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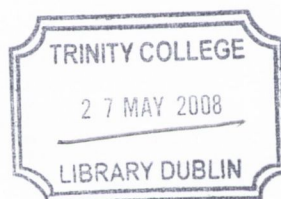
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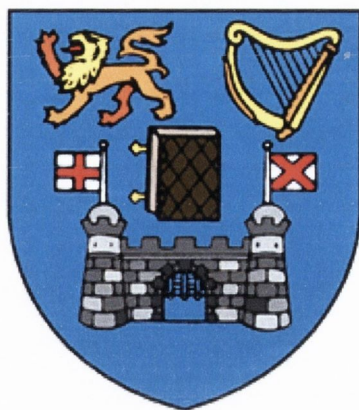
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thesis
8424



Organic Light Emitting Diodes -

New Emissive Materials and Device Architecture

By

Adam Strevens

A thesis submitted in partial fulfilment for the degree of

Doctor of Philosophy

School of Physics

Trinity College Dublin

November 2006

Declaration

I declare that the work in this dissertation has not been previously submitted as an exercise for a degree to this or any other university.

The work described herein is entirely my own, except for the assistance mentioned in the acknowledgements and collaborative work mentioned in the list of publications.

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Adam Strevens
November 2006

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“The supreme task of the physicist is to arrive at those universal laws from which the cosmos can be built up by pure deduction” - Albert Einstein.

Abstract

“Organic Light Emitting Diodes – New Emissive Materials and Device Architecture” by Adam Strevens.

Organic materials are now used for a variety of electronic devices including organic light-emitting diodes (OLEDs). However, most organic electronic display applications require more efficient red, green and blue OLEDs with improved lifetimes. Significant improvements are possible by developing better materials and device structures pertaining to charge-injection, -transport, -recombination and radiative exciton decay.

In this thesis single and multilayer LEDs were made from four poly(phenylene-vinylene) (PPV) light-emitting polymers: MEH-PPV control homopolymer (orange emitter), TPD-M3EH-MEH-PPV (red emitting copolymer), TPA-MEH-PPV (green emitting copolymer) and TPD-MEH-PPV (green emitting copolymer). The copolymers contain TPD and TPA backbone moieties intended to improve hole-transport and blue-shift emission with respect to the homopolymer. Single-pixel brightness levels of 100 – 1000 cd/m², sufficient for many electronic display applications, were achieved. New fluorene type emitters were also studied. These included a PFO-PPV copolymer and the small molecule *9,9-bis[4-(diphenylamino)-phenyl]fluorene* which resulted in green and blue electroluminescence respectively.

This thesis details the development of a new nanodot-array-anode, produced by planarisation of a nickel-filled porous alumina membrane, designed to reduce the effects of Joule heating which often cause early failure in devices and limit maximum current density and brightness. Nanodot-array OLEDs (NA-OLEDs) with the TPD-MEH-PPV copolymer as emissive layer reached current densities of 10⁵ A/m² - amongst the highest values reported for constant current driving. Nano-pixelation did not significantly alter the LED emission spectrum. The results for OLEDs using this new nanodot-array anode device architecture are encouraging from the point of view of passive matrix displays and achieving an organic laser-diode.

1	INTRODUCTION.....	18
1.1	ORGANIC ELECTRONICS	19
1.1.1	<i>Light-Emitting Organic Materials</i>	20
1.1.2	<i>Processibility of Light-Emitting Organic Materials</i>	20
1.1.3	<i>Organic Light-Emitting Diodes</i>	22
1.2	THE ELECTRONIC DISPLAY INDUSTRY	23
1.2.1	<i>Organic Light Emitting Diodes for Electronic Displays</i>	24
1.2.2	<i>The Trouble with Using Inorganic Materials for Electronic Displays.....</i>	26
1.2.3	<i>Challenges to be Met by the Organic Display Community.....</i>	28
1.3	OVERVIEW OF THESIS CHAPTERS 2 - 7	29
2	AN OVERVIEW OF BONDING, EXCITED STATES, AND ELECTRONIC TRANSITIONS IN CONJUGATED ORGANIC MOLECULES.....	32
2.1	MATERIALS CLASSIFICATION BY BAND-STRUCTURE.....	33
2.2	CARBON-CARBON BONDING.....	37
2.2.1	<i>sp₂-Hybridised Organic Molecules.....</i>	39
2.2.2	<i>The Prediction of a Zero-Bandgap for Polyacetylene</i>	42
2.2.3	<i>The Finite Bandgap in Peierls-Distorted Polyacetylene</i>	44
2.3	THE SU-SCHRIEFFER-HEEGER ELECTRONIC BANDSTRUCTURE MODEL	46
2.3.1	<i>Solitons: The Fundamental Excitations in Polyacetylene.....</i>	48
2.3.2	<i>Polarons in Conjugated Polymers</i>	49
2.3.3	<i>Creation Energies of Solitons and Polarons in Polyacetylene.....</i>	50
2.3.4	<i>The Adaptation of the SSH Model to Nondegenerate-Ground-State- Polymers</i>	52
2.4	EXPERIMENTAL EVIDENCE FOR POLARONS AND BIPOLARONS	53
2.4.1	<i>Synopsis of SSH and Other Models</i>	54
2.5	EXCITONS AND THE TRANSITIONS CONCERNING THEIR FORMATION AND SUBSEQUENT DECAY	55
2.5.1	<i>Upward Transitions in Energy: Exciton Formation by Absorption</i>	58
2.5.2	<i>Downward Transitions in Energy: Radiative Decay Routes</i>	60
2.5.3	<i>Allowed and Forbidden Electronic Transitions.....</i>	60
2.5.4	<i>The Origin of the Stokes Shift in Organic Chromophores.....</i>	64
2.5.5	<i>Quantifying Absorption and Fluorescence</i>	66
2.6	THE IMPORTANCE OF ELECTRON-ELECTRON INTERACTIONS IN MODELLING THE ELECTRONIC TRANSITIONS IN π -CONJUGATED POLYMERS.	69
2.6.1	<i>Use of the Band-Model Versus the Molecular Model for Interpreting the Nature of the Pimary Excitations in pi-Conjugated Polymers from Experimental Observations.....</i>	70
2.6.1.1	<i>Interpreting Experimental Results of conjugated polymers.....</i>	72
2.6.2	<i>Binding Energy Synopsis</i>	78
2.7	INTERMOLECULAR ENERGY TRANSFER	79
2.7.1	<i>Excimers and Exciplexes.....</i>	81
2.7.1.1	<i>Emmissive and Non-emissive Inter-chain Excitations in pi-Conjugated Polymers.....</i>	82

2.7.2	<i>Polaron Pairs, Excimers, and Aggregates in Cojugated Polymers</i>	83
2.7.2.1	Evidence for Non-Radiative Polaron Pairs	84
2.7.2.2	Consideration of Other Species Contributing to Non-radiative Decay ...	84
2.7.2.3	Excimer Emission in PPV-type Polymers.....	85
2.7.2.4	Tackling the Problem of Non-Emissive Polaron Pairs.....	87
2.7.3	<i>Synopsis of Interchain Interactions in Conjugated Polymers</i>	87
3	CHARGE TRANSPORT IN AND ELECTROLUMINESCENCE OF π-CONJUGATED THIN FILM ORGANIC LEDS.	93
3.1	ELECTRICAL TRANSPORT IN CONJUGATED POLYMERS.....	94
3.1.1	<i>The Energy Band Model</i>	94
3.1.2	<i>The Tunnelling Model</i>	94
3.1.3	<i>The Hopping Model</i>	95
3.1.4	<i>Charge-Carrier Traps</i>	97
3.2	CURRENT INJECTION FROM ELECTRICAL CONTACTS.....	98
3.2.1	<i>The Work Function of the Metal Electrodes</i>	99
3.3	TYPES OF ELECTRICAL CONTACT	100
3.3.1	<i>Neutral Contacts</i>	100
3.3.2	<i>Ohmic Contacts</i>	100
3.3.3	<i>Blocking Contacts</i>	101
3.3.4	<i>Schottky Barriers and the Schottky Effect</i>	102
3.3.5	<i>Electrical Contacts in Organic Devices</i>	102
3.4	ELECTRODE-LIMITED INJECTION CURRENT	103
3.4.1	<i>Thermionic Emission</i>	104
3.4.2	<i>Field Emission and Fowler Nordheim Barrier Tunnelling</i>	105
3.4.3	<i>Incorporating Disorder in Injection Models</i>	106
3.5	BULK LIMITED CURRENT FLOW	106
3.5.1	<i>One Carrier Space Charge Limited Currents without Traps</i>	108
3.5.1.1	The Condenser Model	108
3.5.2	<i>Current Flow in an Ideal Trap-Free Solid</i>	110
3.5.2.1	One Carrier SCLC with Traps.....	110
3.5.2.2	The Transition from Ohmic to Space-Charge-Limited Current.....	112
3.5.2.3	The Trap-Filled Limit.....	113
3.5.3	<i>Bipolar Space Charge Limited Conduction</i>	114
3.6	ELECTROLUMINESCENCE IN ORGANIC MATERIALS	117
3.6.1	<i>Choice of Electrodes for Carrier Injection</i>	117
3.6.2	<i>Balanced Charge Transport</i>	119
3.6.3	<i>Recombination and Subsequent Radiative Decay</i>	121
3.6.3.1	The Singlet-Triplet Ratio in Organic LEDs	122
3.6.4	<i>Injection- and Volume-Controlled Electroluminescence</i>	128
3.7	MATERIALS DEPOSITION TECHNIQUES	129
3.7.1	<i>Sputtering and Evaporating Techniques</i>	129
3.7.2	<i>Spincoating</i>	130
3.8	DEVICE PERFORMANCE	132
3.8.1	<i>Quantum Efficiency</i>	132
3.8.2	<i>Luminous Efficiency</i>	135
3.8.3	<i>Device Lifetime</i>	135

3.8.3.1	Environmental Factors Effecting Device Lifetime	136
3.8.3.2	Importance of Cleanliness	137
3.9	TYPES OF ORGANIC LIGHT EMITTING DIODE	138
3.9.1	SMOLED	138
3.9.2	PLED	138
3.9.3	PHOLED and DOLEDs	139
3.9.4	WOLED	140
3.9.5	TOLED and FOLEDs	140
3.9.6	Passive Matrix and Active Matrix OLED Displays	141
4	RED, GREEN AND BLUE ORGANIC LIGHT EMITTING DIODES.....	146
4.1	ORGANIC THIN FILMS	147
4.1.1	Preparation Method	147
4.1.2	Absorption Measurements	148
4.1.3	Photoluminescence Measurements	149
4.1.4	Device Fabrication	149
4.1.4.1	Single Carrier Device and LED Structures	149
4.1.4.2	Evaporation and Sputtering of Metal Electrodes	151
4.1.4.3	Current-Voltage-Luminance Measurement	152
4.2	LIGHT-EMITTING POLYMER POLY-PHENYLENE VINYLENE	153
4.3	TUNING EMISSION COLOUR IN LIGHT-EMITTING POLYMERS	155
4.3.1	Other Consequences of Chemical Structure	156
4.4	LIGHT-EMITTING POLYMER MEH-PPV	158
4.4.1	Single Layer Devices	159
4.4.2	Characterization of Single and Multi-Layer LEDs	160
4.5	LIGHT-EMITTING POLYMER TPD-4M-MEHPPV-M3EH PPV	162
4.5.1	Single Layer Devices	164
4.5.2	Characterization of Single and Multi-Layer LEDs	165
4.6	POLYMER TPA-MEH-PPV	166
4.6.1	Single Layer Devices	168
4.6.2	Characterization of Single and Multi-Layer Devices	169
4.7	POLYMER TPD-MEH-PPV	171
4.7.1	Single Layer Devices	172
4.7.2	Combined Characterization of Single and Multi-Layer Devices	173
4.7.3	Discussion of MEH-PPV Polymer Results	174
4.7.3.1	Absorption and Emission Spectra	174
4.7.3.2	Overview of Absorption and Luminescence Parameters	176
4.7.3.3	Carrier Mobilities and Trap Energies in Single Carrier Devices	177
4.7.3.4	LED Performance	179
4.8	BLUE-EMITTING LIGHT-EMITTING POLYMERS	181
4.8.1	Overview of Fluorene-Based Blue Emitters	182
4.9	A NEW POLY(PHENYLENE-VINYLENE)-POLY(FLUORENE) COPOLYMER	186
4.9.1	Chemical Structure, Absorption and Photoluminescence	187
4.10	A NEW BLUE-EMITTING 9,9-BIS[4-(DIPHENYLAMINO)- PHENYL]FLUORENE SMALL MOLECULE	192
4.10.1	Chemical Structure, Absorption and Photoluminescence	192

4.10.2	<i>I-V and EL Spectra of Single and Multi-Layer Devices</i>	194
4.10.3	<i>General Conclusions on the Red, Green and Blue Emitters Tested</i>	197
5	DEVICES WITH NOVEL NANODOT-ARRAY ANODES	203
5.1	INTRODUCTION	204
5.1.1	<i>OLED Performance Limited by Joule Heating</i>	204
5.2	OLEDs FABRICATED BY HIGH-RESOLUTION PATTERNING	207
5.2.1	<i>Top-Down Patterning</i>	207
5.2.2	<i>Porous Templates</i>	208
5.2.3	<i>The Proposed Nano-array-PLED Device Structure</i>	208
5.3	THE CHOSEN TEMPLATE: POROUS ALUMINA	209
5.3.1	<i>Using Cu-filled PAMs for the Proposed Device Structure</i>	210
5.3.2	<i>Imaging Techniques Used to Monitor PAMs</i>	210
5.3.3	<i>Formation of PAMs</i>	212
5.3.3.1	<i>Theory of Pore Formation</i>	212
5.3.3.2	<i>Cleaning of Aluminium Foils</i>	215
5.3.3.3	<i>Anodisation of Aluminium Foils</i>	216
5.4	BARRIER LAYER FORMATION AT THE FOIL:POROUS ALUMINA INTERFACE	219
5.4.1	<i>Reduction of The Barrier Layer Thickness</i>	221
5.4.2	<i>Complete Removal of The Barrier Layer</i>	221
5.4.3	<i>Electrodeposition Techniques Used to Fill Porous Alumina</i>	222
5.4.3.1	<i>DC Electrodeposition</i>	222
5.4.3.2	<i>AC Electrodeposition</i>	223
5.4.3.3	<i>Pulsed Electrodeposition</i>	224
5.5	COPPER-FILLED PAM DEVICES	225
5.5.1	<i>Production and Characterisation of Cu-filled Nanowire Arrays</i>	225
5.5.2	<i>Current Voltage Characteristics of Cu-filled PAMs Devices</i>	230
5.5.3	<i>Electroluminescence of a Cu-filled PAM Device</i>	233
5.5.4	<i>Synopsis of Devices Using Cu-filled Porous Alumina Arrays</i>	235
5.6	NICKEL-FILLED PAMS FOR OLEDs	236
5.6.1	<i>Planarisation of Ni-filled PAMs</i>	238
5.6.2	<i>Electrical Resistance of a 20 nm Thick Barrier Layer</i>	245
5.6.3	<i>Characterisation of Ni-filled Array Electrode PLEDs</i>	249
5.6.3.1	<i>Current Densities Under Forward Bias</i>	249
5.6.3.2	<i>Rectification Ratios</i>	251
5.6.3.3	<i>EL Spectra and Estimated Light Output</i>	253
5.6.4	<i>A Thermal Model for OLEDs</i>	254
5.7	CONCLUSIONS AND IDEAS FOR FUTURE RESEARCH DIRECTIONS	256
5.7.1	<i>Synopsis of Devices Incorporating Nanowire Array Electrodes</i>	256
5.7.2	<i>Inline Nanowire Device Arrays</i>	259
5.7.3	<i>Bulk Heterojunction Solar Cells</i>	261
6	CONCLUSIONS	266

List of Figures

Fig. 1 Above: Chemical structures of AlQ ₃ (left) and TPD (right) which are typical small molecules used for electroluminescence.....	23
Fig. 2 Chemical structure of the prototypical light-emitting conjugated polymer PPV	23
Fig. 3 Magnified image of RGB pixels in an electronic display.	24
Fig. 4 Graph of bandstructure for silicon showing bandgap versus wavevector k for different crystal orientations. The smallest gap between the upper conduction bands and the lower valence bands is clearly an indirect gap (minimum of green band is not in line with maximum of red band).	27
Fig. 5 Polymer solutions; conducting (black: PEDOT:PSS), semiconducting (coloured: red: TPD MEH M3EH PPV, green: TPD MEH PPV and blue: PFO). A solution of the insulator PMMA (not shown) would be transparent and would be on far right above. The bandgap of these materials increases going from left to right.	29
Fig. 6 Energy bands in insulators (a), semiconductors (b) and insulators (c) (dotted line is the Fermi energy level and the grey boxed area represents filled energy levels and the white boxed area empty energy levels.).....	36
Fig. 7 The structures of diamond (left) and graphite (right) are shown above.	38
Fig. 8 Chemical structures of C ₆₀ , SWNT & MWNT.....	39
Fig. 9 Ground state structures of benzene including (a) 2p _z orbitals of C atoms, (b) resonance forms, (c) delocalised form. In benzene the carbon bonds are sp ² hybridised. From the boundary surface plots it is immediately obvious that bonding involving 2p atomic orbitals occurs when there is overlap of a 2p orbital lobe with another 2p lobe or another atomic orbital as all the electron density is in the lobes.....	40
Fig. 10 Degenerate (energetically equivalent) ground state chemical structures for trans-polyacetylene.	42
Fig. 11 Schematic of delocalised electrons (dotted line) along the backbone of trans-polyacetylene.	43
Fig. 12 Energy bands calculated for a Hubbard chain of carbon atoms after condensed matter theory course 1024 by Dr. S. Sanvito TCD 2005. Top: band structure. Bottom: corresponding total density of states (DOS).....	44
Fig. 13 E(k) for a linear chain with equidistant spacing of atoms (left) and for a dimerised chain (right). Note the opening of a gap at $k = \pi/2a$ for the dimerised chain due to a Peierls instability.	45
Fig. 14 Band structure (left) and DOS (right) for a dimerised chain of polyacetylene using the SSH model.	47
Fig. 15 Schematic showing midgap soliton states associated with inclusion of positive charge on a polyacetylene chain.	48
Fig. 16 Polaron states and allowed optical transitions. Left: positive polaron. Right: negative polaron.	50
Fig. 17 Different possible spin combinations.....	55
Fig. 18 Top ground state benzoid structure of PPV. Bottom: quinoid exciton in PPV formed from an electron polaron (EP) and a hole polaron (HP). Note the same kind of orbital overlap seen in Fig. 9 for benzene will result in an electron cloud above and below the backbone plane of PPV and other conjugated polymers.	56
Fig. 19 Jablonski state diagram for a molecular system also showing energy levels for an oxygen molecule outside the system. Horizontal lines: energy levels of the S and T states (S on LHS and T on RHS to emphasise S and T possess different electronic spin configurations.) Note T ₁ is at a lower energy than S ₁ , reflecting the effects of spin correlation. Further horizontal lines represent higher energy vibrational levels for each state. Wavy lines within a manifold of levels indicate vibrational relaxation.....	57
Fig. 20 Franck-Condon diagram for S ₀ to S ₁ absorption transitions.....	63
Fig. 21 Illustration of what is meant by the binding energy. Note the polaron pair is not connected to the ground state. The two-photon energy transition is shown for comparison. E _r is the polaron pair binding energy, E _b and E _b ' are polaron-exciton binding energies.	71
Fig. 22 Predicted DOS for 1, 2 and 3-dimensional systems.	72
Fig. 23. General scheme for radiative and non-radiative decay of an excited species in a conjugated polymer. A* and B* represent an intrachain and an inter-chain excitation respectively. X* is the initially excited state. K denotes the first order rate constant for the transitions indicated by	

the lines between the relevant species. The arrows leaving A^* and B^* represent radiative and non-radiative routes (characterised again by the route rate constant) back to X, the ground state. k_{BA} is expected to be small compared with the decay channels of B^*	88
Fig. 24 Isoenergetic tunneling of an electron wavefunction, ψ , through a potential barrier, U_0	95
Fig. 25 Difference between shottky and P-F barriers: the Schottky effect is associated with field-enhanced thermionic emission from the metal, whereas PF emission (right) is field enhanced thermal excitation of trapped carriers.	102
Fig. 26 Generic diagram illustrating the relative positions of the relevant energy levels in a multilayer LED. For the case of a single layer LED simply ignore the ETL and HTL.....	120
Fig. 27 Photopic curve corresponding to the human eye's response to light (λ).....	133
Fig. 28 Example of a single unlevelled trace AFM image of a cut made in a polymer film of MEH-PPV which was spin-coated from a 15 g/l chlorobenzene solution at a spin speed of 1500 rpm.	148
Fig. 29 Dimension of masks for bottom (left) and top (middle) contacts for a single-carrier device, and the resultant overlap (right: shaded) defining the active area for all devices.....	150
Fig. 30 Left: Final substrate with 6 devices per/substrate showing the generic schematic (not to scale) of a triple layer OLED where the device structure from bottom to top is: Glass, etched ITO, PEDOT:PSS, LEP/small molecule, AlQ ₃ , aluminium. Middle: OLED top-view, looking down on the aluminium electrodes. Right: schematic of OLED operation, seen through the ITO-glass substrate (a black background layer is used to improve contrast, a technique commonly employed in the electronic display industry).....	152
Fig. 31 Left: Unsubstituted PPV. Right: MEH-PPV, the first fully room-temperature-soluble PPV.	154
Fig. 32 left: absorption (dashed), PL (dotted) and SL (72 nm) EL (solid) line for MEH-PPV. Right: Chemical structure of MEH-PPV (top) and M3EH-PPV (bottom).....	159
Fig. 33 Left: Current density versus electric field characteristics for single carrier devices: electron-only (squares), hole-only (circles) and single-layer LED: forward bias (triangles), modulus of reverse bias (inverted triangles). Right: Fowler-Nordheim plots for single-carrier MEH-PPV devices.	159
Fig. 34 left: Current density versus electric field for single and multilayer MEH-PPV LEDs. Right: Current versus voltage characteristics for single and multilayer MEH-PPV LEDs.....	160
Fig. 35 left: EL from single- and multi-layer MEH-PPV LEDs and an Alq ₃ LED. Right: Luminance versus current plots for single- and multi-layer MEH-PPV LEDs.	161
Fig. 36 Chemical structure of TPD-4M-MEHPPV-M3EHPPV.....	162
Fig. 37 Left: absorption (dashed) and photoluminescence (solid) of thin films of TPD-4M-MEHPPV-M3EHPPV on quartz-glass substrates. Right: FeCl ₃ doping-induced absorbance versus energy for a solution of this terpolymer.	163
Fig. 38 Left: Current density versus voltage for a single-carrier device and a single-layer TPD-4M-MEH-PPV-M3EH-PPV LED (120 nm thick). Right: Overlap of doping-induced polaron absorption (open circles) and single layer EL (solid line) spectra.	164
Fig. 39 Left: Current density versus electric field characteristics for single and multilayer TPD-4M-MEHPPV-M3EHPPV LEDs. Right: I-V characteristics for single and multilayer TPD-4M-MEHPPV-M3EHPPV LEDs.	165
Fig. 40 Left: EL spectra of single- and multi-layer TPD-4M-MEHPPV-M3EHPPV LEDs. Right: Luminance versus current plots for single- and multi-layer TPD-4M-MEHPPV-M3EHPPV LEDs. In order to display the luminance data on the same plot a semi-logarithmic plot of the data was made.	166
Fig. 41 Chemical Structure of TPA-MEH PPV.....	166
Fig. 42 Left: absorption (dashed) and PL (solid line) of TPA-MEH-PPV thin films. Right: FeCl ₃ doping-induced absorption in TPA-MEH-PPV solutions.	167
Fig. 43 left: Current density versus electric field for single-carrier devices a single layer LED (150 nm) for TPA-MEH-PPV. Examples of the linear fits to the single-carrier data from which carrier mobilities were extracted are included. Right: FeCl ₃ doping-induced absorbance and single-layer LED EL spectral overlap.	168
Fig. 44 Left: Current density versus electric field characteristics for single (150 nm) and multi-layer TPA-MEH-PPV LEDs. Right: current versus voltage characteristics for single and multi-layer TPA-MEH-PPV LEDs.....	169

Fig. 45 Electroluminescent ITO/TPA-MEH-PPV/AlQ₃/Al demonstration panel which I designed and fabricated.....	169
Fig. 46 EL spectra for single and multilayer TPA-MEH-PPV LEDs and right: luminance versus current plots for TPA-MEH-PPV LEDs.....	170
Fig. 47 Chemical Structure of TPD -MEH -PPV	171
Fig. 48 left: absorption (dashed) and photoluminescence (solid line) of thin films of TPD-MEH PPV and right: FeCl ₃ doping-induced absorption of polymer a polymer solution of TPD-MEH-PPV.	172
Fig. 49. Left: Current density versus electric field for single carrier devices (60 nm) and a single-layer TPD- MEH-PPV-LED. Right: FeCl₃ doping-induced absorption overlap with EL from a single layer TPD-MEH-PPV LED.....	172
Fig. 50 left: Current density versus electric field characteristics for single and multilayer TPD-MEH-PPV LEDs. right: Current versus voltage characteristics for TPD-MEH-PPV LEDs.....	173
Fig. 51 Left: EL from single layer and multilayer TPD-MEH-PPV LEDs and a single-layer AlQ₃ LED. Right: Luminance versus current curves for single and multilayer TPD-MEH-PPV LEDs.....	174
Fig. 52 Chemical structure of the monomer of unsubstituted polyfluorene (PF).	182
Fig. 53 Mechanism proposed for the formation of keto defects in polyfluorenes.	184
Fig. 54 Chemical structure and synthesis route for PFO-PPV.....	187
Fig. 55 Left: UV/Vis absorption spectra of PFO-PPV in dilute benzonitrile solution (2.6×10^{-4} mM) and in thin film. Right: PL of PFO-PPV in solution. The bluest PL is for the most dilute solution and the PL redshifts as concentration increases (2.1×10^{-6}, 2.6×10^{-4}, 8.7×10^{-3}, 2.6×10^{-2}, and 0.5 M).....	188
Fig. 56 Left: Quenching of photoluminescence from that observed in dilute solution (main plot,) to that observed (weak signal around 500 nm) for thin film. Right: EL spectrum of multilayer PFO-PPV (solid line) LED. The EL spectrum of a similar PFO multilayer LED is included (dashed line) for comparison.....	190
Fig. 57 Left: Current density versus voltage for single-layer PFO (open squares) and PFO-PPV (open circles) LEDs. Right: Current-voltage characteristics for PFO-PPV and PFO multilayer LEDs. The inset shows the blue electroluminescence from the PFO LED.	191
Fig. 58 Left: Chemical structure of DPA-F small molecule. Right: Geometry-optimised structure using Hyperchem TM and a Fletcher-Reeves convergence algorithm.	192
Fig. 59 Left: Absorbance thin film (purple line), Polaron absorption due to FeCl₃ doped DPA-F solution (green line), PL thin film (light blue line), EL DL DPA-F LED (dark blue line). Right: 0.25 M FeCl₃ doping-induced absorption of a 9 g/l toluene solution of DPA-F.....	193
Fig. 60 Left: Current versus voltage for DPA-F devices (80 nm) with Right : Temperature dependent I-V data for a ITO/(ozone)PEDOT/DPA-F (110)/LiF/Al device.	194
Fig. 61 Emitting lifetime at constant current for DPA-F devices. Clearly the ozone treatment of ITO improves the stability of the treated devices which exhibit a lower voltage drift for a constant current density, than the single layer device or the double layer device without any ozone treatment.....	195
Fig. 62 Left: Temperature dependent EL spectra of an ITO(ozone)PEDOT/DPA-F/LiF/Al device. Right: Close up of the same temperature dependent EL data in the the blue region of the spectrum.	195
Fig. 63 An example of black spot formation which is due to localized electrode melting and is a major cause of early device failure.	205
Fig. 64 Idealised nanowire array device schematic showing the device bias. The device structure is as follows: aluminium foil substrate (dark grey); filled and unfilled porous alumina regions (thick black and thick white. vertical lines respectively); SiO (dark grey horizontal bar); spin-coated light-emitting polymer TPD-MEH-PPV (shaded layer); evaporated aluminium top contact (uppermost light grey layer).	208
Fig. 65 Schematic of an anodized aluminium foil (a) depicting the aluminium foil (black substrate, the porous oxide layer on the surface, and a barrier oxide layer separating the two and top down view of the hexagonally ordered porous oxide surface (b). The pores are often illustrated as being hexagonally ordered cylindrical pores but they are in fact hexagonal in shape (c).....	212
Fig. 66 Vertical lines represent the different stages during anodisation. i) barrier oxides starts to grow, ii) fine featured pathways form on outer oxide surface iii) the surface features start to propagate into barrier oxide, enlarging as they do so, iv) steady state pore structure is formed.....	212

Fig. 67 Cartoon of vacancy condensation mechanism for void formation in anodic oxide films. i) vacancies condense at Al/Al ₂ O ₃ interface, ii) Decohesion of oxide from metal film, iii) void formation. Clearly the field will be stronger in regions between voids on the film surface and hence that is where pore formation by anodisation occurs.	213
Fig. 68 Typical SEM images of an untreated aluminium foil x 200 (left) and a cleaned foil x 250 (right) where the scale is 200 µm.	216
Fig. 69 Anodisation setup showing external circuit, aluminium foil (held in position using a rubber o-ring clamp fixture), glass container with water cooling, stirrer, and lead plate (holding clamp not shown). Left of the schematic is the power supply used and on the right is the temperature control unit.	216
Fig. 70 Left: SEM image showing thin oxide walls of natively oxidized aluminium foil after removal of oxide from the first anodisation (80 V). Right:, e-beam image taken with a dual beam FIB instrument, of the surface of PAM after second anodisation.	217
Fig. 71 Electron-beam images of the PAM surface (left) and of a crack in the PAM (right).....	218
Fig. 72 False colour AFM images: standard tapping mode image (left) and surface plot corresponding to the AFM image on the left for the same sample (right).	219
Fig. 73 A regularly prepatterned foil by way of a long first anodiation (left) helps to achieve well ordered straight, parallel pores (right). Note the interpore spacing is larger than the pore diameter (even allowing for asymmetrical cleaving).....	220
Fig. 74 Left: Al/barrier oxide/PA/Au Right: Al/barrier oxide/PA/SiO ₂ /Au	220
Fig. 75 images after barrier layer removal for 25 nm pores (right: x 150k, left: x 400k). As expected, the order is better at the pore bases, which are the growth front, than at the pore mouths.	222
Fig. 76 Typical pulse-times and -currents for PED.	224
Fig. 77 Above is the surface of an empty 40 V PAM (an underfilled PAM will also look the same) with the coloured line indicating the boundary of an ordered domain with pore orientation which differs from the surrounding regions. Thus, the PAMs used here are polycrystalline.	226
Fig. 78 Top left: SEM surface images showing filling of a PAM anodized at 40 V, filled with copper by AC electrodeposition., Top right: high resolution SEM of same sample. Bottom left: Non-uniform filling as only where some areas are heavily overplated. Bottom right: Extreme overplating where the whole surface is covered in copper /copper oxide.	227
Fig. 79 Digital Camera Images of AC Cu- filled PAMs, left: empty anodized PAM, middle: underfilled PAM, right: completely overplated PAM.....	227
Fig. 80 left to right: SEM of 4, 6, and 8 min AC filled Cu PAMs Each PAM is anodized under the same conditions, barrier layer is 36 ± 3 nm. Oxide is 6 – 8 micron thick for each PAM.	228
Fig. 81 Left: A cross-section SEM image of the 8 minute Cu-filled PAM. The upper inset shows a surface image of the PAM (scale bar 1 micrometer) and the lower inset shows a cross-section of an overfilled pore (scale bar 0.5 micrometer). Right: cross-section showing the 36 nm barrier layer and Cu-filling near the pore base.....	229
Fig. 82 Left: SEM of polymer on PAM at a crack in the dry polymer film. Right: actual AC plated (7 min) device.	230
Fig. 83 Current Density vs. Voltage for the unfilled PAM (open circles), four (open squares), six (open triangle), seven (inverted open triangle) and eight (open diamond) minute Cu-filled PAMs and the planar Cu-electrode device (solid circles). The inset shows the positive and negative bias characteristic for the 7 minute Cu-filled PAM device.	231
Fig. 84 PL of empty PAM with the laser harmonic of the pulsed mini-Yag laser used to excite the PA at 266 nm.	233
Fig. 85 Electroluminescence spectra for the 7 minute Cu-filled PAM (open circle and dotted line) and the Cu planar electrode device (open square and dash dot dot line). Photoluminescence spectrum for the emissive material (open triangle and solid line). The inset shows the chemical structure of the emissive polymer.	234
Fig. 86 a) Left: cross section SEM image Ni-filled PAM. Note that tilt of the sample belies actual membrane depth here. b) Right: TEM image of a bundle of Ni nanowires liberated from the filled PAM in fig xx a.....	237
Fig. 87 Unpolished (left) and polished (right) SEM surface images of empty 40 V PAMs.....	239
Fig. 88 SEM cross-section image of a polished, empty 40 V PAM.	239

Fig. 89 Top left: unpolished PAM Left: Surface SEM image (2 kV, x 25k) of a Ni-filled PAM. Right: Surface SEM image (2 kV, x 25,000) of the same sample using BS (backscattered mode). Inset: cropped section from the BS-Mode image revealing good short range hexagonal ordering of metal nanodots with a diameter of about 48 nm and interpore spacing of 73 nm.....240

Fig. 90 Left: Surface SEM image of an empty polished 40 V PAM. Right: Surface SEM image of an equivalent, polished, Ni-filled PAM. Some charging is evidenced as these samples were not gold-coated.....241

Fig. 91 Left: SEM surface image (20 kV, x 35k) of a polished Ni-filled PAM. Right: SEM surface image (5 kV, x 35k) of the same sample. In yellow is an example of six nanodots which are hexagonally distributed.242

Fig. 92 Surface SEM images (20 kV, x 150k) of 40 V PAMs. Top left: Empty unpolished PAM. Top right: Empty, polished PAM. Bottom left: Ni-filled unpolished PAM with some overplating. Bottom right: Filled polished Ni-filled PAM243

Fig. 93 Left: AFM section of empty unpolished PAM. Right: AFM section on empty polished PAM.244

Fig. 94 A polished Ni-filled PAM reflecting the light from a micropipette which was dipped in light-emitting polymer solution.....244

Fig. 95 EDX of a polished Ni foil. Al, O and S are the other main peaks.....245

Fig. 96 Left: SEM cross section image of a polished Ni-filled PAM which is about 2 micron thick. Right: High resolution 5kv cross section image of the same sample clearing showing branching of the pores at the barrier layer and a barrier layer thickness of approx. 20 nm after a voltage reduction was performed.....245

Fig. 97 I-V of an over plated 40 V Ni PED filled PAM. Top left: Using Ag to contact area = 6 mm². (right: low voltage region). Bottom : left: Using point probe to contact surface.(Right: low voltage region)..... 246

Fig. 98 The structure of all the above devices is X/poly/Al where X is the anode – the structures are listed in the plot legend.249

Fig. 99 log log plot of I-V for planar and nanowire array devices.....249

Fig. 100 Fowler-Nordheim plots for all the devices.250

Fig. 101 Temperature dependence of FN tunneling for a 40 nm barrier Ni nanodot array device.251

Fig. 102 Negative and positive bias I-V data for Ni-Ni sheet electrodes (left) and Ni nanowire array electrode (right) showing rectification.....251

Fig. 103 Semilog plot showing rectification in thick barrier layer, unpolished devices, thin barrier layer, polished devices and planar devices.252

Fig. 104 EL spectra of nanowire-array and sheet-electrode devices.253

Fig. 105 Generic model for a thermal equivalence circuit describing heat flow in a Polymer LED.254

Fig. 106 Left: proposed structure for an in-line nanowire array device where the green represents the emissive organic material. Right: variations of the inline structures possible (blue: emissive material, grey: electrodeposited metal, white: transparent conducting oxide.260

Fig. 107 In the ideal solar heterojunction device the CDS would need to be shallow enough to use Ni nanowire/cds or composite wires.....261

List of Acronyms

OLED	Organic Light-Emitting Diode	LUMO	Lowest Unoccupied Molecular Orbital
TOLED	Transparent OLED	HMO	Huckel Molecular Orbital
NA-OLED	Nanodot-Array OLED	DOS	Density of States
LEP	Light-Emitting Polymer	FS	Fermi Surface
PED	Pulsed Electrodeposition	CDW	Charge Density Wave
AC	Alternating Current	SSH	Su-Schrieffer-Heeger
SEM	Scanning Electron Microscope	2-D	2-dimensional
DIT	Dublin Institute of Technology	tPA	Trans-polyacetylene
CMA	Centre for Microscopy and Analysis	IRAV	Infrared-active Vibrations
	Programme for Research in Third Level		
PRTL	Institutions	PA	Photo-induced Absorption
HEA	Higher Education Authority	DGS	Degenerate Ground State
FIB	Focused Ion Beam	NDGS	Non-Degenerate Ground State
MI	Materials Ireland	RT	Room Temperature
PPV	Poly(phenylenevinylene)	S-T	Singlet-triplet
MEH	Methoxy-ethylhexyloxy	1-D	1-dimensional
PFO	Polyfluorene	NMR	Nuclear Magnetic Resonance
DPAF	9,9-bis[4-(diphenylamino)-phenyl]fluorene	HOMO	Highest Occupied Molecular Orbital
AIQ3	Tris(8-hydroxyquinoline)aluminium(III)	ee	Electron-only
TFT	Thin Film Transistor	hh	Hole-only
PANI	Polyaniline	BO	Born-Oppenheimer
EL	Electroluminescence	PSS	Poly(styrene sulfonic acid)
PL	Photoluminescence	SWNT	Single Walled Nanotube
IV	Current-Voltage	MWNT	Multi Walled Nanotube
IVL	Current-Voltage-Luminance	LuPo	Luminescent Polymer
TPD	Triphenyl-diamine	HBL	Hole blocking layer
TPA	Triphenyl-amine	ETL	Electron transport layer
PMMA	poly(methylmethacrylate)	HTL	Hole transport layer
RGB	Reg-Green-Blue		
WXGA	Digital Display Standard		
PLED	Polymer Light-Emitting Diode		
LCD	Liquid Crystal Display		
FPD	Flat Panel Display		
TFEL	Thin Film Electroluminescence		
FEM	Field Emission		
CRT	Cathode Ray Tube		
SID	Society for Information Display		
OTV	Organic Television		
WOLED	White Organic Light-emitting diode		
PEDOT	Poly(3,4-ethylenedioxythiophene)		
STO	Slater Type Orbital		
SE	Schrodinger Equation		
LCAO	Linear Combination of Atomic Orbitals		
AO	Atomic Orbital		
MO	Molecular Orbital		
3-D	3-dimensional		
IR	Infrared		

Chapter 1

INTRODUCTION

1.1 ORGANIC ELECTRONICS

This introduction first explores some of the basic forms and terminologies in organic electronics, in particular organic displays, and then briefly outlines the main content of each chapter in this thesis.

Organic electronics is, as the name suggests, concerned with electronic circuits comprised of organic materials through which electrical current flows. Organic materials are predominantly composed of carbon and hydrogen atoms bonded together. With regard to organic materials, only small molecules and polymers are considered in this thesis. A small molecule has a low molar mass whereas *Oligomers* only have a few repeat units (usually between 3 and 12). A polymer or “*polymer chain*”, typically consisting of several thousand repeat units - hence the name poly-mer, has a high molar mass. While all the polymers considered in this thesis are synthetic in nature, polymers do occur naturally - in proteins, for example.

Many people think of a plastic bag or other plastic objects such as toothbrushes etc, as representative of the class of materials called polymers and they are correct in this in many respects. However, polymers can be a lot more exotic than the electrically insulating polymers used to make such items. The term *organic electronics* refers to electronic devices or circuits which use organic materials as the active material. The first impetus for research in the field of organic electronics was the discovery of high levels of electrical conductivity in the conjugated organic polymer *polyacetylene*. Here the term *conjugated* refers to the particular form of carbon-carbon bonding found in this material, i.e. alternating double and single carbon bonds along the polymer backbone, the details of which are discussed in chapter 2. High-tech conjugated polymers actually have something in common with the ancient peat bogs of Ireland! – both materials are organic, carbon-based materials.

For small molecules and polymers with a large degree of conjugation, the extended overlap of atomic orbitals provides a band structure with high enough intrinsic charge mobilities to make low operating-voltage optoelectronic and other devices, such as organic thin-film-transistors (TFTs), organic solar cells, and organic light-emitting

diodes (OLEDs), based on thin films of these materials. Note that OLEDs is a generic term encompassing both small molecule- and polymer-based LEDs.

The term *synthetic metals* refers to polymers which are conducting in their solid state. Polyacetylene was the prototypical synthetic metal. Others exist but have conductivities lower than that of polyacetylene. However, polymers that conduct well have small bandgaps, are usually not fluorescent and, therefore, are not useful for optoelectronics where materials with bandgaps corresponding to the wavelengths of light in the visible range of the electromagnetic spectrum are required.

1.1.1 Light-Emitting Organic Materials

Fluorescence, defined as the emission of visible light from a material upon absorption of light, is the primary driver for the use of organic materials for electrofluorescent applications. The term fluorescence was coined by the famous Irish-born physicist George Gabriel Stokes who named the phenomenon after the mineral fluor spar, or calcium fluoride, (1852) following observations of this phenomenon in quinine sulphate solution originally made by Herschel in 1845. Organic fluorescence was first observed in urea salt which was the first synthesised organic material (1828) and is a small organic molecule. Fluorescent organic materials include small organic molecules, the first of which to be synthesised was *Mauveine*. Fluorescent small molecules are widely used as efficient chromophores or dyes in dilute solution. The discovery of strong photoluminescence (PL) or *fluorescence* from a light-emitting-polymer (LEP) in the solid state caused much interest in the optoelectronics community as these materials can easily be altered to change the emission colour and allow for simple solution-based processing. This makes LEPs interesting and useful and potentially useful for LED applications.

1.1.2 Processibility of Light-Emitting Organic Materials

To date a primary and crucial benefit of LEPs over small molecules is that for polymers thin films may be formed by solution processing. Depending on the type of polymer and the procedure used to make it, the polymer may exist as a powder, a fibrous

mat or a homogeneous thin film (electrochemically grown). LEPs come in the first two forms and can be redissolved with solvent in order to produce homogeneous thin films.

Aromatic small molecules or dyes, however, require the use of either an inert matrix, such as polymethymethacrylate, in solid state or a dilute solution of the dye for most practical optical applications. The reason for this is that small molecule solution cannot be used to spincoat thin films and also aggregation induced quenching of fluorescence is reduced in a matrix. This is due to the size of the small molecules which means they do not form viscous enough solutions to produce films from. Small molecules can be sublimated but are not very efficient used on their own in an OLED, requiring extra charge transport layers to produce efficient devices. Although organic dyes exhibit some of the highest PL quantum yields (PLQY) known in solution, the aforementioned processability factors somewhat limit the use of these molecular organic chromophores in solid state applications. Small molecules may, however, be doped into light-emitting polymer films to achieve energy transfer to the more efficient dye emitter.

LEP films, however, *can* be formed from solution because the intrinsic viscosity of their solutions is often very high. The viscosity of large molecules depends on the size, shape and molecular weight of the macromolecules as described by the Flory-Huggins equation below:

$$\eta = \frac{\lim_{c \rightarrow 0} \frac{\eta_{sp}}{c}}{\lim_{c \rightarrow 0} \frac{1}{c}} \ln \frac{n}{n_0}$$

$$[\eta] = KM^a$$

where a falls between $\frac{1}{2}$ and 2 and is a parameter related to the shape of the molecule¹. The high viscosity of concentrated polymer solutions arises from the entanglement of polymer chains flowing along with the solvent. When the solute molecule is nearly spherical, a (the constant in the equation above) is about 0.5 (case for small molecules), but when the molecule is long, extended or rod-shaped (polymers), its value may reach 1.7 to 1.8. The equation predicts higher viscosity for polymers than for small molecules, and polymer solution viscosity can be high enough to enable thin film formation.

1.1.3 Organic Light-Emitting Diodes

Active, organic-based electronic components exhibit good enough electrical and optical properties for them to be used in place of some traditional semiconductor components and are of huge technological and commercial interest. This is largely because of the highly processable, plastic nature of organic materials and the possibility of roll-to-roll production of flexible electronic devices, potentially over large areas, on a low-cost basis. To date, thin-film organic memory devices based on charge storage², transistors⁴, photovoltaic cells⁵, and batteries⁶ have all been demonstrated and, in all but the first case, commercialised. Historically, thin-film organic photodetectors (solar cells) were demonstrated prior to the invention of thin-film display type electroluminescent cells⁷ which are now a major focus of the electronic display industry.

An OLED is the same as an inorganic diode in that current flows more easily in forward than reverse bias. The device acts as a light switch with light emitted as a function of current above a threshold voltage when the device is under forward bias. This, however, is where the similarity ends. The details of the electroluminescence (EL) process are quite different for inorganic and organic materials and are described in relation to OLEDs in detail in chapter 3 of this thesis.

Although discovered much later than fluorescence, organic EL is closely related to the PL in conjugated organic materials. As visible in Fig. 5, these materials are highly fluorescent, making them good candidates for EL applications.

Some small molecules, such as AlQ₃, (Fig. 1), for example, have been specifically designed for use as the light-emitting active layer in an OLED. AlQ₃, like other dyes, cannot be solution-processed and must be deposited using thin film evaporation/sublimation techniques which require a high-vacuum environment. A solution-processible polymer analogue of AlQ₃ has also been synthesized and it is of course possible to polymerise or co-polymerise small molecules – the monomers from which polymers are made are essentially small molecules.

For physical and economic reasons, vacuum-processing using shadow-masks ultimately limits the area of display panels made using AlQ₃ and similar materials.

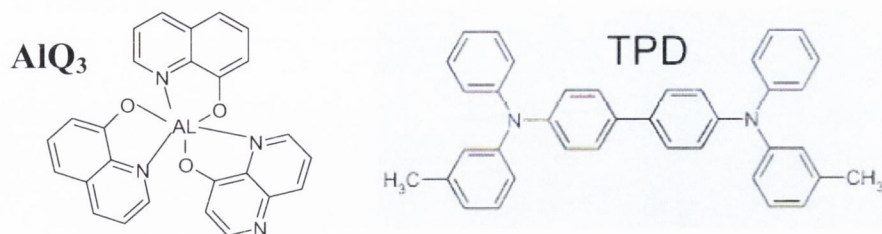


Fig. 1 Above: Chemical structures of AlQ₃ (left) and TPD (right) which are typical small molecules used for electroluminescence.

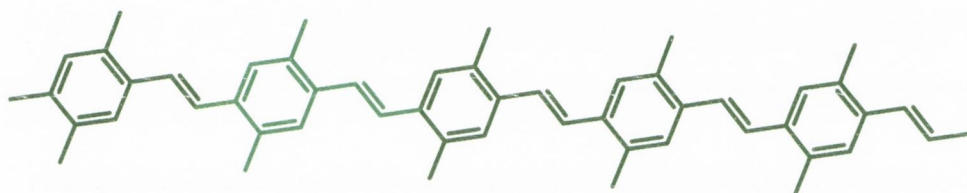


Fig. 2 Chemical structure of the prototypical light-emitting conjugated polymer PPV

The structure in Fig. 2 is essentially that of an oligomer (pentamer), with the repeat unit highlighted. However, in reality, there are thousands of repeat units. Despite this, the photophysical properties typically depend on conjugated segments not much longer than a pentamer.

1.2 THE ELECTRONIC DISPLAY INDUSTRY

OLED displays currently represent a only a small fraction of the many flat panel display (FPD) technologies available which include cathode ray tube (CRT), field emission (FEM), thin-film electroluminescent (TFEL) – an inorganic EL technology, liquid crystal display (LCD), plasma, projection, electrochromic, electrophoretic aswell as OLED displays.

1.2.1 Organic Light Emitting Diodes for Electronic Displays

The advent of organic electroluminescence from thin sublimed films of small molecules and solution processed conjugated polymers heralded the birth of the organic electronic display industry. Efficient LEDs made from these materials possess the basic requirement of light emission across the visible spectrum necessary for full colour RGB (Red, Green, and Blue) displays.

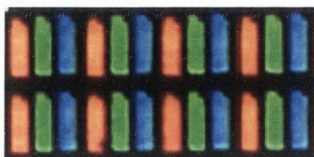


Fig. 3 Magnified image of RGB pixels in an electronic display.

Large (>14 inch diagonal) high resolution (WXGA) full colour video rate displays represent one of the most advanced electronic display applications seen and are found in laptops, for example. Larger TV displays are also very challenging to produce but do not require the high resolution of laptop displays because of the increased viewing distance. In order to achieve full-colour electronic displays, pixels are subdivided into red green and blue sub-pixels. WXGA is a high resolution electronic display industry standard and simply means that there are 600 pixels per inch. Generally displays are rectangular with a longer horizontal edge. To compensate for this, pixels are scaled roughly 3:1 vertical height to horizontal length. At 600 pixels per inch, the pixels are about 42 micron : 14 micron which is at the resolving limit of detection for the human eye.

