       | 0.86       |           |           |           |
|                   |                     | 1.48     | 0.74       | 0.86       | 0.87       |           |           |           |
| 90PFO/10PFB β-    | 3.8                 | 1.31 @   | 0.79 @     | 0.80 @     | 0.73       | 0.151, 0.118 |
| phase             |                     | 5.6 V    | 4.4 V      | 5.6 V      | 5.6 V      |           |           |           |
|                   |                     | 1.21     | 0.78       | 0.80       | 0.73       |           |           |           |
|                   |                     | 1.28     | 0.65       | 0.78       | 0.78       |           |           |           |
| 95F8:5BSP Glassy | 3.2                 | 4.05 @   | 2.62 @     | 2.40 @     | 2.30       | 0.149, 0.175 |
|                   |                     | 6.2 V    | 4.0 V      | 6.0 V      | 6.0 V      |           |           |           |
|                   |                     | 3.80     | 2.50       | 2.40       | 2.30       |           |           |           |
|                   |                     | 4.00     | 1.90       | 2.39       | 2.39       |           |           |           |
| 95F8:5BSP β-      | 3.2                 | 3.60 @   | 2.44 @     | 2.40       | 2.44       | 0.145, 0.123 |
| phase             |                     | 5.6 V    | 4.2 V      | 5.6 V      | 5.6 V      |           |           |           |
|                   |                     | 3.60     | 2.10       | 2.44       | 2.44       |           |           |           |
|                   |                     | 3.50     | 1.50       | 2.37       | 2.37       |           |           |           |
In terms of PLED efficiency, PFO glassy EML devices show a peak $\eta = 0.43$ cd/A at 6.8 V, a peak $\eta_w = 0.22$ lm/W at 5.6 V and a peak $\eta_{eqe} = 0.31\%$ at 6.6 V, with 1000 cd/m$^2$ luminance at 7 V. The PFO $\beta$-phase EML devices show a significant improvement, with peak efficiencies of $\eta = 0.70$ cd/A at 6.2 V, $\eta_w = 0.38$ lm/W at 5.4 V, $\eta_{eqe} = 0.43\%$ at 6.0 V and 1000 cd/m$^2$ luminance now at 5.9 V. This improvement is consistent with previous reports for $\beta$-phase PFO devices.\cite{48,50,217,246,247} Figure 5.15(b) shows, however, that the efficiency gains are at the expense of a detrimental change in EL emission colour. The shift from glassy (peak $\lambda = 425$ nm) to $\beta$-phase (peak $\lambda = 440$ nm) alters the CIE ($x$, $y$) coordinates from (0.155, 0.098) to (0.157, 0.117), with a corresponding shift in dominant wavelength from 470 to 475 nm and a decrease in colour saturation from 86 to 82%. This behavior limits the achievable display colour gamut. It also helps to explain why the $\eta_{eqe}$ enhancement is more modest than the gains in $\eta$ and $\eta_w$; a shift to the green leads to a better overlap with the photopic eye sensitivity function that peaks at 555nm.

The 90PFO/10PFB blend EML PLEDs show significantly better efficiency characteristics than for the corresponding PFO devices (Figure 5.14), with the PFB fraction strongly assisting hole injection (Figure 5.13(b)).\cite{230,234} The glassy blend EML gives peak efficiencies $\eta = 1.52$ cd/A at 5.6 V, $\eta_w = 0.97$ lm/W at 4.6 V and $\eta_{eqe} = 0.89\%$ at 5.6 V, with a luminance of 1000 cd/m$^2$ at 6.3 V, whilst $\beta$-phase blend EML devices show peak efficiencies $\eta = 1.31$ cd/A at 5.6 V, $\eta_w = 0.79$ lm/W at 4.4 V and $\eta_{eqe} = 0.80\%$ at 5.6 V and reach 1000 cd/m$^2$ at 6.2 V. $\beta$-phase devices are, therefore, somewhat less efficient than glassy devices but in terms of CIE ($x$, $y$) colour coordinates $\beta$-phase segment formation leads to a shift from (0.162, 0.174) to (0.151, 0.118), resulting in a highly desirable, deeper-blue emission (Figure 5.15(b)). The corresponding dominant wavelength shifts from 478 to 474 nm and colour saturation increases from 73 to 83%. This colour shift also helps to explain at least in part the proportionately larger decrease in $\eta$ and $\eta_w$ values than in $\eta_{eqe}$ as the emission then has reduced overlap with the photopic eye sensitivity function.
Figure 5.15: (a) EL spectra at 6 V for PFO homopolymer, 95F8:5BSP copolymer and 90PFO/10PFB blend devices with glassy (black) and β-phase (red) EML microstructures. (b) Colour coordinate (CIE(x,y)) diagram showing the EL emission coordinates for PFO (square), 95F8:5BSP (circle) and 90PFO/10PFB (triangle) for glassy (filled black symbols) and β-phase (filled white symbols) EMLs. Inset shows EL emission coordinates on expanded scale; arrows indicate colour shift from glassy to β-phase for PFO (green arrow), 95F8:5BSP copolymer (blue arrow) and 90PFO/10PFB blend (purple arrow).

Glassy and β-phase 95F8:5BSP copolymer EML devices show yet further enhanced PLED efficiency (Table 3). Glassy devices give peak efficiencies $\eta = 4.05 \, \text{cd/A}$ at 6.2 V, $\eta_w = 2.62 \, \text{lm/W}$ at 4.0 V and $\eta_{eqe} = 2.40\%$ at 6.0 V, with a luminance of 1000 cd/m$^2$ at 6.6 V, whilst for β-phase devices $\eta = 3.60 \, \text{cd/A}$ at 5.4 V, $\eta_w = 2.44 \, \text{lm/W}$ at 4.2 V and $\eta_{eqe} = 2.40\%$ at 5.6 V, with 1000 cd/m$^2$ at 7.2 V. Interestingly, here $\eta_{eqe}$ is unaltered by β-phase induction whilst (see
Figure 5.1(b)) the CIE (x, y) coordinates still shift positively from (0.149, 0.175) to (0.145, 0.123), resulting in a dominant wavelength decrease from 479 nm to 474 nm and a colour saturation increase from 77% to 85%. Figure 5.16 shows the deconvolution of the EL spectra of β-phase copolymer and blend devices, showing β-phase emission accounts for ~67% of the total EL emission in the copolymer device, and ~80% emission in the blend device.

![Deconvolution of EL spectra](image)

Figure 5.16: Deconvolution of EL spectra for 95F8:5BSP copolymer β-phase sample (left) and 90PFO/10PFB blend β-phase sample (right). The red dashed line shows residual PFB-like CT emission, whilst the blue dashed line shows the vibronic β-phase emission. The fractional contribution from each component was deduced by integration over their deconvoluted spectra.

The copolymer EML efficiency improvement is largely attributed to the BSP units both assisting hole injection and, due to their sparse distribution, acting as deep hole-traps. Glassy PFO EML devices display the highest turn-on voltages (defined as the applied bias at which L = 1 cd/m²), namely 4.2 V, reducing to 4.0 V on induction of β-phase chain segments, consistent with previous reports.[50,217,246] The 90PFO/10PFB blend devices conversely show the same turn-on voltage (3.8 V) irrespective of glassy or β-phase microstructure, as also do the 95F8:5BSP copolymer devices (3.2 V); injection is clearly controlled by BSP rather than β-phase units. The better turn-on behaviour for the copolymer devices is likely due to the more uniform distribution of BSP units; they are present within every 95F8:5BSP polymer chain whilst the 90PFO/10PFB blend EML shows phase segregation (see AFM data in section 5.3.5).
Overall, the performance of the 90PFO/10PFB blend devices is poorer than for the 95F8:5BSP copolymer devices. Thus, the volume fraction of BSP moieties is not the determining factor in this regard but the distribution of moieties within a polymer chain and through the bulk of a film also matter. In the blend, the BSP moieties are incorporated within PFB polymer chains at high density (alternating with 9,9-dioctylfluorene moieties) and these chains are then mixed with a majority (90%) of PFO polymer chains from which (at least partial) phase separation will occur. Evidence for phase separation is provided by the EL spectrum for glassy blend EML devices that shows a glassy PFO contribution (c.f. shoulder at ~ 425 nm on the blue edge of the spectrum) indicating incomplete energy transfer to PFB CT like emission sites.

Other studies have additionally shown that such copolymers have three to four orders of magnitude lower time-of-flight photocurrent hole mobility ($\mu_{h\text{ToF}}$) than equivalent films of PFO and *alternating* fluorene-arylamine copolymers.$^{[230,233,234]}$ The measured $\mu_{h\text{ToF}} \approx 10^{-7}$ cm$^2$/Vs for glassy films indicates substantially deeper hole trapping than for $\beta$-phase segment formation in PFO. The electrochemical measurements for 95F8:5BSP films suggest that the trap depth is ~ 0.3 eV above the ~ 5.80 eV HOMO level of PFO. This trapping effect is also evident in the reduction in current density between the PFO homopolymer and 95F8:5BSP copolymer EML devices. We find $J = 231.4$ mA/cm$^2$ at 7 V for glassy PFO, and only 41.4 mA/cm$^2$ at the same voltage for glassy 95F8:5BSP despite the turn-on voltage for the copolymer (3.2 V) being 1 V lower than for PFO (4.2 V).

In summary, the device efficiency and display colour parameter data (*Table 5.6*) show that in the absence of BSP units (PFO homopolymer) the induction of $\beta$-phase chain segments is advantageous to device efficiency but only at the expense of a shift away from desirable deep-blue emission. The introduction of BSP units into the EML (blend and copolymer) yields a significant overall enhancement in device efficiency and colour stability with the copolymer performing substantially better than the blend. Again, though, the efficiency enhancement is achieved at the expense of colour response with the BSP-related CT-like emission yielding less deep-blue colour coordinates (green shift in dominant wavelength and reduction in saturation). Induction of $\beta$-phase chain segments is then strongly beneficial to the colour response and for copolymer EML devices this occurs without any appreciable decrease in quantum efficiency; the $\beta$-phase copolymer EML PLEDs thus provide the best overall combination of efficiency and colour performance.
Table 5.6: Display colour parameters for PFO, 90PFO/10PFB blend and 95F8:5BSP copolymer EML PLEDs. Note the close agreement for β-phase EML colour saturation and dominant wavelength for all three EML types and likewise the close agreement for glassy EML copolymer and blend devices.

<table>
<thead>
<tr>
<th>EML Type</th>
<th>EQE (%) @ 1000 cd/m²</th>
<th>CIE (x,y)</th>
<th>Dominant Wavelength (nm)</th>
<th>Colour Saturation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFO Glassy</td>
<td>0.31</td>
<td>0.155, 0.098</td>
<td>470</td>
<td>86</td>
</tr>
<tr>
<td>PFO β-phase</td>
<td>0.43</td>
<td>0.157, 0.117</td>
<td>475</td>
<td>82</td>
</tr>
<tr>
<td>90PFO/10PFB Glassy</td>
<td>0.87</td>
<td>0.162, 0.174</td>
<td>478</td>
<td>73</td>
</tr>
<tr>
<td>90PFO/10PFB β-phase</td>
<td>0.78</td>
<td>0.151, 0.118</td>
<td>474</td>
<td>83</td>
</tr>
<tr>
<td>95F8:5BSP Glassy</td>
<td>2.39</td>
<td>0.149, 0.175</td>
<td>479</td>
<td>77</td>
</tr>
<tr>
<td>95F8:5BSP β-phase</td>
<td>2.37</td>
<td>0.145, 0.123</td>
<td>474</td>
<td>85</td>
</tr>
</tbody>
</table>

5.3.7 Spectral stability and PLED lifetime

A well-known drawback to using PFO as the EML in PLEDs is its low spectral stability under operation due to the appearance of a low energy ‘green-band’ emission when driven at higher voltages, the origin of which is inter-chain emission from fluorenone-based defects.\[214,241,246,248\] Figure 5.17 shows EL spectra as a function of applied voltage for glassy and β-phase PFO and 95F8:5BSP devices. As the voltage is driven beyond 7 V for the glassy PFO device and beyond 9 V for the β-phase PFO device, the emergence of a broad, low energy component (‘green-band’) is clearly observed. However, for both glassy and β-phase 95F8:5BSP devices, no green-band is observed when driving devices between 5 and 13 V, indicating that 95F8:5BSP devices show much improved colour stability compared with PFO PLED devices. This is likely to be due to the bulky BSP units causing increased disruption in the packing structure between the polymer chains, thereby preventing green band emission; similar reductions in green band have been observed when small amounts of carbazole units or large amine group end caps have been incorporated into polyfluorene chains.\[249,250\]
Figure 5.17: EL spectra as a function of voltage for (a) glassy phase PFO, (b) β-phase PFO, (c) glassy phase 95F8:5BSP and (d) β-phase 95F8:5BSP PLED devices.

As a final device test, motivated by literature reports that β-phase formation in PFO increases device lifetime,[241] encapsulated pre- and post-SVA 95F8:5BSP copolymer PLEDs were subjected to accelerated lifetime testing under nitrogen (Figure 5.18) using a constant current source set to deliver 4 mA (i.e. $J \approx 90$ mA/cm$^2$ for the 4.5 mm$^2$ pixels under test). The luminance was measured at 60-second intervals starting from 2821 cd/m$^2$ for glassy and 2300 cd/m$^2$ for β-phase devices. Initially, the glassy and β-phase 95F8:5BSP PLED luminance values decayed at a similar rate, with half decay times $T_{50\%}$ (glassy) = 176 mins and $T_{50\%}$ (β-phase) = 180 mins. The subsequent decay was much more rapid in the glassy copolymer EML devices, especially beyond 400 mins. The luminance took 490 mins to drop to 30% of its starting value for the glassy 95F8:5BSP PLED but took 630 mins to reach the same fractional output for the β-phase device, and whilst the latter was still emitting some 250 cd/m$^2$ at 1200 mins the glassy device luminance had fallen below 4 cd/m$^2$ by that time. The operational stability of β-phase 95F8:5BSP copolymer devices is, therefore, significantly greater than that of otherwise equivalent glassy devices.
Figure 5.18: Accelerated luminance decay measurements for encapsulated 95F8:5BSP copolymer PLEDs driven at a constant current density $J \approx 90 \text{ mA/cm}^2$. Results are shown for both glassy (black line) and β-phase (red line) EML devices.

It is expected that the initial luminance decay is caused by degradation of the reactive LiF and Ca layers in the composite cathode that is used for both device types. The subsequent degradation is slower for the β-phase EML structures for which the emission is dominated by F8 centred excitonic states. In addition to the known stabilising effect of β-phase on extended F8 sequences, this difference suggests a reduced stability for the BSP moiety centred CT like states that dominate emission from glassy copolymer EML structures.

