
Role of Thin Organic Interlayers inserted at the Electrode Interfaces for Efficient Polymer LEDs

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Preface

This thesis describes work undertaken in the Experimental Solid State Group at Imperial College London between February 2010 and November 2013. I gratefully acknowledge the Engineering and Physical Sciences Research Council, Erasmus Mundus Program, and World Class University Project in Korea (Grant No. R32-10051) for funding my research.

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Declaration of Originality

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

Jim Bailey
London, February 2014

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Abstract

This thesis discusses role of thin organic interlayers at the electrode interfaces of polymer light-emitting diodes (LEDs) in increasing their efficiencies.

The effect of varying the anode-side IL material, its thickness, and its p-doping level on poly(dioctylfluorene-alt-benzothiadiazole) (F8BT) PLEDs is examined. Then the impact of varying the IL material is explored in Lumation Green 1300 PLEDs to determine whether a relation exists between the role of the IL and the light emitting layer's properties. It is found that excitons are formed in F8BT adjacent to the interface with the IL and are thus exceptionally sensitive to the energetics at that interface, with wide energy gaps helping to reduce luminance quenching significantly.

The general effects of ionic cathode-side ILs on PLED efficiencies and response times are investigated. The novel materials used contain imidazolium cationic groups. The impact of varying the ionic IL main conjugated backbone on PLED characteristics is studied, since the conjugated backbone is primarily responsible for the optoelectronic properties of semiconducting polymers. Efficiencies of $\sim 15 \text{ lm W}^{-1}$ at 3 V are achieved. The light emitting layer is varied from F8BT to Super Yellow to probe the influence of the active layer's properties on the role of the IL in determining device characteristics. The exact combination of active layer and IL strongly influence device performance. The influence of the mobile anion and the immobile cationic group of cathode-side ILs on PLED performance is investigated. Our investigation focused on ionic ILs with a F8BT conjugated backbone. Ionic ILs with various mobile counter ions are created to study the role of the mobile ion on charge injection. Increased size of anion leads to poorer device performances.

Experiments were carried out to understand what factors determine the response times and efficiencies of PLEDs with ionic cathode-side ILs. Response times of 4.24 μs are recorded and Scanning Kelvin Probe Microscopy (SKPM) experiments on thin films of the ionic polymers are conducted to shed light on the movement of ions within the IL during PLED operation. Good energy level matching with the cathode metal is found for the ionic cathode-side ILs, allowing for good electron injection properties.

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1 Introduction

Worldwide, electric lighting accounts for 1.9 Gt of CO₂ emission, which is the equivalent of 70% of the emissions from cars^[1]. CO₂ emissions must be cut back to mitigate the effects of climate change, and with the world facing an ever increasing demand for energy consuming goods and a drive towards higher quality of life across the globe, it is important to develop technologies with low energy production methods and which are efficient in their energy consumption.

Plastic electronics offers the potential of lowering manufacturing costs of electronic and optoelectronic devices considerably compared to traditional inorganic devices, as well as allowing novel light-weight and flexible designs. With applications from light-emitting diodes^[2–4] and photovoltaic cells^[5–7] to field effect transistors^[8–11] this new field of research is growing rapidly. The elasticity and solution processability of polymers lends itself to roll-to-roll mass production methods employing flexible plastic substrates.

Simple design solutions to further increase polymer LED efficiencies are still required though. Recent work in hybrid organic-inorganic polymer LEDs has realized high luminous efficiencies in an inverted structure with a metal oxide cathode layer.^[12,13] Yet the highest luminous efficiencies in such devices are only achieved by replacing the ultra-thin light emitting polymer (LEP) layer with a micrometre thick polymer layer, yielding high operating voltages and consequently low power efficiencies. The most successful modification to the thin-film PLED structure has been the inclusion of a 10-15 nm interlayer (IL) of poly(9,9-dioctylfluorene-co-N-(4-butylphenyl)-diphenylamine) (TFB) between the hole transport layer (HTL) and the poly(dioctylfluorene-alt-benzothiadiazole) (F8BT) active layer.^[14] The dominant mechanism of the efficiency increase has not yet been clearly identified. Similarly ~15 nm layers of conjugated polyelectrolytes (CPEs) have been used as electron injection layers in PLEDs. Imidazolium-based CPE polymers with a poly(9,9-dioctylfluorene) (PFO) backbone similar to those discussed in this thesis have been published in the literature,^[15–17] but their role in electron injection in PLEDs has not been fully explored. The main aim of this thesis is to investigate the role of both the anode- and cathode-side ILs in enhancing efficiencies and in charge injection.

Chapter outline

Chapter 2 will present a review of organic semiconductors, from the basic physics, excitations, and charge transport models, to the basic operating mechanism of a PLED.

Chapter 3 will cover the experimental methods used in this research, including sample preparation and the techniques used to analyse the samples.

In Chapter 4 research and conclusions on the role of a ~ 10 nm polymeric IL at the anode interface will be presented. The effect of varying the IL material and thickness are probed, as well as the effect of p-doping the IL and of varying the light emitting layer material. The results are compared to 3D Kinetic Monte Carlo simulations of the system.

In Chapter 5 the role of ~ 10 nm conjugated polyelectrolyte (CPE) in electron injection in PLEDs is studied. Efficiencies of $\sim 15 \text{ lm W}^{-1}$ at 3 V are achieved in F8BT PLEDs with a CPE based on F8BT with imidazole units at the end of the side chains and bromide counter ions. Unlike other such materials with mobile ions, PLEDs using this electron injection layer show electroluminescence turn-on times of under 10 μs .

Further characterisation of the CPE injection layers is performed in Chapter 6 to understand the origin of the fast response times and good electron injection properties reported in Chapter 5. Electroluminescent and current density transient measurements of PLEDs are performed with various pulse frequencies to probe ion movement. The vertical stoichiometry and energy levels of the CPEs in relation to already well-characterised light emitting layers is probed.

Finally, Chapter 7 summarises the main conclusions of this thesis and includes suggestions for future work.

2 Review of Polymer Light Emitting Diodes (PLEDs)

This chapter will contain the background information for this report, including a brief explanation of the materials used in plastic electronics and the excitations that occur in organic semiconductors. It will then address the OLED's operation, from charge injection to light reception in the human eye.

2.1 History of PLED Research

The basis of all light emitting diodes (LEDs) is electroluminescence (EL), by which light is emitted from the solid state of a material when a voltage is applied across it. This phenomenon was first discovered in 1907 by H. J. Round, who was working at Marconi Labs, by employing a crystal detector to a silicon carbide crystal. It was almost 20 years later, in 1927, that the first LED was created by O. V. Lossev.^[18] Interest in the discovery was low, however, and in the following decades little progress was made.

The second half of the century saw the start of an increasing amount of attention directed towards the study of both EL and its applications. In the early 1950's EL was discovered for the first time in an organic material (in thin crystalline films of quinacrine and acridine orange)^[19–23] and by the late 1960s inorganic LEDs had entered the mass production phase — they were being manufactured for use as indicator lights.^[24] In the late 1960s organic light emitting diodes (OLEDs) had a breakthrough of their own, when the use of reactive cathodes greatly improved device performance by increasing electron injection.^[25]

In general it was not until the 1970s though that plastics were considered to be anything other than insulators. Plastics were used as insulators for electrical wiring, for example. Fuelled by the 1973 discovery of high conductivities in the inorganic polymer polysulfur nitride, research into conducting plastics began in earnest in the 1970s. 1974 brought about the synthesis of polyacetylene which could be processed as a thin film of metallic appearance — yet it was not conducting.^[26] In 1977, Shirakawa *et al.* conducted the research that would later win them the 2000 Nobel prize in Chemistry for “the discovery and development of conducting polymers”, by oxidising polyacetylene to make it electrically conducting.^[27]

Meanwhile in 1976 Pearsall et al had created LEDs well matched to the transmission wavelengths of optical fibres,^[28] ensuring that LEDs would play a big role in telecommunications and would therefore receive much funding for further development. The first OLEDs had their breakthrough in the mid-80s when Tang and van Slyke fabricated a highly efficient, low voltage EL device based on the organometallic complex Alq3 at Kodak.^[29] Yet it was the 1990 demonstration of EL conjugated polymers by Burroughes, Bradley, Friend *et al.*^[2] at Cambridge University that finally united the research areas of conducting polymers and organic EL. These electroluminescent conjugated polymers are semiconducting. As they are plastics, they are commercially very interesting due to facile solution processing. This makes them a good candidate for large area mass through put printing for light, cheap, robust, and flexible applications in a large variety of fields. Currently displays from small molecules are already a commercial reality in many smartphones, although they rely on expensive ultra-high vacuum deposition methods. In contrast, polymers promise cost effective roll-to-roll printing in future.

2.2 Organic Semiconductors

2.2.1 Semiconducting Properties in Organic Materials

Modern electronics relies on semiconductors for use in transistors, LEDs and in digital and analogue integrated circuits. A semiconducting material has electrical conductivity intermediate somewhere between that of a conductor and an insulator. In solid-state physics the difference between these types of materials is described in terms of their electronic band structures. The bands describe energy levels and according to Pauli these energy levels can each be occupied by only two electrons (each with a differing spin state). The lowest energy levels are filled first. The most relevant bands in electronics and optoelectronics are those with energy near the Fermi level. In a semiconductor or insulator the Fermi level lies in the band gap of the material with the band below it being occupied (termed the valence band) and the band above it being the closest unoccupied band (termed the conduction band). In a metal the Fermi level is inside of one or more bands. Fig. 2.1 illustrates the band diagrams for conductors, insulators and metals; in a metal the conduction and valence band overlap, while the gap between the conduction and valence band that is common to both insulators and semiconductors is larger for insulators. In metals the conduction band is partially filled, which allows for electrons to move throughout the solid freely. The small energy gap of semiconductors (generally 3 eV or below) allows

for electrons to be promoted into the unoccupied levels. To understand the properties of organic semiconductors it is useful to start with a brief review of some carbon chemistry, since organic materials are carbon based.

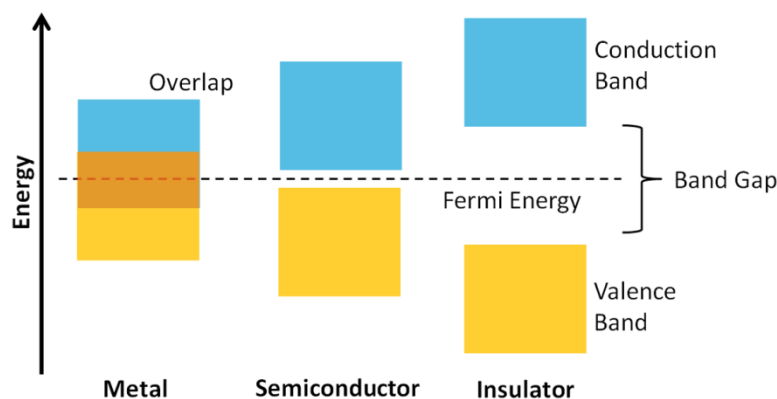


Figure 2.1: Illustration of the band gaps for a metal, a semiconductor and an insulator.

Carbon and its Bonds

The most common isotope of Carbon is ^{12}C ; it has six electrons located in the following four orbitals: two in the 1s orbital, followed by two in the 1p orbital, and one each in the $2p_x$ and $2p_y$ orbitals, while there are none in the $2p_z$ orbital. In this notation the first number refers to is the principle quantum number and the number of electrons in each bond can be written as a superscript; thus: $1s^2 2s^2 2p^2$. Like most elements Carbon forms bonds. Only the p_x and p_y orbitals are incomplete orbitals, each missing one electron, so it might be assumed that carbon undergoes only two bonds. However, due to the intermediate steps of electron promotion and hybridisation it forms four bonds. Hybridised orbitals are the intermediate step between atomic and molecular orbitals. Carbon can be hybridised in three different ways in bonds based on the four orbitals in Carbon (1s, 2s, $2p_x$ and $2p_y$). They are called sp, sp^2 and sp^3 hybridisations which result in differing number of orbitals to be available for molecular bonding (Fig. 2.2).

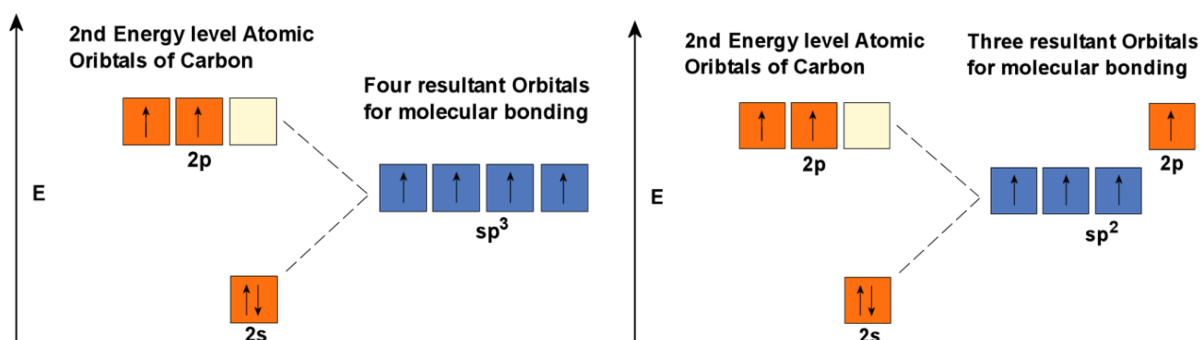


Figure 2.2: The hybridisation of the atomic orbitals to form the orbitals that are involved in the molecular bonding of carbon.

There are two basic types of covalent bonds, the σ -bond and the π -bond. A σ -bond is formed when two of the resultant atomic orbitals overlap, sharing electrons to produce a molecular orbital with a lower energy. In an sp^2 hybridised atom only the $2s$, $2p_x$ and $2p_y$ orbitals are hybridised to form bonds; the p_z orbitals remains un-hybridised. While the other three lie in one plane, the p_z orbitals are perpendicular to that plane. The p_z orbitals overlap forming one delocalised orbital above and below the molecular axis, termed a π -bond (Fig. 2.3).

An example of an sp^3 hybridised molecule is methane in which the unfilled orbitals contain an unfilled orbital — this unfilled orbital can be filled by sharing an electron with an atom, *e.g.* hydrogen in the case of methane. The four bonds between the carbon atom and four hydrogen atoms, which create a tetrahedral structure, are termed σ -bonds (or 'single' bonds). Together one π - and one σ -bond are called a double bond. When a molecule has alternating (and oscillating) single and double bonds it is termed conjugation. While the electrons in the σ -bond are localised, those in the π -bonds are less localised and it is these weakly bound electrons that give rise to semiconducting properties in conjugated polymers.



Figure 2.3: A delocalised π -bond above and below the molecular plane is formed by two p -orbitals.

Molecular Orbitals and Energy Levels

As delocalised π -orbitals overlap to form the π -bonds splitting of the p_z orbitals into bonding and anti-bonding levels gives rise to quasi continuous bands as the delocalisation extends that form a small gap, namely the gap between the highest occupied molecular orbital (HOMO) level and lowest unoccupied molecular orbital (LUMO) level (Fig. 2.4). This energy gap gives rise the emission colour of a light emitting polymer.

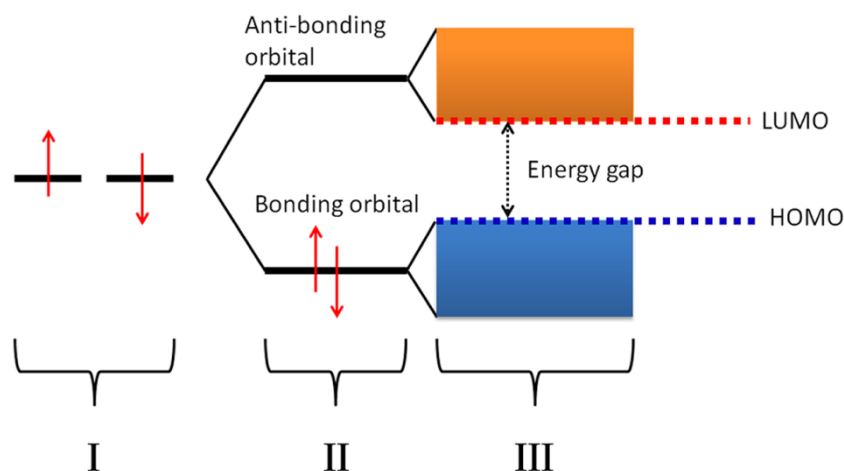


Figure 2.4: Diagram illustrating (I) degenerate π -levels, (II) non-degenerate molecular orbital levels, (III) the energy bands that result from the overlap of many π orbitals along the polymer backbone and the HOMO – LUMO energy gap between them.

2.2.2 Small Molecules

Small organic molecules are increasingly gaining importance for applications in the commercial display sector as light emitting and charge carrier transport layers. They are well studied as they were among the first type of light emitting molecules to be used in OLED fabrication, e.g. the small green-emitting organic molecule tris(8-hydroxyquinolino)aluminium (Alq3).^[29] Other well studied small molecules include the hole transporters N, N'-diphenyl-N, N'-bis(3-methylphenyl) 1, 1'-biphenyl-4, 4' diamine (TPD) and N,N'-di(naphthalen-1-yl)-N,N'-diphenyl-benzidine (NBP) (chemical structures shown in Fig. 2.5). The benefits of small organic molecules is that they have well defined structures and therefore a specific molecular weight, which allows for high reproducibility of results and fewer defects in the organic layer. As they are evaporated under ultra-high vacuum conditions high purity films can be achieved as well as multi-layer structures. The downside

to the vacuum evaporation technique is that it is not compatible with high through put roll-to-roll production methods. Small molecules do not readily form thick, uniform layers when processed from solution. Many new materials are being developed though, such as dendrimers, which have many backbones that branch out from a common centre. These materials can behave like small molecules when their backbones are short (a couple of repeat units), but they can also have properties in common with conjugated polymers when their backbones are longer.

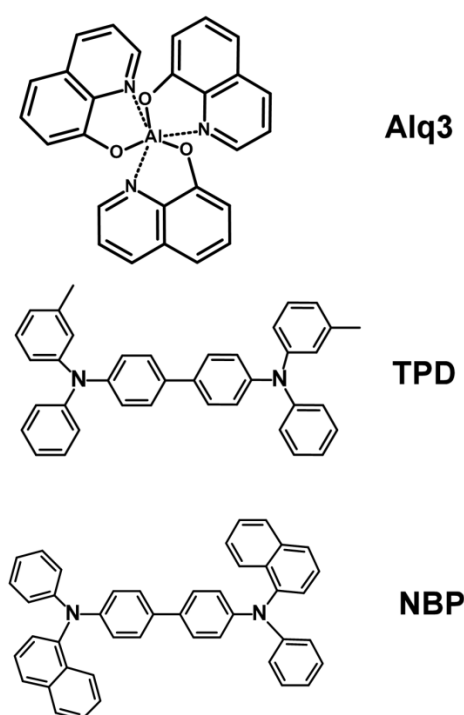


Figure 2.5: Chemical structures of three small molecules commonly used in OLEDs: Alq3, TPD and NBP.

2.2.3 Polymers

Polymers are long chain carbon based molecules. The material is held together in a disordered manner by Van der Waals forces. Since this force is weak and decreases rapidly with increasing distance between the molecules, polymers are more flexible than inorganic materials, which is one of their main attractive qualities. On the other hand such disorder has the consequence that the excitations of the molecules cannot delocalise over the whole of a crystal lattice, as is the case with inorganic materials.

A conjugated polymer is a system of alternating single and double (or triple) bonds. This structure creates intermolecular torsion which helps planarise the molecule's backbone and gives it rigidity. The backbone conjugation is broken when single and double bonds no longer follow each other alternately. Regardless of whether a conjugated polymer was designed to have uninterrupted conjugation on the backbone or short, repeated, conjugated segments, disorder in the molecules leads to a dispersion of the conjugation lengths around an average. This is due to kinks in the chain that break the conjugation. The isolated conjugated segments on the main chain are named chromophores, as it is these conjugated segments that determine the optical (and electrical) properties of the material.

2.2.4 Excitations in Organic Semiconductors

The molecules in organic semiconductors can be excited into a higher energy state in a variety of ways; they can be excited by light or the introduction of charges. As it is the excited states of the molecules that allow light emission and charge transport, it is important to understand them.

Charges on conjugated polymers

There are several ways to introduce charges onto conjugated polymers. The main one of note for OLEDs is through charge injection in a diode structure. However, there are other ways in which charges are introduced, such as chemical doping; the dissociation of excitons due to impurities, interfaces or high electric fields, or the excitation of the polymer at high energies. A hole on a polymer can be described as a cation-radical, as an electron is removed from the HOMO, while an electron can be described as an anion-radical, as an electron is added to the LUMO. When an electron is added or removed, though, the molecule relaxes to its minimum energy level, which brings with it a distortion in the polymer's lattice. The coupling of this lattice relaxation and the charge is termed polaron,^[30] or bi-polaron,^[31] if two charges are involved. Depending on whether the charge is a hole (or electron) the polaron is described as a hole (or electron) polaron respectively. The polarons reside in a sub-gap level which is further inside the energy gap than the energy levels a bound electron-hole pair (exciton) occupies. This neutral excitation is discussed next.

Excitons

Excitons^[32] are a neutral excitation with very short lifetimes in the order of pico- to nano-seconds. An exciton can be formed through an electron and a hole polaron becoming

coulombically bound or through photo-excitation, where an electron in the LUMO is excited to the HOMO *via* photon absorption. Although it is a neutral excitation, the position of an electron has changed, meaning a redistribution of the electrons in the π -bonding and anti-bonding orbitals must take place. This leads to a change in the structure of the polymer chain near the exciton as well as to a change in the charge density in that area.

The degree of delocalisation is determined by the binding energy of the electron and hole. Three different degrees of delocalisation are as follows:^[32]

- **Frenkel** excitons are electron-hole pairs with a delocalisation that is limited to one polymer chain or small molecule. These tightly bound excitons have binding energy of typically around 1 eV. The Frenkel exciton can be visualised as a neutral particle with an exciton radius the size of (or smaller than) the molecule it is localised on (< 0.5 nm). Another way to think of them is as an excited state of a single atom that may hop from one site to the next as these excitons are able to move from site to site and have discrete molecular states in an energy level diagram. Frenkel excitons are generally observed in noble gasses and in ionic crystals.
- **Charge-Transfer (CT)** excitons^[33] are an electron polaron-hole polaron pair coulombically bound on two close chains. The delocalisation across neighbouring molecules leads them to have an exciton radius intermediate between that of Frenkel and Wannier-Mott Excitons. The CT exciton can move from site to site or be trapped.
- **Wannier-Mott** excitons are not found in organic semiconductors, but are commonly found in crystalline materials such as Si or GaAs. Wannier-Mott excitations are more delocalised than Frenkel and CT excitons with exciton radii of 4-10 nm.

Conjugated polymers typically have Frenkel like excitons with binding energies of ~ 0.5 eV. Such excitons have a strong coupling to intramolecular vibrations (these can be observed as vibronic structures in the absorption and emission of the materials). These intramolecular vibrations also lead to the large splitting between singlet and triplet exciton levels. As excitons are formed from the combination of two spin 1/2 particle there are two types of excitons, singlet and triplet: singlet excitons are a spin of 0 (magnetic momentum can only equal 0 in this case), while triplet excitons have a spin of 1 (magnetic momentum can be -1, 0, or 1 in this case). The triplet levels are degenerate unless a magnetic field is applied. In singlet excitons the spin of the LUMO electron can pair with the spin of the HOMO electron, while in triplet excitons the spin of the LUMO electron does not pair with the spin of the HOMO electron. Singlet excitons can recombine to emit light in fluorescent and

phosphorescent materials, but triplets can only recombine to emit light in phosphorescent materials. Phosphorescent emitters generally show higher efficiencies as spin statistics suggest the triplet:singlet ratio is 3:1, however this ratio is not found in all materials.^[34]

2.2.5 Charge Transport

An important aspect of polarons is their role in charge transfer. In organic materials the charge carriers are strongly localised to a single molecule and so charge transport along a polymer chain is in the limit of strong electronic coupling, i.e. band-like transport is possible. Transport between molecules on the other hand is in the limit of weak electronic coupling between molecules — the charges 'hop' from one chain to the next, where 'hopping' refers to phonon assisted tunnelling. Band-like transport is found in ordered organic small molecule crystals, such as rubrene and pentacene.^[35] The probability of hopping transport in disordered semiconductors such as amorphous polymers is dependent on the temperature, electric field, molecular separation and disorder of the polymer film. The energetic and spatial disorder gives rise to a broadening of the available range of energy states which can transport the charge carriers so both electrons and holes hop through a distribution of localised states or shallow traps (once they have overcome the barriers to hopping between sites). Charge carrier mobilities in amorphous polymers are limited as the transfer integrals of the initial and final state wavefunctions of a charge are small in disordered polymer systems, due to little physical overlap of the polymer chains. Chemical defects, conformation, configuration, regioregularity, end groups, and polydispersity all effect charge transport. The hopping transport in organic semiconductors is disordered due to the dispersion of HOMO and LUMO energy levels — some HOMO levels are so shallow that they act as traps. If there is a long tail of traps then it is the charge density that governs the mobility. When the electron density is high the most mobile electrons experience an increase in mobility, as they are not caught in the traps, whereas most electrons lie in deep traps when the density is low. Still, charges can drift through the material under the influence of an electric field or can move *via* diffusion as a result of density gradients.

The hops a charge makes as it is transferred from one discrete site to another are uncorrelated to one another; they occur with a rate that is described by two main models, Miller-Abrahams^[36] and Marcus Theory.^[37]

Miller-Abrahams

According to Miller-Abrahams the charge transport is better the smaller the intermolecular distance, as the electronic coupling is higher then. To increase the coupling between the initial state, i , the charge is in and its final state, j , after the hop, energy needs to be put into the system in the form of phonons (for hops to higher energy states) or molecular motions. This is reflected in the following equation in the Boltzman factor, $(E_i - E_j)$, where E_i and E_j are the energies of two sites i and j :

$$k_{ij} = \nu_0 e^{-2\gamma R_{ij}} \begin{cases} e^{-\frac{E_i - E_j}{k_B T}} & E_j > E_i \\ 1 & \text{else} \end{cases} \quad \text{Equation 2.1}$$

where k_{ij} is the transition rate from site i to side j , ν_0 is the phonon frequency and the term $e^{-2\gamma R_{ij}}$ is the tunnelling factor (R_{ij} is the separation distance between sites i and j and γ is the overlap factor). Polaronic effects (i.e. the relaxation of the local site configuration) is not taken into account.

Marcus Theory

In Marcus theory the polaronic effect is taken into account through the inclusion of the polaronic reorganisation energy, λ , in the rate equation:

$$k_{ij} = c\nu_0 e^{-2\gamma R_{ij}} e^{-\frac{E_i - E_j + \lambda^2}{4\lambda k_B T}} \quad \text{Equation 2.2}$$

In this rate equation the difference in the initial and final transport site energies is used, and assumes a tunnelling through the energy barrier between the two sites. This theory can be expanded, however, to include the height of the barrier, for instance, or to include a quantum mechanical treatment of the vibrational modes (Marcus-Levitch-Jortner equation, for example). Fig. 2.6 illustrates potential energy surfaces: the y axis is energy, and the x axis is the configuration coordinate, which includes all the changes that occur in the positions of the nuclei as the state changes from the initial to the final one. So for an initial energy state, ε_i , and a final energy state, ε_f , the vertical transitions (dashed lines) are shown, with the normal displacement mode ΔQ and the relaxation energies λ_1 and λ_2 . The sum of those two relaxation energies gives the total polaron reorganisation energy, which is the energy that is necessary for the distortion of the nuclear configuration without the transfer of an electron occuring. It is useful to know the value of this energy, since the rate constant for electron transfer is maximum when the free energy is equal and opposite to the reorganisation energy.

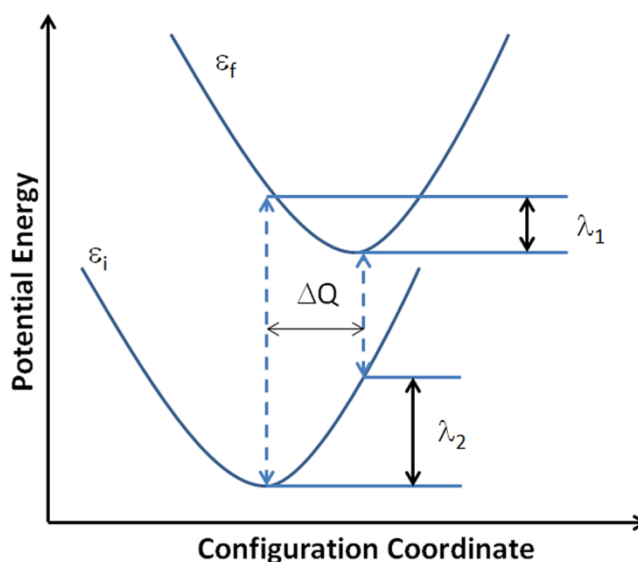


Figure 2.6: When the nuclear co-ordinates of the two chains are the same, they are at the same potential energy, so charge transfer can occur without a further change to the nuclear positions.

2.2.6 Optical Transitions in Organic Materials

Optical transitions in organic semiconductors allow light emission from OLEDs and so it is important to discuss their nature. Photon absorption and emission processes of organic semiconductors can also be studied to understand the electronic properties of the materials.

In conjugated polymers the spin-orbit coupling is typically weak and so the electronic ground state of a molecule (HOMO) is a singlet level, designated as S_0 . Each state has vibrational energy levels associated with it, which are separated by around 0.15 eV. The lowest energy level is the lowest vibrational level of the ground state, which most bonds occupy at room temperature. The first (lowest) excited state (LUMO) is termed S_1 , which is followed by S_2 and so on. The different arrangements of the electrons and spin states also give rise to triplet excited states (as discussed earlier), in which electrons have anti-symmetric spatial wavefunctions, which are termed T_1 , T_2 and so forth. All states occupy a distinct energy level. The energy levels of the triplet states are lower than the corresponding singlet state as the coulomb repulsion is lower for the anti-symmetric triplets. The energy by which the S_1 and T_1 states are separated is the exchange energy (typically 0.3 to 1.0 eV).

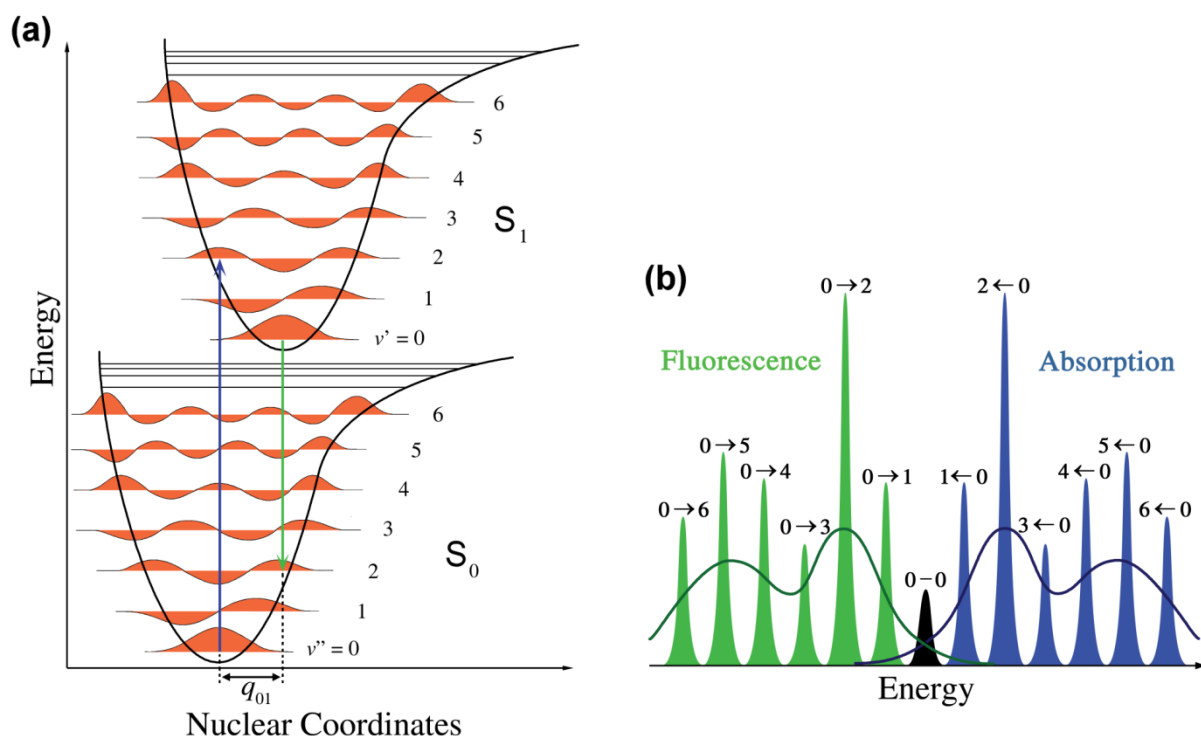


Figure 2.7: Diagram a) shows the ground state, S_0 , and first excited state, S_1 , and vibrational energy levels, v . A vertical absorption transition ($0 \rightarrow 2$ vibronic transition) is represented by a blue arrow, while fluorescence emission from S_1 is represented by a green arrow. Diagram b) shows the ideal absorption and emission spectra of a chromophore. They are mirror images of each other, overlapping at the $0 \rightarrow 0$ vibronic transition. In disordered polymers the fluorescence spectrum will appear shifted to lower energies due to structural relaxation of the system.^[33]

Bonds in S_0 can be excited by the absorption of an incident photon, giving them a higher energy, which puts them into one of the vibrational levels of S_1 (Fig. 2.7). Energy transitions that involve photons are only allowed when the wavefunctions of the initial and final state have opposite symmetry and the same total spin. For example, optical transitions from the ground state to the excited T_1 state are forbidden due to spin. The transitions occur so that the wavefunction undergoes as little change as possible; this means that the nuclear co-ordinates do not shift in the first instance (Franck-Condon^[33] transitions, i.e. ones in which the Born-Oppenheimer approximation, amongst other approximations, holds true). This is represented by plotting the transitions as straight, vertical lines perpendicular to the nuclear co-ordinate axis. The nuclear co-ordinates shift to their excited geometry by relaxation of the bonds from the higher vibrational energies of S_1 to the lowest vibrational energy of S_1 . The overlap integral of the initial and final vibrational states weakly determines the transition strength, which is given by the Franck-Condon factor ($\int \psi_v'^* \psi_v d\tau_n$). Here ψ_v is

the individual vibrational wavefunction. Other quantum mechanical selection rules also apply.

In absorption the transitions are labelled from 0 (the lowest energy) to 1, 2, 3 ... n, according to which vibrational level of the excited state they are elevated to. The more 'vertical' the transition, *i.e.* the less shift in the nuclear co-ordinates, the more likely the transition is. The 0-0 transition is a non-vertical transition, which is called a zero phonon transition as the transition is to the lattice relaxed S_1 state. The sharp absorption peaks of the transition are smeared out in polymers, as on the polymer chains the size of the exciton varies.

Fluorescence efficiency for organic polymers in the thin films can reach values between 40% and 80%. Emission does not occur from the states into which the bonds were excited, as relaxation to the lowest vibrational state occurs — diffusion of the excitons from chromophores with a large to a small energy gap happens rapidly; the fluorescence spectrum lies at lower energy therefore. The splitting between the two spectra is termed Stokes shift. Real absorption and emission spectra are smeared out due to the disordered nature of the polymer.

Transitions can occur from S_1 (spin = 0) to T_1 (spin = 1) through a process called intersystem crossing (Fig. 2.7). Once in the triplet state though the optical transition from T_1 to S_0 is both dipole and spin forbidden, unless an even lower energy mixed singlet-triplet state can be created (for example by including heavy metal atoms).

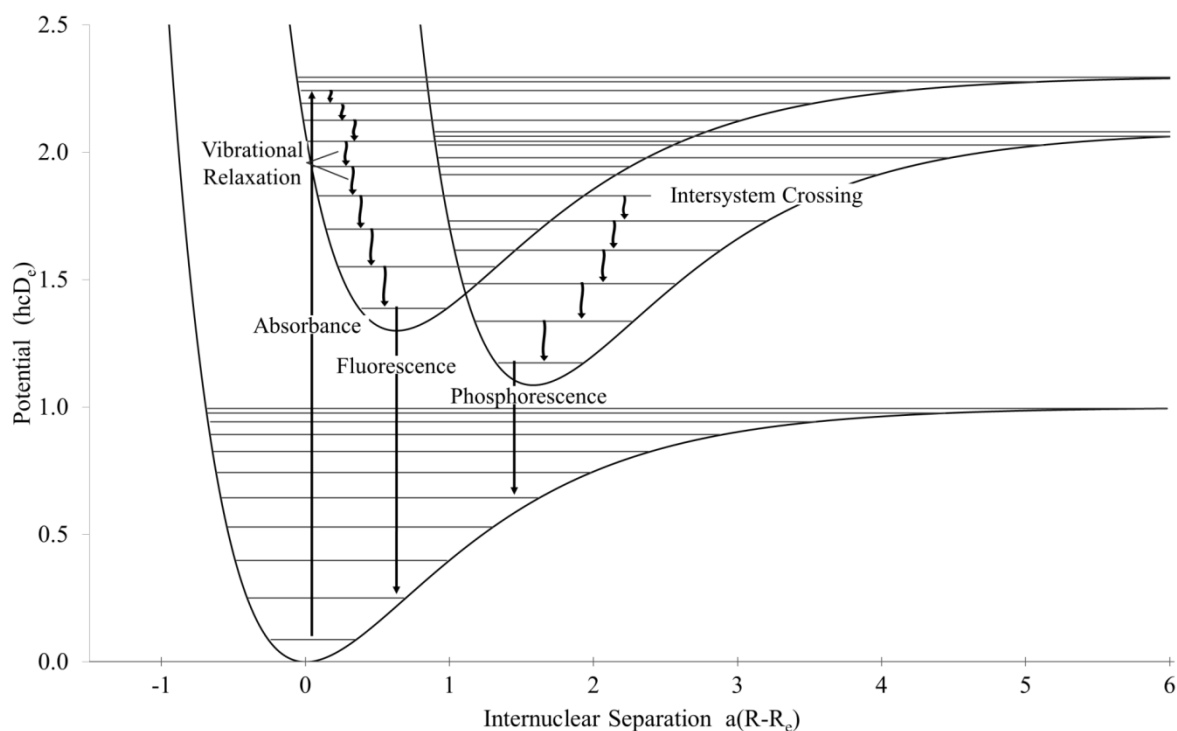


Figure 2.8: Schematic diagram of absorption, fluorescence, phosphorescence transitions and intersystem crossing.

Each of these transitions happens on a different time scale. While absorption is the fastest (around 10^{-6} ns), vibrational relaxation happens on a scale of 10^{-4} to 10^{-3} ns and fluorescence has a time-scale of around 1 ns, phosphorescence is the slowest of all, at a hundred to a hundred thousand times the time-scale of fluorescence.

2.3 PLEDs

2.3.1 PLED Architecture

The PLED architecture, first demonstrated by Burroughes *et al.*^[2] has a single light emitting polymer layer. Between the emissive layer and the electrodes there are often additional layers (Fig. 2.7) to modify the injection of charges, prevent quenching of excitons or control the balance of the charge carriers. Polymeric hole injection and transport layer are often used at the anode to increase PLED efficiencies.

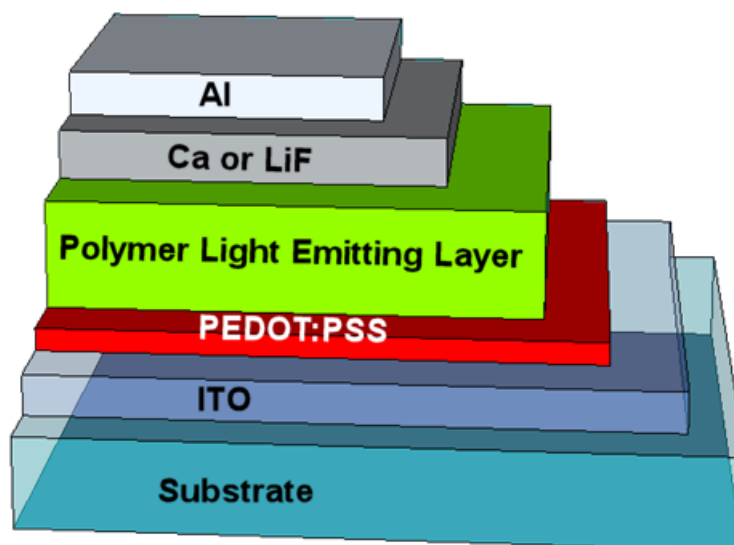


Figure 2.9: Cross-section through a typical PLED without an interlayer.

Water soluble PEDOT:PSS is placed between the anode and light emitting layer to aid hole-injection by helping to overcome the injection barrier, planarise the surface and prevent doping of the light emitting layer from the anode. It has been shown to quench radiative excitons, though, thereby reducing the efficiency of the devices.^[38] An interlayer can produce an improvement.^[14] This layer can be created on top of PEDOT:PSS and through annealing above the glass transition temperature (T_g) can form a thin ($\sim 10\text{-}15\text{ nm}$) insoluble layer.^[14]

For device operation there has to be a large difference in the workfunctions of the electrodes; so often a low workfunction metal is chosen as the cathode, such as calcium, barium or magnesium. These metals are all very reactive and so they are capped with aluminium. The capping results in poor stability in air, so rigorous airtight encapsulation is needed, which may not be suitable for the high throughput flexible processing that plastic electronics aims to achieve. A better solution is the deposition of a flexible organic electron transport layer on top of the light emitting layer. Recently conjugated polyelectrolytes have emerged as one candidate for a solution processable electron injection layer.

2.3.2 PLED Operation

Injection

Electroluminescence is the consequence of holes from the anode and electrons from the cathode combining radiatively in the light emitting material sandwiched between them. The first step of this process is the injection of the charges into the active layer. This process plays an important role in the efficiency of PLED devices, as the charge carrier densities should ideally be in balance for maximum efficiency and should be high enough so that the injected charges in the bulk material are transported away without a build-up of charge. An ohmic contact can be formed when the workfunctions of the electrodes match with the HOMO and LUMO levels.

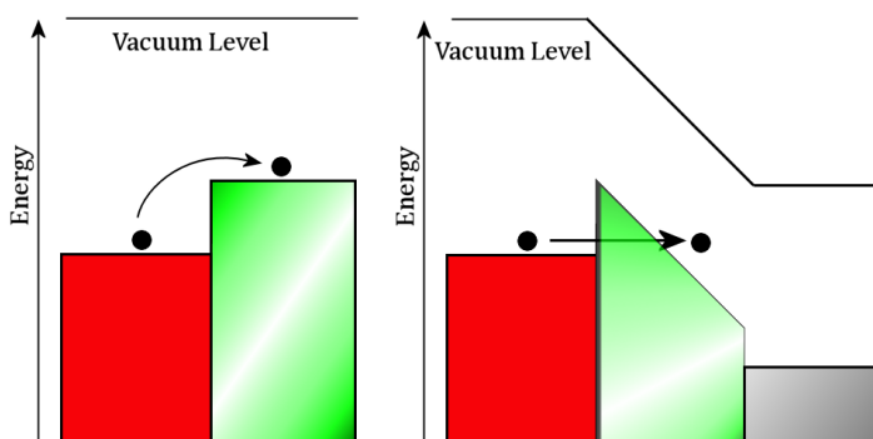


Figure 2.10: a) Representation of thermionic emission of an electron and (b) representation of tunnelling through a triangular barrier.

For injection to occur charge must cross from one material into another. This can happen either through thermionic emission or Fowler-Nordheim tunnelling (Fig. 2.10). In thermionic emission the driving factor is thermal excitation and subsequent transfer into the other materials. Fowler-Nordheim tunnelling is driven by the application of large enough electric fields. When an electric field is applied thermionic emission is increased as the charges flow in a specific direction. At high enough field strengths band bending occurs so that charges can tunnel through a triangular barrier. In inorganics the workfunction of a metal is the energy to remove an electron from the material. This corresponds to the ionisation potential in organic materials.