Full-colour electronic displays based on OLEDs can be made using separate, coplanar LEDs for each colour or by using stacked LEDs. Using organic materials as active components for displays is not new as liquid crystals (used in LCDs) are organic materials. However, the main attraction of OLED displays is that they are *self-emissive* whereas LCD displays are not. The requirement of a backlight for LCD displays offers potential for OLED displays to be more power efficient.

OLED technology has advanced greatly since the discovery of low-voltage EL in small molecules and polymers and promises to become the principle next generation display technology. Advantages offered by OLEDs include: (i) wide viewing angle

(>170 view angle), (ii) fast response time (microseconds) enabling video rate display of images and smooth playback of fast moving images, (iii) high contrast ratio (>200:1 dark contrast (ratio of black to white in darkness)), (iv) a slim, lightweight display module, (v) and flexible displays. Polymer LEDs (or *PLEDs*), in particular, can offer the added advantage of low fabrication costs through solution processing.

OLEDs are the most immature of the FPD technologies but are rapidly gaining a foothold in the overall electronic display market and development of this display type has seen phenomenal expansion since the late 1980s. Campus companies (Princeton: Uniax, Cambridge: CDT and Oxford's Opsys, for example, and more recent start-ups like MED (Edinburgh) and NovaLED (Dresden), have played a huge role in the development of OLEDs. In-house research by the large consumer electronic corporations, among them Phillips, Dow, Dupont, UDC, MEI, Seiko-Epson, Sony, Samsung, Toshiba, and Kodak, to name but a few, has also greatly contributed to OLED development. As a measure of the seminal nature of their innovative research and development, some of these campus companies are now listed on the Nasdaq. The commercial potential of this technology has been recognized by the display industry's representative body, the Society for Information Display (SID) in the form of numerous industry and research awards. Included here is the recent awarding of the '*Jan Rajchman Fellowship*' to Prof. Forrest and Prof. Thompson of Princeton University for their development of efficient organic electro-phosphorescent devices.

The delivery of OLED products to the market will largely follow the trend exhibited by LCD displays in that, initially, small mobile applications will be targeted and, later, larger flat panel displays will follow. Kodak's digital camera (Easyshare, 2002 model) electronic display was one of the first examples of a small molecule based OLED display and the Sony MP3 player (2005) is an example of an OLED display based on polymers. The race is on to bring the first single panel organic television or "OTV" to the market. To date the largest prototype demonstrated is an impressive 40" Samsung polymer-based television (2005). Small molecule prototypes (Sony 14" single panel 2001) have also been made and CDT only recently demonstrated a full colour, flexible polymer, single panel display (2006). OLEDs will not only be excellent for full colour electronic displays but may also soon find application for efficient LCD backlighting and

low-cost general illumination where white OLEDs or '*WOLEDs*' are used. Recent lab data is encouraging indicating power efficiency⁸ competitive with the long-established fluorescent tube lighting. Inorganic LEDs, not common in small electronic displays for cost reasons), are being used as colour and white-light sources. Increasingly inorganic LEDs are replacing filament bulbs for lighting applications including spot-lighting, torches, traffic lights, automotive lighting, outdoor signs, advertising, and instrument panels. In the future, OLED-based modules will compete in all these areas.

1.2.2 The Trouble with Using Inorganic Materials for Electronic Displays

Though the active organic material used in organic electronics may be crystalline (as in the case of pentacene) or amorphous (molecules and polymers), the vast majority of organic solids are amorphous, weakly bound materials, which show very little long range order. Covalently bound inorganic solids, on the other hand, are typically quite rigid due to their makeup of strongly bound networks of atoms. Silicate, which makes up 50 % earths crust, is an obvious example. Inorganic semiconductors are rigid, covalently bound, crystalline materials which, unfortunately, do not make for easy processing. The term semiconductor is usually associated with inorganic materials whose extrinsic doping permits control over charge densities and mobilities. Extrinsic semiconductors are widely exploited to produce high quality transistors and optical devices such as transistors, LEDs and laser diodes - all based on p-n junctions. Despite a very high degree of control over production and performance parameters, applications are still, nonetheless, limited by epitaxial growth constraints and the rigid nature of the crystalline films. Furthermore the most ubiquitous semiconductor, silicon, has in fact got limited usefulness in optoelectronic applications due to its indirect bandgap. The reason radiative recombination is not possible in bulk indirect-gap semiconductors is because of the requirement for momentum conservation. The momentum offset between an electron at the bottom of the conduction band and the top of the valence band is too great for any photon to match, so the small momentum kick associated with an absorbed photon requires additional momentum from a phonon producing event such as a lattice collision. The probability of both a photon being absorbed and a suitable phonon energy event occurring simultaneously is small resulting in inefficient non-radiative recombination.

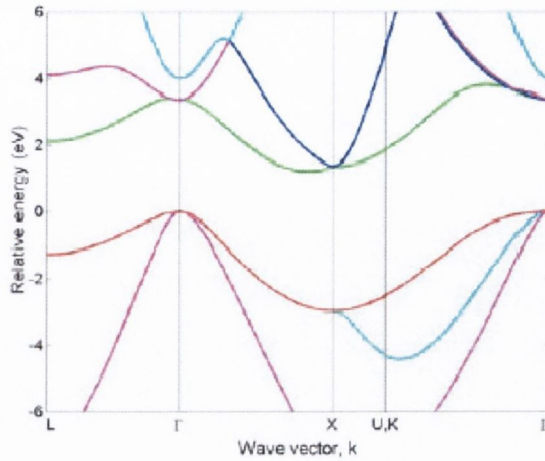


Fig. 4 Graph of bandstructure for silicon showing bandgap versus wavevector, k , for different crystal orientations. The smallest gap between the upper conduction bands and the lower valence bands is clearly an indirect gap (minimum of green band is not in line with maximum of red band).

The only way of overcoming the indirect gap constraints of silicon and other indirect gap materials is to exploit the effects of quantum confinement. Although this has been achieved, with visible fluorescence observed from silicon nanocrystals, fluorescence yields are low, and mass production of these materials is not feasible at the moment.

Electronic components based on silicon and other semiconductors perform very well on criteria such as reproducibility, switching speed, device lifetime and power consumption. However, these positive aspects are limited by the facts that inorganic materials are difficult and expensive to process and that inorganic device yields per wafer (transistors) and panel sizes (detectors) are limited by the size of the high purity, single crystals from which they are made. Ironically, organic devices, which form the basis of this thesis, are currently also limited by inorganic wafer size. This is because as yet, the driving circuitry relies on inorganic-semiconductor technology and will remain to do so until organic-based logic circuitry can compete.

1.2.3 Challenges to be Met by the Organic Display Community

Despite their promise, OLEDs still present certain issues of major concern for companies considering organic display technology over semiconductors. These issues are predominantly related to the relatively rapid degradation of the organic materials which makes CRT and LCD technologies preferable for large displays from a display lifetime point of view. This degradation usually manifests itself in a decrease in electrical conductivity, carrier injection, shifting charge balance or changes in the optical properties of the active materials caused by susceptibility to environmental factors like exposure to moisture⁹, excessive heat¹⁰ and UV irradiation¹¹, or, indeed, all of these factors together. The reason for the greater susceptibility of organics to such environmental effects can be linked to the type of chemical bonding in the molecules, and to their amorphous packing. This makes it relatively easy for oxygen, for example, to penetrate an organic film. It will also be shown later that any defects or impurities present alter the structure of the organic material significantly on a localised basis to the extent that the physical properties of the material may be irreversibly modified. However, control of defect and impurity densities is neither as easy nor as exact as it is with inorganics. The electronic structure of a material determines its optical and electronic properties. In polymers it is important to understand the ground-state chemical structure and how excitations, which alter that structure, are formed. This is essential if we are to be able to design new compounds which take account of the inherent electronic features of organic materials and so that we may exploit organic electronics better. Although chemical synthesis of more stable molecules is one approach to improving device stability, the inherent electronic structure of conjugated molecules means that optimising device architecture to improve device lifetime, will always also be a very important device engineering issue.

The display of information electronically is a major part of the knowledge-based society in which we now live. As energy costs and sources become more of an issue for society, - lighting accounts for a huge proportion of all the energy consumed - the need for more efficient, low cost lighting will intensify. With record gross revenue from the electronic display market as a whole expected to top 100 billion dollars (up 8 % on 2006)

by the end of 2007, it is clear that OLEDs which are increasingly in demand are largely responsible for driving the organic electronics industry.

1.3 OVERVIEW OF THESIS CHAPTERS 2 - 7

Chapter 2 covers background theory, drawing connections between chemical structure, excited states, electrical and optical behaviour of conjugated organic materials. The huge diversity of organic materials is due to the readiness of carbon to hybridise its orbitals to form a wide range of chemical bonds. This is due to the fact that the energies of electrons in the 2s and 2p orbitals in carbon are quite close, allowing the orbitals to combine to form a new hybrid orbital so that carbon can bond with itself. Also, since carbon is element 6 and has 4 valence electrons, it can bond in a wide range of valence states, allowing it to bond to different elements, and to form different carbon-carbon bond types. To understand what makes a conjugated polymer conductive, an explanation of the electronic structure which gives rise to this chemical bonding is given. Polymers have carbon-carbon bonding between the repeat units and since the length of a carbon bond is only a few Angstroms and there are a large number of repeat units, linear polymer chains have very large aspect ratios. The implications from an electronic point of view, of having quasi-1 dimensional materials, are discussed. Polymers may be classed as insulating, semiconducting or conducting according to their electronic properties.

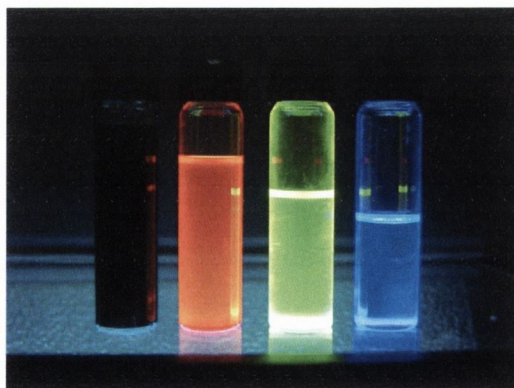


Fig. 5 Polymer solutions; conducting (black: PEDOT:PSS), semiconducting (coloured: red: TPD MEH M3EH PPV, green: TPD MEH PPV and blue: PFO). The bandgap of these materials increases going from left to right. A solution of the insulating polymer, PMMA (not shown), would be transparent and be on the far right above.

Chapter 3 is the second background theory chapter and discusses the 4 main requirements for electroluminescence, from the point of view of organic electroluminescence, in detail. These are charge injection, transport, recombination and decay. The interesting issue of the maximum EL efficiency possible in polymeric devices is discussed, and the main classes of OLED material and device architecture are introduced. It is worth bearing in mind that many of the original theoretical concepts for describing the electrical behaviour of materials and electronic devices were developed for crystalline inorganic materials and later modified for disordered organic systems.

Chapter 4 is the first experimental chapter of the thesis and describes how I fabricated and characterised OLEDs with a selection of new organic emitters using typical device structures. I designed and installed virtually all of the test equipment, fabrication and test processes used. As can be seen from the chemical structure of PPV in Fig. 2, the polymer chain is not highly symmetrically bonded, with substituted side groups breaking the symmetry. The steric interactions of these side groups alter the overlap of the π orbitals along the labile polymer chain. Because the bandgap depends on molecular structure, synthetic chemists can attempt to control the bandgap by design at the molecular level. Often, there is a trade-off in structure related properties. Larger side-groups, for example, can make a polymer more soluble but may also alter the bandgap with respect to a chain with shorter side groups. Similarly, large side groups may help to reduce interchain interactions in solid state (typically required in order to maximize the photoluminescence quantum yield), however, this may also reduce mobility and increase the drive voltage.

Chapter 5 is the second experimental chapter and marks my most original thesis work, as I designed the device architecture used and developed the materials components required. In this chapter a new anode was developed comprised of an array of injecting points, each with an injection area of equivalent to a square of side 45 nm.

Chapter 6 summarises the main conclusions drawn from each chapter, some more general comments on the field of OLED research and suggests possible future directions for research in these areas.

References

1. P. J. Flory Principles of Polymer Chemistry, *Cornell Univ. Press NY* **1953**.
2. J. Ouyang, C-W Chu, C.R. Szmanda, *Nature Mat.* **2004** 3
3. M. Halik, H. Klauk, U. Zschieschang, *Nature* **2004** 431
4. M. Granstrom, K. Petritsch, R. H. Friend, *Nature*, **1998** 395
6. A. Mirmohseni, R. Solhio, *Eur. Poly. J.* **2003**, 39
7. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, *Nature* **1990** 347
8. <http://Novaled.com>
9. S. Xiao, M. Nguyen, A. Heeger, *Adv. Funct. Mat.* **2003** 13
10. Y. T. Lim, T-W. Lee, *Opt. Mater.* **2002** 12
11. U.S. Pat. No. 6936355UV stability
12. Paul Semenza VP iSuppli Inc., May 23, 2007, <http://isuppli.com>

Chapter 2

2 AN OVERVIEW OF BONDING, EXCITED STATES, AND ELECTRONIC TRANSITIONS IN CONJUGATED ORGANIC MOLECULES.

2.1 MATERIALS CLASSIFICATION BY BAND-STRUCTURE.

The electronic structure of a material determines how it is chemically bonded and what its energetic band-gap, if any, will be. Knowledge of bond formation requires knowledge of the electron distribution as a function of energy or the electronic structure in a group of atoms or electronic system (hereafter referred to simply as the *system*) one needs to be able to describe a system mathematically. The total electronic energy of a system is given by the quantum mechanically based Shrodinger equation (SE):

$$\left\{ \frac{\hat{p}}{2m} + V(x) \right\} \psi(x) = E\psi(x)$$

where $\hat{p}$ is the momentum operator defined by the position-momentum commutation relation following experiments such as the Stern-Gerlach experiment, m is electron mass, E is the electron energy in an eigenstate of the associated electron wavefunction $\psi(x)$. Grouping the operators in S.E. defines the Hamiltonian operator, simply reffered to as the *Hamiltonian*, for one dimension as follows:

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

The Schrodinger equation, may then be simply written as:

$$\hat{H}\psi(x) = E\psi(x)$$

The *Hamiltonian*, named after Sir William Rowan Hamilton, arguably the most renowned Irish mathematician, can in principle be used to provide solutions for the allowed energies of discrete energy levels (atomic orbitals) or energy bands (molecular orbitals) of a *system* (i.e. eigenvalues or their corresponding eigenvectors) if the wavefunctions of the electrons of the atoms in the *system* are known. Analagous to light-wave intensity, and allowing for complex electronic wavefunctions, Max Born

defined the probability density, which must be a real number, as $|\psi|^2 = \psi^* \psi$. The radial part of the electron wavefunction depends on the radial distance of the electron from the nucleus (quantum numbers n and l) which describes how $|\psi|^2$ varies out from nucleus. The spherical polar co-ordinate dependent part of the electron wavefunction (which depends on the quantum numbers l and m_l) gives information on electron (often denoted by 'e') orbital shape. Consideration of the allowed wavefunctions and the definition of $|\Psi|^2$ enables us to view the spatial properties of atomic orbitals in terms of the probability distributions of their electrons on a Cartesian plot. The knowledge both of atomic orbital shapes formed by combining different atomic orbitals using the superposition principle and of probability density distributions readily accounts for the types of bonds which may be formed, including hybridized bonds (section 2.2), and hence for the shape imposed on molecules by different bond types.

Quantum number	Magnitude of associated vector ($l\hbar$)	Space quantization of associated vector	Orbital implications
n (principal) = 2	-	-	-
l (azimuthal) $(n-1) = 1$ orb. Ang. momentum	$l = [l(l+1)]^{1/2}\hbar = \sqrt{2}\hbar$	$l_z = m_l \hbar ; -\hbar, 0, +\hbar$	Cones due to indep axial components
m_l (magnetic) -1,0,1 orb ang. momentum			3 orbitals
s (spin) = $1/2$ (fermions) spin ang. momentum	$s = [s(s+1)]^{1/2}\hbar = (\sqrt{3}/2)\hbar$	$s_z = m_s \hbar$ Where $m_s = +1/2$ or $-1/2$	2 e/orbital at most

Table 1 Summary of situation for a single 2p electron in a carbon atom. 2p electrons are of primary interest in conjugated materials. The total spin or orbital angular momentum is found by summing the individual s or l over all electrons present in the atom. The 2p atomic orbital is dumbbell shaped

In many-electron atoms, where one also has e-e repulsion terms, the central field approximation is used a potential energy is obtained by averaging the electron repulsion over all of the other electron positions, over all angles, in order to generate a spherically symmetric potential similar in form to that for the simple case of the electron in a hydrogen atom. The corresponding one-electron orbitals are called Slater-Type Orbitals¹ (STOs). For many electron atoms, the simplest example of which is the Helium atom, a quantity called spin multiplicity is defined as being $2S + 1$, where S is

the sum of electron spins, $\sum s_i$. Since s itself is fixed (m_s though, has two values), S can only be 3 and 1 which correspond to triplet and singlet states respectively.

In order to describe the bulk properties of a solid material focus is no longer on atoms but rather molecules or at least many atomic orbitals. When atoms approach each other atomic orbitals coalesce to form molecular orbitals. Using the S.E. to describe molecular *systems*, one can simplify the calculations involved using the Born-Oppenheimer¹ (B.O.) approximation which rationalises factorizing the time independent molecular wavefunction into nuclear, N , and electronic, E , motion parts ($\psi = NE$). Because of the heavier masses of the nuclei (2×10^{-26} kg for carbon), the electron (9.1×10^{-31} kg) motion occurs on a faster timescale compared to the nuclear motion. Thus, changes to the electronic structure such as excitation or de-excitation of an electron, occur with the nuclei essentially stationary during the transition. Similarly because electron motion is so fast, any changes to vibrational and rotational nuclear motions are accompanied by essentially instant response of electronic wavefunction to the new nuclear coordinates. The BO principle is also very useful when describing electronic transitions. Because the exact electronic wavefunction is still very complex for a molecular system, simpler approximate wavefunctions called basis functions which form a basis set are used to yield expectation values in accordance with the variation theorem. The use of the BO approximation and the variation theorem allows for comparison of *systems* rather than extraction of absolute *system* energies.

Implementing the approximations above, it is possible to write the molecular electronic wavefunction Ψ as a product of A.O. wavefunctions ϕ . This involves the LCAO (linear combination of atomic orbitals) method initially proposed² by John Edward Leonard-Jones in 1929 where:

$$\Psi = \sum_j c_j \phi_j = c_1 \phi_1 + c_2 \phi_2 + \dots$$

How the AOs wavefunctions, ϕ , are combined depends on ϕ symmetries and antibonding, bonding and nonbonding MOs may be produced. MO theory based upon the LCAO method, produces energy bands, as a consequence of the Pauli exclusion principle, as more atoms are bonded together. As isolated atoms approach the interatomic spacing they have in any given solid, the wavefunctions of the outer, or

valence, electrons in particular begin to distort because of electrical interactions and the exclusion principle. For N identical atoms the discrete energy levels shift and split to form separate bands. Ordinarily in 3-D systems $N \sim 10^{23}$ so the bands consist of N closely spaced energy levels with a continuous energy distribution. Fundamentally, however, the more orbitals that overlap, the larger the bandwidth and the charge carrier mobility. Metallic levels of electrical conductivity require a continuous, partially-filled band of overlapping valence electron orbitals. The concepts of energy bands, and the degree of mobility carriers have in the respective bands are used to explain the electrical properties of solids.

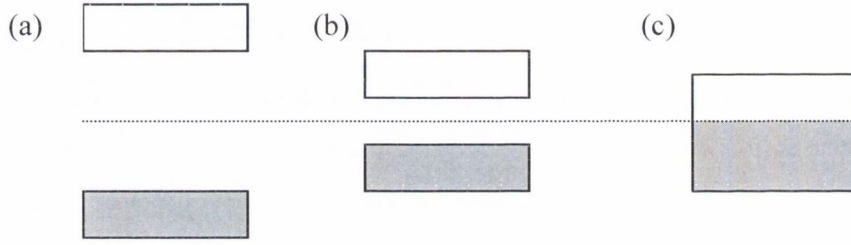


Fig. 6 Energy bands in insulators (a), semiconductors (b) and insulators (c) (dotted line is the Fermi energy level and the grey boxed area represents filled energy levels and the white boxed area empty energy levels.)

In semiconductors, the Fermi-Dirac distribution function defines the probability of band occupancy by an electron:

$$F(E) = \frac{1}{e^{(E-E_F)/kT} + 1}$$

where E_F is the fermi energy, T is temperature and k is Boltzman's constant. In insulators and semiconductors at 0 K, the highest occupied band, the valence band, is completely filled by valence electrons. The next highest band, the conduction band, is completely empty and the energy gap E_g separating the two is $\sim 1 - 5$ eV. At any finite temperature there are a few electrons in the conduction band so no material is a perfect insulator. In intrinsic semiconductors like silicon ($E_g = 1.14$ eV) or germanium ($E_g = 0.67$ eV) there are very few free electrons at low T and they actually behave as insulators. At room temperature few electrons can jump the gap and contribute to conduction. The conductivity can be improved through the use of dopants which provide

acceptor or donor states close to (within 0.01 eV) either the valence or conduction band edge. The small difference in energy between intrinsic and dopant energy levels means it is facile to thermally excite electrons into the acceptor band or from the donor levels into the conduction band providing electrons, thus indirectly providing electrons in the conduction band and holes in the valence band.

2.2 CARBON-CARBON BONDING

Pi-conjugated organic molecules containing alternating carbon-carbon single and double bonds form the basis of organic electronics. Carbon bonds with itself in several ways by combining the s orbitals of one carbon atom with the p orbitals of another carbon atom. When it is possible to draw more than one valence bond or Lewis structures for a substance, the actual Lewis structure is said to be a resonance hybrid of the resonance forms. The notion of a resonance hybrid structure is made plausible by the theory of orbital hybridisation suggested by Linus Pauling³ in 1930. Generally, when VB theory fails to correctly predict the structure for a compound, hybridisation theory must be used. It requires energy to form hybrid orbitals, but this is more than recovered when forming MOs by overlapping the hybrid orbitals with the AOs centered on other atoms. In the case of a sp^2 hybridised carbon atomic orbital, three σ bonds and one π bond are formed. In this case there is one electron in each of the three sp^2 hybrid orbitals and one in the remaining unhybridized p orbital. The combination of a σ bond and a π bond produces a carbon-carbon double bond. In sp^3 hybridisation four σ bonds (tetrahedral shaped molecule) only are formed and thus single bonds are longer than double bonds. Sp hybridisation, where two σ bonds and two π bonds are formed, results in the formation of a carbon-carbon triple bond, however, this type does not exist in any of the materials under discussion in this thesis. The allotropes of carbon are diamond and graphite.

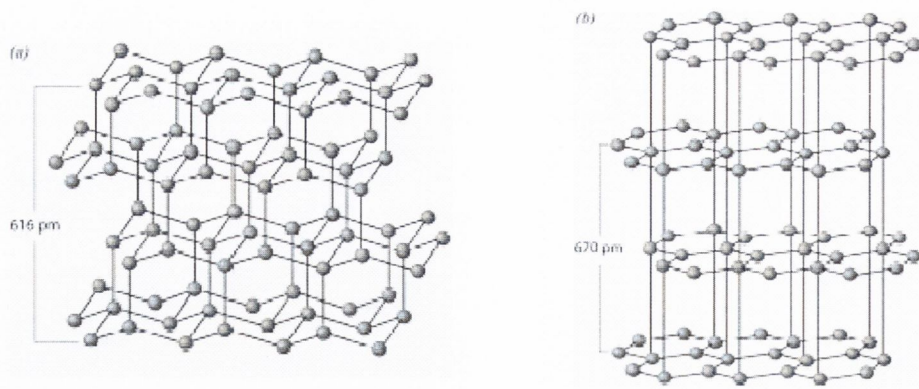


Fig. 7 The structures of diamond (left) and graphite (right).

The sp^3 bonding in diamond renders it an insulator with a bandgap⁴ of 5.4 eV and its high symmetry gives it isotropic physical properties. Although diamond is an insulator there is a significant amount of research being carried out on synthetic diamond films (diamond like carbon) which may be doped with Boron (for P type diamond) and Phosphorus (for n type diamond) in a similar manner to traditional semiconductors. For example in B-doped diamond Boron has an electron acceptor level just above the valence band edge in diamond allow mobile hole carriers to be generated in the valence band. Doped diamond films have most potential in high temperature electronic applications as contacts and for semiconductor p-n junctions⁵.

Graphite is another pure form of carbon, like diamond, but unlike diamond the carbon bonds are sp^2 hybridised and graphite has a multi-sheet structure, very loosely bound by weak Van der Waals forces. The $2p_z$ orbitals contain one electron each and overlap to form bands so that the π electrons are highly delocalised above the plane of the carbon atoms in a sheet, making graphite a highly anisotropic metallic conductor. The parallel to perpendicular conductivity ratio⁶ is about 10^6 . In practice bulk graphite is highly conductive in all directions due to the presence of many microscopic fragments of crystalline sheet material oriented randomly towards each other.

Other forms of sp^2 hybridised carbon are the fullerene family of cage-like structures discovered by Kroto *et al* in 1991⁷ (e.g. C_{60} molecule) and single and multiwalled carbon nanotubes⁸ which were subsequently discovered. C_{60} has been used in organic solar cells⁹ to increase their efficiency due to the fast, efficient photoinduced electron transfer to C_{60} . Multiwalled tubes have been used to make polymer composites

and fibres.¹⁰ The quasi-1d nature of single wall nanotubes makes them very interesting materials electronically. The electrical conductivity of the tubes depends strongly on the tube chirality¹¹. Insulating, semiconducting and metallic nanotubes exist. Metallic tubes are of interest for tiny integrated circuit interconnects since a single tube can exhibit ballistic charge transport. This is because the mean free path of electrons can be much greater than the size of the nanotube, simply because of the small size of the nanotube, and means that electrical resistivity due to scattering is negligible. In the case of ballistic transport, when a constant electric field at a speed $\ll c$, the speed of light, is applied to the material, electrons will continue to accelerate according to Newtonian physics. However, high contact resistance means that device characteristics are limited by the contacts.¹² Semiconducting tubes have been used as active components in nanoscale transistors¹³. Selective processing, resulting in one specific type of tube, and controlled positioning of individual nanotubes are still major challenges in this field.

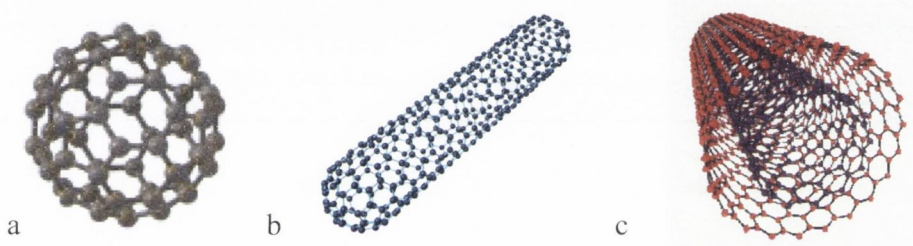


Fig. 8 Chemical structures of C_{60} , SWNT & MWNT.

2.2.1 sp_2 -Hybridised Organic Molecules

Organic molecules are comprised of the elements C, H, O, and N. There are many naturally existing organic compounds but synthetic organic chemistry (and the end of vitalism) dates from 1828 when crystals of urea were synthesised by Friedrich Wohler. Benzene, the molecule of which is the basis of aromatic (organic) chemistry, was first isolated in 1825 by Michael Faraday. Its chemical formula was shown to be C_6H_6 in 1834. Benzene, a hydrocarbon, exists as a colourless liquid at room temperature with its absorption peak at 280 nm (4.4 eV).

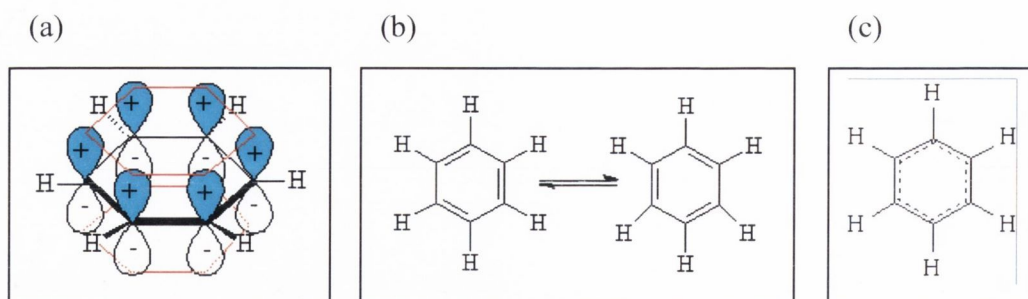


Fig. 9 Ground state structures of benzene including (a) 2pz orbitals of C atoms , (b) resonance forms, (c) delocalised form. In benzene the carbon bonds are sp^2 hybridised. From the boundary surface plots it is immediately obvious that bonding involving 2p atomic orbitals occurs when there is overlap of a 2p orbital lobe with another 2p lobe or another atomic orbital as all the electron density is in the lobes.

Kekule (1865 – 1872) suggested the conjugated (alternating single and double C-C bonds) structure for benzene (Fig. 9b) to be two rapidly switching isomers which existed in equilibrium. The Kekule structure could not account for the stability of benzene which was later explained by Pauling's resonance theory (hybridization) which predicts equal bond lengths and highly delocalised electrons in electron clouds above and below the benzene ring (Fig. 9a). However, Kekule's idea of resonance forms could be considered to represent the dawn of organic electronics.

Benzene is the repeat unit of the *-acenes* (anthracene, tetracene, pentacene etc) which are crystalline organic semiconducting hydrocarbons known as molecular crystals. Most of them have a wide energy-bandgap and low melting point and low carrier mobility. They are called semiconductors because their dark electric conductivity increases exponentially with temperature and some other properties are similar to those of inorganic semiconductors. Most of the initial research into organic electronics was done using films of these materials (e.g. first EL seen using anthracene). The electrical conductivity of their polycrystalline films is low (10^{-20} to 10^{-16} ohm $^{-1}$ cm $^{-1}$ for anthracene for example) because the intermolecular separation is quite large. However good quality organic field effect transistors (OFETs)¹⁴ have been demonstrated from pentacene thin films which have high mobilities. These materials all require high vacuum deposition techniques, and do not lend themselves to cheap or large area organic electronics applications. Solution processed OFETs have been made from

polythiophenes and a solution processible pentacene material, however, mobilities are lower than single crystal pentacene.

Soluble and highly fluorescent (in dilute solution) aromatic dye molecules (e.g. rhodamine and coumarin laser dyes^{14b}) are known as small molecules. Some small molecules are electroluminescent (e.g. AlQ₃¹⁵). Such materials can possess good mobilities and photoluminescence yields, however, they possess limited processibility as amorphous thin films are only formed upon sublimation under high vacuum. The photophysics of larger organic molecules (macromolecules) is based on that developed for small molecules.

Macromolecules are essentially molecules with a large number of atoms where often there are repetitive identical molecular subunits which add to produce large cyclic (*macrocyrcles*) or linear (*polymers*) molecules. For most organic compounds, including those studied by Nobel prize-winners Staudinger, Natta, Ziegler and Flory, there is no delocalisation of charge possible throughout the molecule. This is because they are saturated (sigma bonded) polymers with no extended overlap of atomic orbitals. With wide bandgaps (>5 eV), saturated synthetic organic polymers such as poly-ethylene are excellent electrical insulators and are commonly used in the packaging industry. They are readily processed using solution-based, thermal or mechanical-assisted-molding methods which are low-cost and industrially scaleable.

Organic materials which *combine* electrical functionality *and* processability are desirable. In *conjugated polymers* the sp²pz bonding (π bonding) with one electron per unhybridized pz orbital, leads to extensive orbital overlapping and electron delocalisation along the polymer backbone and provides a route for charge carriers along the polymer chain. The number and type of atoms in the repeat unit of the chain (i.e. the chain symmetry) determines the electronic structure in conjugated polymers. *Poly-acetylene* is the prototypical conjugated polymer.

Polyacetylene (CH=CH)_n was first made by Natta *et al* in 1958 as a black powder. In 1967 Hideki Shirakawa *et al* used a Ziegler-Natta type catalyst to produce a thin nanofibular film of the thermodynamically stable trans-isomer of polyacetylene. Electrical measurements on these thin films and on powder pellets indicated that the intrinsic properties of polyacetylene did not change much between powder and film.

During efforts to use the film as a source of graphitic carbon, strong IR film absorption peaks were observed, when trace amounts of chlorine were added to the film. At high chlorine doping levels, the material became opaque and the spectrum for Cl-polyacetylene became clearer. It is now known that the three bands at 1397, 1288 and 888 cm^{-1} are 'doping induced'. Observed isotope shifts (in NMR data) imply that the bands are of vibrational origin in the vicinity of a carbon cation (positively charged carbon atom) on the chain. In 1976, intentional doping of polyacetylene with bromine by Heeger et al, resulted in a seminal paper on conducting polymers¹⁶ describing metallic levels of electrical conductivity in polyacetylene which was the basis upon which the Chemistry Nobel prize was awarded in 2000. The cationic carbon species responsible for the high conductivity is known as a positively charged soliton after Heeger *et al*¹⁷ 1979.



Fig. 10 Degenerate (energetically equivalent) ground state chemical structures for trans-polyacetylene.

Trans-polyacetylene is a degenerate ground state polymer because of its symmetry. The angle between any two of the three sp^2 orbitals of a C atom in trans-polyacetylene is close to 120° , which tends to constrain it a plane. Neighbouring carbon atoms are strongly sp (sigma) bonded forming a bonding and antibonding energy level with a separation of approximately 20 eV. The σ electrons contribute to the rigidity of the polymer but not the electronic properties. There is a small coupling between neighbouring sp^2 orbitals not oriented toward each other, giving the σ electrons a small bandwidth, but this coupling is neglected in most tight binding MO calculations.

2.2.2 The Prediction of a Zero-Bandgap for Polyacetylene

Modelling polyacetylene as a chain of equidistantly spaced carbon atoms (regular Hubbard chain), the 1-D particle-in-a-box model can be applied. Consider a row of N atoms separated by a distance d, the total length of the chain is (N-1)d or, for large N, Nd. The energy required to excite an electron from the HOMO (highest occupied molecular orbital) to the LUMO (lowest unoccupied molecular orbital), ΔE , for large N is

$\Delta E \approx (h^2 / 8m) / N$. The model therefore predicts polyacetylene to be a metal at long chain lengths.



Fig. 11 Schematic of delocalised electrons (dotted line) along the backbone of trans-polyacetylene.

Huckel MO theory (or HMO) is a simple subset of LCAO-based MO theory, developed by Erich Hückel in 1930¹⁵. HMO theory successfully predicts the delocalisation energy for benzene when the electrons are completely delocalised around the ring, in support of the hybridisation theory. HMO also correctly predicts the guiding of substitution by an N atom in the benzene ring to the ortho and para positions. HMO may also be applied to polyacetylene. In HMO theory (which only considers nearest neighbour overlap integrals), only the $2p_z$ orbitals are considered. HMO theory postulates that the π MOs are considered to be separate from the σ framework since the p_z orbitals are perpendicular (orthogonal) to the σ orbitals. HMO theory can, therefore, be used to describe the π MOs of planar, unsaturated ethenic and benzenoid hydrocarbons. In common with the particle-in-a-box model, each carbon atom contributes one electron to the π system in HMO and polyacetylene is predicted to be a metal. This is due to the extended overlap of half-filled p_z orbitals along the chain for a long polyene chain resulting in a half-filled π -band and a large delocalisation energy.

Electronic bandstructure calculations using a more detailed tight-binding Hamiltonian for a regular Hubbard chain provide the widths of the energy bands and their distribution in k -space. Again with this approach to modeling the bandstructure of polyacetylene, the main results support those of the particle-in-a-box and HMO models:

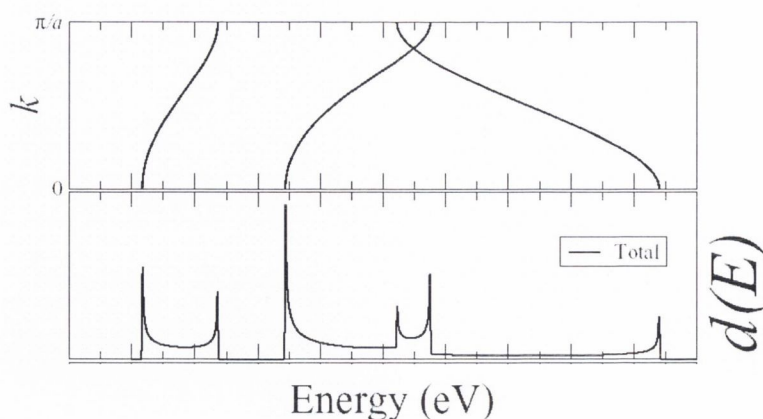


Fig. 12 Energy bands calculated for a Hubbard chain of carbon atoms after condensed matter theory course 1024 by Dr. S. Sanvito TCD 2005. Top: band structure. Bottom: corresponding total density of states (DOS)

The singularities in the DOS are characteristic of 1-D *systems* like polyacetylene¹⁹. The bandstructure calculation includes p and s orbitals and the central band in the DOS (Fig. 12) is largely due to the p_z or π -band. This band has no energy gap, again indicating that polyacetylene is a metal with uniform charge distribution and equal C-C bond lengths along the chain, in agreement with the other models already described.

Polyacetylene in the undoped state is, however, not metallic and has a finite band gap. Furthermore, the observed progression in absorption wavelength on going from butadiene to hexatriene does not follow the particle-in-a-box equation. This fact suggests an upper limit for the absorption and that there is a point beyond which further increased chain conjugation length does not change the bandgap, ΔE . This convergence has been confirmed by several predictions including those by Lennard-Jones and Peierls.

2.2.3 The Finite Bandgap in Peierls-Distorted Polyacetylene

A 1-d metal would be the ultimate solid state conductor, however, it was shown, before polyacetylene was discovered, that such a system is unstable and exists only as a theoretical model. Intuitively one expects that the physical properties of a linear chain will be more sensitive to the precise position of each atom in the chain than in the case of a 2-d or 3-d metal where interacting orbitals in two and three dimensions provide the bands for charge transport. Strictly speaking no atomic system can be truly 1-d as atoms by definition are 3-dimensional. However, reducing the *system* to the electrons

from a particular orbital which overlap with those of its nearest neighbours for all the atoms in the chain, then the system may be considered quasi-1-dimensional.

The hypothetical case of an equidistantly spaced linear chain of sodium atoms was first considered by Rudolph Peierls²⁰. Sodium has a half filled 3s valence shell so each atom on the chain is expected to contribute one electron to the band formed by the overlap of these orbitals along the chain. As per the simple models above, one would expect the chain to be metallic. Peierls showed, however, that upon dimerisation of the chain, the overall chain energy could be lowered because the resulting reduction in electronic energy of the system is greater than the gain in elastic energy caused by the chain deformation known as “Peierls distortion”. The Peierls instability itself is a result of the nesting property of the Fermi Surface²¹ (FS). Overlapping of parts of the FS as a result of a translation is called nesting. For a 1-d chain the crossing points of the energy band with the Fermi energy can be shifted exactly onto each other using the translation $|k| = 2 k_F$. The Peierls instability opens an energy gap at the new Broullian-zone boundary^{20,21} and the total energy is reduced. Peierls Distortion provokes a modulation of the charge density along the chain resulting in a charge density wave (CDW) state. Regions of greater electron density correspond to shorter bonds. The Peierls transition to the CDW state, is a general result applicable to all theoretical 1-d systems.

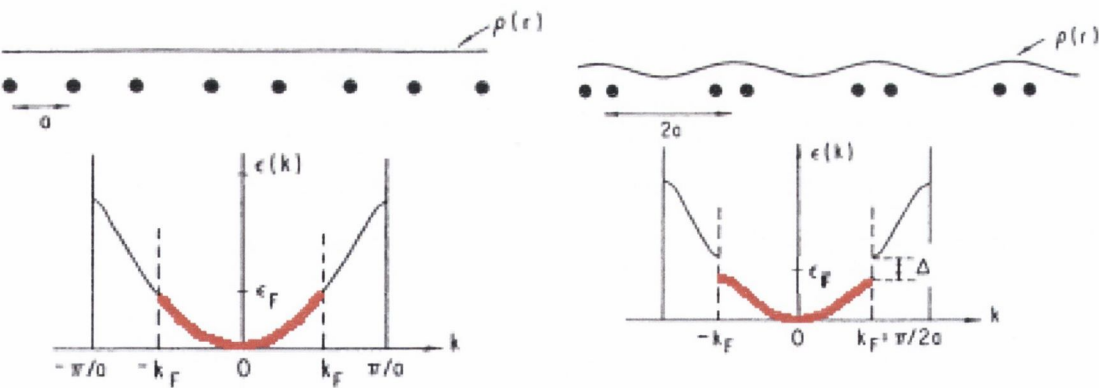


Fig. 13 $E(k)$ for a linear chain with equidistant spacing of atoms (left) and for a dimerised chain (right). Note the opening of a gap at $k = \pi/2a$ for the dimerised chain due to a Peierls instability.

Displacement of every r^{th} atom on the chain means that the basic cell in reciprocal space changes from $-\pi/a < k < \pi/a$ to $-\pi/ra < k < \pi/ra$. Since the states on either side of the breaks coincide exactly or very nearly with the edge of the Fermi distribution, then the

states which are displaced downwards in energy are occupied and those raised are empty, so that there is a net reduction in energy. The total (electronic plus elastic) energy change, ΔE , due to dimerisation (or any Peierls distortion) can be calculated using second order perturbation theory²² on the lattice potential.

$$\Delta E \approx \frac{L|V_k|^2}{\hbar v \ln|V_k|}$$

Since V_k large ΔE will always negative and lattice distortion will be entropically driven.

It is due to Peierls distortion that every second bond in undoped trans-polyacetylene has double bond character, that it is a semiconductor with an energy gap of 1.4 eV between π and π^* sub-bands and that it has an electrical conductivity⁶ of $4.4 \times 10^{-3} \text{ Sm}^{-1}$. Dimerisation in polyacetylene is confirmed by X-ray diffraction measurements. These show a herringbone structure with a length differential of 0.07 Å between single and double bonds which is much less than that in ethene or methane.

2.3 THE SU-SCHRIEFFER-HEEGER ELECTRONIC BANDSTRUCTURE MODEL

In the Su-Schrieffer-Heeger Hamiltonian (SSH) and its continuum version²³ polyacetylene is modeled by taking a regular Hubbard chain (i.e. chain zig-zag is ignored) and incorporating chain dimerisation (Peierls distortion) by using a dimensionless electron-lattice (electron-phonon) coupling constant, α . The Hamiltonian is:

$$H_{el} = -\sum_{n=1}^N [t_0 + \alpha(u_n - u_{n+1})][c_{n+1}^\dagger c_n + c_n^\dagger c_{n+1}] + \frac{1}{2}K \sum_n (u_n - u_{n+1})^2 + \frac{1}{2}M \sum_n \dot{u}_n^2$$

K is a stiffness force constant, taken to be the bond-strain for sigma bonded electrons, M is the mass of a C-H group, t_0 is value of the transfer integral, $t (= t_0 + \alpha(u_n - u_{n+1}))$, between nearest neighbour electronic wavefunctions for an equidistantly spaced chain of carbon atoms, u_n is the displacement of the CDW for the atom at position x_n on the chain, $\dot{u}$ is the momentum of an atom at site n , and $c_n^\dagger$ and c_n are the creation and annihilation

operators for a π -electron on the n^{th} C atom with N being the total number of C atoms on the chain. H_{el} , the electronic part (kinetic energy of π electrons) is the first sum, the second sum is the sigma bond strain energy and the third sum gives the lattice kinetic energy. The corresponding eigenvalues of the Peierls distorted state are:

$$E_k = \pm \left[(2t_0 \cos ka)^2 + (4\alpha u_0 \sin ka)^2 \right]^{1/2}$$

,where, u_0 is a constant called the frozen-in distortion.

The first term is the energy of an electron of wave vector k in a uniform Hubbard chain.

In the Su-Schrieffer-Heeger (SSH) model, for a Peierls-distorted chain of polyacetylene, the Peierls gap is $2\Delta_0 = 8\alpha u_0$. The π - π^* band gap, $(2\Delta_0)$, is determined by the dimensionless electron-phonon coupling constant, λ , through the relation⁶:

$$\Delta_0 = 8t_0 \exp\left(-\left(1 + \frac{1}{2\lambda}\right)\right), \text{ where, } \lambda = \frac{2\alpha^2}{\pi t_0 K}$$

Electron-phonon coupling is usually incorporated in the Hamiltonian as a variation of the strength of the transfer integral as a function of the distance between nearest neighbour atoms in the chain. Usually t is taken as a parameter adjusted to fit macroscopic properties making the SSH model semi-empirical. By finding values of u_0 and α which minimise the *system* energy (sum of all states at 0 K in the lower π band) and the associated elastic energy, a Peierls gap of 1.4 eV is obtained for polyacetylene.

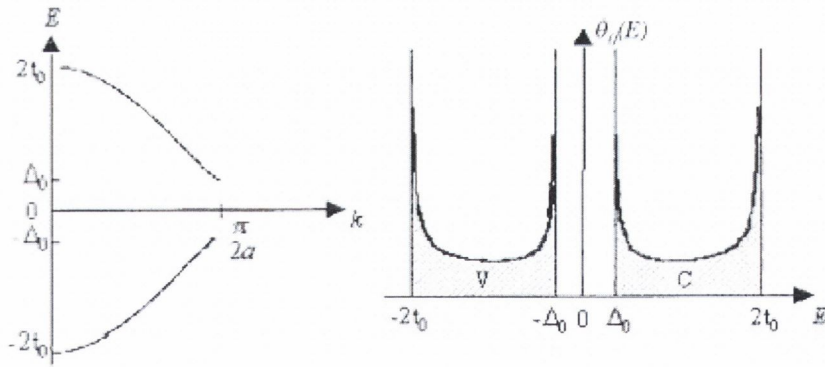


Fig. 14 Band structure (left) and DOS (right) for a dimerised chain (ref) of polyacetylene using the SSH model.

In Fig. 14 the polyacetylene bandstructure has a gap due to the formation of π and π^* star sub-bands. The π band (or valence band, V) is full and the π^* band (or conduction band, C) is empty. In some respects it might have been guessed that there might be two π -bands for the p_z

MOs of polyacetylene since the unit cell for graphite (an extended p_z system) which contains two atoms, has two parts to the p_z band¹⁶ (bonding and antibonding or π and π^*). However, graphite is 2-D so an equidistant lattice spacing of atoms is allowed, the bonding arrangement is stable and graphite is a good electrical conductor.

2.3.1 Solitons: The Fundamental Excitations in Polyacetylene

Apart from being used to model the bandgap, the SSH model¹⁷ can also describe the lowest energy or fundamental excitations in polyacetylene. When two degenerate chemical structures (Fig. 10) occur on the same chain they are separated by a domain wall or *soliton*. Such solitons are neutral, occurring on all trans-polyacetylene chains with an odd number of (-CH)'s since chains are more stable with double bonds at each end. SSH theory predicts the formation of solitons in polyacetylene. The soliton is associated with a characteristic lattice distortion, which is a modulation of the Peierls distortion and takes place over several lattice sites. The fourth electron of the carbon at the center of the soliton is, although still bound to the nucleus, neither bonding nor antibonding and to a first approximation resides in a midgap level. Addition or removal of charge to a chain with a neutral soliton results in a negative or positive soliton respectively. Chemical doping can produce negative (Cl^- or Br^- dopants) or positive (Fe^{3+} dopant) solitons. Doping may also be by optical, thermal, electrical and chemical means. All solitons are mobile excitations which means their characteristic distortions move. Charge transport in electrically poled polyacetylene occurs by solitons moving along a chain as a solitary wave and/or hopping between chains.

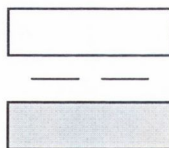


Fig. 15 Schematic showing midgap soliton states associated with inclusion of positive charge on a polyacetylene chain.

Experimental evidence of solitons in polyacetylene is provided by electron spin resonance measurement which, based on the characteristic g value of a π - electron, imply 1 spin/1000 to 3000 atoms. Experimentally measured diffusion rates for these spins agree well with theoretical predictions for neutral solitons. The large creation energy for

solitons, means that the high concentration of spins at RT may have resulted from the creation of neutral solitons during cis-trans isomerisation. These are prevented from recombining by cross-link defects, for example. The number of spins decreases on doping, as expected, since charged solitons have no spin. Magnetic susceptibility is low and suggests spinless conductivity for doped samples. Solitons are also evidenced by changes in the sub-bandgap optical absorption. The predicted midgap absorption peak for polyacetylene is observed for a variety of both donor and acceptor dopants implying the midgap level is associated with the polymer chain, rather than the electronic states of the dopant. Furthermore, the π - π^* interband absorption is bleached upon doping. In addition to midgap absorption, two strong infrared absorption lines, at 900 and 1370 cm^{-1} are seen for lightly doped samples for any dopant. These grow linearly with increasing doping. A third weaker vibration is also observed at 1270 cm^{-1} . The first is caused by oscillations of the charged soliton in the Coulomb field of the impurity ion to which it is bound. The second two are due to IRAV (Infrared-Active Vibrational) modes occasioned by coupling of the excess soliton charge on the polyacetylene chain with the C=C and C-C stretch modes respectively. The latter results from increased dipole moments along the chain. Finally, as expected for photogenerated solitons in polyacetylene, only two photoinduced absorption lines close to the two aforementioned IRAV lines are observed.