In summary, induction of β-phase chain segments in 95F8:5BSP copolymer EMLs not only improves PLED CIE coordinates, but also spectral stability and operational lifetime.

5.3.8 Discussion

This section considers further the effects of β-phase formation on the energy transfer of emissive species in order to explain the desirable PLED emission for 95F8:5BSP copolymer EML devices, in particular, the origin of efficient energy transfer to β-phase F8-centred excitons, with concomitant net increase in mean photon energy and deeper-blue emission.

The HOMO and LUMO of glassy phase PFO homopolymer films were deduced from CV measurements to be 5.80 eV and 2.10 eV respectively, similar to previously reported values. Upon β-phase chain segment formation a smaller optical gap component is introduced into the ensemble of absorbing chromophores, with the resolved $S_0-S_1$ 0-0 peak at 433 nm. Additionally, as a result of rapid energy migration to β-phase segments, there is a ~ 16 nm red-
shift in S₁-S₀ 0-0 PL emission. CV-measurement-based HOMO and LUMO values were also determined for PFB and 95F8:5BSP, yielding 5.05 eV and 2.00 eV and 5.49 eV and 2.10 eV respectively.

The schematic energy level diagram for glassy 95F8:5BSP copolymer chains (Figure 5.19(a)) shows how the energy levels vary spatially along the copolymer chain, with the electron-rich BSP unit being raised in energy relative to the F8 units. Whilst electrical excitation should (at least initially) predominantly produce CT excitons due to the strong hole trapping nature of the BSP units,[207,228],[233] under optical excitation exciton states will also form on longer F8 segments (labelled I in Figure 5.19). In this case, efficient inter- (not shown) and intra-chain energy transfer of F8 excitons to CT states (labelled II in Figure 5.19) is observed.[236]

Figure 5.19: Schematic energy level diagrams (left column) for intra-chain energy transfer processes in 95F8:5BSP (a) glassy- and (b) β-phase chains following optical excitation. Jabonksi diagrams for each process are shown to the right of each schematic. See text for explanation of numbering I, II, and III.

Upon β-phase formation, the corresponding F8 HOMO level will move up and the LUMO down, forming a Type I quantum-well-like structure along the polymer chain (Figure 5.19(b)).[251] Under optical excitation, excitons formed locally on glassy F8 segments undergo efficient energy transfer to either a β-phase F8 segment[37,51,239] (labelled III in Figure 5.19) or BSP-based CT states[236] before decaying (Figure 5.19(b)). As such, the 95F8:5BSP β-phase PL spectrum is a superposition of both PFO-like β-phase emission (~62% of total emission)
and residual CT emission (~38%). The reason β-phase emission dominates the spectrum despite the film having roughly the same proportion of β-phase segments and BSP units (~5%) is likely to be a result of the faster decay for β-phase F8 excitons. Longer-lived CT states will be more prone to thermal energy transfer before decay. Nevertheless, as expected, the fraction of CT type emission increases (and β-phase emission correspondingly decreases) as more BSP units are incorporated into the copolymer chain (see Figure 5.7).

The low temperature photoluminescence measurements (Figure 5.11) support the energy transfer model outlined above since energy transfer in β-phase PFO has been proposed to be a two-step process of thermally assisted exciton diffusion followed by Forster resonance energy transfer from high energy glassy phase F8 to low energy β-phase segments.[42] The decrease in β-phase emission at low temperature could then be explained as a result of energy transfer to β-phase units being more dependent on thermally assisted diffusion than is the case for BSP sites. Alternatively, enhanced polaron formation has been previously observed for β-phase PFO and polarons are known to act as emission quenching sites, especially at low temperatures where their lifetimes are long, leading to an increasing β-phase exciton quenching at low temperatures.[42]

Under electrical excitation of copolymer EML devices, it is likely that a much greater fraction of initially formed excitations are CT states, due to the hole trapping nature of the BSP unit (trap depth ~0.3 eV). Despite this, F8 β-phase emission provides the dominant (~67%) contribution to the EL spectrum, with residual CT-like emission delivering a more modest (~33%) contribution. This suggests that either endothermic energy transfer from BSP-centred CT states to β-phase F8 excitons or ‘trap-filling’ of BSP sites occurs. In the latter case, as the BSP ‘traps’ fill, β-phase F8 charge localization is expected to play an increasing role. Evidence for this is clearly seen in Figure 5.20, where the relative fraction of β-phase exciton EL emission increases with voltage. The shorter emission decay time for F8 β-phase segment- than BSP-localized states also feeds into the higher relative fraction of β-phase EL.
Figure 5.20: Voltage dependent EL spectra for a β-phase 95F8:5BSP PLED with an EML layer thickness of ~95 nm. The fraction of residual CT like emission appears to reduce with increasing voltage as BSP sites become saturated and β-phase F8 segments become filled with excited species. This can be seen by a reduction in intensity between 445-495 nm with increasing voltage.

A key difference for 90PFO/10PFB blend samples is that inter-molecular energy transfer between neighbouring PFB and PFO chains becomes important. Under optical excitation of the glassy-phase blend, excited states are formed directly on both PFO and PFB chains. However, due to the raised HOMO and LUMO energies of PFB relative to PFO, a type II heterojunction occurs at the PFO/PFB interfaces, resulting in exciplex formation.[17] At room temperature, the exciplex undergoes endothermic energy transfer to the emissive PFB CT state yielding its characteristic spectrum (Figure 5.21(a)).[17] However, not all the PFO excitons generated will form an exciplex and we consequently also observe PFO exciton emission as a shoulder at 425 nm. Under electrical excitation, as holes will tend to localize on PFB chains and electrons on PFO (see Figure 5.13 energy levels) it is likely that exciplexes are directly formed by electron-hole Coulomb capture[65] before undergoing endothermic energy transfer to PFB CT states (Figure 5.21(c)). Consistent with this, Figure 5.15(a) indeed shows a much weaker 425 nm PFO emission shoulder for glassy phase blend EL than PL.
For $\beta$-phase blends, the majority of optically excited glassy segment F8 excitons will tend to transfer their energy to $\beta$-phase sites without forming exciplexes (Figure 5.21(b)). Additionally, under electrical excitation, exciplex states that form between PFB and $\beta$-phase PFO chains (from direct electron-hole capture) will likely undergo endothermic energy transfer to PFO $\beta$-phase excitons (Figure 5.21(d)). As a consequence, both the PL and EL $\beta$-phase spectra are dominated by structured vibronic emission. Some residual CT emission remains, respectively 18% and 20% for PL and EL, but these values are significantly lower than for the 95F8:5BSP copolymer case despite the same volume fraction of BSP units being present. This
is most likely due to the greater fraction of $\beta$-phase segments generated and the consequences of phase separation.

In summary, a novel route to high-efficiency, deep-blue emitting PLEDs has been demonstrated by introducing a simple molecular-level conformation change in the F8 sequences of 95F8:5BSP copolymers from the disordered glassy phase to the rigid $\beta$-phase microstructure via annealing in a toluene solvent atmosphere. The BSP units enhance hole injection and act as hole-trapping sites that assist efficient exciton formation. The BSP units also undesirably shift the EL to a CT-state-based sky-blue emission spectrum (CIE $(x, y) = (0.149, 0.175)$). Subsequent introduction of $\beta$-phase chain segments within the copolymer restores a more desirable deep-blue, vibronically-structured EL emission with CIE $(x, y) = (0.145, 0.123)$ whilst retaining the bulk of the efficiency enhancement and increasing operational stability.

5.4 Conclusion

In this chapter, it has been demonstrated that the structural, optical and electrical properties of two types of fluorene copolymer can be altered via simple molecular conformational control. Here, $\beta$-phase segments were introduced to a series of F8:BSP copolymers by solvent vapour annealing in toluene. UV-visible absorption and PL spectroscopy measurements of solvent annealed F8:BSP copolymers at 3%, 5%, 10% and 20% BSP fraction showed $\beta$-phase formation in the F8 segments, with the appearance of characteristic red-shifted absorption peaks and the promotion of well-structured vibronic emission.

Incorporating 5% BSP units into the conjugated backbone of an otherwise F8 polymer (thus yielding 95F8:5BSP) produces a five-fold performance enhancement in PLED luminous efficiency and luminous power efficiency relative to PFO (i.e. 100F8). The BSP units (with significantly lower ionization potential) enhance hole injection and act as hole-trapping sites that assist efficient exciton formation. The BSP units have an additional benefit in increasing the color stability of the PLEDs by suppressing green-band emission when driven at higher voltages. The BSP units also, however, undesirably shift the EL to a CT-state-based sky-blue emission spectrum (CIE $(x, y) = (0.149, 0.175)$). Subsequent introduction of $\beta$-phase chain segments within the copolymer restores a more desirable deep-blue, vibronically-structured EL emission with CIE $(x, y) = (0.145, 0.123)$ whilst retaining the bulk of the efficiency enhancement; it also increases operational stability. The overall best PLEDs, using $\beta$-phase
95F8:5BSP EMLs, then have $\eta = 3.60$ cd/A at 5.4 V and $\eta_w = 2.44$ lm/W at 4.2 V, with 1000 cd/m$^2$ luminance at 7.2 V.

The spatial distribution of BSP units in the PLED active layer is also found to be significant to device function, with 95F8:5BSP copolymer (homogeneous) and 90PFO/10PFB blend (heterogeneous) EMLs showing distinct properties despite containing the same volume fraction of BSP units. Both the glassy- and $\beta$-phase 90PFO/10PFB blend devices performed less well than equivalent copolymer devices with luminous efficiency, luminous power efficiency and EQE lower by a factor 2.5-3.0 but still significantly better than for PFO-only EML devices.
Chapter 6: Controlling Molecular Conformation of Fluorene-Benzothiadiazole Copolymers

6.1 Introduction

Organic light emitting diodes containing a single polymeric emissive layer have been the subject of intense research efforts since their discovery in 1990.[3] For single layer polymer light emitting diodes (PLEDs) to be effective, the polymeric emissive layer often contains a combination of hole- and electron-transporting moieties as well as emissive units contained within one polymer chain.[163,252,253] By controlling the relative proportion of each group, the HOMO and LUMO energy levels as well as charge transport within the emissive layer can be tuned to achieve charge carrier balance within the film as well as maintaining a high PLQY.[163]

This approach is desirable to simplify fabrication and processing, as well as offering greater control of the active layer morphology. In this chapter, a series of octyl-fluorene(F8):benzothiadiazole(BT) alternating copolymers consisting of different ratios of F8 and BT units are investigated as active layer materials in PLEDs.

When the ratio of F8 and BT units are equal, this is more commonly known as poly[2,7-(9,9-di-n-octylfluorene)-alt-4,7-(2,1,3-benzothiadiazole)] (F8BT). F8BT is widely used in a range of optoelectronic devices including the active layer of PLEDs,[73,254] as an electron accepting polymer in organic photovoltaics[160] and as an n-type electron transporting material in organic thin film transistors.[255] The strong electron withdrawing properties of the BT unit causes localisation of the LUMO onto it, whilst the HOMO is relatively delocalised across the polymer chain.[18,256] This in turn determines the charge-transport and energy transfer properties within the copolymer. Additionally, the chain morphology of F8BT can have a significant effect on the copolymer properties. Annealing F8BT to induce ordered crystalline domains increases the high energy emission of F8BT and PLQY, but correspondingly decreases the electron mobility.[161]

Here, the thin film optical and electronic properties of a (100-x)F8:xBT series of copolymers are studied in a systematic way by controlling the proportion of BT within the copolymer. The morphology of the copolymer is then modified by introducing β-phase segments into the fluorene units to examine how β-phase can alter the optoelectronic properties of F8:BT copolymers and the corresponding PLED device properties (see Chapter 5 for more
information on β-phase). It is found that the F8:BT copolymers at 1%, 5% and 10% BT fraction can form β-phase, however the PL is dominated by F8-BT CT emission with only minor fractions of F8 β-phase emission visible. Incorporating β-phase into the active layer of F8:BT copolymer devices can aid in both increasing the efficiency of the device and stabilising the EL emission, demonstrating potential for the system to be used for white light emitting OLEDs. The intensity of F8 emission also increased with β-phase incorporation, leading to a shift towards the white colour point from (0.335, 0.551) to (0.327, 0.521).

6.2 Materials

The 100-xF8:xBT copolymers were provided by Prof. Do-Hoon Hwang at Pusan National University, Korea. Here, x = 0, 1, 5, 10, 20, 30 and 50. Where x = 50, the copolymer takes the form of the well-known polymer poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT). The chemical structure is shown below in Figure 6.1.

The 100-xF8:xBT copolymers were synthesised by the Suzuki coupling reaction from 50 mol% of fluorene bis boronic acid and 50 mol % of arylhalide (fluorene + BT) using a Pd(0) catalyst (tetrakis(triphenylphosphine)-palladium (0.04 g, 0.036 mmol)). The polymer was end-capped with bromobenzene and phenylboronic acid to yield benzene end-groups. Similarly to the synthesis route for F8:BSP copolymers, this synthesis allows F8-F8 and F8-BT linkages, however BT-BT bonding is not possible.

The methods of inducing β-phase in F8:BT copolymers is the same as described for F8:BSP copolymers in Chapter 5.
6.3 Controlling Molecular Conformation of F8:BT Copolymers

To demonstrate another application of conformational control of fluorene copolymers, the effects of solvent vapour annealing were studied on a series of (100-x)F8:xBT (F8:BT for short) copolymers. The F8:BT copolymer series are another example of statistical copolymers whereby BT units are randomly inserted into a fluorene backbone with varying amounts of BT incorporation (here x = 1, 5, 10, 20, 30 and 50, where the 50% case is known as F8BT). Unlike the electron rich (electron donating) BSP unit, the BT unit is strongly electron withdrawing giving the F8:BT copolymers a donor-acceptor type nature. This causes localisation of the LUMO on the BT unit, whilst the HOMO is largely delocalised over the entire backbone of the molecule.[256] Previous measurements dilute solutions of an F8:BT series reveal the emergence of a low-energy charge transfer absorption band (centred at ~450 nm for F8BT) as BT units are incorporated into the polymer backbone. Similarly, the PL spectra shows low-energy (relative to PFO) charge transfer emission at ~550 nm. The emission is red-shifted to a greater extent in comparison the F8:BSP copolymers due to stronger LUMO localisation and energy level offset. This is illustrated by the smaller band gap of F8BT (~2.4 eV)[160] compared to PFB (~2.9 eV).