Increasing the applied electric field reduces the tunnelling distance, leading to an exponential dependence of the applied field and the tunnelling probability. At high field strengths tunnelling naturally comes to exceed thermal processes. Both methods contribute to the overall current and can be added linearly.

In an organic semiconductor diode current can either be limited by the injection properties of the electrodes or by the properties of the bulk. If limited by the bulk of the material, then generally low current densities from thermal excitation of the charge carriers would be observed at low voltages, up until such a voltage at which the carriers can readily enter and flow through the organic semiconductor, resulting in higher current densities. High uncompensated charge carrier densities result in a field gradient causing an electrostatic 'push-back' effect, thus limiting the current density: space charge limited behaviour takes over. This voltage is typically only a few millivolts in polymers, because polymers have very low charge densities. They do however contain a lot of traps, which have to be filled first before the material can go from the space charge limited trap regime to space charge limited trap-filled regime. If a PLED is bulk limited it is in the space charge limited regime, but enters the trap-free regime at higher voltages. In a real device the trap energies are distributed so that the field dependence varies locally. Space charge limited current is thus what we are seeing in the current-voltage characteristics of OLEDs and should be expressed in terms of applied voltage if possible, as the field may vary due to space charge build up.

The mobility dependence in an organic polymer is influenced by many factors such as the distribution of the traps as already mentioned. The mobility can be described by its relationship to the applied electric field (for tunnelling) and the temperature (for thermionic emission) by the Poole-Frenkel relationship, where β and μ_0 are temperature dependent parameters:

$$\mu = \mu_0 e^{(\beta\sqrt{E})} \quad \text{Equation 2.3}$$

Charge Transport

Once the charges have been injected, they then need to be transported to the recombination zone (RZ). They must hop from one localised state on a chain to the next — this is the bottleneck in charge transport in polymers. Charge mobility is critical to the efficiency of light emission in OLEDs; it also influences the degradation of the materials and the losses that are incurred due to resistivity.

Typically the transfer integral is small due to the small overlap of the chains, which leads to the polymers having low charge mobility. Morphology is important as the overlap integral depends heavily on the local chain alignment. In highly crystallised materials higher mobility is expected compared to more amorphous materials. In the amorphous materials used in PLEDs the transport occurs intra-chain along the chromophores through delocalisation of the excitation and through hopping for inter-chain transport. Since the HOMO and LUMO levels have a Gaussian distribution of states due to disorder there is a dependence of charge transport on the charge density; at low electron densities, most electrons would lie in traps, while at high densities there would be more highly mobile electrons available for hopping transport, leading to an increased hopping rate — this is described by Bässler's Gaussian disorder model.^[39]

Recombination

To increase the probability of charge recombination within the active layer it is important to control the charge densities. The aim is always for the excitons to form away from the electrodes where they might be quenched. One thing that can be done is to prevent the majority carrier from crossing straight through to the electrode by introducing an energy barrier against it doing so. Another method to control the recombination rate is by localising charges, which allows some static charges to capture the mobile charges. This can be achieved by having a bi-layer device in which there are separate hole and electron transporting materials that meet in the middle of the device; through a blend of electron and hole transporting materials; or through co-polymerisation of electron and hole transporting moieties.

Exciton Decay

In PLEDs not all excitons relax into a state that will produce light emission. There are triplets that are non-emissive, which can place a limit on light emission. The internal quantum efficiency of a PLED in which phosphorescent complexes don't play a significant role is equal to the fluorescent efficiency of the fraction of injected charge carriers which form singlet excitons. With phosphorescent complexes included there is a second term for this, which is simply added to the singlet exciton term.

Triplets could still be harvested for their light emission *via* phosphorescence. Phosphorescence, unlike fluorescence, is not the direct re-emission of an absorbed photon. Instead, the re-emission occurs on far slower time scales. Through intersystem crossing the

absorbed photon energy goes from the singlet to the triplet state, from which it is classically "forbidden" for the energy to transition to the ground state. Quantum mechanically the transitions may still occur, however. These transitions are kinetically unfavourable enough to lead to slower re-emission time scales for phosphorescent than for fluorescent materials. The intersystem crossing from the singlet to the triplet state can be promoted by going through a mixed triplet-singlet state that is introduced through strong spin orbit coupling brought about through the inclusion of heavy metal complexes with iridium or platinum³⁴ in the organic semiconductors. Incorporating such heavy metal atoms into polymers can reduce solubility. To prevent back-transfer issues, the mixed state must lie lower than the triplet state. This proves difficult in blue emission, where finding such a high lying triplet state can be a problem. Additionally, compared to blue fluorescent organic semiconductor devices, blue phosphorescent devices can suffer from a reduced lifetime due to the higher recombination rate; so despite the blue phosphorescent devices having a higher emission efficiency, the lifetime remains one of the main hindrances for the commercialisation of flexible PLEDs.

Light Outcoupling

Once the charges have recombined to emit light, the light must leave the devices in the forwards direction to be viewed. Total internal reflection is a big problem in PLEDs due to the high refractive indices of the polymer layers as well as the ITO layer.^[40] A possible solution to this problem would be to find materials with a more suitable refractive index. There have been efforts to use patterned substrates and gratings, but these are generally quite complicated to implement on a large scale.

Losses and measuring Degradation

The external quantum efficiency is proportional to that fraction of the photoluminescence quantum efficiency that is not lost due to electrons and holes recombining into non-radiative states (lost due to quenching, mismatch of charge carrier densities) and that is coupled out of the device.

There are many quenching mechanisms: the formation of triplets that don't decay radiatively, exciplex/excimer/aggregate states that have a low efficiency;

- I. Formation of triplets that decay non-radiatively
- II. Exciplex/excimer/aggregate states that have a low efficiency
- III. Exciton dissociation due to traps, electric fields, interfaces, impurities, defects etc.

- IV. Non-radiative decay of singlets due to electrical charges on the polymer chains and
- V. Luminescence quenching near the conducting electrodes, especially if they are metallic.

Effective device design and choice of materials in the system can help reduce all of these, although the heavy metal complex is the only way to do anything about the non-emissive triplet states.

A problem for commercial application is that organic devices degrade, so it is important to measure how long-lived the devices are. Device degradation can be due to irreversible chemical changes that introduce an increasing number of deep traps during the device operation,^[41,42] heating during the flow of the electrical current through the device, causing changes in morphology and the interface morphologies with the electrodes, and diffusion of ions from ITO or PEDOT:PSS into the polymer, which will act as luminescent quenching sites.

To measure the degradation of a device, the devices are usually encapsulated in an inert atmosphere, so that no H₂O or air can reach the materials of the device. The 't₅₀' lifetime of a device is defined as the time taken for the light from a pixel or from the whole display to reduce by half from its starting value.

2.3.3 Human Perception of Light

Rods and Cones

The human eye perceives certain wavelengths at a higher intensity than other colours. This means that red diodes have to 'work' harder than green diodes. So that we can analyse LEDs for practical applications we need a system that takes this into account for our measurements. The Commission Internationale de l'Eclairage (CIE) produces the standard models and curves which the solid state lighting industry uses. LED measurements collect the number of photons of each energy received by the detector but then a correction curve is applied to factor in the way the eye perceives light depending on its colour and intensity.

In our eyes there are two types of light sensitive cells, the rods and the cones. The cones are active at normal light levels and when light levels are low the rods have a stronger influence on what we see. The correction curve for normal light intensities is the photopic curve and is the one that is most useful, as we do not generally deal with low light levels in display applications. The peak in the photopic curve at which our eyes are most

sensitive is 555 nm, green light. The maximum sensitivity of the cones at this wavelength is 683 lm W⁻¹, the efficiency of an ideal, 100% efficient 555 nm light source. To quantify the light, what is used are the (CIE) chromaticity coordinates, the correlated colour temperature (CCT), and the colour rendering index (CRI).

When radiance leaving a surface or point is weighted with the photopic curve the result is 'luminance' — a approximate measure of bright we perceive something to be when viewed from a given direction. The units for luminance are lumens per square meter per steradian or candela per square metre.

Power efficiency and luminous efficiency

The way the human eye perceives some colours with a greater intensity than others also has an impact on how we talk about the efficiency of a LED.

The luminous efficiency, η_L , is a measure of the number of photons emitted to the number of electrons injected with a weighting applied to these measurements that takes the photopic response of the human eye into account. Green light is weighted heavily, while emissions in the infrared or ultra violet would be set to zero. Green devices will always appear more efficient, so it is important to list the spectrum of the device along with its luminous efficiency. The luminous efficiency for a pixel can be calculated with the following formula assuming Lambertian emission from the device, where I_{pixel} is the current the device draws through the pixel and A_{pixel} is the area of the pixel. Luminous efficiency is expressed in candela per ampere (cd A⁻¹).

$$\eta_L = \frac{\text{luminance}}{I_{pixel}/A_{pixel}} \quad \text{Equation 2.4}$$

Although the current through a pixel is used to calculate this efficiency, it does not take into account at which voltage this current was achieved — an important factor in solid state lighting. A better measure of efficiency is the power efficiency, η_P , given in lm W⁻¹, which is the power in lumen (for the forward direction only) over the electrical power needed to drive the pixel (note: [1 cd] = [1 lm]/ π)

$$\eta_P = \frac{\text{luminance} \cdot \pi}{V \cdot I_{pixel}/A_{pixel}} \quad \text{Equation 2.5}$$

A full description of a PLED that takes the human eye's perception into account thus includes the luminous efficiency plotted against voltage, the spectrum, the power efficiency plotted against the applied voltage and the current density *vs.* voltage.

3 Experimental Methods

3.2 Materials

Most of the organic materials used in this research are co-polymers containing polyfluorene moieties (Fig. 3.1). The name fluorene is derived from the fact that the material has interesting fluorescent properties; polyfluorenes are the only family of conjugated polymers whose emission properties can be tuned to allow them to emit light across the whole of the visible spectrum.

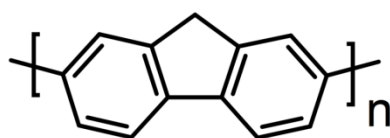


Figure 3.1: Chemical structure of polyfluorene; the fluorene unit takes on a rigid, planar state.

Structurally, polyfluorenes have a planar component in their backbone consisting of phenylene rings that are fused together with a bridging carbon unit to restrict the movement of the phenylene rings. They make good light emitting layers as they have high photoluminescence (PL) efficiencies and are generally air-stable. The energy gap of polyfluorene co-polymers can be tuned with the careful selection of suitable electron donating/withdrawing moieties to be inserted into the backbone.

Alkyl side chains are attached to the bridging carbon in the polyfluorene unit; this generally has only a minor effect on the backbone chemistry, however, through their bulkiness they can affect the packing structure and subsequently the material's properties. Side chains are necessary as they allow the polymer to be dissolved in a variety of organic solvents and achieve thin, uniform films when spin coated. They can also add functionality, e.g. cross-linkable side chains.

The method of choice for producing the co-polymers is Suzuki coupling, which leads to a distribution of chain lengths in the final polymer (compared to living polymerisation, which gives a much smaller polydispersity; living polymerisation is well suited for block-polymer creation). Suzuki coupling is an organic reaction that couples boronic acids to aryl- or vinyl-halides, relying on a palladium(0) complex as a catalyst.^[43] The method is tolerant

to the functional groups on the backbone, as well as allowing for a directly alternating A-B structure and makes high molecular weights possible to achieve. However, the polymerisation technique can leave foreign atoms at the end of the chains that can act as impurities. The effect of these impurities is reduced in long polymer chains and more pronounced in short polymers with fewer than ten repeat units, so-called oligomers.

3.2.1 F8BT

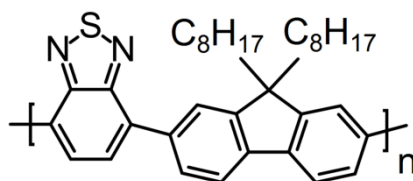


Figure 3.2: The chemical structure of F8BT.

Poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT) is a polyfluorene co-polymer with benzothiadiazole moieties (Fig. 3.2). Benzothiadiazole is very electron deficient, which means that it forms a low band gap when it is copolymerised with an electron rich monomer. In the case of F8BT, the polyfluorene is in itself electron poor though. This leads to an overall electron poor polymer, hence its excellent H₂O and air-stability with an I_p of 5.9 eV^[44,45] and a relatively high E_a of 3.3 eV.^[44,45] The benzothiadiazole unit on its own is not very soluble due to the slightly heavier atoms in it and the lack of side chains, so it must be balanced with the polyfluorene groups. The hybridisation of the acceptor and donor components leads to a reduced energy gap compared to the parent monomers, with the LUMO primarily located on the benzothiadiazole (BT) units.^[46]

3.2.2 PFO

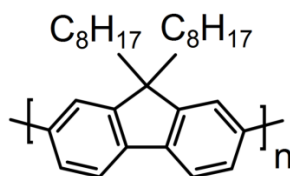


Figure 3.3: The chemical structure of PFO.

Poly(9,9-dioctylfluorene) (PFO or F8) is a blue emitting polymer (Fig. 3.3). It is the basis of all the above polymers, and as already mentioned, the moieties in this chain are relatively

electron poor, and thus should be quite air stable — the polymer is prone to oxidative degradation, though, leading to quenching sites and the loss of its pure blue colour.^[47] The degradation mechanism is not unique to PFO, it has been identified in other light emitting polymers, but it does affect the blue colour strongly.

3.2.3 TFB and PFB

A lot of interlayer work has focused on using arylamine containing polyfluorenes. TFB [poly(2,7-(9,9-di-n-octylfluorene)-alt-(1,4-phenylene-((4-sec-butylphenyl)imino)-1,4-phenylene))] and PFB [poly(9,9-dioctylfluorene-2,7-diyl-co-bis-N,N'-(4-butylphenyl)-bis-N,N'-phenyl-1,4-phenylenediamine)] have similar energy levels: the electron affinity (E_a) of TFB is 2.3 eV^[48] and the ionisation potential (I_p) is 5.3 eV,^[49] while PFB has an I_p of 5.09^[49] — its E_a is the same as TFB's.^[50] The chemical structures of TFB and PFB are shown in Fig. 3.4.

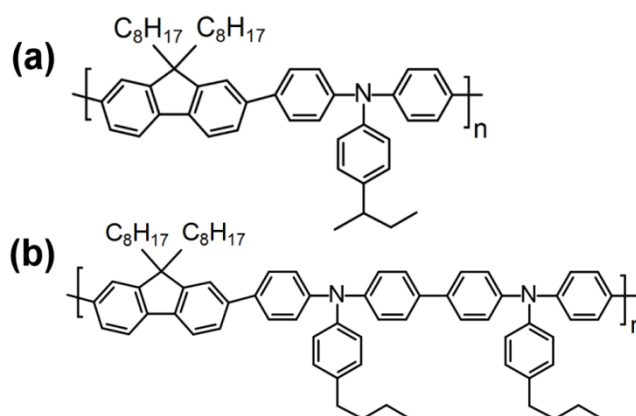


Figure 3.4: The chemical structures of a) TFB and b) PFB are shown.

Both materials are polyfluorene-triarylamine copolymers. Electron rich triarylamine enables good transport properties and preserves the amorphous phase, due to its geometry, which also acts as a conjugation blocker; this blocking of the conjugation means that the conjugated segments are very small, which also means a lower lying HOMO level, which leads to a wider bandgap with good ambient stability in air.

3.2.4 F8T2

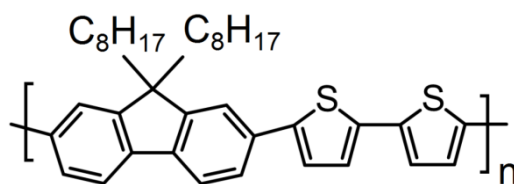


Figure 3.5: The chemical structure of F8T2.

Poly(9,9-dioctylfluorene-co-bithiophene) (F8T2) is a polyfluorene copolymer with dithiophene moieties (Fig. 3.5), which give the material its characteristically good hole transporting properties. As such it is often used in transistors. The electron mobility, as measured in transistor configuration, is very high too, due to the thiophene units, which are electron rich. It is a glassy nematic polymer, with reasonable ambient stability and charge mobilities of up to $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,¹⁷ which is still over an order of magnitude less than top organic semiconductors for transistors. F8T2 has a deep I_p of 5.5 eV^[51,52] and an E_a of 3.2 eV.^[51]

3.1 Sample Fabrication

For device fabrication glass substrates were used that were pre-patterned with stripes of ITO (ITO: thickness $\sim 140 \text{ nm}$; $12 \text{ mm} \times 8 \text{ mm}$; sheet resistance $\sim 15 \text{ } \Omega/\square$; conductivity $\sim 4000 \text{ S cm}^{-1}$). These were solvent cleaned in an ultrasonic bath to remove the photo resist: first with acetone, then isopropanol, finally with a 2% by weight solution of Hellmanx detergent in deionised water. The substrates were then rinsed in deionised water to remove any solvent traces; they were blown dry with nitrogen gas and left on a hotplate at $\sim 125^\circ\text{C}$ for 15 minutes. Then they were plasma ashed for 3 minutes at 80W (Emitech K1050X plasma asher). Quartz substrates ($12 \text{ mm} \times 12 \text{ mm} \times 1.5 \text{ mm}$) for optical analysis of materials were cleaned in the same manner.

Polymer solutions (in concentrations between 0.5 mg ml^{-1} – 10 mg ml^{-1} by weight) were all heated to temperatures of around 60°C to help dissolve them, although they were spin coated from room temperature.

PLEDs were fabricated by first spin-coating a 35 nm layer of PEDOT:PSS (Baytron P VP AI4083) onto ITO-coated glass substrates and then thermally annealing this layer at 135°C for 30 minutes. For those devices without an IL, a 60 nm layer of F8BT/70 nm layer of SY/70 nm layer of Lumation Green Series 1300 (LG 1300) was then spin-coated on top of

the PEDOT:PSS from a toluene solution (F8BT and SY) or chlorobenzene solution (LG 1300). For those devices with a conventional low-workfunction metal cathode these devices were then completed by thermally depositing 20 nm of Ca capped by 140 nm of Al. The evaporation took place in a thermal evaporator in a nitrogen atmosphere glovebox at pressures lower than 10^{-6} mbar. Each pixel, as defined by the spatial overlap of the anode and cathode, had an area of 4.5 mm^2 . For those devices with a CPE/Al cathode, a ~ 10 nm layer of CPE was spin-coated on top of the light emitting polymer layer from a 2-methoxyethanol solution in a nitrogen glovebox ($< 0.1 \text{ ppm H}_2\text{O}$, $< 0.1 \text{ ppm O}_2$). 2-methoxyethanol is a polar solvent in which commonly used light emitting polymers such as F8BT do not readily dissolve, which prevents intermixing with the emission layer. All CPE devices also contained a TFB IL. The IL devices were fabricated in the same way, except that a 10-15 nm TFB/PFB or 2-5 nm F8T2 layer was deposited on top of the PEDOT:PSS from toluene solution and thermally annealed at 180°C for 60 minutes prior to spin-coating F8BT/LG 1300/SY. The annealing step helps to prevent the IL material being washed away or intermixing with the emission layer material when the latter is deposited on top from organic solvent solution.³ These IL thicknesses represent the thickest insoluble layers of each material that could be formed *via* thermal annealing. Thinner ILs were created by spin-coating from more dilute solutions. Doped ILs were spin-coated from toluene solutions of the IL material together with 1, 3 or 7% F₄TCNQ by weight. For hole-only diode structures the Ca/Al top contact was replaced with Au.

UV-visible absorption and photoluminescence (PL) spectroscopy measurements of single layers of the polymers were deposited on quartz substrates. PL and UV-visible absorption studies of the PEDOT:PSS/IL component of the device stack were, for simplicity, performed on samples deposited on quartz substrates. For ultraviolet photoelectron spectroscopy (UPS) measurements the same structure was used, but with glass/ITO as the substrate instead of quartz. The doped and undoped IL series studied in Chapter 4 were annealed prior to UPS measurements. They were excited with a He I, 21.2 eV beam, with an Au electrode as reference. The CPE films, F8BT/CPE and SY/CPE samples for UPS and x-ray photoelectron spectroscopy (XPS) measurements were deposited directly onto ITO and were not annealed. They were excited with a He II, 40.8 eV beam, with an Au electrode as reference. Raman measurements were carried out on films drop-cast or spin-coated onto quartz substrates.

3.2 Analysis Techniques

3.2.1 Optoelectronic Characterisation of PLEDs

PLEDs were held in an air tight testing chamber under nitrogen for analysis. This chamber was connected to a Keithley SourceMeter 2400 *via* a mechanical control box, which enabled switching between the six pixels on the device. The source meter applied the voltage to one pixel at a time and recorded the corresponding current through the PLED, while a Minolta LS100 luminance meter recorded the pixel brightness. The source meter was connected and controlled through a PC with a programme written in LabVIEW. The electroluminescence spectrum of a pixel was recorded using an Ocean Optics USB 2000 CCD spectrophotometer. Its CCD records the spectrum in $\mu\text{W}/\text{cm}^2/\text{nm}$.

3.2.2 UV-Visible Absorption Spectroscopy

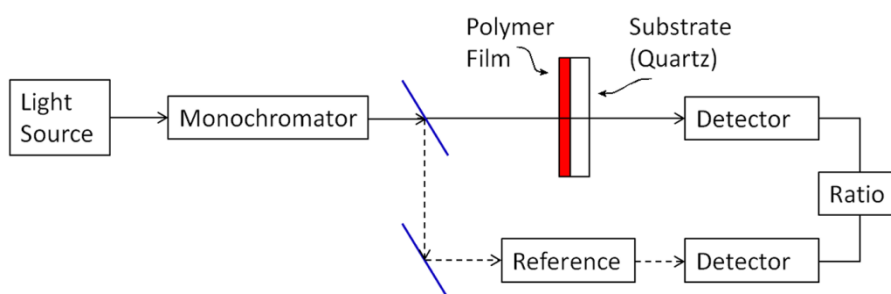


Figure 3.6: Schematic of experimental set-up of UV-visible absorption measurements of polymer film samples.

An ATI Unicam UV-visible spectrophotometer was used to determine the absorption spectra of thin polymer films. The experimental setup is shown in Fig. 3.6. The light from the ultra-violet and visible light sources converges to form a single beam which is then passed through a monochromator. The monochromator works by using two gratings to disperse the light to separate the different wavelengths. A slit at the exit controls which narrow range of wavelengths are allowed through. The beam is split into two identical parts, one that travels to the "sample" and one that travels to the "reference", though they travel the same distance through the air. The recorded transmittance, T , is given in percentage and is equal to the ratio of the intensities and intensities of the sample and reference beam. Light at the sample is either absorbed, reflected or scattered, so reflection and scattering is kept to a

minimum in order to determine the polymer's absorbance, A , which can be calculated as follows:

$$A = -\log_{10}\left(\frac{\text{"transmittance of film and substrate"}}{\text{"transmittance through air"}}\right) \quad \text{Equation 3.1}$$

Absorbance obeys Beer's law, so thicker or thinner films have different values — it is not a material property, but specific to each sample. Samples of the same layer thickness should therefore be compared. The absorption coefficient, α , which is independent of film thickness is calculated from the transmission if the layer thickness, d , is known:

$$T = e^{-\alpha d}, \quad \text{Equation 3.2}$$

which can also be expressed in terms of A :

$$\alpha = \ln(10) A/d \quad \text{Equation 3.3}$$

To determine α accurately samples with different layer thicknesses are measured.

3.2.3 Photoluminescence Measurements

A Spex FluoroMax Jobin-Yvon spectrofluorometer was used to measure photoluminescence (PL) of thin polymer films. The machine uses a R928P photomultiplier tube and a xenon arc lamp (150 W) and was equipped with an integrating sphere for photoluminescence quantum yield (PLQY) measurements. Focused light from a 150 W continuous output xenon lamp is sent through a monochromator, which disperses the light into constituent wavelength components using a reflection grating. It is then refocused and sent either directly to the sample (or into the integrating sphere for PLQY measurements) and the output is recorded with a R928P photomultiplier tube. The beam is split so that ~8% of the light is collected by a reference detector (a photodiode) — this signal is used to correct for the wavelength response of the xenon lamp and the monochromator. Random fluctuations in the lamp's output can also be corrected for this way. The band-pass of the incident light is determined by the width of the excitation spectrometer's slits, which can be controlled through the Datamax spectroscopic software package. While wider slits allow for higher counts, spectral resolution can be lost. The slit width of the emission beam determines the intensity of collected signal.

The alignment of the film in the beam path can alter the optical path length and thus the absorption from the excitation beam. For most PL measurements the samples were

placed at an angle of $\sim 60^\circ$. PLQY is measured with an integrating sphere to account for absorption of the samples. PLQY is useful because it can be combined with the fluorophore lifetime measured by TCSPC to give the radiative and non-radiative decay rates. To determine the PLQY of a sample three PL measurements under identical optical and geometric conditions are required. First the empty integrating sphere is measured (a), then another measurement is taken with the sample placed inside the sphere, but outside of the beam path (b). In the final measurement the sample is placed inside the integrating sphere and inside the beam path (c). The set-ups are illustrated in Fig. 3.7 (a), (b) and (c) along with the results of the three measurements (d) for a 70 nm film of F8BT on quartz. The three peaks at 455 nm correspond to the detection of the excitation signal and the integrated area under these peaks (L_a , L_b and L_c) can be used to determine how much light was not absorbed by the sample in each of the measurements. At longer wavelength the fluorescence from the sample is visible and this signal can be corrected for the absorption of the integrating sphere to yield the amount of light emitting from the sample (the integrated areas under these curves are P_b and P_c). Then the PLQY is given by:

$$\eta = \frac{P_c - (1-A)P_b}{L_a A}, \quad \text{Equation 3.4}$$

where A is defined as $A = 1 - (L_c/L_b)$. The experimental procedure for PLQY measurements is described in more detail in reference ^[53].

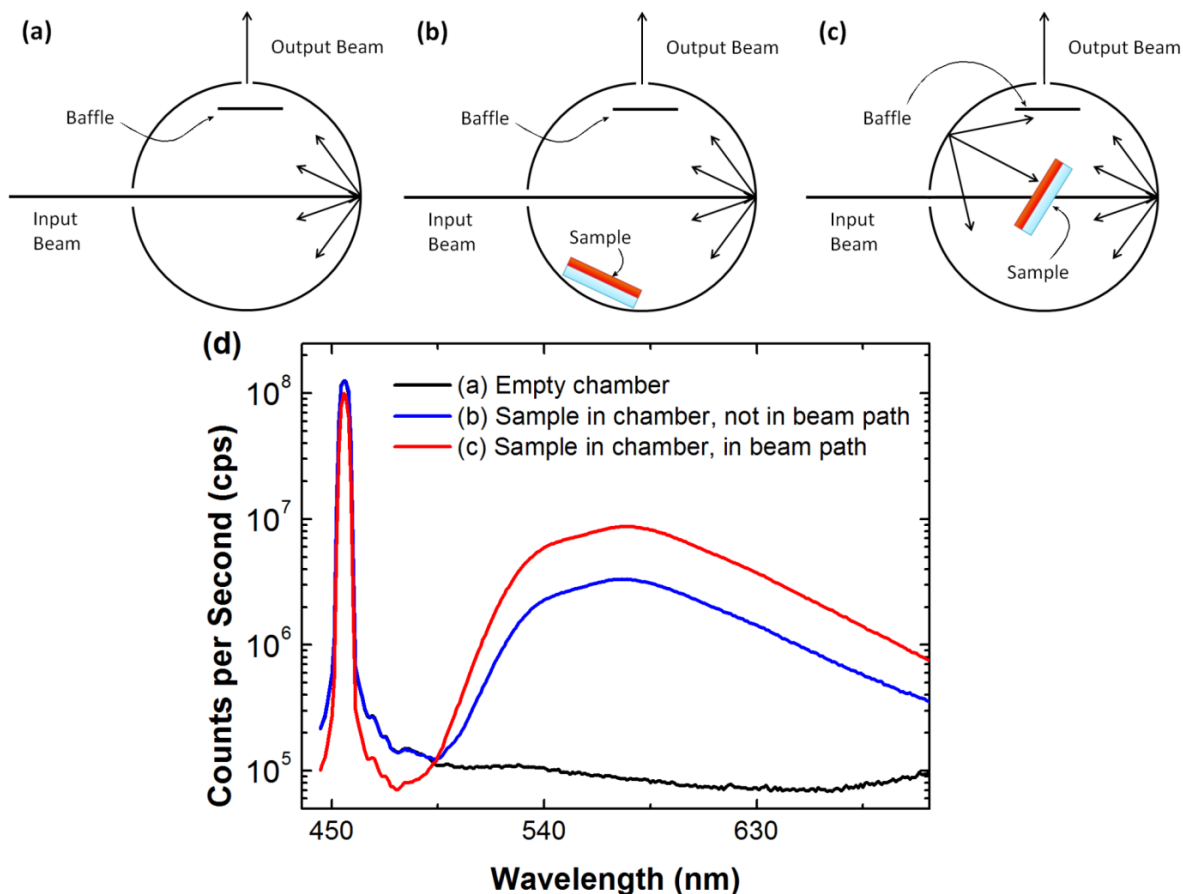


Figure 3.7: Schematic of experimental set-up of PL measurements of polymer film samples for PLQY (a-c) and graph showing the corresponding measurements for each set-up condition for a 70 nm film of F8BT. (Adapted from de Mello *et al.*^[53]).

In Chapter 4 the effect of annealing was studied for both doped and un-doped IL samples by measuring their PL behaviour before and after the annealing step. The measurements were carried out for samples held within an integrating sphere using scattered laser light to excite them. Excitation wavelengths were selected to lie close to the respective absorption maxima, namely 380 nm for TFB and PFB, and 360 nm for F8T2. The samples were placed inside an integrating sphere, again offset from direct illumination by the excitation beam.

Time-correlated single photon counting (TCSPC) is a technique with which PL can be recorded with picosecond time resolution. Single photons from a periodic PL signal (generated from a pulsed laser excitation of the sample) are detected, the time of the detection is logged and the waveform is reconstructed from the individual time measurements. The probability of detecting one photon in each signal period should be

much less than one to allow an accurate histogram of the photon detection times to be created. The sensitivity of the measurement is limited by the dark count rate of the detector.

When an excited state in a molecule decays back down to the ground state it does so in an exponential fashion according to,

$$I(t) = I_0 e^{-t/\tau}, \quad \text{Equation 3.5}$$

where I_0 is the intensity at time zero (upon excitation) and τ is the lifetime. The PL decay signals were therefore fitted in OriginPro 8 software package with the function

$$y = y_0 + A_1 e^{-x/t_1} \quad \text{Equation 3.6}$$

for mono-exponential decays or with

$$y = y_0 + A_1 e^{-x/t_1} + A_2 e^{-x/t_2} \quad \text{Equation 3.7}$$

for bi-exponential decays to extract τ from the data. For the fitting the parameters were bounded so no parameters could go negative and for bi-exponential fits the limits were based on those found for mono-exponential fits of the first few ns of the decay curve and the final few ns of the decay curve respectively (generally limits an order of magnitude either side of those values were chosen).

Transient photoluminescence data presented in this thesis was collected by using a Horiba Jobin Yvon IBH Fluorocube. The films were excited from the front and back (through the quartz) to check for any variations of the signal. The results reported in this thesis are the results from front excitations. The PL decay of the samples were measured following excitation from a pulsed laser (repetition rate of 1 MHz, wavelength 467 nm and 80 $\mu\text{W cm}^{-2}$ average intensity). The instrument response function (IRF) had a 250 ps full width at half maximum.

3.2.4 Electroluminescence and Current Density Transient Measurements

PLEDs were held in an air tight testing chamber under nitrogen for analysis. This chamber was connected to a Keithley SourceMeter 2400 *via* a mechanical control box, which enabled switching between the six pixels on the device. The source meter applied the voltage to one

pixel at a time and recorded the corresponding current through the PLED, while a Minolta LS100 luminance meter recorded the pixel brightness. The source meter was connected and controlled through a PC with a programme written in LabVIEW. The electroluminescence spectrum of a pixel was recorded using an Ocean Optics USB 2000 CCD spectrophotometer. Its CCD records the spectrum in $\mu\text{W}/\text{cm}^2/\text{nm}$.

For current density and EL transient measurements the PLEDs were held in an air tight testing chamber under nitrogen. This chamber was connected to a HP 3325B pulse generator *via* a mechanical control box, which enabled switching between the six pixels on the device. The light emission from the pixel was measured by a PDA36A-EC photodiode from ThorLabs. The output from the pulse generator, the photodiode and the PLED testing chamber were fed to a Tektronix 4-channel oscilloscope for simultaneous measurement. The pulse generator applied voltage pulses of 4-8 V to one pixel at a time. To lower the noise the average of up to 200 individual measurements was used to determine the delay time, t_d , and rise time, t_r , between the on-set of the voltage pulse and the on-set of the EL signal (Fig. 3.8). The rise time of the PLED is deduced from the intersection of lines on the rising edge of the EL and its final value. It represents the time after which the EL tends to saturate and therefore reflects the build-up of the minority carrier density in the RZ.^[54] The delay time, t_d , is the time from the on-set of the voltage pulse and the EL pulse (the onset is found in each case through extrapolation the slope of the rising edge of the signal) and represents the time until the holes and electrons meet and recombine radiatively in the device.^[54]

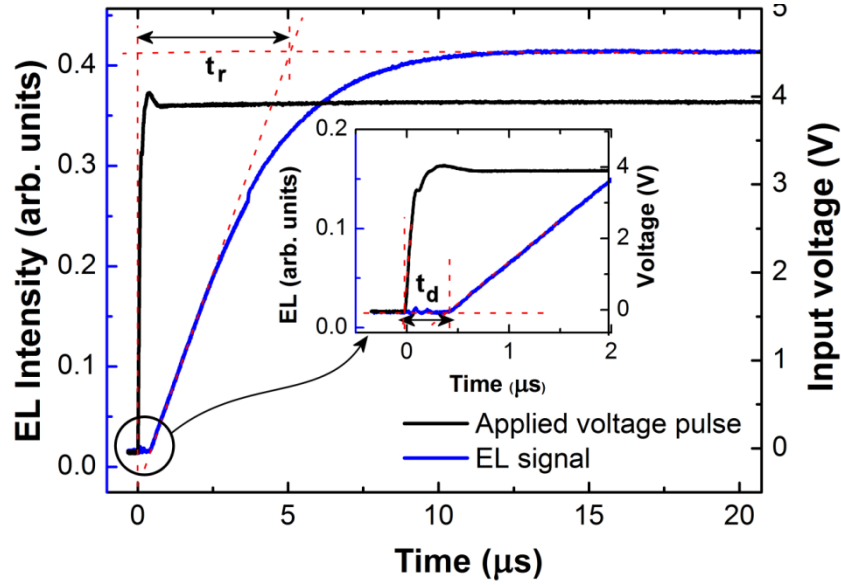


Figure 3.8: EL transient measurement of a F8BT PLED with CPE EIL illustrating how the rise time, t_r , and delay time, t_d , (inset) is determined.

3.2.5 Scanning Kelvin Probe Microscopy Transient Measurements

Scanning Kelvin Probe Microscopy (SKPM) is a variation of Atomic Force Microscopy (AFM). In SKPM the 2D distribution of the potential at the sample surface on nanometre scales. The measured potential map can be related to doping at the surface, bend-bending in semiconductors, or trapped charges amongst other things. The method works by measuring the potential offset between a probe tip and the sample surface. The AFM cantilever, onto which the probe tip is mounted, acts as reference electrode to form a capacitor with the sample surface. The tip is scanned laterally over the sample surface (without being in direct contact with it) with a constant separation to produce the 2D map of the surface potential.

In AFM mode the cantilever would be driven at its mechanical resonance frequency, however, in SKPM it is not; but an alternating current ($V_{ac}\sin(\omega t)$) is applied at its resonance frequency instead. A DC offset voltage is then applied to the cantilever; it is controlled in a feedback loop so that the output the lock-in amplifier measuring the ω signal is zero. The value of the DC offset that zeros the ω signal then gives us the data with which we can construct the map of the absolute surface potential.

For the fabrication of the scanning kelvin probe microscopy (SKPM) samples thin (~ 10 nm) layers of polymer were spincoated onto solvent cleaned substrates with

interdigitated electrodes (20 μm channel separation). The substrates were silicon wafers that had a 230 ± 10 nm SiO_2 (thermal oxidation) layer on their surface followed by 30 nm Au electrodes with 10 nm high work function adhesion layer (ITO) on top (Fig. 3.9). They were purchased from the Fraunhofer-Institut (Photonische Mikrosysteme). SKPM transient measurements were carried out by applying either a positive or negative voltage pulse of between 1 and 10 minutes in length to one electrode, while the change in surface potential was recorded at the edge of the ground electrode with a NCST Au cantilever in non-contact EFM mode on a Park System NX-10. The applied voltage was supplied and supplied by the Park System NX-10 and controlled through the supplied software interface.

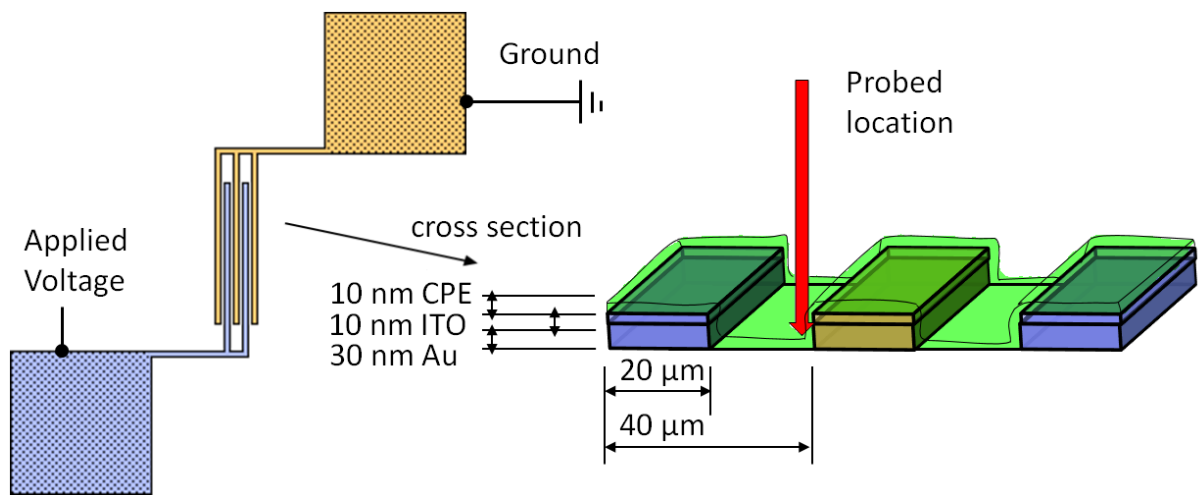


Figure 3.9: Top-down view and cross section through interdigitated Au/ITO electrodes for SKPM sample fabrication with ~ 10 nm CPE layer deposited on top. Probed location indicated by red arrow near at the edge of the grounded electrode.

4 Role of Ultra-thin Anode Polymeric Interlayers in Improving Efficiency of Polymer Light Emitting Diodes

Insertion of ultra-thin polymeric interlayers (ILs) between the poly(3,4-ethylenedioxythiophene):polystyrene sulphonate (PEDOT:PSS) hole injection and poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT) light emission layers of polymer light emitting diodes (PLEDs) can significantly increase their efficiency. In this paper we investigate experimentally a broad range of probable causes of this enhancement with an eye to determining which IL parameters have the most significant effects. The importance of hole injection and electron blocking was studied through varying the IL material (and consequently its electronic energy levels) for both PLED and hole-only diode structures. The role of IL conductivity was examined by introducing a varying level of charge-transfer doping through blending the IL materials with a strong electron-accepting small molecule in concentrations from 1% to 7% by weight. Depositing ILs with thicknesses below the exciton diffusion length allowed the role of the IL as a physical barrier to exciton quenching to be probed. IL containing PLEDs were also fabricated with Lumination Green Series 1300 (LG 1300) light emission layers. The PLEDs were modeled using a 3D multi-particle kinetic Monte Carlo simulation coupled with an optical model describing how light is extracted from the PLED. The model describes charge carrier transport and interactions between electrons, holes, singlets and triplets, with the current density, luminance and recombination zone (RZ) locations calculated for each PLED. The model shows F8BT PLEDs have a narrow charge RZ adjacent to the anode, while LG 1300 PLEDs have a wide charge RZ that is evenly distributed across the light emitting layer. Varying the light emitting layer from F8BT to Lumination Green Series 1300 we therefore experimentally examine the dependence of the IL function, specifically in regard to anode-side exciton quenching, on the location of the RZ. We found an exponential dependence of F8BT PLED luminance on the difference, δ , in the highest occupied to lowest unoccupied molecular orbital energy gap between the light emitting polymer and a semiconducting polymeric IL, with δ consequently the most important parameter determining efficiency. Understanding the exponential effect that wider energy gap IL materials have on exciton quenching may allow δ to be used to better guide PLED structure design.

This work was carried out in collaboration with Mr. Edward N. Wright, Department of Physics, University of Bath, Bath, BA2 7AY, United Kingdom, who carried out the modelling work.

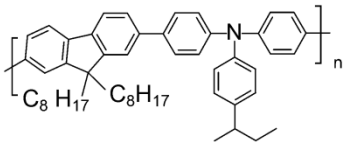
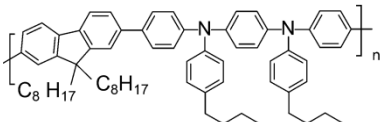
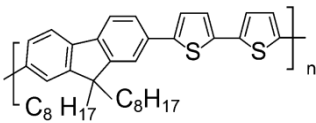
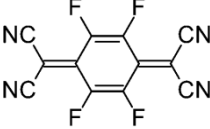
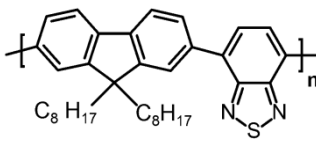
4.1 Introduction

Light-emitting, vacuum-deposited organic small-molecule LEDs are increasingly being used in commercial displays for mobile phones and televisions. Polymer light emitting diodes (PLEDs) have not yet achieved a corresponding commercialization but impressive demonstrators have been shown and there is a view that their ability to be manufactured using printing methods offers significant cost advantages. In that regard it is worth noting that for lighting applications there is already a consensus that small molecule OLEDs will need to be solution processed in order to reach a reasonable price point. Simple design solutions to further increase PLED efficiency and to enhance other characteristics are still required. Recent work in hybrid organic-inorganic LEDs has realized high luminous efficiencies in an inverted structure with a metal oxide cathode layer.^[12,13,55,56] Yet the highest luminous efficiencies in such devices are only achieved by replacing the standard ~ 100 nm thickness light emitting polymer (LEP) layer with a micrometer thick LEP layer, yielding high operating voltages and consequently low power efficiencies. The inclusion of a 10-15 nm interlayer (IL) of poly(9,9-dioctylfluorene-*co*-N-(4-butylphenyl)-diphenylamine) (TFB) between the PEDOT:PSS hole injection layer and the poly(9,9-dioctylfluorene-*alt*-benzothiadiazole) (F8BT) emission layer significantly enhances performance,^[14] also for inverted structures.^[57] The dominant mechanism of the efficiency increase has not yet been clearly identified although it has been carefully studied for related PLEDs with poly(9,9-dioctylfluorene-*alt*-bithiophene) (F8T2) light emission layers.^[58]

In simple thin-film PLEDs a transparent indium tin oxide (ITO) anode typically injects holes into the light-emission layer *via* a PEDOT:PSS conducting polymer layer, while electrons are injected *via* a low work function metal cathode. The PEDOT:PSS layer increases the ITO anode work function from $\sim 4.6 - 4.8$ eV to $\sim 5.1 - 5.2$ eV, thereby assisting hole injection.^[59] In this structure the IL is applied on top of the PEDOT:PSS where it forms a physical barrier that improves device performance, probably by both preventing the acidic PEDOT:PSS from degrading the active layer and also by limiting exciton quenching through moving the recombination zone (RZ) away from the ITO anode.^[14,58,60] The IL could also improve hole injection, hinder electrons from reaching the anode, and promote a better charge balance within the LEP layer.^[58] Previous work in the literature has focused on

studying the role of the IL as an electron blocking and/or hole injecting layer^[61–63] and in promoting charge balance within the emission layer.^[61,64] The IL effect on pinning of the light emission layer's Fermi level to that of the PEDOT:PSS hole injection layer^[65] has also been considered.^[58] IL conductivity, a parameter that should also have an effect on efficiency, has not been adequately investigated in the literature^[61] although the contributing effect of mobility has.^[58] There are clearly many parameters to take into account, but no study has investigated them all. This study focuses specifically on investigating the relative effect that the major IL parameters have on the performance of thin-film F8BT PLEDs.