2.3.2 Polarons in Conjugated Polymers

The SSH also predicts the formation of polarons in polyacetylene. Addition of charge to a kink-free chain cannot create a soliton since it would require changing all the bonds to one side or other which would cost too much energy. In this case a polaron is formed. Again the bond order in the vicinity of the added charge is modified.

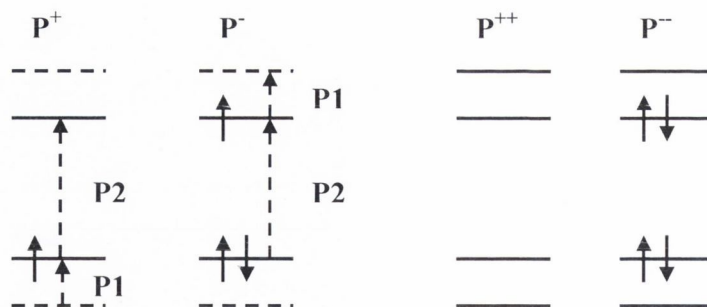


Fig. 16 Polaron states and allowed optical transitions. Left: positive polaron. Right: negative polaron.

In a conjugated polymer if there is no empty level in the valence band, an added electron will cause the chain it is on to deform around it, creating a characteristic pattern of bond deformation about 20 sites long called a negative polaron. In this process a level is pulled out of the HOMO with its two electrons and a level is pulled out of the LUMO. Two levels in the bandgap are created, the lower filled with the two electrons brought up from the HOMO level and the upper with the added electron. The stability of the polaron is due to the reduction in the total electronic energy of the molecule, brought about when the electron moves from the HOMO level into a lower level, exceeding the elastic energy required to form this level. Although its energy levels are in the band-gap, the polaron can move freely on its own chain (assuming an otherwise perfectly conjugated charge-free chain), its lattice distortion moving with it. By extension of these arguments, addition of an electron and a hole, far apart from each other on the chain, would result in a polaron-pair being formed on the chain. In theory, for polycetylene, if the polarons were free to move through the chain, when they met they would be annihilated if the charges were unlike or, for like charges, would be transformed into a pair of solitons since solitons have lower energy.

2.3.3 Creation Energies of Solitons and Polarons in Polyacetylene

In terms of excitation creation, it is important to note that quantum fluctuations prepare the lattice for acceptance of injected charge (electrical excitation) just as when charge carriers are formed upon photo-excitation or chemical doping. In other words the excitations are the same for a given material no matter how the excitation is generated. Note that whereas solitons must occur in pairs polarons may occur singly. Also, if two electrons or holes were added directly to the chain close to each other, two charged solitons would be formed directly. For polyacetylene the soliton creation energy from

the SSH continuum²³ model is $E_s = (2\Delta_0 / \pi)$ and, is lower than that for polarons so the SSH-predicted *polarons for polyacetylene are not observed in reality*. Whereas solitons originate from kink defects, polarons are charge defects and may occur in low density doping. For defects such as solitons or polarons, the dimerisation pattern varies slowly on the scale of the lattice constant and is described in the SSH model by an order parameter (different from the disorder concept discussed in section 2.6.1.1), $\tilde{u}$, defined as

$$\tilde{u} = (-1)^n u_n$$

,where u_n is the displacement of site n , corresponding to a particular carbon atom, on the chain. The spatial extent of a polaron is given by:

$$\frac{u}{u_0} = 1 - \frac{1}{\sqrt{2}} \left[\tanh \left(\frac{(x+x_0)}{\sqrt{2\xi}} \right) - \tanh \left(\frac{(x-x_0)}{\sqrt{2\xi}} \right) \right] \quad \text{where } \xi = 2t_0 a / \Delta_0$$

where x is the distance from the coordinate for the centre, x_0 , of the polaron. For a polaron, the form of the order parameter is that of a soliton-antisoliton pair, with one soliton charged and the other neutral, which explains why the polaron localises two levels in the energy gap. The two polaron levels due to the soliton-like lattice deformations, which would be at midgap for large x_0 , couple significantly and split into an upper level and a lower level in the energy gap (see Fig. 16). The extent of polarons in SSH theory is in line with the original theory by Frölich where small values of m^* , the effective mass, and α , lead to small, strongly lattice-coupled polarons.

One might ask whether doped polyacetylene is widely used as a cheap alternative to copper as an electrical conductor. The answer is no because, although the extrinsic material is highly conductive, the chemical doping of this material renders it relatively unstable over a very short period of time. Furthermore, doped polyacetylene is quite an intractable (insoluble and infusible) material and is, therefore, not attractive from a processing point of view. More stable and processible conducting polymers have been discovered, including PANI and polythiophene but their conductivities are lower.

2.3.4 The Adaptation of the SSH Model to Nondegenerate-Ground-State-Polymers

In 1981 Brazovski and Kirova²⁴ extended the SSH model to non-degenerate ground state (NDGS) polymers. NDGS polymers have a more complex structure than polyacetylene (non-degenerate ground state polymers can have several different π bands contributing to the band structure.) All conjugated polymers other than polyacetylene, including the ones in this thesis, are NDGS polymers with a lower degree of structural symmetry than polyacetylene. Examples of typical NDGS conjugated polymers include conducting polymers (e.g. chemically doped poly aniline and poly pyrole) and pristine light-emitting or fluorescent polymers like poly-phenylene vinylene and poly-fluorene. Polyacetylene and other conducting polymers do not fluoresce because²⁵ of the ordering of the B_u and A_g energy levels which means the transition is forbidden by symmetry. Fluorescent polymers may be rendered solution processible with appropriate side group functionalisation making them very attractive for electronic displays particularly large area displays.

For NDGS polymers the SSH predicts the stable excitations to be polarons and bipolarons and does not alter the predictions for polyacetylene. Addition of two electrons far removed from each other along the chain of a NDGS polymer results in two separate negative polarons (P-). If these P- meet, a single distortion called a bipolaron (BP- -) with two gap levels filled with four electrons is formed. Bipolarons are more likely to form at higher excitation densities and in well ordered systems. For NDGS polymers a bipolaron is usually more stable than two separated P- s. Polarons exist in all NDGS conjugated polymers at room temperature, even in the dark and without injection of charge, due to the presence of impurities and structural defects on the polymer chain.

Peierls distortion contributes exclusively to the formation of the bandgap polyacetylene. NDGS polymers contain larger monomers which result in a number of π bands with the highest occupied band being completely filled. They are semiconductors due to their inherent structure. For NDGS the extrinsic contribution, Δ_e , to the bandgap, 2Δ , is larger than the Peierls contribution, Δ_0 ²⁶ where $\Delta = \Delta_0 + \Delta_e$. In the SSH model

adapted for NDGS, Δ_e is related to the the electron – phonon coupling constant, λ , and the bandgap by a confinement parameter, γ , as follows:

$$\gamma = \frac{\Delta_e}{2\lambda\Delta}$$

The degree of nondegeneracy can be parametrized by the confinement parameter via an experimentally accessible ratio ω_0/Δ , where $2\omega_0$ is the separation of intra-bandgap polaron levels. For the polaron exciton (section 2.5) and the bipolaron²⁷:

$$\gamma = \frac{\frac{\omega_0}{\Delta} \sin^{-1}\left(\frac{\omega_0}{\Delta}\right)}{\sqrt{1 - \left(\frac{\omega_0}{\Delta}\right)^2}}$$

Clearly, when ω_0 is 0, then the gap 2Δ is reduced to the Peierls gap, so for the case of near degeneracy (Δ_e small) polarons levels are near the centre of the bandgap whereas strong breaking of degeneracy keeps them close to the band edges.

2.4 EXPERIMENTAL EVIDENCE FOR POLARONS AND BIPOLARONS

Photoinduced absorption (PA) is a very useful technique for studying excited states such as polarons²⁸. The technique involves exciting a film with a pump beam around the absorption maximum of the sample and then investigating the transmission of a probe beam at different wavelengths. In PA a positive peak in a $\Delta T/T$ versus probe wavelength plot is obtained for effective probe amplification or gain (due to photoluminescence) and a negative $\Delta T/T$ signifies probe intensity reduction due to photo-induced absorption. Both polarons and bipolarons have two levels in the gap but for the latter they are either both filled or both empty (see Fig. 16). Therefore, polarons have three absorption lines (two of same magnitude) whereas bipolarons have two which allows for differentiation between polarons and bipolarons using PA spectroscopy. For example for poly- pyrole (PPy), at low and high doping, there are three and then only two peaks observed⁶. Steady state PA carried out by Vardeny et al³⁰ shows only a few spins

left after microseconds (presumably due to remaining polarons) which is direct evidence for bipolarons. Improving the order of the material studied by annealing means that no photogenerated spins were detected. This indicates that polarons can exist at long times and in low concentration in samples in which defects and imperfections are sufficiently numerous to restrict polaron mobility and thus inhibit bipolaron formation. The observation of bipolarons in steady state PA experiments (signal obtained microseconds after illumination) characterised by two peaks, is by default evidence of polarons since bipolaron formation requires the presence of two like sign polarons. Also, the steady state PA and the photo-induced IRAV peaks are similar to the absorption and IRAV peaks of doped samples suggesting the same species are dominant in both cases. Indirectly, photoluminescence and UV-Vis spectroscopies also confirm the presence of polarons as vibronic features are revealed, consistent with the notion of localized polarons, and polaronic excitons and strong electron-lattice vibrational coupling.

2.4.1 Synopsis of SSH and Other Models

- The SSH model was developed for a single isolated chain of polyacetylene.
- For close-packed chains in a film, Takayama's continuum version where for energies close to the gap the energy varies smoothly within a narrow band.
- Single particle (*one-electron*) model neglecting onsite and inter-site electron-electron interaction.
- Electron-electron interaction is implicitly included via the order parameter which determines the strength of electron-phonon coupling.
- Predicts fundamental excitations to be solitons for polyacetylene and polarons for non-degenerate ground state conjugated polymers. As correlation effects are ignored reliable modeling of higher excited states is not possible.
- Disorder manifested by different electron-phonon coupling strengths for different conjugated segment lengths, may be included, in SSH models by using a Gaussian in the energy distribution function.
- The low dimensionality of all conjugated polymer structures dramatically influences the electronic states of these materials.

2.5 EXCITONS AND THE TRANSITIONS CONCERNING THEIR FORMATION AND SUBSEQUENT DECAY

Excitons are neutral excitations formed by the promotion of an electron from the highest occupied energy level to the lowest unoccupied energy level. The simplest to describe quantum mechanically is the excited Helium atom. Solutions for this 2-level system containing two electrons provide the two types of excitation possible in all energetically bound electron-hole type excitations. The different possible combinations of the electron spins may be described using arrows as follows:

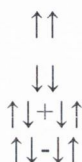


Fig. 17 Different possible combinations of parallel and anti parallel electron-hole spins

In Fig.17 the first three have symmetric wave functions and correspond to triplet states and the last one is antisymmetric and corresponds to a singlet state.

An exciton can be considered a Frenkel exciton if the e-h pair is confined to one molecular unit on a polymer chain or a Mott-Wannier exciton if it extends over several molecular units. Both of these are molecular in nature and in stark contrast with the Wannier exciton found in semiconductors which is part of the band picture and is not bound. Whereas excitons in small molecules are by definition Frenkel excitons, the question of which picture to adhere to for polymers will be discussed in section 2.6.1 but for now discussion will be confined to Frenkel excitons. Frenkel excitons or *polaron-excitons* form when oppositely charged polarons become electrostatically bound and are thus neutral and cannot carry current. Polaron-excitons are formed by combining oppositely charged polarons upon photoexcitation or, by injection of oppositely charged carriers, as in an organic LED. Bredas et al³¹ showed that for a NDGS conjugated polymer the polaron exciton is characterised by the aromatic rings becoming slightly quinoid. This means that the horizontal bonds shorten while the other bonds lengthen.

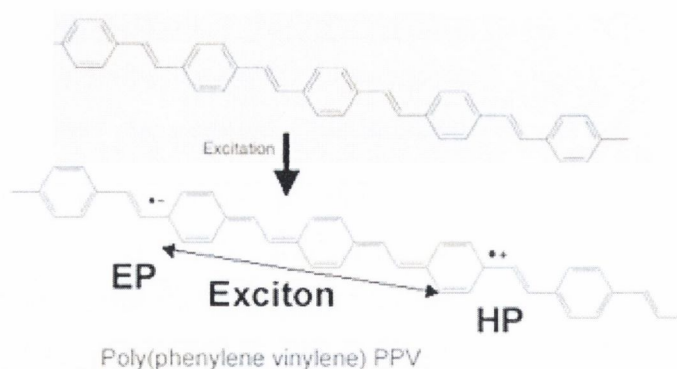


Fig. 18 Top: Ground state benzoid structure of PPV. Bottom: Quinoid exciton in PPV formed from an electron polaron (EP) and a hole polaron (HP). Note the same kind of orbital overlap seen in Fig. 9 for benzene will result in an electron cloud above and below the backbone plane of PPV and other conjugated polymers.

Singlet and triplet excitons differ in energy, in size and lifetime. Understanding the nature and energetics of the charged and neutral excitations in conjugated polymers is very important for designing materials for energy efficient organic devices.

The vibrational wavefunctions of the nuclei must be taken into account to describe the formation and decay of an exciton. Early theoretical description of chemical bonds used the notion of atoms joined by springs and indeed this serve as a basis for the interpretation of molecular vibrations. The potential function used in most Franck-Condon diagrams is that of the one-dimensional Morse oscillator whose eigenvalues are:

$$E_{vib} = hc\omega(v + \frac{1}{2}) - hc\omega x(v + \frac{1}{2})^2$$

, where x is the anharmonicity constant and is related to terms in the potential energy function (which reduces to that of the simple harmonic oscillator at $x = 0$.) The lowest energy is the zero point energy (not actually zero due to indeterminacy). These nuclear vibrations are associated with bond stretches in FTIR spectra.

The classification of molecules and MOs according to the symmetry elements¹ they possess is dealt with by group theory. A molecule possesses a symmetry element if the molecule's appearance as observed by a stationary observer, is invariant under a particular symmetry operation (e.g rotation about a given bond axis). Symmetry arguments may also be applied to AOs and MOs (for example π and π^* orbitals belong to the B_1 species). Since mathematical functions possess certain symmetry properties

we can choose these functions or products of these functions as a basis for symmetry operations. Integration of a function will return a zero result if the function does not serve as a basis for the totally symmetric irreducible representation of the point group to which it belongs. Since electronic transitions are described by the integrals of products of wavefunctions, knowledge of the symmetries of the initial and final state wavefunctions can tell us whether the transition is likely to be observed.

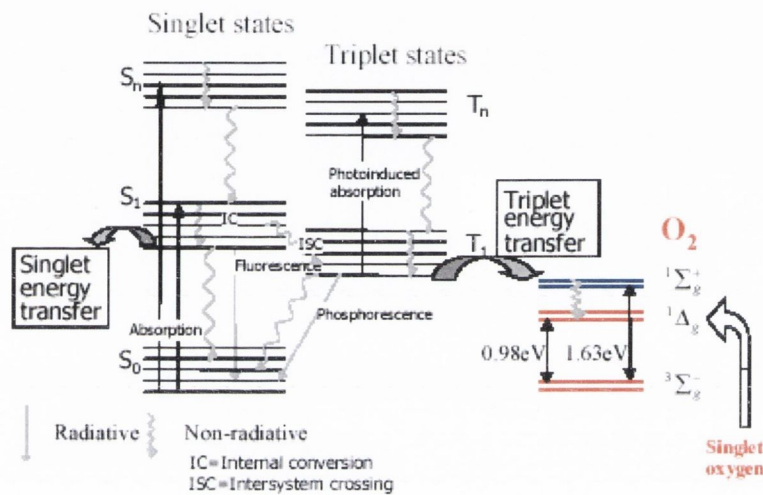


Fig. 19 Jablonski state diagram for a molecular system also showing energy levels for an oxygen molecule outside the system. Horizontal lines: energy levels of the S and T states (S on LHS and T on RHS to emphasise S and T possess different electronic spin configurations.) Note T₁ is at a lower energy than S₁, reflecting the effects of spin correlation. Further horizontal lines represent higher energy vibrational levels for each state. Wavy lines within a manifold of levels indicate vibrational relaxation.

Radiative transitions are ‘vertical’ transitions and involve a change in total energy of the molecule. Nonradiative transitions are ‘horizontal’ transitions involving conversion from one state to another state at constant energy. Nonradiative energy conversion between states of the same multiplicity is called internal conversion (IC) and for states of different multiplicity the term intersystem crossing (ISC) is used. IC and ISC (for S₁ – T₁ and T₁ – S₀) leave the molecule with excess vibrational energy which is dissipated by vibrational relaxation (i.e. interaction with surrounding molecules either in solution or solid state.) The main detractor from fluorescence quantum yield in the light-emitting polymers is quenching of singlet emission by energy transfer to non-emissive states.

2.5.1 Upward Transitions in Energy: Exciton Formation by Absorption

The strongest electromagnetic radiation-induced energy transition is when the electric component of the radiation (the E field) interacts with the electric dipole of the molecule. The one dimensional form of the Maxwell equation describing the space and time dependence of the electric field associated with electromagnetic radiation or a photon beam is:

$$\frac{\partial^2}{\partial x^2} E(x, t) = \epsilon_0 \mu_0 \frac{\partial^2}{\partial t^2} E(x, t)$$

where, ϵ_0 is the dielectric permittivity of free space and μ_0 is the permeability of free space. Upon exposure to the E field, the oscillating electric vector sets up an equivalent oscillation in the electron charge distribution when the oscillation frequency matches that corresponding to the difference in energy of two electronic levels as set by the angular momentum selection. Upon absorption of the photons in a beam by a material, the photons will exhibit the properties of a given quantum state. The absorption of a photon must conserve angular momentum. Thus, the energy transferred upon absorption can excite an electron in a molecule and this electron must exhibit the angular momentum possessed by the photon. Since the latter is fixed, this provides us with the basis of an angular momentum selection rule. That is to say, only electron transitions between states which differ by ± 1 in the orbital angular momentum quantum number will be possible. It should be noted that this only applies for excitation processes involving one photon. Lasers can be used to exploit multiphoton absorption processes in atoms and molecules. Examples of such exploitation include 3-D patterning using femtosecond lasers³², upconversion³³ and other processes.

The promotion of an electron from one level to another forms an electric dipole, which is defined as a pair of equal and opposite charges separated by a distance r and is characterized by the magnitude of the dipole moment μ where $\mu = qr$. This radiation-induced dipole moment called a transition dipole moment. In terms of the total Hamiltonian, light interaction may be viewed as a time dependent perturbation¹. Perturbation theory is a way of finding approximate solutions of the S.E. for complex molecular systems and is based not on separating wavefunctions into basis functions but rather on using a suitable model system whose wavefunctions and energies are known.

The *Hamiltonian*, H , of the real system is $H = H_0 + H'$, where H_0 is the zeroth order Hamiltonian, H' is a time dependent perturbation and the real wavefunctions are:

$$\psi_n = \psi_n^0 + \sum_m \frac{\langle \psi_n^0 | \hat{H}' | \psi_m^0 \rangle}{E_n^0 - E_m^0} \psi_m^0$$

where the term $m = n$ should be excluded. Perturbation theory, as will be evident later, is useful in situations where there is coupling between or mixing of states. The magnitude of the interaction is given by $\hat{H}' = \mu \cdot E$. A transition from a lower state ψ_m with energy E_m to a higher state ψ_n with energy E_n may be described mathematically using time dependent probabilities. It can be shown that the progress of the transition, given by P_n , the probability the molecule is in ψ_n depends on the time dependent Dirac integral called the transition matrix element which represents the extent of coupling of the two states ψ_m and ψ_n by the E field.

$$\frac{\partial}{\partial t} a_n = -\frac{i}{\hbar} \langle \psi_n | \hat{H}' | \psi_m \rangle$$

which can be rewritten another Dirac integral containing μ_x , called the transition dipole moment, such that $\mu_{xnm} = \langle \psi_n | \mu_x | \psi_m \rangle$. The probability of a transition is:

$$\frac{d}{dt} P_n \approx \frac{d}{dt} \left(\frac{4E_0(x)^2 |\mu_{xnm}|^2 \sin^2 \frac{1}{2} \Delta \omega t}{\hbar^2 \Delta \omega^2} \right)$$

Often a transition occurs to a manifold of levels as in a large molecule. For the manifold case, an energy integration of the product of P_n and the density of states results in an analogous expression for $d/dt P_n$ called Fermi's golden rule. Fermi's golden rule is used because in a large molecule there is a large number of closely spaced levels with energies corresponding to the excitation energy and also because there is always a spread of energies in the excitation beam. It can be shown that as the oscillating E field frequency approaches the transition frequency, the transition is more probable. Thus, P_n

depends on the square of the amplitude of the radiation field (which is related to the intensity of the radiation), and the square of the transition dipole moment. Obviously one can only have partial control over P_n as the transition dipole moment is an intrinsic property of the molecule. In the case of radiative transitions the scalar product of the E field and dipole moment vectors is the perturbative part of the Hamiltonian responsible for driving the transition whereas intramolecular interactions, responsible for the mixing of the zeroth order model wavefunctions, drive the nonradiative transitions between different quantum states.

2.5.2 Downward Transitions in Energy: Radiative Decay Routes

A radiative transition is termed fluorescence (~ns decay) if it originates from the de-excitation of an excited state that has the same multiplicity as the ground state. The emission is termed phosphorescence (μs – ms decay) if it originates in de-excitation of an excited state of different multiplicity to ground state (eg $T_1 - S_0$). Without significant ISC and phosphorescence, radiative emission from photoexcited conjugated materials is from an excited singlet state decaying to the ground singlet state. Though higher energy states exist, only the first excited states of S and T are relevant in this thesis. Crucially for full colour display applications, luminescence from $\pi \pi^*$ transitions in organic chromophores spans the whole visible range of the electromagnetic spectrum corresponding to wavelengths between 370 nm and 690 nm as per the human eye response function or photopic curve.

2.5.3 Allowed and Forbidden Electronic Transitions

Clearly the link between the nature of the molecular structure and the transition intensity lies in the transition dipole moment, μ_{nm} . However by inspection of the wave functions involved, it is relatively easy to determine if μ_{nm} will be zero or not¹. This can provide a basis for electric dipole transition selection rules. Transitions forbidden by certain selection rules may be weakly allowed in reality and may have small intensities in absorption spectra. The use of such selection rules is made possible by using the B-O

approximation and knowing the μ vector only operates on the electronic spatial (as opposed to spin) wavefunctions. Using the BO principle one can write:

$$\mu_{nm} = \langle \varphi_n | \mu | \varphi_m \rangle \langle \mathcal{S}_n | \mathcal{S}_m \rangle \langle \mathcal{A}_n | \mathcal{A}_m \rangle$$

Where the overlap integrals on the right of the equality are the electronic spatial, electron spin and nuclear (or vibrational) overlap integrals respectively. The nuclear overlap integral will always be non-zero, however, the first two integrals may be zero and may prevent the pure transition occurring. However, by mixing integrals a transition may be at least weakly allowed.

$\mu_{nm} = \langle \varphi_n | \mu | \varphi_m \rangle = 0$ implies a symmetry forbidden transition (at least one symmetry component vanishes¹).

$\langle \mathcal{S}_n | \mathcal{S}_m \rangle = 0$ implies a spin forbidden transition (e.g. S-T). S-O (spin-orbital) coupling, renders a spin-forbidden transition allowed. Discussion of the spin overlap integral is relatively straightforward as there are only 2 (spin up and spin down) wavefunctions for each electron. Given that most organic molecules possess paired outer electrons (closed shell configuration), S_m is most often a singlet spin function. If the original spin orientation is preserved upon electronic excitation, S_n will also be a singlet function of the same form as S_m . The spin overlap integral will then be 1 and so the transition is spin allowed. If the S_m is inverted upon electronic excitation, the spin overlap integral will be zero because of the overall wavefunction symmetry and the transition is spin forbidden. The same applies for T-T transitions.

$\langle \mathcal{S}_n | \mathcal{S}_m \rangle = 0$ but $\langle \varphi_n | \mu | \varphi_m \rangle$ and $\langle \mathcal{A}_n | \mathcal{A}_m \rangle$ couple which implies $\mu_{nm} \neq 0$ and the transition is weakly allowed due to the symmetry of the coupled wavefunction. Perturbation theory involving mixing of states can show how otherwise spin forbidden transitions occur. In this case the zeroth order wavefunctions are pure singlet or triplet wavefunctions and are mixed together by coupling of the spin and orbital angular momenta of the electrons. Where there is s-o coupling, the singlet state takes on some triplet character and vice versa and intensity in the allowed S-S transition is lost to the s-o coupled, weakly allowed S-T transition. The most important factor in determining the

extent of mixing and the intersystem crossing rate is the size of the spin-orbit coupling constant which determines the magnitude of the matrix coupling element. The s-o constant is proportional to Z^4 , (where Z is the atomic number) and the effect is therefore strongest when heavy atoms are present either in the molecule undergoing the transition (internal heavy atom effect) or in an adjacent molecule (external heavy atom effect.)

A symmetry forbidden transition may be vibronically allowed if there is simultaneous coupling of $\langle \varphi_n | \mu | \varphi_m \rangle$ and $\langle \mathcal{N}_n | \mathcal{N}_m \rangle$ (i.e. BO approximation not valid). This coupling is associated with a change in symmetry of the molecule upon excitation. The coupling which renders a transition vibronically allowed is again described using perturbation theory.

Not all final wavefunctions with the same symmetry as the initial state wavefunction will be final states owing to the probability of the transition ultimately depending on the magnitude of the Franck-Condon factor. The square of the nuclear (or vibrational) overlap integral, $|\langle \mathcal{N}_n | \mathcal{N}_m \rangle|^2$, is called the Franck-Condon (FC) factor and tells us which of the excited vibrational levels of the electronically excited state (vibronics) are most likely to be populated in the transition. A S-S transition in Fig. 20 is depicted as a vertical line based on the BO approximation. However, since the electron distribution is different after the transition with respect to that of the ground state, some redistribution of the nuclei is expected after the transition. This is the FC principle and in Fig. 20 is described for a non-specific diatomic molecule, using Morse-potential curves, where the potential energy curve for the electronically excited state is shown to be displaced to higher energy (potential) and to larger equilibrium internuclear separations with respect to the ground state, consistent with the promotion of an electron into an antibonding state. In the FC diagram the exciton corresponds by default, to a Frenkel exciton for a small molecule but may be applied to a conjugated polymer chain where there can be significant geometrical rearrangement. The fact that the excited state is created with additional vibrational (and rotational) energy has implications for the observed absorption and fluorescence spectra.

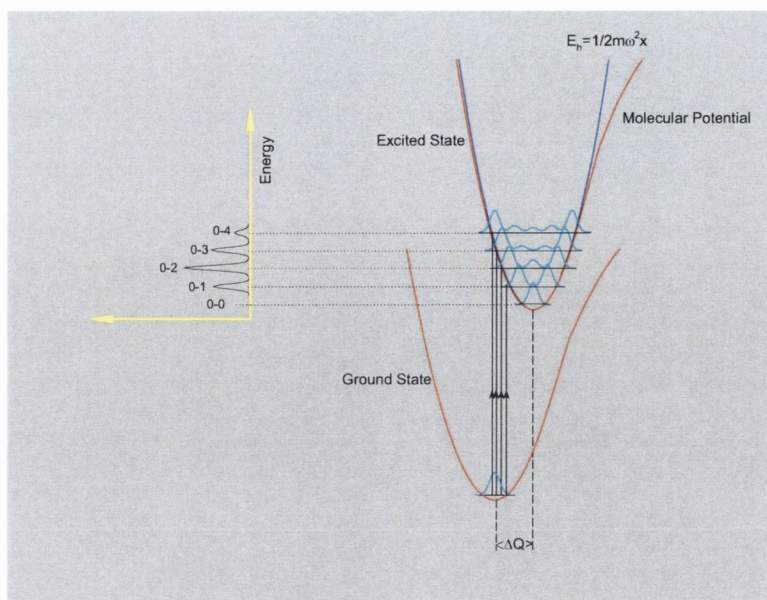


Fig. 20 Franck-Condon diagram for S_0 to S_1 absorption transitions.

For molecules with very similar ground and excited state geometries the F-C factor will be largest for the 0-0 transition (where the numbers refer to the levels of vibrational excitation in the ground and excited states). However, if these geometries are significantly different, the F-C factor is likely to be largest for a non 0-0 transition (0-2 for example). The magnitude of the various F-C factors for the various transitions is reflected in the absorption spectrum where the most dominant peaks correspond to transitions with the largest F-C factors. According to Siebrand's theory for non-radiative transitions, the F-C factor decreases rapidly with increasing energy difference between the vibrationless levels of the states involved, in agreement with IC being more dominant for S_2 - S_1 or S_3 - S_2 transitions than a S_1 - S_0 transition. Due to a small FC factor, the IC rate is a lot less than the fluorescence decay rate for S_1 - S_0 transitions.

For polyatomic molecules such as conjugated polymers, the ground and excited states have potential energy surfaces with many dimensions and many vibrational motions and as a result, the absorption profiles are quite featureless and are referred to as an F-C envelope. Features in the absorption spectrum are due to the vibronic structure in the excited state since separation of ground state and vibronic levels is less than kT at room temperature. Similar force (spring) constants in the excited and ground

states imply only a small distortion of the lattice represented by ΔQ (atomic displacement parameter). This means that, for a small increase in internuclear separation from the ground state configuration, the absorption and emission spectra resemble each other (with the 0-0 peak most intense), obeying the mirror symmetry rule.

Prompt fluorescence¹ (or simply fluorescence, is that due to singlet decay. There is also P type and E type *delayed* fluorescence. The P type involves triplet-triplet annihilation and, consequently, a high accumulation of triplets which causes the delay. E type fluorescence is thermally activated and depends on non-radiative excited triplet state processes. E type fluorescence occurs if vibrational levels of the S_1 and T_1 levels are very close in energy, facilitating reverse ISC.

2.5.4 The Origin of the Stokes Shift in Organic Chromophores

The red shifting of the fluorescence maximum from the absorption maximum is called the Stokes shift and, for small monodisperse molecules in very dilute solution of single molecules, is due to dissipation of vibrational energy to the solvent molecules. The FC principle means that excited molecules have vibrational energy initially, which may be lost by emission of IR radiation of frequency corresponding to the vibrational energy spacing. When this emission ceases, fluorescence or phosphorescence may occur. The energy spacings between vibrational levels are usually larger than the thermal energy kT , so one may assume the excited molecule relaxes to the lowest vibrational level prior to luminescence.

In thin films of conjugated polymers the Stokes shift is chiefly due to two contributions— structural and spectral relaxation.

Upon excitation the molecule relaxes structurally, having a different geometrical configuration (different internuclear separation distance) to that of the ground state (Fig. 18). The excitation couples to the lattice deformation, which leads to vibronic features, particularly in the PL and EL.

Conjugated polymers usually have a range of conjugation lengths and hence lattice coupling strengths for the associated polarons, which contributes to broadening of their absorption spectra. Upon excitation, vibrational relaxation to the lowest vibrational level in the excited state occurs with a time constant $\tau_{fc} \sim 0.1\text{ps}$ which is much faster than

the characteristic singlet decay for organic materials (0.1-1.0 ns). The fact that absorption samples all conjugation lengths and that internal conversion occurs faster than fluorescence, results in red shifted emission with a less broadened or ‘sharper’ emission peaks with more pronounced vibronic structure. This red-shifting of emission is called spectral relaxation. The vibrational levels are themselves broadened by rotational motion of the molecules though rotational energy levels are usually not depicted in Jablonski or FC diagrams. This type of broadening due to disorder is inhomogeneous whereas lifetime broadening of an electronic transition is homogeneous. The fact that Site Selective Fluorescence (SSF) experiments³⁴ demonstrate a red shift of emission spectrum with time on different timescales is evidence of exciton migration and of many conjugation lengths in the sample. This migration is more responsible than structural relaxation for the observed Stokes shift. Migration of excitons to low energy emission or quench sites (carbonyl generally) is dependent on sample crystallinity, conjugation length, and amount of interchain contact. Conventional chromophores spectrally relax but conjugated polymers have a major structural relaxation component in spectra also (e.g. quinoid form of PPV compared with benzenoid form).

Once the FC factor becomes non-zero, intensity is stolen from the 0-0 peak³⁵. This results from vibronic transitions due to lattice coupling, the extent of which is characterised by the Huang-Rhys parameter³⁶, S_i , as follows:

$$S_i = \frac{\frac{1}{2} M \omega_i^2 (\Delta Q_i)^2}{\hbar \omega_i}$$

,where M is the reduced mass for the vibrational mode Q_i , associated with the change, ΔQ_i , in equilibrium configuration coordinate between ground and excited state and ω_i is the phonon frequency. S_i can be experimentally obtained via the Stokes shift³⁷. A synopsis of electron-lattice coupling is:

1: A non-zero ΔQ is needed for a non-zero S

2: A dominant 0-0 peak means a small delta Q and weak e-phonon or e-lattice coupling (S small. An initially dominant 00 peak decreases as S increases.

3: Large S means hw small and therefore vibronic peaks easily smeared out by inhomogeneous broadening.

4: Short chains have higher S and longer chains have lower S and can reveal vibronic structure. Vibronic structure is more easily resolved if there is less energetic disorder also (i.e narrower distribution of chain or conjugated segment lengths). If this factor is X for small molecules then for a polymer the change in bond order is expected to be of order X/N where there are N atoms in polymer.

Polaronic excitation is a manifestation of lattice coupling, i.e. parts of the exciton (the oppositely charged polarons) are strongly coupled to the chain. Halliday *et al* have shown that the improved order in stretched films of PPV³⁸ and improved PPV containing fewer defects both result in much sharper vibronic features in the emission.

2.5.5 Quantifying Absorption and Fluorescence

Absorption of light by a material is described by the Beer Lambert law:

$$-\log(I/I_0) = A = \epsilon cl$$

where I_0 is the incident radiant intensity, I is the transmitted intensity, ϵ is the wavelength dependent decadic absorption coefficient, and A is the decadic absorbance. The absorption cross section, σ , can be thought of as the area a molecule presents to an incoming photon which, if hit by a photon, will lead to its absorption.

$$\sigma = \frac{10^3}{N_A} 2.3026\epsilon = 3.82356 \times 10^{-21} \epsilon$$

Where C is the concentration of absorbing material in units of molecule cm^{-3} and l is the path length in cm. Sigma has units of $\text{cm}^2/\text{molecule}$, often abbreviated to cm^2 .

A measure of the transition intensity or oscillator strength, f_{nm} , is obtained by integrating ϵ over the whole absorption feature $\mathcal{A}$, which is approximated as being a Lorentzian. f_{nm} is equal to $6.784 \times 10^{-9} \epsilon_{\max} \Gamma$, where Γ is the FWHM (full width half max) of the Lorentzian, and can be related to μ_{nm} , the transition dipole moment:

$$f_{nm} = 4.702 \times 10^{-7} \frac{1}{\lambda_{\max}} |\mu_{nm}|^2$$

Fluorescence or spontaneous emission is the random radiative decay of electronically excited molecules and follows first order kinetics:

$$-\frac{d}{dt}[M^*] = k_r^0 [M^*]$$

In other words, the decrease in M^* depends on the first power of $[M^*]$. The so-called natural lifetime, τ_r^0 of a radiative process is defined as the inverse of k_r^0 , the decay rate, and by integration one can see that in a time $t = \tau_r^0$, $[M^*]$ has fallen to $1/e$ of its initial value. k_r^0 is also denoted A_{nm} , the Einstein coefficient for spontaneous emission where n and m refer to the upper and lower levels of the transition respectively. The Strickler-Berg³⁹ relation states:

$$\tau_r^0 = \frac{1}{A_{nm}} = \frac{3.417 \times 10^8 \lambda_{\max}}{n^2 \mathcal{A}}$$

This approach to calculating τ_r^0 has been applied to conjugated polymers as well as inert polymer matrices doped with organic small molecule dyes⁴⁰. The measured decay rate coefficient, k_r , never equals the actual rate, k_r^0 , because additional processes including non-radiative ones like IC and ISC, contribute to the reduction in $[M^*]$.

$$-\frac{d}{dt}[M^*] = k_f^0 [M^*] + k_{ISC} [M^*] + k_{IC} [M^*]$$

k_f is the sum of the all decay rates and τ_f is the inverse of this sum so that τ_f always $< \tau_r^0$. In conjugated polymers, for example, significant non-radiative decay causes the measured lifetime to be shorter than the natural lifetime. Oxygen free PPV has the longest τ (1.2 ns) reported for PPV (film). This is because of the number of non-radiative routes decreases with oxygen removal.

For steady state sample illumination the fluorescence quantum yield, Φ_f , is:

$$\Phi_f = I_f / I_{abs} = \tau_f / \tau_0$$

Φ_f is often measured using known standards or an integrating sphere and experimentally measured values of τ_f and Φ_f can be used to calculate τ_f^0 which can then be compared with the theoretical/semi-empirical value of τ_f^0 based on Strickler-Berg equation. As for singlet fluorescence, the phosphorescence yield, Φ_p , based on triplet emission may be obtained. However, the excitation and emission beams are modulated to avoid fluorescence detection and, since molecular oxygen tends to interact with triplet excited states, experiments should be done in the absence of oxygen.

$$\Phi_p = \Phi_T \frac{\tau_p}{\tau_0}, \text{ where } \Phi_T = \Phi_{ISC}$$

Measurement of the absorbed light intensity and the integrated ESR (electron spin resonance) peak allows triplet yields to be obtained directly.

$$\Phi_T = t_f k_{ISC}$$

Since τ_f and Φ_T can be measured experimentally k_{ISC} can be easily calculated. Once k_{ISC} is known, k_{IC} can also be estimated from:

$$k_{IC} = \frac{1 - (\Phi_f + \Phi_T)}{\tau_f}$$

k_{IC} is typically too small to compete with fluorescence or ISC so that $\Phi_f + \Phi_T = 1$.

2.6 THE IMPORTANCE OF ELECTRON-ELECTRON INTERACTIONS IN MODELLING THE ELECTRONIC TRANSITIONS IN π -CONJUGATED POLYMERS.

Electrons in orbitals in any material will always try to interact by repelling one another due to coulombic effects. This repulsion will be greatest in a confined situation and its effects are in evidence in conjugated polymers. Electron-electron (e-e) repulsion and electron-hole (e-h) attraction can be viewed as being of the same origin and the effects of these interactions are often referred to as *correlation effects*⁴¹. Hund's rule and the energetic ordering of S and T are simple correlation effects - singlet and triplet excitons are no longer either of the same energy or of the same size since triplets are more localised. Shuai and Beljonne *et al*⁴² have shown for PPV and its oligomers that the triplet is stabilised by 0.65 eV with respect to the singlet. It is worth noting that if e-e interactions were too strong then semi-conducting polymers like PPV would be anti-ferromagnetic Mott insulators. Subtle correlations (qualitative failures of orbital theory) are typically seen in narrow bands, low dimensionality, and excited states – conjugated polymers having all three. Generally speaking, even parity singlets are lower in energy than odd with, for example, energies of 2.5 and 2.9 eV respectively for PPV. The former is a one-photon singlet (1_B) where as the latter is a two-photon singlet (2_A). The ordering is a subtle correlation and explains why light-emitting polymers fluoresce since daylight is intense enough to excite one-photon transitions (if the ordering was reversed laser light intensities would be required). So, in many respects fluorescence resulting from linear absorption is manifestation of a subtle correlation effect.

Inclusion of electron-electron interactions in essentially “non-interacting” one electron SSH-type Models through the electron-phonon coupling constant alone is only implicit and fails to describe many excitonic features in conducting polymers. Examples of these failures are that predicted absorption peak intensities differ from those observed experimentally for t-PA, for NDGS fluorescence is predicted to be at bipolaron separation levels (actually it is much higher in energy) and that all photoexcited states should decay radiatively. Non-radiative decay, which occurs to some extent in all conjugated

polymers, requires breaking of charge conjugation symmetry. This may be achieved by introducing e-e interaction terms into the Hamiltonian. Non-interacting π -electron models are, however, useful for comparing conjugated polymers with similar backbones.

In terms of modelling, going from uncorrelated (band) to correlated, e-e interactions or correlations may be switched on either by turning on a Hubbard potential, $V(R)$ or, by varying the transfer integral t discussed in section 2.3. This is analogous to controlling the binding energy, E_b . In practice variation of t is used as it is accessible experimentally via the optical bandgap of the polymer. Maki et al and Baeriswyl *et al*⁴³ calculated the effects of modifying U_0 in t-PA. Calculations of the effects of on-site and inter-site e-e interactions for strong lattice coupling predict PA absorption peak intensity ratios consistent with experiment. Weak coupling is sufficient to explain the asymmetric displacement of the levels.

Using a Peierls-Hubbard Hamiltonian, Shimoï showed,⁴⁴ for a NDGS polymer, that including e-e interactions renders two polarons more stable than a bipolaron. Long range Coulomb interactions (further than nearest neighbour) promote exciton formation in pristine polymers. Peierls-Hubbard models leave out these long range interactions but the Pariser-Parr-Pople (PPP) model includes them by using the Ohno potential. PPP models therefore account for both electron lattice and electron-electron interaction well. Modelling of higher energy excitations is only realistic in PPP type models. One can also use configuration interaction (CI) methods, where the geometry-optimised structure is used as an input for the calculations, to model the bandstructure of polymers. CI involves a general treatment of correlations and quantitative results are limited to small molecules for computational reasons. The UV absorption spectrum of, PPV can be described using CI⁴⁵ or PPP methods⁴⁶.

2.6.1 Use of the Band-Model Versus the Molecular Model for Interpreting the Nature of the Primary Excitations in π -Conjugated Polymers from Experimental Observations.

In the band model photoexcitation of a conjugated polymer produces weakly bound polaron pairs. Singlet polaron-excitons with large binding energy, E_b , are produced in the molecular model, where the molecular “model” or “picture” is based on the photophysics of fluorescent small molecules. Strong e-e interactions favour

formation of correlated electron-hole (e-h) pairs otherwise described as localised molecular-type excitons whereas weaker e-e interactions may be described better using a band model with an additional electron-phonon coupling parameter (e.g. the SSH model). In conjugated polymers both models have been used to explain many of the observed optical properties. Which model to use depends on the e-e interaction strength (characterized by E_b) relative to bandwidth and to electron-lattice interaction.

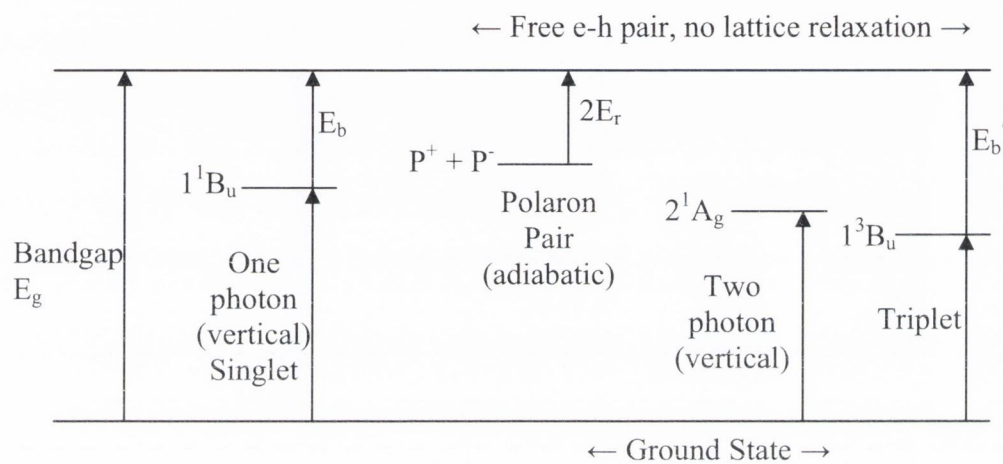


Fig. 21 Illustration of what is meant by the binding energy. Note the polaron pair is not connected to the ground state. The two-photon energy transition is shown for comparison. E_r is the polaron pair binding energy, E_b and E_b' are polaron-exciton binding energies.

Whether the primary excitations (e.g. by photo- or electro-excitation) are polaron pairs or bound neutral excitons is very important with respect to LEDs because the spin statistics are different in each case. If the lowest energy elementary excitations are bound excitons, EL efficiency can only reach a maximum of 25 % of the PL efficiency. This is due to simple spin statistical arguments considering the degeneracy of the singlet and triplet excited states. In the band model for electroluminescence (EL), singlet excitons are intermediates in the recombination of free P^+ and P^- injected at the electrodes in which case the maximum possible EL quantum efficiency can be 1 ('unity') or 100%. EL quantum yield > 25% requires a spin dependent singlet:triplet formation cross-section ratio in the presence of a spin dependent relaxation channel (see section 3.6.3.1). The limit of EL QY depends on the value of E_b .

2.6.1.1 Interpreting Experimental Results of conjugated polymers

For molecular crystals the argument in favour of a molecular excitonic model is based on XRD data which show molecular units rather than an extended system. The molecular model is also adopted, on account of small molecular size, for small molecules in sublimed thin films for SMOLEDS, where there is a lack of an extended band in the amorphous sublimed films. The different excitation energy thresholds for singlets and triplets in PPV etc resemble those for molecular solids like anthracene and suggest confined (molecular) excited states. Interestingly, however, much light-emitting conjugated polymer data may be interpreted using both models – a first example is the absorption lineshape for conjugated polymers. The Density of States (DOS) equation for a 1-dimensional DOS⁴⁷ similar to that expected to exist in a linear conjugated polymer is:

$$g(E)_{1D} dE = \frac{1}{\pi} \left(\frac{2m}{\hbar^2} \right)^{1/2} \sum_i \left(\frac{n_i H(E - E_i)}{(E - E_i)^{1/2}} \right) dE$$

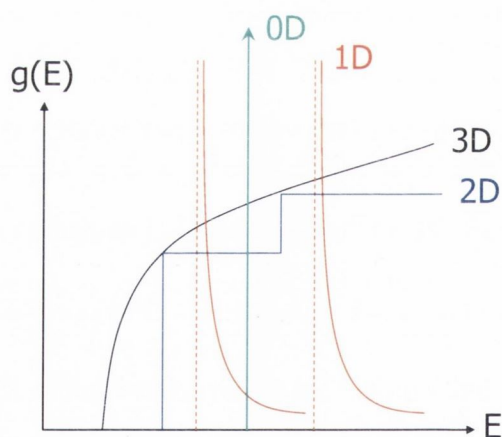


Fig. 22 Predicted DOS for 1, 2 and 3-dimensional systems.

A potential problem with using the band model (and why it is questioned for conjugated polymers) is that polydiacetylene (PDA) *crystals* are definitely excitonic⁴⁸ and display symmetric absorption and electroabsorption profiles. Conjugation is assumed to be similar in PDA *films* which also exhibit excitonic behaviour. Although disorder is partly

responsible for varying E_b values, it cannot be the primary reason since both PDA crystals and spin coated films give E_b of 0.5 eV. Because PDA is a conjugated material with strong e-e interactions, this behaviour could be assumed to be the same in other conjugated materials like PPVs. However, the fact PDA cannot be described by the band model provides merely a circumstantial reason for believing this approach is not applicable to other conjugated polymers like PPV. For example, although the structures are similar, the $1_B/2_A$ ordering is different in PDA to that in PPV.

In practice, in films of NDGS polymers the chains are believed to consist of a range of "conjugation lengths" (CL) separated by twists, kinks, meta-links etc., due to the chemical structure and the resultant chain-packing. The idea of CL contrasts with a delocalisation-based band model with thousands of untwisted repeat units. However, in conjugated polymers Van Der Waals contacts are indicative of weak inter-chain interactions, and π -electron delocalisation is restricted to one dimension and is associated with the backbone which contains thousands of repeat units, inherently demanding a band approach. In ordered, oriented MEH-PPV, which is actually a blend of MEH-PPV and PE which has been stretch-aligned⁴⁹, the CL is considerably longer than usual, making it a good sample to test the band model. Asymmetric linear absorption spectra of highly oriented MEH-PPV samples produced by stretch aligning polymer strands in thin films demonstrate that the observed asymmetry (square root singularity) is intrinsic to a 1-D semiconductor, implying the band model is applicable. One might expect asymmetry in lineshape to decrease with respect to the molecular model which uses a superposition of absorption spectra from a range of CL to explain the observed lineshape for oriented material. In fact it the asymmetry increases significantly. From the band model point of view, the ordered material is expected to exhibit a 1-d lineshape and disorder is expected to suppress the perfect 1-d square root singularity and make the absorption lineshape more symmetric. So the intrinsic lineshape of these materials should be based on oriented samples like this in which the lineshape is well characterized by a square root singularity inhomogeneously broadened and rounded only slightly by a small degree of disorder. Furthermore, trying to apply a superposition of Lorentzian or Gaussian lineshapes corresponding to different CL to explain the oriented sample spectra means using a disproportionate number of short segments.⁵⁰ Fits to the linear absorption using

the SSH model for oriented PPV are very good and suggest that fundamentally the exciton model can only be consistent in the weak binding limit.