6.3.1 Optical Measurements

Here, the thin film properties of the F8:BT series are examined along with the effect of inducing β-phase within the F8 units. Figure 6.2 shows the UV-vis absorption for as-cast thin film samples PFO, 99F8:1BT, 95F8:5BT, 90F8:10BT, 80F8:20BT, 70F8:30BT and F8BT.
The absorption spectra of the F8:BT thin films show two interesting features: (i) an increase in intensity and red shift of the low energy absorption charge transfer band with increasing BT content from ~448 nm (for 5% BT) to ~468 nm (F8BT) and (ii) a blue shift of the high energy absorption band from ~380 nm to 322 nm with increasing BT content. This can be explained by considering the low energy transition as that between the HOMO and BT-localised LUMO, whilst the high energy transition is between the HOMO and the LUMO+4 energy level which is delocalised over the F8 units. As the proportion of BT units increases, the HOMO-LUMO oscillator strength will increase (hence the increase in intensity of the low energy CT band), whilst the relative fraction of F8 units decrease, the F8 localised LUMO (LUMO+4) becomes localised over less units and hence increases in energy.\[18\]

The PL spectra of both dilute solution and thin film samples of F8:BT polymers are shown below in Figure 6.3.
The dilute solution PL spectra of the F8:BT copolymers show a strong F8 emission component (S$_1$-S$_0$ 0-0 peak at 420 nm) for low BT loadings (1-10% BT), which gradually weakens for larger BT fractions before becoming negligible for the F8BT sample. This is expected since the low concentration of BT units means there exists blocks of F8 units extending further than the Förster transfer radius for energy transfer from F8 to F8-BT CT states. As the BT loading increases, the lower energy charge transfer emission band increases in intensity, indicating an increase in energy transfer from F8 centred excitons to F8-BT charge transfer centred species and a reduction in number of F8 blocks larger than the Förster transfer radius.

By contrast, the thin film PL spectra of the polymers shows a drastic reduction of the F8 centred emission, even at small loadings of BT units. The ratio of peak intensities at 420 nm and 550 nm (I$_{420}$/I$_{550}$) is 0.07 for 99F8:1BT and 0.005 for 95F8:5BT, with negligible F8 emission for higher BT fractions. Deconvolution reveals the emission from the F8 units accounts for only 3.4% of the total emission for 99F8:1BT, with the emission <0.1% for higher loadings. This

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**Figure 6.3:** Normalised PL spectra of (a) dilute toluene solutions and (b) thin film samples of (100-x)F8:xBT polymers. Inset of (b) shows thin film PL spectra plotted on a logarithmic scale. All samples were excited at $\lambda_{ex} = 360$ nm.
implies that in thin film, Förster energy transfer can occur from F8 segments to BT units. Unlike in dilute solutions, the F8-BT charge transfer emission band red-shifts with larger BT incorporation, from ~529 nm (99F8:1BT) to 550 nm (F8BT). This is could be caused by the highly polarisable environment of the thin film compared to solution. Increasing the BT content (itself a polarised unit) increases the polarisability of the thin film, thus the interaction of the F8-BT CT state with the environment leads to a red shift in the PL emission.\textsuperscript{161,166,169} Alternatively, the increase in intensity of the CT absorption peak with BT content could cause self-absorption of the high energy emission also causing a red-shift in PL spectra.

To investigate the β-phase generation in F8:BSP copolymers, the thin films were subject to a solvent vapour anneal in a toluene atmosphere (under the same conditions as the F8:BSP copolymers). The subsequent UV-vis absorption spectra are shown in Figure 6.4 and a summary of the β-phase fraction formed is given in Table 6.1.
Figure 6.4: UV-vis absorption spectra for as-cast (black) and SVA (red) films of (a) 99F8:1BT, (b) 95F8:5BT, (c) 90F8:10BT, (d) 80F8:20BT, (e) 70F8:30BT and (f) F8BT.
Table 6.1: Summary of β-phase fraction formed in SVA annealed F8:BT thin filmed samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>β-phase fraction formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>99F8:1BT</td>
<td>9%</td>
</tr>
<tr>
<td>95F8:5BT</td>
<td>7%</td>
</tr>
<tr>
<td>90F8:10BT</td>
<td>5%</td>
</tr>
<tr>
<td>80F8:20BT</td>
<td>Unable to be determined</td>
</tr>
<tr>
<td>70F8:30BT</td>
<td>Unable to be determined</td>
</tr>
<tr>
<td>F8BT</td>
<td>0%</td>
</tr>
</tbody>
</table>

As can be observed from the UV-vis absorption spectra, β-phase formation occurs in 99F8:1BT, 95F8:5BT and 90F8:10BT samples with the appearance of the characteristic lower energy absorption peak at ~433nm. The fraction of β-phase formed is 9%, 7% and 5% for 99F8:1BT, 95F8:5BT and 90F8:10BT copolymers respectively. The β-phase fraction formed in F8:BT copolymers appears larger than for equivalent loadings of BSP units (see Table 6.1), most likely because the BT unit is relatively small and hence causes less disruption to β-phase formation than the large and bulky BSP unit. The β-phase fraction at higher BT loadings is unable to be fully determined as the CT absorption dominates the region of the absorption spectrum where β-phase is located, however the it is likely to be negligible due to the F8 sequence length being too short to support β-phase formation.[235]

Photoluminescence spectra of glass and β-phase PFO, 99F8:1BSP, 95F8:5BSP and 10F8:10BSP thin films are shown below in Figure 6.5 along with PLQE measurements.
Figure 6.5: (a) PL spectra and (b) PLQE values of glassy and β-phase 99F8:1BT, 95F8:5BT and 90F8:10BT copolymers. 80F8:20BT, 70F8:30BT and F8BT measurements are also included for figure (b). Figure (a) inset is PL spectra plotted on a semi-logarithmic scale.

The β-phase F8:BT PL spectra reveal that the spectra remain mostly unchanged. The spectra are still dominated by the broad, low energy emission of the F8-BT centred excitons. The minor emission from the F8 segments is however shifted to β-phase emission, with the characteristic β-phase emission appearing at ~437 nm for the $S_1-S_0$ 0-0 vibronic peak. The β-phase F8 emission appear to increase in relative intensity compared to their glassy counterparts. For 99F8:1BT, F8 β-phase emission however only accounts for ~5.6% of the total PL emission, implying that inducing β-phase increase the F8 contribution to the PL spectra. Interestingly however, the total PLQE decreases from ~24% to ~19% in 99F8:1BT, suggesting the induction of β-phase may increase non-radiative pathways within the film, perhaps by increasing the formation of polarons.[182] The β-phase F8 contribution to the 95F8:5BT and 90F8:10BT copolymers is ~0.1%. These results suggest that unlike in the F8:BSP case, energy transfer takes place from β-phase F8 segments to F8-BT centred charge transfer excitons. Photoluminescence excitation (PLE) spectra were recorded for the 99F8:1BT and 95F8:5BT samples and shown below in Figure 6.6. The samples were excited between 270-450 nm and their emission recorded at ~540 nm, where the CT emission band will be strongest.
Figure 6.6: PLE spectra for glassy (black) and β-phase (red) samples of (a) 99F8:1BT and (b) 95F8:5BT. The samples were excited at wavelength range of 270 – 450 nm and collected at 540 nm.

The PLE spectra of the β-phase 99F8:1BT and 95F8:5BT samples show clearly a peak at ~433 nm, coincidental with the β-phase absorption peaks shown in Figure 6.4. This shows that excitons created on β-phase F8 segments undergo energy transfer to F8-BT CT centred states before decaying radiatively provided there is a BT unit within the Forster transfer radius of the β-phase segment. If not, the exciton will decay radiatively.

6.3.2 PLED Device Measurements

As previously discussed, inducing β-phase in PFO-based PLED devices can improve the efficiency by improving charge balance as the β-phase segments act as energetic traps.[48,50,246,247] In light of this, the effects of both (i) BT unit incorporation and (ii) β-phase formation on PLED device performance were studied. F8:BT active layer PLEDs were fabricated in an ITO/PEDOT:PSS/TFB/F8:BT/Ca/Al conventional bottom-emitting structure. Figure 6.7 below shows the J-V-L and efficiency values for the glassy PLED devices for 99F8:1BT, 95F8:5BT, 90F8:10BT, 80F8:20BT, 70F8:30BT and F8BT.
Figure 6.7: (a) J-V-L measurements and (b) luminous and luminous power efficiencies for glassy phase F8:BT devices.

The J-V-L measurements show several clear trends with the incorporation of the BT unit. As the fraction of BT unit increases, the turn-on voltage for luminance decreases from ~4.2 V for 99F8:1BT, to ~2.6 V for F8BT. This could be explained by the shift in LUMO level with increasing BT content from ~2.1 eV for PFO (100F8) to ~3.4 eV below vacuum,\cite{18} aiding in electron injection and decreasing turn-on voltage. The BT unit is also responsible for electron transport within F8:BT copolymers with F8BT displaying a relatively high electron mobility of ~$10^{-3}$ cm$^2$/Vs\cite{161,255}. With the J-V data, it can be observed that the current density above turn-on increases with increasing BT incorporation from 10-50% BT. However, the 99F8:1BT copolymer EML device shows a larger current density than the 95F8:5BT device. This is likely
due to the BT unit acting as an electron trap and suppressing electron transport at only 5% loading. Below this, electron polarons could be transported through F8 segments as BT units are not present in enough density to cause substantial electron trapping. Above 5% BT loadings, electrons can begin to find transport pathways through the BT units.

The 95F8:5BT device showed the highest peak efficiencies of all devices with $\eta = 0.75$ cd/A and $\eta_w = 0.43$ lm/W, whilst 90F8:10BT and 80F8:20BT showed the lowest efficiencies. Unlike the F8:BSP case, there does not appear to be a correlation between efficiency and BT unit content. The relatively low PLQE of the F8:BT copolymers (shown in Figure 6.5 (b)) suggests the material quality could be low, the cause of which could be chemical defects or leftover catalyst. Literature values of thin film F8BT PLQE are reported to be up to 60%,$^{[161]}$ whilst the F8BT measured here is surprisingly only ~11%. However, since increasing BT content can tune colour emission (as observed in the PL), the EL spectra for each device was measured at 8 V and CIE co-ordinates calculated. The EL spectra and associated CIE co-ordinates (plotted on a CIE diagram) for each copolymer are shown below in Figure 6.8.

Figure 6.8: (a) EL spectra recorded at 8 V and (b) associated CIE co-ordinates for 99F8:1BT, 95F8:5BT, 90F8:10BT, 80F8:20BT, 70F8:30BT and F8BT PLED devices.

Similarly to the spectra observed in the PL, the EL spectra of the (1-x)F8:xBT copolymer devices shows a red-shift of the main CT emission peak with increasing BT content from ~529 nm (for 1% BT) to ~550 nm (50% BT). This shift alters the colour of the emission from blue-green ($1\%$ BT CIE $(x, y) = 0.335, 0.551$) to green-yellow ($50\%$ BT CIE $(x, y) = 0.442, 0.547$). Additionally, the colour saturation increases as more BT units are incorporated into the copolymer, with the saturation at only 69% for 99F8:1BT copolymer device, increasing up to 96% for F8BT. As observed in the PL, the 99F8:1BSP copolymer shows a small amount of
residual F8 emission located at ~420 nm which is absent for higher BT fractions. The device data is summarised below in Table 6.2.

**Table 6.2:** Summary of device parameters for (1-x)F8:xBT EML PLED devices.

<table>
<thead>
<tr>
<th>EML layer</th>
<th>Turn-on Voltage (V)</th>
<th>Luminous Efficiency (cd/A)</th>
<th>Luminous Power Efficiency (lm/W)</th>
<th>CIE (x,y)</th>
<th>Colour Saturation</th>
</tr>
</thead>
<tbody>
<tr>
<td>99F8:1BT</td>
<td>4.2</td>
<td>0.4 @ 12 V</td>
<td>0.11 @ 8V</td>
<td>0.335, 0.551</td>
<td>69%</td>
</tr>
<tr>
<td>95F8:5BT</td>
<td>4.0</td>
<td>0.74 @ 5.8 V</td>
<td>0.43 @ 5.2 V</td>
<td>0.396, 0.574</td>
<td>88%</td>
</tr>
<tr>
<td>90F8:10BT</td>
<td>4.0</td>
<td>0.16 @ 8 V</td>
<td>0.07 @ 7 V</td>
<td>0.378, 0.582</td>
<td>93%</td>
</tr>
<tr>
<td>80F8:20BT</td>
<td>3.6</td>
<td>0.17 @ 10 V</td>
<td>0.07 @ 4.6 V</td>
<td>0.401, 0.575</td>
<td>93%</td>
</tr>
<tr>
<td>70F8:30BT</td>
<td>3.2</td>
<td>0.44 @ 4.6 V</td>
<td>0.31 @ 4.2 V</td>
<td>0.403, 0.571</td>
<td>94%</td>
</tr>
<tr>
<td>F8BT</td>
<td>2.8</td>
<td>0.46 @ 5.8 V</td>
<td>0.32 @ 3.8 V</td>
<td>0.442, 0.547</td>
<td>96%</td>
</tr>
</tbody>
</table>

To examine how β-phase formation in F8:BT copolymers affects electrical properties, PLED devices were fabricated with 99F8:1BT and 95F8:5BT β-phase EML layers. Since β-phase can act as charge traps, it could be that the β-phase helps to device performance as an exciton formation site and improving charge balance. The PLED device characteristics are shown below in Figure 6.9.
The J-V-L measurements (Figure 6.9(a)) for both 99F8:1BT and 95F8:5BT devices show only very small differences between glassy and β-phase devices. However, Figure 6.9(b) shows an increase in peak luminous and luminous power efficiencies for 95F8:5BT β-phase devices, indicating that the β-phase segments aid in charge carrier balance and exciton formation within the PLED devices. Here, the peak luminous efficiency increased from 0.74 cd/A to 0.82 cd/A, whilst the peak luminous power efficiency increased from 0.42 lm/W to 0.52 lm/W. For 99F8:1BT, the peak luminous efficiency shows a slight decrease from 0.40 cd/A to 0.37 cd/A, however the peak luminous power efficiency increases from 0.11 lm/W to 0.12 lm/W. The EL spectra of each device are shown below in Figure 6.10.
Figure 6.10: (a) EL spectra recorded at 8 V and (b) associated CIE co-ordinates for glassy and β-phase 99F8:1BT and 95F8:5BT PLED devices.