Table 4.1: Material chemical structures and their electronic energy levels.

Material	Chemical structure	$E_a^{a,d}$ (eV)	$I_p^{b,d}$ (eV)	E_g^c (eV)
TFB		2.3 ^[48]	5.3 ^[49]	3.0
PFB		2.3 ^[50]	5.1 ^[49]	2.8
F8T2		3.2 ^[51]	5.5 ^[51,52]	2.3
F ₄ TCNQ		5.24 ^[66]	-	-
F8BT		3.3 ^[44,45]	5.9 ^[44,45]	2.6
LG 1300 ^e		2.9 ^[67]	5.4 ^[63,67]	2.5

^a E_a is the electron affinity.

^b I_p is the ionization potential.

^c E_g is the energy gap, $I_p - E_a$.

^d E_a and I_p values are accurate to ± 0.1 eV and taken from the literature on the basis of being measured by the same method for comparability.^[44,45,48,49,51,52,66]

^eLG 1300 is a complex copolymer containing fluorene moieties, arylamine moieties for hole injection and benzothiadiazole moieties, which allow for good electron injection properties and which are responsible for the polymer's green electroluminescence emission. LG 1300 was supplied by the Sumitomo Chemical Company.

F8BT emission layer PLEDs were fabricated with three different semi-conducting polymer IL materials, two arylamine-fluorene copolymers (TFB and poly(9,9-dioctylfluorene-

co-bis(N,N'-(4-butylphenyl))bis(N,N'-phenyl-1,4-phenylene)diamine) (PFB)) and one bithiophene-fluorene copolymer (poly(9,9-dioctylfluorene-co-bithiophene) (F8T2)). Their different energy levels (listed alongside their chemical structures in Table 4.1) allow the role of electron blocking and hole injection barriers to be studied. The strong electron acceptor tetrafluoro-tetracyanoquinodimethane (F₄TCNQ) was blended with the IL materials in varying concentrations to p-dope them in order to examine the role of IL conductivity on PLED performance. To investigate whether ILs with thicknesses below the exciton diffusion length (~ 15 nm)^[14,68,69] can prevent luminance quenching by the anode, we spin-coated < 5 nm thick layers by using concentrations of < 1 mg/ml of the IL materials. F8BT has a relatively deep lowest unoccupied molecular orbital (LUMO) and a reasonably high electron mobility,^[44,70] which combined with a relatively deep highest occupied molecular orbital (HOMO) may lead to preferential electron injection and transport and consequently an electron-hole RZ lying adjacent to the anode. Another green emitting active layer, Lumination Green Series 1300 (LG1300, also known as Green K)^[55,71,72] was used to study the effect of RZ location on the role of the IL. LG1300 has relatively balanced electron and hole mobilities and should therefore have a broad, centrally located RZ.^[73,74] 3D multi-particle Kinetic Monte Carlo (KMC) simulations that include the transport of and interactions between electrons, holes, singlets and triplets, coupled with an optical model describing how light is extracted from the PLED, have been used to calculate the current density, luminance and the location of the RZ in both LG 1300 and F8BT PLEDs with and without ILs. KMC modeling offers many benefits over other simulation techniques. The simulation parameters used within KMC are linked to molecular properties unlike the conventional drift diffusion models concerned with average properties across a layer of the device. In addition to this, the KMC model explicitly calculates the coulombic interactions between electrons and holes, making exciton formation, transport and recombination possible to model, something which is typically lacking in the approach of finding steady state solutions to the 3D Pauli master equation.

We demonstrate the importance of preventing exciton quenching at the anode and cathode sides of the light emitting layer. Small changes in the energy gap differences of the LEP and adjacent organic layers can have a large effect on the luminance, especially when the RZ lies adjacent to the interface. Based on the results of our study, we propose that ILs with wider energy gaps could lead to the design of more power efficient PLEDs while retaining a thin-film device structure.

4.2 Experimental Methods

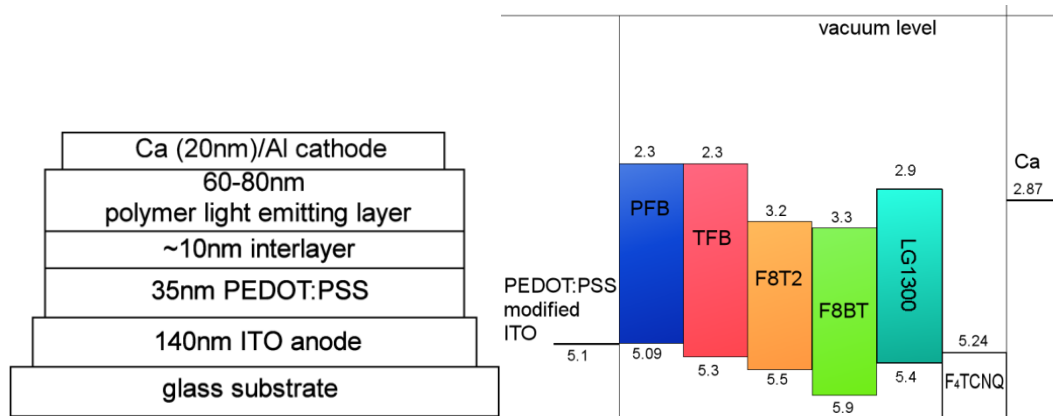


Figure 4.1: On left, schematic PLED device structure used for our experiments. Right, energy level diagram. F8BT and LG 1300 were used for the light emitting polymer layer. TFB, PFB and F8T2 were used as IL materials and F₄TCNQ was used as a p-dopant. In addition, some devices were fabricated without ILs. Hole-only diode structures used Au as top contact in place of Ca/Al.

Structure of PLEDs studied in this chapter is detailed in Fig. 4.1. The results of simulations performed using a combined multi-particle 3D KMC and optical model are compared to the experimental PLED data. The electronic and optical processes are calculated within the simulation for voxels placed on a regularly spaced user designed 3D Cartesian lattice of lattice constant $a = 1.0$ nm, a typical value used in Monte Carlo simulations^[75–77] and a good approximation to the physical volume of a monomer unit. Each voxel represents a hopping site available to electrons, holes, singlets or triplets with certain parameters describing separately how each of these species interacts with the material the voxel is representing (F8BT, PFB, TFB, or F8T2). Periodic boundary conditions are always applied in the y and z dimensions, with electrodes at $x = 0$ and $x = LX$, where LX denotes the thickness of the device. The electrodes are assumed parallel to the (y,z) plane. Bipolar charge injection and extraction through electrodes is governed by the conventional Miller-Abrahams rate equation,^{21–24} and charge transport through the bulk of the device is governed by a Marcus-theory-derived hopping process between voxels,^[75,78] where the energy of each site is randomly selected from a Gaussian distribution of width σ , centered on the HOMO and LUMO level of each polymer material.^[79] The Marcus hopping rate is proportional to a material dependent mobility fitting parameter, μ_{iso} , which represents the high temperature limit of carrier mobility within the material. Charges within the device electrically interact with each other and their induced image charges, and charges of opposite polarity can

combine to form either singlets or triplets. Diffusion of singlets is described using the Förster energy-transfer rate,^[80] which is considered a good representation of singlet diffusion in our coarse grained model, which does not distinguish between intra- and inter-chain hopping processes.

$$R_E = \frac{1}{\tau_s} \times \left(\frac{r_F}{d_j}\right)^6 \times e^{-\left(\frac{E_i - E_j}{k_B T}\right)}, \quad \text{Equation 4.1}$$

where R_E is the exciton diffusion rate, τ_s is the singlet lifetime. The term $E_i - E_j$ represents the change in the energy between the initial site, i , and destination site, j , when the initial and destination sites are located on polymer chains of different materials the term is equivalent to the difference in energy gaps of the two materials. The second term of the equation describes the effect that the distance between donor and acceptor sites affects the rate, with the sixth power term originating from a point-to-point dipole-dipole interaction; r_F is the Förster radius. F8BT has an experimentally determined singlet diffusion length of approximately 15 nm,^[14,68,69] so a value of 10.5 nm for the Förster radius was chosen, since this gave a simulated singlet diffusion length of 15nm. The distance between donor and acceptor is d_j . This approximation does not obviously hold for polymer chains in which the excited state can be extended over distances comparable to or larger than the chain-chain separation distance; weaker power dependences would then apply.^[81] For simplicity, however, we have assumed here that the point-to-point dipole-dipole interaction description suffices to first approximation. Triplet diffusion is governed by Dexter energy transfer which is approximated by a Miller-Abrahams type hopping between nearest neighbors:^[82]

Singlets and triplets are assumed to be generated in a 1:3 ratio due to spin statistics, where interaction between singlets and triplets are governed by the pathways described by Zhang *et al.*^[83] The recombination and dissociation of singlets and triplets are modelled with respective rates dependent on the material and include triplet-triplet annihilation reactions that can cause a higher than 25% yield of singlets, as modelled in reference [83].

The core of the model works as follows: if each event (hole hop, singlet recombination, *etc.*), i , has an associated rate, k_i , then the time, t_i , it takes for the event to occur is calculated by,

$$t_i = -\ln(R_i)/k_i, \quad \text{Equation 4.2}$$

where R_i is a uniformly distributed random number between 0 and 1. The simulation proceeds by calculating all available events and then executing the event with the lowest

time, t_i , associated with it. Once the fastest event has been executed all possible events in the system are recalculated based on the new state of the system, and the simulation clock changes by $t_{sim} + t_i$. An optical model exploiting the equivalence between an oscillating dipole antenna in a non- absorbing medium and the probability of a recombinative dipole transition in thin-film microcavities has been used to calculate the outcoupling probability, $E_{out}(x)$, of a photon escaping the device once generated by the radiative recombination of a singlet. Further details of the model can be found in the literature.^[84] The optical model is also used to adjust the radiative decay rate of singlet excitons due to the microcavity. Luminance, L , and current density, J , measurements can be compared with our combined electrical and optical simulations. The current density is the flow of charge per unit area that has passed through the electrodes, and the luminance is calculated as,^[85]

$$L = \left(\frac{1}{\pi}\right) h\nu k_m \int_0^x E_{out}(x) S(x) dx, \quad \text{Equation 4.3}$$

where k_m is the maximum spectral efficacy defined by CIE and is equal to $k_m = 683 \text{ lm W}^{-1}$. The simulation assumes a monochromatic emitting green PLED of wavelength $\lambda = 560 \text{ nm}$. $S(x)$, calculated directly from the KMC model, is the singlet recombination profile and is given as the positional likelihood that photons will be generated within the device per unit area.

4.3 Varying the Interlayer (IL) Material

Fig. 4.2 shows current density-voltage (J - V (a)), luminance-voltage (L - V (a)), cd A^{-1} (c) and lm W^{-1} (d) efficiency, and EL spectral (e) data for the F8BT PLEDs with and without ILs. J - V data for hole-only (ITO/PEDOT:PSS/IL/F8BT/Au) devices with the same IL series are also shown in (b). The EL spectra for the PLEDs with ILs have a reduced full-width-at-half-maximum (FWHM) linewidth relative to the IL-free device, with a loss of intensity from the long wavelength side of the peak. In the literature a strong PL emission peak at $\sim 625 \text{ nm}$ is found in PFB:F8BT blends due to exciplex states at the PFB:F8BT heterojunction.^[86–88] No clear exciplex features are visible at low energies although there is a slight increase in deep-red emission from the PLED with a PFB IL, which indicates that some exciplex emission may be present in that device.

Below turn-on the J - V curves are symmetric at low bias voltages (below 1.5 – 2.0 V) which indicates that there is a small number of shunt paths between the anode and cathode causing short circuit currents.^[71,89] PLEDs with F8T2 ILs display currents in this regime that

are an order of magnitude higher than in the other PLEDs, implying increased shorting. The current threshold (where conduction through the semiconductor becomes more important than the short circuit currents) varies with the IL material used (1.50 V for PFB, 1.74 V for TFB, 1.96 V for F8T2, and 2.11 V without an IL with an error of ± 0.15 V). These values were obtained from the intersection of straight line extrapolations of the J - V curves around the current turn-on. The trend in the threshold values corresponds clearly with the increasing energy injection barriers between the IL materials (or PEDOT:PSS when no IL was used) and F8BT (see Table 4.1).

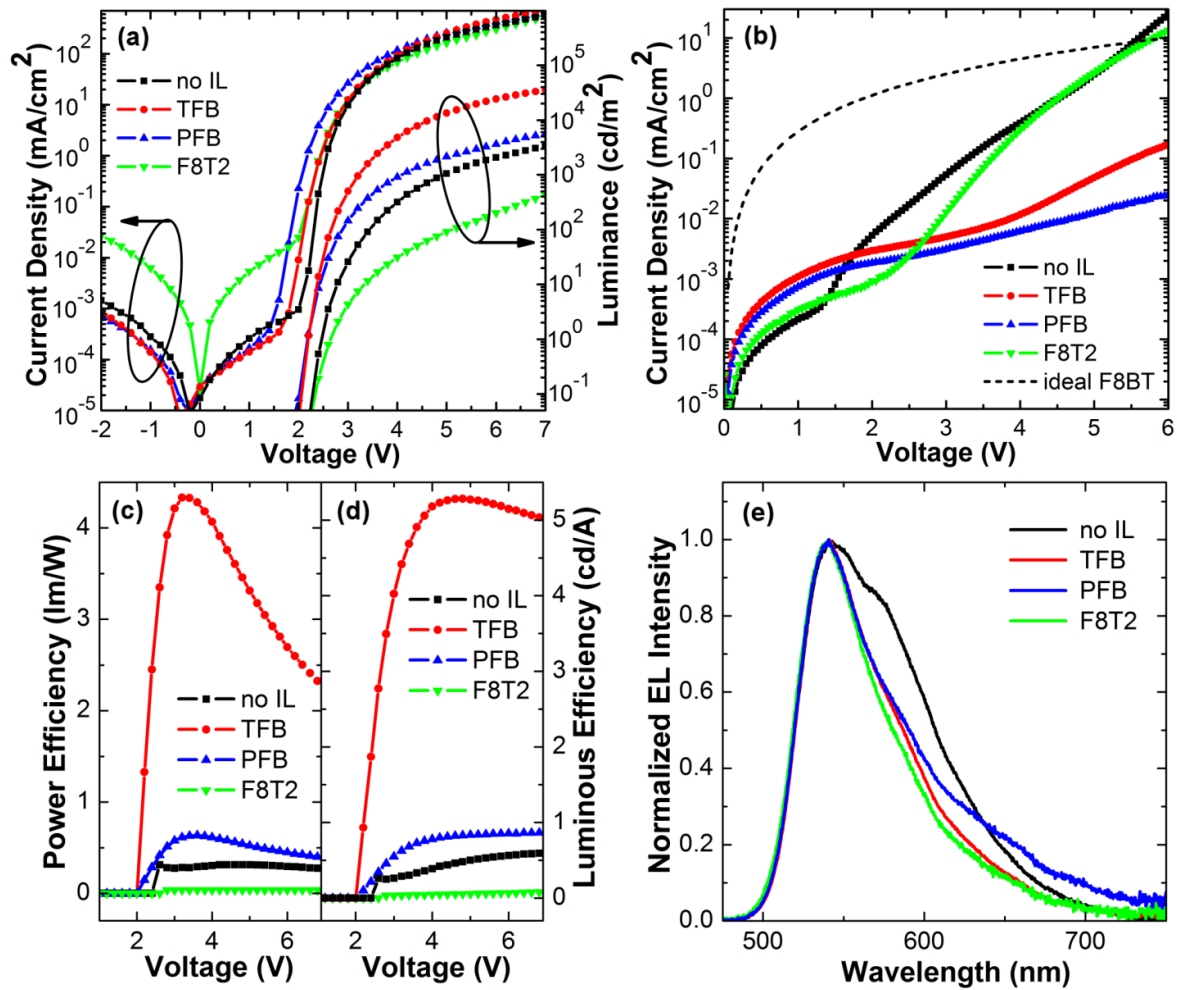


Figure 4.2: (a) J - V and L - V curves for F8BT PLEDs with and without ILs; (b) J - V curves for hole-only ITO/PEDOT:PSS/IL/F8BT/Au devices and the estimated SCLC density of an F8BT PLED without an IL (see text for details). Efficiencies derived from the curves in (a) are presented in (c) lm W^{-1} and (d) cd A^{-1} . The PLED EL spectra are shown in (e).

The high current density regime above 100 mA cm^{-2} in Fig. 4.2 (a) is relatively unaffected by changing the IL material, in contrast to the luminance, which varies by around two orders of magnitude in the same voltage range. Compared to the IL-free PLED, inclusion of a F8T2 IL causes a drop in luminance, while use of a PFB IL raises it, with the highest luminance for a TFB IL. The maximum power efficiencies of the devices correlate with their maximum luminance values. TFB IL devices achieved 4.33 lm W^{-1} at 3.2 V whilst PFB devices reached 0.43 lm W^{-1} at 2.8 V. F8T2 IL devices meanwhile showed a maximum efficiency of 0.04 lm W^{-1} at 7.2 V, lower than the devices without an IL which gave 0.31 lm W^{-1} at 4.8 V. The F8T2 IL device performance also lags that of F8T2 PLEDs in which a 60 nm F8T2 film was used as the emission layer, sandwiched between 50 nm of PEDOT:PSS (Clevios P AI4083) and a 20 nm Ba/100 nm Al bilayer cathode.^[51] In this latter case, a maximum 2 lm W^{-1} efficiency was achieved, falling to 1.2 lm W^{-1} at 1000 cd m^{-2} .

Both TFB and PFB display a relatively large ($1.0 \pm 0.1 \text{ eV}$) electron blocking LUMO offset relative to F8BT, yet PFB IL devices perform considerably worse than TFB IL ones. This suggests that electron blocking might not be the primary cause of efficiency increases. F8T2 IL PLEDs have only a negligible barrier for electron blocking such that TFB has previously been used as an IL when F8T2 is used as emission layer.^[58]

If reduction of the hole-injection barrier were the crucial factor, we would expect PFB IL devices to be the most efficient but they are not. Furthermore, the lowered luminance of F8T2 IL devices — where the hole-injection barrier is reduced relative to IL-free devices — also implies that hole-injection barriers alone are not the dominant factor in achieving the highest efficiencies in the F8BT PLED system studied here.

The hole-only devices were fabricated with Au contacts to block electrons from being injected. At high bias voltages, such a contact may not provide sufficient electron blocking, so only the data up to 6 V are shown. Using the space charge limited current (SCLC) equation^[90] the ideal current density curves for an F8BT PLED without an IL were calculated for comparison. A hole mobility of $2 \times 10^{-7} \text{ cm}^2 \text{ Vs}^{-1}$ was used in the calculation, which had been determined through hole-only device measurements on the same batch of F8BT polymer as used in this experiment.^[91] The SCLC equation is valid for diodes operating in the SCLC regime ($I \propto V^2$) in which Ohmic charge injection occurs and transport is substantially trap-free. Additionally a uniform field across the diode and a single mobility across both the IL and F8BT films must be assumed. The J - V characteristics of the hole-only devices in Fig. 4.2 (b) show that for significant (*i.e.* $>10^{-2} \text{ mA cm}^{-2}$) hole-injection to occur from the

ITO/PEDOT:PSS/IL stack into F8BT, higher voltages are required than when the IL is absent. This is in contrast to the trend in the threshold voltages in the bipolar devices and indicates that electron build-up at the interface plays a non-trivial role in PLED hole-injection. The current densities achieved above turn-on are lower by more than an order of magnitude in devices using TFB and PFB ILs. However, as the hole currents in a F8BT PLED make up a small percentage of the overall current density, due to the electron mobility of F8BT being substantially higher than the hole mobility,^[44,45] this observation is not in contradiction to the results from the bipolar devices, which did not show significant variations in J between the various IL devices. Interestingly, the results indicate that the triarylamine containing ILs decrease the hole-only diode stack's hole transporting abilities, compared to the dithophene containing IL, although the triarylamine ILs both have lower hole injection barriers to PEDOT:PSS. The hole mobilities for TFB,^[92,93] PFB,^[92] F8T2,^[70] and F8BT^[94] recorded in the literature vary significantly not only between the materials, but also for the same materials; they are, however, generally within the same order of magnitude. The larger hole currents in the F8T2 IL hole-only devices do not translate into higher efficiencies in the PLEDs.

To summarize, we have shown that in our IL devices electron blocking does not play a dominant role in achieving the highest device efficiencies. Luminance changes do not correlate with the hole injection barriers in bipolar devices or with the current densities of hole-only devices. Hole injection and electron blocking effects therefore seem not to play a major role in the function of the ILs.

4.4 Doping the IL

4.4.1 Raman Spectroscopy

Previous research has shown that F₄TCNQ is a good p-dopant of organic semiconductors^[95] and enhancement of the conductivity of both TFB and PFB *via* F₄TCNQ doping.^[66] Fig. 4.3 shows 633 nm excited Raman spectra for F8T2, F₄TCNQ and a drop-cast film deposited from a solution of F8T2 blended with 15% w/w F₄TCNQ. A vibrational peak appears at 1370 cm⁻¹ in the Raman spectrum of the F₄TCNQ doped F8T2 film that is not present in either of the other two spectra. This peak originates from the charged F₄TCNQ⁻ dopant molecule adopting a non-planar conformation.^[96] In addition, the strong F8T2 PL background emission (rising from left to right in the F8T2 Raman spectrum) associated with the 0-2 PL vibronic peak^[51] is absent in the doped film. This is consistent with the formation of exciton-

quenching charged polaron/bipolaron states within the HOMO – LUMO energy gap^[97] and therefore confirms that F8T2 is oxidatively doped with F₄TCNQ.

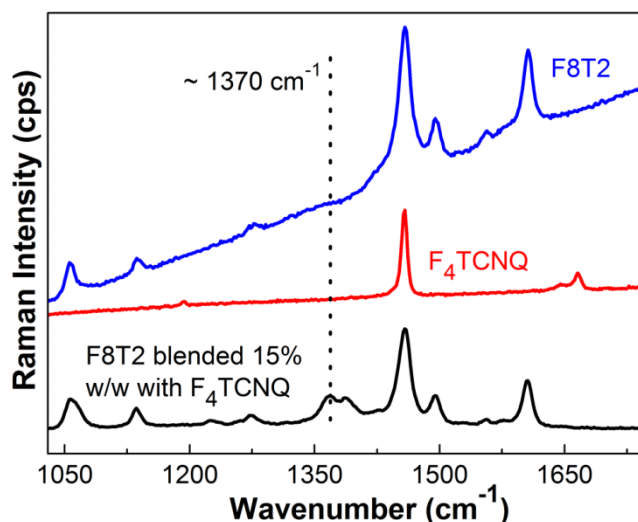


Figure 4.3: Raman spectra of (from bottom to top) a drop-cast blend film of F8T2 with 15% w/w F₄TCNQ, and neat F₄TCNQ and F8T2 films. The PL background evident in the latter is quenched for the 15% doped F8T2 sample.

4.4.2 Photoluminescence Studies

During thermal annealing of the ILs above their respective T_g values, a step required for PLED fabrication, the F₄TCNQ molecules might phase separate from the blend. This possibility has been investigated by monitoring the IL PL emission before and after the annealing step for samples comprising quartz/PEDOT:PSS/IL, with both undoped and F₄TCNQ doped ILs. The annealing conditions were the same for all IL materials at 180°C for one hour under nitrogen. This is above the glass transition temperature of all the materials, so morphological changes may be expected as the polymer chains might move to take on a more energetically favourable configuration, while the dopant molecules might phase-separate out of the blend. The results in Fig. 4.4 ((a) and (b)) were obtained by placing the samples inside an integrating sphere, offset from direct illumination by the excitation beam so that the excitations of the samples would be comparable. The PL emission from the samples is therefore weak, and in the case of F8T2 so weak that the background PL emission (visible here at shorter wavelengths) dominates. F8T2 PL emission has only one peak at ~540-550 nm, but Fig. 4.4 (c) shows another peak, stronger peak, at short

wavelengths. This PL peak is attributed to emission from the EDOT moieties in PEDOT:PSS.^[98]

The PL data shows that annealing undoped TFB and PFB IL films causes a quenching of the PL signal for both. We propose that this may be due to the diffusion of PSS ions from the PEDOT:PSS film into the TFB and PFB ILs. 7% F₄TCNQ doping led to a stronger PL quenching in both PFB and TFB ILs than seen following the annealing of undoped ILs. Annealing the doped TFB and PFB IL films showed an increase in their PL emission though it still fell below that seen for the annealed undoped films. This reduction in quenching is likely to indicate partial de-doping of the film, which we propose may occur through phase separation of F₄TCNQ. F8T2 IL films, unlike PFB and TFB films, showed no significant change in the PL emission upon annealing (Fig. 4.4 (c)). This is true for both doped and undoped samples. Doping does reduce the PL relative to undoped samples but to a much lesser extent than for TFB and PFB. Fig. 4.4 (d) shows the F₄TCNQ doping fraction dependence of the PL quenching both before (crosses, dotted line) and after (filled symbols, solid line) annealing. Peak wavelength PL amplitudes measured at 436 nm for TFB, 456 nm for PFB and 530 nm for F8T2 are plotted for undoped, 1, 3, and 7% doped IL samples. Higher doping concentrations generally lead to weaker PL signals and annealing generally reduces the effect of doping. F8T2 shows the smallest changes, albeit starting from a low PL emission efficiency even for undoped films. Due to clearly identifiable vibronic structure in the absorption spectrum, F8T2 is thought to have a relatively linear polymer backbone, which allows for close-packing of the polymer chains. Due to close-packing of the F8T2 chains it may then be harder to dope F8T2 films but once doped they may be less susceptible to de-doping during annealing than more loosely packed PFB and TFB IL films.

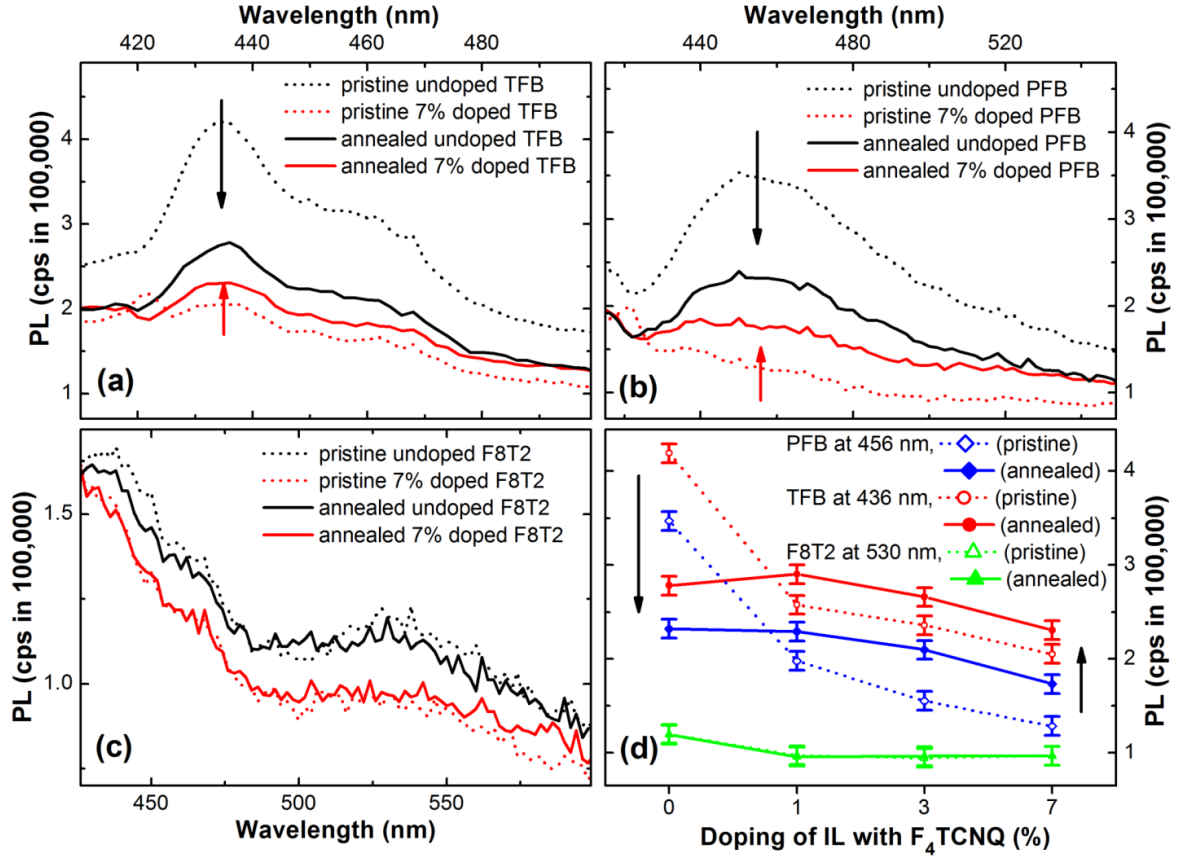


Figure 4.4: PL measurements for quartz/PEDOT:PSS/IL samples. Comparisons are made between 7% F₄TCNQ doped and undoped IL films, both before (dotted lines, open symbols) and after annealing above the IL T_g (solid line, filled symbols) for (a) TFB, (b) PFB, and (c) F8T2 IL films. (d) Peak wavelength PL amplitudes for undoped, 1, 3, and 7% doped IL samples, both before (dotted line, crosses) and after annealing above the IL T_g (solid line, filled symbols). N.B. the before- and after-annealing datasets wholly overlap for F8T2.

4.4.3 Device Characterisation

Fig. 4.5 (a)-(c) show the L - V , J - V , and power efficiency vs. voltage curves of F8BT PLEDs with TFB, PFB, and F8T2 ILs respectively. F8T2 IL PLEDs with doped ILs had higher leakage and reverse bias currents than the reference IL-free PLED, which can be explained by increases in conduction *via* shunt paths. In contrast, the leakage currents for devices with doped PFB and TFB ILs are of the same order of magnitude as that of the reference IL-free device. The absence of an increase in the reverse bias currents in TFB and PFB IL PLEDs indicates clearly that no doping of the adjacent F8BT layer is occurring. The PLEDs containing ILs with 7% F₄TCNQ dopant achieved maximum power efficiencies of 2.02 lm W⁻¹

at 4.4 V for TFB, 0.43 lm W⁻¹ at 3.8 V for PFB, and 0.05 lm W⁻¹ at 4.0 V for F8T2. In all cases only minor differences in current density are recorded after *J* turn-on for doped and undoped ILs. Luminance values are also minimally affected.

The EL spectrum of IL-free F8BT PLEDs (Fig. 4.5 (d), dashed line) displays a strong peak centered on 545 nm with a broad shoulder at around 575 nm. The EL spectra for PLEDs with 7% F₄TCNQ doped TFB and F8T2 ILs have the same spectral characteristics as each other — with a slight increase in shoulder/red-edge emission relative to the IL-free device. The 7% F₄TCNQ doped PFB IL device is somewhat different, with a significant increase in long wavelength EL emission. In contrast to the situation for the undoped-IL PLEDs (*c.f.* Fig 4.2 (e)), doped-IL devices have a higher proportion of the long wavelength (575 nm) shoulder EL. We propose the changes may be due to the dopant molecules changing the IL surface, leading to a different packing of the F8BT polymer chains, which may cause changes in EL emission^[99] or due to exciplex emission.

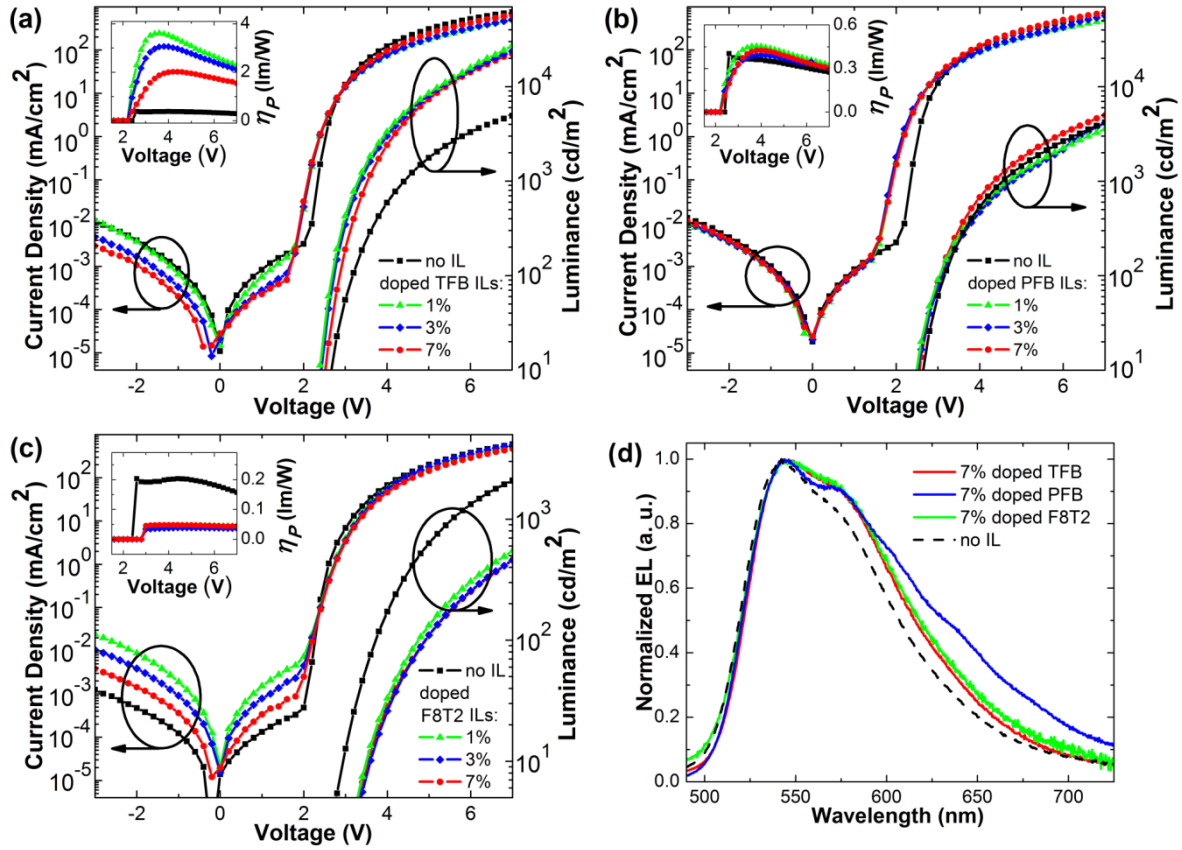


Figure 4.5: J - V and L - V data for F8BT PLEDs with 1-7% by weight F_4TCNQ doped (a) TFB, (b) PFB, and (c) F8T2 ILs. IL-free reference devices were also fabricated for each IL series and the corresponding data are shown in each panel. EL spectra recorded at 5V for the 7% F_4TCNQ doped-IL and IL-free devices are shown in (d).

Fig. 4.6 shows J - V data from hole-only devices with 7% F_4TCNQ doped ILs and for a reference device without an IL. The voltages at which the hole-only devices turn-on did not change appreciably upon doping the ILs, consequently the data for the undoped ILs is not shown. Doping slightly decreases current density in hole-only diodes with F8T2 ILs. When a doped PFB IL is used the current density below 4 V is lower compared to device with an undoped PFB IL by around an order of magnitude; above 4 V the current density approximately matches that of the undoped PFB IL device. With a TFB IL the current density in the hole-only diode structure is reduced consistently by around an order of magnitude. The decrease in the hole-only diode current when adding dopant to the TFB IL is significant, however, the decreases in current are larger compared to differences between a TFB IL and an IL-free hole-only devices — in the latter case the efficiency is significantly increased, while it is slightly decreased in the former case. This implies that the current densities of the hole-only devices are a poor predictor of PLED efficiencies.

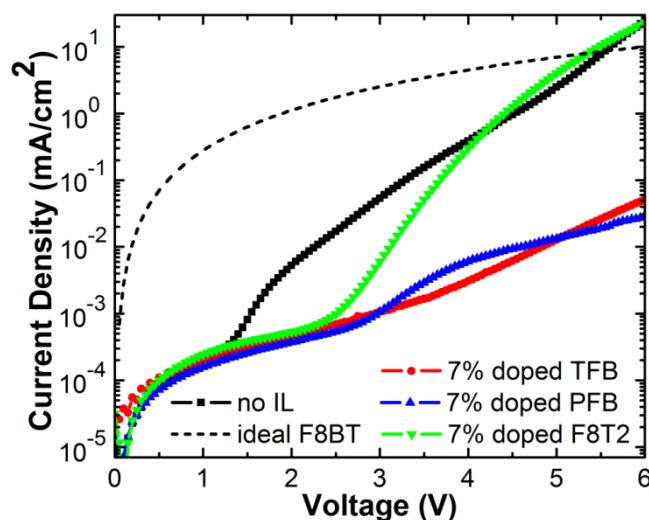


Figure 4.6: Current density vs voltage data for Au-cathode, hole-only devices with 7% F₄TCNQ doped ILs and for a reference device without an IL. The estimated SCLC density of an F8BT PLED without an IL is indicated with a dashed line (see text for details).

4.4.4 Ultra-violet Photoelectron Spectroscopy

Fig. 4.7 shows ultraviolet photoelectron spectroscopy (UPS) results for ITO/PEDOT:PSS/IL samples with and without addition of 1%, 3%, and 7% F₄TCNQ dopant. The effect of the dopant on the electronic energy levels of the IL is visible in the low binding energy region, which corresponds to the delocalized π -band (extending from 0 to 2 eV). It shows additional peaks that do not appear in the UPS spectra of F₄TCNQ alone.^[95] The localized π -state (visible from 2 eV) UPS peaks shift to higher energies upon doping in the triarylamine containing polymers. Both of these observations are consistent with the formation of polaronic charge states within the energy gap.^[100]

The energy level parameters extracted from Fig. 4.7 are listed in Table 4.2 and give a more detailed picture of the influence of the PEDOT:PSS layer on the IL. These thin film samples were prepared as for PLED fabrication, including the annealing step. UPS is a surface sensitive technique that probes depths of up to 10 nm, which is around the thickness of the TFB and PFB IL films studied here. F8T2 ILs are less than 10 nm thick but even then the strongest signals in UPS spectrum will still originate from the IL, due to the exponential decay of the signal with increasing probe depth. Here, the ionization potential (I_p) was measured as 5.5 ± 0.1 eV, which is in good agreement with the literature value of 5.5 eV listed in Table 4.1, thus confirming that the electronic states of the F8T2 IL film are

being probed. The doped ILs show smaller I_p values that should decrease the hole injection barrier from PEDOT:PSS coated ITO electrodes (workfunction = 5.2 ± 0.1 eV). The I_p values of the TFB and PFB ILs are within 0.5 eV and 1.0 eV of commonly cited literature values. Doping the PFB and F8T2 ILs decreases their I_p values while this effect is only visible for the lowest dopant concentration in TFB, with higher dopant concentrations returning I_p to its undoped value. In all three cases, the 1% dopant concentration has the biggest effect on I_p , with higher dopant concentrations showing a lesser, if any, effect. This could indicate that the morphology of the polymer:dopant blend in TFB and F8T2 is optimal for a doping concentration of 1%. At higher doping concentrations the morphology might shift towards something less favourable, which could occur either through increased dopant crystallisation or through increased disruption of the polymer's morphology. If that is the case, the data indicates that in PFB the dopant remains well dispersed/does not disrupt the polymer structure even with dopant concentrations as high as 7%.

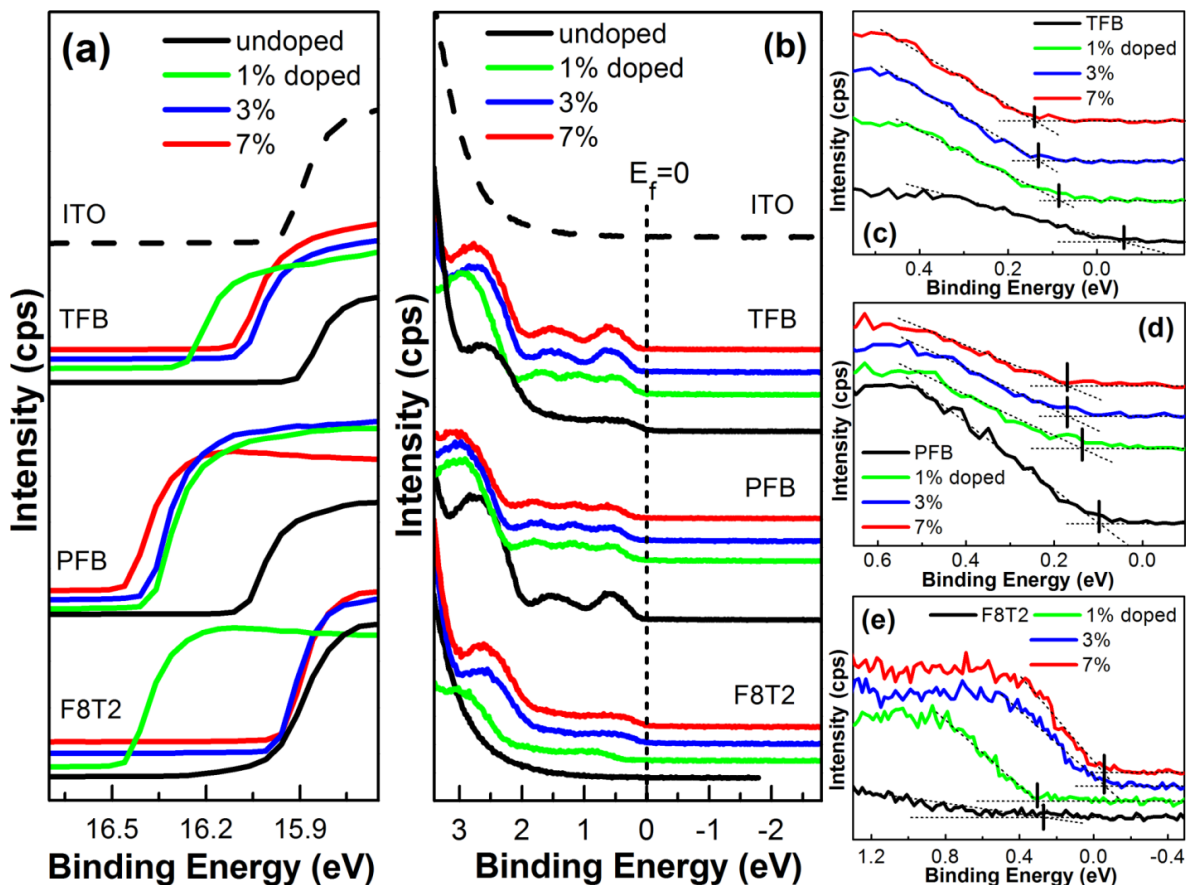


Figure 4.7: He I 21.2 eV excitation UPS data relative to an Au reference for ITO/PEDOT:PSS/IL structures. Data are reported for TFB, PFB and F8T2 ILs both without and with (1, 3, 7%) F₄TCNQ doping. A bare ITO substrate spectrum is also included for reference. Panel (a) shows the high binding energy region and panel (b) the low binding energy region. In panel (c), (d), and (e) the HOMO level cut-off is shown for the TFB, PFB, and F8T2 samples respectively.

To summarize, both PLED current density and luminance vary minimally with IL doping level. There was similarly no correlation between PLED efficiencies and current densities in corresponding hole-only diode structures. In addition, decreased I_{ps} were deduced from the UPS spectra.

Table 4.2: Energy level parameters extracted from Fig. 4.7.