It must be stated that for unaligned thin films there is much evidence for the existence of CL. Conjugation length is defined as the length of a chain over which there is no interruption of conjugation due to defects or severe out-of-plane twisting of the chain. The energy of an exciton on a chain is, therefore, dependent on the conjugation length on which it resides. Broad linear absorption and narrow fluorescence point to energy transfer to long segments in PPV. This implies that a range of conjugation lengths (CL) is present in the material. The disorder associated with flexible segments resembles more traditional non-conjugated polymers. Generally speaking, experiments are performed on films (rather than extended chains) where conformational degrees of freedom generate short conjugation lengths. Thus, finite segments account for the photophysics of PPV and its derivatives where 5-10 phenyl rings become the “molecular units” forming long flexible strands that comprise the backbone. Site-selective fluorescence (SSF) experiments also support the common held view of a molecular exciton in conjugated polymers³⁴. Singlet excitons can inter-site hop by tunneling or Förster transfer of energy. All excitons are mobile and theory suggests excitons migrate to long chain segments which have smaller gaps and lower energy excited states. These may then decay radiatively. In SSF experiments³⁴, the existence of a localisation threshold in a plot of 0-0 emission peak energy versus excitation energy has been interpreted as being due to a CL distribution in PPV – below the threshold the emission is excitation energy dependent since excitons do not have enough energy to hop to lower energy sites. Vibronic structure in absorption and emission spectra is also evidence of a confined molecular picture or CL picture since the Huang-Rhys parameter implies there is stronger lattice coupling associated with confined excitations. Vibronic features could not be observed in the absorption and emission spectra of conjugated polymers if the equilibrium positions of ground and excited states were identical. These features oppose the notion of a truly delocalised band picture.

Since Electroabsorption (EA) is a third order NLO (nonlinear optical) process, and since χ_3 depends strongly on localization length (or conjugation length), EA preferentially probes the longest segments presumably since longer segments will have

greater polarizability. EA as such is particularly useful as it naturally focuses on the more intrinsic electronic properties of a pristine polymer. In this regard, EA is best used to analyse oriented polymers. Identical linear absorption and EA onsets point to long segments in oriented PPV dominating both spectra. The fact that the EA lineshape follows the first derivative of the absorption (as it does in PDA in which excitons are the fundamental excitation) is not necessarily proof of the exciton model being applicable since this relationship is in fact well explained by perturbation theory. Considering the relative peak intensities in the EA spectra is also of interest. The EA max:min peak intensity ratio is asymmetric for ordered MEH-PPV (3:1) but is (1:1) for PDA. It has been shown 3:1 is inconsistent with excitonic absorption. The EA spectrum of MEH-PPV was quantitatively fitted with band theory by Pakbaz et al. Using SSH theory for highly oriented MEH-PPV, the parameters extracted from the fitted data were used to show that excited state wavefunctions are delocalized over at least 400 Å (about 50 unit cells)

Photoconductivity experiments may also be interpreted using both models. Since the energy gap measured from the onset of absorption is the *relaxed* gap, the single particle energy gap is given by adding the binding energy to this value. The difference between absorption and photoconductivity (PC) onsets for PDA and PPV is notable. The offset of these points is 0.5 eV for PDA but is coincidental for PPV, suggesting a very much smaller E_b within the molecular model for the latter since PC requires free carriers whereas excitons are bound⁵¹. In the molecular model, charge generation must be seen as a secondary process, preceded by direct exciton formation. In the band model mobile carriers are directly photogenerated and so photoconductivity (PC) is viewed as a primary process, not an artifact.

In the context of steady state PC onset coincidence with absorption it is interesting that, using DeVore's analysis⁵² (which assumes every photon absorbed creates a pair of charge carriers (i.e. charge carriers are primary photoexcitations), the PC response calculated from the absorption profile agrees well with PC experimental data, in support of the band model. Based on the molecular model, the energy dependence of the PC response should match the thin-film absorption. This, however, is not seen for MEH-PPV where both steady state and transient (ps) PC onsets coincide with the optical

absorption onset, implying a small E_b (<0.1 eV), in favour of the band model. The fast transient photocurrent is temperature independent and is linearly proportional to the external electric field. These facts mean the quantum efficiency of carrier generation is independent of temperature and electric field. Also, because the fast transient is linearly proportional to light intensity, carrier generation efficiency is independent of the level of excitation. The sharp rise-time for PC (nano-pico-seconds after photoexcitation) and the fact that photo-induced charge transfer studies⁵³ of PPV- C_{60} mixtures occur on a femtosecond indicate very easy, fast electron-hole separation. The remarkable temperature independent sensitization of PC by C_{60} seen in transient PA studies implies that initial photo-excitations are mobile, charged polarons and sets an upper limit of E_b of less than kT even at 100 K. These facts all point to a first order carrier generation process that cannot be attributed to interactions between excitations and strongly demonstrates neutral polaron-excitons are not the primary excitation for MEH-PPV. Other reports also suggest this is the case for polyfluorene.⁵⁴

Disorder in PC (photoconductivity) data is manifested by the existence of a threshold⁵⁰ energy E_t below which a modulated steady state PC decreases faster with chopping frequency than above it. This threshold probably corresponds to a mobility edge separating localized states from extended states. Below the edge, activated mobility of localized carriers leads to a slower response. This threshold agrees with Rauscher's localization threshold. The PC data show no dependence⁵⁰ of activation energy on excitation energy in contradiction with Onsager theory, exciton dissociation and the molecular model. Although disorder limits the mobility, it does not dominate the threshold for charge generation which is decided by the E_b . In the band model, $E_b \ll E_{opt}$ and the absorption leading edge essentially determines the carrier- generation threshold. In the molecular model⁵⁰ used in Rauscher's SSF experiments, the lower energy sites below the threshold are associated with longer conjugation lengths and less localisation. In the band model states below the mobility edge in the PC data are more localized. Despite different interpretation, the threshold energy is equal in the PC and SSF experiments, allowing the PC data to be interpreted by either the exciton or band model.

Field dependent photoconductivity and photoluminescence data can be interpreted with either model too. The transient PC is linear for fast transients up to $E = 10^5$ V/cm

but above this is nonlinear. The crossover point from a linear to a nonlinear regime depends on the degree of chain alignment (i.e structural disorder or sample quality). The better the chain alignment, the sooner the response goes nonlinear. At low T (77 K) measurements were done with respect to field-quenched PL (photoluminescence) and PC (photoconductivity) nonlinear onsets for a conjugated polymer. In the exciton model a linear relation between the changing photocurrent and PL intensities should exist but this is not so⁵⁰. Not only are onsets different, above the onset values the PC response is sublinear with respect to the PL quenching. This is contrary to expectations from the molecular model as it indicates that field-induced carrier generation is not significant – i.e. quantum efficiency of carrier generation is quite independent of electric field (E) even in the nonlinear range. This again suggests that these high field effects are best explained using the band model. It is important to distinguish between generation and subsequent transport. The reasons for the threshold are transport rather than generation related. The nonlinearity in the data is essentially obeying a nonlinear transport equation which may be due to field-assisted detrapping, for example.

The relatively low field required for the onset of PL quenching is consistent with a weak E_b . Estimates for E_b based on this onset and the spatial extent of the exciton in PPV, yield values of the order of kT (at room temp) i.e. approx 2×10^{-2} eV, in favour of the band model. Field-induced quenching of PL is a general phenomenon and not necessarily indicative of exciton dissociation by an electric field. Injected carriers may also act to quench PL. Indeed, as field increases, there may be more of these. Steady state illumination can also cause PL quenching due to photogeneration of charge carriers. Deusen *et al*⁵⁵ state PL quenching in blends under forward bias was higher than under reverse bias at the same field. This is correlated with the higher photocurrent in forward bias than reverse bias. In the weak binding limit, for times less than 50 ps after photogeneration, a mobility value of 2×10^{-2} cm²/Vs was obtained which is reasonable given that pre-trapping transport is dominant. This value is higher than time-of flight data and appears more consistent with the value of 5 cm²/Vs reported by Virgili *et al*, derived from an optically determined Langevin recombination rate constant⁵⁴.

The PL quenching data is consistent with the band model and electric field induced quenching of PL from mobile polaron-pairs.

2.6.2 Binding Energy Synopsis

Unfortunately, similar to the range of values seen in the literature for singlet exciton yields in PLEDs (section 3.6.3.1) a wide range in singlet exciton binding energies of LEPs has also been reported ($kT - 1 \text{ eV}$)⁵⁶. E_b values have been obtained from a wide range of experiments including internal photoemission in LEDs, electroabsorption and absorption, ultraviolet photoemission spectroscopy, light-emitting electrochemical cell measurements, photoinduced absorption, nanosecond photoconductivity, and electrochemical doping as well as theoretical calculations. The experimental challenge is to obtain accurate results that distinguish clearly between the band gap, polaron pairs, and the exciton. If E_b is much larger than kT and the disorder-induced band-tailing, bound excitons would then be stable. On the other hand, if E_b is less than or comparable to kT and the disorder-induced band tailing, then excitons would not form, rather polaron pairs would be stable. The band and the exciton models are not conceptually different: the issue that must be resolved is the strength of the binding energy relative to the single particle continuum (the LUMO or lowest unoccupied molecular orbital band). Referring to Fig. 21, relaxation is important in defining what one means by the energy gap. In order conclusively to prove the existence of excitons, one needs accurate knowledge of E_b and E_g values. It is possible that from coincidence of good clear experimental data from photoconductivity, absorption and EA experiments, one can be confident in singlet E_b values for some materials.

Triplet state identification was confirmed using photoinduced absorption (PA), for PPV, by Wei *et al*⁵⁷. Bipolarons are the other sub gap peaks that have been identified. Sometimes only the T-T* transition sub-gap peak is seen and its lineshape is asymmetric in oriented samples. The T-T* absorption signal is polarized parallel to the chain axis meaning it is an intrachain excitation which is intrinsic and well defined. Although, as evidenced from the foregoing, there is controversy over the value of the singlet binding energy, triplets are well understood as bound e-h pairs. A large triplet binding energy means a stable triplet which gives plenty of time for intersystem crossing to occur. Although the dynamics of triplet state formation are not well established, the intersystem

crossing time is, however, expected to be slower than 1 ns. This is the case for polythiophene which has heavier atoms in the molecular structure than PPV and therefore exhibits more spin-orbit coupling than PPV.

Data for ordered MEH-PPV suggests that mobile charge carriers (charged polarons) are the primary photoexcitations in the MEH-PPV poly-arylene vinylene (PPV) family. However, disorder induced localization in conjugated polymers can cause a conjugated polymer to exhibit more molecular type behaviour. So, clearly disorder does have important effects in both the band and molecular interpretations. In conjugated polymer films there is, typically, sufficient resolution to assign spectra but not definitively so. Finite conjugation lengths and variable environments should be considered in any analysis since these variables offer adjustable parameters that produce deceptively accurate fits. Heeger points out⁵⁰ that, since some results have been interpreted (e.g. SSF) using either a band or molecular model, it is unwise to assume that a certain experimental result for a given polymer is proof positive of the suitability of either model.

2.7 INTERMOLECULAR ENERGY TRANSFER

Radiative energy transfer simply requires that the emission of one excited molecule overlaps the absorption of another. Nonradiative energy transfer can be either coulombic or electron-exchange energy transfer. Non-radiative energy transfer may be thought of as a nonradiative transition in a single (M^*Q) super molecule so that much of the non radiative theory already alluded to for single molecules still applies here. The interaction Hamiltonian may be split into two parts: $H = H_c + H_{ee}$ which exert influences at different intermolecular distances.

Coulombic energy transfer is dominated by long range dipole-dipole interactions which cause mutual perturbations of the electronic structures of the energy donor and acceptor. Via the electromagnetic fields of the molecules, a dipole oscillation of M^* may introduce a corresponding oscillation in Q . This process may occur at intermolecular separations up to 100 Å and in this mode, an electron on M^* will remain on the the deexcited M . Here we focus on the coulombic part of the interaction

Hamiltonian, H_c . The excited electron in the HOMO of M^* can excite an electron from the HOMO of Q into the LUMO of Q provided the latter is not of a greater energy than the HOMO of M^* . Looking at H_{nm} (electronic coupling matrix element) for the process, it can be represented by β_e which is given by:

$$\beta_e = \frac{\mu_M \mu_Q}{r^3}$$

Where μ_m and μ_q are the dipole moments of M^* and Q and r is the distance between M^* and Q , Forster identified these quantities with the transition dipole moments $M-M^*$ and $Q-Q^*$ and related them to experimentally accessible quantities such as τ_r .

$$K_{D \rightarrow A} = \frac{3f}{64\pi^5 \tau_{nat}^d R^6} \int_0^\infty \frac{E_F^d(\lambda) \sigma_{abs}^a(\lambda) \lambda^4}{n^4(\lambda)} d\lambda$$

where $E_F^d(\lambda)$ is the fluorescence quantum distribution spectrum for the donor, σ_{abs}^a is the acceptor absorption spectrum, $n(\lambda)$ is the refractive index of the environment, f is an orientation factor, equal to $2/3$ for randomly orientated species, and τ_{nat}^d is the natural lifetime of the donor species.

$$K_{D \rightarrow A} = \frac{1}{\tau_D} \left(\frac{R_o}{R} \right)^6$$

where the Forster radius, R_o , is given by:

$$R_o = \left[\frac{3f}{64\pi^5} \int_0^\infty \frac{E_F^d(\lambda) \sigma_{abs}^a(\lambda) \lambda^4}{n^4(\lambda)} d\lambda \right]^{1/6}$$

The spin selection rules which apply are those that apply to the individual molecules i.e. multiplicity changes are forbidden.

In the case of short range energy transfer, the H_{ee} term is relevant and involves the physical transfer of electrons from energy donor to energy acceptor and is described using Dexter's electron-exchange theory⁵⁹.

$$\frac{d}{dt}P_n = \frac{2\pi}{\hbar} Z^2 J$$

Where Z is just a parameter found to behave as:

$$Z^2 \propto e^{-2r/l}$$

In contrast to Forster transfer, electron exchange energy transfer requires much closer contact (6- 20 Å) between M^* and Q since overlap of orbitals is required to facilitate the electron transfer mechanism.

2.7.1 Excimers and Exciplexes

An excimer is an excited dimer and is only stable in an electronically excited state, owing to the mutual repulsion felt by both molecules at small intermolecular separation. Excimers may form in concentrated organic solutions containing excited molecules or in thin solid films containing excited molecules. The absence of a bound ground state means that emission must lead to dissociation of the complex. All the photophysical processes already described also occur for excimers. Excimer emission is structureless because the FC envelope now includes a multitude of levels associated with the low-frequency vibrations of the excimer. Also, it is always red-shifted with respect to that of the monomer. Excimer formation represents a form of quenching since the emission intensity from free M^* is reduced. Accordingly, excimer quenching is often referred to as concentration quenching. It is worth noting that excimers may also be formed by triplet-triplet annihilation, resulting in excimer fluorescence, introduced earlier as p-type delayed fluorescence. An excimer is thus the result of emitter-emitter interaction.

An exciplex is an excited complex, differs from an excimer in that the two molecules are different. It differs also insofar as a degree of electron transfer is involved in exciplex formation, but not in excimer formation. In common with excimers, exciplexes have no bound ground state. If the electron migrates between the two components there is a charge transfer resonance and if there is complete charge transfer then an ion pair exciplex is formed. An exciplex could form in a PLED between for example an emissive hole transporter (HT) molecule, as many amine-based HTs are, and the desired emitter. The best way to avoid excimers and exciplexes is to keep molecules with similar energy levels well separated or, if two emitting moieties exist in a single molecule, to keep them well separated or reduce the overlap of their absorption and emission spectra.

2.7.1.1 Emissive and Non-emissive Inter-chain Excitations in π -Conjugated Polymers

Because of the S-T branching ratio argument whereby $EL_{\max} = PL/4$, the photophysics and factors which limit ϕ_{PL} are of interest. The latter should be referred to as a quantum yield rather than a quantum efficiency as it is likely to vary for different batches of the same material. ϕ_{PL} is wavelength dependent and yet at the different excitation wavelengths the PL decay is similar. This suggests that excited species other than intrachain singlet excitons are formed upon photoexcitation and, thereby, offering non-radiative decay routes. These routes are due to the existence of long-lived polaron type carriers which, in turn, are more likely to quench intrachain polaronic excitons. More evidence of interchain interaction is that ϕ_{PL} decreases due to non-emissive polaron pairs as concentration increases. Also, at a given concentration, increases in conjugation length are also associated with reduced ϕ_{PL} , probably due to chain-folding. Generally speaking, one might conclude that a long-lived photoinduced absorption (PA) species and a concentration-dependent PL yield point towards interchain species.

2.7.2 Polaron Pairs, Excimers, and Aggregates in Conjugated Polymers

Bound polaron pairs are considered as bound coulomb charges on adjacent chains which are formed by separation of hot intrachain singlet excitons on a subpicosecond timescale and which recombine geminately. The wavefunction overlap of negative and positive polarons in the pair is very poor so that radiative recombination is extremely improbable (the transition dipole moment, therefore, is small and the likelihood of a transition also small). Polaron pairs are also variously referred to as excimers, CT excitons or indirect excitons. However, the terminology chosen here is for polaron pair to refer to a non-radiative species and excimer to refer to a species which may be radiative or non-radiative. The term polaron pair was first introduced in 1992 by Frankevich et al and later by Rothberg et al⁶⁰. A separated polaron pair is one where the coulombic attraction is reduced with respect to a polaron pair for adjacent chains but is still greater than kT (otherwise there would be free polarons).

Initial evidence of aggregates/excimers can be obtained from film and concentration-dependent solution absorption spectra and photoluminescence spectra. Both excimers and aggregates have broad emission but the aggregates may show some phonon structure because of ground state stability. Using the term excimer, as opposed to exciplex, implies that two identical (in practice, at least, very similar) conjugation lengths are facing each other. Excimers are formed by resonant Förster energy transfer from one chain to another. For excimers to decay radiatively there must be good overlap between adjacent chains. For this, a relatively small Förster radius or, in other words, close interchain spacing (3 – 4 nm) is required. The Förster transfer is usually irreversible in organics. An excimer, typically, has a lower emission energy maximum than the isolated exciton. Aggregates differ from excimers in that they have stable ground states which implies stronger interchain coupling. Whether excimer or aggregate emission is seen can often just be sample dependent. Focus in this chapter will be on polaron pairs (non-radiative) and excimers (emissive) because PPV and MEH-PPV do not form aggregates with lower excited state energy than isolated chain segments.

2.7.2.1 Evidence for Non-Radiative Polaron Pairs

In picosecond transient pump probe experiments, the calculated amplification due to stimulated emission is less than that expected. This is due to PA by an excited state species characterised by a peak in the n-IR for PPV. The species in the n-IR has different decay dynamics (longer lifetime) to the stimulated emission for a solid film, suggesting it is not associated with the singlet exciton. For MEH-PPV it has been shown that the negative peak in the PA spectrum increases on going from solution to solid blend to homogeneous thin film, linking the excited state absorption with chain-packing or interchain-spacing. Broadening in PA spectra due to polaron pairs is not only due to disorder but also to the opposing polarons in the pair moving away to a position where they vibrate in their potential wells which are shallow and quite broad. Broadening is also due to separated pairs.

The PL for MEH-PPV has similar decay times in solution and film. In fact, ϕ_{PL} in solution is much higher than for film and this suggests another, different, non-radiative excited state species also exists in the film.

For Rothberg's study of PPV which is definitely well described by the molecular model with intrachain excitons, he assigns this species to non-emissive polaron pairs⁶⁰ which have a quantum yield formation of 0.9. Mizes and Conwell have calculated the PA for interchain polaron pairs which supports Rothberg's data⁵⁰.

2.7.2.2 Consideration of Other Species Contributing to Non-radiative Decay

If polarons are, in fact, the other excitation aside from the singlet exciton, and they are the main species contributing to non-radiative decay, one might expect to find incident light polarizaton (with respect to polymer axis) dependence for photocurrent and PA measurements. This is not however the case. One would also expect the PA feature to have a bimolecular decay which is not the case either. Furthermore, the excitations observed in solid state PA measurements, do not occur in dilute solution where there is very little inter-chain interaction.

Separated pairs can be seen in PLODMR – indicating the presence of polaron pairs. Evidence for separated pairs comes from the magnetic field dependence of PC and PLODMR signals (time scale μs – ms).

If the *other* excitations are bipolarons, one might expect a long formation time which was not seen. Since triplets do not absorb at 0.5 eV (the peak seen in the PA) combined with the observations just discussed, it is reasonable to assume the PA signal is due to polaron pairs.

Rothberg et al concluded that the singlet quantum yield is just 0.1 whereas Greenham *et al* conclude a very high singlet quantum yield of almost 1 based on ϕ_{PL} of 0.27 for their PPV. The fact that their PL yield calculations do not take into account self-absorption is not enough to make Rothberg's analysis⁶⁰ acceptable. Such a yield of non-emissive excited state species in Rothberg's case cannot explain a high PL yield in other PPV samples like Greenham's. For PPV, there is no evidence for *emission due to interchain species*⁵⁰ (i.e. excimer emission). For example, PPV oligomers, after 6-7 monomers, the PL stops decreasing in energy and the PL of the oligomers in solution is the same as that seen for PPV thin films. This indicates that intrachain excitons are responsible for emission in PPV films. The lifetime and other exciton parameters obtained using the Strickler-Berg relationship also suggests that emission is intrachain.⁴⁰ The behaviour of PPV means that an excited state formed by intermolecular energy transfer, probably non-emissive polaron pairs, is only responsible for *reducing* the intrachain singlet emission. The short lifetimes of around 1 ns for PPV would tend to support the notion of intrachain exciton decay. It is generally assumed that there *are*, however, excimers in stretch aligned crystalline PPV (interchain spacing of 0.34 nm) and MEH-PPV. Emission due to aggregates is ruled out on account of the long radiative lifetimes (aggregates would have short lifetimes due to the good ground state coupling).

2.7.2.3 Excimer Emission in PPV-type Polymers.

Time-resolved work must be done for a range of excitation and emission wavelengths in order to help separately identify migration of excitations and their decay.

From studies of fluorescence lifetimes and PL quantum yields, Samuel et al find that, for cyano-PPV (CN PPV), the high PL quantum yield in solid state is due to excimer emission and reduced non-radiative decay rates. They⁶¹ have shown CNPPV exhibits long-lived, unstructured emission and have assigned it to excimers with emission lower in energy than the intrachain exciton emission.

The reason non-radiative decay is reduced in CN-PPV is probably due to the excimer being less mobile than an intra-chain exciton. CN-PPV solution lifetime is 1.7 ns but 16 ns in film. Clearly CN-PPV is intra-chain in solution but inter-chain in solid film. Long radiative times are characteristic of excimers since the transition from excimer to ground state is usually forbidden by symmetry. The fact that excimer emission can be observed, means an alternative view to Rothberg's must be that recombination involving a polaron pair can be expected to be non-radiative in most cases but that emission from polaron pairs is possible. Also the PLQY is higher in film than in solution – in general for LEPs the opposite is seen due to exciton migration to quench sites. This implies an emissive inter-chain species exists, where the inter-chain exciton mobility must be low due to (the presence of) excimer or dimer regions where excitons are stopped before they can reach non-radiative decay sites. The inter-chain radiative decay oscillator strength will be less. However, the yield may be high since although the radiative rate constant is reduced, the non-radiative rate constant is reduced even more. Friend et al⁵⁰ use the term “inter-chain exciton” when discussing CN-PPV rather than “excimer” or “polaron pair” because the latter two terms are frequently associated with non-emissive species.

Identifying the emissive species in MEH-PPV is less clear cut than for PPV or CN-PPV⁵⁰. MEH-PPV solution excited at 560 nm (low energy side of absorption) has a lifetime of 0.9 ns, similar to PPV solutions and films, but MEH-PPV film has a lifetime of 5.8 ns which lies between that for PPV and CN-PPV. Clearly, MEH-PPV is intra-chain in solution but in solid state some aspects of PL can be explained by inter-chain (excimer) and some by intra-chain (vibronic structure) emission.

Monte-Carlo cooling algorithms yield the approximate spacing of polymer chains in a layer (chains side by side) – the larger spacing for MEH-PPV (0.41 nm) than CN-PPV (.34 nm) implies poor overlap and, therefore, longer radiative lifetimes in

MEH-PPV than CN-PPV. Since they are so long, the non radiative decay is more likely a de-excitation route for excimers in MEH-PPV. Based on overlap probability as a result of interchain spacing, excimer emission in MEH-PPV is about 20 times less than for CN- PPV. Since the lifetime is 16 ns for CN-PPV, this means that the interchain excitations in MEH-PPV are likely to be non-emissive polaron pairs.

2.7.2.4 Tackling the Problem of Non-Emissive Polaron Pairs

Knowledge and control of interchain interactions⁶² is very important. Pressure dependent PL may be a way to study change from intra to inter molecular excitation (shown for PPV already.) Blends are another way of studying inter-chain interactions. PPV in polycarbonate shows improvements in PL yield with respect to the pure film.⁶³ The development of polymers like CN-PPV where excimer or aggregate emission is efficient is one way to circumvent the problem of non emissive polaron pairs, which have been identified in PPV. This requires materials with immobilized interchain species and good overlap of chains. Alternatively, focus should be on eliminating interchain species altogether by drastically reducing close chain packing. In this regard poor interchain registry (e.g. using photophysically inert norbornene:PPV copolymer) has been achieved using short conjugation lengths and using rotaxanes. Rotaxanes, however, might have the disadvantage that operating voltage would increase due to reduced film mobility.

2.7.3 Synopsis of Interchain Interactions in Conjugated Polymers

Reported values for ϕ_{pl} for films of CN-PPV, PPV and MEH-PPV are 0.27, .35 - .46, .1-.15, respectively, which means that MEH-PPV suffers most from non-radiative decay routes, most of which are considered to be due to interchain interaction.

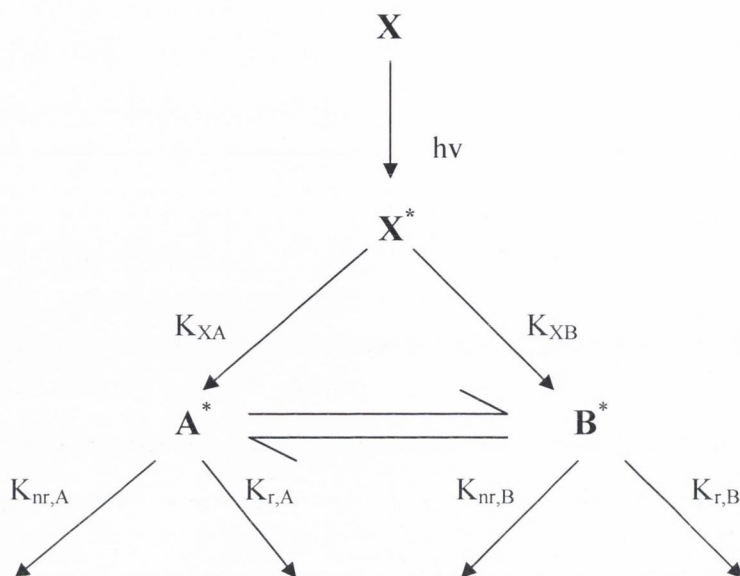


Fig. 23. General scheme for radiative and non-radiative decay of an excited species in a conjugated polymer. A^* and B^* represent an intrachain and an inter-chain excitation respectively. X^* is the initially excited state. K denotes the first order rate constant for the transitions indicated by the lines between the relevant species. The arrows leaving A^* and B^* represent radiative and non-radiative routes (characterised again by the route rate constant) back to X , the ground state. k_{BA} is expected to be small compared with the decay channels of B^* .

The general excitation scheme in Fig. 23 above is very good and should be used as it will always be valid no matter what molecular engineering developments are made. From the fore-going discussion of interchain interactions here is a brief synopsis.

- Both intra and inter chain excitations can decay radiatively or nonradiatively
- The magnitude of the non-radiative decay rate versus the radiative decay rate is what determines ϕ_{pl} .
- Avoiding interchain species altogether would be the best way of having high PLQY and consequently efficient devices.

References

1. A. Gilbert, J. B., "Essentials of Molecular Photochemistry", Blackwell Scientific Publications: Oxford, **1991**.
2. Lennard-Jones, J. E., *Trans. Faraday Soc.* **1929**, 25, 668.
3. Atkins, P. W. (**1998**) "Physical Chemistry."
4. a) "CRC Handbook of Chemistry and Physics", 72nd ed. (CRC Press, Boston **1991-1992**).
b) Baba, K.; Aikawa, Y.; Shohata, N., "Thermal-Conductivity of Diamond Films". *Journal of Applied Physics* **1991**, 69, (10), 7313-7315.
5. Teraji, T.; Hamada, M.; Wada, H.; Yamamoto, M.; Arima, K.; Ito, T., "High rate growth and electrical/optical properties of high-quality homoepitaxial diamond(100) films". *Diamond and Related Materials* **2005**, 14, (3-7), 255-260.
6. E. M. Conwell, H. A. M., "Handbook on Semiconductors": "Conjugated Polymer Semiconductors: An Introduction". Elsevier Science Publishers B.V.: **1992**; Vol. 1, Ch.11.
7. H.W. Kroto, W.R. Heath, S.C.O'Brien, R.F.Curl and R.E.Smalley, *Nature*, 118 162 **1985**.
- 8 S. Iijima, *Nature*, **1999**, 354
- 9 "Polymer-C60 transfer" P. Lane et al. *Phys.Rev.B*. **2005**
- 10 S. Curran, P.M. Ajayan, W. Blau, D.L. Carroll, J. Coleman, A. Dalton, A.P. Davey, B. McCarthy, and A. Strevens. "A Composite from Poly(m-phenylenevinylene-co-2,5-dioctoxy-p-phenylenevinylene) and Carbon Nanotubes: A Novel Material for Molecular Optoelectronics" *Advanced Materials*, 10, 1091 (**1998**). b) R. Andrews, M.C. Weisenberger, *Curr. Opp. Sol. State and Mat. Sci.* **8**, **2004**.
- 11 D. A. Waters, M. J. Casavant, X. C. Qin, C. B. Huffman *Chem. Phys. Lett.* **2001** 338.
12. M. Terrones, "Carbon nanotubes: synthesis and properties, electronic devices and other emerging applications" *International Materials Reviews*, **2004** 49
13. S.J. Tans, A.R.M. Vershueren, and C. Dekker, *Nature*, **1998** 393
14. Bao, Z. N., "Recent progress in materials for organic electronics". In *Polymers for Microelectronics and Nanoelectronics*, **2004**; Vol. 874, pp 1-14
- 14b. Jones, G., II, Jackson, W. R., Chol-yoo, C. and Bergmark, W. R. (**1985**). "Solvent effects on emission yield and lifetime for coumarin laser dyes. Requirements for a rotary decay mechanism." *Journal of Physical Chemistry* 89(2): 294-300.
15. M. Colle and W. Brutting, *Phs. Stat. Sol. (a)*, 201, **2004**
16. Shirakawa, H.; Louis, E. J.; Macdiarmid, A. G.; Chiang, C. K.; Heeger, A. J., "Synthesis of Electrically Conducting Organic Polymers - Halogen Derivatives of Polyacetylene, (Ch)X". *Journal of the Chemical Society-Chemical Communications* **1977**, (16), 578-580. b). Heeger, P. A. J., "Semiconducting and metallic polymers: The 4th generation of polymers", Nobel Prize Speech.
<http://nobelprize.org/chemistry/laureates/2000/heeger-lecture.pdf>, **2000**.
17. Su, W. P.; Schrieffer, J. R.; Heeger, A. J. "Solitons in Polyacetylene" *Physical Review Letters* **1979**, 42, (25), 1698-1701. Su, W. P.; Schrieffer, J. R.; Heeger, A. J., "Soliton Excitations in Polyacetylene". *Physical Review B* **1980**, 22, (4), 2099-2111. b) Heeger, A. J.; Kivelson, S.; Schrieffer, J. R.; Su, W. P., "Solitons in Conducting Polymers". *Reviews of Modern Physics* **1988**, 60, (3), 781-850. c) Kivelson, S.; Heeger, A. J., "1st-Order Transition to a Metallic State in Polyacetylene – a Strong-Coupling Polaronic Metal". *Physical Review Letters* **1985**, 55, (3), 308-311.
18. Hückel, E., *Z.Physik* **1931**, 70, 204.
19. Sanvito, S., "Condensed Matter Theory". *University of Dublin*,
<http://www.tcd.ie/physics/people/Stefano.Sanvito/TEACHING/4012.html> **2005**.
20. a) Peierls, R., "More Surprises in Theoretical Physics",. Princeton University Press: **1991**. b) Peierls, R. E., "Quantum Theory of Solids". Oxford University Press: **1955**.
21. Dressel, M., "Peierls Instability and Charge Density Waves" *Physikalisches Institut, Universität Stuttgart* <http://www.pi1.physik.uni-stuttgart.de/indexjs.html>. **2002**.
22. Fowler, M., "Electron in a One-Dimensional potential", *Univ. Virginia, U.S.A.*, <http://galileo.phys.virginia.edu/classes/752.mf1i.spring03/PeierlsTrans.htm>.
23. M. Takayama, Y. R. L.-L., K. Maki "Continuum model for solitons in polyacetylene". *Phys. Rev. B* **21** **1980**, 21, 2238.

24. Brazovski, S. A. and Kirova, N. N. (1981). "Excitons, polarons and bipolarons in conducting polymers." *Pis'Ma V Zhurnal Eksperimental'noi i Teoreticheskoi Fiziki* **33**(1): 6-10
- 25 why PA not fluorescent mazumdar
- 26 kirova bishop
- 27 N.C. Greenham and R. H. Friend in "Semiconductor Device Physic" **1995**, Cambridge University Press.
- 28 polarons study by PA
- 29 E. M. Conwell, H. A. M., "Handbook on Semiconductors": "Conjugated Polymer Semiconductors: An Introduction". Elsevier Science Publishers B.V.: **1992**; Vol. 1, Ch.11.
- 30 . Lane, P. A., Wei, X. and Vardeny, Z. V. (1997). "Spin and spectral signatures of polaron pairs in pi - conjugated polymers." *Physical Review B-Condensed Matter* **56**(8): 4626-37.
- 31 Shuai, Z., Bredas, J. L. and Su, W. P. (1994). "Nature of photoexcitations in poly(paraphenylene vinylene) and its oligomers." *Chemical Physics Letters* **228**(4-5): 301-6.
- 32 fs laser patterning
- 33 upconversion Grace
- 34 Rauscher, U.; Schutz, L.; Greiner, A.; Bassler, H., "Site-Selective Spectroscopy of Matrix-Isolated Conjugated Polymers". *Journal of Physics-Condensed Matter* **1989**, *1*, (48), 9751-9763. b) Schindler, F., Lupton, J. M., "Single chromophore spectroscopy of MEH-PPV: Homing-in on the elementary emissive species in conjugated polymers". *Chemphyschem* **2005**, *6*, (5), 926-934. c) Mahrt, R.; Yang, J. P.; Greiner, A., Bassler, H., Bradley, D. D. C., "Site-Selective Fluorescence Spectroscopy of Poly(P-Phenylenevinylene)s and Oligomeric Model Compounds". *Makromolekulare Chemie-Rapid Communications* **1990**, *11*, (9), 415-421. d) Lupton, J. M.; Samuel, I. D. W.; Burn, P. L., "Origin of spectral broadening in pi-conjugated amorphous semiconductors". *Physical Review B* **2002**, *66*, (15).
35. Bronold, F. X., Saxena, A. and Bishop, A. R. (1993). "Radiative decay of polaron-excitons in poly(phenylene vinylene)." *Physical Review B-Condensed Matter* **48**(17): 13162-5.
36. Henderson, B. and Imbusch, G. F. (1989). "Optical spectroscopy of inorganic solids."
37. Reddy, N. R. S., van Amerogen, H., Kua, S. L. S., van Grondelle, R. and Small, G. J. (1994). *Journal of Physical Chemistry* **98**: 4729-4735.
38. Halliday, D. A.; Burn, P. L.; Bradley, D. D. C.; Friend, R. H.; Gelsen, O. M.; Holmes, A. B.; Kraft, A.; Martens, J. H. F.; Pichler, K., "Large Changes in Optical-Response through Chemical Preordering of Poly(P-Phenylenevinylene)". *Advanced Materials* **1993**, *5*, (1), 40-43. 59.
39. S.J. Strickler, R.A. Berg, *J. Chem. Phys.* **37**, 814 (1962)
40. S Berg Horhold paper
41. Sariciftci, N. S., "Primary Photoexcitations in Conjugated Polymers: Molecular Excitons versus Semiconductor Band Mode" I. World Scientific: Vol. 1. . b) Bassler, H.; Gailberger, M.; Mahrt, R. F.; Oberski, J. M.; Weiser, G., "Exciton Versus Band Description of the Absorption, Luminescence and Electroabsorption of Poly(Phenylphenylenevinylene) and Poly(Dodecylthiophene)". *Synthetic Metals* **1992**, *49*, (1-3), 341-352. c) Ramasesha, S.; Galvao, D. S.; Soos, Z. G., "Exact Eigenstates of the Pariser-Parr-Pople Model for Anthracene". *Journal of Physical Chemistry* **1993**, *97*, (12), 2823-2829. d) McBranch, D.; Long, F. H.; Hagler, T. W.; Robinson, J. M.; Swanson, B. I., "Luminescence Excitation Spectroscopy in Poly(P-Phenylene-Vinylene) Derivatives - Implications for a Semiconductor Band Vs Exciton Model in Conjugated Polymers". *Molecular Crystals and Liquid Crystals Science and Technology Section a-Molecular Crystals and Liquid Crystals* **1994**, *256*, 499-505.
42. Beljonne, D., Shuai, Z., Friend, R. H. and Bredas, J. L. (1995). "Theoretical investigation of the lowest singlet and triplet states in poly(paraphenylene vinylene) oligomers." *Journal of Chemical Physics* **102**(5): 2042-9.
43. Sariciftci, N. S., "Primary Photoexcitations in Conjugated Polymers: Molecular Excitons versus Semiconductor Band Mode" I. World Scientific: Vol. 1
44. Shimoi, Y., Abe, S. and Harigaya, K. (1995). "Theory of optical absorption in doped conjugated polymers." *Molecular Crystals & Liquid Crystals* **267**: 329-34.

45. Cornil, J., Beljonne, D., Friend, R. H. and Bredas, J. L. (1994). "Optical absorptions in poly(paraphenylene vinylene) and poly(2,5-dimethoxy-1,4-paraphenylene vinylene) oligomers." *Chemical Physics Letters* **223**(1-2): 82-8. b) Bredas, J. L., Cornil, J., Meyers, F. and Beljonne, D. (1998).
46. Chandross, M.; Mazumdar, S.; Jeglinski, S.; Wei, X.; Vardeny, Z. V.; Kwock, E. W.; Miller, T. M., "Excitons in Poly(Para-Phenylenevinylene)". *Physical Review B* **1994**, 50, (19), 14702-14705.
47. Kittel, C. (1996). "Introduction to Solid State Physics."
48. Soos, Z. G.; Ramasesha, S.; Galvao, D. S., "Band to Correlated Crossover in Alternating Hubbard and Pariser-Parr-Pople Chains - Nature of the Lowest Singlet Excitation of Conjugated Polymers". *Physical Review Letters* **1993**, 71, (10), 1609-1612. b) "Electronic Structure and Optical Response of Highly Conducting and Semiconducting Conjugated Polymers and Oligomers" in "Handbook of Conducting Polymers". T. A. Skotheim, R. L. Elsenbaumer and J. R. Reynolds: 1-27.
49. Hagler, T. W.; Pakbaz, K.; Heeger, A. J., "Polarized-Electroabsorption Spectroscopy of a Soluble Derivative of Poly(P-Phenylenevinylene) Oriented by Gel Processing in Polyethylene - Polarization Anisotropy, the Off-Axis Dipole-Moment, and Excited-State Delocalization". *Physical Review B* **1994**, 49, (16), 10968-10975. b) Hagler, T. W.; Pakbaz, K.; Voss, K. F.; Heeger, A. J., "Enhanced Order and Electronic Delocalization in Conjugated Polymers Oriented by Gel Processing in Polyethylene". *Physical Review B* **1991**, 44, (16), 8652-8666. c) Hagler, T. W.; Pakbaz, K.; Heeger, A. J., "Polarized Electroabsorption Spectroscopy of Highly Ordered Poly(2-Methoxy, 5-(2'-Ethyl-Hexoxy)-P-Phenylene Vinylene)". *Physical Review B* **1995**, 51, (20), 14199-14206.
- 50 Heeger in Linz book
51. Moses, D.; Okumoto, H.; Lee, C. H.; Heeger, A. J.; Ohnishi, T.; Noguchi, T., "Mechanism of carrier generation in poly(phenylene vinylene): Transient photoconductivity and photoluminescence at high electric fields". *Physical Review B* **1996**, 54, (7), 4748-4754.
- 52 De Vore
53. Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F., "Photoinduced Electron-Transfer from a Conducting Polymer to Buckminsterfullerene". *Science* **1992**, 258, (5087), 1474-1476.
54. Virgili
- 55 Deussen, M.; Scheidler, M.; Bassler, H., "Electric-Field-Induced Photoluminescence Quenching in Thin-Film Light-Emitting-Diodes Based on Poly(Phenyl-P-Phenylene Vinylene)". *Synthetic Metals* **1995**, 73, (2), 123-129
56. Yang, Y.; Pei, Q.; Heeger, A. J., "Efficient blue light-emitting diodes from a soluble poly(paraphenylene): Internal field emission measurement of the energy gap in semiconducting polymers". *Synthetic Metals* **1996**, 78, (3), 263-267. b) Leng, J. M.; Jeglinski, S.; Wei, X.; Benner, R. E.; Vardeny, Z. V.; Guo, F.; Mazumdar, S., "Optical Probes of Excited-States in Poly(P-Phenylenevinylene)". *Physical Review Letters* **1994**, 72, (1), 156-159. c) Yu, G.; Yang, Y.; Cao, Y.; Pei, Q.; Zhang, C.; Heeger, A. J., "Measurement of the energy gap in semiconducting polymers using the light-emitting electrochemical cell". *Chemical Physics Letters* **1996**, 259, (3-4), 465-468. d) P. Gomes da Costa, E. M. C., *Phys. Rev. B* **1993**, 48, 1993. 60. Shuai, Z.; Bredas, J. L., "Polaron-Pair Binding Due to Interchain Coupling in Conjugated Polymers". *Physical Review B* **1995**, 52, (19), 13730-13733. e) Shuai, Z.; Pati, S. K.; Su, W. P.; Bredas, J. L.; Ramasesha, S., "Binding energy of 1B(u) singlet excitons in the one-dimensional extended Hubbard-Peierls model". *Physical Review B* **1997**, 55, (23), 15368-15371 f) Bredas, J. L.; Cornil, J.; Heeger, A. J., "The exciton binding energy in luminescent conjugated polymers". *Advanced Materials* **1996**, 8, (5), 447-&. g) Fahlman, M.; Logdlund, M.; Stafstrom, S.; Salaneck, W. R.; Friend, R. H.; Burn, P. L.; Holmes, A. B.; Kaeriyama, K.; Sonoda, Y.; Lhost, O.; Meyers, F.; Bredas, J. L., "Experimental and Theoretical-Studies of the Electronic-Structure of Poly(P-Phenylenevinylene) and Some Ring-Substituted Derivatives". *Macromolecules* **1995**, 28, (6), 1959-1965. h) Eckhardt, H.; Shacklette, L. W.; Jen, K. Y.; Elsenbaumer, R. L., "The Electronic and Electrochemical Properties of Poly(Phenylene Vinylenes) and Poly(Thienylene Vinylenes) - an Experimental and Theoretical-Study". *Journal of Chemical Physics* **1989**, 91, (2), 1303-1315.
57. Wei, X.; Hess, B. C.; Vardeny, Z. V.; Wudl, F., "Studies of Photoexcited States in Polyacetylene and Poly(Paraphenylenevinylene) by Absorption Detected Magnetic-Resonance - the Case of Neutral Photoexcitations". *Physical Review Letters* **1992**, 68, (5), 666-669.
- 58 Forster, T. (1946). *Naturwissenschaft* 33: 166. b) Forster, T. (1948). *Ann. Phys.*
59. Dexter, D. L. (1953). *Journal of Chemical Physics* 21: 836

60. Hsu, J. W. P., Yan, M., Jedju, T. M., Rothberg, L. J. and Hsieh, B. R. (1994). "Assignment of the picosecond photoinduced absorption in phenylene vinylene polymers." *Physical Review B-Condensed Matter* 49(1): 712-15.
61. Samuel, I. D. W., Rumbles, G. and Collison, C. J. (1995). "Efficient interchain photoluminescence in a high-electron-affinity conjugated polymer." *Physical Review B-Condensed Matter* 52(16): R11573-6.
62. Nguyen, T.-Q., Schwartz, B. J., Schaller, R. D., Johnson, J. C., Lee, L. F., Haber, L. H. and Saykally, R. J. (2001). "Near-Field Scanning Optical Microscopy (NSOM) Studies of the Relationship between Interchain Interactions, Morphology, Photodamage, and Energy Transport in Conjugated Polymer Films." *Journal of Physical Chemistry* 105(22): 5153-5160. b) R.H. Friend, R. W. Gymer, Electroluminescence in conjugated polymers, *Nature*, **1999**, 397
- 63 R. Stevenson, R. Riehn, R. G. Miller, *Appl. Phys. Lett.* **2001**, 79
- 64 F. Cacialli, J. S. Wilson, J. J. Michels, " Cyclodextrin-threaded conjugated polyrotaxanes as insulated molecular wires with reduced interstrand interactions" *Nature Materials*, 1, **2002**

Chapter 3

3 CHARGE TRANSPORT IN AND ELECTROLUMINESCENCE OF π -CONJUGATED THIN FILM ORGANIC LEDS.

3.1 ELECTRICAL TRANSPORT IN CONJUGATED POLYMERS.

Although carriers in organic films may be optically and or thermally generated, the focus in this chapter is on electrical transport mechanisms of carriers generated by injection from electrodes. Charge carrier generation is distinct from carrier conduction but it does provide the impetus for the latter as typically upon carrier generation redistribution of charge by diffusion or drift (or both) of charge carriers is required to reach neutrality and equilibrium. In conjugated polymers the mobility is anisotropic where in plane (intramolecular) transport and is only usually observed in AC measurements. This anisotropy is not evident in conjugated small molecule thin films.

3.1.1 The Energy Band Model

Energy band formation was described in chapter 2. A negative temperature coefficient of carrier drift mobility (mobility due to an applied electric field) is the mark of band transport, where Fermi-Dirac statistics apply. This is observed in conventional semiconductors and organic crystals. However, the uncertainty principle regarding energy and time requires that the carrier mean free path is larger than the lattice constant and, even in molecular crystals, these criterion are barely met. Despite this, band theory can successfully predict many transport phenomena including the lattice components of carrier drift mobility and its temperature dependence in organic crystals such as anthracene, naphthalene and pentacene. Band theory which treats electron lattice interactions as a small perturbation, works well for inorganic semiconductors but is not appropriate for highly amorphous conjugated polymer and small molecule films which have very narrow bands and very low carrier mobilities.

3.1.2 The Tunnelling Model

Quantum mechanical tunneling of an electron through a potential barrier is a very general phenomenon and was proposed originally by Josephson¹. The transmission probability, P , for a general barrier, of length $x_2 - x_1$, is given by integral calculus as:

$$P_{x_1 \rightarrow x_2} \propto \exp\left(-2 \int_{x_1}^{x_2} \sqrt{2m(V(x) - E)} / \hbar dx\right)$$

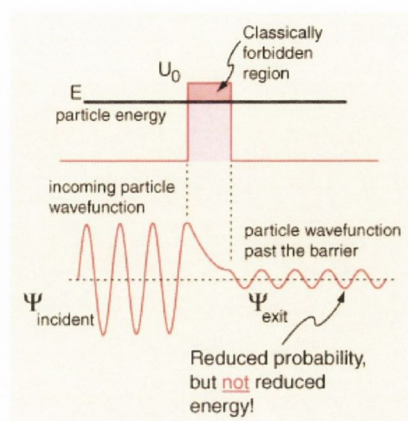


Fig. 2.4 Isoenergetic tunneling of an electron wavefunction, ψ , through a potential barrier, U_0 .

The tunneling conductivity model assumes a charged particle (e.g. an electron in a negative polaron) can tunnel, conserving energy, through a potential barrier to a new site on a neighbouring molecule, forming a polaron there. In this model, tunneling of an electron to a neighbour is more likely than its relaxation to ground state and is most likely, therefore, for long lived triplet states. The tunneling model can be considered a band model if tunneling is over a large number of molecules with a small periodic potential barrier of width ($< 10 \text{ \AA}$). These criteria are not normally met in a disordered material, however, if there are nano-crystallites present, separated by a thin barrier, fluctuation-induced tunneling may occur on a highly localized scale.

3.1.3 The Hopping Model

For narrow bands, carrier scattering is a multiphonon process, and carrier motion is random and incoherent, unlike the Bloch wave case for band motion in a crystal. This means a hopping model (Mott 1969²) where a carrier can move from one molecule to another via an excited state, by jumping over a potential barrier, is most likely for amorphous materials. Band transport involves coherent transport with mobility dependent on the number of oscillators whereas hopping transport is a random process. Hopping is inherently a quantum mechanical tunneling process but it is phonon assisted.