Whilst the EL spectra of the 95F8:5BT devices remain relatively unaffected, the EL of the 99F8:1BT β-phase device shows a clear red-shift in the high energy F8 emission part of the spectrum (from ~420 to ~437 nm) indicating a shift from glassy to β-phase based F8 emission. Additionally, the intensity of the F8 emission increases, with β-phase F8 emission accounting for 11% of the total EL emission of β-phase 99F8:1BT device (compared to ~3.5% emission for glassy device). This causes a shift in CIE (x,y) colour co-ordinates from (0.335, 0.551) to (0.327, 0.521). By tuning both β-phase fraction and BT unit incorporation, this system could be used to fabricate efficient white light emitting diodes since emission occurs in both the high energy (F8 units) and low energy (F8-BT centred charge transfer emission) parts of the electromagnetic spectrum. The spectral stability of the EL emission also increases with β-phase incorporation. Figure 6.11 below shows voltage dependent EL measurements for both glassy and β-phase 99F8:1BT devices.
Interestingly, the 99F8:1BT glassy devices show an increase in F8 emission intensity as voltage increases whilst the \( \beta \)-phase devices do not show a change in the proportion of F8 emission as voltage is varied. This could be due to saturation of BT centred and \( \beta \)-phase centred emission sites for the 99F8:1BT devices, even at 6 V. This indicates the emission of \( \beta \)-phase 99F8:1BT devices is more stable than glassy phase devices, and thus are more suitable for use as the EML for PLED devices.

To summarise, \( \beta \)-phase formation has been demonstrated in a series of (1-x)F8:xBT copolymers from 1-10% BT loadings. At 20%, 30% and 50% BT, no \( \beta \)-phase formation is observed. The PL spectra of the \( \beta \)-phase F8:BT copolymers are dominated by F8-BT centred charge transfer emission with a minor component of F8 emission visible. This is unlike the F8:BSP copolymers where F8 \( \beta \)-phase emission dominated and is because the F8-BT CT exciton is much more stabilised in energy compared to the F8-BSP CT exciton. Incorporating \( \beta \)-phase into the active layer of F8:BT copolymer devices can aid in both increasing the efficiency of the device and stabilising the EL emission, demonstrating potential for the system to be used for white light emitting OLEDs.

### 6.4 Discussion

In this chapter the formation of \( \beta \)-phase segments in thin films of 99F8:1BT, 95F8:5BT and 90F8:10BT copolymers is observed post solvent vapour annealing at a fraction of 9%, 7% and 5% respectively. However, the PL spectra is dominated by F8BT centred CT emission; \( \beta \)-phase 99F8:1BT films shows \(~96\%\) CT emission in PL whilst 95F8:5BT and 90F8:10BT films show...
>99% CT emission. The EL spectra of the β-phase 99F8:1BT and 95F8:5BT PLED devices are similarly dominated by CT emission.

This case is different to the β-phase microstructure F8:BSP copolymers (see Chapter 5) where, for 97F8:3BSP and 95F8:5BSP, β-phase makes up the majority of the PL and EL emission (69 and 62% respectively). This is despite less β-phase being formed in equivalent 95F8:5BSP copolymers than 95F8:5BT. This can be explained by the differences in the optoelectronic properties between the copolymers. In F8:BT copolymers, the LUMO is strongly localised to the BT unit due to the large separation in energies between the LUMOs of the F8 and BT monomers (ΔE ~ 1.5 eV).\cite{256} By contrast, the HOMO energies are well matched thus the relatively delocalised across the backbone of the polymer.\cite{256,257} This manifests itself in a lower energy CT type absorption at ~430 nm and emission at ~550 nm. The F8:BSP copolymers however, show an energy offset in both the HOMO and LUMO, causing localisation of the HOMO on the BSP unit whilst the LUMO is relatively localised on the F8 units.\cite{236} The offset in energy is not as great at in the F8-BT case (ΔE ~ 0.3 eV), thus the CT-type emission observed is much higher in energy which is centred at ~455 nm.

The differences in chemical structure influences the type of intra- and inter-molecular energy transfer within the copolymers. As previously discussed in Chapter 5, energy transfer in F8:BSP copolymers from glassy F8 segments to the F8-BSP centred CT excitons occurs via transfer of the hole to the BSP unit to form a CT-like state; this happens on a time scale of ~1.5 ps.\cite{236} Forster energy transfer does not occur due to the lack of separate CT absorption band that lies in the energy range of the F8 emission. However, for β-phase F8:BSP copolymers, thermally-assisted Forster energy transfer can occur from the glassy F8-segments to β-phase F8-segments; this process happens on a timescale of ~3 ps.\cite{49} The competing processes result in a superposition of BSP-centred CT emission and β-phase excitonic emission (see Chapter 5). Energy transfer between β-phase F8 excitons and F8:BSP CT states does not occur. By contrast, in F8:BT copolymers energy transfer from glassy F8 segments to F8-BT CT states occurs via Forster energy transfer due to the overlap in glassy F8-emission and the F8-BT CT absorption band.\cite{18,239,258,259} However, when β-phase F8 units are also present, Forster energy transfer can still occur from β-phase F8 segments due to overlap from β-phase emission with the F8-BT CT absorption band. This results in only a small fraction of β-phase emission present in the PL and EL spectra of β-phase microstructure F8:BT films. The energy transfer mechanisms in glassy and β-phase F8:BT copolymers is summarised in Figure 6.12.
Figure 6.12: Schematic energy level diagram of energy transfer occurring in (a) glassy F8:BT copolymers and (b) β-phase F8:BT copolymers.

6.5 Conclusion

UV-visible absorption measurements of solvent annealed F8:BT copolymers at 1%, 5% and 10% BT fraction also showed β-phase formation, however the PL was dominated by F8-BT CT emission with only minor fractions of F8 β-phase emission visible. Incorporating β-phase into the active layer of F8:BT copolymer devices can aid in both increasing the efficiency of the device and stabilising the EL emission, demonstrating potential for the system to be used for white light emitting OLEDs. The intensity of F8 emission also increased with β-phase incorporation, leading to a shift towards the white colour point from (0.335, 0.551) to (0.327, 0.521).
Chapter 7: Interfacial Energetics and Surface Photovoltage of Mixed Halide Perovskite Semiconductors

The work carried out in this chapter was performed in collaboration with Matyas Daboczi and is in preparation for publication. Matyas Daboczi fabricated and characterised the perovskite solar cells.

7.1 Introduction

Hybrid organic-inorganic lead halide perovskites are a novel class of semiconductors that have attracted significant interest from the research community in the last six years.[5] These materials have several properties that make them ideal materials for optoelectronic devices such as high absorption coefficients, low exciton binding energies, optical band-gap tenability and high photoluminescence quantum yield.[98,260–262] Additionally, these materials can be solution-processed, making them attractive from a manufacturing perspective. Despite the facile methods used to deposit lead halide perovskite materials, there has been a rapid increase in device performance of perovskite-based photovoltaics from 4% in 2009[99] to over 20% in 2017.[113] However, issues regarding the lifetime and stability of perovskite devices remain a challenge for commercialisation.

Whilst the initial research on lead halide perovskites has focused on methylammonium lead iodide (MAPI),[263,264] subsequent efforts have focused on tuning the properties of the perovskite crystal by introducing mixtures of halide anions (I\(^-\), Br\(^-\) and Cl\(^-\)).[110,122,265,266] In particular, mixtures of bromide and iodide ions (MAPI\(_{1-x}\)Br\(_x\)) have been shown to alter the band gap of the perovskite from 1.6 eV (for MAPI) to 2.3 eV (in MAPBr).[110,267] In conventional mesoporous titanium oxide (TiO\(_2\)) based solar cells, increasing bromide content up to 25% lead to improvement in solar cell efficiencies primarily by an increase in the open-circuit voltage (V\(_{OC}\)). However, incorporating greater amounts of bromide beyond 25% lead to a decrease in device performance, primarily because of a decrease in short circuit current (J\(_{SC}\)) due to the blue-shift of the absorption onset[110,265] as well as an abrupt reduction in V\(_{OC}\).[121,265] Phase segregation of the perovskite into iodide and bromide rich phases has been suggested as the main challenge in maximising the device efficiency of mixed halide perovskite solar
However, careful selection of hole-extracting materials can increase the device efficiency of wide band gap perovskites. Tuning the halide content towards bromide also provides additional benefit in increasing the stability and lifetime of the perovskite.

When designing the device structure of mixed halide solar cells, knowledge of the energy levels of each layer is critical. Considering the HOMO, LUMO and Fermi levels ($E_f$) of the active perovskite layer (as well as the hole transport layer (HTL) and electron transport layer (ETL)) are key in understanding how to improve device efficiency. In this chapter, several techniques are used to gain a deeper understanding of both the energy levels of mixed halide perovskite layers and their interactions with HTLs and ETLs. Ultraviolet ambient pressure photoemission spectroscopy (UV-APS) is used to measure the HOMO values of CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ perovskites at 0, 25, 50, 75 and 100 mol% Br loadings whilst Kelvin probe microscopy (KPM) is used to determine the surface Fermi level (workfunction) in dark. Further measurements are taken of the Fermi level under illumination. The difference between the Fermi levels taken in dark and under white light illumination is known as the surface photovoltage (SPV) and is induced by the redistribution of photogenerated charge carriers within the photoactive layer under influence of an internal electric field caused by a space charge region (see Chapter 3 for more details). Thus, this technique allows tracking of light-induced cancellation (flattening) of band-bending at either the surface of the semiconductor layer or at a buried interface. Since the Kelvin probe method is contactless, the photovoltage of device stacks can be measured layer-by-layer and thus information relating to the contribution of each layer to the photovoltage can be revealed. Previous measurements of perovskite layers reveal that the SPV is closely related to the $V_{oc}$ and that selection of electron and hole transporting contacts plays a large role in determining the SPV values.

In this study, the above techniques are utilised along with UV-vis and PL measurements to investigate the behaviour of mixed halide CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ perovskites as the active layer in inverted perovskite solar cells. Here, the energy levels of each perovskite layer, along with the hole and electron transport layers are considered in the explanation of device behaviour, whilst low temperature measurements help explain the stability and phase behaviour of each perovskite material and how that impacts photovoltaic performance. This work allows greater insights into the photovoltaic processes within perovskite solar cells and how the materials and device structure can be designed to offer greater PV performance for mixed halide perovskites.
7.2 Materials

The perovskite materials used in this chapter are mixed halide perovskites of the form CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ where $x = 0, 0.25, 0.5, 0.75$ and $1$ molar ratio. Perovskite precursor solutions were prepared by separately weighing the methylammonium halide (either iodide or bromide) and lead halide powders using an electronic balance before transferring to a single vial. A solvent mixture of γ-butyrolactone (GBL) and dimethyl sulfoxide was added in a ratio of 7:3 to reach a concentration of 1 M. Mixed halide solutions of methylammonium lead bromide and methylammonium lead iodide were then produced by blending the individual solutions in the desired ratio. PCBM dissolved in chlorobenzene at a concentration of 20 mg/ml was used to deposit the electron transport layer.

For SPV measurements, three different device stacks were prepared (shown in Figure 7.1): a) ITO/CH$_3$NH$_3$PbI$_{1-x}$Br$_x$, b) ITO/PEDOT:PSS/CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ and c) ITO/PEDOT:PSS/CH$_3$NH$_3$PbI$_{1-x}$Br$_x$/PCBM.

![Figure 7.1: Schematic diagram of sample structures for SPV measurements. (a) shows CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ deposited on bare ITO, whilst (b) shows CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ deposited on an ITO/PEDOT:PSS layer. (c) shows the stack as in (b) but with a PCBM ETL deposited as the final layer.](image)

For fabrication of solar cells (performed by Matyas Daboczi), the stack was completed by the evaporation of calcium and aluminium cathode. For optical measurements (UV-vis absorption, photoluminescence spectroscopy and TCSPC) each CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ layer was deposited on a quartz spectrosil slide.
7.3 Relationship between Optical Band Gap and Halide Content

![Figure 7.2](image)

**Figure 7.2:** (a) Normalised absorption spectra for CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ perovskites as a function of wavelength. Inset shows absorption spectra as a function of energy showing the energy of the band gap increases with increasing bromide content. (b) shows diagram of energy gaps with increasing bromide content.

To investigate how the optical properties of the mixed halide vary with halide composition, UV-visible absorption measurements were taken for CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ (where $x = 0, 0.25, 0.50, 0.75$ and 1) and shown in **Figure 7.2**.

The onset of the absorption band is blue shifted with respect to increasing bromide content. As the bromide content increases, the absorption onset wavelength shows a systematic decrease from 785 nm (for MAPI) to 723 nm, 656 nm, 593 nm and 540 nm for 25% Br, 50% Br, 75% Br and MAPBr respectively. This causes the energy gap, $E_g$, to increase from 1.58 eV for MAPI to 1.71, 1.90, 2.08 and 2.30 eV as the Br content increases. This shows that the energy band gap can be finely tuned with bromide composition allowing band gap tailoring for use in multi-coloured solar cell and LED applications.

7.4 Characterisation of Mixed Halide Perovskite Photovoltaics

Solar cell devices for each mixed halide perovskite were fabricated in an inverted (TiO$_2$ free) structure comprised of ITO/PEDOT:PSS/CH$_3$NH$_3$PbI$_{1-x}$Br$_x$/PCBM/Ca/Al. These structures have been previously used before for MAPI active layer solar cells and show an advantage over traditional TiO$_2$ cells in that they do not show hysteresis at room temperature.\textsuperscript{[277]} The average reverse scan JV curves illuminated under 1 sun intensity are shown below in **Figure 7.3** whilst a summary of the key photovoltaic parameters are shown in **Table 7.1**. A comparison of the average forward and reverse scans are shown in **Figure A.1** in Appendix A. Interestingly, the 50% and 75% Br devices show a strong dynamic hysteresis between the forward and reverse
scans whilst the MAPI, 25% Br and MAPBr devices show only minimal hysteresis. This is likely to be linked to both phase segregation and ionic movement within the cell.[278]

![Figure 7.3: Reverse current voltage scan for mixed halide CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ perovskite solar cells in an ITO/PEDOT:PSS/CH$_3$NH$_3$PbI$_{1-x}$Br$_x$/PCBM/Ca/Al structure under 1 sun illumination intensity.](image)

**Table 7.1:** Summary of average device performance for mixed halide CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ perovskite solar cells in an inverted device architecture with associated errors.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{oc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>Fill Factor</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPI</td>
<td>13.72 ± 0.22</td>
<td>0.86 ± 0.01</td>
<td>0.74 ± 0.02</td>
<td>8.71 ± 0.24</td>
</tr>
<tr>
<td>25% Br</td>
<td>12.01 ± 0.19</td>
<td>0.98 ± 0.01</td>
<td>0.76 ± 0.01</td>
<td>8.93 ± 0.21</td>
</tr>
<tr>
<td>50% Br</td>
<td>6.41 ± 0.10</td>
<td>0.76 ± 0.05</td>
<td>0.37 ± 0.01</td>
<td>1.76 ± 0.12</td>
</tr>
<tr>
<td>75% Br</td>
<td>1.77 ± 0.05</td>
<td>0.58 ± 0.01</td>
<td>0.36 ± 0.01</td>
<td>0.37 ± 0.02</td>
</tr>
<tr>
<td>MAPBr</td>
<td>1.12 ± 0.08</td>
<td>0.74 ± 0.06</td>
<td>0.41 ± 0.05</td>
<td>0.35 ± 0.09</td>
</tr>
</tbody>
</table>

The MAPI solar cell achieved an average power conversion efficiency (PCE) value of 8.71 ± 0.24%, similar to values achieved previously in this structure,[277] whilst the largest average PCE achieved was 8.93 ± 0.21% which was achieved using the 25% Br perovskite. However, the uncertainty in the MAPI and 25% Br PCEs do not conclusively show that the 25% Br is
more efficient than MAPI, though previous literature indicates the addition of 20-25% Br atoms is beneficial to perovskite solar cell performance.\cite{110,267} From here the PCE decreases as more bromide content is added with PCE values of 1.76 ± 0.12%, 0.37 ± 0.02% and 0.35 ± 0.09% for 50% Br, 75% Br and MAPBr active layers respective. The primary reasons for this appear to be a decrease in $J_{sc}$, $V_{oc}$ and FF as bromide content is added beyond 25% Br.