Samples	E_h^a (eV)	W_{sp}^b (eV)	E_l^c (eV)	I_p^d (eV)	Δ_{vac} (eV)
TFB	15.91	15.7	-0.1	5.3	-0.06
1% doped TFB	16.25	16.2	0.1	5.1	0.28
3% doped TFB	16.09	16.0	0.1	5.3	0.12
7% doped TFB	16.11	16.0	0.2	5.3	0.14
PFB	16.09	16.0	0.1	5.2	0.12
1% doped PFB	16.38	16.3	0.1	5.0	0.41
3% doped PFB	16.40	16.2	0.2	5.0	0.43
7% doped PFB	16.38	16.2	0.2	5.0	0.41
F8T2	16.00	15.8	0.3	5.5	0.03
1% doped F8T2	16.46	16.1	0.3	5.1	0.49
3% doped F8T2	15.98	16.0	0.0	5.2	0.01
7% doped F8T2	15.96	16.0	0.0	5.2	-0.01

^a E_h is the high energy cut-off, which was determined with an error of ± 0.02 eV.

^b W_{sp} is the spectral width.

^c E_l is the low energy cut-off, the HOMO edge, which was determined with an error of ± 0.1 eV.

^d I_p (ionization potential) = Photon energy (21.22 eV) – (spectral width). We use the cut-off position at high binding energies to calculate I_p . If the midpoint value on the slope of the high binding energy side were used instead, then the value of I_p would be increased by around 0.2–0.4 eV.

4.5 Varying the Emissive Layer Material

4.5.1 Modelling the Charge Recombination Zone and Electron and Hole Profiles

Fig. 4.8 shows the KMC model predicted electron (solid line) and hole (dashed line) profiles for F8BT and LG 1300 devices with and without ILs. The electron and hole profiles are calculated by taking snapshots of particle locations once the model has reached a steady state. Also shown is the recombination zone of singlets, $S(x)$, (shaded area), calculated in a similar manner as Staudigel *et al.* [85] by recording the locations of all singlet recombination events. The anode is located at $x = 0$ nm. These data suggest that for LG 1300 PLEDs the recombination zone (RZ) is more evenly distributed across the active layer of the device, while that for F8BT PLEDs it is localized on the anode side.

This is reasonable on the basis that the conjugated backbone of LG 1300 contains fractions of arylamine, benzothiadiazole, and fluorene moieties within a chain architecture that allows for balanced electron and hole mobilities.^[101] Trivially, for both F8BT and LG 1300 PLEDs the RZ is moved away from the anode by the thickness of the added IL but in LG 1300 PLEDs there is also a significant increase in recombination near the cathode and a sharper peaking in the recombination at the anode side of the device. In both F8BT and LG 1300 PLEDs with an IL the electron densities peak near the cathode side and drop towards zero near the anode side of the devices. In both types of PLEDs the TFB IL causes the maximum of the electron density to shift from the cathode to the anode side of the devices, with a smaller, but still significant peak in electron-densities remaining near the cathode, which indicates some degree of electron-blocking at the cathode-side.

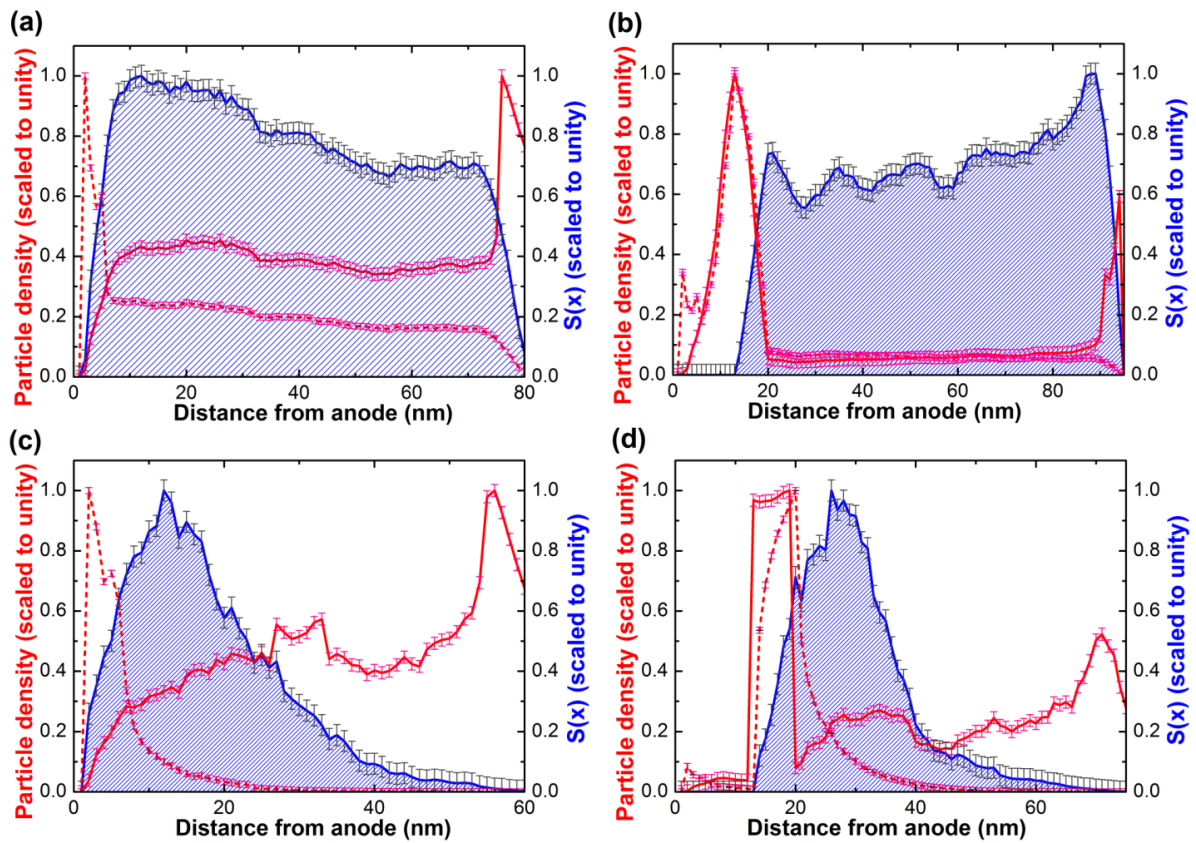


Figure 4.8: Device simulations at 5.2 V bias of the hole (dashed) and electron (solid) densities scaled to unity, and the singlet recombination zones, $S(x)$ (shaded), for a LG 1300 PLED (a) without an IL (cathode located at 80 nm from the anode) and (b) with a TFB IL (cathode located at 95 nm from the anode). Data are also shown for a F8BT PLED (c) without an IL (cathode located at 60 nm from the anode) and (d) with a TFB IL (cathode located at 75 nm from the anode).

4.5.2 PLED Characterisation

The J - V and L - V curves of LG 1300 PLEDs with and without ILs and their corresponding efficiencies in cd A^{-1} and in lm W^{-1} are shown in Fig. 4.9 (a), (b) and (c), respectively. The introduction of ILs in this system somewhat reduces the above turn-on current density (Fig 4.9 (a), left ordinate) for all ILs. As the IL is applied to the anode-side of the PLEDs (c.f. Fig. 4.8) it is likely that this effect is predominantly the consequence of a reduction in hole current density. More widely varying luminance values are observed (Fig. 4.9(a), right ordinate), however. This suggests that the ILs must also cause changes in exciton quenching and/or in the balance of electron and hole densities within the active layer. Efficiency increases are seen above 3.5 V when using a TFB IL and above 6.1 V when using a F8T2 IL (Fig 4.9 (b) and (c)). Fig. 4.9 (d) shows the EL spectra of the LG 1300 PLEDs with and without ILs. In each case the main EL peak arises at ~ 541 nm with a more or less prominent shoulder at longer wavelengths. According to:^[102]

$$E_x = IP_D - EA_A - C, \quad \text{Equation 4.4}$$

where E_x is the energy of an exciplex state, IP_D the donor ionization potential, EA_A the acceptor electron affinity, and C the Coulomb stabilization energy associated with the charge-transfer interaction, the LG 1300:PFB exciplex emission would be expected to appear around 605 ± 30 nm (Table 4.1 gives a PFB HOMO to LG 1300 LUMO gap of 2.2 eV and C is assumed to be 0.15 ± 0.10 eV).^[102] A peak attributable to such emission is centred at 620 nm when the spectra of the IL-free device is subtracted from the PFB IL device.

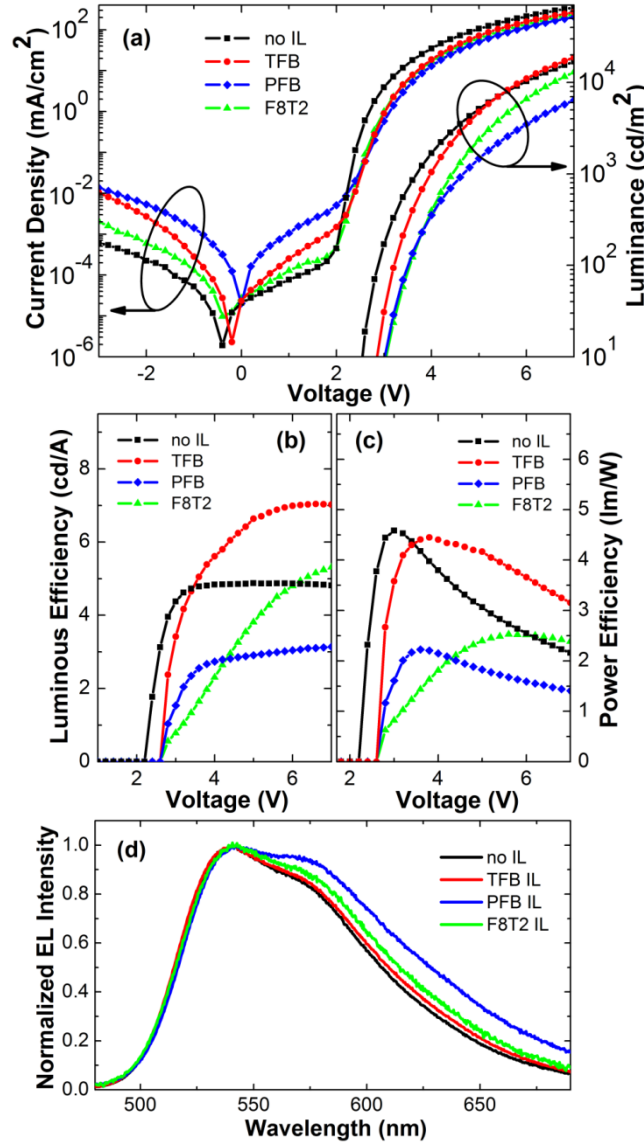


Figure 4.9: (a) J - V and L - V , (b) luminous efficiency and (c) luminous power efficiency curves, and (d) EL spectra of TFB, PFB, and F8T2 IL PLEDs with a LG 1300 active layer.

Fig. 4.10 (a) and (b) show the luminance values of the F8BT and LG 1300 PLEDs, respectively, plotted against δ , the energy gap energy difference (in eV) between the emission and IL materials. The error in δ was estimated in each case from the associated uncertainties in the gap energies. Though no clear correlation between the luminance and δ is observed in the LG 1300 IL PLED series, the results from the F8BT PLEDs showed an exponential dependence of the luminance on δ , fitted according to:

$$L(\delta) = L_0 \times e^{\delta/b}, \quad \text{Equation 4.5}$$

where $L(\delta)$ is the luminance at a specified electric field as a function of δ and where $L(\delta = 0) = L_0$ represents the luminance of an IL-free PLED. The parameter b represents the energy required for L to increase by one factor of e . Exponential curves were fitted to the luminance values at various electric field strengths between 3.3×10^5 and $8.0 \times 10^5 \text{ V cm}^{-1}$ yielding an average value $b = 0.15 \pm 0.02$. The field strengths roughly cover the entire voltage range from 2.0 V to 7.0 V and an exponential dependence on the luminance was observed within this range and is therefore independent of the applied voltage. It is expected (considering the simulation results presented in 4.5.3) that Boltzmann statistics apply in so far as the luminance is L_0 adjusted for luminance lost due to quenching or blocking of excitons by the material adjacent to the anode-side of the emission layer. However, b is around 5.8 times the value of $k_B T$, which may possibly be explained by polaronic effects that lead to additional energy barriers being present in the movement of the excitons.

This exponential dependence of the luminance on δ provides evidence that in F8BT devices — in which the majority of excitons will be within a diffusion length of the IL — exciton quenching processes at that interface are of primary importance for PLED performance.^[14] It should be expected that $L(\delta)$ will saturate at large enough values of δ , when the overwhelming majority of excitons are blocked from entering the IL. For values of $\delta < 0$ a flattening off of the curve should also be expected, since all excitons within the exciton diffusion region should be quenched equally by any quencher, regardless of how narrow its energy gap according to the Miller-Abrahams rate equation (eqn. 2.1). The fact that the exponential dependence appears to continue in the $\delta < 0$ region is in agreement with exciton hopping transport in the bulk being governed by Marcus theory (eqn. 2.2) — in the classical Marcus theory of electron transfer reactions the reaction rates become higher with increasing exergonicity of the reaction (until a very negative domain of the Gibbs free energy is reached).

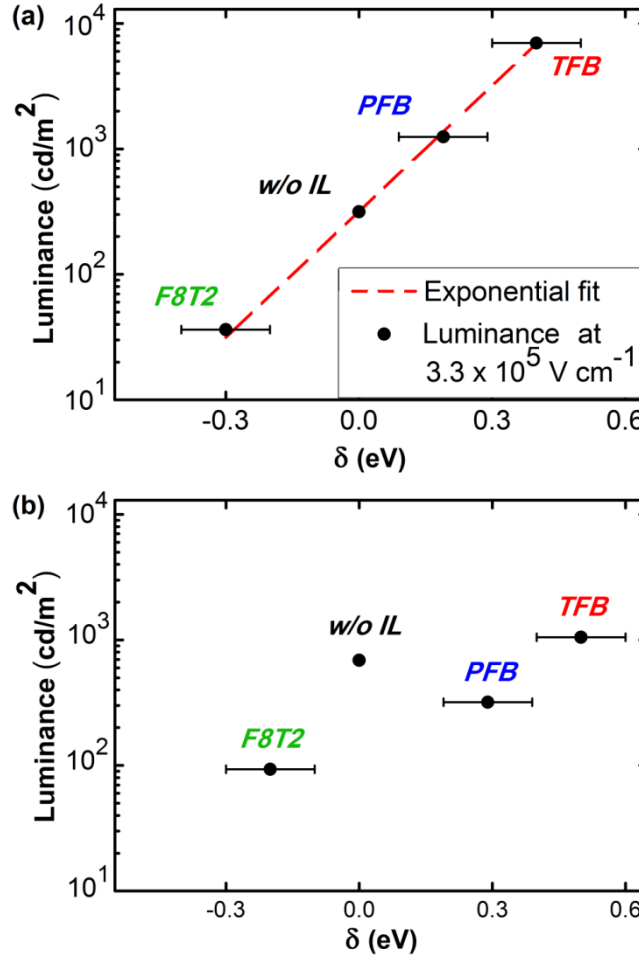


Figure 4.10: Luminance recorded at $3.3 \times 10^5 \text{ V cm}^{-1}$ (corresponding to voltages near the efficiency maximum of the PLEDs (*ca.* 2.5 V)) for (a) F8BT and (b) LG 1300 PLEDs without an IL and with TFB, PFB and F8T2 ILs, plotted as a function of δ , the difference in energy between the energy gaps of the IL and emission layer materials. The without interlayer device data are placed at $\delta = 0$ for convenience.

4.5.3 3D Kinetic Monte Carlo Simulation

Fig. 4.11 (a) shows good fits to the luminance for the F8BT PLEDs (with and without ILs) have been achieved with the 3D KMC simulation. In these simulations the singlet diffusion length was assumed to be 15 nm, and therefore any singlets that entered the IL were considered to be immediately quenched; this is justified by noting that the emission profile for each PLED device showed no emission from their respective ILs. The transport of excitons across the interface between F8BT and the IL is dependent on the energy gap offset δ which is accounted for in the $E_i - E_j$ term in Eqn. 4.1. The $E_i - E_j$ terms can be thought of as a Boltzman penalty for hops that are unfavorable in energy and acts to restrict

the diffusion of excitons into an IL with a wider energy gap or to restrict the diffusion of excitons in the IL back into the active layer, if the active layer has a larger gap. In Fig. 4.11 (b) luminance values from simulations of the F8BT IL PLED series run at 8V are plotted against δ . We assumed the excitons enter the IL rather than tunnelling through and simulated two cases: (i) all excitons that diffuse from F8BT into the IL or to the anode are considered non-radiative (solid line, filled symbols), and (ii) the IL does not quench excitons (dashed line, open symbols). The lower the value of δ , the more significant the change in luminance between (i) and (ii). It is clear that when the energy gap offset favors exciton diffusion into the interlayer (as is the case for F8T2) there is a significant difference between the quenched and unquenched luminances. However, as the energy gap offset becomes unfavorable to exciton diffusion, this difference in quenched and unquenched luminance decreases.

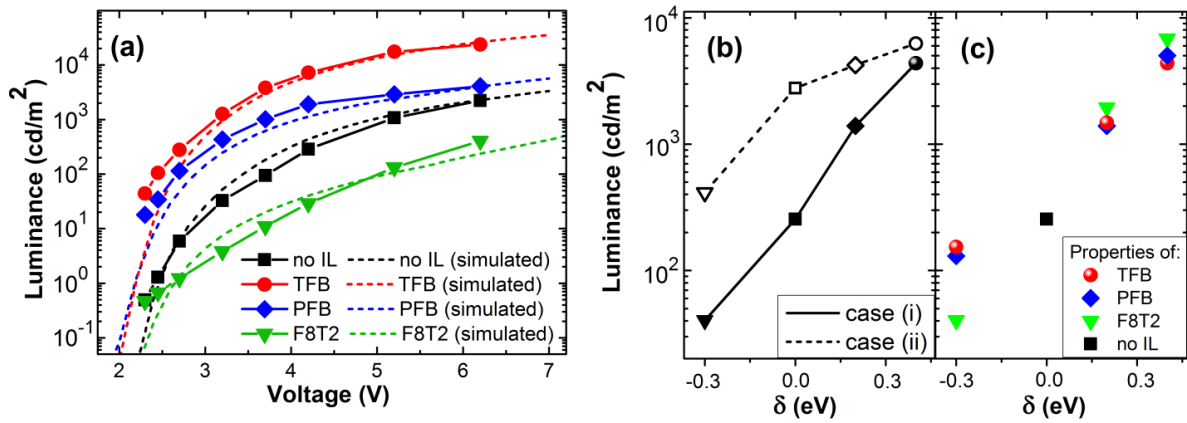


Figure 4.11: (a) Comparing the experimental (solid lines) and simulated (dashed lines) luminance of an F8BT light emitting layer PLED with various ILs. (b) How the luminance is affected by quenching due to δ for case (i) with quenching, case (ii) without quenching, and (c) depending on other IL parameters (see text for details).

We used our model to determine whether the difference in the energy gap between the IL and F8BT alone was accountable for the exponential dependence we observed. We modelled PLEDs with ILs that had a difference in energy gap of $\delta = -0.30$ eV to F8BT (equivalent to using a F8T2 IL), $\delta = 0.19$ eV (equivalent to using a PFB IL), and $\delta = 0.40$ eV (equivalent to using a TFB IL). Excitons at the interface moved into the IL or stayed within the light emitting layer according to the resulting probabilities based on the energy gap difference. In our model electron and hole movements are determined by the LUMO and HOMO levels, the resulting injection barriers, and the hopping constants. These can be set

independently from the energy gap difference. The results in Fig. 4.11 (c) show the modelled luminance values for set values of δ , where the properties that determine electron and hole movement (electron and hole mobility as well as electron and hole injection barriers) have been artificially set to those of F8T2, PFB, and TFB at each of the three values of δ we probed. The results demonstrate that quenching effects due to the energy gap offset in the simulation (shown in Fig. 4.11 (b)) had a far larger effect on the luminance than varying the other parameters. For the case $\delta = -0.3$ eV higher luminance values are recorded when using the parameters for TFB and PFB compared to using those for F8T2; the luminance values are none the less still lower than for cases with higher δ values with F8T2 parameters.

4.5.4 Summary

To conclude this section, an exponential dependence of the luminance seen in the experimental results of the F8BT devices is reproduced by the 3D KCM simulation, and variation of the simulation parameters demonstrated that the most important factor is exciton quenching. This is likely due to the RZ being located close to the anode interface, since an exponential dependence of the luminance on δ is observed in this system, but not in the LG 1300 PLED IL series for which the RZ spreads across the device.

4.6 Varying IL Thickness

The J - V curves in Fig. 4.12. show no noteworthy change in current density between the thick (~ 5 nm for F8T2 and ~ 10 -15 nm for TFB and PFB) and the thin (~ 2 nm for F8T2 and ~ 5 nm for TFB and PFB) ILs. For TFB, however, a drop in luminance is visible when the < 5 nm IL is used rather than the < 15 nm TFB IL. Assuming that the exciton diffusion length in alternating fluorene-based copolymers is ~ 15 nm^[14,68,69] the drop in luminance with a TFB layer < 5 nm can be explained through the RZ being located closer to the anode, thus increasing luminance quenching. The overall trend in the device efficiencies with various IL materials is not altered by using thinner layers. While thinner TFB ILs had lower luminance values than the thicker ones, the drop in luminance was not as large as would be expected if the primary function of the IL was to reduce excitation quenching by PEDOT:PSS through physically removing the RZ away from the anode, therefore other parameters, such as a large energy gap are also important in blocking excitons at the IL/light emitting polymer interface.

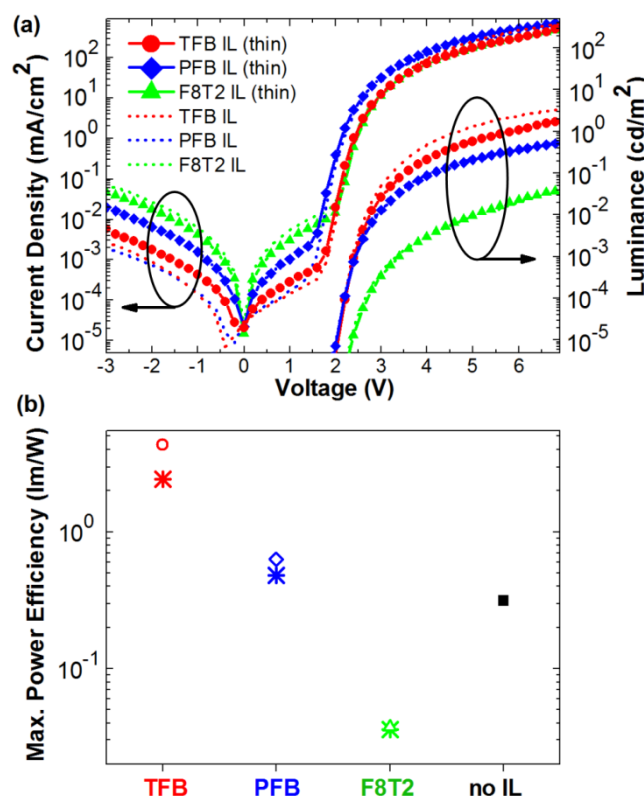


Figure 4.12: (a) J - V and L - V curves of F8BT PLEDs with <15 nm (dotted lines) and <5 nm (solid lines, filled symbols) TFB, PFB, and F8T2 ILs. (b) Maximum power efficiency values on a log scale for an IL-free device and for <15 nm (open symbols) and <5 nm (star symbols) TFB, F8T2, and PFB IL devices.

4.7 Conclusion

The aim of this work was to shed light on the origin of the large increases in efficiency that are found when a TFB IL is used at the anode-side of F8BT PLEDs. We investigated a broad range of IL parameters to establish which of them had the most significant effect. When we varied the IL material we found minimal changes in current densities, but large variations in the luminance. The changes in the luminance do not correlate with the hole injection barriers in the PLED structure nor with the current densities in the hole-only diode structure. Neither is a strong correlation between the luminance values and the IL's electron blocking barrier found. PLEDs with ILs doped with 7% F₄TCNQ by weight did not display higher efficiencies nor did the corresponding hole-only diode structures reveal a correlation between their current densities and device efficiency. However, there was evidence to suggest that exciton blocking plays a major role. Reducing the thickness of the IL below the exciton diffusion length was shown to reduce efficiencies

by a small amount. The most important role of the TFB IL in increasing PLED efficiencies in F8BT devices was therefore found to be exciton blocking *via* the differences in the energy gap between the LEP and the IL. PLED luminance showed an exponential dependence on the IL-LEP energy gap difference both experimentally and in 3D KCM simulations. The importance of exciton blocking is likely of particular importance in thin-film F8BT PLEDs because the singlet RZ is adjacent to the anode in such devices. The implications of this study are that ILs, hole injection layers and electron injecting layers in organic LEDs with active layers <100 nm should, as a first consideration, have very large energy gaps in order to limit losses from exciton quenching. Electrode quenching strongly affects the excitons created adjacent to the charge injection layers. Some small molecule OLEDs have active layer thicknesses in the region of 30 nm, which could lead to large losses due to quenching. Sourcing materials for HIL and EIL with larger energy gaps than currently current used is therefore expected to increase PLED and OLED efficiencies.

5 Efficient Polymer Light-Emitting Diodes using an Imidazolium-incorporated Conjugated Polyelectrolyte (CPE) as Electron Injection Layer

In this chapter we investigate experimentally the effect of novel CPE materials as electron injection layers (EILs) in PLED and electron-only diode structures to determine the role of the CPE main conjugated backbone on device efficiencies and response times. The PLED characteristics of F8BT-based CPEs with various anions are also measured to investigate the role of the anion choice. CPE EIL containing PLEDs were also fabricated with F8BT and Merck Super Yellow (SY) light emission layers. The effect of the ionic groups on UV-visible absorption and PL emission is examined in thin films. Raman spectroscopy is used to evaluate the effect of the ionic groups on the vibrational properties of the CPE molecules. We explored the exciton quenching effect of the light emitting layer/CPE component of the device stack through TCSPC and PLQY measurements.

This work was carried out in collaboration with Dr. Minwon Suh and Mr. Kyungmok Kim in the Department of Materials Science and Engineering, KAIST, Republic of Korea, (synthesis of CPE materials) and Mr. Sebastian Wood (Raman spectroscopy) at The Blackett Laboratory, Imperial College London.

5.1 Introduction

Ionic conduction through liquids and solids is common in many biological functions, such as in the neural pathways of our brain. Ionic conduction has been explored in the field of plastic electronics in PLEDs,^[103,104] polymer light-emitting electrochemical cells,^[105–108] dye-sensitized solar cells,^[109–111] and polymer FETs.^[112,113] CPE materials are a particularly interesting sub-set of organic semiconductors as they have the potential for both ionic and electronic charge transport.

CPEs are semiconducting polymers with ionic groups at the end of some or all of the solubilising alkyl side-chains. The ionic groups allow for processing in highly polar solvents which do not dissolve most commonly used light emitting conjugated polymers. This allows for a CPE layer to be deposited on top of a light emitting polymer film without intermixing

between the two layers. Therefore the ability to form the CPE layer on top of the polymer layer opens the door to inexpensive multilayer structures using solution-based techniques.

The use of CPE layers as EILs has been reported to improve PLED efficiencies.^[114–117] Recently some studies have suggested the role of CPEs in electron injection is to lower an, otherwise high, electron injection barrier through the formation of dipoles at the CPE/metal cathode interface.^[118,119] Others have proposed the role of the CPE layer is to enhance the local electric field at the electrode *via* the redistribution of its mobile ions.^[120,121]

An underexplored aspect of CPEs is the role of its main conjugated backbone in device performance. The novel CPE polymers investigated here both have imidazolium (Im) cationic side-groups compensated by mobile bromide (Br⁻) counter-ions. The charge on the imidazolium is delocalized on the aromatic ring leading to a relatively low average charge density, however, the separation of the cationic and anionic charge is minimal since the Im ring offers little steric hindrance in that regard.^[122] Additionally, the imidazolium ring is a versatile organic cation with a relatively high ionic conductivity and high thermal and chemical stability.^[123,124] Recent studies have found efficient charge carrier injection and good transport properties in imidazolium-based materials.^[125,126] The CPEs studied here are 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) and poly[(9,9-bis(8'-(3''-methyl-1''-imidazolium)octyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)] dibromide (F8im-Br). The conjugated backbone of these CPE materials are based on the electro-active conjugated polymers F8BT and PFO respectively. PFO has a wider HOMO - LUMO energy gap (~ 3.0 eV) than F8BT (~ 2.4 eV).

PLEDs with CPE EILs typically show slow response times on the order of seconds,^[104,127] which are undesirable in displays, where fast switching speeds are required. These slow EL luminance turn-on times have been linked to the mobility of the counter-ions, since zwitterionic CPE PLEDs, in which ions are covalently bonded to the ionic group and thus immobile, show fast turn-on times of ~ 10 μ s.^[128] However, even zwitterionic CPE PLEDs display unfavourable properties for display applications. The human eye will perceive changes in the luminance of $\sim 5\%$, but with the zwitterionic CPE increases in the PLED luminance of $\sim 33\%$ over a duration of 0.01 s are reported.^[128] Achieving both fast response times and luminance values that do not vary greatly over time have still not been reported with CPE EILs. Here, the response times of F8BT PLEDs with F8imBT-Br and F8im-Br EILs are probed through transient EL and current density measurements and response times of

<10 μ s are observed, with variations of the luminance of only $\sim$ 5% over a time period of 0.5 s.

Research on using CPEs as EILs with mobile ions has primarily focused on materials with ammonium cationic groups (Am), which adopt a tetrahedral structure leading to relatively large separation distances of the anionic and cationic charges.^[103,120,129] The charge on imidazolium cationic units ((CH)₂N(NH)CH⁺) is highly delocalized and the imidazolium group ((CH)₂N(NH)CH) is highly planar.^[122] By comparing an imidazolium and an ammonium containing CPE (F8imBT-Br and F8amBT-Br respectively) as EILs the role of the anionic and cationic charge separation is probed. By varying the anion counteracting the imidazolium cation of F8BT based CPEs from bromide (Br) to trifluoromethanesulfonate (Tf) and tetrakis(1-imidazolyl)borate (BIm₄) anions we study of the role of the anions on device performance. It has been suggested in the literature that larger anions improve device performance.^[114] Here we investigate whether the size of the anions has an effect on device efficiencies (of the anions we investigate here Br is the smallest and BIm₄ the largest). The size of the anions may play a role due to the ease with which they can move and rearrange within the CPE layer when an electric field is applied across the device. Alternatively the anion size may affect device performance due to steric hindrance posed by the bulky anions causing a physical separation between the anionic and cationic charges — an increased separation distance between the anion and cation causes both a larger dipole moment and a weakening of the ionic bond. Raman spectroscopy measurements were carried out on these samples as a probe of the molecular vibrational modes, which are very sensitive to the molecular conformation of the conjugated polymer backbone. Slight changes to the molecular conformation that cannot be detected through UV-visible absorption measurements can thus be probed with Raman spectroscopy.^[130]

Imidazolium-based CPE polymers with a PFO backbone similar to those reported here have been published in the literature,^[15–17] but their role in electron injection in PLEDs has not been fully explored. To investigate this is the main aim of the study pursued here.

5.2 Effects of CPE EIL on PLED performance

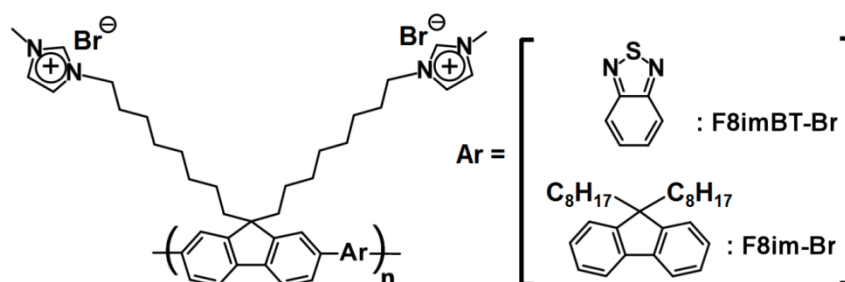


Figure 5.1: Chemical structures of novel imidazolium incorporated CPE materials with two different main conjugated backbones. The CPE materials are F8imBT-Br and F8im-Br, which have F8BT and PFO conjugated backbones respectively.

Two novel CPE materials, F8imBT-Br and F8im-Br, were synthesised *via* a palladium-catalysed Suzuki condensation polymerization and successive quarterisation reaction processes. The synthesis and characterisation of these CPE materials have been carried out by Dr. Minwon Suh and Mr. Kyungmok Kim (see Figure 5.1 for chemical structures and Appendix A for synthesis and characterisation details).

5.2.1 UV-Visible Absorption and PL Emission

UV-Visible absorption spectroscopy and PL emission of thin polymeric films were carried out to reveal any differences in optoelectronic properties between F8imBT-Br and F8im-Br compared to F8BT and PFO, respectively.

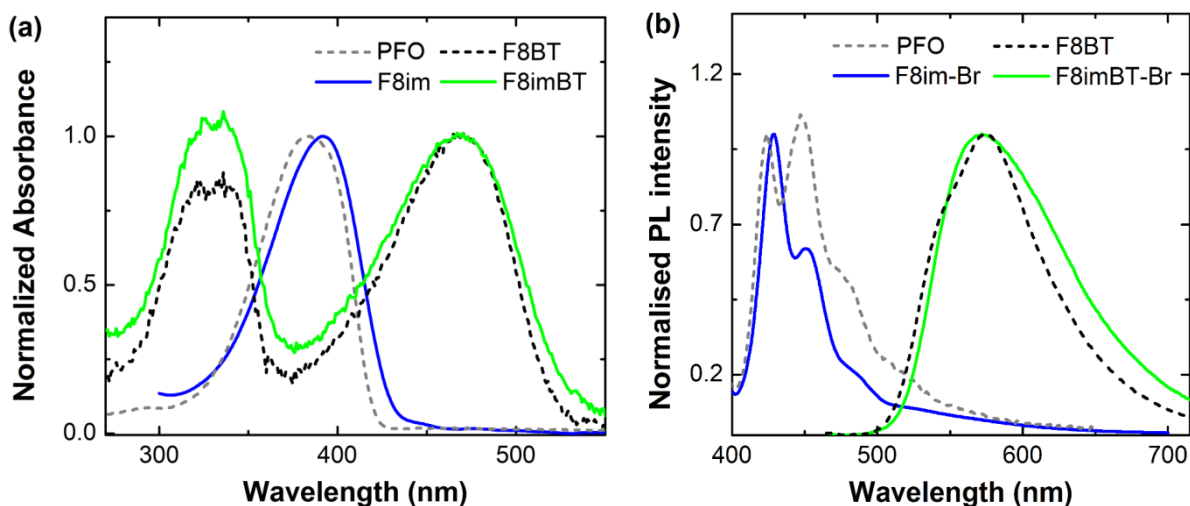


Figure 5.2: Normalised UV-visible (a) and PL (b) spectra of F8imBT-Br, F8im-Br, F8BT, and PFO. Data taken in collaboration with Dr. Minwon Suh at KAIST and Mr. Nathan Chander at Imperial College London.

In Fig. 5.2 (a), UV-Visible absorption spectra of novel CPEs are compared to the spectra of F8BT and PFO films. The F8BT and F8imBT-Br UV-visible spectra both show two absorption peaks. The one at around 470 nm is related to transitions between the HOMO and LUMO, where the LUMO is spatially localised on the BT unit,^[46,131] and is reported to have some degree of charge-transfer character.^[131,132] The one around 330 nm is related to transitions between the HOMO and higher lying unoccupied molecular orbitals, which are either centred on the 9,9'-dioctylfluorene units^[46] or more widely delocalised, encompassing the BT moieties too.^[132] The 470 nm absorption peak was chosen for the normalisation because it showed a lower level of noise. As the CPEs were dissolved in a polar solvent, a blue-shift in the spectra might be expected due to solvatochromic effects since the CPE films were spincoated from a polar solvent. However, PFO and F8im-Br both show only one absorption peak (associated with a series of inhomogeneously broadened vibronic transitions from the ground, S_0 , to the first excited electronic state, S_1)^[133] which appears slightly red-shifted in F8im-Br. A red shift in PFO absorption spectra is linked to PFO adopting the glassy or crystalline phase.^[134]

The ratio of the high to the low energy absorption peak ($I_{330\text{ nm}}/I_{470\text{ nm}}$) is ~ 0.86 in F8BT and ~ 1.07 in F8imBT-Br. The ratio for F8BT is in agreement with the literature, where it is reported that the 330 nm transition has marginally stronger absorption compared to the 470 nm transition.^[135] Studies on $F8_{(1-x)}BT_{(x)}$ copolymers (in which the fraction of BT moieties was varied from $x=0.06$ to 0.5) and star-shaped BT containing truxenes indicate that a

weaker peak at 470 nm is linked to a decrease in spatial overlap of the molecular orbitals.^[131,135] It is therefore possible that the presence of the ions disrupts the degree of localisation of the LUMO on the BT unit,^[131,135] which may be affected by the interaction of ionic groups with the backbone. Another possibility may be that the change is related to a quenching of intramolecular charge transfer transitions due to changes in the packing structure due to the ionic groups.^[132] Yet another possible explanation are that the change in the peak ratios is due to changes in inter-unit torsion.^[136]

Fig. 5.2 (b) shows the PL spectra of the CPE materials compared to the PL spectra of F8BT and PFO respectively. The PL emission spectrum of F8BT is comprised of two main peaks centred at ~540 nm and ~570-590 nm.^[14,99] Changes in the position and relative intensities of these peaks may be linked to changes in the polymer packing structure, since those two peaks are believed to have excimer character.^[14] An enhanced long-wavelength emission is observed in F8imBT-Br, which is reported to be associated with an increased torsional angle at the BT unit and a packing structure with increased electron mobility.^[130]

The PL spectra of F8im-Br and F8 were normalised to the highest energy peaks of each spectra and show clear vibronic structures. F8im-Br shows a red-shift in the PL 0-0 transition, which is consistent with the red-shift observed in the absorption spectra due to changes in crystallinity. A change in the ratios of the relative peak heights, combined with the red-shift, may indicate increased coplanarity of the backbone rings.^[137]

5.2.2 Electron Only Devices

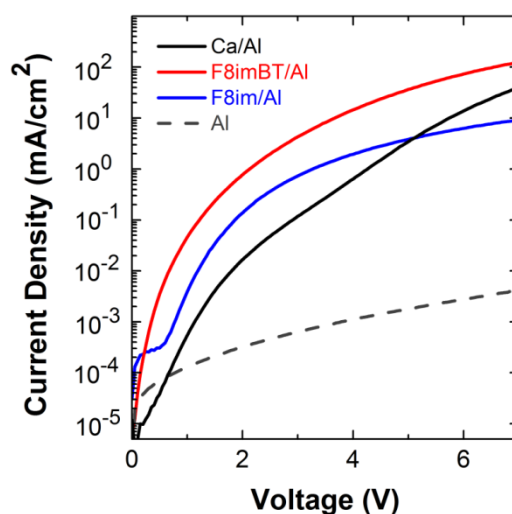


Figure 5.3: J - V curves in F8BT electron-only devices with Ca/Al and Al cathodes, as well as with CPE F8imBT-Br/Al and F8im-Br/Al cathodes.

We investigated the effect of the main conjugated backbone of the CPE on electron injection by studying electron-only devices (ITO/Al/F8BT/CPE (or Ca)/Al). The differences in the electron current densities of devices with F8imBT-Br/Al, F8im-Br/Al, Ca/Al, and Al cathodes are shown in Figure 5.3. . The thickness of the CPE layer is ~ 10 nm, while that of the Ca layer is ~ 20 nm. The results highlight how electron injection can be increased by using CPE layers: with F8imBT-Br current density is significantly increased compared to both Ca/Al and Al electrodes. The F8imBT-Br and Ca/Al devices both show no distinctive current turn-on voltage (defined as the voltage at which the current density in forward bias starts to rise steeply), meaning that charge injection is ohmic or near ohmic. In contrast the F8im-Br device displays current turn-on at ~ 0.7 V, which corresponds to a non-negligible energy barrier to electron injection being present at the interface between the F8BT active layer and the F8imBT-Br/Al cathode.

5.2.3 PLEDs

Figure 5.4 shows J - V (a), L - V (a), cd A^{-1} and lm W^{-1} efficiencies (b) for F8BT PLEDs with Ca/Al, F8imBT-Br/Al, and F8im-Br/Al cathodes. The turn-on voltage was unchanged between the two CPE devices at $1.6 \text{ V} \pm 0.2 \text{ V}$ and was also the same for the Ca/Al PLED. It has been reported that doping from positive ions, such as K^+ and Na^+ , leads to higher reverse bias currents through doping of the active layer.^[138] Here, the presence of Br^- in the CPE layer

did not show a significant effect on the reverse bias and leakage currents, which are comparable for all the devices.

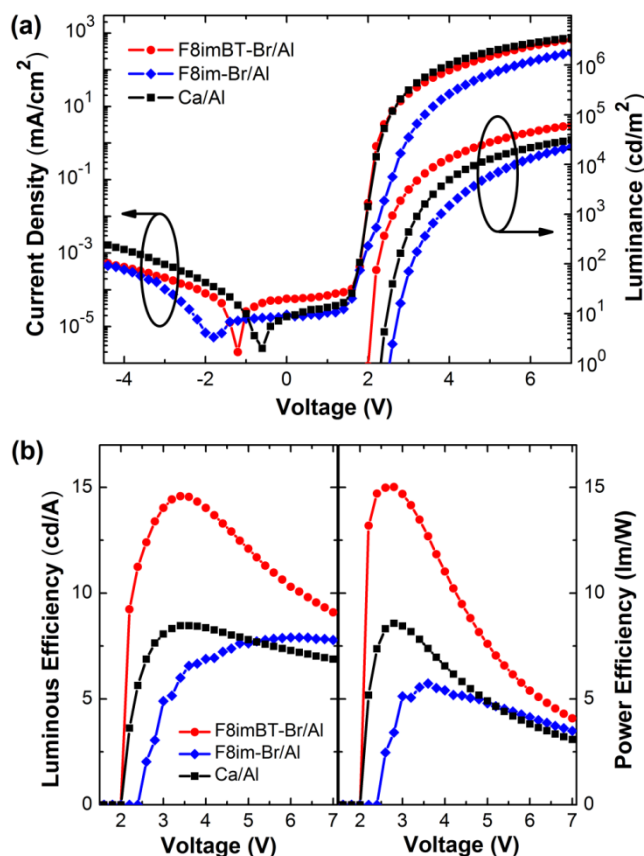


Figure 5.4: (a) The J - V and L - V characteristics of F8BT PLEDs with ~ 5 nm F8imBT-Br and F8im-Br cathode interfacial layers. PLEDs with Ca (20 nm)/Al cathode included as reference in black. (b) Luminous (cd A^{-1}) and power (lm W^{-1}) efficiencies extracted from data in (a).

After current turn-on, the Ca/Al and F8imBT-Br/Al PLEDs display very similar current densities (7.4 mA cm^{-2} and 7.6 mA cm^{-2} at 2.6 V respectively), while the F8im-Br/Al PLED shows lower current densities (0.1 mA cm^{-2} at 2.6 V). We observe the highest luminance values for F8imBT-Br EILs, while F8im-Br EIL device results in lower luminance values compared to PLEDs with Ca/Al cathodes. At a current density of 100 mA cm^{-2} a luminance of $14,900 \text{ cd m}^{-2}$ is measured in F8imBT-Br/Al PLEDs, which is 5.3 and 2.0 times higher than the F8im-Br/Al and Ca/Al PLEDs, respectively. Table 5.1 lists the luminance values and efficiencies of all the devices. The F8imBT-Br/Al PLED shows a maximum power efficiency of 15.0 lm W^{-1} at only 2.8 V . Previously 12.6 lm W^{-1} at 6.4 V was the maximum power efficiency reported for a single-layer F8BT PLED fabricated with either a CPE EIL or a metal oxide EIL in an inverted device structure.^[139]

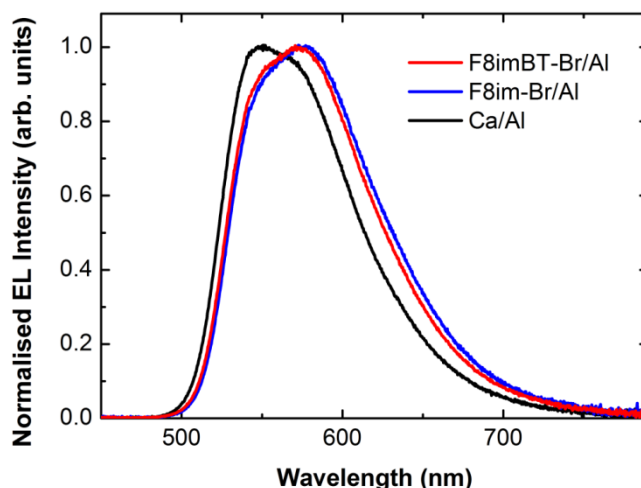


Figure 5.5: Normalised EL spectra of F8BT PLEDs at 4.5 V with F8imBT-Br/Al, F8im-Br/Al, and Ca/Al cathodes.