Whether hopping or band transport applies depends on the strength of electron-lattice interactions. If the electron relaxation time, t , is less than the intermolecular vibration period, ν_{inter} , and the latter is less than the intramolecular vibration period, ν_{intra} , the band model is applicable and if $t_{\text{intra}} < t < t_{\text{inter}}$, then the lattice is polarized, resulting in polaron formation where the electrons are trapped by phonon-interaction, in self-induced potential wells. Basically, if the phonon bandwidth is large in comparison with the polaron bandwidth, hopping will predominate. The probability of finding the electron in a trap level different in energy to its initial trap level is proportional to the product of the probability of finding the electron displaced by a distance r from its initial trap position and the phonon energy, E , required to make the transition:

$$p(r, \varepsilon) \propto e^{-\left(\frac{2r}{r_o} + \frac{\varepsilon}{kT}\right)}$$

where r_o is known as the localisation length and E is positive for conduction processes. The displacement and energy dependence of the hop are reflected in the first and second terms in the exponent in the equation above. At lower temperatures low energy hops over relatively large hopping distances will be most likely and, conversely, higher energy hops over shorter hopping distances will be more probable at higher temperatures. For a given temperature, conductivity based on hopping will be governed by the *average* hopping distance, $\langle r \rangle$. To see what the most probable hopping distance is one must consider the energy difference ε as a function of r . For a hop to occur from an initial state at the centre of a spherical volume there must be one final state of energy ε_F between 0 and $\varepsilon(r)$ within that volume. In other words $n(\varepsilon_F)$, the density of states, = 1 for a given r within this sphere. It follows that:

$$\varepsilon(r) = \frac{3}{4\pi r^3 n(\varepsilon_F)}$$

Substitution of $\varepsilon(r)$ into $p(r, \varepsilon)$ yields a maximum for $p(r, \varepsilon)$ when

$$\langle r \rangle = \left[\frac{8\pi}{9r_o} kT n(\varepsilon_F) \right]^{\frac{1}{4}}$$

Substituting $\varepsilon(r)$ and $\langle r \rangle$ into $p(r, \varepsilon)$, a hopping conductivity, σ , is obtained:

$$\sigma = \sigma_o e^{-\left(\frac{T_o}{T}\right)^{\frac{1}{4}}}$$

where T_o is given by:-

$$T_o = \frac{f}{kn(\varepsilon_F)r_o^3}$$

f is a scale factor equal to .30907 and is due to a combination of dimensionless factors.

Variable range hopping characteristics are obtained by plotting $\ln \sigma$ against $(1/T)^{\frac{1}{4}}$. The $1/4$ index denominator is representative of an effective dimensionality characteristic of the hopping phenomenon (d spatial dimensions and one energy dimension). In the presence of an applied electric field, E, σ is given by Mott *et al*² as:

$$\sigma = \sigma_o e^{(-e\langle r \rangle E)}$$

3.1.4 Charge-Carrier Traps

Amorphous organic films contain a high density of structural defects and/or impurity related defects which are difficult to avoid and impossible to remove. These defects play an important role in conduction, acting as trapping sites for charge carriers. In a film, the vast majority of these traps are structural but chemical traps due to oxygen, or impurities which remain after synthesis, are also prevalent. Electrochemically grown conjugated polymer films also contain trap-forming ionic defects and impurities. Charge carriers will fill empty traps below the quasi Fermi level at any given operating voltage so that traps can lower the room temperature mobility by an order of magnitude. Hopping, though not a microscopic theory, inherently accounts for traps and disorder. Although all microscopic theories for conduction are based on a perfect, trap-free, *ideal* crystal structure, trapping effects may be included. SCLC (space charge limited current) conduction is an example of a microscopically based theory which can include trapping effects and is frequently used to model transport in organic devices.

The Poole-Frenkel (PF) effect³ is usually associated with field assisted hopping. It is analogous to an internal Schottky (section 3.3.4) effect in so far as the potential barrier to liberating a carrier from a trap level into the conduction band is reduced by ΔE_{PF} by the presence of an applied electric field, F . The magnitude of the PF effect for a 1-D planar model is governed by the factor β_{PF} .

$$\Delta E_{PF} = \beta_{PF} F^{1/2}$$

ΔE is twice as large in the PF effect as in the Schottky effect since the positive charge is fixed rather than being a mobile image charge. Field enhanced carrier generation based on this effect is common in amorphous semiconductors where ion traps are found. In conjugated organic materials, traps are mostly structural, being neutral when empty and charged when filled rather than vice versa. Therefore, there is a lack of coulomb interaction and the PF effect does not play an important role in conduction in theory. However, a PF type ($\mu \propto F^{1/2}$) field dependent mobility has often been observed.⁴

3.2 CURRENT INJECTION FROM ELECTRICAL CONTACTS

When electrical contacts (electrodes) are used to generate an electric field across a sample film to inject carriers, one of a range of different equations is used to describe the total current flow depending on whether it is electrode-limited or bulk-limited. Electrical injection results in an increase in the conductivity over the dark conductivity. The nature of an electrical contact, which may be simply defined as a contact between a metal and a non-metallic material, is very important. When two materials with different Fermi levels are brought into contact, Fermi level alignment occurs by movement of carriers of one type from one material to the other. This causes two oppositely charged space charge regions to form either side of the interface. The field produced by the space charge region maintains a state of equilibrium and Fermi level alignment by preventing further net movement of charge. The space charge regions are often referred to as a neutral

electrical double layer or potential barrier. As with conduction processes, the potential barrier will be greatly affected by chemical or structural surface traps or surface states.

3.2.1 The Work Function of the Metal Electrodes

The simplest, ideal contact is between a metal and a vacuum and is used to define the metal workfunction, ϕ , which originates in the discovery of the photoelectric effect⁵.

$$\phi_m = \zeta - E_{Fm}$$

ζ is the difference between the potential energies of electrons inside and outside the metal and E_{FM} is the metal Fermi level. ϕ depends on the binding energy of the electron (strong binding will increase ϕ_m) and on the energy needed to move the electron through the electrical double layer of the contact which is determined by the dipole moment of the double layer. With a metal-vacuum contact, the discontinuity facing surface electrons in the metal results in double layer formation similar to that caused by net charge flow when Fermi level align as a solid-solid interface forms. ϕ is modified in the presence of an adsorbed layer of foreign atoms on the surface. An electronegative surface layer pushes surface electrons in the metal away from the surface, increasing ϕ . For example, ϕ is higher for an ozone-treated ITO (indium tin oxide) surface than untreated ITO. ϕ_m is determined mainly by the top few layers of atoms. For semiconductors and insulators the work function is defined as:

$$\phi = \chi + (E_c - E_F)$$

where χ or E_a is the potential between the lowest energy electrons in the conduction band at the surface and the vacuum level and is called the *electron affinity*. E_c is the conduction band edge and E_F the Fermi level in the semiconductor and E_a or $\chi \cong I_p - E_{opt}$ where I_p is the *ionization potential* of an isolated molecule and E_{opt} is the optical band gap measured from the absorption edge. The contact potential, V_d , for two solids is:

$$V_d = \frac{1}{q}(\phi_m - \phi_s) = \frac{1}{q}[\phi_m - \chi_s - (E_c - E_F)]$$

where contact is between a metal and a semiconductor. For organic materials ionization potential is defined as the energy to remove an electron from the HOMO (adding a hole) to the vacuum level and the electron affinity is the energy required to add an electron from the vacuum level to the LUMO. In a sandwich configuration with a semiconductor between two dissimilar metal electrodes, the built-in field is V_d/d and can be quite high for organic thin films.

3.3 TYPES OF ELECTRICAL CONTACT

3.3.1 Neutral Contacts

Neutral contacts, by definition, mean that there is no space charge and therefore no band bending caused by varying space charge density. Neutral contacts occur when the metal and semiconductor work functions are equal. If a bias is applied the current in the semiconductor layer follows Ohm's law:

$$J = qn_0\mu\frac{V}{d}$$

3.3.2 Ohmic Contacts

In an ohmic contact (also called a reservoir or injecting contact) the contact impedance is negligible compared to the impedance of the material being contacted. A contact is ohmic as long as *the injected* carrier density is less than the thermally-generated carrier density⁶. An ohmic contact may be achieved for a metal: n-type junction if $\phi_{\text{metal}} < \phi_{\text{semic}}$ for electrons from the metal and for a metal: p-type junction if $\phi_{\text{metal}} < \phi_{\text{semic}}$ for hole injection. The current will remain ohmic as long as a flatband condition ($dE/dt = 0$) exists, the mobility is independent of E (i.e. Joule-heating is insignificant), and the current in the semiconductor is less than the saturated thermionic cathode current. In the ohmic regime a relatively small voltage drop exists across the contact itself. An ohmic contact behaves as an infinite reservoir of carriers. Although the

contact may be ohmic, the I-V (current-voltage) characteristic may be highly non-linear due to space charge effects. If the electric field, E , becomes too large, the contact ceases to be ohmic and becomes blocking. In this case, the I-V characteristic from ohmic contacts becomes electrode-limited.

3.3.3 Blocking Contacts

A contact is blocking when $\phi_m > \phi_{\text{semi}}$ (n type) for electrons and the resulting space charge causes bending of the conduction and valence bands. Since the metal electrode is highly conductive, there is an image charge of sheet or planar charge of electrons (or holes) in the metal upon injection of electrons (or holes) into the organic. However the space charge extends well into the organic due to the low charge mobility in the organic. The potential due to the space charge in the organic varies inversely with the distance of the injected charge from the interface. An electron blocking contact has been observed for aluminium:organic interfaces in OLEDs. Since $\chi_{\text{organic}} < \phi_{\text{Al}}$, electrons will flow from the organic to the metal at 0 bias to align the Fermi levels. For diagrammatic clarity, a line is usually used to denote the interface between the materials as the barrier it represents is so thin it is transparent to tunnelling and all the potential at the interface is effectively dropped over the space charge region in the organic material.

It is worth noting that an ohmic contact for electrons is blocking for holes and so simply changing bias can make an ohmic electron injecting contact an electron blocking contact. Thus one can go from two ohmic or, one ohmic and one blocking, to two blocking contacts, by simply switching bias. Therefore, it is no surprise that there is current rectification when these types of contacts are involved.

Injection in an organic LED cannot actually occur until the flat band voltage, which is equal to the built-in voltage due to the difference in electrode workfunctions, is exceeded. After this point electrons in the low workfunction cathode material are at a higher potential to those in the LUMO (allowing electron injection) and electrons in the HOMO are at a higher potential to those in the high workfunction anode material, allowing hole injection. Thus the lines depicting the HOMO and LUMO in the organic material in an LED can be thought of as pivoting around a central point such that

their slopes change going through the flat band voltage, V_{bi} , as the voltage is increased from 0V to $V > V_{bi}$.

3.3.4 Schottky Barriers and the Schottky Effect

A potential barrier, ϕ_B , formed by a space charge double layer at a solid-solid interface, with voltage dependent barrier width and height is called a Schottky barrier. They exist in principle at ohmic and blocking contacts though the magnitude will be a lot smaller for the former and they are usually associated with the latter. If ϕ_B is close to kT in height or close to the wavelength of a charge carrier, it will not perform effectively as a barrier. The Schottky effect describes the lowering of ϕ_B by the external field.

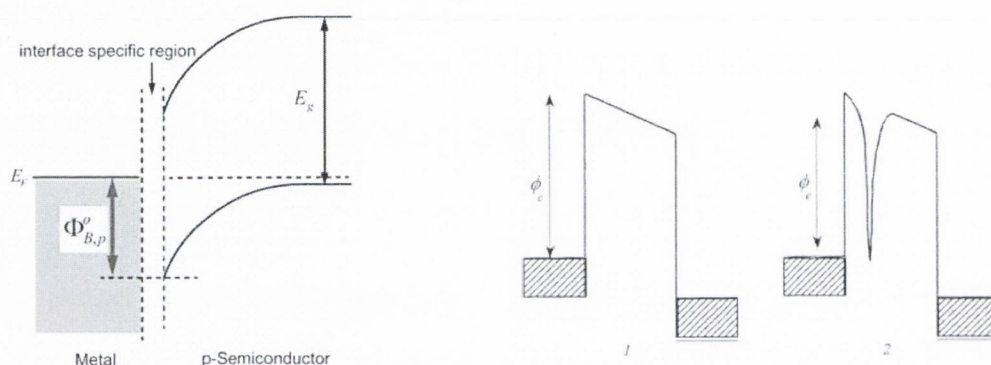


Fig. 25 Difference between Shottky and P-F barriers: the Schottky effect (left) is associated with field-enhanced thermionic emission from the metal, whereas PF emission (right) is field enhanced thermal excitation of trapped carriers.

3.3.5 Electrical Contacts in Organic Devices

Although contact diagrams for semiconductors are quite straight forward, this is not so for their organic counterparts. For example, a metal-semiconductor interface is described by the energy difference between the Fermi levels or the built-in potential. In organics, however, it is difficult to determine the Fermi level before injection and to know exactly how the charge which causes the built-in potential is distributed in the film. The fabrication of organic devices results in polycrystalline metal electrodes which are rough at the molecular length scale. The bottom electrode may be coated with a native oxide while the top electrode often reacts chemically with the organic and the organic

may be unintentionally doped. Quite apart from the contacts, the fact that injection will take place into an amorphous material with localized states with a lot of energetic disorder complicates matters. Disorder, low bandwidth, electron-phonon interactions and temperature all work together to localize charges in organic materials, and it is safe to assume in virtually every case of interest that charge carriers are localized at room temperature. Hence, injection consists of a transition from an extended band-like state in the metal electrode to a localized molecular polaronic state in the organic material⁷. Regardless of the theoretical approach to injection, the relative energies of the metal Fermi level and the organic HOMO and LUMO levels are critical. Experimentally, Ultraviolet Photoelectron Spectroscopy (UPS) is used to determine the organic HOMO or ionization potential level and then the LUMO or electron affinity is inferred using knowledge of the onset for optical absorption since there are no electrons to remove in that case. Seki *et al*⁸ have done much work on characterizing metal-organic interfaces and have found that even for the thinnest of organic layers on a metal, the UPS spectrum is shifted with respect to that of the uncoated metal. The shift also varies for each metal-organic combination. The Kelvin-probe method allows for thicker layers to be used, up to 500 nm, to measure the surface potential directly. Buried interfaces, and the small ratio of molecules at the interface with those in the bulk, make determination of the Fermi level in the organic problematic.

3.4 ELECTRODE-LIMITED INJECTION CURRENT

The electrodes of an organic device either inject or remove charge from the device and provide contact with external systems such as circuit drivers used to power the device. Efficient injection of charge across the metal-organic interface is critical to performance. The most important factor in this process is the energy barrier which charge carriers must overcome when crossing the interface. The primary event in the charge injection process is tunnelling from a thermally excited extended state in the metal into a localized polaronic state (HOMO or LUMO) in the organic. The main tunnelling mechanisms⁶ are summarized below.

3.4.1 Thermionic Emission

Thermionic emission of an electron from a metal with workfunction, ϕ , into a vacuum is described by the Richardson-Dushman equation as follows:

$$J = AT^2 \exp(-\phi / k_B T), \text{ where } A = \frac{emk_B^2}{2\pi^2\hbar^3}$$

For injection from a metal into a crystalline semiconductor m^* , the effective mass is used and A becomes A^* and the corresponding thermionic emission equation (for a triangular barrier) is referred to as the thermionic Richardson equation which is:

$$J = A^* T^2 e^{\left(\frac{e\phi}{kT}\right)}$$

The barrier height gives the activation energy that dominates the temperature dependence of thermionic emission. Bethe produced an equation taking account of applied voltage and the Schottky effect. Field enhanced thermionic emission is described by the first part of Bethe's equation:

$$J = A^* T^2 \exp\left(\frac{\phi\sqrt{E}}{kT}\right)$$

The barrier height ϕ has a field dependence of $\sqrt{E}$ for neutral contacts and $\sqrt[4]{E}$ for blocking contacts. Since the tunnelling rate depends strongly on the width of the barrier, thermal excitation can significantly increase the tunnelling current. A similar equation, the diode equation, describes current across the Schottky barrier across a p-n junction as:

$$J = J_0 \left[\exp\left(\frac{qV}{nkT}\right) - 1 \right]$$

The diode equation was used to model PPV LEDs at low voltages where low values of n and good fits suggested the current was electrode limited by the PPV/Al interface.⁹

In all cases above, the injection process is inherently a quantum mechanical process. In amorphous organic semiconductors the electronic states are highly localized and charge transport is by hopping. Schottky *et al* solved the drift diffusion equation

across the barrier and thereby produced an expression which is not explicitly quantum mechanical, where the pre-exponential factor is proportional to the density of states and carrier mobility. Various other thermionic emission models exist^{10,11} but are not discussed in this thesis.

3.4.2 Field Emission and Fowler Nordheim Barrier Tunnelling

FN emission corresponds to tunnelling from states in the metal Fermi level directly into states beyond the maximum in the potential barrier where the electric field emission is temperature independent. When a triangular barrier, ϕ , is used to describe the smoothly varying potentials (in preference to a square barrier) F-N theory gives:

$$J = \frac{A^* T^2}{\phi} \left(\frac{eE}{kT\kappa} \right)^2 e^{-\left(\frac{2\kappa\phi^{\frac{2}{3}}}{3eE} \right)} \quad \kappa = \frac{4\pi\sqrt{2m^*}}{h}$$

In a linear plot of $\ln J/E^2 \propto 1/E$ the slope, $m = \frac{4(2m^*)^{1/2}}{3\hbar e} \phi^{3/2}$ can be used to obtain ϕ

In F-N theory there is little consideration as to whether final states in the semi conductor are propagating (as hot states would be) or localized (as they would be in an organic semiconductor.) F-N emission¹² is often considered for injection but is frequently inappropriate since it is based on extremely high fields. As yet, there is no completely satisfactory analytical theory to describe the field and temperature dependence of the injection current in organic devices which, for well characterized interfaces, exhibits behaviour relating to both thermionic emission and field induced tunnelling. Partly this is because the field dependence of the Schottky effect and of the carrier mobility are identical ($\exp\sqrt{E}$) and, furthermore, both injection and hopping mobility are thermally activated processes. This means it is difficult to isolate the field and temperature dependences of the injected current. When there is an oxide or other contaminant on the electrode surface, the primary role of the overlayer is as an *insulator*. Since this layer is usually sufficiently thin, electrons will still tunnel through from metal to localized states in the organic material but the tunnelling rate reduces exponentially with insulator

thickness. With an insulating layer present, the charge density in the first few organic molecular layers is not so easily replaced and an injection-limited current is more likely.

3.4.3 Incorporating Disorder in Injection Models

The first model to accommodate the localized nature of organics was the two step Gaussian disorder model of Bassler *et al*¹³ where the initial step is tunnelling from the metal into one of the organic delocalized states. The second step is escape from a localized state into the bulk of the organic. The hopping attempt frequency is taken to be the same for both steps. Disorder creates a tail of low lying states which are more likely to be thermally occupied and provide preferred sites for the initial hop, thereby enhancing the injection current. Typically, the current in organic devices is bulk limited at normal operating currents but at very high fields the F-N analysis has been quite successfully used to model the currents, providing reasonable values for the interface barrier height. However, it is often the case that the device will have broken down before reaching the stage of high-field F-N limited current flow.

3.5 BULK LIMITED CURRENT FLOW

Lampert and Mark note that by insulator they mean $E_g > 2$ eV and, by semiconductor they mean $E_g < 2$ eV, making amorphous organic materials insulators for from a theoretical electrical modeling point of view. Although the starting point to describe bulk limited current flow is with an ideal trap or defect free insulator, a realistic model must account for the high densities of traps which exist in organic thin film samples.¹⁴ At low temperatures the capture of electrons (or holes) by traps is stable and so trapping effects may be more significant. Traps may be of a single energy (discrete) or distributed gaussianly, exponentially or uniformly in energy throughout a film. The total density of trap states ($\sim 10^{12} \text{ cm}^{-3}$ - 10^{18} cm^{-3}) depends on sample purity or quality. Mathematically, traps are described using Fermi-Dirac statistics¹⁴. The probability, f_n , for a trap to capture an electron is given by:

$$f_n(E) = 1 \left\{ 1 + g_n^{-1} \exp \left[(E - E_{Fn}) / kT \right] \right\}$$

Traps of a single energy (i.e. discrete traps) may be shallow or deep: traps are shallow if $E_t > F > F_0$. Shallow traps are characterized by the thermal concentrations of electrons contained in them. Traps are deep if $E_t < F_0$. Deep traps are characterized by the thermal concentrations of holes in such traps. Positionally, both types may, in principle, be distributed throughout a film. However, in practice, there are usually many deep electron traps near interfaces. This holds true for metal cathode:organic interfaces in particular and has important implications for organic LEDs, for example, since non-radiative recombination routes may be enhanced.

The Gaussian trap distribution function as a function of trap energy ε_t is:

$$D_T(\varepsilon) = \frac{D_{T_0}}{\sqrt{2\pi}\sigma_t} e^{-\frac{1}{2} \left(\frac{\varepsilon - \varepsilon_t}{\sigma_t} \right)^2}$$

where D_{T_0} is trap density, and σ_t is the standard deviation of the Gaussian function.

The exponential distribution function is given by:-

$$D_T(\varepsilon) = \frac{D_{T_0}}{kT_c} e^{-\left(\frac{\varepsilon_{LUMO} - \varepsilon}{kT_c} \right)}$$

where T_c is the characteristic trap temperature given by $T_c = \frac{\varepsilon_t}{k}$. In the exponential trap distribution, the trap concentration per unit energy decreases exponentially with energy from the band edge. This means that for electrons, close to the LUMO there are a lot of traps of low energy and away from the band edge there are fewer high energy traps.

The uniform trap distribution function (if $T > T_t$) is viewed as a limiting case for the exponential distribution function and is given by:

$$N_n = N_0 \exp \left(\frac{F_0 - E_C}{kT_t} \right) = \text{constant.}$$

When there is a quasi thermal equilibrium between trapped and free carriers the term quasi Fermi level or steady state Fermi level is used¹⁴. Quasi thermal equilibrium is assumed for steady state injection as long as the applied field is not strong enough to affect electron capture from the conduction band into a trap, or, re-emission from a trap into the conduction band. Because. In the presence of traps in organic semiconductors it is only sensible to take about a quasi Fermi level which, for electrons or holes, shifts as more carriers are injected. Shallow and deep traps are, therefore, not absolute concepts since the definition of these traps based on their characteristic energy depends on the quasi Fermi level position which in turn depends on applied voltage.

3.5.1 One Carrier Space Charge Limited Currents without Traps

Charge transport is a dynamic process, and the relative lengths of times associated with dielectric relaxation and carrier transit in a film determine whether space charge effects are important. The dielectric relaxation time, t_d , is the time taken for a material to restore charge neutrality after the injection of a small excess charge. The transit time, t_t , comes from the Einstein–Smoluchowski equation. The crossover from ohmic to space charge limited conduction occurs at⁶:

$$t_d = \frac{\epsilon}{p_0 e \mu} = \frac{\epsilon}{\sigma} \cong \frac{d^2}{\mu V} = t_t$$

where ϵ is the dielectric constant, e is unit charge, p_0 is free carrier density, μ is mobility, d is thickness, V is voltage, and σ is electrical conductivity.

As soon as $t_d > t_t$, the dielectric fails to relax the injected charge before more charge is injected and space charge forms in the bulk. Consequently an internal field is established which ultimately limits further injection of charge and therefore current flow in the bulk – hence the term SCLC (space charge limited current) conduction.

3.5.1.1 The Condenser Model

It is apparent that materials with a large dielectric constant and small mobility, e.g. LEPs are going to be obvious candidates for exhibiting SCLC. The simplest

description of SCLC is a phenomenological one which assumes average values for the variables involved¹⁴. In the condenser model, the injection and geometric capacitances are approximately the same since the injected charge distribution is generally non uniform. Considering a solid state analogue of the thermionic vacuum diode ($J = Q/t$, where Q is the total charge, and $p_0 = 0$), an approximate SCLC for pure holes is:

$$J = C_0 v V / L .$$

Assuming the drift velocity, v , is field dependent, for moderate fields when one uses the Einstein-Smoluchowski relation, the last equation can be altered to give:

$$J = \epsilon \mu \left(\frac{V^2}{L^3} \right)$$

SCLC is described analytically for the vacuum case where there is no scattering, giving Child's law. Including thermally generated carriers by equating t_t to t_d gives:

$$J = e p_0 \mu (V / L)$$

To include the effect of traps, a prefactor, θ , to the trap-free mobility, μ , is included. θ is the ratio of free total charge, $\frac{p}{p + p_t}$, and $\theta \mu$ is called the effective mobility, μ_{eff} . For trapping, i.e. $\theta < 1$, $\mu_{eff} < \mu$. Generally $\theta \ll 1$ and the single carrier SCLC is much reduced from the trap-free SCLC. For discrete, shallow traps, θ will be a constant, independent of injection level. There may well be several discrete trap levels in which case the one with the smallest θ value will dominate the SCLC.

To obtain more information about the variables involved in conduction, the completely phenomenological approach must be cast aside in favour of a more analytical approach. Both simplified and complete analytical approaches involve Poisson's equation. The latter uses position dependent free and trapped carrier concentrations. The assumptions made in the simplified analytical theory render it still quite phenomenological and are listed below.

- Planar, 1-dimensional DC current flow is considered.
- Mostly a low field, field independent mobility regime is considered.
- Diffusion currents are only sizeable in the immediate vicinity of the electrode and are ignored.
- The detailed micro or nano structure of the injecting contact is irrelevant as $E = 0$ at the electrode interface.
- p_i , injected carrier density, is infinite at the interface and finite in the bulk.

3.5.2 Current Flow in an Ideal Trap-Free Solid

The perfect, trap-free insulator is the direct solid state analog of the thermionic vacuum diode. In this case $n_0 = n_{t0} = 0$ and the combined continuity and Poission equations give:

$$E(x) \frac{dE(x)}{dx} = \frac{J_{SCLC}}{\epsilon \mu}$$

$V = \int_0^d E(x) dx$ and using the boundargy condition, $E(0) = 0$, and integrating yields :

$$J = \frac{9}{8} \epsilon \mu \frac{V^2}{d^3}$$

This simple analytical solution is the Mott-Gurney or trap-free square law, or, sometimes, Child's law for solids. The full analytical solution for SCLC in an insulator without traps and with $p_o \neq 0$ involves the regional approximation method and, though exact, does not explicitly relate J to V . The simplfied analytical theory is used in this thesis as a convenient way of extracting sample mobilities from I-V data.

3.5.2.1 One Carrier SCLC with Traps

For shallow traps described using the simple analytical approach the trap-free Mott Gurney square law simply contains the additional factor θ as a mobility multiplier.

Using the simplified analytical theory for the Gaussian and exponential distribution functions, satisfying the Poisson and continuity equations gives:

$$J = n(\varepsilon_{HOMO})\mu e^{1-l} \left(\frac{l}{(l+1)} \frac{\epsilon}{D_t} \right)^l \left(\frac{2l+1}{l+1} \right)^{l+1} \frac{V^{l+1}}{d^{2l+1}}$$

where $l = \frac{T_c}{T}$ for the exponential distribution and $l = \sqrt{1 + \frac{2\pi\sigma_t^2}{16k^2T^2}}$ for the Gaussian distribution, $n(\varepsilon_{HOMO})$ is the density of HOMO states and T is the absolute temperature. With regard to the exponential distribution, as a device is cooled, E_t continuously decreases. E_t is directly related to the steepness and depth of the exponential trap distribution, with the smaller values indicating a much steeper distribution closer to the N_{HOMO} levels. So with cooling, E_t must decrease and the positive carrier quasi Fermi level move closer to the HOMO levels. So, at lower temperatures, the Fermi level will be sweeping across regions of the trap distribution close to the N_{HOMO} . The exponential distribution reduces to a discrete shallow distribution when $T_t < T$. Actually, it has been suggested that the trap distribution is not a true exponential but is in fact a much steeper function of energy closer to the HOMO levels. Assuming a constant N_{HOMO} , the Fermi level as a function of applied voltage is¹⁵:

$$E_f = kT \ln \left[\frac{(2m+1)N_{HOMO}q\mu V}{((m+1)Jd)} \right]$$

This allows one to calculate the energy of the deepest traps in the distribution by using the highest J and V values from J - V data. These trap energies are larger than the characteristic trap energy.⁶ The mobility obtained from a discrete trap level region, or other means, may be used along with an approximate value for N_{HOMO} to do this.

Depending on the film morphology, either one or both of energetic, σ , and positional disorder, Σ , can influence the carrier mobility. Σ describes the spread of energy levels associated with transport. Σ describes the fluctuation of intersite distances and coupling between sites. The Gaussian disorder model (GDM) model is used for

non-dispersive transport (low values of σ and Σ) and the Scher-Montroll method for dispersive transport. Inhomogeneity in a film may also be included in the GDM model.

3.5.2.2 The Transition from Ohmic to Space-Charge-Limited Current

Using the condenser model, the crossover from ohmic to SCLC for a discrete trap level occurs at $t_t \approx t_d$. However, using the simple analytical analysis, it can be shown that $\tau_t = 9/8 \tau_d$ which means that SCLC actually becomes dominant before τ_t exceeds τ_d . The voltage, V_Ω , at which $t_t \approx t_d$ is given by:

$$V_\Omega = \frac{8}{9} \frac{epd^2}{\mu_{\text{eff}}\epsilon}$$

Note the effect of θ , reflected by μ_{eff} , is to increase V_Ω . A significant departure from ohm's law occurs once the Fermi level moves up by about kT in the exponential model or when p_0 comparable to p_i .

Equations involving an exponential distribution do not describe the current density for a shallow trap distribution. For shallow traps a Gaussian distribution governs the current density and a separate V_Ω is used. The exponential distribution, by its nature, has deep lying traps as well as shallow traps. $V_{\Omega\text{exp}}$ for SCLC with deep traps is:

$$V_{\Omega\text{exp}} = \frac{ed^2 D_t}{\epsilon} \left(\frac{p}{n(\epsilon_{\text{HOMO}})} \right)^{\frac{1}{l}} \left(\frac{l+1}{l} \right) \left(\frac{l+1}{2l+1} \right)^{\frac{l+1}{l}}$$

which, for large l , reduces to : $\left(\frac{eD_t d^2}{\epsilon} \right) \left(\frac{p}{n(\epsilon_{\text{HOMO}})} \right)^{1/l}$

where l is related to the slope of the log plot of the I-V curve characterising the exponential trap distribution SCLC. V_Ω can also be calculated for deep Gaussian and uniform trap distributions but discussion in this thesis is confined to shallow and exponentially distributed traps.

3.5.2.3 The Trap-Filled Limit

As more carriers are injected, traps are filled and the Fermi level increases until there are no more trap levels to be filled. This occurs at the trap filled limit¹⁴, V_{tfl} , after which trap-free square law SCLC is seen. From the simple theory, V_{tfl} for exponentially distributed traps to trap-free conduction is given by:

$$V_{\text{TFI}} = \frac{ed^2}{\epsilon} \left\{ \frac{9}{8} \frac{D_t}{n(\epsilon_{\text{HOMO}})} \left(\frac{l+1}{l} \right)^l \left(\frac{l+1}{2l+1} \right)^{l+1} \right\}^{\frac{1}{l-1}}$$

Note that the trap-filled limit problem is apparently unphysical and one must imagine all of the traps, N_t , to be filled prior to the application of voltage. V_{tfl} is nonetheless useful as it provides a limiting description of what happens when the Fermi level passes through a trap distribution.

Generalising, it can be seen that the SCLC current-voltage characteristics follow a power law $J = KV^{m+1}$ where m is related to the depth of the traps. Provided the current-voltage (IV) characteristics follow this bulk-limited process, and data is obtained that includes V_{Ω} and V_{TFI} , the material properties such as mobility, μ , intrinsic or free carrier density, p , trap density, D_t , and densities of states, N_{HOMO} or N_{LUMO} , may be determined. For unipolar devices displaying linear ohmic, and linear quadratic regions in their double logarithmic I-V characteristics it is thus possible to find values for σ , μ_{Ω} , μ_{SCLC} , V_{Ω} and p (charge density). The derivations are outlined fully in other theses but essentially the charge density may be solved for at the point where the ohmic current equals the space charge current as the charge density in both these equations is the same. At this point the time it takes for a carrier to drift across the film from one electrode to the other is equal to the dielectric relaxation time. The charge density is thus arrived at as follows⁶:

1. So $J = \sigma E$ or $J = p_0 e \mu E$

2. At low voltages the mobility is simply given by $\mu = \frac{V_d}{E}$

3. $\tau_t = \frac{d}{V_d} = \frac{d}{\mu E} = \frac{d^2}{\mu V}$ and $\tau_d = \frac{\epsilon}{\sigma} = \frac{\epsilon}{pe\mu}$

4. equating τ_d and τ_t gives $\frac{d^2}{\mu V} = \frac{\epsilon}{pe\mu}$ or $p = \frac{V\epsilon}{ed^2}$. If the Mott Gurney law is used for

J_{SCLC} a prefactor of 9/8 is used in the expression for the charge density.

5. V_Ω is often used to denote the voltage at this point where $p = p_0$. If $V < V_\Omega$ there is an ohmic regime only, and for $V > V_\Omega$ the current is SCLC with a smaller ohmic current flowing simultaneously.

6. From double logarithmic I-V plots it is thus simple to obtain values for μ from the ohmic section (slope approx = 1) and the SCLC section (slope approx = 2).

These values are largely based on the premise $p < p_0$ up to V_Ω which means that SC is negligible till that point, i.e. a carrier can transit the film faster than the dielectric relaxation time. The equations and calculations involved have been outlined in previous theses from TCD. It is worth mentioning that using this approach these values are obtained V_Ω are only valid if one assumes a mobility independent of charge density and electric field. Since V_Ω occurs at low voltages, mobilities extracted are effectively zero field values being up to 4 orders of magnitude less than those seen at typical device operating voltages. Most LEPs, however, exhibit a field dependent Murgatroyd mobility. Based on this fact, curve fits using a field dependent mobility can be used to model the I-V data better. However, the fits are usually only good over a limited range still. Recently Tanase has shown charge density is also important and fits taking it into account can accurately model the whole range of operation of both LEDs and FETs.

3.5.3 Bipolar Space Charge Limited Conduction

In the previous section single carrier currents were discussed, however, injection of carriers of both signs is a prerequisite in electroluminescent devices. Analysis of two

carrier currents in highly disordered systems, is extremely complicated and only a brief overview of bipolar space charge limited conduction (SCLC) is given here.

In double injection devices, recombination kinetics control the electrical properties. Recombination may be bimolecular, band to band or through one or more localized recombination centres. Double injection is best understood using injected plasma theory (where there are equal numbers of free carriers of both signs.) In a two carrier device, apart from space-charge and trapping effects, two additional features, determine the magnitude of the current: - charge neutralization and recombination. For two carrier SCLC currents, the positive and negative carriers tend to neutralize each other's charge and the current is limited by the bimolecular recombination rate. However, since neutralization is never complete, not only is the plasma injected into an insulator recombination-limited, it is, simultaneously, recombination- and space-charge-limited. In an ideal insulator there are no thermally generated free carriers to relax injected space charge which means that the latter plays an important role in limiting the injected plasma. Essentially, however, recombination limits bipolar current, much like how space charge limits single carrier current. In simple terms, the current-voltage behaviour of bipolar devices might be thought of as unipolar SCLC by two simultaneous, parallel pathways. This would be valid if both electron and hole-currents are injection limited and space charge effects are negligible. Thus, the two-carrier problem could then, essentially, be treated as a superpositioning of two single carrier currents. However, this scenario neglects the recombination of charge carriers. Mark and Lampert have discussed double- injection plasmas (i.e there are no traps or "recombination centers".) They obtain an analytical solution for a bimolecular recombination plasma in the injected plasma limit. Lampert *et al* have shown¹⁴ that the current voltage behaviour, incorporating recombination in the plasma limit, is of the form:-

$$J = (9/8) \epsilon \mu_{eff} (V^2 / L^3)$$

which is, clearly, a square law. Substituting μ_{eff} into the equation above, where

$$\mu_{eff} = (2/3) \left[2\pi\mu_p\mu_n(\mu_p + \mu_n) / \mu_R \right]^{1/2}$$

and

$$\mu_R = \varepsilon_r \varepsilon_0 (\langle v \rangle \langle \sigma_R \rangle) / 2q,$$

yields the following expression for the two-carrier current density:

$$J = (9\pi/8)^{1/2} \varepsilon \left\{ \mu_p \mu_n (\mu_p + \mu_n) \mu_R \right\}^{1/2} (V^2 / L^3)$$

This solution for the two-carrier current density is known as the Parmenter-Ruppel equation¹⁶. Since this excludes trapping effects, it represents the upper limit of recombination current. Sometimes σ_R is called the recombination constant and is labelled B in that case. The key point to note here is that upon increasing μ or decreasing ε , the recombination increases and the measured current decreases. This equation is only really of use if trapping is negligible.

The other limits for a bimolecular recombination plasma are for a one carrier SCLC current (σ_R infinite or $\mu_{eff} = \mu_n$) and for a pair of one carrier SCLC currents ($\mu_{eff} = \mu_n + \mu_p$). The former was discussed previously in one carrier theory and the latter is given by:

$$J = (9/8) \varepsilon (\mu_p + \mu_n) (V^2 / L^3)$$

Due to neutralization, despite recombination, the total charge can far exceed the net charge and so the overall magnitude of bipolar currents can exceed those in unipolar devices. That is to say the current density can be greater in a two carrier device than in a single carrier device for the same material. As seen from the Parmenter-Ruppel equation, the current flow will be limited by the recombination of carriers which reduce the amount of neutralisation. Without this recombination, the double carrier current

would be infinite. Thus the difference in J in single and double layer devices should qualitatively provide information about the strength of recombination.

Because the analytical equations for bipolar currents involving traps and recombination centers are quite formidable, it is, more meaningful to try and extract information from single carrier analysis on unipolar devices. In fact, in many cases single carrier models have been quite successfully applied to OLED J-V data where it is assumed that the current is dominated by one carrier type. In summary, the main difference between single carrier devices and bipolar ones is there is a recombination term in bipolar ones.

Although consideration of traps has been omitted thus far, trapping plays an important role in double injection. A trap may act as a carrier trap exclusively, or, as a recombination centre. A carrier in a trap is more likely to be thermally re-excited to the nearest energy band than to recombine with an oppositely charged carrier. If the converse occurs, the trap is known as a recombination centre. A demarcation level exists analogous to a Fermi level, insofar as at this energy level a carrier has the same probability of being re-excited as of recombining. Thus, the regions between the demarcation levels for holes and electrons and their respective bands are occupied by traps whereas the region between demarcation levels is occupied by recombination centres.

3.6 ELECTROLUMINESCENCE IN ORGANIC MATERIALS

Electroluminescence (EL) is the phenomenon responsible for light emission in LEDs. The four main requirements for EL are (i) carrier injection, (ii) balanced charge transport, (iii) recombination and, (iv) radiative decay.

3.6.1 Choice of Electrodes for Carrier Injection

Charge injection theory was discussed in section 3.2. Typical contact materials for organic devices are now discussed. For LEDs one contact is highly transparent to visible light and generally the other is opaque and highly reflective. Most often to date the anode is an ITO (indium tin oxide)-coated glass substrate upon which organic layers

and a non-transparent cathode are subsequently deposited. However, increasingly, for high resolution active matrix displays the device is built on CMOS (complimentary metal oxide semiconductor) integrated circuitry, demanding a surface or 'top' emitting device. One approach to a top-emitting structure is to use an inverted structure where the layer next to the substrate with the driving circuitry is the cathode. The other is to use conventional layer ordering, with a highly reflective anode and a transparent cathode, and is more viable for interface formation reasons. In both cases ITO is usually the uppermost layer. Performance of top-emitting devices is, however, poorer than conventional ones because sputtering ITO onto an organic surface requires extra interlayers and even then great care is necessary to avoid damaging the organic layer.

High workfunction, transparent materials such as ITO, which match the organic layer I_p well, are used as ohmic hole-injecting contacts in LEDs. In a multilayered LED, this organic layer may or may not be light-emitting itself. Motivated by the rapidly rising price of indium cost-effective performance enhancing alternatives to ITO are under investigation and include other TCOs (transparent conducting oxides) and conducting polymers like polyaniline and full name PEDOT¹⁷ (BaytronP). Recently, transparent sheets of single wall nanotubes have also been used but the tube network density needs to be increased to make this a viable option for top-performance LEDs. In all cases, it is crucial to have a very low anode sheet resistance (and hence line resistance). TCOs and ITO in particular remain the materials of choice, even for flexible substrates for flexible displays. Partly this is because ITO has long been used in the LCD industry, enabling the OLED industry to simply transfer the relevant fabrication techniques. For hole-only devices, other high workfunction metals can be used including Au, Pt, and Ni since transparency is not a requirement.

Low workfunction metals which match the E_a of the adjacent organic layer provide good ohmic electron-injecting contacts. The lowest workfunction air-stable metal is aluminium but its use generally results in a blocking contact. To achieve an Ohmic contact Calcium is typically deposited first (1-10 nm) and capped with a protective aluminium layer (80 – 200 nm). Ca electrode devices¹⁸ are not air stable and need encapsulation after electrode deposition without breaking the vacuum. MgAg may also be used as a low workfunction material, but controlling deposition is difficult and

target composition is variable. Another approach to ohmic electron injection is to evaporate 1-5 nanometer thick alkali-metal interlayers such as LiF, BaF, and CsF onto the organic, followed by a thick Al capping contact layer. More complex cathodes like LiF/Ca/Al¹⁹ have also been used. Actually, the first ever OLEDs made by Pope *et al* employed sodium-salt solutions to inject electrons, but this rendered the device unstable.

3.6.2 Balanced Charge Transport

Charge transport theory was discussed in section 3.1. In an LED, which is, of course, a two-carrier device, in order to promote recombination, the carrier transport must be balanced. Ideally, devices employing light emitting materials possessing ambipolar mobilities and injection materials and barriers leading to equal injection rates should be used. This is never the case and as a result recombination occurs close to one of the electrodes - the cathode in the case of p-type organic emitters. At electrodes and interfaces generally, EL quenching rates are increased, lowering device quantum efficiency and therefore OLEDs are typically multilayer devices, with layer(s) intended solely for transport purposes as well as an emissive layer. Sometimes the transport layers are also emissive but in this case provided the energy can transfer from the transport layer, the emission will primarily occur from the intended emissive layer

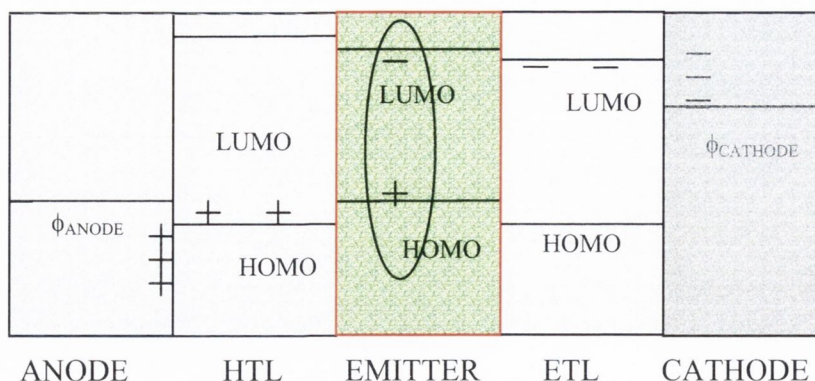


Fig. 26 Generic simplified diagram illustrating the relative positions of the relevant energy levels in a multilayer LED. For the case of a single layer LED, simply ignore the ETL and HTL.

The transport layers are often not just high electron or hole-mobility materials but they also offer a reduced barrier to carrier injection providing a greater supply of carriers also at a given voltage. In the case of holes for example, the barrier to hole injection is reduced by using an organic hole transport layer (HTL) with an ionization potential (I_p) between that of the emissive layer I_p and the ITO workfunction. Furthermore, an HTL can often act as an electron blocking layer to prevent electrons travelling straight through to the anode which can help reduce vertical leakage current. Blocking in this manner also confines the recombination zone to a specific location in the device, away from the electrodes, thereby increasing device efficiency.

PEDOT is a common HTL for PLEDs and TPD²⁰ (see Fig. 1) for SMOLEDs. In the case of PEDOT, ozone-treated ITO improves PEDOT layer formation. Because PEDOT is aqueous, it is very important to dry it fully by baking at high temperature prior to depositing subsequent organic layers. PEDOT is thought to smooth spikes on the sputtered ITO surface which is not polished like, for example, a silicon wafer is. PEDOT's conductivity is not high enough that it can be used without ITO. PEDOT is also thought to quench emission in some cases and the use of a further thin layer between the PEDOT and the LEP may be beneficial²¹. It is also thought to dedope with time²², possibly causing decay by upsetting charge balance due to hole starvation in the device.

One of the most common types of ETL in use is AlQ_3 ²³ which is an emissive small molecule. Polymeric ETLs include PBD and oxadiazole-based²⁴ materials. ETLs are less common than HTLs and there is a distinct lack of really high mobility ETLs.

3.6.3 Recombination and Subsequent Radiative Decay

The capture of electrons and holes to form bound, neutral excited states (excitons or emissive polaron pairs) is a prerequisite for light emission in any LED. Langevin recombination states that a bound excited state will form when an electron and hole approach within a distance r_c , at which point the Coulombic binding energy dominates the thermal energy, kT . Equating these energies gives r_c which is inversely proportional to the dielectric constant, ϵ_r :

$$r_c = \frac{q^2}{4\pi\epsilon_s kT}$$

For example, for $\epsilon_r = 4$, at 300K, r_c will be 14 nm. For electrons and holes, with number densities n and p , approaching each other with velocity, v , the recombination cross section, σ_r , equals the product $G_E npv$, where the generation rate, G_E , is:

$$G_E = npF(\mu_e + \mu_h)\sigma_r$$

The simplest model has $\sigma_r = \pi r_c^2$ which assumes isotropic mobilities. The recombination zone (RZ) is where emission occurs and is that region in the LED emissive layer(s) whose width is defined by r_c and whose location is defined by the balance of charge transport. For example in a hole-dominant device, EL efficiency increases when cathode workfunction is lowered because the quasi Fermi level for electrons is brought closer to the LUMO (conduction band) and so more negative carriers are available for recombination. Also, as electron mobility is increased (related to increase in n), the recombination zone widens and electrons travel further from the quenching cathode before recombination occurs. Finally, what was essentially a unipolar device is now considered bipolar since bipolar current exceeds unipolar current.

3.6.3.1 The Singlet-Triplet Ratio in Organic LEDs

One of the first reports of a polymer with a singlet-triplet (S-T) ratio, r , greater than that predicted by simple spin statistics was made by Heeger et al in 1999²⁵ and since then there has been much research aimed at better understanding exciton yields and formation rates in conjugated polymers. Heeger's results involved using an integrating sphere to separately measure EL and PL efficiencies from an OC1C10-PPV : BuPBD blend. The PL quantum efficiency is shown to be temperature-independent over the range measured (20 – 90° C). However, the EL QE at 85° C is about twice that at room temperature for the blend device, giving a singlet yield of 50% at 85° C. If their device does not have good charge balance, quenching effects at the electrodes will dominate and a reduced singlet yield will be observed at elevated temperatures. Therefore, the authors stress this is a lower limit as it does not take into account any field-induced PL-quenching and also because EL efficiency suffers a greater reduction due to electrode quenching than PL efficiency. Due to the weak spin-orbit coupling in conjugated polymers, it is unlikely that the singlet population is increased in devices through triplet-to-singlet conversion via triplet annihilation. Thus the high singlet yield must be due to either a small exciton binding energy or enhanced singlet formation cross-section at 85° C, or in other words, a spin-dependent formation cross-section. At room temperature the singlet yield observed was already at the simple spin-statistical threshold of 25%. Since the S-T exchange energy is ~ 0.7 eV, one must favour the notion of a spin-dependant exciton formation rate or cross-section. This idea requires then also that there are competing channels for recombination. Although it is not yet clear what these are, some candidates include spin-lattice relaxation, spin-orbit coupling, spin-dependent e-h capture radii and competition between exciton cooling rate and exciton dissociation by the electric field. Using spin-lattice relaxation as an example, Vardeny et al²⁶ have shown how r (which depends on the formation cross-sections which are related to the formation rates) determines $n_{\max}$ in the case of two important limits. They show that $n_{\max} \xrightarrow{k_{SL}=0} 0.25$ and $n_{\max} \xrightarrow{k_{SL} \ll k_S} \frac{r}{r+3}$. So, for example, if $r = 3$, $n_{\max} = 0.5$. If a rough approximation is made in saying that only 20% of the light in an OLED is extracted, then

we can begin to suspect $r > 1$ if the EQE $> \sim 5\%$. The S-T ratio may be studied experimentally in live OLEDs, though this is made difficult by interference effects in a device. Therefore a technique which combines photoinduced absorption (PA) and optically detected magnetic resonance (ODMR) techniques has been used on thin films²⁷. By manipulating exciton formation rates in thin films using electron spin resonance in thin films where the changes in excited state absorption are simultaneously measured, PA-ODMR can be used to obtain $r = \sigma_S/\sigma_T$, the S-T formation cross-section ratio, directly from experiment. In order to enhance the PA signal spectra, samples were UV-irradiated for 3 hours using a filtered 450-W xenon lamp. This latter process has been shown not to alter the $P^+ P^-$ recombination kinetics.

$$r = \frac{1 + 3(\delta T / \Delta T)^{1/2}}{1 - (\delta T / \Delta T)^{1/2}}$$

where $\delta T/\Delta T$ is the magnetic resonance-induced change in the transmission, ΔT , in the PA-ODMR experiment. In these experiments, the spin $1/2$ magnetic resonance reduction of triplets was compensated by an increase in the singlet population, and therefore PL intensity is enhanced under magnetic resonance. Also, an absorption band at 1 eV was attributed to excited state (singlet) absorption due to the excess singlets formed. For an oligo-thiophene (12-mer), r from the low temperature PA and PADMR data = 2.2 whereas for the equivalent polymer $r = 4$. It has been shown using these techniques that $r \sim 1$ in small molecules, in agreement with reports of a singlet yield of 22% in AlQ₃ devices, and that r increases as the conjugation length increases, again implying that r is spin-dependent. In OLEDs the quantum efficiency, η_{EL} , equals $n_1 n_2 n_3$ where n_1 is the singlet emission quantum efficiency, n_2 is the fraction of the total exciton population that are singlets, and n_3 is the probability the injected carriers form e-h pairs. Both n_1 and $n_3 < 1$ hence $\eta_{EL} < n_2 = \eta_{max}$. Since r can be found experimentally, $\eta_{max} = (1 + 3r^{-1})^{-1}$ can also be estimated. Importantly, it has been shown that $r^{-1} \propto CL^{-1}$, where CL^{-1} , the inverse of the conjugation length was varied by changing n , the number of rings for a set of oligothiophenes. Using literature data, polymers such as PFO and MEH-PPV were also shown to fit well in this scheme, indicating the universality of the trend, irrespective of chain length, backbone structure or side-groups. The conjugation lengths of different polymers can be inferred since polaron absorption peak energy, P , is linearly dependent

on $1/CL$ and r^{-1} is linearly proportional to P , the polaron energy (making $r^{-1} \propto 1/CL$ also linear). By linear extrapolation, $r = 1$ was found for $n = 2$ ($= 7\text{\AA}$) and so exciton formation is spin-dependent at lengths greater than this.