The short circuit current ($J_{sc}$) decreases from 13.72 ± 0.22 mA/cm$^2$ for MAPI to 1.12 ± 0.08 mA/cm$^2$ for MAPBr. This downward trend in $J_{sc}$ has been noted previously in TiO$_2$ conventional perovskite cells and has been attributed to the blue-shift in absorption onset as more Br ions are incorporated into the active layer, leading to less photons absorbed and hence less photogenerated current produced.\cite{110,121}

There is an increase in $V_{oc}$ from 0.86 ± 0.01 V for MAPI to 0.98 ± 0.01 V for the 25% Br device, however the $V_{oc}$ then begins to decrease as more Br ions are added; the 50% Br device shows an open circuit voltage of 0.76 ± 0.05 V whilst the 75% Br device displays an even smaller $V_{oc}$ of 0.58 ± 0.01 V. When using MAPBr however, the $V_{oc}$ then begins to increase slightly again, showing a value of 0.74 ± 0.06 V. Whilst the initial increase in $V_{oc}$ is due to the wider band gap of the 25% Br perovskite, the decrease in $V_{oc}$ at Br content above this could be due to phase segregation of iodide and bromide ions.\cite{123,269}

Finally, the fill factor decreases with bromide content from 0.74 ± 0.02 and 0.76 ± 0.01 (for MAPI and 25% Br) to 0.36 ± 0.01 (for 75% Br), with the MAPBr device showing a slight increase to 0.41 ± 0.05. The decrease in FF is likely to be due to an increase in the series resistance ($R_s$) of the cells. The main contribution to $R_s$ is active and interfacial layer resistances within the cell, indicating that either incorporating Br ions into the active layer may increase resistance, or the increasing mismatch of the perovskite and PCBM LUMOs may increase $R_s$ within the cell. Optimising the electron transport layer material with a higher lying LUMO may further increase device efficiency for the 25% Br and MAPBr solar cells,\cite{271} however the poor performance of the 50% and 75% Br devices is likely to be due to phase segregation of iodide and bromide ions.\cite{123,270}

In summary, the performance of inverted structure MAPI perovskite solar cells is marginally increased by adding 25% Br ions into the perovskite layer. The origin of the increase in PCE is due to an increase in $V_{oc}$ (from 0.86 to 0.98 V) which is brought about by an increase in the energy gap of the perovskite layer (from 1.58 to 1.71 eV). The increase in $V_{oc}$ is however accompanied by decrease in $J_{sc}$ (13.72 to 12.01 mA/cm$^2$), due to a reduction in the generated
photocurrent. Further increasing the bromide content within the perovskite layer leads to large reductions in PCE due to further reductions in $J_{sc}$, ionic phase segregation and charge recombination.

### 7.5 Surface Topography

To check for the film quality and uniformity between samples, atomic force microscopy (AFM) measurements were taken for each mixed halide perovskite film deposited on ITO. Figure 7.4 below shows the AFM topography scan for ~150 nm CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ films along with a diagram of the perovskite unit crystal cell structure. Table 7.2 shows the r.m.s. roughness values of each sample.

**Figure 7.4**: 10 x 10 µm AFM topography images of (a) CH$_3$NH$_3$PbI, (b) CH$_3$NH$_3$PbI$_{0.75}$Br$_{0.25}$, (c) CH$_3$NH$_3$PbI$_{0.5}$Br$_{0.5}$, (d) CH$_3$NH$_3$PbI$_{0.25}$Br$_{0.75}$ and (e) CH$_3$NH$_3$PbBr deposited on ITO substrate. All perovskite layers are ~150 nm thickness. (f) shows the perovskite crystal structure where X$^-$ = Br$^-$ or I$^-$. 

[Image of AFM topography scans and perovskite crystal structure diagram]
**Table 7.2:** Surface roughness values for mixed halide perovskites on ITO substrate.

<table>
<thead>
<tr>
<th>Perovskite composition</th>
<th>R.M.S Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPI</td>
<td>9.88</td>
</tr>
<tr>
<td>25% Br</td>
<td>13.60</td>
</tr>
<tr>
<td>50% Br</td>
<td>7.85</td>
</tr>
<tr>
<td>75% Br</td>
<td>6.90</td>
</tr>
<tr>
<td>MAPBr</td>
<td>16.0</td>
</tr>
</tbody>
</table>

The AFM reveals that all films show a uniform, pinhole free layer that are relatively smooth for ~150 nm thick films, similar to those found in literature.\[279,280\] The roughness value for MAPI films were 9.88 nm whilst MAPBr films showed the highest roughness with an r.m.s. value of 16.0 nm. This is due to the larger crystals formed by MAPBr compared to MAPI. Interestingly however, the mixed halide (25, 50 and 75%) all showed smoother films compared to MAPBr, with 50% and 75% films showing even smoother films than MAPI itself. The smoother films of 50% and 75% Br could be due to greater phase segregation compared to the 25% Br sample.

**7.6 Mapping the Energy Levels of Perovskite Materials**

**7.6.1 HOMO Determination via Air Photoemission Spectroscopy (APS)**

Air photoemission spectroscopy (APS) is a technique used to measure the absolute workfunction for metals and the ionisation potential (IP) or highest occupied molecular orbital edge (HOMO) for organic semiconductors/perovskites. A deuterium lamp acts as a source of ultra violet (UV) light of 3.5-7.0 eV energies which are incident upon a sample. Incident radiation above the threshold energy of the sample (i.e. energies greater than the HOMO) will cause photoelectrons to be ejected, which will then ionise the surrounding O\(_2\) and N\(_2\) air molecules. A positively charged non-vibrating Kelvin probe tip is then used to detect the charged air molecules. The lateral resolution of the technique is determined by the spot size of the UV illumination, which is 4-5 mm.\[133,134\] The technique is sensitive to only the surface of the sample since the vertical depth that can be probed is 5-10 nm below the surface.\[131\]
Figure 7.5: (a) APS spectra for CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ perovskites on an ITO substrate. HOMO levels were found by extrapolating the linear part of the curve to the baseline signal level. (b) energy of extrapolated HOMO levels.

**Figure 7.5 (a)** shows the photoemission spectra of the mixed halide CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ perovskite films on ITO substrates whilst **Figure 7.5 (b)** shows the extracted HOMO levels. The cube root of the photoemission is plotted against energy because for most semiconductors, the density of photoemission current increases linearly with the cube root of the photon energy above ionisation potential.[138] By extrapolating the linear part of the photoemission curve to the baseline, the HOMO energy can be found. Since the APS measurement only probes the first 5-10 nm of the sample, and that ITO has a much weaker photoemission spectrum (thus cannot be measured using the APS), it is very unlikely the APS spectra is influenced by the layer beneath the perovskite.

The extrapolated HOMO value for MAPI (CH$_3$NH$_3$PbI) was found to be 5.32 ± 0.05 eV. Previous APS and high vacuum UV photoemission spectroscopy (UPS) have shown MAPI to have HOMO value between 5.3 and 5.4 eV, closely matching the value found here.[124,267,281] The HOMO value extracted for MAPBr (CH$_3$NH$_3$PbBr) is 5.63 ± 0.05 eV, significantly deeper than MAPI. This agrees well with previous UPS measurements found in the literature which put the HOMO of MAPBr between 5.6 - 5.9 eV.[282–285] Interestingly, the values for the mixed halide perovskite samples show only a small systematic increase in HOMO energy from MAPI; the values found were 5.35 ± 0.05, 5.36 ± 0.05 and 5.40 ± 0.05 for 25%, 50% and 75% Br loadings respectively. This indicates that the APS spectra are dominated by MAPI emission at low energies. Whilst this would be understandable at low (25%) Br loadings, the fact that the emission spectra still show significant MAPI emission at 50% and 75% Br loadings lends evidence for phase segregation of iodide and bromide regions in these samples. These
measurements indicate the first HOMO values recorded in literature for mixed halide perovskite materials.

Figure 7.6: Ambient pressure photoemission spectoscopy data for (a) CH$_3$NH$_3$PbI (MAPI), (b) CH$_3$NH$_3$PbI$_{0.75}$Br$_{0.25}$, (c) CH$_3$NH$_3$PbI$_{0.5}$Br$_{0.5}$, (d) CH$_3$NH$_3$PbI$_{0.25}$Br$_{0.75}$ and (e) CH$_3$NH$_3$PbBr (MAPBr). The blue shaded area between photoemission curve, extrapolated fit and baseline indicates trap/defect density of states within the perovskite. (f) shows value of each shaded area.

In general, semiconductor materials often contain sub-band gap states that exist near the top of the valence band (often referred to as trap, defect or tail states) which are often caused by disorder within a material and can be occupied by thermally excited electrons.[286–288] The APS
can be used as a tool to measure the relative density of trap or defect states within a semiconductor as has previously been shown in silicon. The trap states can be identified on an APS spectra plot by the low energy photoemission intensity between the baseline (orange dashed line in Figure 7.6) and the linear part of the spectra (blue dashed line in Figure 7.6). The area between the baseline, linear photoemission and trap photoemission gives an estimation of the trap density of states. Figure 7.6 (a) – (e) shows the individual photoemission spectra for each of the mixed halide CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ perovskite layers. The blue shaded area shows the relative trap density of states for each sample in arbitrary units, and the extrapolated area is then plotted as a function of bromide content in Figure 7.6 (f).

The data shows that the relative trap density of states increases with the amount of bromide content incorporated into the perovskite layer with the 100% Br (MAPBr) sample showing the largest density of trap states and MAPI sample showing the least. This could be due to more defects within the perovskite crystal as more bromide ions are added; the origin of which is likely to be more unreacted Pb$^{2+}$ ions that are not incorporated into the perovskite crystal structure. This could be due to different solubilities and film formation of bromide ions in comparison to iodide ions – thus the greater the amount of Br ions within the perovskite film there is likely to be a greater density of trap states. Greater density of trap states within perovskite crystals has been linked to an increase in non-radiative recombination which causes loss mechanisms in perovskite solar cells, reducing both the J$_{sc}$ and fill factor. The increase in trap state density correlate with the decrease in solar cell device performance presented in section 7.7 which show a reduction in J$_{sc}$ and fill factor with increasing bromide content.

In summary, the HOMO values of MAPI and MAPBr measured via APS were found to be 5.32 and 5.63 eV respectively which correlate well to literature values. However, mixed halide perovskites show only a small increase in HOMO energies as more bromide is incorporated (from 5.35 to 5.40 eV), indicating MAPI domains largely control the HOMO energies of mixed halide perovskites. The APS measurements also revealed the trap (defect) density of states increases with bromide content, with MAPBr showing a 1.8x larger TDoS than MAPI. This is could be related to the larger quantity of unreacted lead (Pb$^{2+}$) ions brought about by the difference in solvency of iodide and bromide ions and may cause charge recombination within the perovskite solar cells, leading to reduced device performance.
7.6.2 Fermi Level Measurements

To investigate the Fermi level (workfunction) values for the mixed halide CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ perovskite materials, contact potential difference (CPD) measurements were carried out using a vibrating gold-plated Kelvin probe tip, firstly on mixed halide perovskite layers deposited onto bare ITO, and then on the perovskite layers deposited onto ITO/PEDOT:PSS substrates to monitor how the workfunction of the perovskite changes with hole transport layer.

![Figure 7.7](image.png)

**Figure 7.7**: (a) contact potential difference measurements in dark for CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ perovskites on ITO and (b) workfunction measurements of CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ perovskites. Workfunction found by adding the contact potential difference to Kelvin probe tip workfunction.

**Figure 7.7** (a) shows the contact potential difference values as a function of time whilst **Figure 7.7** (b) shows the extracted Fermi level value for ITO and the mixed halide CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ perovskites deposited on ITO. As can be observed from **Figure 7.7** (a), all samples show a very stable contact potential difference indicating little degradation occurs within the measurement timeframe. The stable Fermi level of bare ITO was found to be 4.69 eV, whilst the ITO/perovskite samples showed Fermi levels of 4.710 ± 0.005, 4.720 ± 0.005, 4.810 ± 0.005, 4.960 ± 0.005 and 5.00 ± 0.005 eV for MAPI, 25% Br, 50% Br, 75% Br and MAPBr respectively.

Interestingly, the MAPI and 25% Br Fermi levels show very little change from the ITO Fermi level, with increases of only 20 and 30 meV respectively. This could imply that both the MAPI and 25% Br samples have relatively low carrier concentration levels (i.e. have low levels of doping) and as such have relatively large depletion regions – larger than the thickness of the perovskite layer. This would cause the observed Fermi level to shift towards the HTL. Indeed, previously the depletion width of MAPI has been measured to be up to 300 nm thick,$^{[289]}$ which
given that the perovskite layer used is only 150 nm thick means that the perovskite Fermi level is likely to be strongly influenced by the HTL it is deposited on.

Beyond 25% Br, the Fermi level of the mixed halide perovskite samples on ITO begins to increase up to 5.00 eV for the MAPBr sample. This could imply that as bromide content increases, the level of p-doping increases which decreases the width of the depletion region.

Figure 7.8: (a) contact potential difference measurements in dark for CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ perovskites on ITO/PEDOT:PSS and (b) workfunction measurements of CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ perovskites on ITO/PEDOT:PSS.