Fig. 5.5 shows that the normalised EL spectra measured at 4.5 V of both CPE/Al PLEDs are the same. They display a reduction in the low energy emission shoulder compared to the spectra of a Ca/Al PLED. This change at low energies may be due to a difference in the microcavity structure of the PLED, since an additional 10 nm layer has been inserted into the PLED device stack, which may cause changes in the constructive or destructive interference patterns.^[140]

Table 5.1: Maximum luminous efficiencies (LE) and power efficiencies (PE) extracted from Figure 5.4.

	Ca/Al	F8imBT-Br	F8im-Br
Max. LE (cd A^{-1})	8.5 (at 3.6 V)	14.6 at (3.4 V)	7.9 (at 6.2 V)
Max. PE (lm W^{-1})	8.6 (at 2.8 V)	15.0 at (2.8 V)	5.7 (at 3.6 V)

In summary, an F8imBT-Br EIL increases F8BT PLED efficiencies compared to PLEDs with Ca/Al cathodes. The EL spectra of F8im-Br/Al PLEDs show no contribution from the PFO CPE backbone, which indicates that the thin CPE layer does not contribute to the EL. Electron-only devices with an F8imBT-Br EIL had significantly higher current densities than when a F8im-Br or Ca EIL was used, demonstrating the excellent electron injection properties of F8imBT-Br. The increase in the efficiencies when using a F8imBT-Br/Al compared to a Ca/Al cathode in PLEDs is due to an increase in luminance in the CPE device. A higher luminance could be explained through either an increase in charge balance or a reduction of exciton quenching in the light emitting layer. The high electron mobility in

F8BT¹⁵ causes the current densities in F8BT PLEDs to be dominated by electron currents; so it is unlikely that increased electron injection might cause large increases in PLED efficiencies beyond those observed when a Ca/Al cathode is used. Exciton quenching by metal electrodes is known to cause significant loss of luminance.^[141] It is possible the CPE layer provides either a physical or energetic barrier to the metal of the Al which is able to reduce luminance quenching.

5.2.4 PL Decay Transients and PLQY

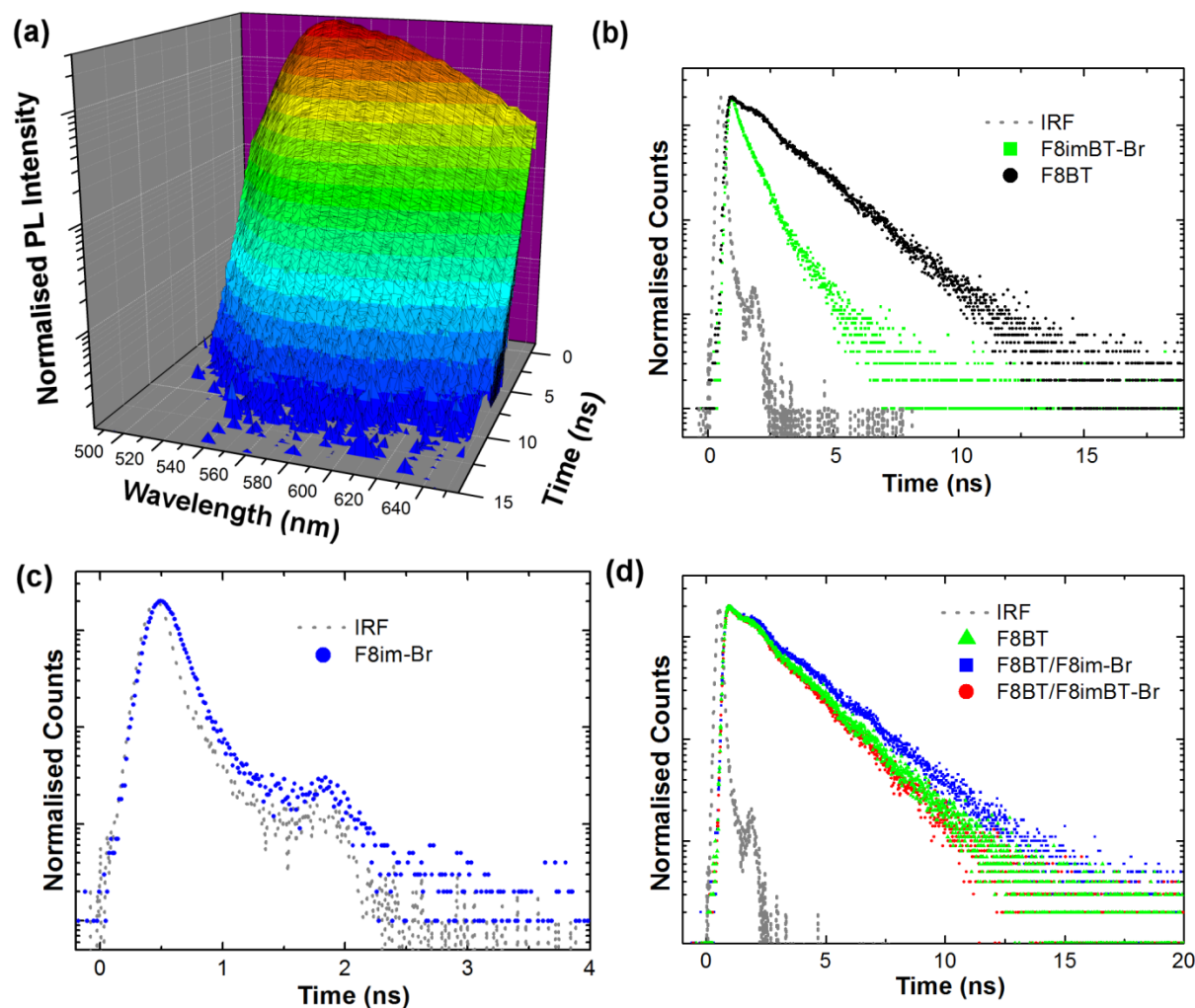


Figure 5.6: (a) 3D plot of PL decay curves as a function of wavelength for a F8BT (70nm)/F8imBT-Br (10 nm) sample. (b) Normalised PL decay curves measured at 467 nm excitation at 550 nm for single layers of F8imBT-Br (10 nm) and F8BT (70 nm). (c) Normalised PL decay curves measured at 467 nm excitation at 550 nm for single layer of F8im-Br (<10 nm). (d) PL decay curves measured at 467 nm excitation at 550 nm for F8BT (70 nm), F8BT (70 nm) /F8imBT-Br (10 nm), and F8BT (70 nm) /F8im-Br (<10 nm). The instrument response function (IRF) is shown in grey in panels (b)-(d).

PL decay transients were measured as a function of wavelength and decay time for thin film F8BT and CPE layers and F8BT/CPE samples on quartz. Fig. 5.6 (a) shows the shape of the PL decay curves as a function of wavelength and decay time for a F8BT/F8imBT-Br sample. At ~ 550 nm the PL emission is strongest so the results at this wavelength were used to compare between samples.

Pristine films of F8BT (~70 nm), F8imBT-Br (~10 nm) and F8im-Br (~10 nm) on quartz were studied *via* TCSPC (Fig. 5.6 (b) and (c)). On a semi-logarithmic scale the transient decays from all samples follow an almost straight line — this corresponds to a mono-exponential decay. The data was therefore fitted with an exponential decay function and the fitted lifetimes are listed in Table 5.2. Exciplex or charge transfer emission is generally visible in the PL decay transients as a second exponential with far longer life time ($\tau = 30 - 90$ ns)^[142,143] and is not visible in any of our data. In the 10 nm F8imBT-Br sample on quartz a ~66% reduction (from $\tau = 2.0$ ns to 0.7 ns) of fluorescence lifetime is observed compared to a 70 nm F8BT layer on quartz (note: the literature reports no significant change in the fluorescence lifetime between a 65 nm ($\tau = 1.71$ ns), 35 nm ($\tau = 1.82$ ns) and a 10 nm ($\tau = 1.77$ ns) layer of F8BT on quartz).^[144] The F8BT used in our study was supplied by Cambridge Display Technology (CDT) and a fluorescence lifetime of 2.0 ns is in agreement with reported values for F8BT supplied by CDT.^[135] F8im-Br has a fluorescence lifetime of 0.1 ns, which is almost thirty times shorter than F8BT; this is expected, as PFO generally shows such fast fluorescence decay rates.^[133] The samples were excited at 455 nm to determine the PLQY (Table 5.2). The PLQY of the F8BT film is 45%, while that of the F8imBT-Br film is only 10%. Recent studies have attributed PLQY quenching within CPE layers to the formation of weakly emissive long-lived CT states induced by the interaction of the mobile ions with bound excitons within the CPE.^[145] Here, a reduced PLQY in the CPE film was found, however, without the appearance of a long-lived CT emission component in the PL decay. When the fluorescence lifetime and the PLQY are both known the radiative rate constant, k_r , and the non-radiative rate constant, k_{nr} , can be calculated. In the F8imBT-Br film k_r is only slightly lower than in the F8BT film (2.3×10^8 and 1.4×10^8 s⁻¹ respectively), while k_{nr} is almost an order of magnitude greater in the F8imBT-Br film than in the F8BT film (2.7×10^8 and 1.3×10^9 s⁻¹ respectively). The emission of the fluorophores is highly depended on their environment and so increases in k_{nr} indicates processes occurring within nanometre range of the excited molecule that cause it to decay to the ground state non-radiatively.

Table 5.2: Parameters extracted from *PLQY* and *TCSPC* measurements.

	<i>PLQY</i> ($\pm 2\%$)	τ (ns) ^{a)}	k_r (s^{-1}) ^{b)}	k_{nr} (s^{-1}) ^{b)}
F8BT	45%	2.0	2.3×10^8	2.7×10^8
F8im	20%	0.1	2.7×10^9	1.1×10^{10}
F8imBT	10%	0.7	1.4×10^8	1.3×10^9
F8BT/10nm F8im	40%	2.3 ^{c)}	1.4×10^8	2.9×10^8
F8BT/10nm F8imBT	35%	1.8 ^{c)}	1.8×10^8	3.6×10^8

^{a)}Error in τ is ± 0.1 ns.

^{b)}Error in k_r and k_{nr} is $\pm 5\%$.

^{c)}Lifetime of the F8BT fluorophores; explanation given in text. Error in τ is ± 0.2 ns.

We carried out PL transient measurements on F8BT (~ 70 nm)/F8imBT-Br (~ 10 nm) and F8BT (~ 70 nm)/F8im-Br (~ 10 nm) samples to study the effect of the CPE layer on luminance quenching at the LEP layer/CPE interface within the PLED. As the lifetime of F8imBT-Br and F8im-Br is so much shorter than that of F8BT and has decayed to virtually zero after ~ 7 ns (in F8imBT-Br films) and ~ 2 ns (in F8im-Br films), the lifetime of the F8BT fluorophores can be extracted from the tail at 7 – 15 ns (note: extracting the lifetime of a F8BT only film by fitting only the tail or the entire curve produced the same lifetime to within ~ 0.2 ns). This allows us to probe the lifetime of the fluorophores in the F8BT layer (rather than in the CPE layer) of the F8BT/CPE samples to understand how the lifetime of the F8BT fluorophores are affected by the adjacent CPE layer. Alternatively the exponential curve can be fitted with multiple exponentials, however, it was found that more reliable results were achieved by fitting only the tail of the spectrum. The recorded fluorescence lifetime was 1.8 ns in the F8BT/F8imBT-Br sample and 2.3 ns in the F8BT/F8im-Br sample. The decrease in the lifetime of the F8BT fluorophores in the F8BT/F8imBT-Br sample compared to the F8BT sample indicates that the F8imBT-Br layer is causing some PL quenching at the interface with F8BT. The increase in the lifetime of the F8BT fluorophores in the F8BT/F8im-Br sample compared to the F8BT sample could be an indication of a small amount of exciplex or CT emission. The *PLQY* of F8BT/F8imBT-Br and F8BT/F8im-Br samples is 10% and 5% less, respectively, than that of F8BT films. The results from the F8BT/F8imBT-Br and F8BT/F8im-Br samples both show a reduction in k_r and an increase in k_{nr} for the F8BT fluorophores compared to the F8BT sample, which suggests the adjacent CPE layers introduces additional non-radiative decay pathways.

PL transient measurements were also carried out on F8BT (~70 nm)/F8imBT-Br (~10 nm) samples on quartz which were annealed at 45°, 77° and 90°C under nitrogen for 30 minutes each before being allowed to cool back down to room temperature (Fig. 5.7). The measurements were carried out to study the effects that may occur due to electrical driving of the PLED device. No changes are visible in the PL transients after annealing, which demonstrates the strong ionic bonding between the bromide anions and imidazolium cations.

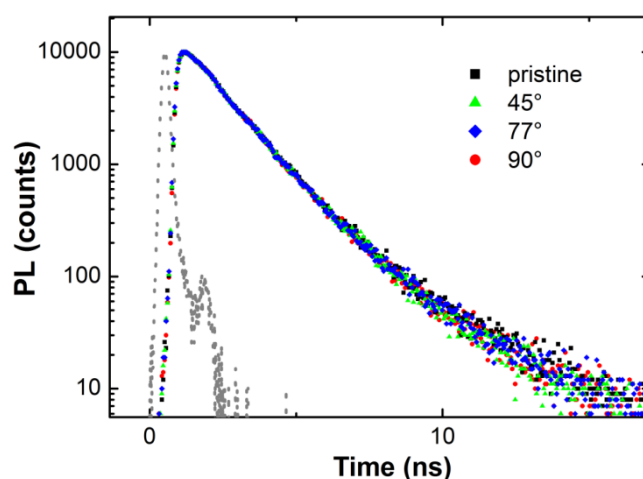


Figure 5.7: PL decay curves at 550 nm for pristine F8BT (70 nm)/F8imBT-Br (10 nm) samples on quartz and for samples annealed under nitrogen for half an hour each at 45°, 77° and 90°C and then measured at room temperature.

To conclude from this section, the thin CPE layer acts as PL quenching layer on top of F8BT. Thin films of F8im-Br deposited on top of F8BT additionally indicate a small amount of emission from longer-lived states. The annealing studies show that samples which had been previously heated up to temperatures of 90°C had similar fluorescence lifetimes as pristine samples, which suggests the ionic bonds in the CPE layer between the anion and cation are strong.

5.3 Electroluminescence and Current Density Transients

The input voltage, the EL signal and the current density responses of PLEDs with F8imBT-Br/Al, F8im-Br/Al, and Ca/Al cathodes are measured simultaneously in our PLED transient set-up. Fig. 5.8 shows the normalised current density (a) and EL (b) transient response of the PLEDs for two consecutive 0.5 s long 4.0 V pulses (c). The Ca/Al device shows a rectangular response function for the current density and EL, while the F8im-Br/Al device

shows a slow rise in both the current density and the luminance — this is in line with previously reported data for CPE EIL layers.^[129] The EL response of F8im-Br/Al PLEDs rises slowly and does not reach its maximum value within the duration of the 0.5 s rectangular voltage pulse, but when a rectangular voltage pulse of 5 s duration is applied we find that EL reaches ~86% of its maximum value after 4.7 s. The F8imBT-Br/Al device shows a fast EL and current density response; over the duration of the 0.5 s pulse the EL signal decreases by 5% though. The second pulse shows that this decay is completely recoverable, however, and therefore not due to a chemical degradation of the material.

In Fig. 5.8 the unnormalised current density (d) and EL (e) response is plotted against the logarithm of time to show the full evolution of the signal from F8imBT-Br/Al and F8im-Br/Al devices during the 0.5 s long voltage pulse. In both devices a large inrush current is visible when the voltage is turned on. An inrush current is normally found in capacitors and is caused by large changes in voltage on short time scales. The presence of an inrush current here can be understood by considering the PLED as a capacitor in series with a resistor. Once the voltage is no longer changing there is no more inrush current and currents through the PLEDs are found to be similar to those found in the J - V curves of the same devices (at ~4.0 V). The current density and EL of F8imBT-Br/Al devices decreases slightly over time, as expected. The F8im-Br/Al devices show an initial decrease in the current density (visible in the inset of Fig. 5.8 (d)) and EL signal (the local minima of the signal at this point are roughly the same in the current and in the EL) before slowly rising again.

The rise time, t_r , of the PLED represents the time after which the EL tends to saturate and therefore reflects the build-up of the minority carrier density in the RZ.^[54] For the F8imBT-Br/Al cathode PLEDs t_r is found to be 5.15 μ s, compared to 3.94 μ s for the Ca/Al PLED. The delay time, t_d , is the time from the on-set of the voltage pulse and the EL pulse and represents the time until the holes and electrons meet and recombine radiatively in the device. Both the CPE/Al and Ca/Al PLEDs have t_d values on the order of hundreds of nanoseconds (Table 5.3). The *apparent* electron mobility, μ_A , as defined in reference ^[54] is calculated as follows:

$$\mu_A = d / (t_d \times (V - V_{bi}) / d) \quad \text{Equation 5.1}$$

Where μ_A is the apparent electron mobility, d is the thickness of F8BT, t_d is the delay time between the applied rectangular voltage pulse and EL response, and $(V - V_{bi}) / d$ is the

applied electric field. From t_d the apparent mobility, μ_A , can be calculated (see Chapter 3.2.4 for further details); both CPE/Al PLEDs have comparable values of μ_A (2.0×10^{-6} for F8imBT-Br and 2.3×10^{-6} for F8im-Br EILs).

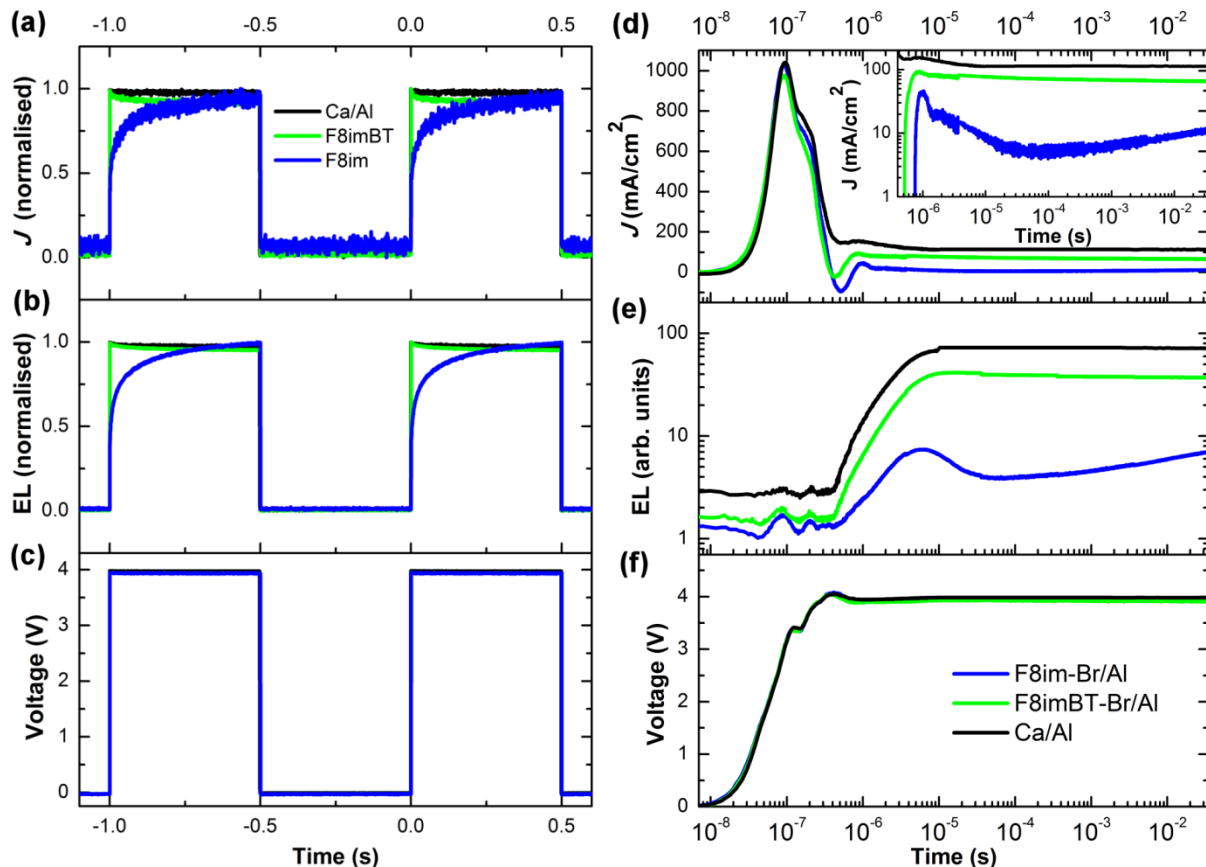


Figure 5.8: Normalised transient response of the current density (a) and EL (b) of F8BT PLEDs with F8imBT-Br/Al, F8imBT-Br/Al and Ca/Al cathodes. Panel (d) shows the absolute rise of the current density of the same PLEDs on a semi-log plot, while the inset in panel (d) shows the current density on a log-log plot starting at 4×10^{-7} s (once the voltage signal has stabilised). Panel (e) shows the rise of the EL in arbitrary units for those devices on a log-log plot. Data obtained at a frequency of 1 Hz for 4 V pulses. Applied voltage is also shown (c) and (f).

To investigate the role and importance of ion migration, PLEDs with varying F8imBT-Br EIL thicknesses were fabricated (Figure 5.9). It is hypothesised that the anions in CPE EILs move under the applied electric field toward the light emitting layer/CPE interface and that the time it takes the ions to move is responsible for the characteristically long delay times^[127] — in thicker films the ions need to travel further. When the thickness of a $\text{PFN}^+\text{BIm}_4^-$ EIL was varied (3, 12, 18, 22 and 45 nm), thicker layers caused very large increases in the response time (0.080 s at 3 nm, 2.9 s at 12 nm and >300 s at 45 nm).^[129]

F8imBT-Br layers spincoated from 1.5, 2.5 and 3.5 mg ml⁻¹ solutions by weight in toluene yielded ~5, ~8 and ~10 nm films respectively (Appendix B.1). Fig. 5.9 shows that the peak of the inrush current appears larger for thicker films, which is expected as the total ionic charge has an influence on the capacitance of the PLED. Although the thickness variation is small, noticeable increases should still be expected if ionic transport is involved in which the ions have comparable mobilities to those of previously reported CPE materials. We find t_r increases with thickness (2.7, 3.1, 4.1 μ s for ~5, ~8 and ~10 nm films respectively). The result does therefore point towards the involvement of ionic movement in the films, although it would appear to be far faster than in F8im-Br. The apparent electron mobility is also increased by the increased layer thickness from 8.6×10^{-7} cm² Vs⁻¹ for ~5 nm films to 2.0×10^{-6} cm² Vs⁻¹ for ~10 nm films. After 0.01 s the current density of the device with the ~10 nm film is ~35 mA cm², while it is ~67 mA cm² with a ~5 nm film. Correspondingly the EL is higher in the PLEDs with the thinner F8imBT-Br EILs. This is also in line with previous results in the literature, although the changes we see are small.^[129]

Table 5.3: Parameters extracted from EL transient measurements of PLEDs with F8BT active layer.

	t_d (ns)	μ_A (cm ² Vs ⁻¹)
Ca/Al	393	8.2×10^{-7}
~5 nm F8imBT-Br (1.5 mg ml ⁻¹)/Al	420	8.6×10^{-7}
~8 nm F8imBT-Br (2.5 mg ml ⁻¹)/Al	487	1.9×10^{-6}
~10 nm F8imBT-Br (3.5 mg ml ⁻¹)/Al	490	2.0×10^{-6}
~10 nm F8im-Br (3.5 mg ml ⁻¹)/Al	391	2.3×10^{-6}

To summarise, varying the CPE backbone from one based on PFO (F8im-Br) to one based on F8BT (F8imBT-Br) caused dramatic increases in the EL response time of F8BT PLEDs. The response times of a few seconds seen in the F8im-Br/Al PLEDs are comparable to data in the literature for F8BT PLEDs containing CPE EILs with mobile ions.^[121] The EL response times of F8imBT-Br/Al PLEDs, however, are <10 μ s and are thus similar to those of Ca/Al cathode PLEDs. Additionally, variations of only ~5% in the luminance are recorded over a time period of 0.5 s. This demonstrates the possibility of achieving fast turn-on times of PLEDs with CPE EILs even in the presence of potentially mobile ions in the CPE layer.

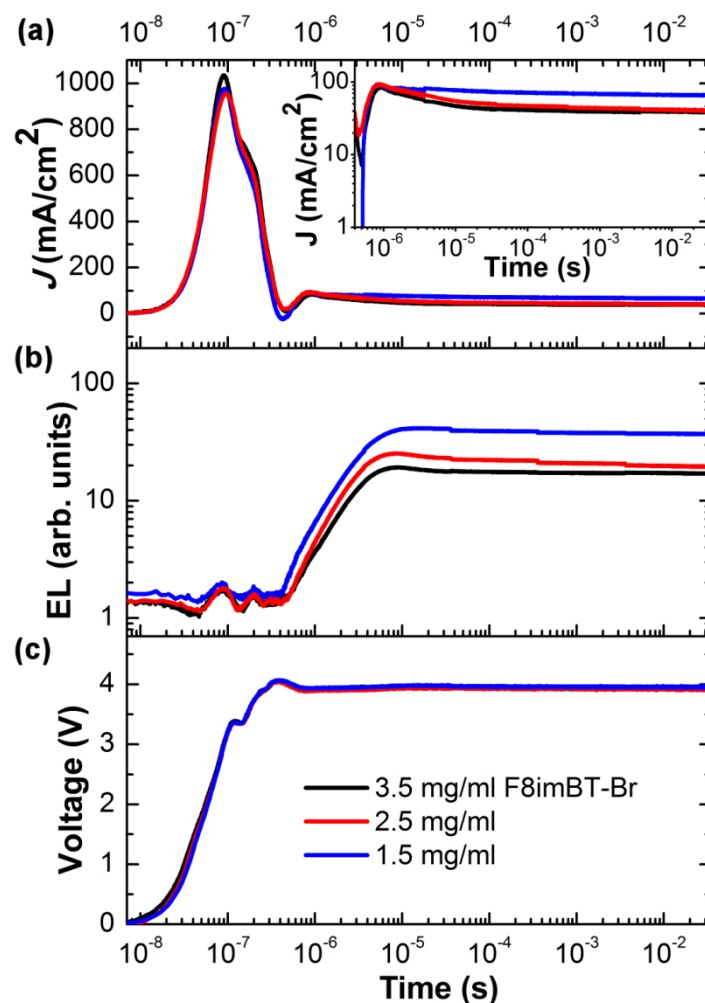


Figure 5.9: Transient response of the current density (a) and EL (b) of F8BT PLEDs with F8imBT-Br EILs. Data obtained at a frequency of 1 Hz for 4 V pulses (c). The thickness of the EIL was varied through spincoating from 1.5 – 3.5 mg ml⁻¹ solutions of F8imBT-Br. Applied voltage is also shown.

5.4 CPE EIL Thickness Dependence

To understand the precise role of the CPE layer in electron injection, we investigated the properties of PLEDs with different CPE layer thicknesses. A thicker CPE layer has a greater number of ions and may also have a different packing structure (and therefore different dipole characteristics).

5.4.1 PLEDs

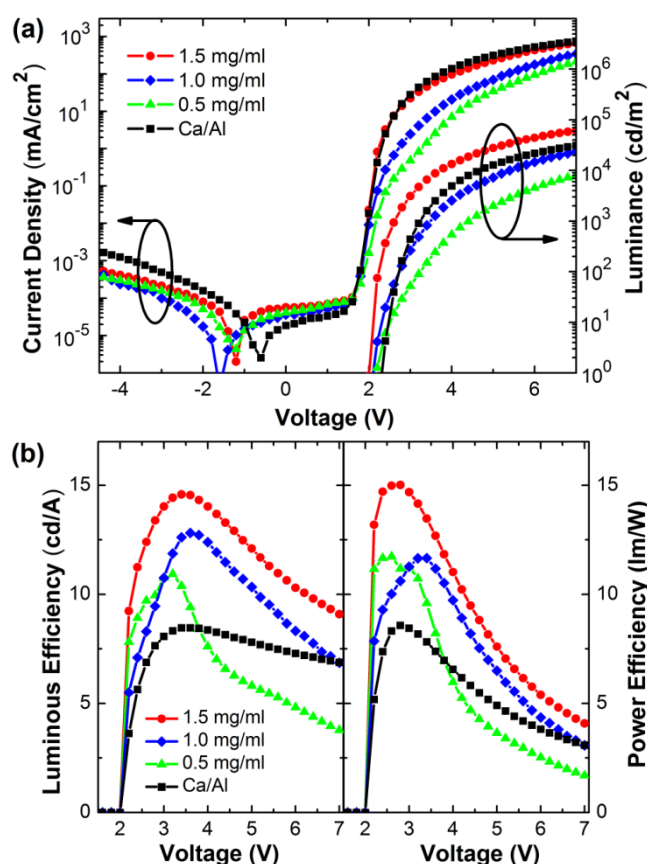


Figure 5.10: (a) J - V and L - V curves for F8imBT PLEDs with different thicknesses of the F8imBT-Br EIL (all under 10 nm, spin-coated from solutions with concentrations from 0.5 – 1.5 mg ml^{-1}), as well as the curves for a Ca/Al cathode PLED. (b) Luminous (Cd A^{-1}) and power (lm W^{-1}) efficiencies are extracted from the data in (a).

The results listed in Table 5.4 show that the optimum thickness of the F8imBT-Br electron injection layer is $\sim 5\text{nm}$ (spin coated from a 1.5 mg ml^{-1} solution by weight in toluene). PLEDs with F8imBT-Br EILs of $\sim 5\text{ nm}$ thickness and below are studied to understand the origin of the CPE's good charge injection properties. The J - V results in Fig. 5.10 show similar reverse bias and leakage currents with different CPE layer thicknesses. After turn-on reduced current densities are observed in the thinner films (at 2.6 V the current densities are 7.6 mA cm^{-2} for 1.5 mg ml^{-1} , 0.7 mA cm^{-2} for 1.0 mg ml^{-1} and 0.2 mA cm^{-2} for 0.5 mg ml^{-1} solutions of F8imBT-Br by weight in toluene). The L - V curves display correspondingly lower luminance values for the thinner films (at 2.6 V the luminances are 939 cd m^{-2} for 1.5 mg ml^{-1} , 56 cd m^{-2} for 1.0 mg ml^{-1} and 15 cd m^{-2} for 0.5 mg ml^{-1} solutions of F8imBT-Br by weight in toluene).

The EL emission from these devices was uniform, even for the 0.5 mg/ml layer, indicating a uniform coverage of the thin F8imBT-Br layers on top of the F8BT layer. The luminous efficiencies decrease as the layer thickness decreases, although the power efficiency of the thinnest layer does not follow that trend. The PLEDs with varying CPE EIL thicknesses all display higher peak efficiencies than the Ca/Al cathode device. The luminous efficiency roll-off of the CPE devices is, however, steeper than in the Ca/Al PLED, which points towards increasing electron and hole imbalances in the light emitting layer at higher current densities.^[146] Table 1.3 lists the luminance values and efficiencies of all the devices in detail. No changes in the EL spectra of the devices with different CPE layer thicknesses were observed (see Appendix B.2). Results from films of increased thickness were obtained in other device runs using a spectrometer to measure the luminance (see Appendix B.3). These data indicate that increasing CPE layer thickness above 10 nm does not lead to ever higher efficiencies, but causes luminance to drop off fast.

Table 5.4: Peak efficiencies and luminance values extracted from Fig. 5.10 and Appendix B.3.

	Max. LE (cd A ⁻¹)	Max. PE (lm W ⁻¹)	L at 7 V (cd m ⁻²)
0.5 mg ml ⁻¹ (< 3 nm)	10.9 at (3.2 V)	11.7 (at 2.6 V)	8 037
1.0 mg ml ⁻¹ (~ 3 nm)	12.8 (at 3.6 V)	11.7 (at 3.4 V)	23 640
1.5 mg ml ⁻¹ (~5 nm)	14.6 at (3.4 V)	15.0 at (2.8 V)	61 510
3.5 mg ml ⁻¹ (~ 10 nm)	12.7 at (3.8 V)	12.7 at (2.8 V)	45 180

Even a <5 nm EIL of F8imBT-Br increases CPE efficiencies over using a Ca/Al cathode. This increase in efficiency occurs even though lower current densities and luminance values are recorded for the <5 nm EIL devices. A peak in device efficiencies is found with ~ 5 – 10 nm CPE EILs; thicker layers cause lower luminance and efficiency values. It has been reported that the thickness of the charge injection layer is important in determining at which field strength the remaining energy barrier between the electrode and the charge injection layer is minimised; thinner layers should perform better at lower electric field strengths while thicker layers should perform better at higher field strengths.^[147] While we do observe this, the lower current densities in the thinner films highlight that the origin of the higher efficiencies is not due to better charge injection of electrons from Al. It is more likely that the CPE layers increase efficiencies by offering additional protection from luminance quenching by the metal electrodes or promoting better charge balance in the active layer.

5.4.2 Quenching with Increased CPE Thickness

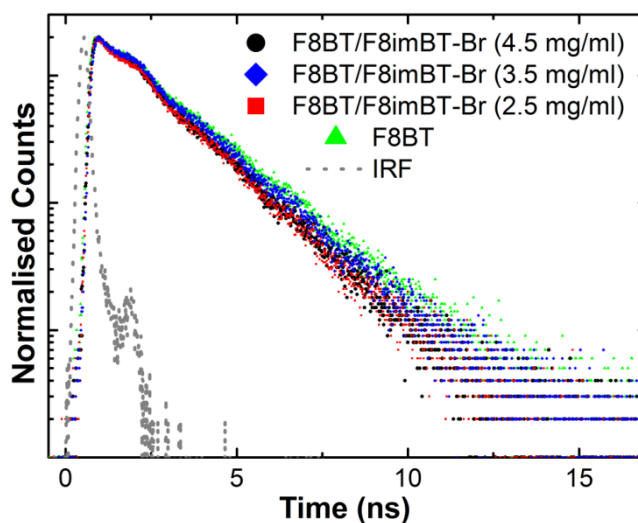


Figure 5.11: Normalised PL decay signal at 550 nm for F8BT (70nm)/F8imBT-Br samples with different thicknesses of the F8imBT-Br layer. The different thicknesses achieved by spincoating from solutions of 2.5, 3.5 and 4.5 mg ml⁻¹ concentrations and are approximately 8 nm, 10 nm and 13 nm respectively. The PL decay of a 70 nm F8BT layer on quartz is also shown, along with the IRF (dotted grey line).

To understand the role the CPE layer might have in quenching luminance we conducted TCSPC experiments on quartz/F8BT (~70 nm)/F8imBT-Br samples with varying thicknesses of the F8imBT-Br layer (Fig. 5.11). CPE layers were spincoated from 2.5, 3.5 and 4.5 mg ml⁻¹ by weight solutions yielding films of ~8 nm, ~10 nm and ~13 nm respectively. Thicker CPE layers contain in total more ions and may have stronger dipole characteristics as a result. A quartz/F8BT sample was also measured for comparison. No long lived emission is observed in any of the samples. The fluorescence lifetimes of the samples were extracted by fitting the tail end of the PL decay, so as to only probe the lifetime of the fluorophores within the F8BT layer (Table 5.5). The fluorescence lifetimes appear to be independent of CPE thickness at 1.8 – 1.7 ns. The differences in the PLQY of the CPE films at various thicknesses are also within error. These results show that the effect of the CPE layer on F8BT PL quenching is independent of thickness within the range of CPE layer thicknesses probed here; any increase in the CPE layer's dipole characteristics at increased layer thicknesses does not cause significantly more PL quenching.

Table 5.5: Parameters extracted from *PLQY* and *TCSPC* measurements.

	<i>PLQY</i> ($\pm 2\%$)	τ (ns) ^{a)}	k_f (s ⁻¹) ^{b)}	k_{nr} (s ⁻¹) ^{b)}
F8BT	45%	2.0	2.3×10^8	2.7×10^8
F8BT/F8imBT-Br (2.5 mg ml ⁻¹)	38%	1.8 ^{c)}	2.2×10^8	3.5×10^8
F8BT/F8imBT-Br (3.5 mg ml ⁻¹)	35%	1.8 ^{c)}	1.8×10^8	3.6×10^8
F8BT/F8imBT-Br (4.5 mg ml ⁻¹)	35%	1.7 ^{c)}	2.0×10^8	3.7×10^8

^{a)}Error in τ is ± 0.1 ns.

^{b)}Error in k_r and k_{nr} is $\pm 5\%$.

^{c)}Lifetime of the F8BT fluorophores; explanation given in text in Section 1.2.4. (error in τ is ± 0.2 ns).

5.5 Vary PLED Light Emitting Layer from F8BT to Super Yellow (SY)

We studied PLEDs with SY light emitting layers to explore the role of the light emitting layer/CPE interface in the PLED device stack on device performance. A set of SY PLEDs and electron only devices with F8im-BT and F8imBT-Br EIL were fabricated. SY has a HOMO level of 5.3 eV, compared to a HOMO level of 5.9 eV in F8BT; the LUMO energy level of SY is 3.2 eV and that of F8BT is 3.7 eV (see Chapter 6.5.1) the energy gap of SY is slightly smaller than that of F8BT. PLEDs with SY should therefore have different energy level alignments at the CPE/light emitting layer interface than F8BT PLEDs. Additionally, varying the active layer from F8BT to SY allows us to study light emitting layer systems in which electron and hole transport are slightly dominant respectively.^[44,70,148]

5.5.1 PLED Characterisation

Fig. 5.12 shows J - V and L - V (a), cd A⁻¹ (b) and lm W⁻¹ efficiency (c) and EL spectra (d) for SY PLEDs with Ca/Al, F8imBT-Br/Al, and F8im-Br/Al cathodes. The turn-on voltage was unchanged between the two CPE devices at 1.5 ± 0.2 V and was slightly higher for the Ca/Al PLED at 1.7 ± 0.2 V. The leakage currents for all the devices were comparable.

After current turn-on, the F8imBT-Br/Al PLED initially displays very similar current densities as the Ca/Al PLED; after around 2.2 V the F8imBT-Br/Al PLED shows over an order of magnitude lower current densities until around 10.0 V, when the current density of F8imBT-Br/Al PLED is only slightly lower. The F8im-Br/Al PLED displays lower current density after current turn-on compared to the F8imBT-Br/Al PLED until over 7.0 V — in that voltage region both CPE/Al PLEDs display similar current densities. The Ca/Al PLED has higher

luminance values at all voltages, while above 5.0 V the PLED with F8im-Br EIL shows higher luminance values than the F8imBT-Br EIL device. At a current density of 100 mA cm^{-2} a luminance of $6,000 \text{ cd m}^{-2}$, $3,900 \text{ cd m}^{-2}$, and 370 cd m^{-2} is found in Ca/Al, F8im-Br/Al, and F8imBT-Br/Al PLEDs, respectively. Table 5.6 lists the luminance values and efficiencies of all the devices in detail. The F8im-Br/Al PLED shows a maximum power efficiency of 5.07 cd A^{-1} at 7.2 V, which is around 1 cd A^{-1} lower than the Ca/Al PLED, but 8.6 times higher than the maximum luminous efficiency of the F8imBT-Br/Al PLED.

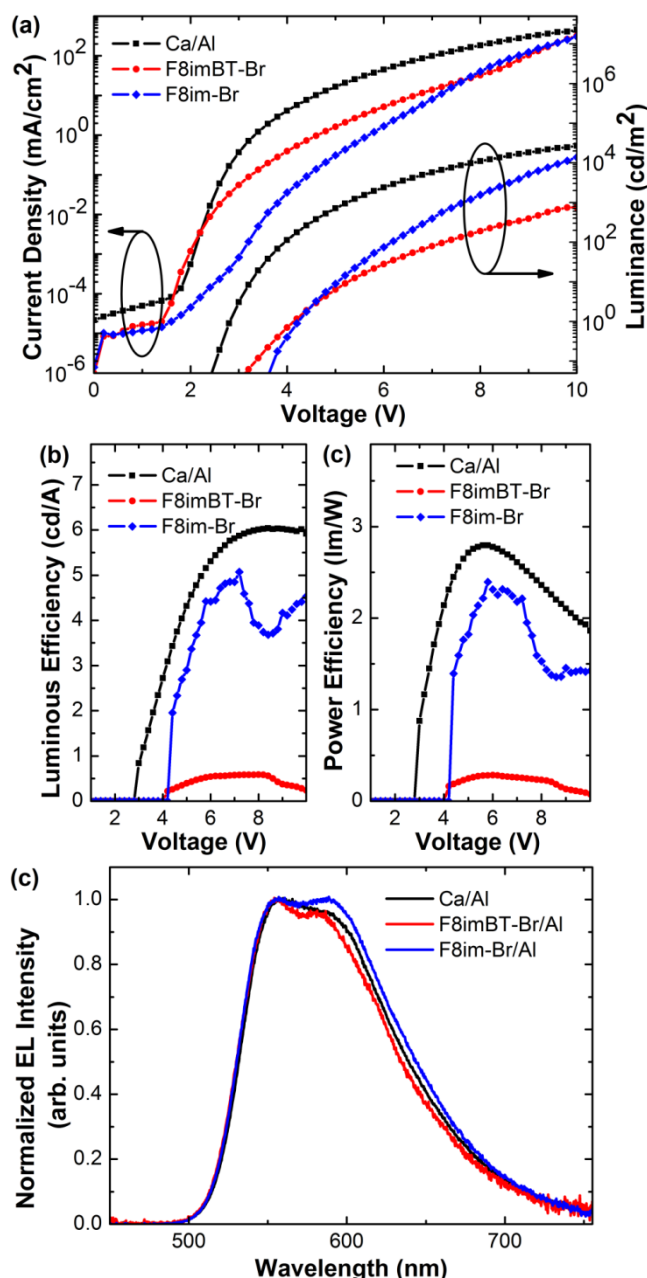


Figure 5.12: Panel (a) shows J - V and L - V characteristics of SY light emitting layer PLEDs with Ca/Al, F8imBT-Br/Al, and F8im-Br/Al cathodes. Panel (b) shows the lm W^{-1} and cd A^{-1} efficiency data extracted from the data in panel (a), and panel (c) shows the corresponding spectra at 7 V.

Fig. 5.12 (c) shows EL spectra at 7 V of all devices normalised to the low energy peak. The SY EL emission displays a main peak at 555 nm, which originates from the π - π^* transition, while the lower energy shoulder at is associated with interchain emission related to the packing structure of the polymer chains.^[149] The low energy shoulder of the spectra appears highest for the F8im-Br/Al PLED, while it is similar for the F8imBT-Br/Al and Ca/Al PLED. SY and PFO form a type I heterojunction and so no exciplex emission would be

expected, however, it is possible that due to differences in the energy level alignment of F8im-Br and PFO that a type II heterojunction is formed in the case of SY and F8im-Br. Subtracting the Ca/Al spectrum does not however reveal a distinctive exciplex peak. The increase in the emission from the shoulder is therefore likely due to something else, such as a change in the location of the RZ to areas within the SY layer with slightly different packing structures. This explanation is most likely, since large changes in the J - V curves are recorded when using the CPE EILs, which points towards differences in the charge balance within the active layer (note: charge balance influences the position of the RZ).^[61]

Table 5.6: Maximum luminous efficiencies (LE) and power efficiencies (PE) extracted from Fig. 5.12.