The reason for this universal dependence of r^{-1} on CL^{-1} is possibly due to the increasing difference in singlet and triplet wavefunction extent as CL increases. Triplets are always confined, even for polymers (e.g. e hole separation in PPV is $3.2\text{\AA}$) but singlet wave functions can be as large as the CL itself. Morphological film changes do not alter the value of r probably because both exciton formation rates are effected similarly by any associated changes.

These observations in relation to CL are in agreement with the results of Wilson²⁸ who found that the singlet generation fraction in EL devices is $22 \pm 1\%$ for a phosphorescent monomer and $57 \pm 4\%$ for the related polymer. The singlet yield for the monomer is close to the 25% expected for a random Langevin capture process. The Langevin capture radius is of the order 14 nm. This is considerably larger than the molecular dimension for a monomer unit, but comparable to the delocalisation length along a polymer chain. Therefore, for molecular materials, the electron-hole capture occurs at a range where only the Coulomb interaction is effective and there is no contribution from electron-hole wavefunction overlap. Consequently, the capture process proceeds as expected for a Langevin mechanism, resulting in excitons, which are independent of the spin states, of the captured charge pair. However, for polymers, when electrons and holes are present on the same chain within the capture radius the interaction also includes a contribution from the direct overlap of electron and hole wavefunctions. The singlet exciton delocalisation is of the same order of magnitude as the Langevin capture radius, while the triplet exciton delocalisation is considerably less than this. Consequently, the formation of singlet excitons can compete with the random charge capture process. Thus the overall capture process becomes spin dependent in favour of the formation of singlet excitons. As a result, polymers displaying greater singlet exciton delocalisation should have increased electro-luminescent efficiency.

More recently, than the above work by Heeger, Wilson, and Vardeny, Bradley et al²⁹ found $n_2 = 0.7$ for polyfluorene (PFO). In this work a PFO LED was reverse biased at room temperature and a 150 fs resolution pump-probe arrangement was used to study

the fundamental dynamics in polymer devices. It was shown that field-induced dissociation of singlet excitons results in free polarons (polaron pairs) as short lived intermediates which subsequently recombine. The polaron pairs exist both with singlet and triplet multiplicity and have differing formation rates, rendering the fundamental event in electroluminescence time-resolved. In order to identify features in the differential transmission spectrum from the LED sample, a chirp-free transient absorption spectrum from a PA experiment (1 ps probe delay) done on PFO coated glass was used as a reference. Clear differences are observed between the differential transmission spectrum taken at 2 ps and 200 ps pump-probe separation or 'delay' times. An interesting feature at 820 nm observed to form at about 50 ps probe delay is attributed to triplet formation based on previous PA work on thin films. This feature is clearly not due to singlets as the intensity of singlet-associated peaks was seen to have decayed to zero already at this stage. Also the decay dynamics at the associated wavelengths of the singlet and triplet species from PFO-coated glass (no field) are identical. Since spin flipping in doublet states occurs at 1 μ s timescales this means the triplets are formed non-geminately by recombination of initially field-induced polarons, as part of a very short time-scale pairing process which results in singlets and triplets being formed. By making population decay fits to the time-dependant ΔT and differential transmission curves a value of 0.7 for n_2 was obtained.

In a separate experiment, using what was essentially a standard LED structure, Dhoot et al³⁰ deduced a singlet yield of 83 $\pm$ 7% for OC1C10-PPV. By measuring the lifetime of an identified triplet species and using a calculated absorption crosssection to get the triplet generation rate. The measured light output of the LED and an optical model of the device was used to obtain the singlet generation rate. The work involved measuring changes in transmission (using partially transmissive electrodes) induced by pulsing the device on and off. The yields of excitons were based on measurements made at 10 K where the triplet absorption signal was greatest. At temperatures above 150 K no triplet absorption was detected due to the short lifetimes of the triplets at higher temperatures.

Barford explains for the first time³¹, starting from degenerate singlet and triplet polaron pairs, the higher than 25% S yields for parallel chains, using a theory where

electron-hole recombination occurs via intermolecular interconversion from intermolecular weakly bound polaron pairs to intramolecular excitons. The interconversion process is a multiphonon process, determined by F-C factors which are exponentially smaller for the triplet manifold than the singlet manifold because of the difference in energy of S and T states (0.7 eV). Therefore, the triplet interconversion rate is slower than the singlet one and is comparable to the ISC rate, making it possible for singlet yields, greater than those predicted by simple spin statistics, to exist. The theory explains how the maximum yield goes from close to 25% for small molecules, and increases with conjugation length, via selection rule changes as the conjugation length and particle hole-separation change from being comparable to quite different. Quantum chemical calculations confirm these predictions³². Barford's finally derived rate equation shows clearly that the singlet yield increases as S_p , the polaron Huang-Rhys parameter (not accurately known but presumed to be similar to the equivalent exciton parameter) decreases because multiphonon emission becomes more difficult. The singlet yield also increases as the exchange energy increases for any v_S (number of phonons emitted) or v_T if $S_p < 1$. Barford³¹ has made recommendations for increased singlet yield from a theoretical analysis of the singlet-triplet ratio problem – these are that the chains should be well conjugated, closely packed, and parallel. This is apparently at odds with many papers which suggest that interchain interaction results in quenching of emission through the formation of excited states not bound to the ground state. However, an enhanced singlet yield could occur with an overall reduction in radiative emission. It seems a balance between maximizing singlet yield and reduced emission intensity due to interchain packing effects is desirable.

Reufer et al³³ observe spin conservation in experiments designed to study recombination of optically and electrically generated excitons. This is apparently contradictory to many of the other studies just reviewed. In order to study the recombination of optically generated excitons dissociated in under an electric field, PL was studied in a sandwich type structure. Recombination following electrical injection of carriers was also studied in PLEDs by applying a reverse bias pulse using a model light-emitting material containing Pd atom sites (at such a low level as not to effect the singlet emission in thin films) which allows both singlet and triplet emission to be monitored.

In both, carriers are field-dissociated and it is assumed that because the resulting polaron pairs are then held in a metastable state for times much longer than the slow triplet formation time (i.e. field pulse width) that there should be plenty of time for any spin-randomization to occur. This is not seen i.e the relative triplet intensity does not change appreciably and so it is concluded that spin conversion does not occur in close or distant pairs (optically generated). Also, use of a strong magnetic field applied to the LED only serves to increase both S and T yields by the same amount but does not promote formation of one exciton over another as would be expected for spin-dependent recombination. The observations are not inconsistent with a higher singlet formation rate than triplet formation rate but they do suggest that the singlet and triplet polaron pairs are not degenerate and that there is still some exchange splitting so that there can be no physical competing channels to carrier recombination. In this case even a large imbalance in exciton formation rates cannot modify overall yields. This paper, although based on a model compound, does suggest that spin conversion during the capture process is not occurring, in agreement with other direct device observations made by Segal et al³⁴ but contrary to the results published by Heeger et al, Virgili et al and many others. The shorter timescales in Virgili's work²⁹ in particular (and the fact a 'standard' LEP was used) should be more appropriate for studying what actually occurs at the initial coulombic encounter. Reufer's approach is the same with respect to starting with dissociated excitons, (polaron pairs) but he studies changes after dissociation on a longer timescale so that it is possible other non-radiative processes have already occurred to give an apparently unaltered exciton ratio in his case. Based on these results he concludes that since single charge is coupled to molecular vibrations, the electronic wavefunction is extended through space, though reduced in mass, and exchange splitting remains large enough to prevent singlet triplet degeneracy in the P₊P₋ state.

If the triplet E_b and corresponding cross-section for forming a triplet from a pair of injected carriers were large then, 25% of the photoluminescence (PL) yield would equate to the maximum electroluminescence (EL) efficiency. If the cross section for formation is small, EL quantum efficiency could in principle be 100% of the PL yield. Although in principal 100 % EL yields may be possible, in reality, disordered, unaligned samples will exhibit more polaron-exciton behaviour. However, since disorder is

distanced from the intrinsic electrical and optical properties, EL efficiencies greater than the limit predicted by simple spin statistics (25 % of PL yield) should be possible even for disordered samples as long as the conjugation length is comparable with the coulomb capture radius.

Exciton decay, $-\frac{dn}{dt}$, depends on the radiative and non-radiative decay times. It is defined as $-\frac{dn}{dt} = \frac{n}{\tau_r} + \frac{n}{\tau_{nr}}$ and has a random natural exponential decay where n, the exciton density is:

$$n = n_0 \exp \left[-\frac{t}{(\tau_r^{-1} + \tau_{nr}^{-1})^{-1}} \right] = n_0 \exp \left(-\frac{t}{\tau} \right)$$

3.6.4 Injection- and Volume-Controlled Electroluminescence

Kalinowski *et al*³⁶ proposed a method of expressing the current density dependence of the EL efficiency, ϕ_{EL} , using a kinetic model. Their method assumes only singlet excited states to be produced homogeneously throughout the sample in the electron-hole recombination process and states:

$$\phi_{EL} = (k_F / k_S) \gamma n_h n_e d$$

where γ is the recombination coefficient for the injected carriers, and $k_F = k_f + k_{nr}$ and is the total decay rate constant including the nonradiative pathways. The kinetic equation describing the free negative carrier population under steady state conditions is:

$$\frac{j_i^e}{ed} - \left(\frac{1}{\tau_T^e} + \frac{1}{\tau_{rec}^e} \right) n^e = 0$$

, where transit time is given by $\tau_T = \frac{d}{\mu F}$ and the recombination time is $\tau_{rec} = 1 / \gamma n$.

In the case of injection-controlled EL, ICEL, there is monomolecular decay of charge carriers since $\tau_T < \tau_{rec}$. Combining these equations for electrons and holes yields:

$$\phi_{EL} \cong \frac{k_F}{k_S} \gamma \frac{j_i^e j_i^h}{e^2 \mu^e \mu^h F^2} d$$

With ICEL, the EL is a side-effect of the current flow and its intensity is proportional to the product of electron and hole currents. Irrespective of the form of the injected current, ICEL predicts a power law dependance of ϕ_{EL} on current density, i.e. $\phi_{EL} \propto \left(j^{e,h}\right)^{n_{e,h}}$.

In the case of volume-controlled electroluminescence (VCEL), the positive and negative space charges will overlap throughout the sample and largely cancel each other out. The decay is bimolecular as it is dominated by the second order process of recombination and so $\tau_T > \tau_{rec}$. It can be shown for VCEL that $\phi_{EL} = (k_F / k_S)(j / e)$ and ϕ_{EL} is always linearly proportional to the current, independent of the extension of space charge overlap which does, however, strongly influence the position of the EL RZ

3.7 MATERIALS DEPOSITION TECHNIQUES

3.7.1 Sputtering and Evaporating Techniques.

Developed in 1858, sputtering involves plasma formation over the target material to be deposited by inert gas ionization using a RF (radio frequency) power supply. The target is negatively charged, and positive argon plasma ions accelerate towards it. Target ion-bombardment causes surface ejection of target atoms towards the substrate overhead. A homebuilt sputterer with a rotary-backed diffusion pump (base pressure of 2x10⁻⁶ mbar) and high purity targets (99.99%) from Testbourne Ltd were used for this thesis work. A low deposition rate (low power) of 2 Å/s was used initially and ramped after 20 nm of material was deposited. Although any conductive material can be sputtered, its use in OLED fabrication is usually limited to coating glass with ITO since sputtering

onto soft organic materials can lead to surface damage and penetration of thin films by high kinetic energy metal particles.

Evaporation is used to deposit cathode materials and small molecules. Thermal evaporation of a source material contained in a boat, coil, baffle or other holder involves passing a sufficiently large current through the boat/holder thereby resistively heating it and, indirectly, the source itself. This causes the source to evaporate or sublime on the substrate overhead (and to a lesser extent on the walls of the chamber). Again, low rates (low boat current and temperature) are used initially, as with sputtering. An Edwards Autovac 306 evaporator with a rotary backed diffusion pump (base chamber pressure of 2×10^{-7} mbar) was used for this thesis work. Although greater control of deposition layer quality may be achieved by controlling substrate temperature, particularly for organics, this was not used in this thesis. Evaporation is useful for thin film (~100 nm) deposition whereas sputtering, can also be used for thick films (microns).

The thickness of the sputtered or evaporated layer was monitored in situ using a quartz-crystal thickness monitor. The fundamental mode of vibration of the water-cooled crystal changes as more material is deposited on it. The instrument may be calibrated for any material knowing the bulk density of the material and the thickness of a layer deposited at a given rate for a given source-substrate distance. Crystals were replaced regularly, with either a new crystal or with a washed, used crystal to ensure reliability.

3.7.2 Spincoating

Spincoating is widely used to produce good optical quality polymer thin films. All the films for this thesis were spun from a fully flooded substrate using a Convac 2000 coater. Nitrogen or argon-purged spin-coaters lower interface trap densities as can using dry vacuum pumps to hold the substrate in place during coating. Typically substrate spin speeds of 1200 – 2000 rpm for different light-emitting polymer solutions of concentration 10 mg/ml - 20 mg/ml yielded 40 -150 nm thick films. The film thickness, t , is related to the spin speed, ω , by a power law of form $t = k\omega^{-b}$. For a given concentration the thickness is proportional to ω^{-b} and for LEPS b is typically $\frac{1}{2}$. The constant k depends on the viscosity and hence the solution concentration and the acceleration to full speed. Film thickness may also be varied by changing the speed

during the 'drying phase' after the main spinning phase also though this was not experimented with here. The thickness was monitored using tapping-mode AFM (Atomic Force Microscopy) with a stepheight analysis function and/or Dektak needle profilometry. White light interferometric measurements may also provide thickness information. All these thickness measurement techniques also provide surface roughness information (e.g. highly volatile solvents result in rougher film surfaces). When making a scratch with a pin or a razor blade edge in a film to measure the film thickness it is very important not to scratch the substrate and to have flat regions either side of the scratch on the same level.

Other deposition methods for OLEDs include ink-jet printing (IJP), organic vapour-phase deposition (OVPD), doctor-blading, and screen printing. OVPD³⁷ normally involves the vacuum deposition of small molecules by sublimation, with excellent control of layer composition, film morphology and crystallinity achievable. Unlike evaporation, OVPD permits the flow rates of the organic species introduced into the chamber to be controlled precisely.

Of the organic deposition techniques IJP is the most innovative and potentially disruptive technologically. Inkjet printing³⁸ offers the inherent ability to deposit very small quantities (~ 3 pL) of highly specialized fluids reliably, accurately and at high speed onto a wide range of substrates. Applications under development include ink jet printing of colour filters, printing LCD spacers and printing metal wiring using nanometal inks. The emissive regions in PLEDs which are based on solution-processable light-emitting polymers may also be assembled using ink jet printing meaning RGB elements can be deposited in a single layer rather than as a stack where there may heavy optical losses. PLEDs offer end-user performance advantages over LCD displays but are also potentially cheaper to produce if ink jet methods are used.

The backlight, colour filter, polarizer and LCD layer, collectively account for about 50% of an LCD panel's functional materials. Inkjet printing will simultaneously deposit and pattern the emissive layer in a PLED display thereby reducing process steps. Furthermore, 3-10 times more efficient use of material, quick tact times (<2 mins) comparable to those for LCDs (and better by a factor of 2, than for OLEDs), a smaller footprint and elimination of masks all make inkjet printing an attractive option to the

device manufacturer. Even spincoating may be replaced by ‘flood’ printing, where a dot pattern is printed and the dots coalesce to form an even film, however, it is not possible to efficiently ink jet materials with a high molecular weight ($> 250,000$).

IJP is, however, technically very challenging. The main issues with inkjet printing are drop formation at the nozzle, drop placement on the substrate, and uniformity of resultant layer. The problems in reducing the drop size have to do with the development of self cleaning print heads which do not clog easily. Low molecular weight materials are best suited to IJP. The wet layer thickness of a single drop is 5 – 20 micron which then dries to about 100 nm thickness. This defines a concentration of about .01 g/L polymer solution concentration to produce a shear viscosity that falls within the range needed for ink-jet printing. However, with LEP inks, small concentrations of high molecular weight polymers can cause unstable jetting conditions. This is due to higher deformation rates in the ink jet head, where the liquid will behave in a non-Newtonian manner. After drop formation the drop flies through the air, lands on the substrate and spreads. Because the pixel size must be fixed in a display, drops are printed between barriers made by photolithography. In common with spincoating, the last step is solvent evaporation and the formation of a flat polymer film. This is a complicated process which depends on the solvent type, polymer, concentration, and substrate wettability. Seiko Epson raised the profile of this technology by printing a 40” diagonal PLED TV screen in 2004 (glass substrate). CDT demonstrated a printed 6” display on a flexible substrate earlier in 2006. Ink jet printing may now be applied to conventional long chain PPV/PFO type polymers but is also being adapted for materials which may be used in PHOLEDs or SMOLEDs and it may even be used for SWNT (single wall nanotube) mat printing.

3.8 DEVICE PERFORMANCE

3.8.1 Quantum Efficiency

The internal quantum efficiency η_{int} of a device is a *theoretical* quantity which considers the maximum possible efficiency by excluding losses due to inefficient light outcoupling and is defined as $\eta_{\text{int}} = \gamma r_{\text{st}} q$, where γ is the ratio of the number of exciton

formation events within the device to the number of electrons flowing in the external circuit, r_{st} is the fraction of excitons formed as singlets, and q is the efficiency of radiative decay of the singlet excitons.

External quantum efficiency, η_{ext} , on the other hand, is an experimentally measurable quantity and is defined as $\eta_{ext} = \#photons_{out} : \#electrons_{in}$, where $\#electrons_{in} s^{-1} m^{-2} = J / e$ and $\#photons_{out} s^{-1} m^{-2} \cong \frac{L_v \lambda}{\mathcal{L} hc}$. L_v is the luminance and is a photometric quantity as opposed to a radiometric one. This means that the luminance accounts for the human eye response which is defined by the photopic function.

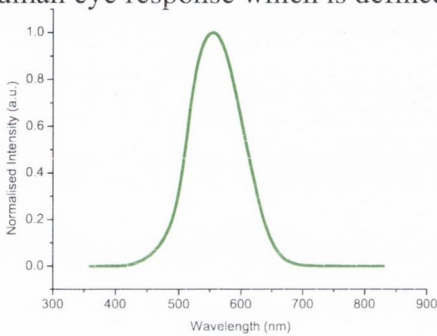


Fig. 27 The photopic curve, peaking in the green region, corresponds to the human eye’s response (λ) to light.

Luminance or *brightness* is the photometric equivalent of radiance which is measured for extended light sources (as opposed to a point source) and is defined as $L_v = \frac{d\phi_v}{dA_v d\Omega}$, where $d\Omega = dA / r^2$ and the luminous flux, ϕ_v , emitted from an area, dA_v , per unit solid angle, $d\Omega$, is:

$$\phi_v = \mathcal{L} \int_{380nm}^{780nm} \phi_e(\lambda) \cdot V(\lambda) d\lambda$$

$\mathcal{L}$ is a lumens to watts conversion factor equal to 683 Lm/W. From these definitions η_{ext} is defined as:

$$\eta_{ext} \cong \frac{J \mathcal{L} hc}{e L_v \lambda}$$

A spectroradiometer is used to measure the emitted power as a function of wavelength and this, in turn, is converted to a luminance reading. An integrating sphere may also be used. The CIE system³⁹ is used to define colour purity of a given pixel EL spectrum.

Though η_{int} is not directly measurable, it may *be estimated* assuming $\eta_{\text{ext}} \cong \eta_{\text{int}} / 2n^2$, where n is the refractive index of the glass substrate. In other words most of the LED inefficiency is due to optical losses caused by poor outcoupling of light through the face of the ITO/glass substrate. Most of the EL is effectively waveguided in the ITO layer and exits at the LED edges. Assuming $n \sim 1.5$, clearly, only $\sim 20\%$ of the internally generated emission is collected externally through the face of the ITO. Improving outcoupling by reducing optical losses due to waveguiding modes in the LED is an important way of increasing outcoupling efficiency. In standard PLEDs (see below), outcoupling elements, such as photonic crystal slabs and microlens arrays built into the ITO glass substrate, increase η_{ext} but result in more directional emission. For WOLEDs (see below) scattering layers on the ITO have been used to assist outcoupling⁴⁰.

Most OLEDs have diffuse emission with an approximately Lambertian or cosine distribution. A Lambertian point source has an angular dependent emission defined by $I = I_0 \cos \theta$ where I_0 is the intensity normal to the source itself. In the case of microcavity OLEDs, one highly reflecting electrode and one partially transmitting metal electrode, results in an etalon or Fabry-Perot arrangement. The resulting emission spectrum is narrowed around a central wavelength λ corresponding to the resonant mode of the cavity given by $2nd \cos \theta = m\lambda$ $m=1,2,\dots$, where d is the cavity thickness, n is the refractive index of the polymer and θ is the emission angle from the cavity. The use of thin multilayer dielectric stacks instead of semitransparent metals enables control of the cavity characteristics. Building an ITO layer as the top layer of the dielectric stack, permits microcavity devices to be made which have sharply directed emission. For any kind of LED, a goniometer is used to measure the emission profile.

3.8.2 Luminous Efficiency

The luminous efficiency η_l (units of Lm/W) is the photometric analogue of the radiometric quantity power efficiency and is defined as $\eta_l = \pi L_v / JV$. A Cd/A value is often quoted with a corresponding operating voltage, V. This has the advantage that, at once, one can see all the main device parameters - brightness, drive current, drive voltage - and η_l can easily be calculated by multiplying the Cd/A value by π/V . Whether Lm/W or Cd/A are quoted, it is important to remember that this efficiency is effectively not sensitive to device architecture changes which cause different outcoupling for different wavelengths, whereas η_{ext} is. Owing to a lack of a spectroradiometer, in the η_{ext} calculations a forced compromise was made by using only the maximum of the EL spectrum.

In terms of portable device performance, luminous efficiency contributes greatly to determining battery lifetime. For the consumer, running cost and convenience are important device parameters. Operating voltage will determine battery size and is most important for mobile applications. When comparing the power efficiencies of various display modules or pixels, it is important the same unit sizes and specifications are used. It is worth noting that as a rule of thumb, there is up to an order of magnitude decrease in performance from one-off, optimised lab devices to similar display production modules.

3.8.3 Device Lifetime

The root cause of the exponential decay observed in OLED lifetimes is still not well understood, though contributing factors are many and depend on synthesis and fabrication methods as these influence the composition, number of trapping states and morphology of materials used. The operational lifetime is often defined as the time to half brightness (t_{50}) from an initial brightness of 400 cd/m^2 under constant current (DC) driving although for many applications a good t_{80} or even t_{90} value from 1000 cd/m^2 would be more appropriate! Lifetimes can be measured directly by running a device under STP or, indirectly, by extrapolation from t_{50} and assuming a constant acceleration factor for the decay (power of exponent used to describe decay curve is constant.)

Clearly the lifetime depends on the initial luminance, the higher the initial luminance the shorter the lifetime – there is no industry standard at the moment for quoting lifetimes and results published must always be treated with caution.

SMOLEDs are more stable than PLEDs at present. The lifetime of blue materials for all OLED types lags behind those of red and green and needs improving before televisions based on OLEDs can compete with LCD TVs. Flexible OLEDs⁴², are particularly unstable environmentally, largely due to difficulties in achieving effective encapsulation.

3.8.3.1 Environmental Factors Effecting Device Lifetime

Oxygen from the atmosphere, or from water, results in the formation of reactive carbonyl groups which promote formation of excited singlet oxygen states which quench luminescence⁴³. Oxygen and moisture also oxidize the electrodes and alter the injection barrier as a result. Lipson et al⁴⁴ confirmed that spincoating Ar-degassed polymer solutions in Ar instead of air, reduced polaron absorption due to oxygen in the resultant films and increased photoluminescence efficiency. In industry, exposure of OLEDs to oxygen or moisture is minimised by fabricating the entire device under high vacuum conditions, including passivation by encapsulation.

Photo stability is the stability of a material to light, particularly UV light, which can have a photobleaching effect⁴⁵. OLED displays are fine for indoor applications but risk being washed out or faded upon prolonged, direct exposure to sunlight. After long periods of operation (> 10000 hours for stable materials) degradation can be due to loss of conjugation due to photobleaching and or oxidation resulting in a blue-shift of the EL. The use of UV filters in the encapsulating layers can somewhat reduce this problem.

Defects in organic films or metal electrodes can lead to shorting and the formation of black spots due to localized heating⁴⁶. Localised joule heating is sufficient to melt the cathode in parts of a single pixel. Black-spot degradation, unlike photo-degradation, gives rise to early failure. Elevated operating temperatures in a device, or the presence of temperature gradients, can also lead to molecular diffusion in SMOLEDs which can cause pixel bloom (spreading of emission beyond the pixel edges defined by the electrodes.). In the case of PLEDs elevated temperatures usually will mean that there is a

burn-in time for a display where the polymer strands rearrange slightly and, after which, the display is quite stable. Clearly, if joule heating can generate large internal device temperatures, then high glass transition temperature (T_g) organic materials are required. A high T_g is also important as organic layers require baking after spincoating in order to drive off excess solvent fully. Although black-spot defects affect display lifetimes, many commercial OLED display modules are being produced with low defect counts and sufficient lifetimes to be competitive in certain display industry sectors. This is largely because for applications like mobile phone displays, a modest brightness is required if AM drivers are used. Joule heating really becomes a problem for high brightness applications. Therefore, for displays using PM drivers (a strobe technique) joule heating is a very important lifetime limiter. In a PM OLED the duty cycle must be at least 50 – 60 Hz, and since brightness is proportional to current, a large pulsed current is required to generate a sufficient average brightness. Another application where Joule heating would be significant is the as yet undemonstrated, electrically pumped organic laser.

3.8.3.2 Importance of Cleanliness

In order to achieve high performance devices cleanliness is crucial at all stages of device production, from chemical synthesis and substrate cleaning to spin-coating and metalisation. Clean room facilities are just as important for organic devices as they are for inorganic devices. For example, the likelihood of pinholes, impeded contacts and filamentary injection, all of which reduce device lifetime, is lowered by using clean room facilities. All layers must be as pure, uniform and homogenous as possible. Cleanliness will reduce trap densities in the material which in turn reduces mobility. Cleanliness affects the nature of an interface (e.g. by changing surface tension) and hence its injection properties, and is ultimately reflected in the emission uniformity, turn-on voltages and efficiency of a device.

3.9 TYPES OF ORGANIC LIGHT EMITTING DIODE

3.9.1 SMOLED

Electroluminescence of an orange colour was first observed⁴⁷ in an organic material in the 1960s upon application of several hundred volts across a very thick, epitaxially-grown anthracene single crystal. This was the first electrofluorescent OLED and could be termed an MCOLED (molecular crystal OLED).

Small-molecule-OLEDs (SMOLEDs) rely on electrofluorescence from small molecules deposited either by thermal evaporation/sublimation or, alternatively by OVPD. The use of vacuum-deposited amorphous thin films of anthracene (Vincett and Barlow) led to EL being observed at 30 V and represented the beginning of SMOLEDs although external quantum efficiencies were still low (0.05%). It was not until Tang *et al*⁴⁸ used a sublimed, two layer SMOLED in 1987, with each layer capable of only monopolar transport, that green EL device with 1% η_{ext} was achieved at 1.5 lm/W. SMOLEDs are limited to quite small panel sizes, generally only up to a few inches diagonal, due high vacuum processing organic deposition requirements. It is difficult to create a uniform thickness layer by sublimation, however, techniques like OVPD may enable these materials to be used in low cost production of larger panels.

3.9.2 PLED

Strictly speaking, PLEDs should be (and sometimes are) referred to as P-OLEDs (polymer OLEDs) although. Polymer EL was discovered serendipitously in 1989⁴⁹ during electrical studies on PPV. The solution processibility of polymers lends itself well to large area device production and to patterning using inkjet printing techniques, making PLEDs, potentially, a very cheap display to manufacture. To an extent, PLEDs may be distinguished from SMOLEDs by the fact that SMOLEDs tend to have more layers since PLED layers tend to be multifunctional so one material is used both for transport and emission. Polymers may also be blended (with other polymers or small molecules) and processed in a single step enabling combination of different functionalities, potentially reducing device production costs. The different classes of

polymer backbone synthesized include PPVs,^{49,50} ladder Polymers⁵¹, polyfluorenes⁵², polythiophenes and spiro-polymers.

3.9.3 PHOLED and DOLEDs

The idea behind PHOLEDs⁵³ is to harvest both radiative singlets and non-radiative triplets in a polymer host material by using simultaneous Forster transfer of singlets and Dexter transfer of triplets from the host to a phosphorescent emitter using the heavy atom effect. The internal quantum yield is thus almost 100 % and the external quantum efficiency is the best of all the OLED types. Pt compounds were initially used but this resulted in loss of efficiency as brightness was increased due to triplet-triplet annihilation. The problem was overcome by using Ir compounds. The first commercial use of a PHOLED was in 2001 when a full colour sub-display in a Fujitsu phone used it. The big development bottle neck is with blue PHOLEDs which lag red and green PHOLED lifetimes and have a low initial brightness, though improvement is ongoing. There is interest now in making an IR (infra-red) two-tone PHOLED display for military use, viewable only by someone with night goggles.

Dendrimers⁵⁴ are the most recently developed class of organic emissive materials and cover the whole spectral range. Dendrimers are particularly interesting materials in that different functionalities (charge transport and luminescence) are very well separated and may be independently varied in a controllable manner. Ordinarily the fact that polymer emission and transport are linked via the chemical structure can be problematic (e.g. quenching due to polarons interacting with excitons and excimer formation between transporting and emitting moieties resulting in reduced EQE.) Dendrimers avoid this problem and it has been shown the influence of the charge-transporting conjugated dendrons on the emission properties of the core are negligible. This allows fine-tuning of the electrical properties of the dendrons independently of the highly fluorescent dye chromophore (or phosphorescent molecule) cores to improve LED efficiency. Dendrons with alkoxy sidechains are designed to ensure these polymer-hybrid systems are soluble, enabling solution processable electro-phosphorescent materials where the core is a

triplet-emitter. Highly efficient PHOLEDs using solution processing have been made using this approach.

3.9.4 WOLED

Inorganic white LEDs⁵⁵ are now widely available as efficient, bright sources for lighting applications ranging from torches to ceiling lighting. Similarly, there is a concerted effort in the OLED industry and in academic circles to develop OLEDs for solid state lighting. Unlike their inorganic counterparts, white OLEDs (WOLEDs) may be produced in thin film format over large areas, desirable for interior illumination in particular. Obviously, if WOLEDs are to replace current the filament bulb and the fluorescent tube, cost and efficiency must be better than for these established technologies. Novaled have reported some of the highest values for WOLEDs to date⁵⁶. WOLEDs are also significant in their own right for use as sub-pixels in RGBW type AM OLED displays where the use of white sub-pixels provides improved display contrast.

3.9.5 TOLED and FOLEDs

Totally transparent-OLEDs⁵⁷(TOLEDs) are useful in situations where one would like illumination while still being able to, for example, read print directly beneath the device. Their surface-emitting structures are also useful for surface-emitting OLEDs on A-Si backplanes. A typical TOLED structure is ITO/poly/ETL/CuPC/LiF/Al.

Using roll-to-roll processing ultimately one could envisage a paper-thin, full-colour, Flexible-OLED (FOLED) display, possibly with an inbuilt organic solar cell which could be used as a refreshable, rechargeable spreadsheet/broadsheet. Other thin, flexible electronic display systems include flexible LCDs, electrophoretic displays and electrochromic displays, all of which are deficient in the following ways: they require backlighting; they only have grey scales and they have slow response times respectively. FOLEDs⁵⁸ offer the best solution for low power, RGB video rate flexible displays. The main area of concern with FOLEDs is in extending the device lifetime by making the flexible substrate sufficiently impermeable to moisture, especially in a country like Ireland!! Flexible substrates used include Mylar, Kaladex (a PEN film) and thin steel

foil. Multilayer barrier films using organic-inorganic repeating layers (Barix and Batelle Inc.) have been used to passivate the device. A further concern is that repeated bending of the FOLED display must not affect its performance for a given bend radius. Recent demonstrations using a paper punch highlighted FOLED durability: - holes made on a live device simply leave the remainder of the pixel still working normally.

3.9.6 Passive Matrix and Active Matrix OLED Displays

In a passive matrix (PM) display, ITO columns and metal cathode rows overlap orthogonally. Each row is addressed sequentially: the picture data cause the pixels to flash for a very short time. By scanning the lines sufficiently fast (c. 72 Hz), the human eye integrates all of the light flashes into a picture without flicker. Because the pixel is on for such a short time, in order to have a clearly visible average luminance the light pulses must be extremely bright. 64 lines means the single pixel must flash 64 times brighter than the luminance the viewer perceives. The flashing rate is called the MUX rate. Anode line power losses and pixel charging/discharging losses limit the size of single panel PM displays to about 4" diagonal. In a PM display, red and blue emissions will have a similar measured radiance will have different luminance intensities which are a lot less than that of the green (due to the photopic curve). It is, therefore, necessary to make the green subpixel smaller than the red and blue ones. PM devices will always command market share being simpler and cheaper to produce than AM OLEDs.

In an active matrix (AM) display all subpixels can of uniform size since each subpixel's brightness is controlled by a single TFT (thin-film-transistor). Often more than one TFT is used so that should one TFT fail, the subpixel can be controlled by a previously redundant TFT. AM displays may be produced using a conventional structure with emission through the anode. In this case the driver circuitry is peripheral to the display. In a more space-efficient design, the OLED part of the display is built directly on top of the driver IC (integrated circuitry). For a conventional pin structure, the type of SOG (Silicon on Glass)⁵⁹ used for the circuitry is important because the mobility of the different types of Si (silicon) employed in AM TFTs determines the TFT size and current-supply capability. The Si type ultimately affects image quality (resolution),

therefore, because TFT size determines the aperture ratio of the display, where the latter is the ratio of emitting area of a sub-pixel to the overall area of a pixel, including non-emissive metallised regions.

References

- 1 Kittel, C. (1996). "Introduction to Solid State Physics."
2. Sharma, B. L., "Metal-Semiconductor Schottky Barrier Functions and Applications". Plenum Press: Newyork, 1984.
- 3 K. C. Kao, W. Hwang., "Electrical Transport in Solids. Pergamon Press" 1981.
- 4 W. F. Pasveer, J. Cottaar, C. Tanase, *Phys. Rev. Lett.* **2005**, 94
- 5 A. Einstein, *Ann.Phys.Lpz*, **1905**, 17
6. K. C. Kao, W. Hwang., "Electrical Transport in Solids. Pergamon Press" 1981.
7. Barth, S.; Wolf, U.; Bassler, H.; Muller, P.; Riel, H.; Vestweber, H.; Seidler, P. F.; Riess, W., "Current injection from a metal to a disordered hopping system. III. Comparison between experiment and Monte Carlo simulation." *Physical Review B* **1999**, 60, (12), 8791-8797.
8. K. Seki, T. Tani, *Thin Solid Films*, **1996** 273
- 9 P.E. Burrows, Z. Shen, V. Bulovic, D. McCarty, S.R. Forrest, *J. Appl. Phys.* **1996** 79
10. J. C. Scott, "Metal-organic interfaces and charge injection", *J.Vac.Sci.Technol.A* **2003** 21
11. Lous, E. J.; Blom, P. W. M.; Molenkamp, L. W.; Deleeuw, D. M., "Schottky Contacts on a Highly Doped Organic Semiconductor". *Physical Review B* **1995**, 51, (23), 17251-17254. . Blom, P. W. M., de Jong, M. J. M. and Vleggaar, J. J. M. (1996). "Electron and hole transport in poly(p-phenylene vinylene) devices." *Applied Physics Letters* 68(23): 3308-10. b) Bozano, L., Carter, S. A., Scott, J. C., Malliaras, G. G. and Brock, P. J. (1999). "Temperature- and field-dependent electron and hole mobilities in polymer light-emitting diodes." *Applied Physics Letters* **74**(8): 1132-4.
12. a) R. H. Fowler, L. N.Nordheim, "Electron Emission in Intense Electric Fields". *Royal Society of London* **1928**, Series A, (119), 173. b) Davids, P. S.; Kogan, S. M.; Parker, I. D.; Smith, D. L., "Charge injection in organic light-emitting diodes: Tunneling into low mobility materials". *Applied Physics Letters* **1996**, 69, (15), 2270-2272.
13. Barth, S.; Wolf, U.; Bassler, H.; Muller, P.; Riel, H.; Vestweber, H.; Seidler, P. F.; Riess, W., "Current injection from a metal to a disordered hopping system. III. Comparison between experiment and Monte Carlo simulation". *Physical Review B* **1999**, 60, (12), 8791-8797.
14. M. A. Lampert, P. M., "Current Injection in Solids". Academic Press: Newyork, 1970.
15. Campbell, A. J., Bradley, D. D. C. and Lidzey, D. G. (1997). "Space-charge limited conduction with traps in poly(phenylene vinylene) light emitting diodes." *Journal of Applied Physics* **82**(12): 6326-42.
16. a) Parmenter R.H. and Ruppel W., *J. Appl. Phys.* 1959 30 b) Blom, P. W. M.; de Jong, M. J. M., "Electrical characterization of polymer light-emitting diodes". *IEEE Journal of Selected Topics in Quantum Electronics* **1998**, 4, (1), 105-112.
17. a) Aleshin, A. N.; Williams, S. R.; Heeger, A. J., "Transport properties of poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate)". *Synthetic Metals* **1998**, 94, (2), 173-177. b) Kraft, A.; Burn, P. L.; Holmes, A. B.; Bradley, D. D. C.; Friend, R. H.; Martens, J. H. F., "Hole-Transporting Compounds for Multilayer Polymer Light-Emitting-Diodes". *Synthetic Metals* **1993**, 57, (1), 4163-4167.
18. Liao, L. S.; Cheng, L. F.; Fung, M. K.; Lee, C. S.; Lee, S. T.; Inbasekaran, M.; Woo, E. P.; Wu, W. W., "Oxygen effect on the interface formation between calcium and a polyfluorene film". *Physical Review B* **2000**, 62, (15), 10004-10007.
19. Fung, M. K.; Lai, S. L.; Bao, S. N.; Lee, C. S.; Lee, S. T.; Wu, W. W.; Inbasekaran, M.; O'Brien, J. J., "Interface between poly (9,9-dioctylfluorene) and alkali metals: cesium, potassium, sodium, and lithium". *Journal of Vacuum Science & Technology a-Vacuum Surfaces and Films* **2002**, 20, (3), 911-918.
- 20 Y. Qiu, Y. Shao, D. Q. Zhang, X. Y. Hong, *Jap. J. Appl. Phys. Part I* **2000** 39
- 21 L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, and J. R. Reynolds, *Adv. Mat.* **2000**, 12
- 22 Bayer AG, Eur. Patent 339340, 1988
23. Li, G.; Kim, C. H.; Lane, P. A.; Shinar, J., "Magnetic resonance studies of tris-(8-hydroxyquinoline) aluminum-based organic light-emitting devices". *Physical Review B* **2004**, 69, (16).

24. Kulkarni, A. P.; Tonzola, C. J.; Babel, A.; Jenekhe, S. A., "Electron transport materials for organic light-emitting diodes". *Chemistry of Materials* **2004**, 16, (23), 4556-4573.
25. Cao, Y.; Parker, I. D.; Yu, G.; Zhang, C.; Heeger, A. J., "Improved quantum efficiency for electroluminescence in semiconducting polymers". *Nature* **1999**, 397, (6718), 414-417.
26. Wohlgenannt, M.; Jiang, X. M.; Vardeny, Z. V.; Janssen, R. A. J., "Conjugation-length dependence of spin-dependent exciton formation rates in Pi-conjugated oligomers and polymers". *Physical Review Letters* **2002**, 88, (19). b) Wohlgenannt, M.; Jiang, X. M.; Yang, C.; Korovyanko, O. J.; Vardeny, Z. V., "Spin-dependent polaron pair recombination in pi-conjugated polymers: enhanced singlet exciton densities". *Synthetic Metals* **2003**, 139, (3), 921-924. c) Wohlgenannt, M.; Jiang, X. M.; Vardeny, Z. V., "Spin-dependent exciton formation rates in pi-conjugated oligomers and polymers". *Synthetic Metals* **2003**, 137, (1-3), 1069-1071. d) Wohlgenannt, M.; Vardeny, Z. V., "Spin-dependent exciton formation rates in pi-conjugated materials". *Journal of Physics-Condensed Matter* **2003**, 15, (3), R83-R107.
27. Wohlgenannt, M.; Vardeny, Z. V.; Shi, J.; Francis, T. L.; Jiang, X. M.; Mermer, O.; Veeraraghavan, G.; Wu, D.; Xiong, Z. H., "Spin and magnetic field effects in organic semiconductor devices". *IEEE Proceedings-Circuits Devices and Systems* **2005**, 152, (4), 385-392. b) Wohlgenannt, M.; Graupner, W.; Osterbacka, R.; Leising, G.; Comoretto, D.; Vardeny, Z. V., "Singlet fission in luminescent and nonluminescent Pi-conjugated polymers". *Synthetic Metals* **1999**, 101, (1-3), 267-268 c) Wohlgenannt, M., "Polarons in pi-conjugated semiconductors: absorption spectroscopy and spin-dependent recombination". *Physica Status Solidi a-Applied Research* **2004**, 201, (6), 1188-1204. d) Sheng, Y.; Nguyen, T. D.; Veeraraghavan, G.; Mermer, O.; Wohlgenannt, M.; Qiu, S.; Scherf, U., "Hyperfine interaction and magnetoresistance in organic semiconductors". *Physical Review B* **2006**, 74, (4). e) Wohlgenannt, M.; Tandon, K.; Mazumdar, S.; Ramasesha, S.; Vardeny, Z. V., "Formation cross-sections of singlet and triplet excitons in pi-conjugated polymers" (vol 409, pg 494, 2001). *Nature* **2001**, 411, (6837), 617-617. f) Wohlgenannt, M.; Tandon, K.; Mazumdar, S.; Ramasesha, S.; Vardeny, Z. V., "Formation cross-sections of singlet and triplet excitons in pi-conjugated polymers". *Nature* **2001**, 409, (6819), 494-497. 53. g) Yang, C.; Vardeny, Z. V.; Kohler, A.; Wohlgenannt, M.; Al-Suti, M. K.; Khan, M. S., "Spectroscopic study of spin-dependent exciton formation rates in pi-conjugated semiconductors: Comparison with electroluminescence techniques". *Physical Review B* **2004**, 70, (24). h) Wohlgenannt, M.; Mermer, O., "Single-step multiphonon emission model of spin-dependent exciton formation in organic semiconductors". *Physical Review B* **2005**, 71, (16).
28. Wilson, J. S.; Dhoot, A. S.; Seeley, A.; Khan, M. S.; Kohler, A.; Friend, R. H., "Spin-dependent exciton formation in pi-conjugated compounds". *Nature* **2001**, 413, (6858), 828-831.
29. T. Virgili, G. Cerullo, L. Luer, G. Lanzani, C. Gadermaier, and D. D. C. Bradley, *Phys. Rev. Lett.* **2003**, 90
30. A. S. Dhoot, D. S. Ginger *Chem. Phys. Lett.* **2002**, 360 b) Dhoot, A. S.; Greenham, N. C., Comment on "Triplet-to-singlet exciton formation in poly(p-phenylene-vinylene) light-emitting diodes". *Physical Review Letters* **2003**, 91, (21).
31. Barford, W., "Theory of singlet exciton yield in light-emitting polymers". *Physical Review B* **2004**, 70, (20). b) Barford, W.; Bursill, R. J., "The electronic structure of conjugated polymers". *Synthetic Metals* **2001**, 119, (1-3), 251-252.
32. Beljonne, D.; Shuai, Z. G.; Ye, A. J.; Bredas, J. L., "Charge-recombination processes in oligomer- and polymer-based light-emitting diodes: A molecular picture". *Journal of the Society for Information Display* **2005**, 13, (5), 419-427. b) Beljonne, D.; Ye, A. J.; Shuai, Z.; Bredas, J. L., "Chain-length dependence of singlet and triplet exciton formation rates in organic light-emitting diodes". *Advanced Functional Materials* **2004**, 14, (7), 684-692.
33. Reufer, M.; Walter, M. J.; Lagoudakis, P. G.; Hummel, B.; Kolb, J. S.; Roskos, H. G.; Scherf, U.; Lupton, J. M., "Spin-conserving carrier recombination in conjugated polymers". *Nature Materials* **2005**, 4, (4), 340-346.
34. Segal, M.; Baldo, M. A.; Holmes, R. J.; Forrest, S. R.; Soos, Z. G., "Excitonic singlet-triplet ratios in molecular and polymeric organic materials". *Physical Review B* **2003**, 68, (7). b) Segal, M.; Baldo, M. A.; Holmes, R. J.; Forrest, S. R.; Soos, Z. G., "Excitonic singlet-triplet ratios in molecular and polymeric organic materials". *Physical Review B* **2003**, 68, (7).
35. Morteani, A. C.; Dhoot, A. S.; Kim, J. S.; Silva, C.; Greenham, N. C.; Murphy, C.; Moons, E.; Cina, S.; Burroughes, J. H.; Friend, R. H., "Barrier-free electron-hole capture in polymer blend heterojunction light-emitting diodes". *Advanced Materials* **2003**, 15, (20), 1708-+. b) Monkman, A. P.; Burrows, H. D.; Hartwell, L. J.; Horsburgh, L. E.; Hamblett, I.; Navaratnam, S., "Triplet energies of pi-conjugated