Figure 7.8 (a) shows the contact potential difference values as a function of time whilst Figure 7.8 (b) shows the extracted Fermi level value for PEDOT:PSS and the mixed halide CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ perovskites deposited on PEDOT:PSS. As with the samples deposited on ITO, the CPDs for each sample are very stable with no changes over the measurement time. The PEDOT:PSS Fermi level was found to be 5.00 eV, whilst the mixed halide samples deposited on PEDOT:PSS showed Fermi level values of 4.83 ± 0.005, 4.94 ± 0.005, 5.04 ± 0.005, 5.27 ± 0.05 and 5.42 ± 0.05 eV for MAPI, 25% Br, 50% Br, 75% Br and MAPBr samples respectively.

All PEDOT:PSS/mixed halide perovskite samples show a deeper Fermi level than their respective values deposited on ITO. This is further evidence of the Fermi level pulling phenomena whereby the deeper Fermi level of PEDOT:PSS causes the Fermi level of the perovskites to be ‘pulled’ downwards. Such observations were previously made for MAPI deposited on titanium oxide (TiO$_2$) substrates. The origin of the Fermi level pulling effect
is due to the mismatch in Fermi level energy between the substrate (either bare ITO or ITO/PEDOT:PSS) and perovskite. To align the Fermi levels, charges will transfer between the perovskite and substrate resulting in a charge depletion region within the perovskite. Figure 7.9(b) shows the energy level diagram of when Fermi level alignment is achieved, and the measured Fermi level of the perovskite is the same as the perovskite Fermi level in isolation ($\phi_{p,1}$). The depletion region is represented by the band bending. However, as perovskite materials generally do not have high levels of doping, the width of the depletion region can be large (up to ~300 nm), which in this case is larger than the thickness of the perovskite layer. This means that in these sample full Fermi level alignment is not achieved and the apparent measured Fermi level of the perovskite is strongly influenced by the substrate Fermi level (see Figure 7.9 (c)).

**Figure 7.9:** Energy level diagram showing semiconductor and ITO (a) not in contact, (b) in contact with full Fermi level alignment and (c) in contact but depletion width is greater than thickness of semiconductor.

Since it appears that the p-doping level of the perovskite appears to increase with increasing Br content, the depletion width will decrease (as depletion width, $w \propto N_d^{-1/2}$) and thus the samples with a larger Br content are less susceptible to the Fermi level pulling effect. A summary of all the measured energy levels (HOMO and Fermi level – solid lines) and estimated (LUMO – dashed lines) of each mixed halide perovskite as well as energy levels for ITO, PEDOT:PSS and PCBM are shown in Figure 7.10.
Figure 7.10: HOMO values (black bars) measured by air photoemission spectroscopy, with LUMO values (red bars) found by adding band gap found via UV-vis absorption spectroscopy. The dark workfunction values measured by Kelvin probe for samples on ITO (blue bars) and on PEDOT:PSS (green bars). Energy levels for PCBM are taken from reference [264].

From these measured energy level values, the expected band bending at the ITO/Perovskite and PEDOT:PSS/Perovskite interfaces can be predicted. The likely band bending for each sample is shown below in Figure 7.11. The measured dark Fermi levels of the perovskite and ITO indicate that when in contact with the ITO, the band bending for each perovskite layer at the ITO/perovskite interface is upward, indicating electrons will tend to accumulate towards the interface and holes will accumulate at the surface. The upward band bending is due to the Fermi level of the perovskites being deeper than the Fermi level of ITO. Since the Fermi level increases with Br content, this band bending will likely increase as more bromide is incorporated into the perovskite.
Figure 7.11: Schematic energy level band diagrams for mixed halide perovskites in contact with either ITO or PEDOT:PSS for (a,b) MAPI, (c,d) 25% Br, (e,f) 50% Br, (g,h) 75% Br and (i,j) MAPBr.
By contrast, as the PEDOT:PSS has a deeper Fermi level than ITO meaning that not all the mixed halide perovskite samples will bend upwards. The Fermi level of PEDOT:PSS is deeper than that of MAPI, 25% and 50% Br, but shallower than 75% Br and MAPBr. Hence, for 0-50% Br perovskites, the band bending is downwards where electrons will accumulate at the sample surface and holes will accumulate towards the interface. This is desirable for charge extraction in solar cells, whereas the upward band bending observed for 75% Br and MAPBr samples is not. This is reflected in the $J_{sc}$ which decreases with Br content (Table 7.1) from 13.72 mA/cm$^2$ (for MAPI) to 1.12 mA/cm$^2$ (for MAPBr) which could indicate hole extraction is worse as Br content increases.

In summary, the effective Fermi level of the perovskite layer is dependent upon two factors, (i) the halide composition of the perovskite and (ii) the buried interface in contact with the perovskite. Changing the halide composition of the perovskite from iodide to bromide, the Fermi level becomes deeper and closer to the HOMO level, thus becoming relatively more p-type. This could be related to the greater density of trap states within the bromide type perovskites as revealed in section 7.6.1. Changing the buried interface type from ITO/perovskite to PEDOT:PSS/perovskite results in a further downward shift of the perovskite Fermi level due to the relatively large depletion region of the perovskite. The resulting band bending shows that PEDOT:PSS is a suitable hole transporting material (HTM) for MAPI, 25% Br and 50% Br perovskites, however 75% Br and MAPBr perovskites may require a HTM with a deeper Fermi level. This may adversely affect the photovoltaic device performance of 75% Br and MAPBr by reducing the $J_{sc}$ due to poorer hole extraction from the active layer.

7.7 Probing the Change in Energetics under Illumination

In this section, the change in energy levels of mixed halide perovskites under illumination is probed via surface photovoltage (SPV). SPV measurements of perovskite materials can be complex due to its nature of being both an ionic and electronic conductor. Additionally, SPV can be generated both by the band bending caused by defect states situated at the surface of the perovskite (Figure 7.12(a)) and band bending caused by depletion between the buried interface of the perovskite at the hole transporting material (Figure 7.12(b)).
Here, SPV measurements are used to probe how the energetics of mixed halide perovskites change under illumination whilst in contact with (i) ITO, (ii) PEDOT:PSS and (iii) PEDOT:PSS and PCBM.

**7.7.1 ITO/Perovskite samples**

The mixed halide perovskite semiconductors are most commonly used as the active layer in solar cell devices.\textsuperscript{[110,121]} A useful technique to characterise the suitability of material stacks for use in solar cell devices is surface photovoltage, whereby the illumination induces changes of the Fermi level of a semiconductor material are monitored. Here, the surface photovoltage of ITO/CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{1-x}Br\textsubscript{x}, ITO/PEDOT:PSS/CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{1-x}Br\textsubscript{x} and ITO/PEDOT:PSS/CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{1-x}Br\textsubscript{x}/PCBM material stacks are measured. **Figure 7.13** shows the surface photovoltage of ITO/CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{1-x}Br\textsubscript{x} samples as a function of illumination intensity between 0 – 200 W/m\textsuperscript{2}. Interestingly, whilst the band bending from the ITO/CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{1-x}Br\textsubscript{x} alone would indicate only holes should be accumulated at the surface, most of the samples show a positive SPV which indicates accumulation of electrons at the surface. This suggests the SPV measured here is caused by predominantly band bending at the surface rather than at the buried interface.
Figure 7.13: Surface photovoltage of mixed halide CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ perovskites deposited on ITO as a function of incident light intensity.

At low light intensities (0 – 25 W/m$^2$), the 50% and 75% Br samples show a sharp increase in SPV, with the 75% Br sample showing an SPV value of 170 meV at only 20 W/m$^2$. The 50% Br sample then quickly plateaus, with only a small increase in SPV from 170 meV to 175 meV between 80 – 200 W/m$^2$. Likewise, the 75% Br sample quickly plateaus at ~20W/m$^2$ before decreasing to 150 meV over 20 – 200 W/m$^2$ intensities. The larger SPV of 50% and 75% Br materials at lower light intensities could be due to larger difference in workfunction energy levels causing greater internal field at the buried ITO/perovskite interface which leads to a larger SPV. The plateau of the SPVs at higher light intensities could be due illumination induced phase separation of the iodide and bromide regions inside the perovskites, leading to inversion of the electric field from ion migration (discussed further below).[291] This is supported further by the large hysteresis observed in the reverse current scans shown in Figure A.1 (Appendix A).

MAPI and 25% Br samples show a slightly slower initial increase in SPV with illumination intensity, with MAPI showing an SPV of 130 meV and 25% Br displaying an SPV of 160 meV at 20 W/m$^2$. Unlike the 50% and 75% samples, both the MAPI and 25% Br samples show a continued increase in SPV, with MAPI showing an SPV value of ~200 meV at 200 W/m$^2$, and 25% Br showing an SPV of ~245 meV. This shows typical photovoltaic material behaviour, implying the ion migration of these samples only a relatively small effect on the SPV. The
larger SPV of the 25%Br sample correlates well to the larger $V_{oc}$ of 25%Br photovoltaic cells, which is likely due to the wider bandgap and a reduction in charge recombination of the 25% Br perovskite at higher light intensities.

The MAPBr sample shows an interesting phenomenon whereby the SPV increases positively at low light intensities up to 120 meV at 30 W/m$^2$ before decreasing as the illumination intensity increases. At 125 W/m$^2$ light intensity, the SPV returns to 0 meV (i.e. the same Fermi level as in dark) before becoming negative. At the highest light intensity (200 W/m$^2$) the SPV is -90 meV, indicating the MAPBr sample is now accumulating holes at the surface rather than electrons. This could be due to reverse migration of ions at high light intensities to reverse the electric field within the perovskite, which also may cause increased charge carrier recombination.

As discussed above (and in Chapter 3), surface photovoltages are produced by movement of photogenerated charge carriers to cancel out internal electric fields within the material stacks. In perovskites however, there exists both electrons/holes and ions that can freely move under the influence of an electric field.$^{[292]}$ To probe further the possible processes that underlie the SPVs for each mixed halide perovskite sample, SPV transients (SPV measurements as a function of time) were measured for each perovskite at 40, 120 and 200 W/m$^2$ intensities. Figure A.2 shows the SPV transients for each mixed halide CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ sample on ITO at (a) 40, (b) 120 and (c) 200 W/m$^2$ respectively.

Here, the 25% Br sample shows the largest SPV at higher (200 W/m$^2$) light intensities whilst 75% Br shows the largest SPV at lower intensities (40 W/m$^2$). The SPV transients for 0-50% Br appear to be made up of a ‘fast’ (<1 s) component which is likely due to mobile photogenerated charge carriers (Figure 7.14 (a)), followed by a positive ‘slow’ component on the order of ~10$^2$ s, likely due to trapped charges or movement of mobile ions to balance out the internal fields generated within the perovskite (Figure 7.14(b)). Upon turning off the light, a sharp decrease (<1 s) in SPV is observed which is likely due to fast recombination of the photogenerated charges (Figure 7.14(c)) followed by a much slower decay (~10$^2$ s) in SPV, again likely due to movement of mobile ions (Figure 7.14(d)).
Figure 7.14: Schematic diagram showing processes within surface photovoltage transients. (a) shows ‘fast’ photogenerated charge carriers under illumination, (b) shows ion migration under illumination, (c) shows recombination of charges after illumination ceases and (d) shows reverse ion migration in dark.

The 75% Br perovskite also shows an initial fast (<1 s) turn on component however the ‘slow’ component (~10^2 s) is negative, implying the mobile ions drift in a different direction than the 0-50% Br samples to reduce the value of the SPV and causing an inversion of the electric field. This is likely due to the deeper Fermi level of the 75% Br. The MAPBr sample shows a positive SPV at low light intensities and a negative SPV at higher light intensities, possibly due to movement of mobile ions causing inversion of the electric field thus causing MAPBr to collect holes rather than electrons. This could be related to the smaller size of the ions in the MAPBr.

To summarise, intensity dependent SPV measurements reveal that 25% Br deposited on ITO has the largest SPV at high intensities (245 meV at 200 W/m²), however at lower intensities 75% Br has the highest SPV intensity. This is likely related to (i) devices made from 25% Br had the largest V_{oc} as shown in section 7.4, (ii) less charge recombination occurs in the 25% whilst light intensity increases than in other samples (most likely due to reduced density of defects) and (iii) the deeper Fermi level values of 75% Br and MAPBr causes a larger depletion region at the buried ITO interface causing reversed ion migration thus allowing negative SPVs to form at higher intensities.
7.7.2 PEDOT:PSS/Perovskite samples

Figure 7.15 shows the surface photovoltage of mixed halide \( \text{CH}_3\text{NH}_3\text{PbI}_{1-x}\text{Br}_x \) perovskites deposited on PEDOT:PSS as a function of illumination intensity. Here, the SPV profiles of each perovskite sample are drastically different compared to the bare ITO case.

![Surface photovoltage of mixed halide CH\(_3\)NH\(_3\)PbI\(_{1-x}\)Br\(_x\) perovskites deposited on PEDOT:PSS as a function of incident light intensity.](image)

**Figure 7.15:** Surface photovoltage of mixed halide \( \text{CH}_3\text{NH}_3\text{PbI}_{1-x}\text{Br}_x \) perovskites deposited on PEDOT:PSS as a function of incident light intensity.