	Ca/Al	F8imBT-Br	F8im-Br
Max. LE (cd A^{-1})	6.04 (at 8.4 V)	0.59 at (8.0 V)	5.07 (at 7.2 V)
Max. PE (lm W^{-1})	2.79 (at 5.6 V)	0.28 at (6.0 V)	2.40 (at 5.8 V)

5.5.2 Electron-only Devices with SY Active Layer

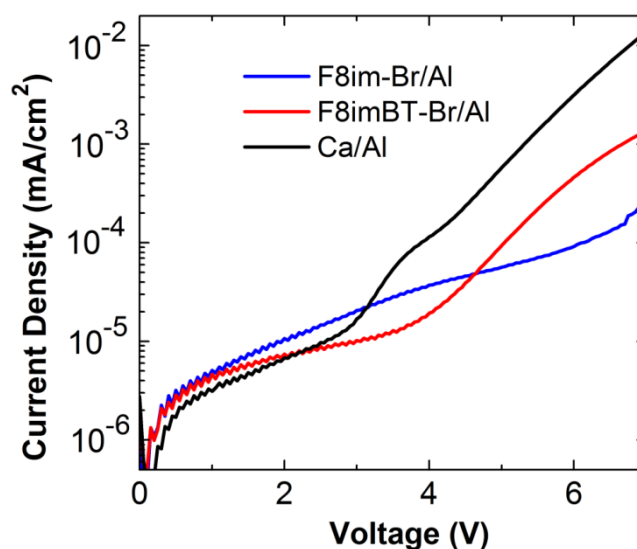


Figure 5.13: Electron-only devices with F8imBT-Br/Al, F8im-Br/Al, and Ca/Al as EIL with a SY active layer.

We investigated the effect of varying the main conjugated backbone of the CPE on electron injection in electron-only diode structures with SY active layers (Fig. 5.13). The electron densities in these SY electron only devices are far lower than in the F8BT devices, which is expected, since F8BT is far superior electron transporter than SY. The electron current

densities of devices with an F8imBT-Br/Al cathode show higher current densities above 4.5 V, while devices with F8im-Br/Al cathodes showed higher current densities initially. The F8im-Br device shows no distinctive current turn-on voltage (defined as the voltage at which the current density in forward bias starts to rise steeply), meaning that charge injection occurs through thermal excitation. In contrast the F8imBT-Br device displays current turn-on at ~ 4.0 V, which corresponds to a large energy barrier to electron injection being present in this system.

5.5.3 Summary

PLEDs with SY light emitting layers showed lower current density turn-on voltages when CPE/Al cathodes were used compared to when Ca/Al cathodes were used; additionally lower current densities were observed over the majority of the voltage range. As the CPE EILs modify primarily the cathode-side of the device stack, these observations suggest lower electron injection. In turn, of course, lower electron injection may cause changes in charge accumulation at the anode-side and thus affect hole injection also. The electron-only devices suggest a non-ohmic contact of the F8imBT-Br layer and Al on SY — this is likely the cause of the low efficiencies observed in the F8imBT-Br/Al SY PLEDs and suggests that the energy level alignment plays a key role. The alignment of the energy levels is explored in Chapter 6.

5.6 Role of Ionic Side Groups of Electron Injecting Polyelectrolytes on PLED Performance

A series of F8BT PLEDs were fabricated with the structure detailed in Fig. 5.14 (a) with different CPE EIL materials, the chemical structures of which are shown in Fig. 5.14 (b). The addition of the ionic side groups causes polymer chains to exhibit amphiphilic behaviour, which would influence the way in which such polymers pack. In the literature the introduction of the ionic groups has been associated with aggregate formation and with increased backbone planarity and molecular ordering due to the nature of CPEs to form lamella structures.^[150–152] To study the packing structures Raman spectroscopy measurements were carried out. For UV-visible absorption spectroscopy, Raman and photoluminescence (PL) measurements thin film samples were prepared on quartz. The PL quantum yield (PLQY) measurements were carried out with an integrating sphere and the values calculated using the method published in reference^[53]. Raman spectra were obtained using a Renishaw inVia Raman spectrometer with a 785 nm excitation laser focused through

a $\times 50$ objective in a back-scattering configuration. The laser power was ~ 186 mW at the sample surface with a total exposure time of 300 s.

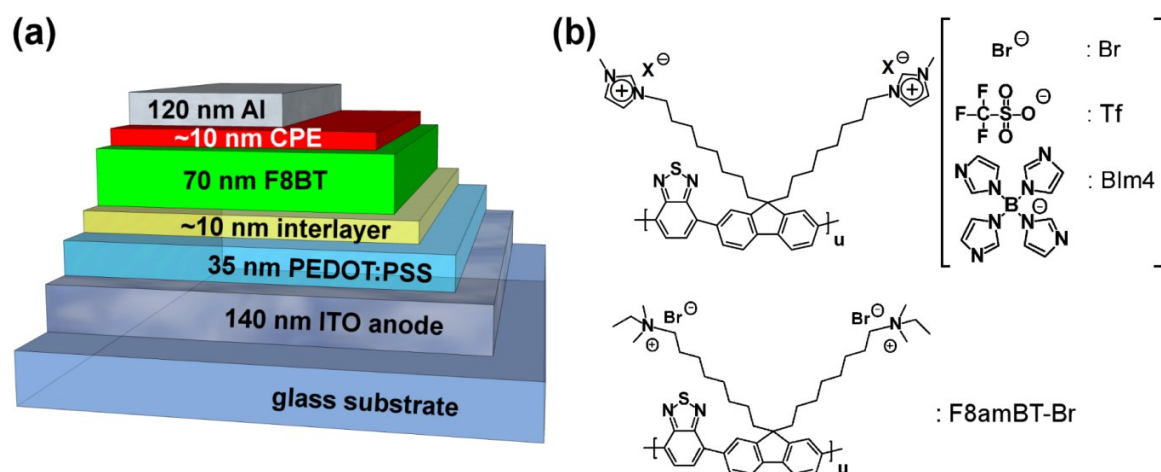


Figure 5.14: PLED diode structure with CPE EIL (a) and chemical structures of F8imBT-Br, F8imBT-Tf, F8imBT-BIm₄ and F8amBT-Br CPE materials used as EILs (b).

All CPE materials were synthesised based on the chemical structure of the F8BT conjugated backbone. CPEs with bromide, trifluoromethanesulfonate, and tetrakis(1-imidazolyl)borate mobile counter ions were created (F8imBT-Br, Poly[(9,9-bis(8'-(3''-methyl-1''-imidazolium)octyl)-2,7-fluorene-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)] trifluoromethanesulfonate (F8imBT-Tf) and Poly[(9,9-bis(8'-(3''-methyl-1''-imidazolium)octyl)-2,7-fluorene-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)] tetrakis(1-imidazolyl)borate (F8imBT-BIm₄) respectively). These all had an imidazolium immobile cationic group attached to the alkyl side-chains. Another CPE with Br counterions and ammonium cation groups was also synthesised, Poly[(9,9-bis(8'-((N,N-dimethyl)-N-ethylammonium)octyl)-2,7-fluorene-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)] dibromide (F8amBT-Br). The synthesis procedure for these materials is listed in Appendix A.3 and is based on procedures found in references ^[114] and ^[153]. All CPE layers were spincoated from solutions of 3.5 mg/ml in 2-methoxyethanol, yielding layers of ~ 10 nm thickness.

5.6.1 UV-visible Absorption and Photoluminescence

The UV-visible absorption spectra of F8imBT-Br, F8amBT-Br, F8imBT-Tf and F8imBT-BIm₄ show two absorption peaks (Fig. 5.13 (a)). The tail end of the main $\pi \rightarrow \pi^*$ electronic transition (~ 220 nm) is just about visible in the high energy region of the graph.^[46] The 330

nm peak is thought to involve transitions between the HOMO and higher lying delocalised unoccupied molecular orbitals, which are either centred on the 9,9-dialkylfluorene units^[46] or more widely delocalised, also encompassing the BT moieties.^[132] The higher energy peak at 470 nm has been related to transitions between the HOMO and LUMO with some degree of charge-transfer character,^[131,132] where the LUMO is spatially localised on the BT unit.^[46,131] There is no visible change in the high energy tail of the spectra, indicating that all the films have similar scattering properties and hence implying similar surface roughnesses. No significant differences in the peak positions of the high and low energy peaks are observed. While all films were spincoated from solutions using the same solvent and the same concentration by weight, it is possible that they differ slightly in thickness. The spectra display similar absorption peak values (high energy peak) for all films except F8imBT-BIm₄, which displays slightly lower values (~ 0.11 absorbance units at 330 nm in F8imBT-Br, F8imBT-Tf and F8amBT-Br samples and ~ 0.09 absorbance units in the F8imBT-BIm₄ sample). The films are too thin to accurately determine their thickness *via* profilometry. The relative peak heights in the absorption spectrum give a rough indication however that spin coating the CPE materials from solutions of the same concentration yields approximately similar thickness values (although F8imBT-BIm₄ films may form slightly thinner films). The ratio of the high to the low energy absorption peak ($I_{330\text{ nm}}/I_{470\text{ nm}}$), which may be related to changes in inter-unit torsion or to changes in the intramolecular charge transfer transition due to changes in the packing structure,^[136] show no significant variations except with regard to the F8imBT-Tf film, in which the low energy peak displays a lower absorbance. A weaker peak at 470 nm is reported to be associated with a decrease in spatial overlap of the molecular orbitals.^[131,135]

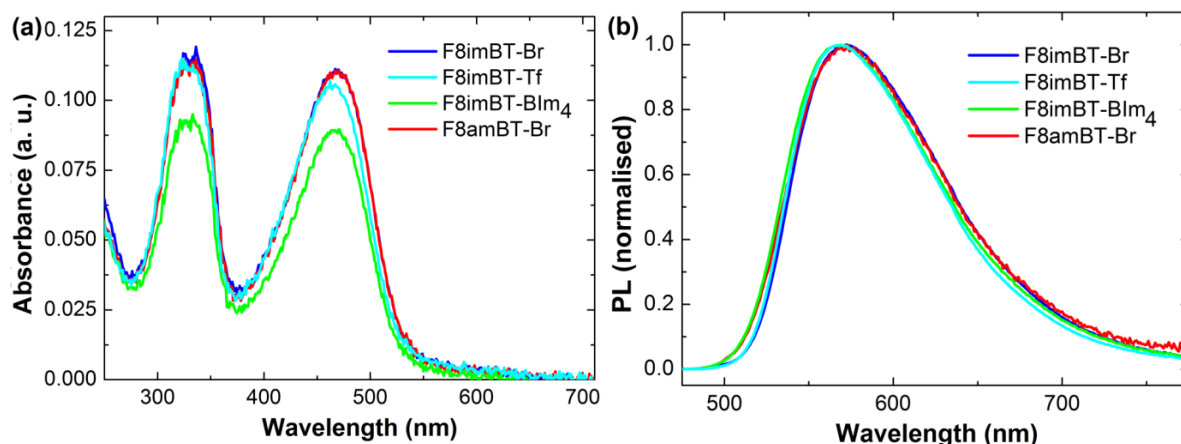


Figure 5.15: (a) UV-visible absorbance, A , and (b) normalised PL spectra of F8imBT-Br, F8imBT-Tf, F8imBT-BIm₄ and F8amBT-Br.

The PL emission from F8BT has two main peaks centred at ~ 540 nm and ~ 570 - 590 nm,^[14,99] which are believed to have excimer character.^[14] Changes in the polymer packing structure could thus show up as changes in the PL spectra. There are, however, no significant differences recorded between the spectra of the various F8BT CPEs in Fig. 5.15 (b).

Table 5.7: *PLQY* measurements of ~ 10 nm thin films on quartz. All values below have an error of ± 2 .^[53]

F8BT	F8imBT-Br	F8imBT-Tf	F8imBT-BIm ₄	F8amBT-Br
45%	10%	23%	15%	15%

PLQY was measured for pristine thin films on quartz at an excitation wavelength of 455 nm, which corresponds to the high energy absorption peak in F8BT. The F8BT reference PLQY measurement is in agreement with literature values for pristine films,^[130] and the results are listed in Table 5.7. The CPE films all show lower PLQY compared to the F8BT film, however, even the lowest PLQY recorded (10% in F8imBT-Br) is still relatively high considering and demonstrates that not all luminance is quenched by the ionic groups. F8imBT-Tf shows the highest PLQY among the CPE films despite displaying slightly lowered absorption in the high energy peak where the sample was excited. Although F8imBT-Br and F8amBT-Br contain the same counter ion (Br), the PLQY of the F8imBT-Br film is 10%, compared to 15% in F8amBT-Br, which has the imidazolium cationic group.

Lower PLQY values in CPE films compared to films of same-backbone material without ionic groups has been reported in the literature and was attributed to the formation

of charge transfer states induced by the interaction of the anions with bound interchain excitons within the CPE.^[145,154] It is noted that bulkier anions decrease those interchain interactions and therefore suffer less PL self-quenching^[145,154] and further that Coulombic interactions with the excitons (and thus PLQY quenching) is also reduced with the use of larger anions due to increased steric separation of the anion from the conjugated backbone.^[145] No trend of PL quenching with respect to the steric hindrance of the cations or anions with regards to each other or to the backbone was observed in this work. It is possible that this is due to analysing only films in the thickness region of ~ 10 nm (which corresponds with the thickness of the CPE EILs used in PLEDs).

5.6.2 Raman

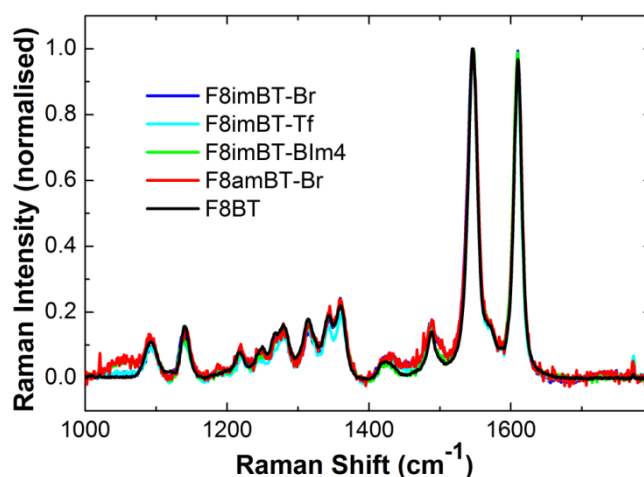


Figure 5.16: Raman spectra of F8BT and F8BT-based CPE materials with different ionic side groups under 785 nm excitation, normalised to the 1545 cm^{-1} peak.

Raman scattering measurements at 785 nm excitation were performed on thin film samples (<15 nm) of F8BT, F8imBT-Br, F8imBT-Tf, F8imBT-BIm₄ and F8amBT-Br and are reported in Fig. 5.16. The spectra in Fig. 5.16 and Fig. 5.17 (a) have two main peaks, one at 1545 cm^{-1} (in-plane BT ring stretch) and the other at 1608 cm^{-1} (in-plane 9,9'-dioctylfluorene ring stretch), which dominate the Raman spectra of all the samples.^[134,155–157] The spectra were normalised to the 1545 cm^{-1} peak. No changes in the peak positions beyond the $\pm 1\text{ cm}^{-1}$ resolution of the instrument are observed. Fig. 5.17 (b) shows carbon stretch modes; of note here is the BT-centred C-C stretching mode frequency (1358 cm^{-1}).^[130]

Both the 1358 cm^{-1} to 1545 cm^{-1} vibrational peaks in the Raman spectra of the F8BT and CPE materials are BT-centred vibrations and their intensity ratio, I_{1358}/I_{1545} (Fig. 5.17

(c)), has been linked to the torsion angle of the BT unit within the F8BT backbone.^[130] The results show I_{1358}/I_{1545} is largest in the F8imBT-Br sample and is decreased in order for F8imBT-BIm₄, F8amBT-Br, F8BT and F8imBT-Tf. I_{1358}/I_{1545} is therefore both increased and decreased by substituting the anion; varying the cation from Im to Am caused an increase in I_{1358}/I_{1545} . It makes sense here to also plot the intensity ratios of the 1545 cm⁻¹ and 1608 cm⁻¹ modes (I_{1545}/I_{1608}), which dominate the spectrum, as they are reported to be only weakly dependent on the exact chemical structure^[155,158] and are also reported to be associated with backbone planarity.^[130] I_{1545}/I_{1608} is lowest in F8imBT-Br and increases in order for F8amBT-Br, F8imBT-BIm₄, F8BT and F8imBT-Tf (Fig. 5.17 (d)), thereby showing a large degree of correlation with the trend observed in the I_{1358}/I_{1545} ratios of the samples.

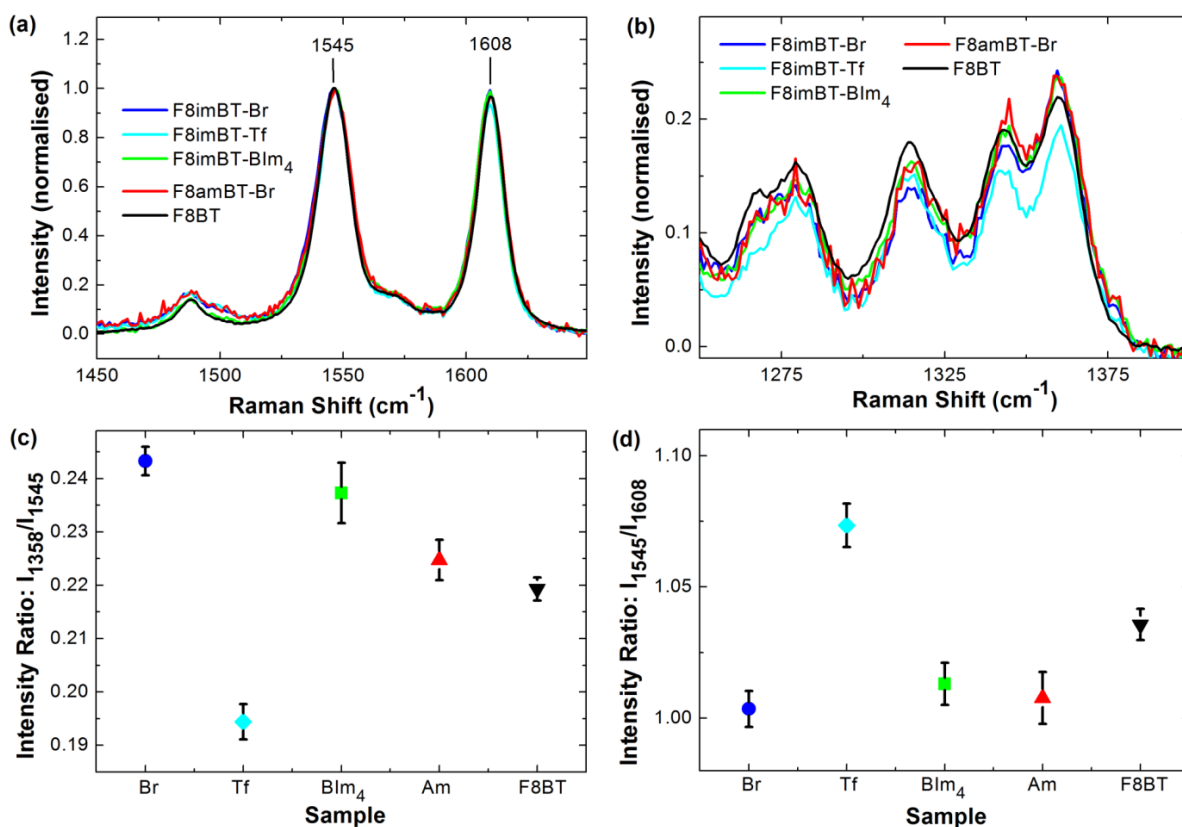


Figure 5.17: Comparison of Raman spectra for F8BT, F8imBT-Br (Br), F8imBT-Tf (Tf), F8imBT-BIm₄ (BIm₄) and F8amBT-Br (Am) thin films in the (a) 1450-1650 cm⁻¹ range, and (b) 1250-1400 cm⁻¹ range, all normalised to the 1545 cm⁻¹ peak. Comparison of (c) 1358 to 1545 cm⁻¹ intensity ratio, and (d) 1545 to 1608 cm⁻¹ intensity ratio, for the same films.

It is reported in references ^[130,157] that high values of I_{1358}/I_{1545} and low values of I_{1358}/I_{1545} relate to increased backbone planarity, but this is disputed by findings from Belton *et al.* ^[135], who state that changes in the wavefunction most likely play a major role in

determining the Raman scattering intensities of these peaks. The changes in both I_{1358}/I_{1545} and I_{1545}/I_{1608} are most pronounced in F8imBT-Tf, which also showed a weaker absorption peak at 470 nm, which has been linked to a decrease in spatial overlap of the molecular orbitals.^[131,135] In our case this may mean a LUMO that is even more localised on the BT unit in F8imBT-Tf than it is in F8BT (or a more planar backbone in F8imBT-Tf than in F8BT, if the results are interpreted as being representative of torsional angles of the BT units in the backbone). F8imBT-Br, F8imBT-BIm₄ and F8amBT-Br on the other hand may have a more delocalised LUMO/less planar structure than F8BT. These trends in the intensity ratios of F8imBT-Br, F8imBT-BIm₄ and F8imBT-Tf correlate with changes observed in the PLQY—the PLQY has been linked to changes in the interchain interactions and the size of the anions, however, we saw no correlation with anion size: it is possible that changes to the backbone wavefunction affect the PLQY. Additionally, more planar backbones of F8BT have been linked to an alternating packing structure that has reduced electron mobilities and increased PLQY,^[130] which may account for the observed trend in our dataset.

5.6.3 Characteristics of PLEDs with F8BT-based CPEs with varied Ionic Groups

The various CPEs were tested as electron injection layers (EILs) with an F8BT active layer. The current density (J) - voltage (V), luminance (L) – voltage (V), and luminance as well as power efficiency - V characteristics are shown in Fig. 5.18. (all CPE layers were spin-coated from a 3.5 mg/ml solution). The EL spectra in Fig. 5.19 do not show significant changes as the CPE layer is varied. Turn-on voltage (defined as the voltage found at the intercept of the leakage and forward bias current densities) is unchanged in the various devices observed at $1.75 \text{ V} \pm 0.2 \text{ V}$ and is the same as for the Ca/Al and Al-only device. This demonstrates that the turn-on voltage in the CPE PLEDs is governed mainly by the hole injection barrier, which also indicates that good electron injection is achieved from the CPE/Al cathodes. All CPE EIL devices display a lower current density and luminance after turn-on compared to the Ca/Al devices. Uniform emission is observed from PLEDs with F8imBT-Br and F8imBT-Tf EILs. These devices also show higher efficiencies compared to PLEDs with Ca/Al cathodes (12.7 lm W^{-1} at 2.8 V for F8imBT-Br/Al, 9.1 lm W^{-1} at 3.0 V for F8imBT-Tf/Al and 8.6 lm W^{-1} at 2.8 V for Ca/Al cathodes), while retaining high luminance values ($45,180 \text{ cd m}^{-2}$ at 7.0 V for F8imBT-Br/Al, $19,010 \text{ cd m}^{-2}$ at 7.0 V for F8imBT-Tf/Al and $51,230 \text{ cd m}^{-2}$ at 7.0 V for Ca/Al cathodes).

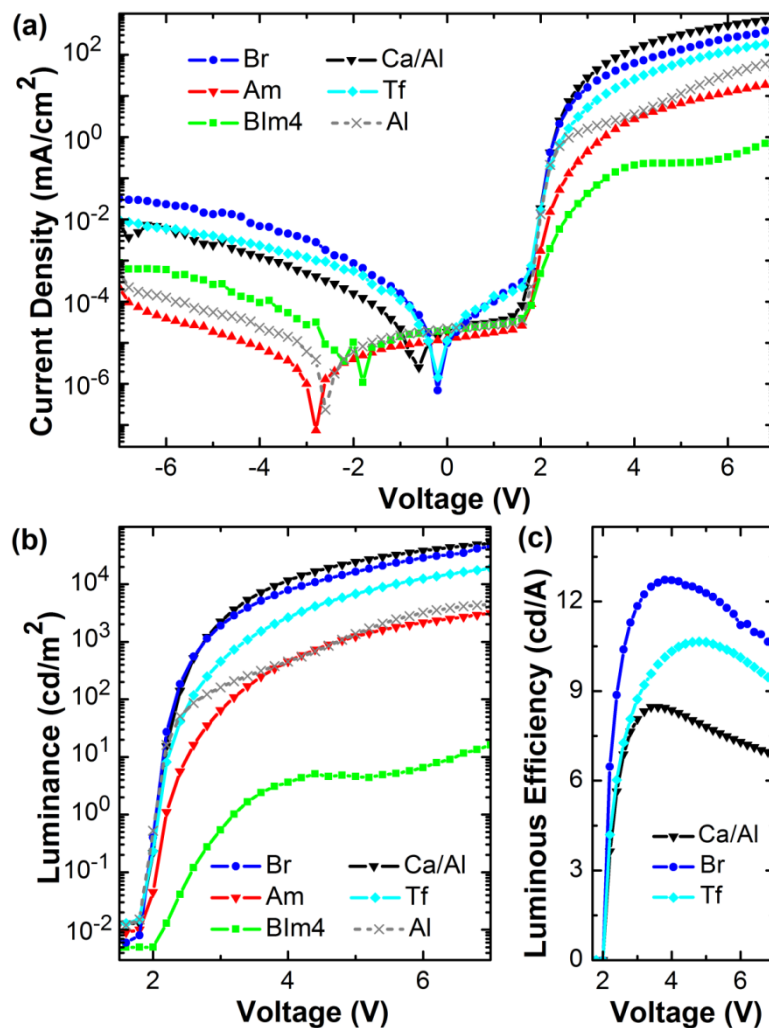


Figure 5.18: (a) J - V and L - V curves of F8BT PLEDs with F8imBT-Br (label: Br), F8imBT-Tf (label: Tf), F8imBT-BIm₄ (label: BIm₄), and F8amBT-Br (label: Am) EILs, as well as Ca/Al and Al cathode devices. (b) Efficiency in cd A^{-1} and lm W^{-1} extracted from data in (a) for the F8imBT-Br and F8imBT-Tf EIL PLEDs, and for the Ca/Al PLED.

In the PLEDs with F8amBT-Br EILs, which has an ammonium cation, we observed around an order of magnitude lower current density after turn-on than in the imidazolium cation containing F8imBT-Br EIL PLEDs. Higher reverse bias currents in the PLEDs are an indication of doping of the light emitting F8BT layer.^[138] Since the anode side is the same in all devices, any change in the reverse bias current is attributed to a difference to the cathode-side. We observe the following trend in the reverse bias currents: F8amBT-Br < Al < F8imBT-BIm₄ < Ca/Al < F8imBT-Tf < F8imBT-Br. F8imBT-BIm₄, F8amBT-Br, and Al devices do not have their lowest current density at 0.0 V, which is likely an effect of charge accumulation causing a hysteresis in the curves. Exchanging the imidazolium ionic group with the ammonium ionic group leads to significantly lower reverse bias currents as well as

lower current densities in forward bias after turn-on. In this case the ammonium group offers a higher degree of steric hindrance than the imidazolium group. The differences in the reverse bias currents of the PLEDs show a correlation with anion size and cation steric hindrance; the smaller the anion, which coincides with reduced steric hindrance, the higher the reverse bias current, which may be due to the increased ability of smaller ions to move into and dope the light emitting layer^[138] (although it should be noted that smaller ions do not always show increased doping).^[138]

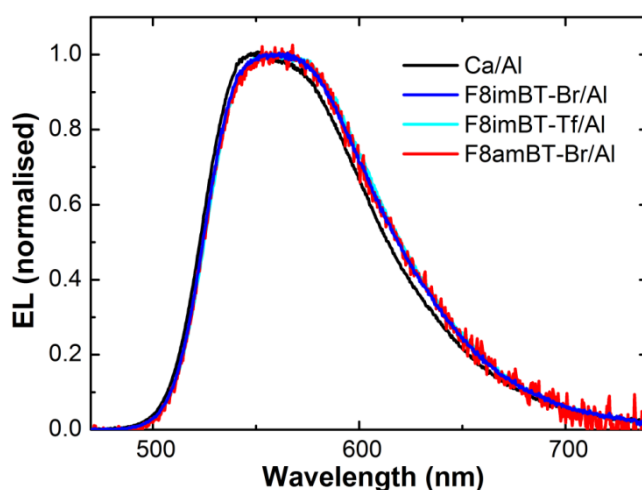


Figure 5.19: EL spectra at 5 V of F8BT PLEDs with F8imBT-Br, F8imBT-Tf, F8imBT-BIm, and F8amBT-Br EILs. EL spectra of an F8BT PLED with a Ca/Al cathode included for reference.

The luminance and current density curves in this PLED set closely match each other, which implies that the low luminances are due to insufficient electron injection at the cathode-side. The larger the anion, the lower the luminance and current density after turn-on ($F8imBT-BIm_4 < F8imBT-Tf < F8amBT-Br$). CPE anions are reported to form charge transfer states by interacting with bound interchain excitons within the CPE.^[145,154] The bulkier the anion, the more those interchain interactions decrease due to increased steric separation of the anion from the conjugated backbone.^[145,154] We point to this correlation to propose the possibility of a link between these interchain interactions and the ability of the CPEs to efficiently inject electrons into the light emitting layer, although further research is necessary to study this possibility.

The efficiencies of F8imBT-Br and F8imBT-Tf EIL PLEDs are higher than those of Ca/Al PLEDs despite having lower current densities and luminances. The efficiencies of the other three devices are not listed here, although they exceed those of the Ca/Al device, as

they did not light up uniformly and are therefore not comparable. As the increases in efficiency when using F8imBT-Br and F8imBT-Tf EIL PLEDs are not due to increases in electron injection the other possibilities are: increased charge balance in the light emitting layer, increased hole-blocking at the cathode-side or reduced luminance quenching by the electrodes. PL decay results in Section 5.4.1 indicate the CPE layers act as exciton quenchers. The increased charge balance due to increased hole-blocking and decreased electron injection over Ca/Al cathodes is a possibility since these devices were fabricated with F8BT active layers, which already have high electron mobilities, and as semi-conductors with relatively low HOMO levels (F8BT has a HOMO level of ~ 5.9 eV) the CPE layers may block holes at the cathode-side better than Ca/Al.

F8imBT-Br and F8amBT-Br have the same anion, but have a different cationic group. The reverse bias currents are far lower with a F8amBT-Br EIL than with an F8imBT-Br one. The forward bias current and luminance after device turn-on is lower in F8amBT-Br devices than in F8imBT-Br ones. The steric hindrance created by the anion is the same, however the steric hindrance of the Am group is larger than that of the Im group. A larger device set would be necessary to study whether this steric hindrance effect is really a determining factor in the device performance or not though.

5.6.4 Summary

Trends in the UV-visible absorption, PLQY and Raman spectroscopic data of films of the F8BT-based imidazolium CPEs with varied anions show correlations with one another: higher PLQY is seen for CPEs with more planar backbone configurations/decreased spatial overlap of the molecular orbitals on the backbone. F8imBT-Br and F8imBT-Tf EILs in PLEDs increase electron injection of Ca/Al cathode PLEDs; this may be due to a promoting increased charge balance in the light emitting layer. A trend was found in the properties of the PLEDs with anion size: the larger the anion, the lower the luminance and current density after turn-on. This highlights the possibility that the ability of the CPEs to efficiently inject electrons into the light emitting layer may depend on interchain interactions involving the anions and the polymer backbone.

5.7 Conclusion

We investigated the effect of varying the CPE backbone chemical structure by first studying F8imBT-Br and F8im-Br as EIL in different device structures (PLED and electron-only) and

through investigating thin films of these layers with a variety of experimental techniques. High device efficiencies of 15.0 lm W^{-1} were recorded for the F8imBT-Br/Al cathode PLEDs; similar current densities, but higher luminance values, were observed compared with Ca/Al cathode PLEDs. The results from characterisation of the CPE materials in an electron-only device structure point toward reductions in the electron injection barriers being responsible for the good electron injection. EL turn-on times of $<10 \text{ }\mu\text{s}$ are observed in F8BT PLEDs with F8imBT-Br EILs, which is comparable to Ca/Al cathode devices. Such fast turn-on times have not been reported previously in the literature for PLEDs with CPE EILs with mobile ions. This demonstrates that varying the backbone of the CPE EIL material can have a drastic effect on device performance.

Through varying the F8imBT-Br EIL layer thickness in the PLED structure and in thin films on quartz it was established that the PL quenching effect of the F8imBT-Br layer is thickness independent, while the device efficiency is highly dependent on the thickness. However, even at current densities lower than those found in the Ca/Al PLED, much higher efficiencies (11.7 lm W^{-1} at 2.6 V) are observed in the F8imBT-Br/Al PLED with the thinnest CPE EIL. This implies that the mechanism responsible for the increase in efficiencies may be a reduction in EL quenching. Since F8BT generally has a very high electron density in the bulk of the film due to having better electron than hole mobilities, it is also possible that through a reduction in electron injection the number of charges 'wastefully' reaching the anode without undergoing radiative recombination is reduced, thus increasing device efficiency.

PLEDs with SY light emitting layers showed poorer efficiencies with CPE EILs were used than when Ca/Al cathodes were used. Electron injection barriers were visible in electron-only devices and point towards the important of the CPE/light emitting layer energy level alignment in achieving sufficient electron injection and high device efficiencies.

The properties of four CPEs based on F8BT were compared (F8imBT-Br, F8imBT-Tf, F8imBT-BIm₄ and F8amBT-Br). F8imBT-Br/Al and F8imBT-Tf/Al cathode PLEDs outperformed the device efficiencies of Ca/Al cathode PLEDs while retaining high luminance values. Higher PLQY was observed for CPE films with more planar backbone configurations/decreased spatial overlap of the molecular orbitals on the backbone. The larger the anion, the lower the luminance and current density in the PLED devices after turn-on. This highlights the possibility that the ability of the CPEs to efficiently inject electrons

into the light emitting layer may depend on interchain interactions involving the anions and the polymer backbone.

The results in this chapter demonstrate the potential of CPE electron injection materials with strongly electronegative units in the backbone to enhance PLED efficiencies.

6 Role of F8BT-Based CPE Material in Fast and Efficient Electron Injection

In the previous chapter an F8BT PLED with a F8BT-based CPE material as EIL showed fast response times and high efficiencies. This chapter explores in more detail the role of the F8BT-based CPE material in providing both good electron injection properties and fast response times.

First voltage, pre-applied bias, and frequency dependent EL and current density transient measurements of PLED with F8BT- and F8-based CPE materials are studied to determine the origin of the fast turn-on characteristics in the devices with the F8BT-based CPE. Varying the frequency of voltage pulses in the transient measurements, the effects of slow orientation polarisation and ion movement are discussed. Next, by comparing the shape of the PLED transients and scanning kelvin probe (SKPM) transients, the influence of the CPE material's chemical structure on ion movement within the CPE layer is explored.

Finally, ultraviolet and x-ray photoelectron spectroscopy is used to determine the energy levels, electron injection barriers and relative atomic composition of thin films of the CPE materials. The results are compared to the PLED J-V curves obtained in the previous chapter.

This work was carried out in collaboration with Dr. Minwon Suh and Mr. Kyungmok Kim in the Department of Materials Science and Engineering, KAIST, Republic of Korea, (synthesis of CPE materials). The energy levels and chemical composition of the samples was determined at Samsung Advanced Institute of Technology (SAIT), Korea, under the supervision by Dr. Yun Dong-Jin et al.

6.2 Introduction

The slow EL rise times (on the order of a few seconds) of PLEDs with CPE EILs^[120,121,129] has been hypothesised to be due to the slow movement of ions within the CPE material,^[127,129] although the role of the ionic group and main conjugated backbone has not been clearly identified so far. Additionally, the polarisation of the polymer due to ionic movement and due to orientation polarisation may occur on similar timescales, yet little is reported on the effects of dipole orientation within the CPE materials. Within polymers the orientation of dipoles in an applied electric field is a major polarisation mechanism and is highly temperature and viscosity dependent.^[159] In crystals orientation polarisation occurs typically within $10^{-11} - 10^{-9}$ s, but in polymers this can take up to seconds (or even years, depending on the system)^[159] and is therefore a candidate for the slow rise time of the EL.

To overcome the slow rise times a zwitterionic CPE was proposed, which has no mobile counterions. The idea with such a material is either for layers of the zwitterionic CPE to possess an intrinsic surface dipole or for the orientation of the material's dipoles under an applied external electric field to occur such that the zwitterionic CPE energy levels match the workfunction of a cathode metal such as Al.^[127] A zwitterionic CPE material with fast EL turn-on times when used as an EIL in a PLED device structure is reported in reference ^[128]. However, the transient EL signal was observed to increase ~33% over a duration of 0.01 s. So while the initial response of the EL was <10 μ s, the EL rise time, t_r , of their device was ~1 ms; the EL response curves appear to rise in the same manner as in devices with conventional CPE EILs. As the zwitterionic CPE has no potentially mobile ionic species in it, it is likely this slow rise time is due to orientation of the dipoles within the material. Considering that this CPE material is likely to have broadly similar (likely within the same order of magnitude at least) viscosities and glass transition temperatures as previously reported CPE materials, it is possible that the slow rise times previously observed in PLEDs with CPE EILs may be due to (or at least in part due to) the orientation of dipoles within the material rather than due to long-range ion movement — especially considering the high energies that ionic bonds have.

In Chapter 5 we demonstrated that F8imBT-Br EILs showed rise times of <10 μ s, comparable to the rise times of Ca/Al cathode PLEDs — this was not observed in F8im-Br EIL PLEDs. To understand the role the BT unit in the backbone has in producing such favourable electron injection layer characteristics further EL and current density transients are carried out and reported in this chapter: the applied bias was varied, a pre-bias voltage

was applied to the PLEDs and the dependence of the transients on the frequency of the voltage pulse was studied. As the PLED structure is complex, transient measurements in a simpler system were also performed: SKPM transient measurements were carried out on thin film samples of PFO, F8BT, F8imBT-Br and F8im-Br on substrates with interdigitated Au/ITO electrodes (20 μm channel separation) by applying either a positive or negative voltage pulse of between 1 and 10 minutes in length. By comparing the behaviour of F8imBT-Br and F8im-Br samples it is possible to make inferences as to the origin of both the slow and the fast rise times of the PLEDs and discuss the role of ionic movement and dipole reorientation within the CPE material. The energy level alignment of the LEP/EIL/Al part of the PLED device stack was investigated *via* UPS to shed light on the differences in the device performances and efficiencies between the F8imBT-Br/Al and F8im-Br/Al PLEDs with F8BT and SY light emitting layers. To determine whether there was any change in the vertical composition of F8imBT-Br and F8im-Br films on F8BT we fabricated F8imBT-Br (10 nm)/F8BT and F8im-Br (10 nm)/F8BT samples, which were studied with XPS, using a large Ar gas cluster ion beam (Ar GCIB) to incrementally ablate the sample surface.

6.3 EL and Current Density Transients

The input voltage, the EL signal and the current density response are measured simultaneously in our EL transient set-up. The responses to rectangular voltage pulses were measured for PLEDs with F8imBT-Br/Al and F8im-Br/Al cathodes. The structure of the PLEDs in this experiment was ITO/PEDOT:PSS (35 nm)/TFB (15 nm)/F8BT (70 nm)/EIL/Al. Further details of the experimental set-up are given in Chapter 3.2.4.

6.3.1 Varying Applied Voltage

By varying the height of the voltage pulse between 4.0 and 7.0 V it can be determined whether the EL delay time, defined as the time from the on-set of the voltage pulse to onset of EL emission, is determined by the accumulation or transport of charges within the device.^[54]

In Fig. 6.1 the EL response is plotted against the logarithm of time to show the full evolution of the signal during the 0.5 s long voltage pulse. The data shows that at low voltages (4.0 and 4.5 V) the EL of F8imBT-Br/Al PLED rises quickly and then decays by $\sim 5\%$ during the 0.5 s voltage pulse. At voltages above 5.0 V the luminance remains roughly constant for the duration of the voltage pulse. The current density curves show a higher in-

rush current for higher voltages, as expected, since the inrush current is linked with capacitive charging and scales with the rate of change of the voltage. There is a drop in current density after the initial inrush current peak, followed by a secondary peak. Both the drop in current density and following peak are less prominent at higher voltages due to the nature of the double log plot.

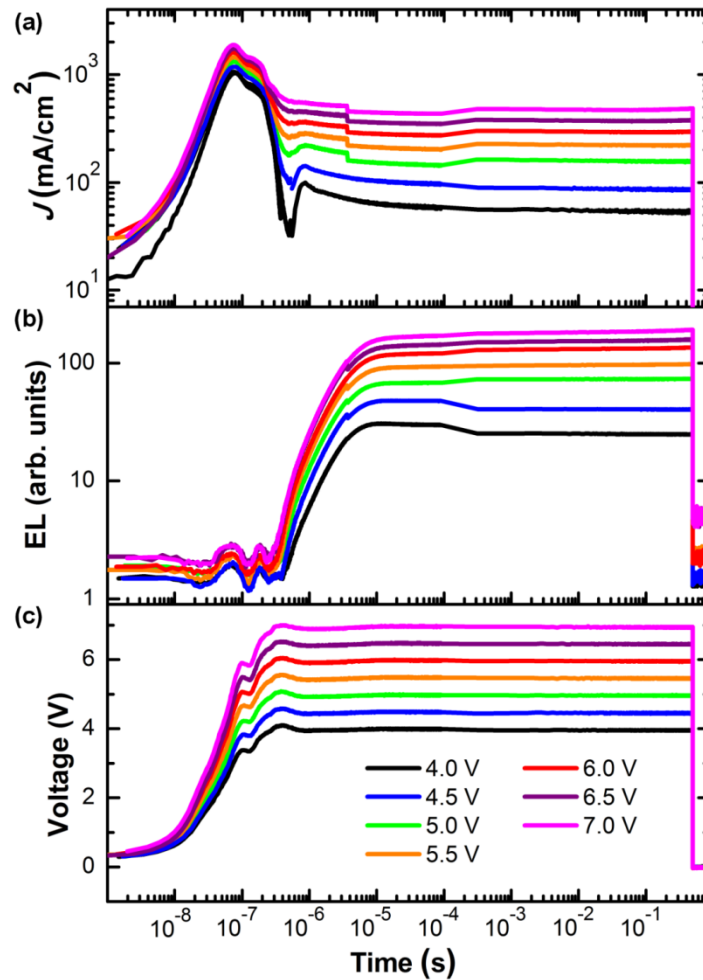


Figure 6.1. Transient response of the current density (a) and EL (b) of F8BT PLEDs with F8imBT-Br EILs. Data obtained at a frequency of 1 Hz for 4.0 – 7.0V V pulses. Applied voltage is also shown (c).

Table 6.1 lists the response and delay times that are extracted from the EL transient measurements of PLEDs with F8imBT-Br EIL with various applied voltages. The rise time, t_r , of F8imBT-Br/Al cathode PLEDs is found to vary between 4.3 μ s at 4.0 V to 5.4 μ s at 7.0 V. The delay time, t_d , between the onset of the voltage pulse and the EL signal decreases from 428 ns at 4.0 V to 325 ns at 7.0 V. This has the effect that the calculated apparent electron mobility, $\mu_{A'}^{[54]}$ (see Section 5.3 for definition) rises steadily with increased voltages, as it is inversely proportional to t_d .

Table 6.1. Parameters extracted from EL transient measurements with F8imBT-Br EIL with various voltages applied.

	t_d (ns)	t_r (μ s)	μ_A ($\text{cm}^2 \text{Vs}^{-1}$)
4.0 V	428	4.3	2.2×10^{-5}
4.5 V	393	4.4	2.6×10^{-5}
5.0 V	363	4.9	3.1×10^{-5}
5.5 V	359	4.8	3.5×10^{-5}
6.0 V	339	4.8	3.7×10^{-5}
6.5 V	333	4.6	4.1×10^{-5}
7.0 V	325	5.4	4.4×10^{-5}

In Fig. 6.2 the EL response shows that at low voltages the EL of F8im-Br/Al PLEDs rises quickly and then rapidly decays by around half before slowly rising steadily again. At higher voltages the luminance rises rapidly and then continues to increase at a much reduced rate. The current density curves show a higher inrush current for higher voltages, as expected. There is a drop in current density after the initial inrush current peak, followed by a secondary peak $\sim 1 \mu\text{s}$ after voltage turn-on. After the secondary peak in current density there is a large drop in the current density at voltages of 4.0 – 4.5 V (from a peak $\sim 1 \mu\text{s}$ after voltage turn-on with current densities in the range of hundreds of mA cm^{-2} to a low of only tens of mA cm^{-2} $\sim 60 \mu\text{s}$ after voltage turn-on). The drop in current density was less pronounced at higher voltages. After the drop the current density rises continuously for all voltages and does not saturate within the 0.5 s duration of the applied voltage pulse.