- polymers". *Physical Review Letters* **2001**, 86, (7), 1358-1361. c) Lee, M. K.; Segal, M.; Soos, Z. G.; Shinar, J.; Baldo, M. A., "Yield of singlet excitons in organic light-emitting devices: A double modulation photoluminescence-detected magnetic resonance study". *Physical Review Letters* **2005**, 94, (13). d) Hong, T. M.; Meng, H. F., "Spin-dependent recombination and electroluminescence quantum yield in conjugated polymers". *Physical Review B* **2001**, 6307, (7). e) Karabunarliev, S.; Bittner, E. R., "Spin-dependent electron-hole capture kinetics in luminescent conjugated polymers" (vol 90, art no 057402, 2003). *Physical Review Letters* **2003**, 90, (7). f) Burin, A. L.; Ratner, M. A., "Spin effects on the luminescence yield of organic light emitting diodes". *Journal of Chemical Physics* **1998**, 109, (14), 6092-6102. g) Kadashchuk, A.; Vakhnin, A.; Blonski, I.; Beljonne, D.; Shuai, Z.; Bredas, J. L.; Arkhipov, V. I.; Heremans, P.; Emelianova, E. V.; Bassler, H., "Singlet-triplet splitting of geminate electron-hole pairs in conjugated polymers". *Physical Review Letters* **2004**, 93, (6). h) Shuai, Z.; Beljonne, D.; Silbey, R. J.; Bredas, J. L., "Singlet and triplet exciton formation rates in conjugated polymer light-emitting diodes". *Physical Review Letters* **2000**, 84, (1), 131-134. i) Shuai, Z.; Ye, A.; Beljonne, D.; Silbey, R. J.; Bredas, J. L., "Singlet and triplet exciton formation rates in conjugated polymer LEDs". *Synthetic Metals* **2001**, 121, (1-3), 1637-1638. j) Das, M.; Ramasesha, S.; Mazumdar, S., "Role of electron-electron interactions on spin effects in electron-hole recombination in organic light emitting diodes". *Synthetic Metals* **2005**, 155, (2), 270-273. k) Yin, S. W.; Chen, L. P.; Xuan, P. F.; Chen, K. Q.; Shuai, Z., "Field effect on the singlet and triplet exciton formation in organic/polymeric light-emitting diodes". *Journal of Physical Chemistry B* **2004**, 108, (28), 9608-9613. l) Bittner, E. R., "Exciton dynamics - Simplifying organic complexity". *Nature Physics* **2006**, 2, (9), 591-592. m) Chakrabarti, A.; Mazumdar, S., "Essential excitations in phenylene-based conjugated polymers". *Synthetic Metals* **1997**, 85, (1-3), 1121-1122. n) Shimoi, Y.; Mazumdar, S., "Energy diagram of triplet and singlet excited states in conjugated polymers". *Synthetic Metals* **1997**, 85, (1-3), 1027-1028. o) Tandon, K.; Ramasesha, S.; Mazumdar, S., "Electron correlation effects in electron-hole recombination in organic light-emitting diodes". *Physical Review B* **2003**, 67, (4). p) Ramasesha, S.; Mazumdar, S.; Tandon, K.; Das, M., "Electron correlation effects in electron-hole recombination and triplet-triplet scattering in organic light emitting diodes". *Synthetic Metals* **2003**, 139, (3), 917-920. q) Karabunarliev, S.; Bittner, E. R., "Dissipative dynamics of spin-dependent electron-hole capture in conjugated polymers". *Journal of Chemical Physics* **2003**, 119, (7), 3988-3995. r) Ye, A.; Shuai, Z.; Bredas, J. L., "Coupled-cluster approach for studying the singlet and triplet exciton formation rates in conjugated polymer LED's". *Physical Review B* **2002**, 65, (4).
36. a) Kalinowski, J.; Cocchi, M.; Giro, G.; Fattori, V.; Di Marco, P., "Injection-controlled electroluminescence in organic light-emitting diodes based on molecularly-doped polymers: II. Double-layer devices". *Journal of Physics D-Applied Physics* **2001**, 34, (15), 2282-2295. b) Kalinowski, J.; Cocchi, M.; Fattori, V.; Di Marco, P.; Giro, G., "Thomson-Like electron-hole recombination in organic light-emitting diodes". *Japanese Journal of Applied Physics Part 2-Letters* **2001**, 40, (3B), L282-L285.
37. Baldo, M. A.; Kozlov, V. G.; Burrows, P. E.; Forrest, S. R.; Ban, V. S.; Koene, B.; Thompson, M. E., "Low pressure organic vapor phase deposition of small molecular weight organic light emitting device structures". *Applied Physics Letters* **1997**, 71, (21), 3033-3035.
38. Xia, Y. J.; Friend, R. H., "Polymer bilayer structure via inkjet printing". *Applied Physics Letters* **2006**, 88, (16).
39. CIE "Commission Internationale de l'Eclairage" **1937**.
- 40 A. Bergh, G. Crawford, A. Duggal, *Phys. Today* **2001** 54
41. a) Morgado, J.; Friend, R. H.; Cacialli, F., "Environmental aging of poly(p-phenylenevinylene) based light-emitting diodes". *Synthetic Metals* **2000**, 114, (2), 189-196. b) *Information Display*, SID, **2006** 22 12. c) Berntsen, A. J. M.; Van de Weijer, P.; Croonen, Y.; Liedenbaum, C.; Vleggaar, J. J. M., "Stability of polymer light-emitting diodes". *Philips Journal of Research* **1998**, 51, (4), 511-525.
42. Gu, G.; Shen, Z. L.; Burrows, P. E.; Forrest, S. R., "Transparent flexible organic light-emitting devices". *Advanced Materials* **1997**, 9, (9), 725-728.
- 43 G. D. Hale, J. B. Jackson, *Appl. Phys. Lett.* **2001**, 78
44. a) Lipson, S. M.; Coleman, J. N.; Drury, A.; O'Brien, D. F.; Blau, W. J.; Cadby, A. J.; Lane, P. A.; Bradley, D. D. C., "Alternating and direct current characterization and photoinduced absorption studies of modified conjugated polymer thin films". *Journal of Applied Physics* **2004**, 95, (11), 6138-6144. b) Cumpston, B. H.; Parker, I. D.; Jensen, K. F., "In situ characterization of the oxidative degradation of a polymeric light emitting device". *Journal of Applied Physics* **1997**, 81, (8), 3716-3720. c) Gill, R. E.; van de Weijer, P.; Liedenbaum, C. T. H.; Schoo, H. F. M.; Berntsen, A.; Vleggaar, J. J. M.; Visser, R. J.,

- "Stability and characterization of large area polymer light-emitting diodes over extended periods". *Optical Materials* **1999**, 12, (2-3), 183-187.
45. Holzer, W.; Penzkofer, A.; Pichlmaier, M.; Bradley, D. D. C.; Blau, W. J., "Photodegradation of some luminescent polymers". *Chemical Physics* **1999**, 248, (2-3), 273-284.
46. Kolosov, D.; English, D. S.; Bulovic, V.; Barbara, P. F.; Forrest, S. R.; Thompson, M. E., "Direct observation of structural changes in organic light emitting devices during degradation". *Journal of Applied Physics* **2001**, 90, (7), 3242-3247.
47. M. E. Pope, C. E. S., *Electronic Processes in Organic Crystals*. Oxford University Press: **1982**.
48. C.W. Tang, and S.A. Vanslyke, *Appl. Phys. Lett.* **1987** 51
49. Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B., "Light-Emitting-Diodes Based on Conjugated Polymers". *Nature* **1990**, 347, (6293), 539-541. b) Lidzey, D. G.; Bradley, D. D. C.; Martin, S. J.; Pate, M. A., "Pixelated multicolor microcavity displays". *IEEE Journal of Selected Topics in Quantum Electronics* **1998**, 4, (1), 113-118. c) 40. Riess, W.; Beierlein, T. A.; Riel, H., "Optimizing OLED structures for a-Si display applications via combinatorial methods and enhanced outcoupling". *Physica Status Solidi a-Applied Research* **2004**, 201, (6), 1360-1371.
50. a) Tak, Y. H.; Pommerehne, J.; Vestweber, H.; Sander, R.; Bassler, H.; Horhold, H. H., "Pulsed electroluminescence from organic bilayer light emitting diodes". *Applied Physics Letters* **1996**, 69, (9), 1291-1293. b) Yang, C. Y.; Hide, F.; Heeger, A. J.; Cao, Y., "Nanostructured polymer blends: Novel materials with enhanced optical and electronic properties". *Synthetic Metals* **1997**, 84, (1-3), 895-896.
51. a) Stoessel, M.; Wittmann, G.; Staudigel, J.; Steuber, F.; Blassing, J.; Roth, W.; Klausmann, H.; Rogler, W.; Simmerer, J.; Winnacker, A.; Inbasekaran, M.; Woo, E. P., "Cathode-induced luminescence quenching in polyfluorenes". *Journal of Applied Physics* b) Lee, K. S.; Kim, Y. H.; Lee, Y.; Jang, J.; Kwon, S. K., "Synthesis and characterization of stable blue light-emitting poly (spirobifluorene) derivatives containing alkoxy group". *Journal of Polymer Science Part a-Polymer Chemistry* **2005**, 43, (11), 2316-2324. c) Palilis, L. C.; Lidzey, D. G.; Redecker, M.; Bradley, D. D. C.; Inbasekaran, M.; Woo, E. P.; Wu, W. W., "High performance blue light-emitting diodes based on conjugated polymer blends". *Synthetic Metals* **2001**, 121, (1-3), 1729-1730.
52. a) Cimrova, V.; Scherf, U.; Neher, D., "Microcavity devices based on a ladder-type poly(p-phenylene) emitting blue, green, and red light". *Applied Physics Letters* **1996**, 69, (5), 608-610. **2000**, 87, (9), 4467-4475. 48. b) Tasch, S.; Niko, A.; Leising, G.; Scherf, U., "Highly efficient electroluminescence of new wide band gap ladder-type poly(para-phenylenes)". *Applied Physics Letters* **1996**, 68, (8), 1090-1092.
53. Zhou, T. X.; Ngo, T.; Brown, J. J.; Shtein, M.; Forrest, S. R., "Stable and efficient electrophosphorescent organic light-emitting devices grown by organic vapor phase deposition". *Applied Physics Letters* **2005**, 86, (2).
54. Markham, J. P. J.; Lo, S. C.; Magennis, S. W.; Burn, P. L.; Samuel, I. D. W., "High-efficiency green phosphorescence from spin-coated single-layer dendrimer light-emitting diodes." *Applied Physics Letters* **2002**, 80, (15), 2645-2647.
55. P.S. Martin, *Laser Focus World*, **2001**, b) Kanno, H.; Giebink, N. C.; Sun, Y. R.; Forrest, S. R., "Stacked white organic light-emitting devices based on a combination of fluorescent and phosphorescent emitters". *Applied Physics Letters* **2006**, 89, (2).
- 56 T.A. Ali, A. P. Ghosh, W.E. Howard, *SID* 1999, Santa Ana, CA, USA.
- 57 a) Gu, G.; Shen, Z. L.; Burrows, P. E.; Forrest, S. R., "Transparent flexible organic light-emitting devices". *Advanced Materials* **1997**, 9, (9), 725-728. b) Kanno, H.; Sun, Y.; Forrest, S. R., "High-efficiency top-emissive white-light-emitting organic electrophosphorescent devices". *Applied Physics Letters* **2005**, 86, (26). c) Baigent, D. R.; Marks, R. N.; Greenham, N. C.; Friend, R. H.; Moratti, S. C.; Holmes, A. B., "Surface-Emitting Polymer Light-Emitting-Diodes". *Synthetic Metals* **1995**, 71, (1-3), 2177-2178.
58. a) Hao, X. T.; Zhu, F. R.; Ong, K. S.; Tan, L. W., "Top emitting poly(p-phenylene vinylene) light-emitting diodes on metal sandwiched polyethylene terephthalate substrates". *Applied Physics B-Lasers and Optics* **2006**, 83, (1), 67-74. 35. Kallinger, C.; Hilmer, M.; Haugeneder, A.; Perner, M.; Spirk, W.; Lemmer, U.; Feldmann, J.; Scherf, U.; Mullen, K.; Gombert, A.; Wittwer, V., b) "A flexible conjugated polymer laser". *Advanced Materials* **1998**, 10, (12), 920-+.

Chapter 4

4 RED, GREEN AND BLUE ORGANIC LIGHT EMITTING DIODES

This Chapter marks the start of the experimental work, which was carried out by me during my thesis. Several emissive materials for organic displays are introduced - two for each of the three basic colours (red, green and blue) required for full-colour electronic displays. LEDs based on these emitters are characterised and discussed.

4.1 ORGANIC THIN FILMS

4.1.1 Preparation Method

OLEDs typically consist of one or more thin layers of organic material sandwiched between metallic electrodes. Clean, flat substrates are required as a starting point for producing good optical quality, thin films. Bought ITO-coated glass substrates (UQG optics) were boiled in acetone followed by isopropanol, to remove any unwanted residual surface stains. The ITO was then photolithographically patterned, recleaned and the organic layer(s) deposited on the ITO surface. In the case of spincoated organic layers, for the desired polymer solution concentration, the appropriate amount of polymer powder/fibrous mat was weighed on an electronic balance and the required volume of spectroscopic grade solvent added to the powder in a clean glass vial using a pipette. The use of a low power sonic bath, shaking by hand, heating, or a combination of these, was used to hasten the dissolution process. Solutions were then filtered using .45 μm Whatman filter paper in a syringe head. The filtered polymer solutions were spin-coated using a Convac 2000 spincoater in a laminar flow hood. Just prior to spincoating, the substrate was blasted with a nitrogen gun at ~ 2 mbar to remove any dust particles that may have lodged on the ITO surface. Where possible, xylene was used preferentially to toluene. This is due to its slightly higher boiling point and the fact volatile solvents generally result in films with a smoother surface. Spin-coated films were then baked for a few minutes in a vacuum oven (fitted with a solvent trap) at 60°C to evaporate off any remaining solvent. A Digital Instruments Nanoscope IIIa atomic force microscope (AFM) was used to image cuts made using a razor blade in polymer films spincoated onto glass substrates. The resulting image, was processed using analysis software which levels the flat regions either side of the cut and (via the stepheight analysis function) calculates the height differential of one side and the base of the bottom of the trench

formed by the blade. AFM traces were taken in tapping mode, adjusting the tip drive-amplitude and feedback gains using a silicon nitride tip to ensure a clean scan. These readings were checked against needle profilometry readings obtained using a Dektac surface profiler.



Fig. 28 Example of a single unlevelled trace AFM image of a cut made in a polymer film of MEH-PPV which was spin-coated from a 15 g/l chlorobenzene solution at a spin speed of 1500 rpm.

4.1.2 Absorption Measurements

In order to characterize the ground state absorption of thin solid organic films and the absorption (excited state) of doped polymer solutions, measurements were carried out using a Shimadzu UV-Vis (Ultra-Violet-Visible) absorption spectrometer. The UV-Vis spectrometer works by passing a high voltage discharge through a xenon or mercury vapour contained in a quartz envelope. These sources are operated at quite high gas pressures to provide a continuous spectral output. Transmission wavelength selection is achieved by dispersing the lamp output using a grating monochromator rotated by an electronic actuator. The Shimadzu system used has a dual-beam monochromator arrangement (one for the sample and one for the reference) with lamp changeover from mercury to xenon occurring at 690 nm. The detector is a photomultiplier tube and the wavelength range using these sources and quartz containers/substrates is 200 – 1000 nm. Spectrosil B quartz glass substrates were used for spincoated thin films (absorption starts at ~ 270 nm) and matched quartz cuvettes (1 cm^3) were used for solution measurements.

Doping of light-emitting polymer (LEP) solutions was done in order to demonstrate excited state (positive polaron) absorption which is expected to be similar to polaron pair absorption since the polarons in a polaron pair are not tightly bound. The

dopant, FeCl_3 solution (0.025 M in DCM), was added to LEP solution (0.25 mg/ml) in a cuvette dropwise until the absorbance saturated. Although solutions were doped, and only the solid state is relevant in this thesis, graphs showing the overlap of doping-induced absorption and electroluminescent spectra illustrate qualitatively, at least, how excited state absorption detracts from electroluminescence intensity.

4.1.3 Photoluminescence Measurements

A high solid state photoluminescence quantum yield (PLQY) is a fundamental requirement for a good electrofluorescent material. Therefore, PL or *fluorescence*, measurements were made, prior to device fabrication, using a Lambda-Instruments (FL40 model) fluorimeter on thin films spincoated on quartz-glass (Spectrosil-B) substrates. The fluorimeter uses similar light sources to the absorption spectrometer, the main difference being that light emitted at right angles to the exciting beam is collected and focused on a second monochromator. The double-monochromator setup means that excitation and emission spectra may be obtained. For some PL measurements, a Rothin UV diode with a peak emission of 370 nm and a narrow spectral distribution (FWHM of 20 nm) was used in conjunction with a CCD detection unit. The PL quantum yield for the LEPs was obtained using a standardised solution of quinine sulphate in 0.1 M H_2SO_4 ($\phi_{\text{PL}}=54\%$). For solid films, an integrating sphere can also measure the external PL quantum yield. Although self-absorption in thin films results in reduced PL yields, to date, it has not been quantified. LEP fluorescence lifetimes were obtained from the literature, where a mode-locked ruby laser (35 ps pulse @ pump wavelength of 347.15 nm) was used to excite the sample.

4.1.4 Device Fabrication

4.1.4.1 Single Carrier Device and LED Structures

In order to characterize the polymer mobilities and trap distributions which govern current flow in OLEDs, single-carrier devices were made on glass substrates. Hole-only devices in a *ITO/ polymer/ Au* format were made, using different masks for

the top and bottom gold contacts to consistently define the active device area. Electron-only devices in an *Al/polymer/Al* format were also made using the same masks.

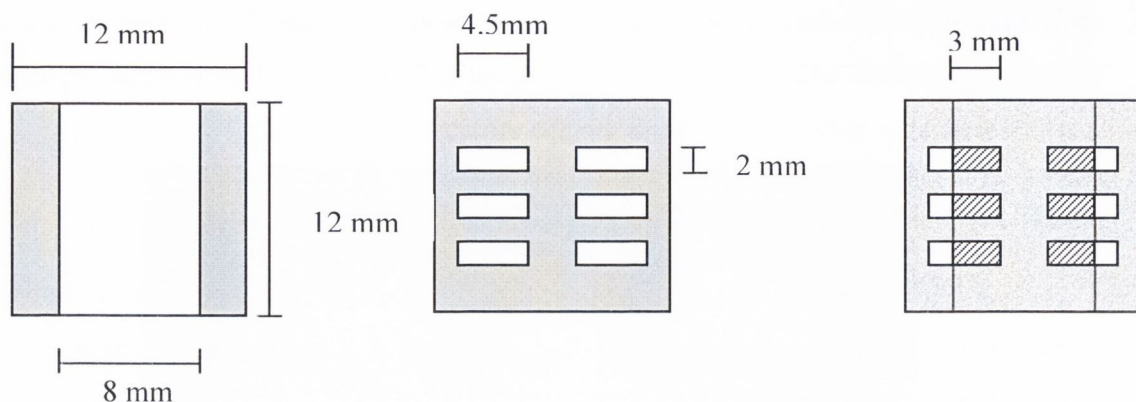


Fig. 29 Dimension of masks for bottom (left) and top (middle) contacts for a single-carrier device, and the resultant overlap (right: shaded) defining the active area for all devices.

For LED structures, an ITO transparent bottom anode was used. Typically ITO is 80% transparent across the visible @ thickness of ~ 80 nm). The bought-in glass substrates used in this thesis were ITO-coated over the whole glass area. The ITO layer, therefore, requires etching in order to achieve electrode isolation and to avoid shorting between the top and bottom contacts when mechanical contact is made to the electrodes. The etching was done photolithographically. This involved spin-coating a negative photoresist (Shipley) at 6000 rpm, on the ITO-glass substrate, curing the spin-coated layer of resist on a hotplate, mask defined exposure of the cured resist layer to UV light, dissolving the the exposed regions of the resist layer by immersion in developer (MMDF), rinsing the remaining partially resist-coated ITO in water, etching the resist-free areas of ITO in hydrochloric acid (10% @ 80 °C), and, finally, removal of undeveloped resist with acetone. Although this work involved exposing the resist surface to UV light, better results may be obtained by exposure through the substrate. The ITO patterning process is tedious but highly reproducible. The completeness of the etching step was monitored by checking substrate resistance using a regular lab multimeter. The masks allowed for batches of 16 substrates to be processed at a time.

4.1.4.2 *Evaporation and Sputtering of Metal Electrodes*

For devices made during this thesis work, evaporated aluminium was used to inject electrons and sputtered ITO, or gold, to inject holes. Aluminium was used as the cathode in LEDs and for both contacts in electron-only devices. Using an Edwards Autovac coating system fitted with a rotary-backed diffusion pump (E05 model), a vacuum of 2×10^{-7} mbar is achievable. However, an order of magnitude less than this is sufficient and was used for making the devices. Aluminium wire (99.99 % purity, Testbourne Inc.) was placed in a tungsten coil (Tesbourne Inc.) and this was evaporated under vacuum by resistively heating the coil to the melting point of aluminium. A high current is passed through a narrow gauge (1mm) coil, 4 cm long, with a coil diameter of 0.5 cm (and a pitch of 0.5 cm). Care was taken to remove the shutter only once a stable low rate of metal deposition had been established. Film thickness was monitored using a water-cooled quartz crystal detector unit. In the absence of a readily available non-emissive electron transporting layer (ETL), evaporated AlQ_3 (tris-(8-hydroxyquinoline)) was used as the ETL in multilayer devices. In this case a quartz crucible (Testbourne Ltd.) containing AlQ_3 (Aldrich Inc.) was plugged with glass wool (to help purify the AlQ_3 and to obtain better control of deposition) and placed in a coiled tungsten crucible holder. With a quartz crucible the resistive heating is less direct than in the case of metal evaporation. Because of this and the fact AlQ_3 sublimes at relatively low temperature, constant careful adjusting of the coil current is required to ensure a uniform deposition rate. Improved control of evaporation rate and layer uniformity, particularly for evaporating organic materials, would be afforded by an automated feedback system for controlling the coil current (and temperature) and substrate temperature. Magnesium-silver composite targets can be sputtered to produce a cathode layer, however, this was found to result in damage of the target with our sputterer, and in poor quality devices.

Hole-only devices were made by RF sputtering gold on the polymer-coated ITO-glass substrates. Although it is possible to evaporate gold, material wastage is high and the boats are easily damaged. Therefore, a gold target was used in a home-built RF sputterer. In this instrument an Ar-plasma is generated using a high voltage discharge in an argon-purged chamber under a vacuum of 2×10^{-6} mbar. To minimise metal diffusion

into the polymer film which can lead to electrically shorted devices, sputtering was done at low power (low deposition rate of 0.1 nm/min). For hole-only devices with sputtered top contacts, a thick organic layer can also help prevent devices being shorted.

Sputtering could also be used to deposit platinum or ITO as an anode, both of which have similar workfunctions to that of gold. However, ITO, is typically deposited using magnetron sputtering which produces better quality films.

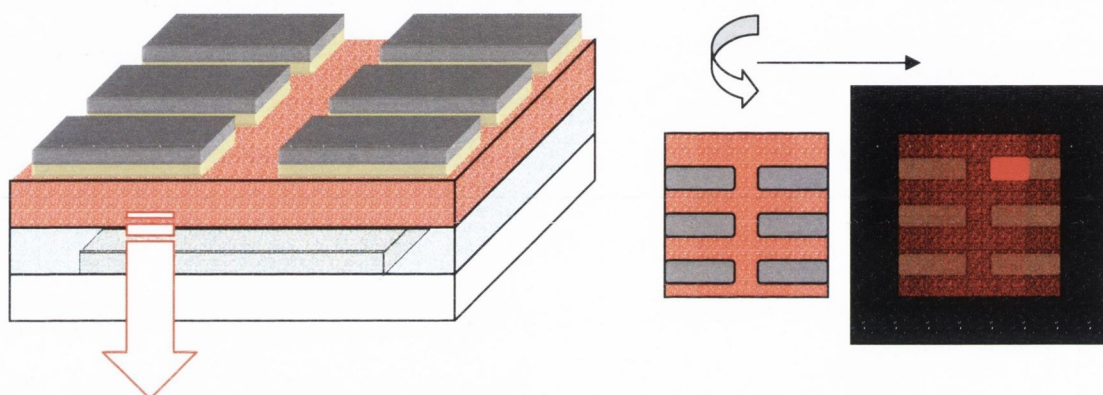


Fig. 30 Left: Final substrate with 6 devices per/substrate showing the generic schematic (not to scale) of a triple layer OLED where the device structure from bottom to top is: Glass, etched ITO, PEDOT:PSS, LEP/small molecule, AlQ₃, aluminium. Middle: OLED top-view, looking down on the aluminium electrodes. Right: schematic of OLED operation, seen through the ITO-glass substrate (a black background layer is used to improve contrast, a technique commonly employed in the electronic display industry).

For the devices in this thesis a PEDOT HTL was spincoated @ 4000 rpm to give 40 nm thick films and an AlQ₃ ETL was formed by evaporation to give a 20 nm thick layer

4.1.4.3 Current-Voltage-Luminance Measurement

To facilitate current voltage (I-V) measurement and data acquisition, a source-meter was interfaced to a PC using an in-house *Visual-Basic* programme. This programme allowed for different test intervals over different ranges. In conjunction with the application of a current compliance limit, the programme was used to ramp the device to a constant current at which luminance could be measured, thereby allowing external quantum efficiencies to be calculated. A device I-V test-rig was designed which allowed switching between the six pixels in the schematic in **Fig. 30** and testing under a rotary vacuum. For testing, the device was placed face down with the Al contacts

located on spring-loaded, gold-coated point probes. A lid fitted with an o-ring and mounted using a bayonett coupling (lid#1), sealed and held the device securely in place.

Electroluminescence (EL) from LEDs was measured in the I-V test rig using lid #1 which was fitted with a quartz-glass (Spectrosil-B) window. EL was detected via a liquid light-guide with one end of the guide against this window and the other coupled to a CCD spectrometer (Andor Technology and Oriel Instruments) interfaced to a PC. The CCD spectrometer was calibrated prior to measurement using the characteristic lines in the emission spectrum of the room-lights which were calibrated using a mercury lamp. A dark background reading was taken with the sample in the test-rig. LEDs were driven in darkness and the background-corrected EL spectra recorded.

LED luminance was measured using the I-V test-rig with lid #2 which was fitted with a silicon photodiode (with optical filters to approximate the photopic response function) rather than a glass window. This enabled luminance and I-V data (I-V-L) to be collected simultaneously. Since the photodiode was uncalibrated, only the relative luminance efficiency was measurable with this setup. Calibrated luminance (cd/m^2) was obtained using a Topcon Luminance Meter (Model BM-09 with AI-08 attachment lens) in conjunction with the I-V rig using lid #1. The luminance meter had a spot size of diameter (0.73 mm^2) which was smaller than the mask-defined pixel area (6 mm^2). Optical losses due to the experimental setup (light guide and lid#1) were not accurately accounted for in the EL quantum efficiency calculations but are of the order of 10% across the visible region of the electromagnetic spectrum.

4.2 LIGHT-EMITTING POLYMER POLY-PHENYLENE VINYLENE

Polyphenylene vinylene (PPV) was the first LEP and has an absorption band of 400 – 420 nm, and emission peaks at 520 nm and 551 nm in thin film¹ although these values do vary somewhat depending on the synthesis and subsequent storage methods used.

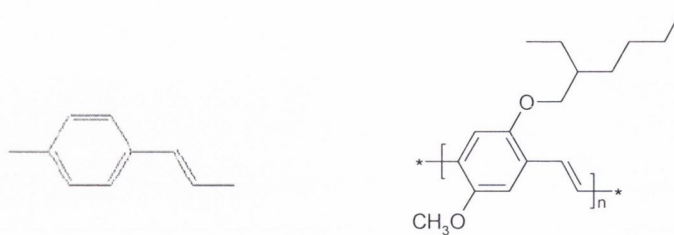


Fig. 31 Left: Unsubstituted PPV. Right: MEH-PPV, the first fully room-temperature-soluble PPV.

The first PPV materials were insoluble² materials formed by the thermoconversion of a soluble precursor. Thermoconversion involving the Wessling Zimmermann precursor route³ for MEH-PPV requires harsh conversion conditions (HCl gas at 220° C). This kind of polymer synthesis involves thermal conversion of a solution-processable sulfonium intermediate. Even with PPV which requires milder conversion conditions, attack of the ITO by HCl can be a problem with this technique. Single-layer (SL) precursor devices have been made with Ca electrodes with η_{ext} of 0.1%.

The first soluble PPV was dihexyloxy PPV (DH-PPV) , however, it was not soluble at room temperature¹. To produce PPV which is soluble at room temperature, a highly asymmetric substituent pattern of methoxy/2-ethylhexyloxy side-groups synthesized, via the Gilch polymerization route was used. The Gilch method⁴ is the most common polycondensation used for PPVs and for MEH-PPV⁵ involves base promoted 1,6 elimination of 1,4bis(chloro/bromomethyl-benzenes) of alkyl and alkoxy substituted monomers. This results in molecular weights of 50,000 – 1,000,000. If the molecular weight is too high, gel formation can occur, so the molecular weight is often controlled using polymer end-capping agents^{6,7}. MEH-PPV⁸ has been and still is the focus of a huge amount of study in the field of light-emitting polymers. The long alkoxy side chains in LEPs (as in MEH-PPV) are primarily for solvation and effects film-forming and device stability. Differences in these long side chains may also cause slight shifts in the emission spectra (e.g. OC₁C₁₀PPV)⁹. A large degree of side-branching can increase the amorphous nature of a film and increase the PLQY relative to a less branched polymer. It has been shown that the main influence of alkyl/alkoxy substituents is to affect the torsion angle between the phenylene and vinylene groups. This affects the planarity of molecules in a film and has implications for the light outcoupling efficiency.

Chemical-vapour-deposition¹⁰ can produce uniform, patterned PPV films but requires heating at 500-700 °C which results in byproduct impurities. The harsh conditions and incomplete halogen removal result in low performance PLEDs.

Solvent orthogonality is a problem in designing multilayer devices. For this reason PEDOT which is aqueous is often used as the hole-transport-layer (HTL). Alternatively the HTL may be soluble in organic solvent in which case water-soluble MEH-PPV¹¹ can be used but this is not common practice as water soluble LEPs are not very fluorescent or stable. Another method is crosslinking polymer layers to prevent their full dissolution.

4.3 TUNING EMISSION COLOUR IN LIGHT-EMITTING POLYMERS

One common method of colour-tuning is by varying the chemical structure by producing copolymers. A copolymer consists of a monomer containing two or more sub-monomers or 'comonomers' in the polymer repeat unit. Heck-coupling can be used for PPVs to produce all-trans material with very few side reactions and is often used to produce alternating PPV copolymers. This involves Pd-catalysed coupling of aromatic dihalide with a divinylbenzene¹². The Wittig (Horner) synthesis is also used for alternating copolymers where different substituents are seen in adjacent phenylene units. This involves condensation between terephthalaldehydes and p-xylenediyolphosphonium salts. Synthesis of copolymers is an effective way of tuning the emission in LEPs as a greater variety of structures are possible with respect to homopolymers. Using thermoconversion, the first copolymer device was made using (MEH-PPV)-PPV. A 30-fold increase in η_{ext} was obtained with respect to the MEH-PPV homopolymer. A soluble copolymer with OC₁C₁₀ alkoxy side groups has been used to make a very efficient LED ($\eta_{\text{ext}} = 6.5\%$) using a graded PEDOT HTL and a Ca cathode¹³.

Apart from changing the HOMO-LUMO gap (and hence emission colour) by using different main-chain or backbone monomers or comonomers, bulky sidegroups can also be used. Alkoxy, alkyl, silyl, and aryl substituted PPVs have been used to achieve this. It has been shown that diphenyl-substituted PPV has a high PLQY of 65 % in solid state and a blue-shifted emission of 490 nm, with respect to PPV, both due to the bulky

nature of the substituent¹⁴. Reducing intramolecular π -stacking by introducing a twist to the backbone reduces conjugation causing a hypsochromic emission-shift.¹⁵ Although bulky sidegroups introduce a twist in the backbone reducing the effective conjugation length and blue-shifting emission, their use slows polymerization, resulting in low molecular weight (M_w) products. One solution to the latter problem is using a second less sterically demanding co-monomer unit. Solid state PLQYs of 61 – 82 % have been achieved for materials with this approach¹⁶. Alkoxy-substituted phenyl-PPVs have good film-forming properties, with 3.1% η_{ext} demonstrated for ITO/polymer/Ca devices¹⁷.

Conjugation length may also be controlled by introduction of non-conjugated blocks or saturated sp_3 “defects”. A non-conjugated block-oligo-PPV copolymer device with EL peaking at 465 nm was made¹⁸. Non-conjugated blocks greatly improve film homogeneity (by reducing crystallinity) and provide more controllable film morphology.

Conjugation may also be controlled by changing the attachment mode of the phenylene unit (e.g. in PmPV¹⁹ and the alternating copolymer PpPV-PmPV²⁰ where m-linkage in the monomer acts as a conjugation break.). PPV emission can be tuned from blue to red, however, even for the bluest PPVs, emission from the green tail results in a low blue colour purity (high CIEy value) and so they are not useful as blue emitters.

4.3.1 Other Consequences of Chemical Structure

Chemical structures with bulky aromatic side-groups or hyper-branched side-groups can quite effectively demonstrate reduced inter-chain interaction due to hindered inter-chain π -stacking, for example. Although inter-chain interactions generally reduce the PLQY in most polymers, efficient excimer emission in CN-PPV is one exception. Aggregation also tends to red-shift emission with respect to matrix-dispersed material. The use of bulky side-groups may reduce aggregation effects, however, it may also reduce hopping probability between chains and hence reduce mobility, resulting in increased drive-voltage.

Chemical structure determines the relative positions of the HOMO and LUMO levels which are very important from the point of view of EL. The HOMO and LUMO levels of PPV are – 6.12 eV and 3.75 eV and of MEH-PPV are – 4.98 eV and – 2.89 eV²⁰ respectively. Chemical structure therefore determines how easily a material is oxidised

or reduced and the mobility of holes and electrons in the material and therefore plays an important part in determining charge balance in a given device structure. Both PPV and MEH-PPV are p-type. For a SL LED, if the HOMO (or LUMO) levels of the emitter are offset from the most suitable electrode workfunctions offered by readily available materials, the introduction of a HTL (or ETL) can improve hole (or electron) injection, reducing the drive voltage and improving the balance of charge transport if the emitter mobility is not ambipolar, resulting in increasing LED η_{ext} .

For p-type polymers one way to improve the charge balance is to have the ET moiety in the backbone of the light-emitting polymer, as one of comonomer units, and has been used to improve the LED efficiency with respect to the MEH-PPV homopolymer. A statistical copolymer of triphenyl-triazole (an ET moiety) substituted PPV and MEH-PPV leads to a more efficient OLED due to improved electron transport²¹. Also, PPV with oxadiazole side groups as an ET moiety resulted in a very efficient device (21 cd/A), much better than the homo-polymer PPV²². Improving the balance of charge transport by blending an essentially hole-transporting polymer with an ET material can also be a means to improve OLED efficiency. An η_{ext} value of 1.3% was achieved by blending a PBD ET material with MEH-PPV. A 2.5% η_{ext} double-layer device was made with a polybenzobisazole ETL and an Al electrode²³. A 2.3 % η_{ext} was achieved for a device using a blend of MEH-PPV with a Li-organophosphate surfactant. 3.8 % η_{ext} was achieved by blending a carbazole-thiophene ET copolymer with MEH-PPV. From the discussion above it can be deduced that improving electron injection and or transport in MEH-PPV devices is beneficial with respect to device performance.

Combining the motivating factors of good hole-transporting properties, excellent solubility, high PLQY and colour tunability, novel copolymers of MEH-PPV with TPA (triphenylamine) and with TPD (triphenyldiamine) were synthesised by Prof Hörhold at Jena University. These materials were designed for use in optical and optoelectronic applications including polymer waveguides and polymer LEDs. This thesis investigates the use of these materials for LED applications.

4.4 LIGHT-EMITTING POLYMER MEH-PPV

MEH-PPV or *poly{2-methoxy-5(2-ethylhexyloxy)-1,4-phenylene-vinylene}*, is a homo polymer and is the first of the Jena materials used in this thesis and has the simplest chemical structure. MEH-PPV is already well known and its intended use in this thesis is as a control material for comparative purposes since the other materials are all derived from this structure. A 1% η_{ext} has been achieved for a single layer MEH-PPV LED with a calcium cathode. This was improved to 2 % using SiO_2 nanoparticles²⁴ blended with MEH-PPV. MEH-PPV has orange emission whereas PPV is a green emitter. MEH-PPV can be made using *Horner-olefination* synthesis as the step-growth polymerisation process or, by using the dehydrohalogenation process (Gilch method). It should be noted that while two synthesis methods may result in the same chemical structure, the product yield and purity may be quite different. The *Horner* method is advantageous in several ways and was used. Firstly, both cross-linking and incomplete double bond formation is avoided. Both of these defects interrupt conjugation, thus modifying the electrical and optical properties with respect to a perfectly polymerised, defect-free polymer chain. Interrupted conjugation reduces mobility along a chain and blue-shifts emission. Secondly, different dialdehyde and bis(phosphonate) monomers may be used to produce strictly alternating copolymers and regular terpolymers. Thirdly, completely soluble materials with a perfect phenylene-vinylene backbone structure are formed (i.e. the backbone is fully conjugated). Fully conjugated backbones result in higher mobilities than more defective materials. MEH-PPV is made by reacting *2-methoxy-5 (2-ethylhexyloxy) xylylene bisphosphonate* directly with *MEH-terephthalaldehyde* and is characterised by a glass transition temperature (T_g) of 65° C and a molecular weight (M_w) of 40,300²⁵.

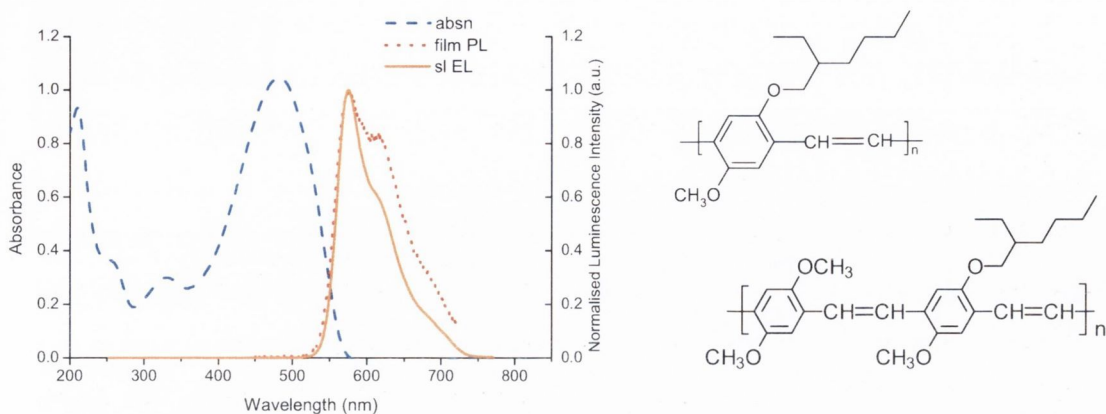


Fig. 32 Left: absorption (dashed), PL (dotted) and SL (72 nm) EL (solid) line for MEH-PPV. Right: Chemical structure of MEH-PPV (top) and M3EH-PPV (bottom).

The PL and absorption spectra for 72 nm thick films spun from chlorobenzene solutions (15 gl/l @ 1500 rpm) are shown in Fig. 32. The PL is orange-red with peaks at 590 nm and 630 nm. In Fig. 32 the EL from a SL LED is included to demonstrate that emission is from S_1 to S_0 states for EL and PL. Changes in the relative peak intensities of PL and EL are likely due to optical effects in the LED caused by interference of waves being reflected from the different optical interfaces.

4.4.1 Single Layer Devices

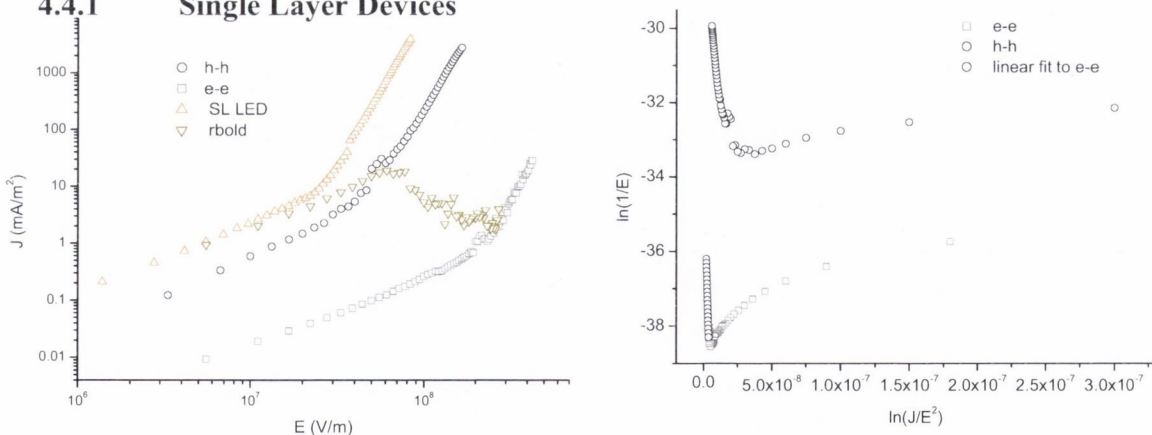


Fig. 33 Left: Current density versus electric field characteristics for single carrier devices: electron-only (squares), hole-only (circles) and single-layer LED: forward bias (triangles), modulus of reverse bias (inverted triangles). Right: Fowler-Nordheim plots for single-carrier MEH-PPV devices.

The current density versus electric field (J-E) characteristics show good rectification ($\sim 10^4$ at 10.3 V) in the single-layer LED and that electron mobility is lower than hole mobility. However, the mobilities are quite similar, as observed by other researchers, including a report that electron and hole-mobilities only differed by one order of magnitude, so the current balance and/or carrier injection must be quite good for a single layer LED. Notably, the single-layer LED has a higher J for a given field than either of the single-carrier devices, consistent with quite well balanced transport and efficient injection of holes and electrons in SL devices.

The Fowler-Nordheim (FN) plot for the electron-only device in Fig. 33, has a linear region at high fields, enabling extraction of a barrier height of 0.55 ± 0.02 eV at the aluminium-polymer interface, using FN theory. This value, although reasonable, is, however, lower than expected given the workfunction of aluminium (3.8 eV) and the electron affinity of the polymer (2.89 eV). F-N theory is not applicable for the hole-hole (h-h) device as there is curvature throughout the corresponding F-N plot. The F-N plots are consistent with a smaller injection barrier for holes than for electrons.

4.4.2 Characterization of Single and Multi-Layer LEDs

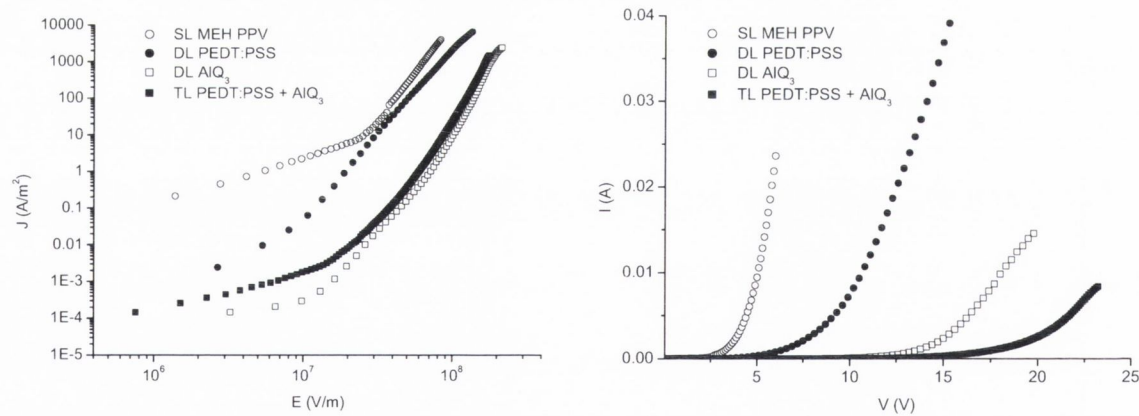


Fig. 34 left: Current density versus electric field for single and multilayer MEH-PPV LEDs. Right: Current versus voltage characteristics for single and multilayer MEH-PPV LEDs

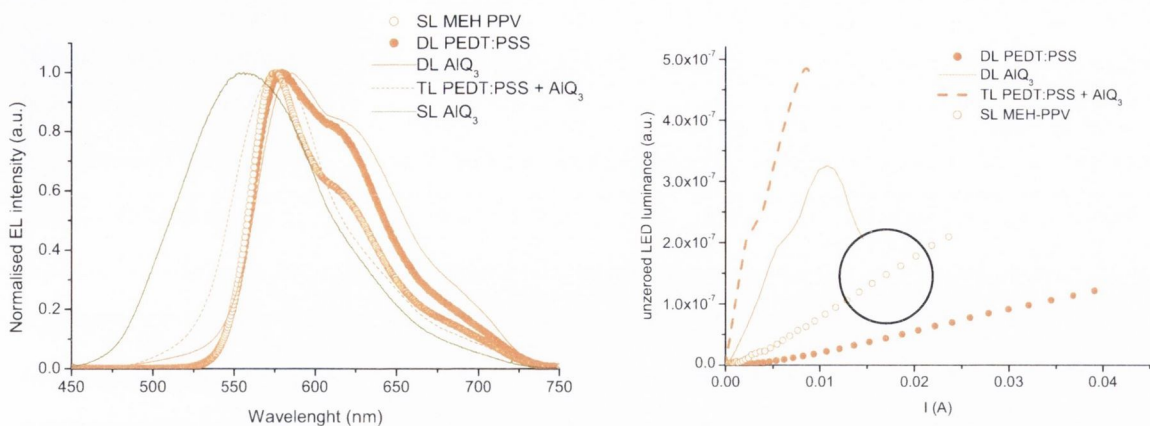


Fig. 35 left: EL from single- and multi-layer MEH-PPV LEDs and an AlQ₃ LED. Right: Luminance versus current plots for single- and multi-layer MEH-PPV LEDs.

From the logarithmic scale J-E plots in Fig. 34 it is apparent that the trapping-dominated transport is similar in all these devices. High currents were observed in the single layer (SL) and double-layer (DL) devices with a PEDOT:PSS HTL which were not as efficient as the DL and triple layer (TL) devices with an ETL as expected. The high drive voltage, V_d , of the ETL-containing devices was unexpected and was probably due to having a low mobility ETL which is too thick owing to the difficulty of controlling its deposition thickness. In Fig. 35 the LED luminance-current (L-I) plots, being volume controlled are linear up to the point where thermal stresses start to degrade the device. At this point the luminance rapidly starts to decrease as exemplified (see circle in Fig. 35) by the DL device with an AlQ₃ ETL. In the case of the DL -AlQ₃ and TL devices, there is a dip in the luminance in the current range 2-5 mA, after which the L-I curve is still linear. Since the current in the corresponding I-V does not drop simultaneously (i.e there is no corresponding drop in current at that field in the I-V curve), this drop may be due to spreading of the recombination zone with increased field to include a more defective, quenching region of the emissive film near an interface. It is also possible that some patches of the device have degraded, leaving the remaining, smaller, pixel area being driven at significantly higher currents, rendering the device less efficient. Plotting η_{ext} versus voltage would help to confirm this. From the time scales involved in our test conditions, it can be concluded that device degradation is in the form of heat-induced damage to the aluminium cathode. The rapid formation of black spots across the pixel area was observed in real-time by viewing the LED during operation

with a microscope objective lens. ITO (or other) dust on the substrate leads to the formation very thin or weak points in a spincoated film, and is the major source of this problem. Without clean-room or glove-box conditions it is impossible to prevent this happening. In the case of vacuum-deposited materials like AlQ₃, any particles on the ITO are coated by the sublimed organic layer, so this problem is not as great. The slope of the L-I plots gives a good indication of the device η_{ext} . The slopes of the SL and DL-HTL devices in Fig. 35 are lower than those of the DL ETL and TL devices, consistent with MEH-PPV being p-type. The EL spectra in Fig. 35 all resemble each other and the PL spectrum in Fig. 32 closely, with several vibronic peaks visible, however, these features are less evident in the TL device. This may be due to emission from the AlQ₃ itself, the high energy portion of which will be largely absorbed by the MEH-PPV. Alternatively the high energy portion may undergo energy transfer to the MEH-PPV.

4.5 LIGHT-EMITTING POLYMER TPD-4M-MEHPPV-M3EH PPV

TPD-4M-MEH-PPV-M3EH-PPV, or, to give it its full name; poly[1,4-phenylene-(4-methylphenyl)imino-4,4'-diphenylene-(4-methylphenyl)imino-1,4-phenylene-ethenylene-2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-ethenylene)-co-(2,5-dimethoxy-1,4-phenylene-ethenylene-2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-ethenylene)] is a terpolymer. That is, it is an ordered ternary (or just *ter*-) condensation copolymer of the general structure TPD-4M-MEHPPV (AB)_x M3EH-PPV(CB)_y, containing two different arylene-vinylene units, A,B,C, where A represents the TPD-vinylene unit and x:y is 50:50.

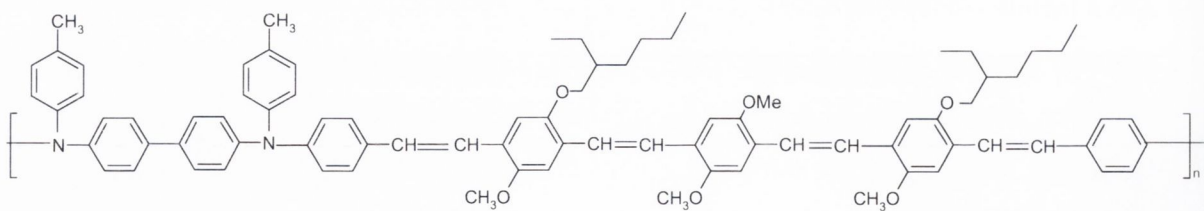


Fig. 36 Chemical structure of TPD-4M-MEHPPV-M3EHPPV

From the chemical structure in Fig. 36, confirmed by NMR and IR spectroscopy, it is apparent that TPD-4M-MEHPPV-M3EHPPV is a triphenyldiamine (TPD) -based PPV.²⁶ The motivation for making this material was two-fold, i) to see what effect the amine rich moiety has on hole transport and hole injection and ii) to see what effect having MEH-PPV and M3EH-PPV linked together in the monomer has on emission colour. The small molecule TPD²⁷ (see Fig. 1) is often used in SMOLEDs as an HTL and it is expected that this moiety in TPD-4M-MEH-PPV-M3EH-PPV will improve hole-injection as the HOMO of TPD is expected to be deeper than that of the amine free MEH-PPV. This has been observed for TPD-PPV with respect to PPV. Although TPD is emissive, it has a wide bandgap with respect to MEH-PPV and emission is still expected to be from the MEH-PPV units (i.e. any emission from the amine moiety is expected to transfer to the phenylene-vinylene moieties.)

The terpolymer combines a reasonably good M_w (35,700) for film-forming with a high T_g (156 C), the values for which were obtained by GPC (Gel Permeation Chromatography) and TGA (Thermo-gravimetric Analysis) respectively. The PLQY for a solid film is 25 %.