In the case of MAPI, the SPV generated when deposited on PEDOT:PSS is much lower at all light intensities compared to when deposited on ITO, reaching only \(~78\) meV at 200 W/m\(^2\). The profile shows a steady increase in SPV over the intensity range and does not appear to saturate. The lower value of SPV on PEDOT:PSS compared to ITO is likely due to charge recombination at the PEDOT:PSS/MAPI interface.\[^{293,294}\]

The 25% Br perovskite also shows a smaller SPV value when deposited on PEDOT:PSS compared to ITO, showing a final SPV of \(~162\) meV at 200 W/m\(^2\) compared to \(~248\) meV on ITO. The 25% Br perovskite shows by far the largest SPV out of the mixed halide series, which correlates well with the increased \( V_{oc} \) observed in 25% Br devices (see section 7.4) and is likely to be due to the increase in the band gap and a reduction in charge recombination at the PEDOT:PSS/perovskite interface. The 50% and 75% Br samples deposited on PEDOT:PSS both show much lower SPVs compared to their ITO counterparts, with both displaying SPV
values of 62 meV and 30 meV at 200 W/m² respectively. The 50% Br sample shows a relatively larger increase in SPV up to ~40 W/m², after which the SPV then increases much more slowly with intensity. The 75% Br sample appears to level off quickly after the initial increase in SPV at low light intensities. This could be due to phase segregation of bromide and iodide ions that causes an increase in charge recombination, hence a lower SPV is observed.\[123\]

Interestingly the MAPBr sample shows drastically different SPV behaviour when deposited on PEDOT:PSS rather than on ITO. Rather than showing a large increase, then subsequent decrease in SPV (eventually becoming negative), the SPV shows a very small, linear increase with light intensity, showing a final SPV of ~27 meV. This shows that the PEDOT:PSS must significantly alter the internal electric field of the MAPBr, leading to only a small increase in SPV even at high intensities. This could be explained by the deeper Fermi level of the PEDOT:PSS reducing the internal electric field of the perovskite compared to when in contact with ITO, where the Fermi energy difference is greater. This may reduce the internal electric field inside the perovskite and hence reduce the ionic migration, hence no reversal in SPV is observed. The small SPV observed could also be caused by increased charge recombination due to the larger trap density of states previously measured (section 7.6). To investigate further the causes of these changes, SPV transient measurements were taken for each mixed halide perovskite sample deposited on PEDOT:PSS at 200 W/m². These are shown in Figure A.3. The SPV transients observed here are more conventional than those observed in Figure A.2, showing fast and slow components but all SPVs appear positive, as previously observed in the literature.\[295,296\] Both the MAPI and 25% Br samples show relatively similar turn-on SPV dynamics, with an initial ‘fast’ (< 1 s) increase in SPV (of ~60 meV in magnitude) followed by a slower, delayed rise in SPV on the order of 10² s, again likely be due to photogenerated charge carriers (fast) and ion migration (slow) respectively. The magnitude of the rise in the 25% Br sample is much larger, with the SPV reaching a value of ~164 meV after 200 s – by comparison MAPI reaches an SPV value of only 119 meV. The 50% and 75% Br samples show similar turn-on and turn-off transients as MAPI and 25% Br transients, albeit with a much slower rise in the SPV after the initial fast increase. The 50% Br only reaches ~70 meV after 200 s whilst the 75% Br levels off at ~40 meV. Finally, the MAPBr sample shows only relatively slow turn-on and off dynamics. The SPV increases slowly to a final value of ~30 meV after 200 s. No ‘fast’ turn-on and turn-off component appears to be observed, indicating the SPV could be generated mainly by ‘slow’ (trapped) charged or ions.
To summarise, all perovskite SPVs showed different SPV characteristics when deposited on PEDOT:PSS compared to ITO due to the deeper Fermi level of PEDOT:PSS causing different interfacial band bending at the buried HTL/Perovskite interface. Again, 25% Br showed the largest SPV due to a reduction in charge recombination at the PEDOT:PSS/Perovskite, likely because of a small defect density compared to 50% Br, 75% Br and MAPBr.

### 7.7.3 PEDOT:PSS/Perovskite/PCBM samples

Finally, SPV measurements were taken for the ITO/PEDOT:PSS/CH$_3$NH$_3$PbI$_{1-x}$Br$_x$/PCBM materials stack. Figure 7.16 shows the SPV of these samples as a function of light intensity. The SPV profiles here show some notable changes compared to both the ITO/CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ and ITO/PEDOT:PSS/CH$_3$NH$_3$PbI$_{1-x}$Br$_x$/PCBM materials structures.

![Figure 7.16: Surface photovoltage of mixed halide CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ perovskites in a PEDOT:PSS/Perovskite/PCBM structure as a function of incident light intensity.](image)

*Figure 7.16*: Surface photovoltage of mixed halide CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ perovskites in a PEDOT:PSS/Perovskite/PCBM structure as a function of incident light intensity.

Table 7.3 summarises the different values of SPV the MAPI, 25% and MAPBr samples for both the PEDOT:PSS/CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ and PEDOT:PSS/CH$_3$NH$_3$PbI$_{1-x}$Br$_x$/PCBM material stacks at low light intensities (25 W/m$^2$) and high light intensities (200 W/m$^2$).
Table 7.3: Summary of SPV values for MAPI, 25% Br and MAPBr samples at low light intensities (25 W/m²) and high light intensities (200 W/m²) deposited on PEDOT:PSS only or between PEDOT:PSS and PCBM.

<table>
<thead>
<tr>
<th>Perovskite composition</th>
<th>PEDOT/Perovskite</th>
<th>PEDOT/Perovskite/PCBM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low intensity (25 W/m²)</td>
<td>High intensity (200 W/m²)</td>
</tr>
<tr>
<td>MAPI</td>
<td>22</td>
<td>78</td>
</tr>
<tr>
<td>25% Br</td>
<td>40</td>
<td>162</td>
</tr>
<tr>
<td>MAPBr</td>
<td>2</td>
<td>27</td>
</tr>
</tbody>
</table>

Here, the MAPI sample shows the largest SPV out of all the perovskite layers, with the SPV continually increasing as a function of light intensity before beginning to level off at the higher intensities. At low light intensities of 25 W/m², the SPV shows a value of ~130 meV whilst the final SPV value reached ~292 meV at 200 W/m². The 25% Br sample by contrast shows an initial rapid increase at low intensities, reaching ~165 meV at 25 W/m². However, the SPV rapidly levels off and does not increase beyond intensities of 50 W/m², recording a final value of SPV of ~185 meV a 200 W/m². Interestingly, the perovskite solar cells devices measured under 1 sun illumination (1000 W/m²) shows the largest V<sub>oc</sub> for 25% Br and not MAPI. This could be due to the Al cathode aiding electron extraction from PCBM layer and preventing accumulation of electrons inside the PCBM that causes recombination.

The intensity dependent behaviour of the 25% Br sample could be due to the ability of PCBM extracting electrons from 25% Br perovskite. At low light intensities, electrons generated within the perovskite layer are able to be extracted into the PCBM layer more efficiently than in the case of MAPI. However as the light intensity increases, there is a greater build-up of charge within the perovskite layer. Due to the poorer LUMO alignment of PCBM (which has a LUMO of ~3.9 eV) with 25% Br (3.63 eV) compared to MAPI (3.73 eV), this leads to faster recombination within the 25% Br perovskite thus the amount of electrons that can be extracted into the PCBM layer is limited at higher illumination intensities. This limitation in SPV increase in the 25% Br/PCBM sample can be shown by the limited increase between low to high light intensities as the SPV increases only by a factor of 1.1 compared to increasing by a factor of 4.1 without the PCBM layer. By comparison, the MAPI SPV increases from low to
high light intensities by a factor of 2.24 with PCBM and by 3.54 without PCBM, showing that the interfacial recombination is reduced in MAPI compared to the 25% Br sample. Previous transient photovoltage measurements of MAPI and 20% Br solar cells also attribute $V_{oc}$ losses to increased recombination with Br loading, however this can be offset by the inclusion of a wider band gap fullerene, ICBA, into the electron extraction layer for better LUMO alignment.\cite{125}

The MAPBr sample again shows the most drastic change when PCBM is deposited on top. The MAPBr sample now shows a relatively large increase in positive SPV at low intensities (similar to the ITO/MAPBr sample) reaching $\sim120$ meV at 25 W/m$^2$, but now the SPV continually increases with intensity before levelling off near 200 W/m$^2$ at a value of 225 meV. This now indicates that the PCBM is efficiently collecting electrons from the MAPBr layer to generate a positive SPV. Further work is required to understand why PCBM appears to be more efficient at collecting electrons from MAPBr than from the 25% Br perovskite; the Fermi level of PCBM may play a role in understanding this.

To understand further the SPV processes for the PEDOT:PSS/CH$_3$NH$_3$PbI$_{1-x}$Br$_x$/PCBM material stacks, SPV transients were measured for each perovskite layer at 200 W/m$^2$ and are shown in the appendix as Figure A.4. Whilst all samples showed a very rapid initial increase ($< 1$ s) in SPV, MAPI and MAPBr SPV stayed constant over 200s, whilst the mixed halides (25%, 50% and 75%) show a slow decrease in SPV over the same time period. This could be due to the recombination occurring within the perovskite (discussed above) because of the poor electron extraction from the PCBM. The 25% Br sample however reaches the highest initial SPV ($\sim213$ meV) after turn on showing that at the highest illumination intensities the interfacial recombination processes play a key role.\cite{125} Further measurements with different ETL layers would be key to confirming this.

In summary, when PCBM is deposited on the mixed halide perovskites, 25% Br has the highest SPV at low light intensities but saturates quickly, thus at higher illumination intensities it no longer has the highest SPV. This is most likely due to offset in the LUMO levels of PCBM and 25% Br (0.27 eV) causing greater charge recombination at higher light intensities. The PCBM is much more efficient at extracting charges from MAPI due to the smaller LUMO energy offset (0.17 eV) and thus has the largest SPV at larger light intensities.
7.8 Monitoring Phase Transitions and Phase Segregation

To further characterise the stability and optoelectronic properties of the mixed halide perovskite materials, temperature dependent PL measurements between 80 – 290 K (Figure 7.17).

**Figure 7.17**: Photoluminescence measurements from 77 to 293 K for (a) CH$_3$NH$_3$PbI, (b) CH$_3$NH$_3$PbI$_{0.75}$Br$_{0.25}$, (c) CH$_3$NH$_3$PbI$_{0.5}$Br$_{0.5}$, (d) CH$_3$NH$_3$PbI$_{0.25}$Br$_{0.75}$ and (e) CH$_3$NH$_3$PbBr mixed halide perovskite samples deposited on quartz. (f) shows a comparison of mixed halide perovskites at 173 K.

*Figure 7.17 (a)* shows the PL spectra for the MAPI (CH$_3$NH$_3$PbI) sample. As the temperature decreases from 290 K to 150 K a red shift in peak position is observed from 1.62 eV to 1.57
eV along with a decrease in the full width half maximum (FWHM) from ~80 meV to ~40 meV. This has been previously observed in MAPI materials and has been attributed to a reduction in electron-phonon scattering as the temperature decreases. At 130 K, two new peaks emerge; a weak, high energy peak at 1.67 eV and a broad, low energy peak at 1.46 eV. As the temperature decreases, the intensity of the high energy peak decreases and the spectra becomes dominated by the low energy peak that shifts to 1.43 eV at 80 K. The high energy peak can be attributed to the phase transition from the tetragonal phase of MAPI to the higher energy orthorhombic phase, whilst the lower energy peak is due to emission from defect related sub-bandgap states.

By contrast, the 25% Br sample shows only one main peak over the duration of the 290 – 80 K emission range shown in Figure 7.17 (b). At 270 – 290 K, there appears to be a low energy tail to the emission that could result from sub-band gap defect state emission, otherwise the main emission peak only shows a very uniform red shift in position from 1.74 eV to 1.68 eV as the temperature decreases. This is accompanied by a decrease in the FWHM from ~100 meV to ~30 meV. This indicates that there is (i) no phase segregation occurring in the 25% Br perovskite and (ii) no evidence of a phase transition as no new peaks appear in the PL. This may mean the 25% Br perovskite has a uniform crystal structure from passivation of the MAPI due to the minor Br component.

The low temperature PL spectra for the 50% Br and 75% Br samples are shown in Figure 7.17 (c) and (d) respectively. Unlike the 25% Br spectra, both the 50% and 75% Br samples show a range of peaks over the 80 – 290 K temperature range. Here, little correlation is observed between the energy of the emission and the temperature of the sample, indicating that both these samples show significant phase segregation into iodide and bromide rich phases.

The MAPBr sample essentially shows just one main emission peak over the entire 290 – 80 K temperature range. Initially, the peak is located at 2.31 eV (at 290 K) before red shifting to 2.26 eV (at 80 K). This is accompanied by a decrease in the FWHM from ~80 meV to ~40 meV, which is due to a decrease in density of states width. A low energy tail emerges at 80 – 90 K, which can be explained as recombination in a band of tail states. No other peaks appear to emerge as a result of phase transitions.

In summary, the low temperature PL measurements show 25% Br is the ideal perovskite to be used in mixed halide perovskite solar cells. Unlike the MAPI and MAPBr samples, no low
energy PL emission is observed at low temperatures due to tail state recombination, indicating less defects are present in the 25% Br. Additionally no extra peaks appear as a result of phase transitions. Unlike the 50% and 75% Br samples, the 25% Br sample shows no evidence of halide phase segregation and is thus more stable to use in photovoltaic devices.

7.9 Discussion

In this study, we have used Kelvin probe, APS, SPV and optical spectroscopy to explain the solar cell device characteristics of mixed halide perovskite solar cells. We find that of the mixed halide perovskite photovoltaic devices fabricated, the most efficient use 25% Br as the active perovskite layer with an efficiency of 8.93%, with MAPI slightly less efficient at 8.71%. The origin for this improvement in efficiency was an increase in the $V_{oc}$ from 0.86 V to 0.98 V (much of which can be explained by the wider energy gap) despite a decrease in the $J_{sc}$ from 13.72 mA/cm$^2$ to 12.01 mA/cm$^2$. Adding more Br beyond 25% results in low efficiency devices with a decrease in $V_{oc}$, $J_{sc}$ and FF.

Optical absorption measurements showed that energy band gap of the perovskites increases with Br content from 1.71 eV (pure MAPI) to 2.30 eV (pure MAPBr). This helps explain the decrease in $J_{sc}$ as more Br is added due to the reduction in absorbed photons, though it also partly explains the increase in $V_{oc}$ from MAPI to 25% Br.$^{110,121}$ The decrease in $V_{oc}$ for devices more than 25% Br is therefore not explained by the increase in optical absorption measurements. AFM measurements revealed that all the films show good surface coverage and uniformity, however the 25% Br and MAPBr films had the largest surface roughness. This implies that there was not a strong correlation between device performance and surface roughness.

APS measurements of the perovskite films revealed that the HOMO values of MAPI and MAPBr were 5.32 and 5.63 eV respectively (correlating well to literature values$^{124,267,268,282–285}$), however measurements on mixed halide films showed that the HOMO was largely controlled by the MAPI domains with only a small increase in HOMO value ($5.35 – 5.40$ eV). The TDoS measured via APS revealed that the trap density of states appeared to increase bromide content; this could be due to an increase in unreacted lead ion defects within the perovskite structure. The increase in trap states have been associated with a subsequent decrease in photovoltaic device performance; this is caused by a reduction in $V_{oc}$ due to trap-assisted recombination.$^{113,287,302}$ The increase in traps also cause anomalous hysteresis within
the solar cells. The 50%, 75% Br and MAPBr show both a reduction in $V_{oc}$ and an increase in hysteresis consistent with an increase in TDoS. X-ray photoelectron spectroscopy would be useful in confirming the relationship between trap states and bromide content.