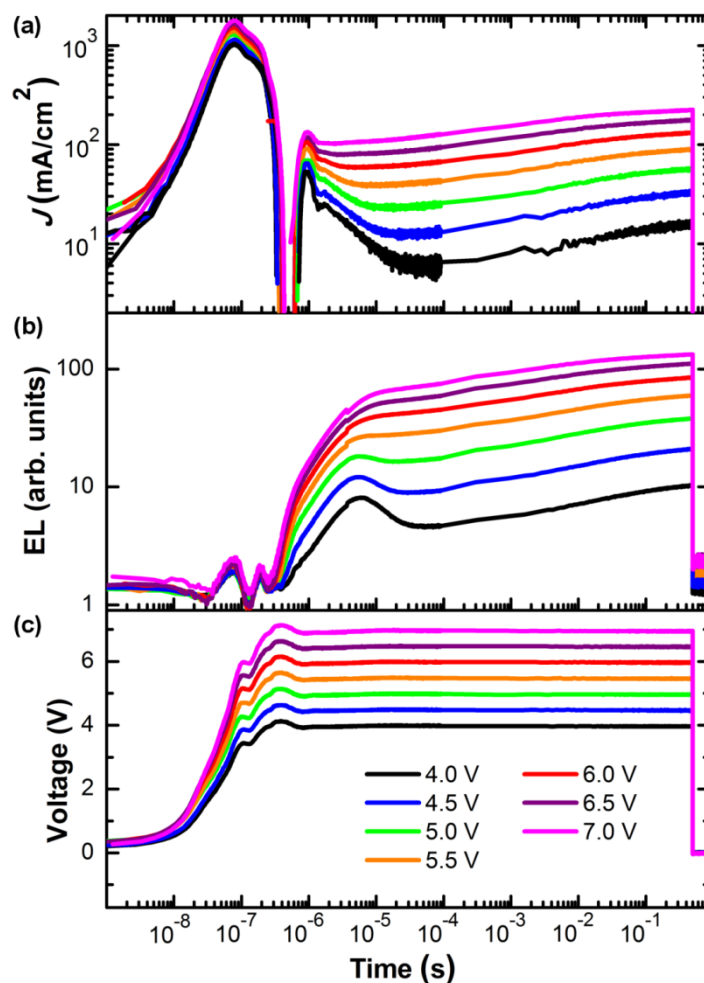


Figure 6.2. Transient response of the current density (a) and EL (b) of F8BT PLEDs with F8im-Br EILs. Data obtained at a frequency of 1 Hz for 4.0 – 7.0V V pulses. Applied voltage is also shown (c).

Table 6.2 lists delay times extracted from the EL transient measurements of PLEDs with F8im-Br EIL with various applied voltages. F8im-Br/Al cathode PLEDs show an initial EL spike at lower voltages, but that peak cannot be used to determine the rise time, since it decays again within only ~ 50 μ s. At 7.0 V the initial EL spike is no longer apparent. Additionally, the EL does not reach saturation within the 0.5 s duration of all voltage pulses. The rise time of the devices is certain >100 μ s in all cases, though. The delay time, t_d , between the onset of the voltage pulse and the EL signal decreases from 441 ns at 4.0 V to 314 ns at 7.0 V. This has the effect that μ_A rises steadily with increased voltages.

Table 6.2. Parameters extracted from *EL* transient measurements with F8im EIL with various voltages applied.

	t_d (ns)	μ_A (cm ² Vs ⁻¹)
4.0 V	441	2.1×10^{-6}
4.5 V	398	2.3×10^{-6}
5.0 V	360	2.5×10^{-6}
5.5 V	353	2.6×10^{-6}
6.0 V	334	2.7×10^{-6}
6.5 V	326	2.8×10^{-6}
7.0 V	314	2.9×10^{-6}

The electric field dependence on the apparent electron mobility indicates that t_d is due to space-charge at interfaces within the PLEDs^[54] at all voltages tested here, both for the F8imBT-Br and F8im-Br EIL PLEDs. The continual rise of the luminance of the F8im-Br/Al cathode PLED is present at all voltages, but is certainly faster at high voltages. The shape of the transient curve of the F8imBT-Br PLED seems comparatively unaffected by the increase in voltage.

6.3.2 Effect of Pre-Biasing the Devices

The EL and current density responses of PLEDs with F8imBT-Br/Al, F8im-Br/Al (Fig. 6.3 and 6.4 respectively) to rectangular voltage pulses were measured, where the voltage pulses rose to 4.0 V from either -1.50, -0.75, 0.00, 0.75 or 1.50 V. By varying the voltage pulse in this way the effect of a pre-applied positive or negative bias of PLED response curves can be observed. Positive pre-bias voltage should lead to a favourable arrangement of the Br⁻ ions toward the light emitting layer.^[127]

In Fig. 6.3 the EL response to positive pre-biasing of F8imBT-Br/Al cathode PLEDs shows that the initial spike in the EL and current density are suppressed, while negative pre-biasing enhances the initial spikes — the larger the positive or negative pre-biasing voltage is, the greater the changes observed are. Further, positive pre-biasing of the PLEDs leads to reduced apparent electron mobilities (Table 1.4), while negative pre-biasing results in increased apparent electron mobilities. Since positive voltages applied across the diode should create an electric field that moves negatively charged ions towards the anode-side,

the results are the opposite of what we might have expected. However, this effect may be due to the changes in the inrush current and might indicate that the inrush current has a significant impact on the device behaviour.

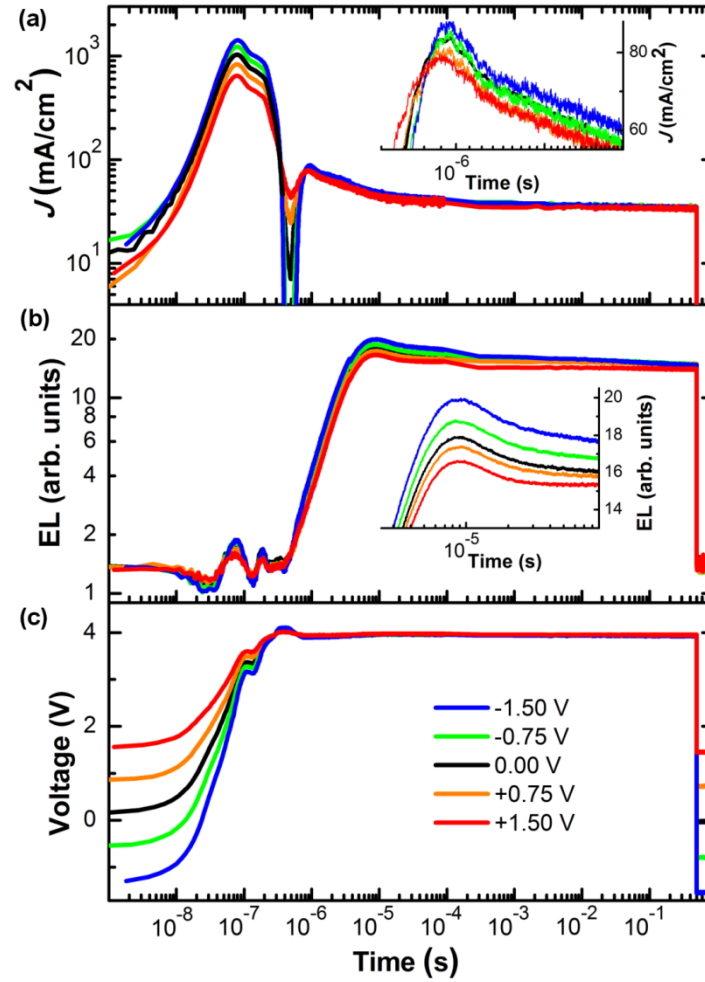


Figure 6.3. Varied pre-bias voltage transient response of current density (a) and EL (b) of F8imBT-Br/Al cathode PLEDs at 4 V, 1Hz. Insets in the top and middle panel show the EL peak and secondary current density peak in greater detail on a log-linear scale. The applied voltage is shown in (c).

Table 6.3. Parameters extracted from *EL* transient measurements with F8imBT-Br/Al cathode PLEDs with various pre-bias voltages applied.

	t_d (ns)	t_r (μ s)	μ_A ($\text{cm}^2 \text{Vs}^{-1}$)
+1.50 V	524	4.3	1.7×10^{-6}
+0.75 V	552	4.2	1.6×10^{-6}
0.00 V	476	4.2	1.9×10^{-6}
-0.75 V	461	4.3	2.0×10^{-6}
-1.50 V	447	4.2	2.0×10^{-6}

In Fig. 6.4 the EL response to positive pre-biasing of F8im-Br/Al cathode PLEDs shows that the initial spike in the current density is suppressed to an equal degree for both 1.50 and 0.75 V pre-biasing, while the EL appear unaffected. Additionally, the rise of the luminance is slightly suppressed over the entire duration of the 0.5 s voltage pulse, although no appreciable change in the corresponding current density curves is visible. Further, positive pre-biasing of the PLEDs leads to no significant changes in the apparent electron mobilities (Table 6.4). Negative pre-biasing enhances the initial current density spike, but reduces the initial EL spike — the larger the pre-biasing voltage, the greater those effects are. After the initial EL and current density spikes the PLED transients do not differ significantly from the case where no pre-biasing voltage was applied. Negative pre-biasing with -1.50 V results in an increase in the apparent mobility by around 1.5 $\times$.

The changes with pre-biasing voltages in F8im-Br/Al cathode PLEDs are small compared to the effects in F8imBT-Br/Al cathode PLEDs. This may be due to a reduced mobility of the Br⁻ counterions in F8im-Br/Al cathode PLEDs under operation, possibly due to a reduction in the local electric field strength across the CPE layer due to changes in charge injection and accumulation, or due to differences in the interaction of the ionic group and the main conjugated backbone of the CPE.

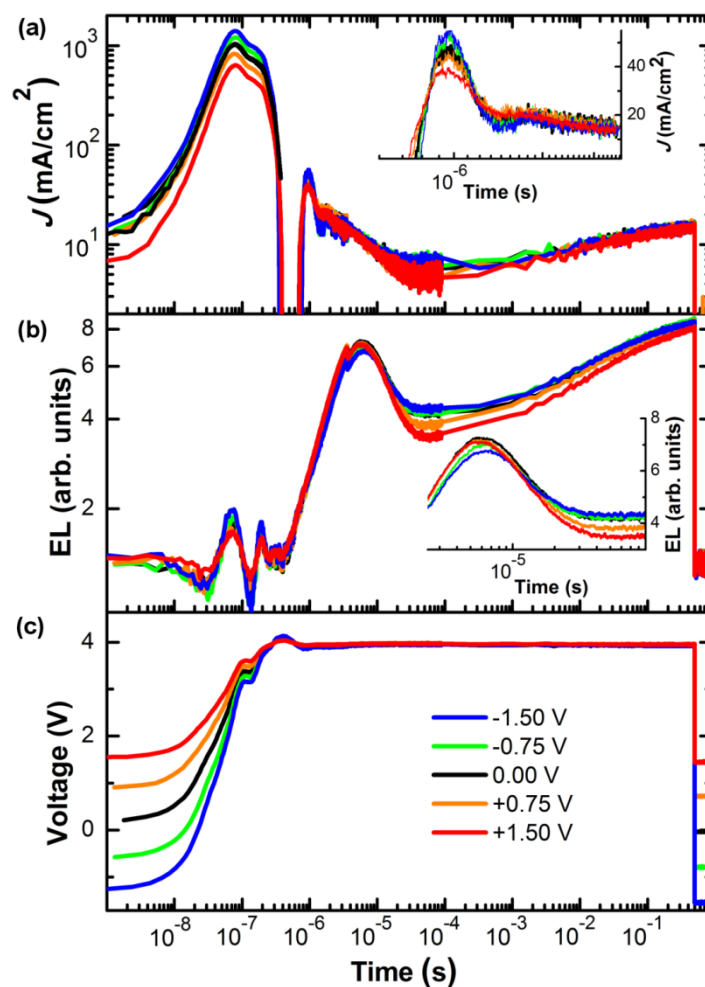


Figure 6.4. Varied pre-bias voltages transient response of the current density (a) and EL (b) of F8im-Br/Al cathode PLEDs at 4 V, 1Hz. Insets in the top and middle panel show the EL peak and secondary current density peak in greater detail on a log-linear scale. The applied voltage is shown in (c).

Table 6.4. Parameters extracted from *EL* transient measurements with F8im-Br/Al cathode PLEDs with various pre-bias voltages applied.

	t_d (ns)	μ_A (cm ² Vs ⁻¹)
+1.50 V	402	2.2×10^{-6}
+0.75 V	444	2.0×10^{-6}
0.00 V	391	2.3×10^{-6}
-0.75 V	373	2.4×10^{-6}
-1.50 V	251	3.6×10^{-6}

6.3.3 Varying Applied Frequency

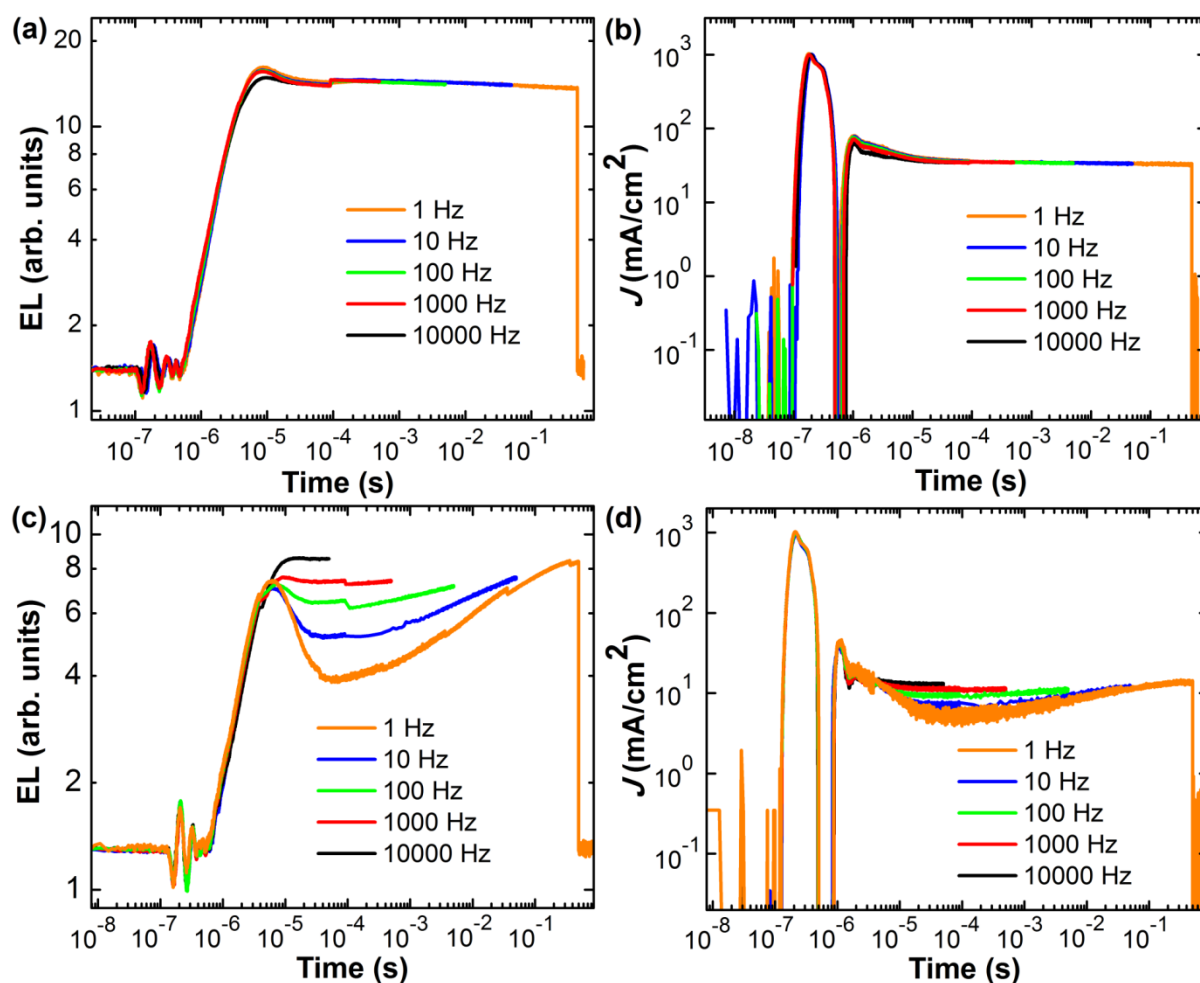


Figure 6.5. (a) EL and (b) current density, J , transient response of an F8imBT-Br/Al cathode PLED to a 4.00 V rectangular voltage pulse at frequencies between 1 and 10,000 Hz. Panels (c) and (d) show the EL and J transient responses of a F8im-Br/Al cathode PLED to a 4.00 V rectangular voltage pulse at frequencies between 1 and 10,000 Hz.

The EL and current density responses of PLEDs with F8imBT-Br/Al (Fig. 6.5 (a) and (b) respectively) and F8im-Br/Al (Figure 6.5 (c) and (d) respectively) cathodes to 4.00 V rectangular voltage pulses were measured — the frequency of the applied pulses was varied from 1 Hz to 10,000 Hz in steps of one order of magnitude. By varying the frequency of the pulse in this way the polarisation of the material due to the applied electric field can be dampened at high frequencies — when ions and molecular dipoles are not given sufficient time to move or align themselves under the influence of the applied electric field.

Increasing the frequency of the voltage pulse applied to F8imBT-Br/Al cathode PLEDs shows no significant effect in either the EL or current density transients, implying any ion

movement or dipole rearrangement either happens in under 100 μs in these PLEDs or does not occur. In contrast, the responses of the F8im-Br/Al cathode PLED to higher frequencies reveal that the drop in both the EL and current density after the initial EL peak and the secondary current density peak is suppressed. The ability of the material to relax back to its initial state is suppressed. This implies that some form of slow ion movement or dipole re-orientation takes places in the F8im-Br layer over time when an electric field is applied and that at frequencies of ~ 1000 Hz this effect does not have time to relax back during the 'off' phase of the rectangular wave. No changes in the inrush current were observed in either case, demonstrating that the capacitance of the devices remained constant, as expected.

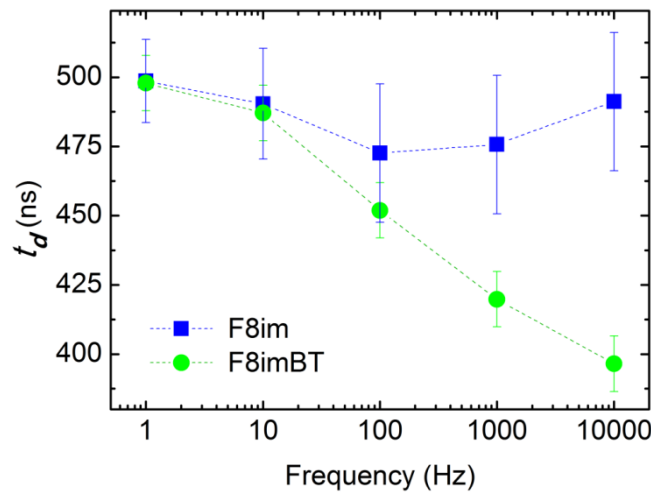


Figure 6.6. Delay time between the applied voltage pulse and the EL signal (t_d) of F8imBT-Br/Al and F8im-Br/Al cathode PLEDs at 4.00 V as a function of pulse frequency.

Fig. 6.6 shows an almost flat response of t_d in F8im-Br/Al cathode PLEDs, whereas t_d decreases in F8imBT-Br/Al cathode PLEDs (Table 6.5 and 6.6 respectively list the delay times, response times and calculated apparent electron mobilities of those devices). The response time of the F8im-Br/Al cathode PLED increases from 2.0 μs at 1 Hz to 5.3 μs at 10,000 Hz. In comparison the response time of the F8imBT-Br/Al cathode PLED varies only by around ~ 0.5 μs across the entire frequency range. We saw that at 4.00 V bias the delay time of the PLEDs is most likely due to accumulation of space charge at layer interfaces within the device, rather than due to charge carrier transit times (Section 6.3.1). Therefore the lack of change of t_d with frequency in the F8im-Br/Al cathode PLEDs reveals that the build-up of space charge at interfaces in the device is not affected by the changes in frequency. On the other hand F8imBT-Br/Al cathode PLEDs show a faster build-up of space charge at higher frequencies. The apparent electron mobility rises with increased pulse

frequency in F8imBT-Br/Al cathode PLEDs, while it remains constant in F8im-Br/Al cathode PLEDs. Further investigation is necessary to understand the implications of this observation.

Table 6.5. Parameters extracted from EL transient measurements with F8im-Br EIL with various pre-bias voltages applied.

	t_d (ns)	t_r (μ s)	μ_A ($\text{cm}^2 \text{Vs}^{-1}$)
1 Hz	499	2.0	1.8×10^{-6}
10 Hz	490	2.5	1.8×10^{-6}
100 Hz	473	2.8	1.9×10^{-6}
1000 Hz	476	4.6	1.9×10^{-6}
10000 Hz	492	5.3	1.8×10^{-6}

Table 6.6. Parameters extracted from *EL* transient measurements with F8imBT-Br EIL with various pre-bias voltages applied.

	t_d (ns)	t_r (μ s)	μ_A ($\text{cm}^2 \text{Vs}^{-1}$)
1 Hz	498	4.0	1.8×10^{-6}
10 Hz	487	4.0	1.9×10^{-6}
100 Hz	452	3.6	2.0×10^{-6}
1000 Hz	420	3.7	2.2×10^{-6}
10000 Hz	397	4.0	2.3×10^{-6}

6.3.4 Summary

The inclusion of the BT unit in the CPE backbone results in EL and current density transients of CPE EIL PLEDs which are independent of the applied frequency (up to 10 000 Hz). Any orientation of the dipoles or movement of the ions in the CPE layer occurs either on timescales faster than what can be measured in this kind of experiment or on timescales far longer than those investigated here. In contrast, the responses of the F8im-Br/Al cathode PLED to higher frequencies reveal that in the presence of an applied electric field slow ion movement or dipole re-orientation takes places in the F8im-Br layer over time.

6.4 Scanning Kelvin Probe Microscopy Transient Measurements

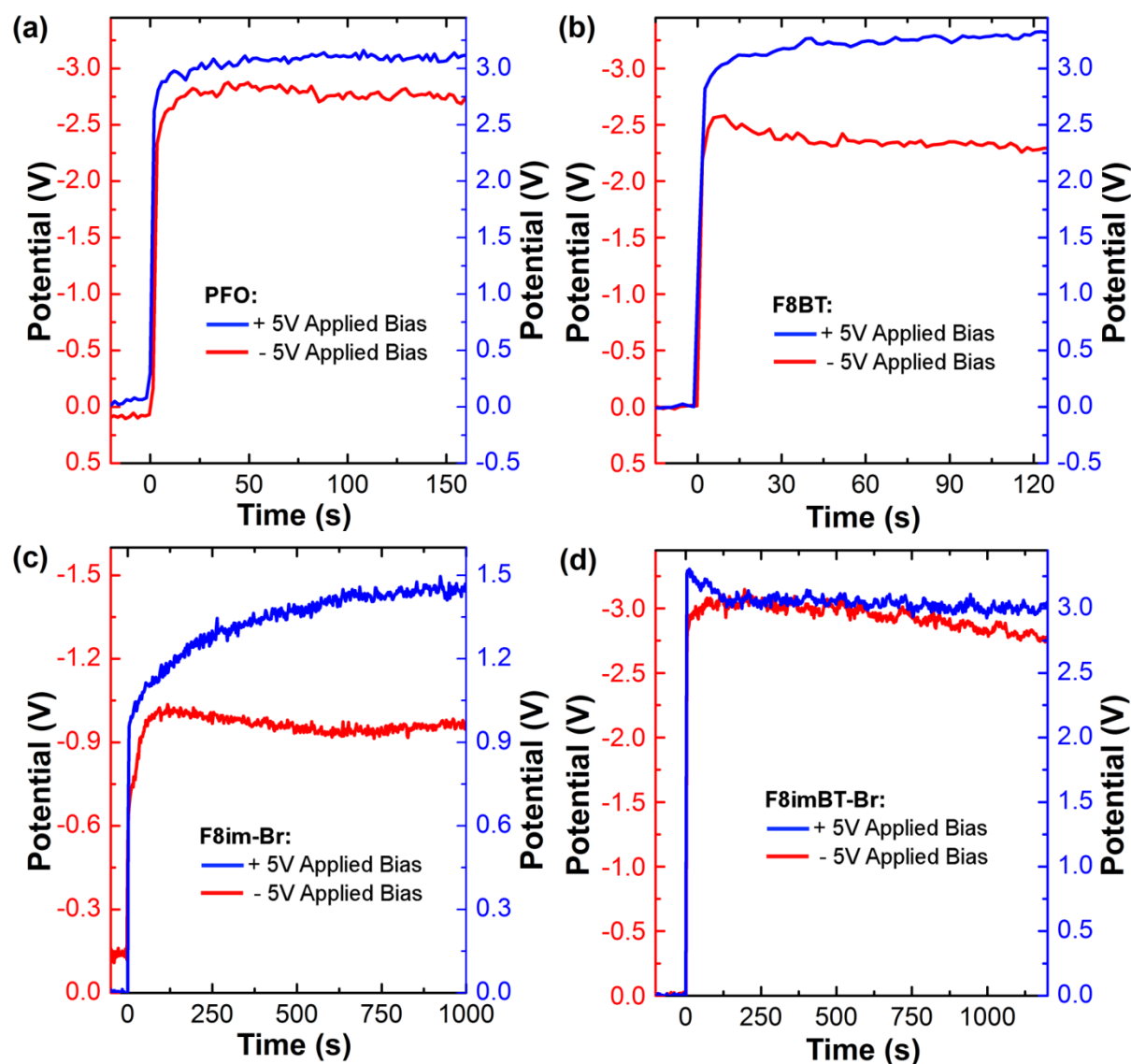


Figure 6.7: Scanning kelvin probe microscopy transient measurements of ~ 10 nm films of (a) PFO, (b) F8BT, (c) F8im-Br and (d) F8imBT-Br on a substrate with interdigitated Au/ITO electrodes ($20\ \mu\text{m}$ channel separation). Voltage pulses of $5.0\ \text{V}$ (right axes) and $-5.0\ \text{V}$ (left axes) were applied to one electrode while the other was grounded. Results shown here from the near edge of the ground electrode.

Polymer films of ~ 10 nm thickness were spincoated onto substrates with interdigitated Au/ITO electrodes that had a channel separation of $20\ \mu\text{m}$. A pluse of positive or negative voltage was applied to one electrode while the other was grounded; the response was measured near the edge of the grounded electrode for voltage pulses of $5.0\ \text{V}$ and $-5.0\ \text{V}$. The full description of the set-up is given in Chapter 3.2.5. Fig. 6.7 shows the evolution of

potential measured at the sample surface from SKPM transient measurements of ~ 10 nm films of (a) PFO, (b) F8BT, (c) F8im-Br and (d) F8imBT-Br samples. Voltage was applied at time = 0 and held constant at 5.0 V or -5.0 V. The F8BT sample quickly reaches a roughly steady potential for both negative and positively applied biases: ~ 3.0 V is reached after ~ 50 s of the positive bias being applied, while ~ -2.7 V is reached after ~ 30 s when the negative bias is applied. The PFO film has a larger difference in the response to a positive or negative bias; it reaches ~ 3.3 V after ~ 60 s when the positive bias is applied, but when the negative bias is applied the transient curve reaches a maximum of ~ -2.5 V after ~ 10 s before settling to ~ -2.3 V at ~ 40 s. In F8im-Br there is an even larger difference between applying a positive and negative bias. Additionally, the time taken to reach a roughly steady-state value in the potential is far larger — it takes ~ 800 s to reach ~ 1.4 V for a positively applied bias (note: this is less than half the potential reached in PFO). When the negative bias is applied a potential of ~ -1.0 V is reached after ~ 100 s, after which the signal shows a decline of < 0.1 V after ~ 500 s. In F8imBT-Br the potential immediately peaks at ~ 3.3 V after positive bias is applied; it then drops to ~ 3.0 V after only 120 s. For the negative bias a peak potential of ~ -3.0 V is observed at ~ 250 s, after which the signal shows a steady decline of ~ 0.2 V over ~ 500 s.

The slow rise in potential in the F8im-Br films and the immediate rise in potential followed by a drop that is observed in the F8imBT-Br films mirrors the behaviour observed in the current density transient measurements of F8BT PLEDs at 4 V (*c.f.* Chapter 5.2.4). This implies that the shape of the PLED transients is due to intrinsic characteristics of the CPE material when exposed to electric fields. The response is dependent on the polarity: the slow rise in potential in F8im-Br and the fast rise followed by a steep drop in F8imBT-Br are only observed under positive bias.

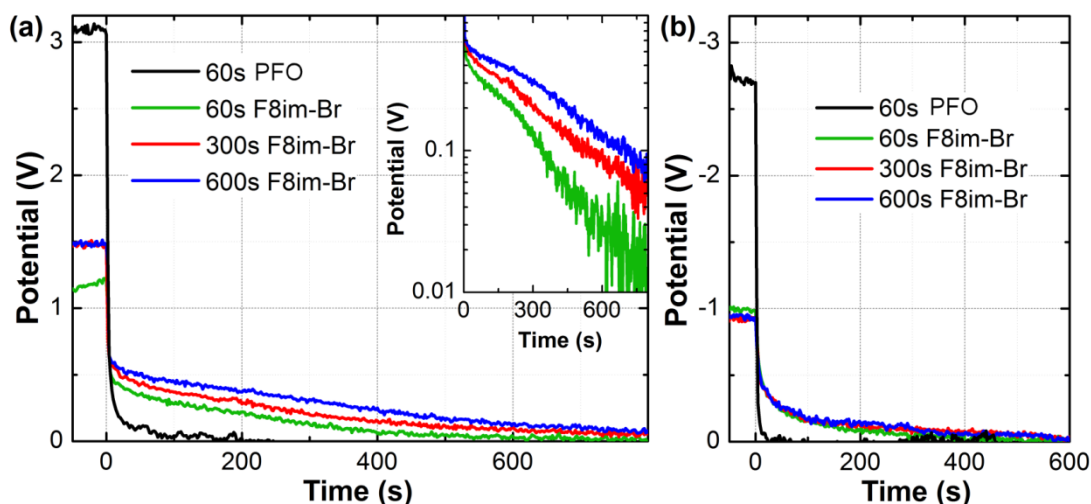


Figure 6.8: Scanning kelvin probe microscopy transient measurements of ~ 10 nm films of F8im-Br on a substrate with interdigitated Au/ITO electrodes ($20\ \mu\text{m}$ separation). Voltage pulses of (a) 5.0 V and (b) -5.0 V were applied to one electrode while the other was grounded for 60 s, 300 s and 600 s and then turned off ($V = 0$) at time = 0. Results shown here from the near edge of the ground electrode. The inset in panel (a) shows the transients of F8im-Br on a semi-log plot. The transient results from a PFO film are included in black.

Fig. 6.8 shows the transient response of ~ 10 nm films of F8im-Br after turn-off of (a) the positive and (b) the negative voltage pulse. By varying the duration of the voltage pulse the effect of ion accumulation can be observed (the length of the voltage pulse was varied: 60 s, 300 s and 600 s). For comparison the potential decay curve of a PFO sample after a 60 s voltage pulse is also shown. After a 60 s pulse of 5.0 V the potential takes longer to decay (~ 600 s) in the F8im-Br sample compared to the PFO sample (~ 180 s), although the initial potential recorded when the voltage was switched off was almost double in the PFO sample. Additionally longer voltage pulses took even longer to decay. While the potential at the end of the voltage pulse was lower after the 60 s pulse than after the longer ones, the potential at $t = 0$ after the 300 s and 600 s pulses was comparable; the decay time after the 600 s pulse was nonetheless longer.

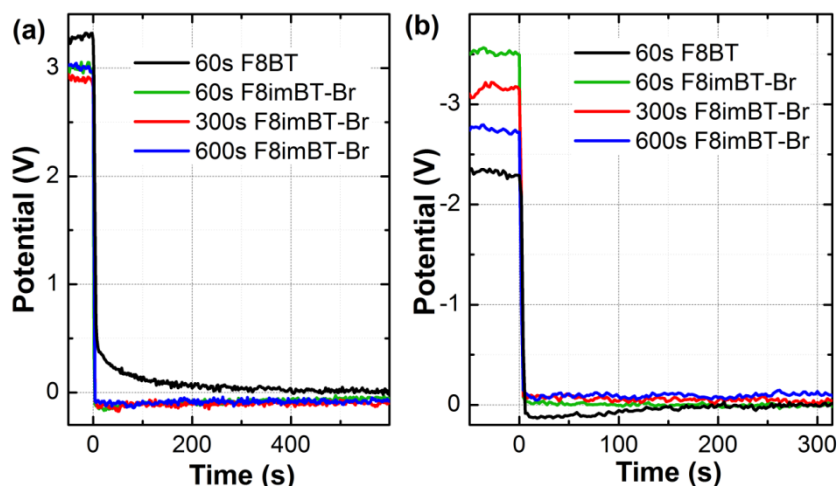


Figure 6.9: Scanning kelvin probe microscopy transient measurements of ~ 10 nm films of F8imBT-Br on a substrate with interdigitated Au/ITO electrodes ($20 \mu\text{m}$ separation). Voltage pulses of (a) 5.0 V and (b) -5.0 V were applied to one electrode while the other was grounded for 60 s, 300 s and 600 s and then turned off ($V = 0$) at time = 0. The transient results from a F8BT film are included in black.

Fig. 6.9 shows the transient response of ~ 10 nm films of F8imBT-Br after turn-off of (a) positive and (b) negative voltage pulses of 60 s, 300 s and 600 s duration. For comparison the potential decay curve of a F8BT sample after a 60 s voltage pulse is also shown. After a 60 s pulse of 5.0 V the potential takes longer to decay (~ 500 s) in the F8BT sample compared to the F8imBT-Br sample, which drops off instantaneously (note: the potential drops to ~ -0.1 V before returning to 0.0 V after ~ 400 s. 0.1 V is around the error in this measurement technique, however). When a negative bias was applied the drop in potential was instantaneous after voltage turn-off for the F8BT and F8imBT-Br samples (note: the potential in the F8BT sample drops to ~ -0.1 V before returning to 0.0 V after ~ 400 s).

The behaviour of the potential decay in the F8im-Br sample corresponds well with behaviour in the rise of the potential observed in the same sample for both the positive and negative applied bias: with negative biases the rise in the potential is faster than under positive bias; it then reaches a relatively stable level of potential that is lower than when a positive bias is applied. In the decay the duration of the voltage pulse has no significant effect on the curve, which implies the polarisation of the F8im-Br layer had already occurred on the timescales probed. With a positive bias, however, the limit of the polarisation is not reached for the probed timescales. The implication of this is that more significant polarisation of F8im-Br is possible with positive biases, but that this polarisation process is

slow to occur (>100 s). In the F8imBT-Br sample the potential decay after applied positive bias reveals no significant difference when the time duration of the voltage pulse is varied, although the pulse durations chosen here correspond to times during which the initial spike in the potential after voltage turn-on has not yet decayed. This implies that the initial spike in the potential is unlikely to be caused by a polarisation process with slow (>10 s) relaxation times. After voltage turn-off the F8imBT-Br sample is able to return to 0.0 V faster than even the F8BT sample, *i.e.* there is a fast (<1 s) polarisation response to the change in potential. This response is unlikely to be due to changes in dipole orientation, since it should be expected that the molecular dipoles of F8imBT-Br and F8im-Br would occur on similar timescales, as the materials should have similar viscosities. Therefore fast ion movement is a likely cause for the fast response of the F8imBT-Br material.

If we entertain the hypothesis that the fast current density and SKPM transient behaviour in the F8imBT-Br samples and F8imBT-Br/Al cathode PLEDs is caused by the fast movement of ions, the difference in behaviour between F8im-Br and F8imBT-Br still has to be explained. In the following we make some tentative suggestions as to the origin of the uncharacteristic behaviour of the F8imBT-Br sample. To state clearly: the results imply that the ions within the F8imBT-Br sample move faster under the influence of electrostatic forces in the CPE material with the BT-moiety. The main difference between F8im-Br and F8imBT-Br chemical structure is the inclusion of the electron-deficient BT unit in the main conjugated backbone, with the LUMO localised to the BT unit.^[46] Recent studies indicate that electron deficient π -rings are excellent candidates for the transport of anions,^[160] as favourable non-covalent interactions between anions and electron deficient aromatic rings and anions with binding energies of 20–50 kJ mol⁻¹ (comparable to hydrogen bonds) have been reported.^[160–163] DFT (Density Functional Theory) calculations for the interactions between several electron deficient aromatic rings, e.g. hexafluorobenzene, octafluoronaphthalene and pentafluoropyridine, with Br⁻ anions indicate a favourable interaction of the anion with the π -cloud of the aromatic ring.^[161] It is possible that the role of the BT unit in the backbone is to facilitate the transport the anions in F8imBT-Br through favourable interactions between the BT unit and the Br⁻ ion. Further study is required to explore this possibility.

6.5 CPE Energy Levels and Surface Stoichiometry

6.5.1 HOMO Level Position and Energy Level Alignment

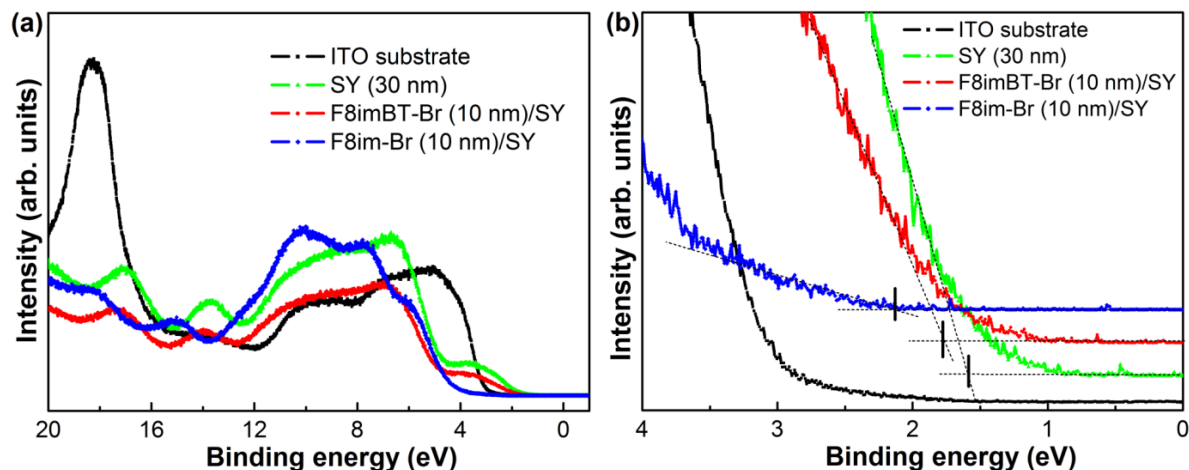


Figure 6.10: High resolution UPS (He II: 40.8 eV) measurements of a cleaned ITO substrate, a 30 nm layer of SY on ITO substrate, and F8imBT-Br and F8im-Br on top of SY on ITO substrate. Panel (a) shows the binding energy spectrum from 0 eV to 20 eV; panel (b) shows the low binding energy region (magnification 0.25 $\times$), where the intersection of the slope of the curve and the baseline give the location of the HOMO edge.

Fig. 6.10 shows high resolution UPS data from the surface of a 30 nm layer of SY as well as from ~ 10 nm layers of either F8imBT-Br or F8im-Br deposited on top of SY. The workfunction of an ITO substrate was also measured (4.6 eV). The HOMO edge is indicated by a black line in the low binding energy region shown in Fig. 6.10 (b). Both CPE materials decrease the HOMO edge from 6.17 eV for SY to 6.36 eV for F8imBT-Br/SY to 6.74 eV for F8im-Br/SY. Fig. 6.11 shows the shift in the HOMO edge when the same CPE materials are deposited on top of F8BT rather than on top of SY. The HOMO edge shifts from 6.03 eV for F8BT to 6.34 eV for F8imBT-Br/F8BT and to 6.72 eV for F8im-Br/F8BT samples. The difference between the location of the HOMO edge when depositing the CPE materials on top of different polymers therefore differs only up to 0.02 eV, which is well within error of ± 0.05 eV for the determination of the HOMO edge.

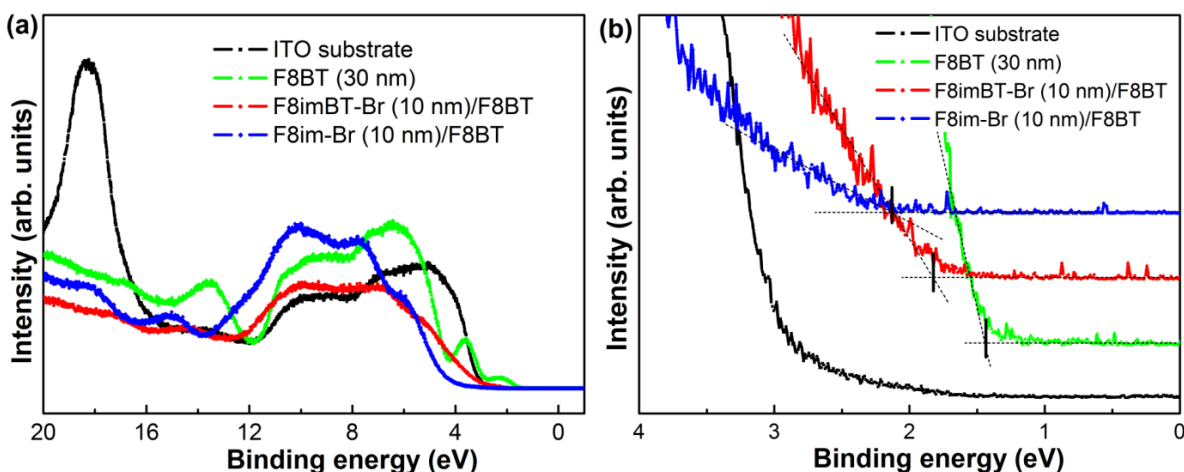


Figure 6.11: High resolution UPS (He II: 40.8 eV) measurements of a cleaned ITO substrate, a 30 nm layer of F8BT on ITO substrate, and F8imBT-Br and F8im-Br on top of F8BT on ITO substrate. Panel (a) shows the binding energy spectrum from 0 eV to 20 eV; panel (b) shows the low binding energy region (magnification 0.25 $\times$), where the intersection of the slope of the curve and the baseline give the location of the HOMO edge.

To determine the energy level alignments in the LEP/EIL/Al part of the PLED device stack we fabricated samples with ~ 10 nm layers of F8BT and SY, as well as samples with ~ 10 nm layers of F8imBT-Br and F8im-Br deposited on top of both the F8BT and SY layers. The energy levels of these samples were then determined by Dong-Jin Yun *et al.* at SAIT: the results of the energy level analysis of the CPE/LEP combinations are presented here in Fig. 6.12. There is a low electron injection barrier to Al (~ 0.14 eV) for F8imBT-Br/F8BT compared to the F8im-Br/F8BT case. The high electron injection barrier of 0.92 eV at the SY/Al interface is lowered by both CPE materials when they are deposited on top of SY. It is noteworthy that the electron injection barrier of the CPEs to Al varies depending on which light emitting layer the CPEs are deposited on.