Dark Kelvin probe measurements of the perovskite layers reveal that the workfunction of the perovskites increases with as more bromide is incorporated. When deposited on ITO, the measurements show that the perovskite energy bands bend upwards away from the ITO at the ITO/perovskite interface (Figure 7.11). This causes a positive space charge region so that electrons accumulate at that interface rather than holes which would not be ideal for photovoltaic devices. However, when in contact with PEDOT:PSS (which has a deeper Fermi level), MAPI, 25% Br and 50% Br samples now bend downwards at the perovskite/PEDOT:PSS interface causing a negative space charge interface thus holes would accumulate at this interface which would be desirable for photovoltaic devices. By contrast there still exists a positive space charge region within the 75% Br and MAPBr samples (due to their intrinsically deeper workfunction which explains lower $J_{sc}$ for 75% and MAPBr samples as the upward band bending would not be desirable for the extraction of holes through the PEDOT:PSS.

Surface photovoltage measurements of mixed halide perovskites on ITO and PEDOT:PSS reveal that the SPV is largest for 25% Br for all intensities, eventually reaching 248 meV at 200 W/m² when on ITO and 162 meV on PEDOT:PSS. This reflects the higher $V_{oc}$ value measured in 25% Br solar cells, which indicates the larger energy gap and reduction in charge recombination (due to low defect density) is responsible for the excellent performance for 25% Br. ITO and PEDOT:PSS/perovskite stacks for 50%, 75% and MAPBr showed much lower SPV, correlating with the lower $V_{oc}$ observed in devices, this is likely due to increased charge recombination due to ion migration (for 50% Br and 75% Br) and large increase in defect states for MAPBr (as measured in section 7.6).

Interestingly, when PCBM is deposited on top of the PEDOT:PSS/perovskite stack, the 25% Br shows the highest SPV at low illumination intensities (25 W/m²) of 165 mV, however at higher intensities (200 W/m²) MAPI shows the largest SPV of with a value of 292 mV whilst 25% Br shows only 185 mV. As previously discussed, this could be due to mismatch with the LUMO of PCBM and the LUMO of 25% Br causing difficulty in extracting electrons from the perovskite layer and hence causing recombination at the 25% Br/PCBM interface. However, device measured under even higher intensities of 1 sun (~1000 W/m²) still shows 25% Br as
having the highest $V_{oc}$. Inside a real device it could be that the aluminium cathode helps aid the extraction of electrons from the PCBM layer and hence reduce recombination. Further studies such as transient photovoltage techniques or SPV on a complete device would be useful in confirming this.

Finally, low temperature photoluminescence measurements show 25% Br is the ideal perovskite to be used in mixed halide perovskite solar cells. Here, no low energy PL emission is observed at low temperatures due to tail state recombination, indicating less defects are present in the 25% Br. Additionally no extra peaks appear as a result of phase transitions as observed in the 50% and 75% Br samples. The resistance to phase segregation of the 25% Br, as well as the smaller TDoS leads to improved photovoltaic device performance as phase segregation has previously been shown to reduce $V_{oc}$.[123] This is consistent with the device performances in section 7.4.

The data presented in this chapter presents a relatively consistent overall picture explaining why 25% Br appears to function as the best choice for a mixed halide perovskite material in photovoltaics. Device measurements indicate that larger $V_{oc}$ due to the wider band gap is responsible for the increase in efficiency of the 25% Br device over MAPI, however further increasing the bandgap does not appear to increase $V_{oc}$ nor the efficiency of the device. APS measurements indicate that the 25% Br has a relatively low trap/defect density of states compared to the 50% Br, 75% Br and MAPBr perovskites which will reduce charge recombination and aid charge transport within the perovskite. SPV measurements showed the 25% Br perovskite had the largest SPV, further correlating with the larger $V_{oc}$ measured. Transient SPV measurements possibly indicated a reduction in ion migration compared to the 50-100% Br samples. Finally, photoluminescence measurements confirmed phase separation of iodide and bromide perovskite in 50% and 75% Br samples, but not in 25% Br which remained stable.

**7.10 Conclusions**

In this chapter, using a range of analytic tools such as APS, SPV, Kelvin probe microscopy and UV-vis and PL spectroscopy, the optoelectronic properties of a range of mixed halide perovskite materials have been characterised and their respective performances in inverted solar cells is rationalised.
The inverted solar cells show that 25% Br perovskite gives the best device performance of 8.91% PCE. This is primarily due to an increase in $V_{oc}$ due to the wider bandgap of 25% Br and less recombination losses and phase segregation losses of ions compared to the other mixed halide devices. At Br levels beyond 25%, the FF, $J_{sc}$ and $V_{oc}$ decrease, leading to drastically reduced device performance. APS measurements show the tail density of states (TDoS) is increases with increasing Br content, implying there is more disorder within the perovskite at higher Br loadings. The larger TDoS is then likely to reduce the $V_{oc}$ in the photovoltaic devices due to trap-assisted recombination. Additionally, dark Kelvin probe measurements reveal that the 75% Br and MAPBr devices have a positive space charge region at the PEDOT:PSS/perovskite interface, which would reduce the hole extraction efficiency subsequently reducing $J_{sc}$ and $V_{oc}$.

These measurements are supported by SPV measurements. For perovskites deposited on PEDOT:PSS only, 25% Br shows by far the largest SPV correlating with the largest $V_{oc}$ in the solar cells, which is likely due to the larger energy gap in 25% Br over MAPI combined with a relatively small trap state density reducing charge recombination within the perovskite. However, when PCBM is deposited on top of the 25% Br the SPV saturates quickly at higher illumination intensities. This is possibly due to the mismatch in LUMO energies between the 25% Br perovskite and PCBM causing the electron extraction from PCBM to be less efficient and increasing interfacial recombination. SPV and $V_{oc}$ could be increased if another ETL was used such as ICBA.

Finally, low temperature PL measurements show that 25% Br shows no phase segregation unlike the 50% and 75% Br cases and shows no tail state signatures at low temperature unlike MAPI and MAPBr. Since both trap state recombination and phase segregation have both negative consequences on device performance, 25% Br is the ideal mixed halide perovskite.
Chapter 8: Conclusions and Further Work

8.1 Conclusions

This study has both underlined the importance of material interfaces to produce high performance, solution processed optoelectronic devices (specifically polymer light emitting diodes and perovskite solar cells) as well as demonstrating how conformational control of the active layers can enhance device characteristics. The key conclusions reached for each study are presented in this chapter, however more detailed summaries can be found at the end of each chapter.

The aim of the work presented in Chapter 4 was to understand how varying the chemical structure of conjugated polyelectrolyte (CPE) materials as electron injection materials in PLEDs produced large differences in (i) the luminous device efficiency and (ii) the current and luminance turn-on times. The device behaviour could be rationalised by considering two main interfaces, the CPE/Al interface and the LEP/CPE interface. By lowering the LUMO of the CPE by including a BT unit into the backbone structure, the barrier for electron injection at the CPE/Al interface is greatly reduced. This allows for ‘fast’ electron injection to occur, and depending on the light emitting polymer used, improved device performance (as was the case in F8BT devices). However, the LEP/CPE interface was found to play a key role in device performance. The F8imBT-Br CPE formed a type II heterojunction with an F8BT-TFB random copolymer and MEH-PPV polymer whilst F8im-Br forms a type I. This means that when F8BT-TFB and MEH-PPV are used as the LEPs, the device performance of F8imBT-Br CPE is drastically reduced due to quenching of the luminescence. For F8im-Br, device performance remained high. Therefore, for a PLED device containing a CPE electron injection layer to have both high luminous efficiencies and fast luminance turn-on for all LEPs, the CPE must be designed to have a deep enough LUMO to allow for ohmic electron injection whilst simultaneously having a wide enough band gap to prevent luminance quenching at the LEP/CPE interface. The work contained in this chapter showed the critical importance of the LEP/CPE interface and the CPE/Al interface in determining the device performance.

Chapter 4 additionally showed that by blending ZnO NPs with an alkoxy containing CPE, a composite CPE:ZnO NP material can be fabricated via solution processing. This material was found to be an effective electron injection layer in hybrid inverted polymer light emitting...
diodes, producing devices with efficiencies > 4 cd/A for a 75 nm thick F8BT device. This result shows the potential of this material as a one-step, low temperature solution processed method to produce flexible inverted light emitting diodes which was previously a great challenge due to the high processing temperatures required for planar ZnO layers.

Chapter 5 discusses how conformation of 95% fluorene:5% arylamine copolymers can be controlled to produce both highly efficient and deep-blue polymer light emitting diodes by incorporating β-phase into the fluorene units. This alters the luminescence of the copolymer from a broad, red shifted charge transfer type emission to a vibronic, structured, higher energy emission. The resultant β-phase copolymer PLEDs produced a deep-blue emission with CIE co-ordinates of (0.145, 0.123), with luminous efficiencies of 3.60 cd/A and 2.44 lm/W. These are a factor of 5 more efficient than corresponding PFO β-phase PLEDs and show a much higher spectral stability with no low energy ‘green-band’ emission present even at higher driving voltages. Using both TCSPC and low temperature PL it can be shown that efficient energy transfer to β-phase segments occurs within a β-phase copolymer film which is the source of the higher energy emission. The work in this chapter shows how molecular conformation control of a fluorene:amine copolymer can enhance both the emission and spectral stability of blue emitting PLEDs.

Chapter 6 extends the concept of inducing β-phase in fluorene copolymers to fluorene:benzothiadiazole copolymers. Here, we find that unlike in the case of fluorene:arylamine copolymers, the emission of (100-x)%F8:x%BT incorporating a β-phase microstructure is still dominated by low energy CT emission. This is because Forster resonance energy transfer can occur from the β-phase F8 segments to the F8-BT CT state. However, when the amount of BT present is small (as in the case of 99F8:1BT copolymer), emission from F8 units is still visible. When incorporating β-phase into the active layer can aid in both increasing the efficiency of the device and stabilising the EL emission, demonstrating potential for the system to be used for white light emitting OLEDs. The intensity of F8 emission also increased with β-phase incorporation, leading to a shift towards the white colour point from (0.335, 0.551) to (0.327, 0.521). Further decreasing the amount of BT unit may allow the colour point of this system to be controlled to a greater extent.

Finally, the work contained in Chapter 7 of this thesis used Kelvin probe microscopy, air photoemission spectroscopy (APS) and surface photovoltage (SPV) techniques to characterise a series of mixed halide (Br:I) perovskite materials. Initially, perovskite solar cells were
fabricated that showed 25% Br sample was the optimum halide composition for device efficiency. This was due to an increase in the open circuit voltage of the device up to 25%, increasing the Br content beyond this causes V_{oc} to drop. Kelvin probe and APS measurements indicated that the density of trap/defect states increases with Br content, which could increase charge recombination within the solar cells and thus decreases the V_{oc}. Phase segregation at 50% and 75% Br was also a reason for reduced V_{oc}. SPV measurements of the perovskites on bare ITO and PEDOT:PSS showed clearly 25% Br had the largest SPV making it the ideal choice for the active layer within a solar cell due to a combination of a larger energy gap and relatively small trap state density reducing charge recombination. Photoluminescence measurements confirmed that the 25% Br is stable and does not show phase segregation, whereas 50% and 75% Br samples indicated strong phase separation which is highly detrimental to solar cell performance.[295]

8.2 Further Work

This work has demonstrated how controlling both interfaces and molecular conformation within polymer light emitting diodes or perovskite solar cells can provide benefits in both device performance and fundamental understanding of the device physics and materials involved.

In the work with conjugated polyelectrolytes, a set of design rules were established that may show high efficiency, fast responding PLEDs that can work for a wide range of light emitting polymer materials. As a result, prospective collaborations with synthetic chemists would provide a way to test these rules by developing a range of CPEs with different conjugated structures with relatively deep LUMOs but wide band gaps. PPV-based CPEs are yet to tested and could be potential candidates for universal electron injecting CPEs due to their wide range of tunable polymers. Other candidates include F8 copolymerised with thiophene or arylamine units. Device worked with a wide range of materials will help build a library of knowledge to allow further understanding to how CPEs control device efficiency and luminance turn-on to realise all-printable PLED devices.

The work where controlling the molecular conformation of fluorene copolymers to enhance PLED device characteristics opens up a previously unexplored route in organic optoelectronic devices. Controlling further the 95F8:5BSP copolymer via different β-phase processing methods (such as using a di-iodooctane additive) could further control the colour point within these polymers. The deep-blue colour point in these β-phase F8:BSP devices could be
controlled further using microcavities to enhance the 0-0 emission peak. Further applications for this system could be in patterning β-phase within these copolymers to achieve colour contrasting films, and perhaps using this material as the gain material in organic laser. The fluorene copolymer example could be extended to a greater range of co-units such as F8:thiophene and F8:BODIPY where F8 is the majority unit. The optoelectronic properties of β-phase analogues of these polymers could then be studied, possibly finding use in transistor and solar cells. Finally, the approach could be extended further to non-fluorene based copolymers such as thiophene or DPP based copolymers.

The mixed halide perovskite work showed that the APS-04 can be used as a tool to explain the varying device performance within the mixed halide series through Kelvin probe, APS and SPV measurements. Additional measurements that could aid understanding of the perovskite system could be temperature dependent SPV measurements; if the decay and rise times of apparently ‘slow’ processes are altered significantly this could confirm ion migration as a possible mechanism for the change in workfunction. SPV measurements with a different range of ETLs deposited on top of the perovskite could also prove useful, especially in the case of the 25% Br. By altering the LUMO of the ETL (by using a material such as ICBA), better electron extraction could be achieved and recombination within the perovskite could be reduced.
Chapter 9: Bibliography


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Appendix A: Supporting information for Chapter 7

Figure A.1: Reverse (solid) and forward (dashed) current voltage scan for mixed halide CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{1-x}Br\textsubscript{x} perovskite solar cells in an ITO/PEDOT:PSS/CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{1-x}Br\textsubscript{x}/PCBM/Ca/Al structure under 1 sun illumination intensity.
Figure A.2: Surface photovoltage transients of mixed halide CH$_3$NH$_3$PbI$_{1-x}$Br$_x$ perovskites deposited on ITO at an intensity of (a) 40 W/m$^2$, (b) 120 W/m$^2$ and (c) 200 W/m$^2$. The left panel shows the light turn-on SPV response whilst the right panel shows the light turn-off response.
Figure A.3: Surface photovoltage transients of mixed halide $\text{CH}_3\text{NH}_3\text{PbI}_{1-x}\text{Br}_x$ perovskites deposited on PEDOT:PSS at an intensity of 200 W/m$^2$. The left panel shows the light turn-on SPV response whilst the right panel shows the light turn-off response.

Figure A.4: Surface photovoltage transients of ITO/PEDOT:PSS/$\text{CH}_3\text{NH}_3\text{PbI}_{1-x}\text{Br}_x$/PCBM at an intensity of 200 W/m$^2$. The left panel shows the light turn-on SPV response whilst the right panel shows the light turn-off response.
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