As the shift in the HOMO edge of the material does not vary when the CPEs are deposited onto either SY or F8BT the changes in the electron injection barriers imply that the ~ 10 nm CPE layers experience changes in their surface dipoles that vary between SY and F8BT. While the differences in the electron injection barriers between the CPE/F8BT samples and Al may explain the fast turn-on times of the F8imBT-Br/Al cathode PLEDs, the electron injection barrier from Al to the F8imBT-Br/SY is similar to that of the F8im-Br/F8BT sample; initial EL and current density transient measurements of SY PLEDs with F8imBT-Br/Al cathodes indicate these too have fast response times (Appendix B.4). The low electron injection barrier to Al from F8imBT-Br/F8BT could explain the high current densities

recorded in the J - V curves of F8BT PLEDs with F8imBT-Br/Al cathodes, though (Chapter 5.2). The current densities in F8BT PLEDs with F8im-Br/Al cathodes were lower, which correlates well to the increased electron injection barrier from Al to the F8im-Br/F8BT sample. Similarly, higher current densities between 2.0 – 7.0 V are observed in SY PLEDs with F8imBT-Br EILs compared to when a F8im-Br EIL is used (Chapter 5.5). This correlates well with the lower electron injection barriers between Al and the F8imBT-Br/SY samples compared to F8im-Br/Al sample. The injection barriers between the CPE and light emitting layer materials were higher in the CPE/SY samples, which may account for the low efficiencies of the SY PLEDs with CPE/Al cathodes.

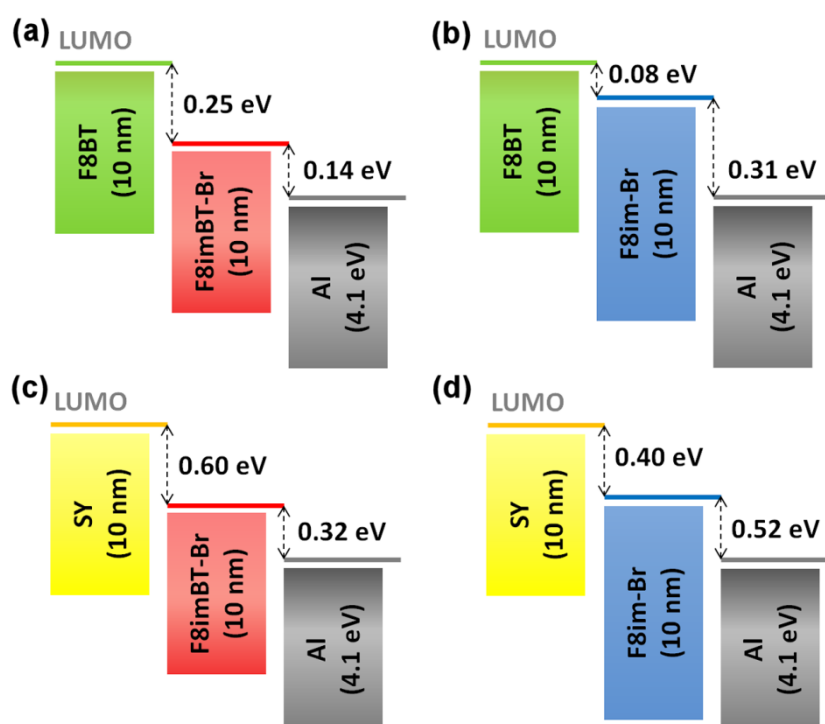


Figure 6.12: Energy level alignment to Al and F8BT (determined for a ~ 10 nm thick layer) of a ~ 10 nm layer of (a) F8imBT-Br and (b) F8im-Br deposited on top of F8BT. Energy level alignment also shown to Al and SY (determined for a ~ 10 nm thick layer) of a ~ 10 nm layer of (c) F8imBT-Br and (d) F8im-Br deposited on top of SY. Energy levels determined by Dong-Jin Yun *et al.* at SAIT through UPS measurements (HOMO level). LUMO levels determined by subtracting the energy gap of the materials.

6.5.2 Depth Profiling through X-ray Photoelectron Spectroscopy

XPS is sensitive to the chemical states at the sample surface. When combined with incremental ablation of the sample surface the vertical chemical composition of the film can be probed. The relative atomic composition of our samples was determined at SAIT by Dong-Jin Yun *et al.* using a large Ar gas cluster ion beam (Ar GCIB) to ablate the surface sample. We fabricated F8imBT-Br/F8BT and F8im-Br/F8BT samples to determine whether there was any change in the vertical composition of the two CPE materials, such as Br leaking into the emissive layer

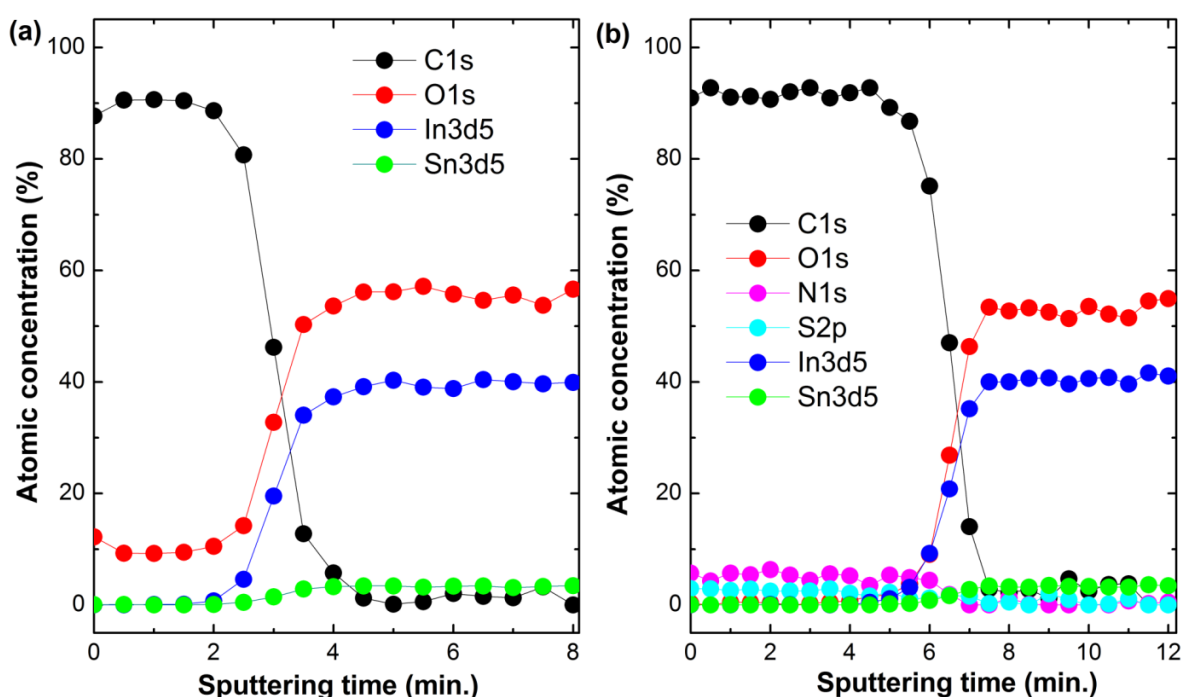


Figure 6.13: The relative atomic composition of 30 nm thick SY (a) and F8BT films (b) on ITO substrates with sputtering time (where increased sputtering time probes deeper into the sample) is shown. For the SY sample the relative atomic composition data is calculated using the C 1s, O 1s, In 3d5 and Sn 3d5 XPS peaks, while the C 1s, O 1s, S 2p, N 1s, In 3d5 and Sn 3d5 XPS peaks are used for the F8BT sample. The Ar GCIB condition used to ablate the layers was 10kV on an area of 2x2 mm².

Fig. 6.13 shows the results for the relative atomic compositions of 30 nm films of (a) SY and (b) F8BT on ITO as a function of Ar GCIB sputtering time. The top surface of SY shows a slight increase in oxygen concentration compared to the bulk. In the bulk both the SY and F8BT films show a homogeneous distribution with depth of their various atomic

components. After two minutes (6 minutes) the SY/ITO (F8BT/ITO) interface shows a slight intermixing of the polymer and metal oxide before the bulk states of ITO are probed.

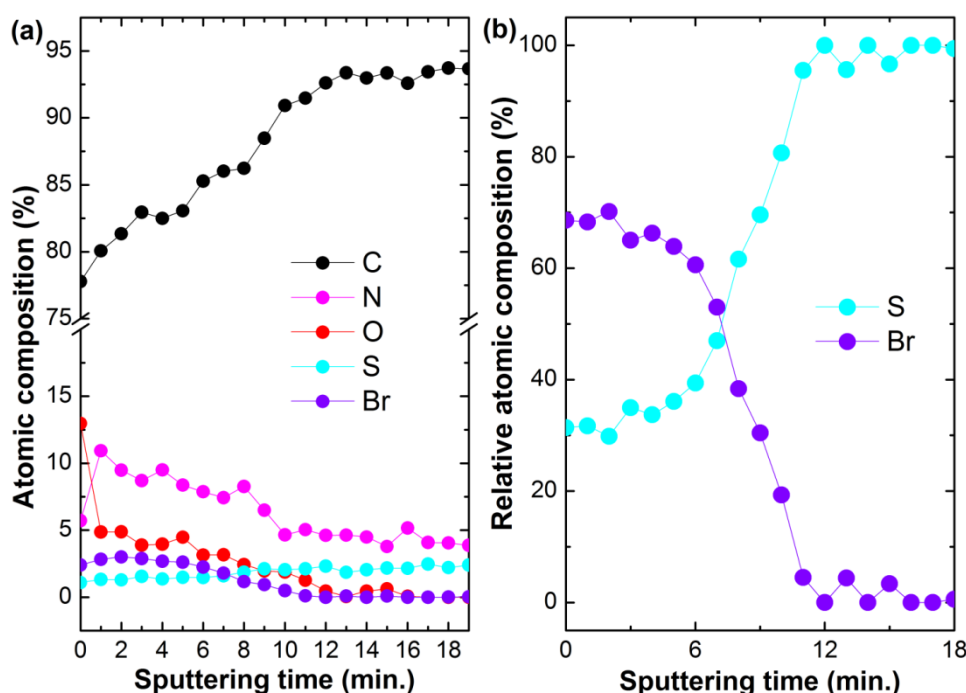


Figure 6.14: The relative atomic composition of 10 nm thick F8imBT-Br layers deposited on top of F8BT films is shown in terms of (a) C, N, O, S, and Br atoms and (b) S and Br atoms. The Ar GCIB condition used to ablate the layers was 5kV on an area of 5x5 mm² with 1 minute intervals in the sputtering.

Samples of 10 nm thick F8imBT-Br layers deposited on F8BT were similarly studied to probe the vertical composition of the F8imBT-Br layer and the F8imBT-Br/F8BT interface. Fig. 6.14 (a) shows the relative atomic composition of the sample as a function of Ar GCIB sputtering time for C, N, O, S, and Br atoms; from this data it can be determined that the F8imBT-Br layer gives way to the underlying F8BT layer at around the 12 minute mark. Before then the data shows a steady rise in the relative carbon content of the film, which is concurrent with a drop in relative oxygen, nitrogen and bromide content (note: the F8imBT-Br molecule does not contain any oxygen in its chemical structure, so this is due to surface oxidation). The F8imBT-Br film shows an inhomogeneous atomic composition with depth where the increasing relative Br and decreasing S atomic composition at the film surface in particular is noted (Fig. 6.14 (b)). In F8imBT-Br the Br signal is a distinct marker of the anion while the S signal is indicative of the conjugated backbone. The ratio of Br to S in F8imBT-Br should be 2.0. At the sample surface we observe a ratio of 2.3, which may imply

that the CPE backbones are preferentially located further away from the interface, with the ionic group closer to the sample surface.

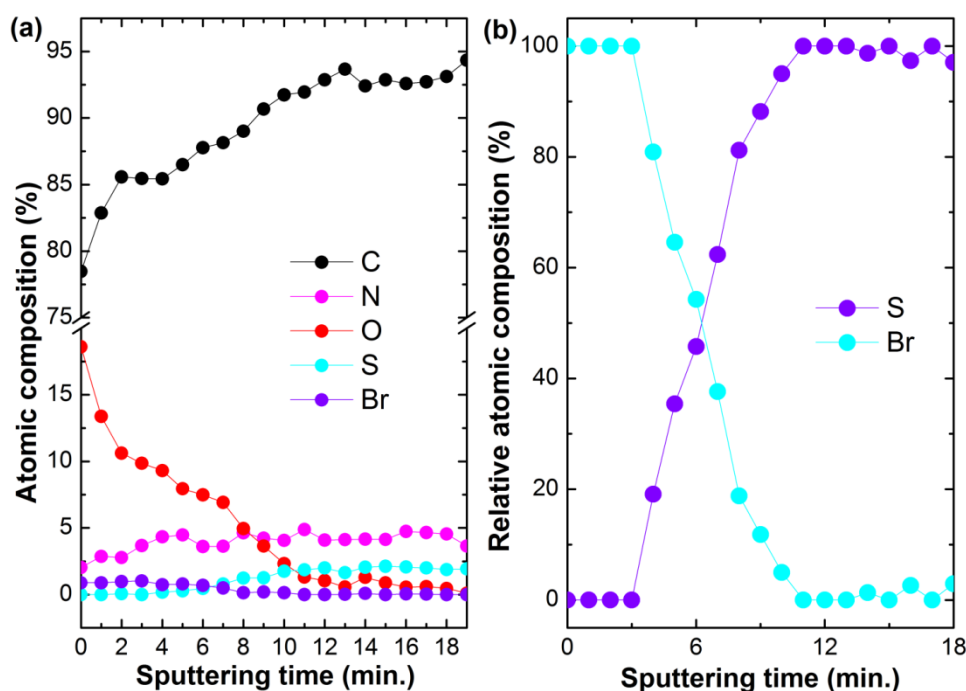


Figure 6.15: The relative atomic composition of 10 nm thick F8im-Br layers deposited on top of F8BT films is shown in terms of (a) C, N, O, S, and Br atoms and (b) S and Br atoms. The Ar GCIB condition used to ablate the layers was 5kV on an area of 5x5 mm² with 1 minute intervals in the sputtering.

The vertical composition of the F8im-Br layer and the F8im-Br/F8BT interface were studied for samples of 10 nm thick F8im-Br layers deposited on F8BT. Fig. 6.15 (a) shows the relative atomic composition of the sample for C, N, O, S, and Br atoms. The F8im-Br layer gives way to the underlying F8BT layer at around the 12 minute mark. Before then the data shows a steady rise in the relative carbon, sulphur and nitrogen content of the film, which is concurrent with a drop in relative oxygen and bromide content. In the bulk of the F8im-Br film a homogeneous atomic composition with depth of the relative Br atomic composition is observed and the Br atoms do not appear to be present in the bulk of the F8BT film (Fig. 6.14 (b)). No significant concentration of Br atoms was present in F8BT layer.

6.5.3 Summary

The electron injection barriers from Al to F8imBT-Br/F8BT, F8imBT-Br/SY, F8im-Br/F8BT and F8im-Br/SY are found to correlate with the CPE/Al cathode PLED current densities. The electron injection barriers of the CPEs to Al were found to vary depending on whether the CPE was deposited on top of SY or F8BT due to changes in the interfacial dipole. XPS depth analysis of the relative atomic composition of CPE/F8BT samples revealed that both CPE films showed a high degree of surface oxidation that was not observed in the SY or F8BT films, which is likely due to the ionic groups. The F8imBT-Br layer appeared to have a preferential alignment of the ionic group toward the sample surface.

6.6 Conclusion

The inclusion of the BT unit in the CPE backbone results in EL and current density transients of CPE EIL PLEDs which are independent of the applied frequencies up to 10 000 Hz, while the responses of the F8im-Br/Al cathode PLED were highly frequency dependent. This suggests that the slow rise times in F8im-Br PLEDs are caused by the orientation of the dipoles in CPE layer or movement of the ions on time scales of several seconds, which is in line with previous reports in the literature.^[120,121,127,129] The polarisation of the F8imBT-Br layer appears to occur on timescales < 100 μ s, though. The shape of the PLED transient curves is reproduced in SKPM transient measurements in thin CPE layers and <1 s relaxation times are recorded in the F8imBT-Br samples. This also points towards the fast movement of ions or fast orientation of molecular dipoles within the F8imBT-Br layer, despite the strong ionic bonds in the material. Since both CPEs have similar chemical structures apart from the inclusion of the BT unit in the backbone it is unlikely that the molecular dipoles in F8imBT-Br would be able to realign themselves orders of magnitudes faster than those in F8im-Br. The polarisation of the CPE materials is therefore likely due to the movement of ions within the layers — in F8imBT-Br, however, the movement is orders of magnitudes faster due to the inclusion of the electron deficient BT unit in the main conjugated backbone. This explains the < 10 μ s rise times observed in F8BT PLEDs with F8imBT-Br/Al cathodes.

The good electron injection properties of F8imBT-Br meanwhile appear to be due to a favourable alignment of the energy levels (as determined *via* UPS) that allows for a ~0.14 eV electron injection barrier from Al into F8imBT-Br. The poorer performance of the CPE layers as EILs in SY PLEDs compared to F8BT PLEDs was due to higher electron injection barriers: the energy level alignment of the CPEs was dependent on interfacial dipoles, which

varied depending on the underlying polymer layer onto which they were deposited. The interfacial dipoles acted to increase the shift in the vacuum energy levels, so the CPE LUMO levels approached the high workfunction of the Al cathode metal. XPS depth analysis of the relative atomic composition of CPE/F8BT samples revealed that the F8imBT-Br layer appeared to have a preferential alignment of the ionic group toward the sample surface; such an alignment of the chains should create a surface dipole.

7 Conclusions and Future Work

The work in this thesis describes series of experiments to probe the role of thin organic interlayers at the electrode interfaces of PLEDs. In the first part, the effect of varying the anode-side IL material, its thickness, and its p-doping level on F8BT PLED efficiencies was examined. In the second part, the role of ionic cathode-side ILs on electron injection in PLEDs was investigated. The response times of PLEDs with various different CPE EILs were measured to gain insight into movement of ions within the devices with applied electric fields.

Role of Ultra-thin Anode Polymeric Interlayers in Improving Efficiency of Polymer Light Emitting Diodes

The aim of the work in Chapter 4 was to shed light on the origin of the large increases in efficiency that are found when a TFB IL is used at the anode-side of F8BT PLEDs. We investigated a broad range of IL parameters and found that the energy gap of the IL had the most significant effect. When TFB, PFB and F8T2 IL were used large variations in the luminance were found, while current densities remained largely unaffected. The luminance changes could not be explained by electron blocking from the LUMO of the IL materials, nor by the hole-injection barriers between PEDOT:PSS and the ILs. The variations in the current densities of hole-only devices with different ILs did not correlate with the observed changes in the PLED luminance. PLEDs with ILs doped with up to 7% F₄TCNQ by weight did not display significant changes in the device characteristics. PLED efficiencies were reduced slightly for devices with thinner TFB ILs compared to those with thicker TFB ILs, pointing towards the importance of exciton quenching in determining the luminance of the devices.

The difference between the energy gap of the IL and the light emitting layer was found to have an exponential dependence on the luminance. TFB has a 0.4 eV larger energy gap than F8BT, which prevents many excitons formed in the light emitting layer from moving into the IL. The IL thereby prevents luminance quenching by the anode, raising the efficiencies of the PLEDs. Through 3D KCM simulations it was found that excitons are formed in F8BT adjacent to the interface with the IL and are thus sensitive to the energetic considerations at that interface. This explains why the insertion of the IL has such a large effect on F8BT PLED efficiencies.

This study could be expanded by testing IL materials with wider energy gaps. The IL materials studied here all had favourable HOMO levels for hole injection from PEDOT:PSS. It could therefore be interesting to test materials with HOMO levels deeper than F8BT. This would create the opportunity to study type I heterojunctions. TFB, PFB and F8T2 all formed a type II heterojunction with F8BT, which should act to promote charge separation, rather than exciton transfer. Both our experimental results and the simulation results suggest exciton transfer is the key mechanism here. As even very thin (~ 2 nm) ILs had a large impact on the efficiency, thin insulating layers might also be considered to test if the IL must have good hole-injection properties to increase PLED efficiency.

Efficient Polymer Light-Emitting Diodes using an Imidazolium-incorporated Conjugated Polyelectrolyte as Electron Injection Layer

The main aim of Chapter 5 was to investigate the role of CPEs as electron injection layers in PLEDs. By studying CPE materials containing imidazolium cationic groups based on either the PFO or F8BT conjugated backbone structure (F8im-Br and F8imBT-Br respectively) it was discovered that through including the electron deficient BT unit in the CPE backbone the electron injection properties of the CPE layer could be enhanced. PLED efficiencies of ~ 15 lm W^{-1} at 3 V and EL response times of < 10 μs were achieved with the use of F8imBT-Br electron injection layer. Through fabricating PLEDs with SY light emitting layers it was found that the precise combination of active layer and CPE EIL strongly influenced device performance. The EIL thickness was varied in PLEDs and also found to have a large impact on device efficiencies. The PLED with the thinnest (< 3 nm) F8imBT-Br EIL showed reduced current densities and brightness, but higher efficiency (11.7 lm W^{-1}) compared to a PLED with a conventional Ca/Al cathode (8.6 lm W^{-1}). This implies that the role of the CPE in increasing efficiencies is not purely due to its good electron injection properties — it may also promote charge balance in the light emitting layer or reduce exciton quenching by the metal cathode.

By using four CPEs with different cation and anion groups as EILs in PLEDs it was found that materials with smaller anions showed higher current densities than those with larger anions. This trend implies a relationship between the electron injection ability of the CPEs and anion mobility, as smaller anions should be able to move more freely through the amorphous polymer. Raman and PLQY studies of CPE thin films showed that an increased spatial overlap of the backbone's molecular orbitals (or possibly decreased backbone planarity) caused increased luminance quenching.

The results invite further study with more CPE materials to understand the electron transport properties. For example, a comparison of the electron mobility between the various materials could be undertaken with a series of electron only devices with thick (~ 70 nm) layers of CPE between a hole-blocking contact and an electron injection contact.

Role of F8BT-Based CPE Material in Fast and Efficient Electron Injection

A more in-depth view of the role of the BT unit in the CPE backbone is demonstrated in Chapter 6. Frequency dependent current density and EL transient studies showed that inclusion of the BT unit in the CPE backbone resulted in electron injection properties that remained the same from 1 Hz through to 10 000 Hz. In contrast the CPE without the BT unit showed slow EL rise times (>0.5 s) at 1 Hz and fast (<10 μ s) at 10 000 Hz. This suggests that without the BT units the ions in the film move through the ~ 10 nm film on time scales of several seconds (in line with previous reports in the literature^[120,121,127,129]) while the addition of the BT unit allows for them to move in <100 μ s. Through Scanning Kelvin Probe Microscopy (SKPM) experiments on thin CPE films the shape of the PLED transient curves could be reproduced, supporting the theory that the cause of the EL transient curve lies in the CPE material's inherent charge transport or polarisation property. The results lend further evidence to the fast movement of the ions within the F8imBT-Br material.

Through UPS analysis of thin film and bi-layer films (CPE deposited on top of light emitting polymer layer) it was demonstrated that the electron injection barrier from Al to the CPEs vary depending on the underlying light emitting layer. This is due to changes in the surface dipoles of the CPE films — it appears these are highly dependent on the thin film morphology. Electron injection from Al into the CPEs is enabled through good energy level matching, with the lowest electron injection barriers corresponding to the best performances in the corresponding PLEDs. The electron injection barrier from Al into F8imBT-Br was only around 0.14 eV. XPS depth analysis of the relative atomic composition of CPE/F8BT samples revealed that the F8imBT-Br layer showed preferential alignment of the ionic groups, which would create an interfacial dipole. This surface dipole may have raised the energy levels of F8imBT-Br so that they happened to match the workfunction of Al. The results support the theory that interfacial dipole give rise to the CPE electron injection properties,^[118] rather than the re-arrangement of ions within the layer.^[127]

The results invite further studies into the control of chain alignment in CPE films, since the surface dipole of these materials appears to be a property of the thin film morphology. For example, it could be attempted to control the CPE morphology through

zone casting^[164] to determine how the morphology can be controlled to produce favourable dipole characteristic in a reproducible manner. Additionally, theoretical simulations into the transport of anions in F8imBT-Br could shed light on the origin of F8imBT-Br's so far unique EIL properties. Various electron deficient units could be incorporated into the backbone structures in such models to estimate their interactions with the anions.

8 Bibliography

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A CPE Synthesis

A.1 Detailed synthesis procedure of the CPEs (F8imBT-Br and F8im-Br)

General details. All commercial chemical reagents were obtained from Aldrich and used as received. ^1H -NMR spectra were collected on a JEOL JNM-AL400 spectrometer at 400 MHz. Molecular weights of the polymer were determined by gel permeation chromatography (GPC) analysis on a Waters Breeze HPLC instrument, using tetrahydrofuran as an eluent and a calibration curve of polystyrene standards.

2,7-Dibromo-9,9-bis(6'-bromooctyl)fluorene (M1)

2,7-dibromofluorene (5 g, 15.4 mmol), 1,8-dibromooctane (13.82 g, 50.8 mmol), and tetrabutylammonium bromide (0.5 g, 1.54 mmol) were dissolved in THF (40 ml) at room temperature under inert atmosphere. To the mixture, KOH aqueous solution (16 ml) was added drop-wise. The reaction mixture was allowed to stir at 70 °C for 6 h and then was diluted with water. The solution was extracted with THF, and the combined organic layer was dried over MgSO_4 , filtered, and concentrated by rotary evaporator. The obtained product was purified by column chromatography (silica gel, hexane) to afford M1 (4.5 g, 41 %) as a white powder. ^1H NMR (400 MHz, CDCl_3 , TMS), $\delta(\text{ppm}) = 7.55 - 7.42$ (m, 6 H; Ar-H), 3.35 (t, $J=6.8$ Hz, 4 H; $-\text{CH}_2$), 1.95 - 1.87 (m, 4 H; $-\text{CH}_2$), 1.81 - 1.72 (m, 4 H; $-\text{CH}_2$), 1.36 - 1.24 (m, 4 H; $-\text{CH}_2$), 1.17 - 0.99 (m, 12 H; $-\text{CH}_2$), 0.63 - 0.52 (m, 4 H; $-\text{CH}_2$).

General procedure for polymerization

Polymerizations were carried out using palladium-catalysed Suzuki coupling reaction. Equivalent molar ratio of a diboronic acid ester monomer to a dibromo monomer (M1), and tetrakis(triphenylphosphine)palladium(0) ($\text{Pd}(\text{PPh}_3)_4$) (0.2-1.0 mol % with respect to the monomer) were dissolved in a mixture of toluene and aqueous 2 M K_3PO_4 . The reaction mixture was refluxed with vigorous stirring for 36 h under nitrogen atmosphere. After the solution was cooled to room temperature, it was poured into methanol. The precipitate was collected by filtration and was washed with acetone. The precipitate dissolved in dichloromethane was further washed with aqueous 2 M HCl to remove any terminal boronates on the polymer chain. Then, the organic layer was separated, dried over MgSO_4 , and concentrated under reduced pressure to yield a crude solid. The solid was redissolved in a minimal amount of chloroform and added to methanol, giving a precipitate. The resulting

precipitate was recovered by filtration and washed successively for 48 h using acetone to remove residual impurities. It was then dried overnight in vacuum at 60°C.

Poly[(9,9-bis(6'-bromooctyl)fluorene-*alt*-(benzo[2,1,3]thiadiazol-4,8-diyl)] (P1)

M1 (1.41 g, 2 mmol), 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (0.78 g, 2mmol), and Pd(PPh₃)₄ (4 mg) in a mixture of toluene (20 ml) and aqueous 2 M Na₂CO₃ (10 ml) were degassed and stirred at 80 °C for 36 h. The desired polymer was precipitated, washed, and dried in vacuum to afford P1 (1.8 g, 63 %) as an orange powder. ¹H NMR (400 MHz, CDCl₃, TMS), δ(ppm) = 8.18 - 7.45 (m, 8 H; Ar-H), 3.35 (m, 4 H; -CH₂), 2.16 (m, 4 H; -CH₂), 1.78 - 1.73 (m, 4 H; -CH₂), 1.32 (m, 4 H; -CH₂) 1.17 (m, 12 H; -CH₂), 0.97 - 0.81 ppm (m, 4 H; -CH₂). GPC: *M_n*, 4790; *M_w*, 9916; PDI, 2.01.

Poly[(9,9-bis(6'-bromooctyl)fluorene-*alt*-2,7-(9,9-dioctylfluorene)] (P2)

M1 (1.13 g, 1.6 mmol), 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di-n-octylfluorene (1.03 g, 1.6 mmol), and Pd(PPh₃)₄ (14 mg) in a mixture of toluene (16 ml) and aqueous 2 M Na₂CO₃ (8 ml) were degassed and stirred at 80 °C for 36 h. The desired polymer was precipitated, washed, and dried in vacuum to afford P2 (1.7 g, 55 %) as a yellow powder. ¹H NMR (400 MHz, CDCl₃, TMS), δ(ppm) = 7.90 - 7.46 (m, 12 H; Ar-H), 3.36 (m, 4 H; -CH₂), 2.13 (m, 4 H; -CH₂), 1.81- 1.70 (m, 4 H; -CH₂), 1.55 - 1.41 (m, 4 H; -CH₂), 1.36 - 1.03 (m, 40 H; -CH₂), 0.85 - 0.78 (m, 10 H; -CH₂CH₃). GPC: *M_n*, 7418; *M_w*, 9370; PDI, 1.26.

General procedure for imidazolium substitution reaction

The precursor polymer and 1-methylimidazole in the ratio of 1:30 by weight were dissolved in toluene at room temperature under nitrogen atmosphere. Upon complete dissolution, the reaction mixture was heated to reflux for 4 h and the precipitate was dissolved by adding methanol. Stirring was subsequently continued for 48 h. After the solution was cooled to room temperature, it was poured into acetone to precipitate the desired polymer. The resulting polymer was recovered by filtration, washed with acetone, and dried overnight in vacuum to obtain the final polymer with the imidazolium substitution. Yield: ~74 %.

Poly[(9,9-bis[6'-(3''-methyl-1''-imidazolium)octyl]fluorene-*alt*-(benzo[2,1,3]thiadiazol-4,8-diyl)] dibromide (F8imBT-Br)

The polymer was derived from P1 by the reaction procedure mentioned above. ^1H NMR (400 MHz, CD_3OD , TMS), $\delta(\text{ppm}) = 8.80$ (br, 2 H, Ar-H), 8.24 - 7.40 (br, 10 H; Ar-H), 4.12 (br, 4 H; $-\text{CH}_2$), 3.88 (br, 6 H; $-\text{CH}_3$), 2.26 - 2.16 (br, 4 H; $-\text{CH}_2$), 1.76 (br, 6 H; $-\text{CH}_2$), 1.17 (br, 12 H; $-\text{CH}_2$), 0.84 (m, 6 H; $-\text{CH}_2$).

Poly[(9,9-bis[6'-(3''-methyl-1''-imidazolium)octyl]fluorene-*alt*-2,7-(9,9-dioctylfluorene))] dibromide (F8im-Br)

The polymer was derived from P2 by the reaction procedure mentioned above. ^1H NMR (400 MHz, CD_3OD , TMS), $\delta(\text{ppm}) = 8.82$ (br, 2 H, Ar-H), 8.25 - 7.44 (br, 14 H; Ar-H), 4.11 (br, 4 H; $-\text{CH}_2$), 3.92 (br, 6 H; $-\text{CH}_3$), 2.27 - 1.99 (br, 6 H; $-\text{CH}_2$), 1.74 (br, 4 H; $-\text{CH}_2$), 1.24 - 0.97 (br, 42 H; $-\text{CH}_2$), 0.84 - 0.74 (br, 10 H; $-\text{CH}_2\text{CH}_3$).

A.2 Solubility of the CPE (F8imBT-Br) in common organic solvents

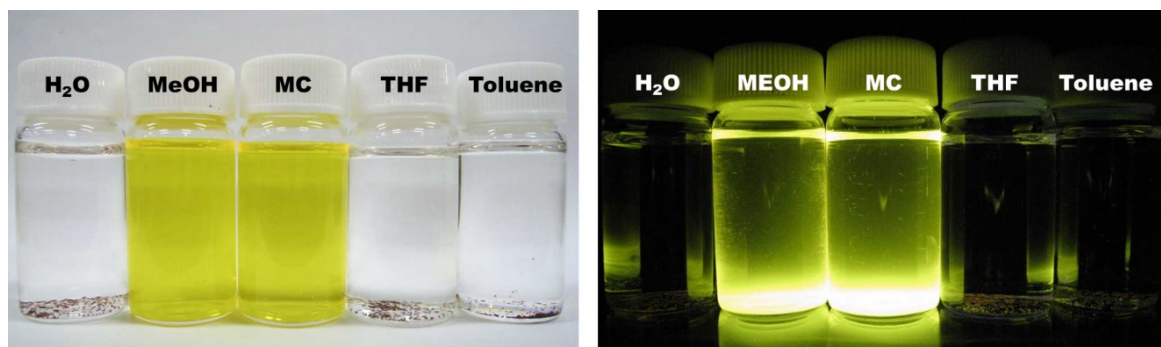


Figure A.2: Photo images of F8imBT-Br dissolved in various solvents under daylight (left), and 365 nm UV-light (right).

The solubility of F8imBT-Br in various organic solvents is summarized in Table A.2. It is found that the substitution of the imidazolium ions on the precursor polymer offers good solubility of F8imBT-Br into polar organic solvents listed above (MeOH and MC) and several others, such as dimethyl sulfoxide and ethanol. However, F8imBT-Br is not soluble in water, which enables to execute a contact angle measurement of the CPE films by water droplet.

Table A.2: Solubility of F8imBT-Br in various organic solvents.

	H_2O	MeOH	MC^a	THF	Toluene
P1 (precursor polymer)	×	×	×	✓	✓
F8imBT-Br	✓	✓	✓	×	×

^aMC = methyl cellosolve (2-methoxyethanol)

A.3 Synthesis of F8amBT-Br, F8imBT-Tf and F8imBT-BIm₄

The precursor polymer, **poly[(9,9-bis(8'-bromooctyl)-2,7-fluorene-*alt*-(benzo[2,1,3]thiadiazol-4,8-diyl)] (F8BT-Br)**, was synthesized *via* Pd-mediated cross-coupling reaction. The detailed procedure is described in Appendix A.1. All other chemical reagents here were provided by Sigma-Aldrich and used without further purification processes.

(1) General procedure for the organic-cation substitution. F8BT-Br and the desired organic substituents (1:30 w/w) were dissolved in toluene and then stirred vigorously under nitrogen. The precipitate occurred after few hours later in the reaction mixture was completely dissolved by adding methanol. It was then left for stirring another 48 hours. The solution was poured into acetone to extract the desired polymer. The resulting polymer was recovered by filtration, washed with acetone in soxhlet apparatus, and eventually dried in vacuum oven for overnight to obtain the final polymer.

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). F8BT-Br and 1-methylimidazole were used to obtain F8imBT-Br by the method (1).

Poly[(9,9-bis(8'-((N,N-dimethyl)-N-ethylammonium)octyl)-2,7-fluorene-*alt*-(benzo[2,1,3]thiadiazol-4,8-diyl)] dibromide (F8amBT-Br). F8BT-Br and N,N-dimethylethylamine were used to obtain F8amBT-Br by the method (1).

(2) General procedure for the counter-anion exchange of F8imBT-Br. A salt with desired anion (x mol) was dissolved in x ml methanol and then added to a solution of F8imBT-Br (x mol) in x ml methanol. The mixture was stirred for three days at room temperature. The resulting polymer was recovered by removing methanol under reduced pressure. It was then further washed with deionized water in soxhlet extractor to remove the residual impurities followed by drying in vacuum oven to yield the final polymer.

Poly[(9,9-bis(8'-(3''-methyl-1''-imidazolium)octyl)-2,7-fluorene-*alt*-(benzo[2,1,3]thiadiazol-4,8-diyl)] trifluoromethanesulfonate (F8imBT-Tf). F8imBT-Br and lithium trifluoromethanesulfonate were used to obtain F8imBT-Tf by the method (2).

Poly[(9,9-bis(8'-(3''-methyl-1''-imidazolium)octyl)-2,7-fluorene-*alt*-(benzo[2,1,3]thiadiazol-4,8-diyl)] tetrakis(1-imidazolyl)borate (F8imBT-BIm₄).

F8imBT-Br and sodium tetrakis(1-imidazolyl)borate were used to obtain F8imBT-BIm₄ by the method (2).

B CPE Analysis

B.1 UV-Visible Absorption

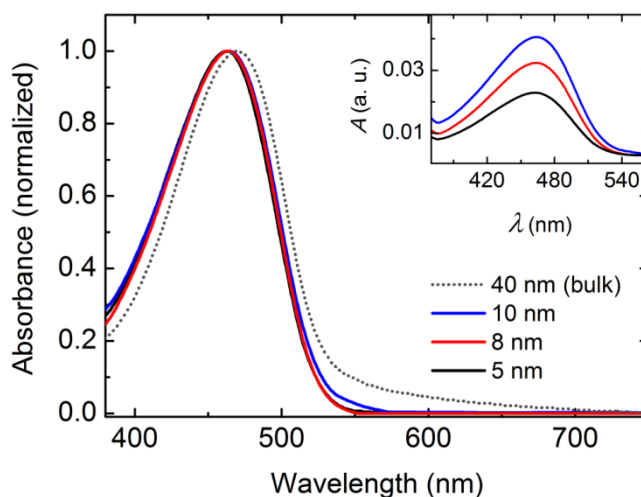


Figure B.1: UV-Vis absorbance spectra of F8imBT-Br CPE layer with different film thicknesses on quartz; F8imBT-Br (40 nm) was 40 ± 2 nm as determined by profilometry.

Ultra-thin layers of F8imBT-Br were spincoated from solutions with 1.5, 2.5, and 3.5 mg ml⁻¹ concentrations (Fig. B.1). A ~40 nm layer was also spincoated onto quartz substrate for comparison. From this absorption data the thicknesses of the CPE layers were estimated to be ~5 nm (1.5 mg/ml), ~8 nm (2.5 mg/ml) and ~10 nm (3.5 mg/ml).

B.2 EL with Varying CPE EIL Thickness

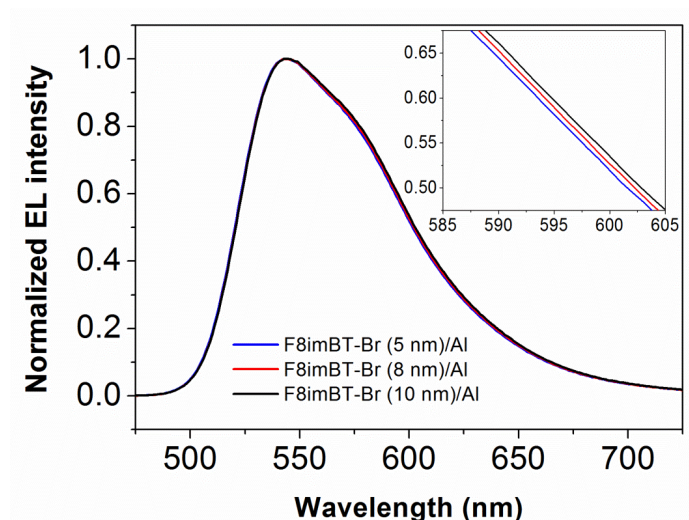


Figure B.2: EL spectra of F8BT PLEDs with different F8imBT-Br EIL thicknesses. The observed changes (inset) are minimal.

B.3 F8BT PLED Efficiencies

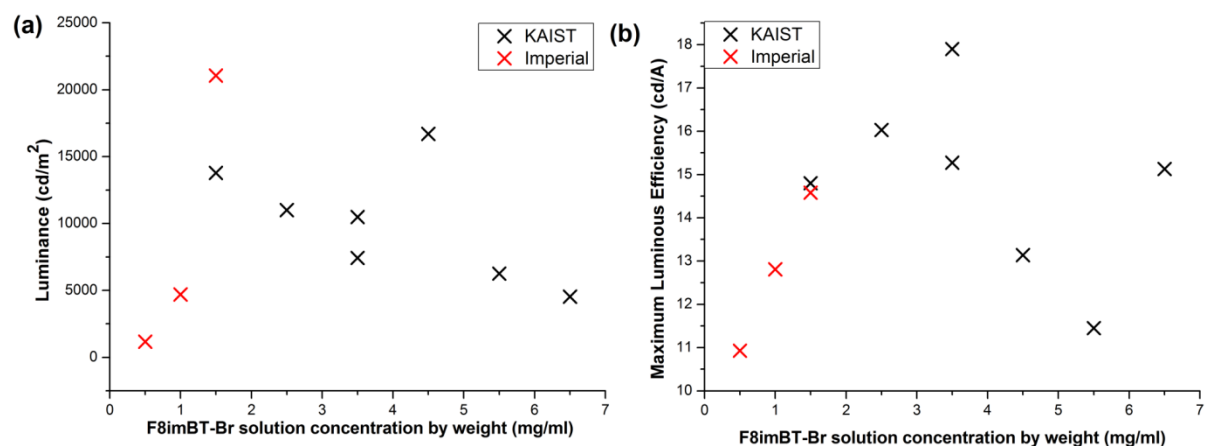


Figure B.3: (a) Luminance at 7.0 V for F8BT PLEDs with F8imBT-Br EILs spincoated from solutions with increasing concentration. (b) Corresponding maximum luminous efficiencies (cd A^{-1}) for the same devices. The PLED data at KAIST was taken in collaboration with Dr. Minwon Suh and was recorded with a spectrometer, while the data at Imperial was recorded with a luminance meter. In both cases a Keithley source meter was used to determine the current density and supply the voltage to the devices.

Fig. B.3 shows the spread of efficiency and luminance recorded with increasing F8imBT-Br thickness in F8BT PLED devices with a CPE/Al cathode. Rather than listing the thickness of the layers, the solution concentration from which they were spincoated is shown. High concentrations of the material by weight should give rise to thicker films. The luminances drop off after concentrations of 1.5 mg ml^{-1} , while the efficiencies show a maximum around 3.0 mg ml^{-1} .

B.4 EL Transients of SY PLEDs with F8imBT-Br EIL

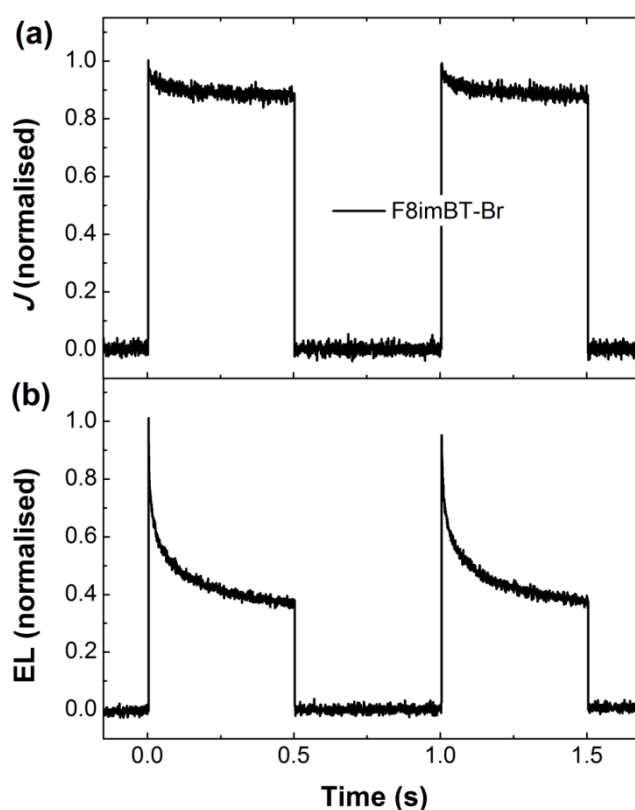


Figure B.4: Current density (a) and EL (b) transient measurements of a SY light emitting layer PLED with a F8imBT-Br/Al cathode for 7.0 V pulses at 1 Hz.

Fig. B.4 shows the EL and current density transient curves for a SY PLED with a F8imBT-Br EIL. The EL turns on fast, however the initial spike is followed by a large drop in the EL. The prominence of the EL drop is explained by the low luminance levels that F8imBT-Br PLEDs showed, even at 7.0 V.