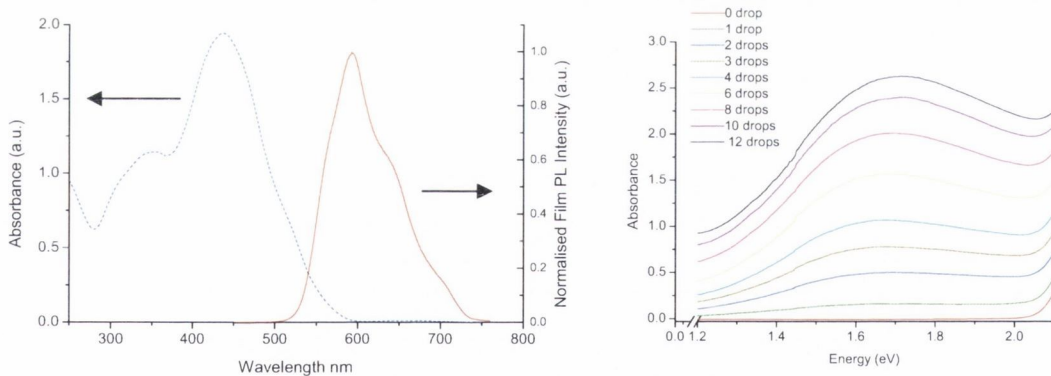


Fig. 37 Left: absorption (dashed) and photoluminescence (solid) of thin films of TPD-4M-MEHPPV-M3EHPPV on quartz-glass substrates. Right: FeCl_3 doping-induced absorbance versus energy for a solution of this terpolymer.

The TPD-4M-MEHPPV-M3EHPPV terpolymer emission (Fig. 37) is red-shifted with respect to MEH-PPV (Fig. 32) due to the presence of the M3EH-PPV moiety. The terpolymer emission is in fact red whereas that from MEH-PPV is more orange in colour. The terpolymer emission is associated with the MEH-PPV unit and good coplanarity

between the phenyls in the MEH- and M3EH-PPV units providing the increased conjugation necessary to observe the longer wavelength emission maximum. It has also been suggested that there may be emission from the TPD moiety also but that it is absorbed and reemitted in a down-conversion process, by the MEH-PPV moieties, thus not directly contributing to a red-shift in emission. The terpolymer solution was easily doped using FeCl_3 and the polaron absorption in Fig. 37 (right) showed little sign of saturating which is consistent with the notion of a rather long straight conjugated backbone section easily accessed by dopant ions. Excited state absorption due to polaron-pairs in thin solid films is expected to be similar and Fig. 38 illustrates the importance of designing materials where non-radiative excimers cannot easily form. Fig. 38 (right) shows that the doping-induced absorption due to positive polarons overlaps the EL emission, quenching the low energy EL.

4.5.1 Single Layer Devices

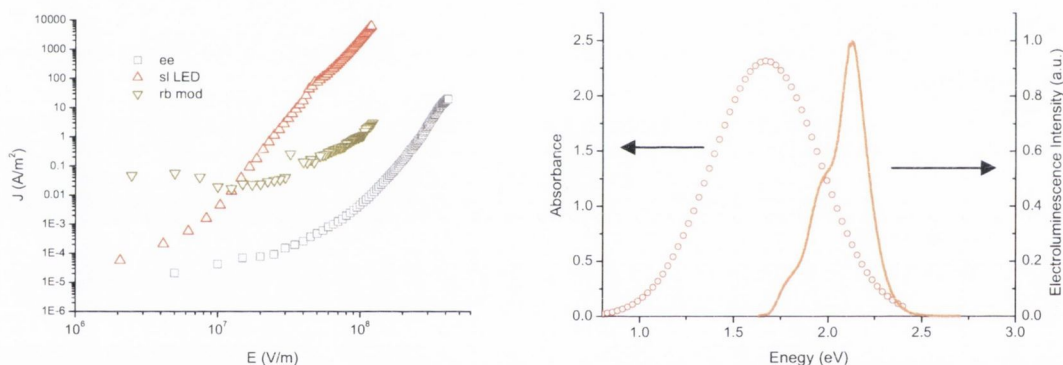


Fig. 38 Left: Current density versus voltage for a single-carrier device and a single-layer TPD-4M-MEH-PPV-M3EH-PPV LED (120 nm thick). Right: Overlap of doping-induced polaron absorption (open circles) and single layer EL (solid line) spectra.

Rectification is quite good again ($\sim 10^3$ at 14.8 V). Hole-hole data was not obtained for this device due to problems with device stability. However, as can be seen from Fig. 38 it is likely there is a larger difference between the magnitude of the electron and hole mobilities for this terpolymer than for MEH-PPV, with the single-layer LED being essentially a hole-only device, consistent with its low η_{ext} of $1.2 \times 10^{-4} \%$.

4.5.2 Characterization of Single and Multi-Layer LEDs

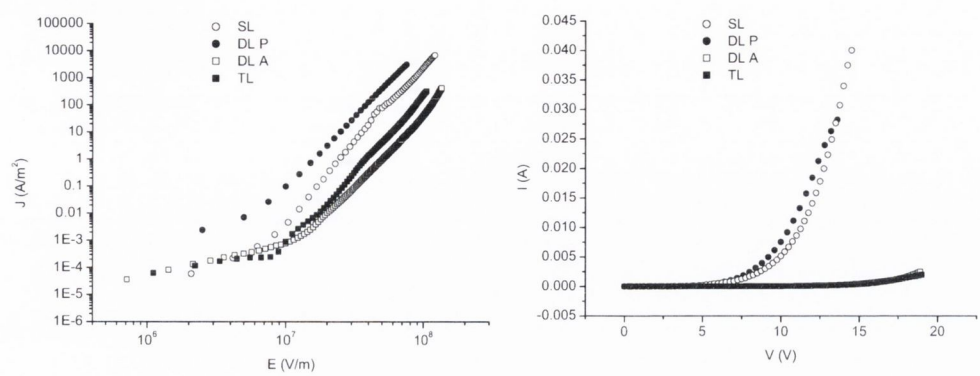


Fig. 39 Left: Current density versus electric field characteristics for single and multilayer TPD-4M-MEHPPV-M3EHPPV LEDs. Right: I-V characteristics for single and multilayer TPD-4M-MEHPPV-M3EHPPV LEDs.

The DL HTL device exhibited a slight reduction in V_d for a given current with respect to the SL device. This effect was also seen in the TL device with respect to the DL ETL device. The improvement in hole-injection afforded by using PEDOT was not reflected by improved η_{ext} of the device. This was probably due to the carrier transport imbalance being increased by using PEDOT and also to difficulties experienced with PEDOT layer formation on an untreated ITO surface, resulting in poor wetting of the ITO and possibly the presence of small particles in the PEDOT solution. Use of an ETL on the other hand resulted in a marked increase in luminance efficiency (Fig. 40) in the DL and TL devices in which it was used, albeit at higher operating voltages. The latter may be due to the thickness and low mobility value of the AlQ₃ layer used.

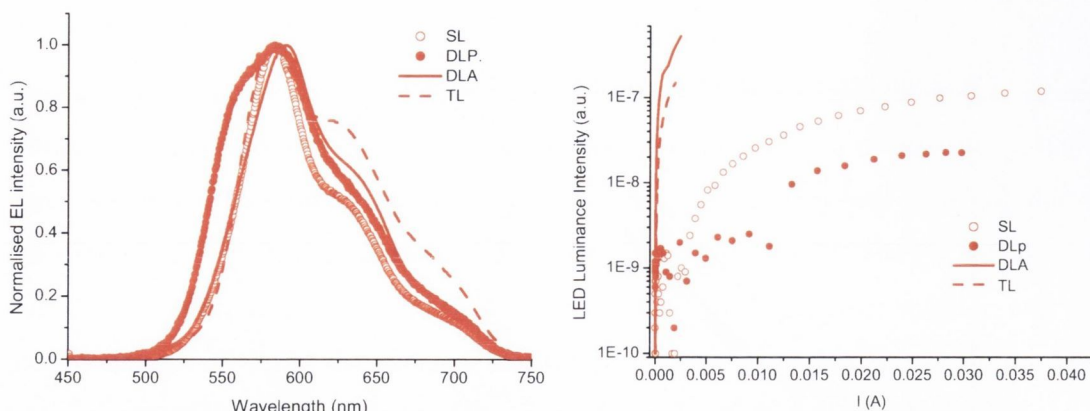


Fig. 40 Left: EL spectra of single- and multi-layer TPD-4M-MEHPPV-M3EHPPV LEDs. Right: Luminance versus current plots for single- and multi-layer TPD-4M-MEHPPV-M3EHPPV LEDs. In order to display the luminance data on the same plot a semi-logarithmic plot of the data was made.

The EL spectra in Fig. 40 show a lot of similarity but the DL HTL device has a strong green component that the others do not have. The reason for the enhancement of this shoulder in this device is unclear as there should be no AlQ_3 in this device. The EL peaks were better resolved overall, than they were for MEH-PPV, consistent with a more linear quasi-1-dimensional material with better order.

4.6 POLYMER TPA-MEH-PPV

TPA-MEH-PPV is a triphenylamine- (TPA) based PPV copolymer and has the full name *poly[phenylimino-1,4-phenylene-ethenylene-2,5-dioctyloxy-1,4-phenylene-ethenylene-1,4-phenylene]*. The structure is similar to the terpolymer except it contains one amine moiety and no M3EH-PPV moiety. The motivation for making this material was two fold: i) to see whether use of a single amine moiety is sufficient to hole injection (the previous terpolymer has two amine-type units) and ii) what effect if any it has on emission colour. The TPA-moiety has previously been observed to reduce the barrier to hole injection for TPA PPV with respect to PPV.

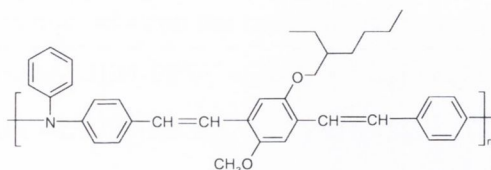


Fig. 41 Chemical Structure of TPA-MEH PPV

TPA-MEH-PPV²⁸ is made by a polycondensation method using the Horner reaction. The TPA moiety is incorporated into the PPV backbone by using TPA dialdehyde for the polycondensation. The Horner reaction allows the preparation of TPA-PPVs (with strongly electron donating and hole-transporting properties), similar to TPD moieties, containing unsubstituted and phenyl substituted double bonds.

The molecular structure of TPA is well defined by NMR and IR spectroscopy. As in the case of MEH-PPV, in this polymer, the methoxy and ethyl-hexyloxy side groups assist solubility. The weight averaged molar mass or molecular weight is 46, 900 which is high enough to permit good film-forming properties when processed from solution. This molecular weight was found by gel permeation chromatography (GPC) using a polystyrene standard in THF. The T_g is 147° C and TPA-MEH-PPV therefore shows a favourable combination of high T_g and high M_w and is soluble in toluene and dioxane²⁸.

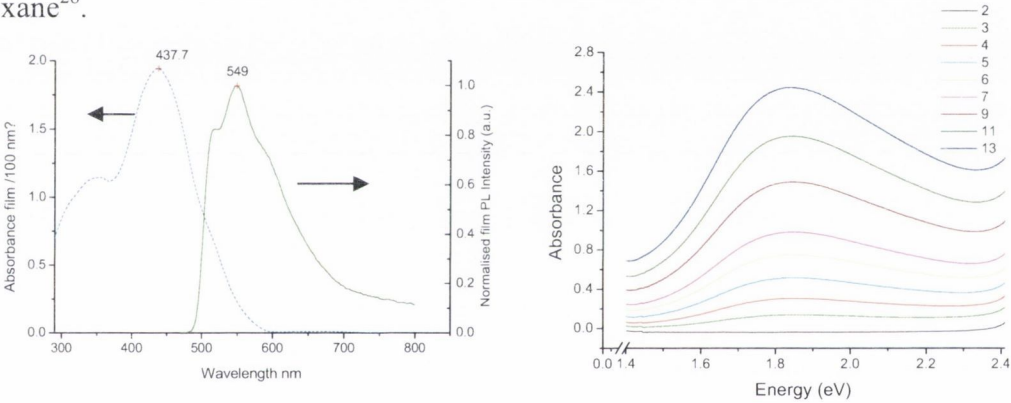


Fig. 42 Left: absorption (dashed) and PL (solid line) of TPA-MEH-PPV thin films. Right: FeCl₃ doping-induced absorption in TPA-MEH-PPV solutions.

Emission from TPA-MEH-PPV is green and is, therefore, blue-shifted with respect to that of MEH-PPV. It has been shown that the emitting chromophore size is about the same as the repeat unit size and it is assumed the lumophore structure is derived from the 4,4'-diamino-distyrylbenzene skeleton. This lumophore is present in the phenylamino, distyrylbenzene, phenylamino segment of TPA-MEH-PPV. This assumption is further backed up by the fact that low molar mass compounds, also containing this lumophore, have similar PL, EL, and ASE maxima to TPA-MEH-PPV. One reason TPA leads to a blue shift but TPD does not may be due to the fact the TPD is

essentially a larger conjugated amine moiety and is probably not as blue an emitter as TPA, and is itself contributing to the emission assuming energy transfer to the PV moieties is not complete.

4.6.1 Single Layer Devices

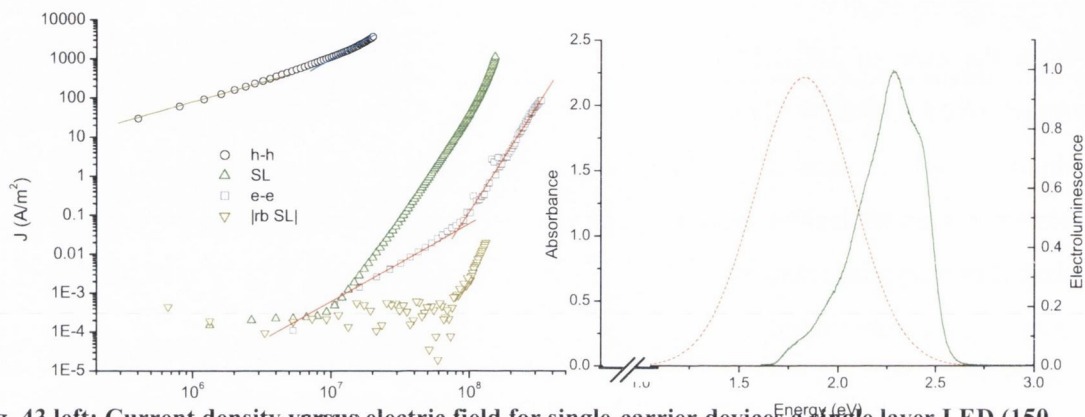


Fig. 43 left: Current density versus electric field for single-carrier devices a single layer LED (150 nm) for TPA-MEH-PPV. Examples of the linear fits to the single-carrier data from which carrier mobilities were extracted are included. Right: FeCl₃ doping-induced absorbance and single-layer LED EL spectral overlap.

From the plots in Fig. 43 it can qualitatively be seen that for single layer devices, the hole mobility is several orders of magnitude larger than the electron mobility for TPA-MEH-PPV. The rectification in the single-layer LED is good ($\sim 10^4$ at 19.1 V). Although EL was not recorded under reverse bias for any of the devices made in this thesis, it is possible. Fig. 43 shows a large overlap of the polaron absorption and the EL emission as with the terpolymer.

4.6.2 Characterization of Single and Multi-Layer Devices.

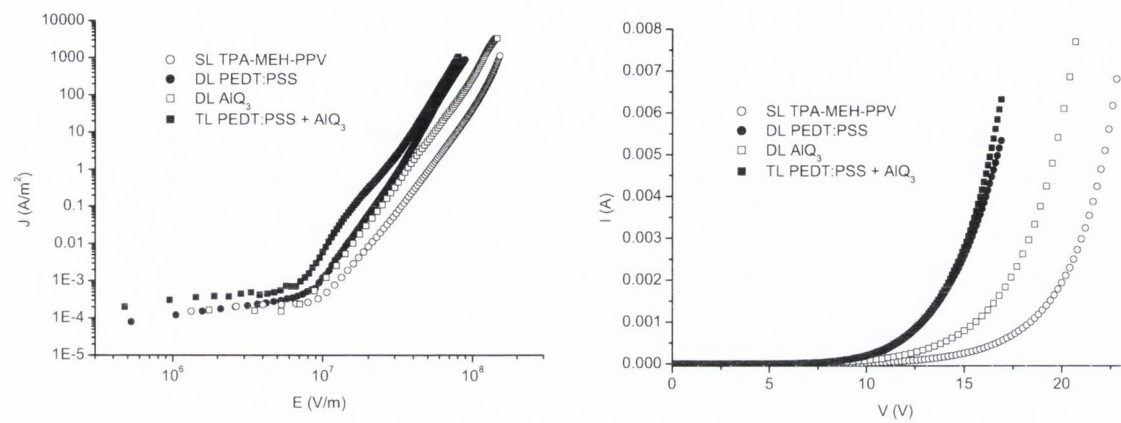


Fig. 44 Left: Current density versus electric field characteristics for single (150 nm) and multi-layer TPA-MEH-PPV LEDs. Right: current versus voltage characteristics for single and multi-layer TPA-MEH-PPV LEDs.

The double logarithmic multi-plot of J v E for all the devices shows the transport is similar in all of them. The use of PEDOT:PSS reduced V_d at a given I in DL HTL with respect to the SL device and this effect was also seen in a reduced V_d for TL with respect to DL ETL devices. For this material the use of AlQ₃ reduced V_d of DL ETL devices with respect to SL and this effect.

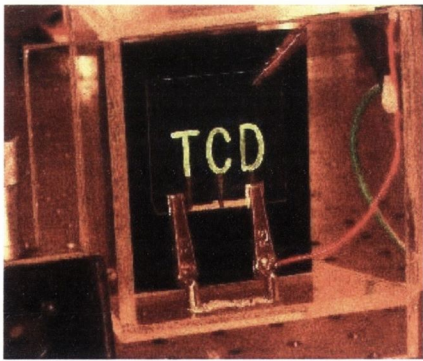


Fig. 45 Electroluminescent ITO/TPA-MEH-PPV/AlQ₃/Al) demonstration panel which I designed and fabricated.

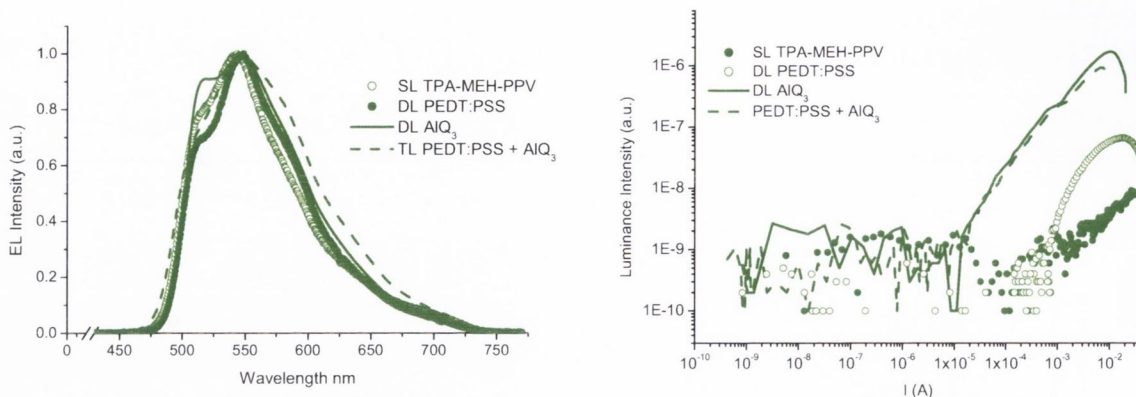


Fig. 46 EL spectra for single and multilayer TPA-MEH-PPV LEDs and right: luminance versus current plots for TPA-MEH-PPV LEDs.

From the double logarithmic plot in Fig. 46 one can see luminance turn-on is ~ 10 μ A and stays on up to currents of ~ 30 mA. The data is noisy in low current regions since there is no appreciable light detection until ~ 10 μ A. For the SL device in Fig. 46 shorting is almost certainly the cause of the spread in data points. At currents of about 1 mA a sublinear correspondence of luminance to current is already observed, indicative of EL quenching or degradation processes which may be heat-induced. This could also be indicative of a change from volume-controlled EL to injection-controlled EL. Such degradation results in black spots and patches of the device being destroyed thereby reducing the luminance per original, undamaged device area. The L-I data shows the AlQ₃-containing devices to be much brighter and more efficient than the SL or DL HTL devices as expected. One might have expected the TL device to be most efficient since PEDOT reduces V_d but the efficiency is slightly worse suggesting charge balance is worse. Also the maximum luminance is less than the DL ETL device probably because the TL devices are less stable due to problems forming a good, uniform HTL layer. The EL spectra are all very similar and have a lot less structure evident than the two orange and red emitters investigated, consistent with the notion that the effective conjugation length is reduced and suggests that TPA-MEH-PPV materials are more disordered.

4.7 POLYMER TPD-MEH-PPV

The full name of this polymer is *Poly[4-methylphenyl) imino-4,4' -diphenylene-(4-methylphenyl)imino-1,4-phenylene-ethenylene-2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene-ethenylene-1,4-phenylene]* and it is a polyconjugated main-chain polymer with TPD units in the arylene-vinylene backbone.

The motivation for making this material was two fold i) to compare with TPA-MEH-PPV which has one not two triphenylamine moieties and ii) to compare with TPD-M3EH-MEH-PPV which has an additional M3EH-PPV moiety but is otherwise the same.

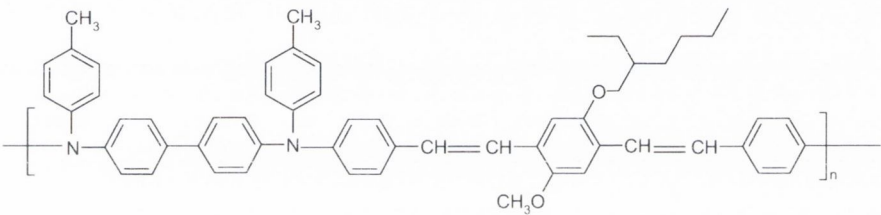


Fig. 47 Chemical Structure of TPD -MEH -PPV

As can be seen from the chemical structure in Fig. 47, TPD-MEH-PPV is an alternating copolymer which is a triphenyldiamine (TPD)-based PPV²⁹ consisting of TPD-vinylene and MEH-phenylene-vinylene units. The TPD moiety is incorporated into the PPV backbone by using the corresponding TPD-dialdehyde for the Horner type polycondensation. The internal PL yield is 15 %. TPD-MEH-PPV combines a high M_w (53,100) with a high T_g (188 °C).

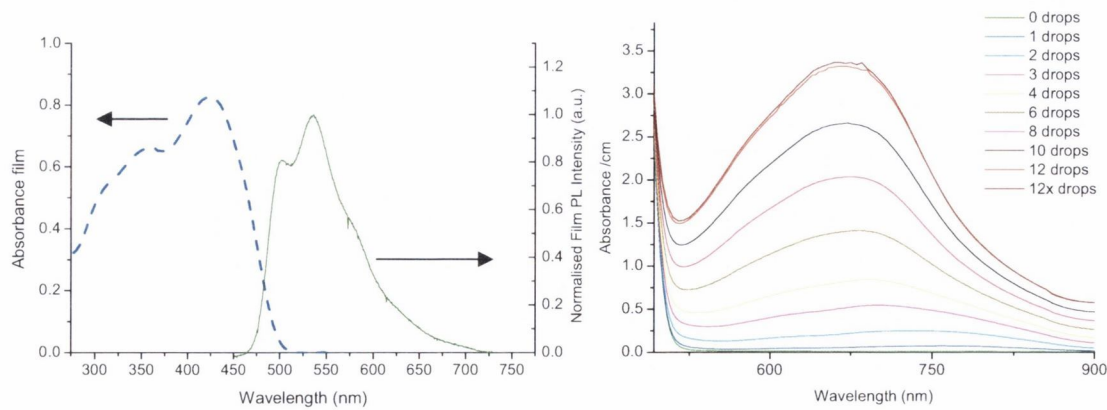


Fig. 48 left: absorption (dashed) and photoluminescence (solid line) of thin films of TPD-MEH-PPV and right: FeCl₃ doping-induced absorption of polymer a polymer solution of TPD-MEH-PPV.

The extension of the arylene-vinylene conjugation over the whole chain leads to a red-shifted luminescence with respect to TPD small molecules or non-conjugated TPD polymers. The latter are blue emitters while TPD-MEH-PPV is a green emitter. PL is blue-shifted slightly with respect to TPA-MEH-PPV. The monomer conformation is expected to be slightly more twisted for TPD-MEH-PPV than TPA-MEH-PPV, from quantum chemistry calculations for isolated heptamers of each polymer (using a Fletcher-Reeves energy minimisation routine with Hyperchem software), consistent with the blue shifted PL. The greener emission with respect to MEH-PPV implies that as with TPA-MEH-PPV exciton formation must also be occurring on the amine part of the molecule. The doping-induced absorption is very similar to that of TPA-MEH-PPV. The polymer is readily doped and does not show signs of saturating. Also there is no evidence of bipolaron formation or of any change in the ground state absorption. The polaron peaks for each MEH-PPV derivative were fitted by a Gaussian function and the peak energy and FWHM obtained. The polaron peak in Fig. 48 is shifted slightly with respect to that in TPA-MEH-PPV and has a slightly larger width at FWHM.

4.7.1 Single Layer Devices

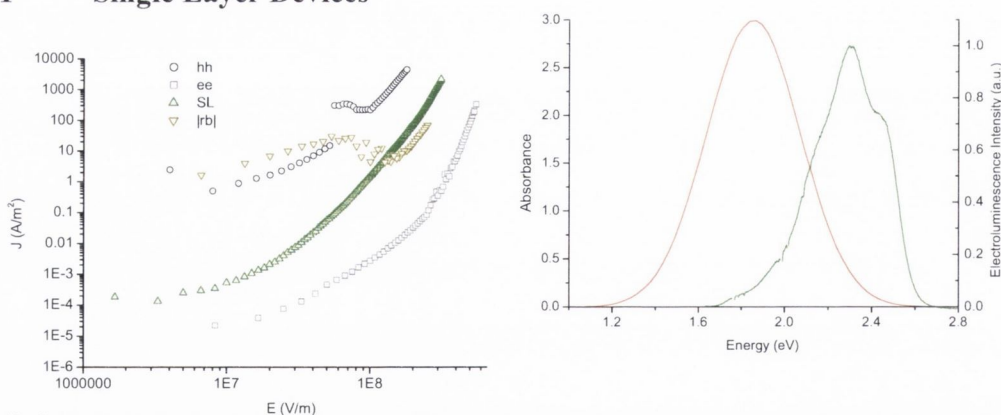


Fig. 49. Left: Current density versus electric field for single carrier devices (60 nm) and a single-layer TPD-MEH-PPV-LED. Right: FeCl₃ doping-induced absorption overlap with EL from a single layer TPD-MEH-PPV LED.

Note that although the data can appear very smooth on a linear scale, this is of course often not the case on a log scale. Despite this it is instructive to plot the different

device types together on a log scale. The rectification is poor in the single layer device ~ 10 at 15.6 V).

One can see the electron-mobility is considerably less than the hole-mobility for this material. The differential observed for this polymer and the other MEH-PPV derivatives would be less, if lower workfunction electrodes were used for the electron-only devices, however, for process reasons Al cathodes were used for this thesis work.

4.7.2 Combined Characterization of Single and Multi-Layer Devices

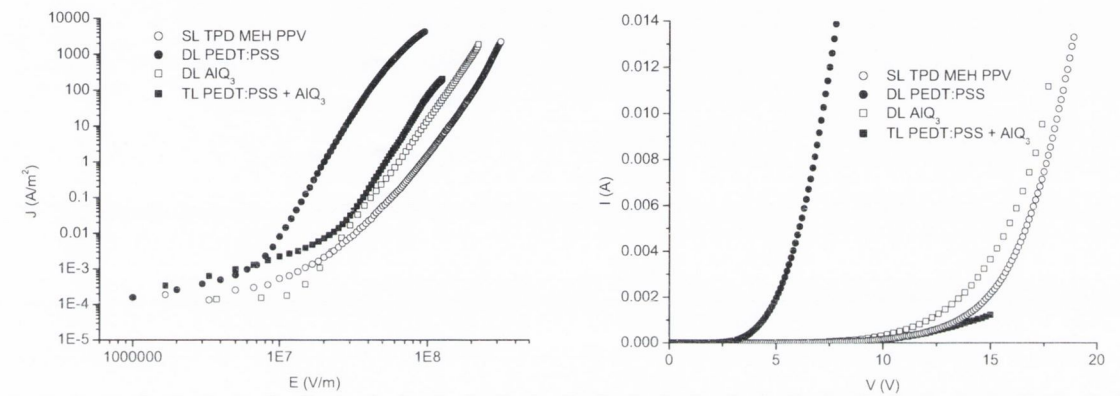


Fig. 50 Left: Current density versus electric field characteristics for single and multilayer TPD-MEH-PPV LEDs. Right: Current versus voltage characteristics for TPD-MEH-PPV LEDs.

From the I-V characteristic in Fig. 50, one can see however that all the devices have similar operating IV characteristics, excepting the DL HTL which had very large currents. This may be due to current flowing through the PEDOT itself (which is a highly conductive conjugated polymer) preferentially where the polmer layer has pinholes. Pinholes are more likely in very thin films such as the one formed by TPD-MEH-PPV. This is more likely than a percolation situation where PEDOT:PSS and polymer layers may have become mixed upon layer formation. This is because PEDOT:PSS is spun from aqueous solutions, whereas the polymer is spun from toluene or xylene and there is good solvent orthogonality and interface mixing of the two materials should not be a problem. This again is most likely due to device fabrication issues. With respect to TPA-MEH-PPV, the increased current by using PEDOT suggests a greater hole-supply due to reduced hole-injection barrier. This implies a deeper HOMO for TPD-MEH-PPV than TPA-MEH-PPV while LUMO levels are similar.

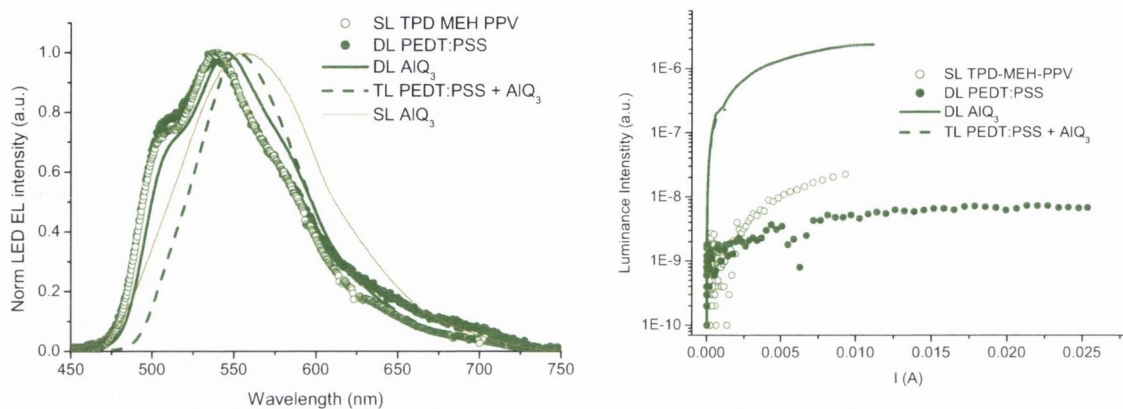


Fig. 51 Left: EL from single layer and multilayer TPD-MEH-PPV LEDs and a single-layer AlQ₃ LED. Right: Luminance versus current curves for single and multilayer TPD-MEH-PPV LEDs.

From Fig. 51 it can be seen that most of the EL spectra resemble the PL spectrum obtained for TPD-MEH-PPV. However, the TL LED spectrum is considerably red-shifted and resembles emission from a pure AlQ₃ SL device, suggesting there is a contribution to the EL from the AlQ₃ layer. This may be due to the AlQ₃ layer being too thick for this device. In that case, optimisation of the AlQ₃ thickness should recover the TPD-MEH-PPV spectrum for the TL device. However, the increased hole-supply may also be responsible, causing a greater charge imbalance with the recombination zone shifted into the ETL emitter itself.

4.7.3 Discussion of MEH-PPV Polymer Results

4.7.3.1 Absorption and Emission Spectra

For all these materials a large stokes shift is clear from the small overlap of the ground state absorption and photoluminescence spectra. The absorption profiles are very featureless owing to inhomogeneous broadening. In all cases the PL and EL spectra are very similar indicating emission is from the same species. TPA-MEH-PPV has the smallest stokes shift and is the least fluorescent of these materials. The PL spectra are

narrower than the absorption spectra and exhibit more structure and sharper, better resolved peaks, consistent with spectral and structural relaxation. Although the PL quantum efficiency is not extremely high, ASE (amplified spontaneous emission) has been achieved for these materials and the peak ASE wavelengths are included in Table 2 which summarises the optical properties of these polymers. In most cases the ASE max is red-shifted with respect to the PL and EL maxima. This red-shift is thought to be due to short-wavelength fluorescence re-absorption by the long-wavelength ground state absorption shoulder and may be reduced by using higher pump intensities than those for the onset of ASE to be observed. The PL and ASE and EL maxima are nearly the same in TPA-MEH-PPV as for the corresponding TPD material, TPD-4M-MEHPPV^{51, 54, 61}.

Clearly non-radiative relaxation of the excited segments in neat films is the dominant decay process in these materials and is due to internal conversion, polaron formation and triplet formation. Emission parameters for the MEH-PPV derivatives looked at in this chapter have been calculated, using ideas from molecular photophysics, and indicate a lumophore about the size of a repeat unit³⁰.

Radiative lifetimes for a repeat unit are of the order of a nanosecond and are also included in Table 2. Hence the device response time is not optically limited. With respect to MEH-PPV, TPD-4M-MEH-PPV emission is blue-shifted. This is because the exciton for MEH-PPV is thought to extend over several repeat units based on fluorescence lifetimes, while for TPD- 4M-MEH-PPV it is thought to be over one repeat unit. Weaker absorption cross-section spectra for MEH-PPV are consistent with this. The absorption of TPD-4M-M3EH-PPV resembles the combined shapes of TPD-4M-MEH-PPV and M3EH-PPV (which is very similar to MEH-PPV), indicating separate TPD-4M-MEH-PPV and M3EH-PPV chromophores with excitation transfer from the former to the latter as evidenced by the dominant emission from the M3EH-PPV.

The doping induced absorption peaks for each polymer were fitted using a double Gaussian function in order to obtain the peak widths and absorption maxima, taking the effect of the ground state polymer absorption edge into account by using a Gaussian to model the absorption edge. The main peak Gaussian fit parameter results were then used to generate a single Gaussian which was superimposed on single-layer LED spectra for each polymer. The fitting was necessary to isolate the polaron absorption spectrum from

the ground state absorption and the background signal due to trapping effects. The doping peak increases linearly with concentration for each polymer despite their structural differences. For other materials, quadratic and higher power law dependences have been observed. For the materials here, the doping-induced absorption is very broad and featureless for the same reasons as given for the ground state absorption and PL. Excited state absorption in the three copolymers is clearly evident from the doping-induced absorption spectra which overlap the EL spectra to a high degree, posing a problem for achieving an electrically pumped laser with these materials.

4.7.3.2 Overview of Absorption and Luminescence Parameters.

Polymer	Abs $\lambda_{\max}$ (nm)	PL $\lambda_{\max}$ (nm)	Polaron Abs $\lambda_{\max}$ (nm)	ϕ_{PL} or PLQY	SL EL $\lambda_{\max}$ (nm)	ASE $\lambda_{\max}$ (nm)	PL Lifetime τ (ns)
A	482.6	574.9*, 617.22		.15	576.7*, 620.6	622	6.2
B	437.9	591.8*, 640.9	743.1	0.25	584*, 640	618	.238 +- 20
C	437.7	514.4, 549*	678.1	.27	511.5, 545.6*	546	0.27+-0.04
D	424	501.8, 535*	669.0	0.15	505, 537.8*	540	.182+- .045

Table 2. Optical parameters of polymer films and devices and polaron absorption in polymer solutions. All film measurements are from films spun from toluene except MEH-PPV which was spun from chlorobenzene. (Asterix indicates main peak.) A is MEH PPV, B is TPD-4M-MEHPPV-M3EH PPV, C is TPA MEH PPV and D is TPD MEH PPV.

In Table 2 ASE pump intensities at onset or threshold (defined as pump pulse energy density required to narrow the spectral emission to half its initial value) are all of the order of $10 \mu\text{J}/\text{cm}^2$ for TPD materials here and for the MEH-PPVs and for TPA materials, they are a bit higher, at about $50 \mu\text{J}/\text{cm}^2$. The threshold is directly related to the effective stimulated emission cross section which is reduced by excited state absorption. Therefore minimising excited state absorption will reduce the thresholds for lasing in these materials. Since ASE is observed for these materials in waveguide structures, this suggests that issues like losses due to absorption by the metal electrodes,

achieving sufficiently high current densities, and promoting singlet over triplet formation, are very important for developing narrow-band electrically driven organic light sources.

4.7.3.3 Carrier Mobilities and Trap Energies in Single Carrier Devices

Polymer	$p_0 = p$ m^{-3} $\pm 20\%$	V_Ω V $\pm 30\%$	μ_Ω $m^2V^{-1}s^{-1}$ $\pm 20\%$	μ_{SCLC} $m^2V^{-1}s^{-1}$ $\pm 50\%$	$\tau_{d\Omega}$ s $\pm 3\%$	E_t (eV) $\pm 3\%$
A ee hh	2.3×10^{23}	6.4	4.6×10^{-14}	4.7×10^{-14}	.016	.0997
	3.8×10^{22}	1.05	8.5×10^{-12}	8.8×10^{-12}	5.2×10^{-4}	.112
B ee hh	3.7×10^{22}	0.45	7.0×10^{-16}	7.0×10^{-16}	6.46	.108
				1.7×10^{-13}		.114
C ee hh				2.4×10^{-14}		.118
	1.1×10^{22}	0.71	3.7×10^{-8}	3.7×10^{-8}	3.4×10^{-7}	
D ee hh	4.3×10^{23}	1.82	1×10^{-17}	2.4×10^{-16}	38.9	.232
	1.4×10^{23}	0.70	3.6×10^{-12}	6.3×10^{-12}	3.4×10^{-4}	.107

Table 3 The electron (e) and hole (h) charge carrier mobilities, charge carrier densities, transition voltage, and dielectric relaxation times for the four Jena materials are summarized. A is MEH-PPV, B is TPD-4M-MEHPPV-M3EH -PPV, C is TPA-MEH-PPV and D is TPD-MEH-PPV.

As can be seen from Table 3 all the polymers are p-tpye, having much greater hole-mobilities (obtained from hh – hole only – devices) than electron mobilities (obtained from ee – electron only – devices). This is consistent with the SL device efficiencies in Table 4 generally being low due to poor charge balance. Ideally a non-emissive electron-transport layer with similar electron mobility to the intrinsic hole-mobility of emissive polymer should be used. The barrier to electron injection using AlQ₃ is larger than for that for holes so that the although devices using an ETL had better charge balance and were the most efficient, these devices were still dominated by hole currents. The reason for poor agreement in the electron mobilities for TPD-4M-M3EH-PPV is largely that there are too few points for a proper fit. The largest sources of error in calculating the parameters in Table 3 are those involving the dimensions of the organic film, i.e. area (length and width) and thickness. Since μ_Ω and μ_{SCLC} agree well for a field independent mobility, $\tau_{d\,SCLC}$ will also be similar to $\tau_{d\,\Omega}$. Hole-only data was difficult to obtain due to shorting of devices made by sputtering a gold top-contact. This could be

avoided in future work by using thicker films (requiring either more concentrated polymer solutions or a lower spin speed. The dye layer time-of-flight method could be used to obtain carrier mobilities to compare with those obtained from electrical data here.³¹

The electron and hole mobilities of the polymers studied here listed in Table 3 are not only very different, they are also rather low compared with the state of the art which is now of the order of $1 \times 10^{-6} \text{ Vm}^2\text{s}^{-1}$ for fluorene-type backbone emitters. The turn on voltage of our devices is therefore quite high, with the exception of MEH-PPV devices, compared with state of the art devices. This is largely due to poor electron transport in the devices and the energy barrier at the AlQ_3 -polymer interface still being quite high. The use of Ca electrodes or aluminium electrodes using alkali-halide interlayers would reduce this barrier and lower the operating voltage of the devices. However, calcium is extremely instable in air and so was not a viable material to use considering air transfer etc., in the test setup used for the work in this thesis. With regard to the use of alkali metal fluorides and oxides like BaO in *composite cathodes* as they are sometimes referred to, extremely thin layers need to be deposited (of the order of 1 nm) and therefore a great degree of control is required over the deposition process in order to achieve reproducible results.

Low mobilities in the materials tested is mostly due to the presence of trapping sites in the MEH-PPV films (largely linked to monomer and hence polymer purity) which reduces the charge carrier mobility. Evidence for trapping in the materials tested is clear from fits to the I-V data which suggest that an exponential distribution of traps exists in all the materials studied here. Moreover, the characteristic trap energy is very similar for these materials as can be seen from Table 3, which is not unexpected as they have common components in their chemical structure and were synthesized, stored and processed using similar methods. It is evident that LED operating currents for useful brightness are all in the range described by space-charged limited conduction in the presence of an exponential trap distribution. In all the single carrier device I-Vs in this work, the trap filled limit and a subsequent trap free current region was not observed.

Trap distribution fits for an exponential distribution can be fit over several decades of device operation for unipolar devices. The electron and hole trap energies at

room temperature are similar (0.1 and 0.2 eV respectively) for all the devices except the electron device for TPD-4M-MEH-PPV which is about twice as deep as that of the others. At lower temperatures these trap energies would be expected to decrease for the same energetic distributions. For the most part the characteristic trap energies obtained are similar to those obtained for PPV, dialkoxy-PPV and AlQ₃ films. Trapping theory can also be applied to LED structures since the basic relation of J being proportional to V^m will remain true although the form of the mobility will be more complex. The trapping levels probably exist in very high densities in these materials despite improved synthesis techniques. Most of these are traps related to structural defects rather than chemical impurities. This may partly explain why fluorene type backbones have mobilities than PPV ones, since the former offer to routes for charge so if one is blocked by a defect there is still a way for charge to be transported.

To increase η_{ext} and lm/watt by improving charge balance, light outcoupling for a given emission colour and keeping V_d down, LEDs need to have all the organic layer thicknesses optimised. The individual layers were not optimised in this thesis and the total thickness of organic layers ranged between 40 and 210 nm. Using higher mobility materials would result in higher brightness levels at a given operating voltage assuming a similarly charge-balanced structure. The lack of suitable non-emissive n-type polymers is thus a bottleneck to all-polymer ultra-efficient devices based on PPV-type emitters.

4.7.3.4 LED Performance

The device efficiencies, taking into account the effect of the photopic curve, are quite similar for each polymer. The use of AlQ₃ significantly reduced the current flowing in the device at a given field yet efficiency is improved, particularly for the terpolymer as it has unbalanced transport. Perhaps for these polymers, the use of AlQ₃ in this instance introduced a lot of trapping sites which reduced the current flow in the device. The use of AlQ₃ should not just improve EL from a charge balance point of view but also because it can act to force recombination to be near the polymer: AlQ₃ interface, away from the polymer:cathode interface where a much higher number of quenching sites are likely to be found. Recombination is likely to be at this interface in a polymer

with a p-type backbone and so the AlQ₃ can act as an exciton confining layer too provided the HOMO of AlQ₃ is not well aligned with that of the LEP as is the case here.

Device Type	Max Brightness Cd/m ² ±5%	Max Measured η _{external} (%) ±15%	Estimate η _{internal} (%) ±20%	Theoretic η _{internal} (%) ±5%	Max Luminous Efficiency Lm/W ±15%
A					
SL	119	2.3x10 ⁻³		6.25	1.6x10 ⁻²
DLH	157	6.8x10 ⁻⁴			1.8x10 ⁻³
DLE	58	6.7x10 ⁻³			1.5x10 ⁻²
TL	230	1.3x10 ⁻²	7.5x10 ⁻²		3.0x10 ⁻²
B					
SL	2.2	1.2x10 ⁻⁴		3.8	9.9x10 ⁻⁵
DLH	1.2	8.6x10 ⁻⁵			7.4x10 ⁻⁵
DLE	158	1.2x10 ⁻¹	7.8x10 ⁻¹		7.1x10 ⁻²
TL	52	4.7x10 ⁻²			2.7x10 ⁻²
C					
SL	2	1.1x10 ⁻⁴		6.8	2.5x10 ⁻⁴
DLH	8	2.4x10 ⁻³			1.7x10 ⁻³
DLE	631	2.7x10 ⁻²			5.6x10 ⁻²
TL	504	3.1x10 ⁻²	2.4x10 ⁻¹		8.1x10 ⁻²
D					
SL	4	1.8x10 ⁻⁴		3.8	4.5x10 ⁻⁴
DLH	0.5	1.2x10 ⁻⁵			6.7x10 ⁻⁵
DLE	510	8.6x10 ⁻²	5.3x10 ⁻¹		5.7x10 ⁻²
TL	52	8.4x10 ⁻²			6.9x10 ⁻²

Table 4 LED Summary of performance parameters for the four MEH-PPV derivative-based LEDs where A is MEH PPV, B is TPD-4M-MEHPPV-M3EH PPV, C is TPA MEH PPV and D is TPD MEH PPV.

The best external quantum efficiency achieved for each EL device was compared with 25% of the internal PL yield in order to see how close to the spin-statistically-limited maximum EL efficiency for each material our devices were. For all these materials the simple spin statistics limit was found to be valid, however, several instances of devices which have exceeded this limit are discussed in section 3.6.3.1.

Despite the relatively low efficiencies of the devices tested here compared with state of the art devices, these materials are certainly excellent candidates for electroluminescent applications. Even with unoptimised layer thicknesses, and cathode materials, multilayer devices with good brightness levels sufficient for many electronic display applications were achieved under constant current driving. Use of Ca cathodes, device encapsulation and fabrication using glove box conditions from start to finish would greatly improve device performance, however, this is mostly the realm of corporate clean-room facilities. Such fabrication improvements would undoubtedly render LEDs made with the LEPs tested here with brightness and efficiency levels improvement by up to an order of magnitude, making these materials competitive with many of the other organic EL materials in the PPV class of emitters. The issue of colour purity of the emitters, very important for EL display applications, is not addressed in this thesis. Colour purity is measured using a colourimeter and is defined by the CIE tristimulus curves which can be used to provide CIE colour coordinates. Without the use of a colourimeter, one can still see from the EL spectra that the emission is quite broad and varying in intensity over the spectral width, with several broad peaks or shoulders. This reduces the colour purity, and is something which must be addressed through a combination of chemical synthesis to achieve narrower emission, selective wavelength outcoupling and microcavity effects enhanced by optimising device architecture.

4.8 BLUE-EMITTING LIGHT-EMITTING POLYMERS

The high energy (~ 3 eV) excited states of blue organic emitters impose higher reactivity (and lower stability) to these materials. Colour purity and device stability for blue OLEDs lag red and green devices considerably³². Blue emission can be obtained from several polymeric emitters including some PPV-based materials, ladder polymers and the most successful type – polyfluorenes. For PPVs, bulky sidegroups can be used to produce³³ fully conjugated PPV materials with a PL max at 442 nm attributed to interruption of conjugation due to oligophenylene substituents, which adopt a nearly orthogonal dihedral angle with respect to PPV in order to minimise steric hindrances. However, a shoulder is seen at 512 nm, which is attributed to aggregate emission. Incorporation of phenyl comonomer units in a PPV copolymer, also reduces conjugation

yielding an EL max of 450 nm. Use of carbazole-PPV³⁴ copolymers resulted in an emission maximum of 480 nm. A triazole PPV-copolymer was made which had a 486 nm PL maximum in thin film with a PLQY of 33%. A non conjugated polymer with oligo-PPV side groups³⁵ had a PL maximum of 475 nm. Although there is a lot of blue emission in these materials, pure blue is not available for fully conjugated PPVs.

Some ladder polymers, such as PPP, are good in terms of colour purity but LEDs based on these materials required a relatively high turn-on voltage.

4.8.1 Overview of Fluorene-Based Blue Emitters.

Fluorene-containing materials are the best blue polymeric emitters as they are easily functionalizable and good pure blue emission can be achieved. Polyfluorene is a polycyclic aromatic compound which received its name due to strong violet fluorescence which arises from the highly conjugated planar π -electron system.

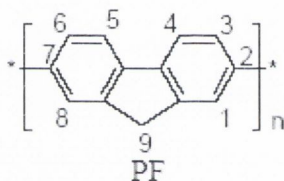


Fig. 52 Chemical structure of the monomer of unsubstituted polyfluorene (PF).

The 2, 7 positions in Fig. 52, are the most reactive towards electrophilic attack, allowing construction of a fully conjugated rigid-rod polymer chain by substitution reactions, whereas the methylene bridge provides scope to modify the processibility by substituents, without perturbing the electronic structure of the backbone. Polyfluorenes are the only class of conjugated polymer that emit right across the visible range of the electromagnetic spectrum with relatively high PL quantum efficiency³⁶. The rigid rod structure³⁷ can result in an overestimation of the molecular weight (M_w), which for PFO ((poly(9,9-di-*n*-octylfluorenyl-2,7'-diyl) or simply 'F8') is estimated to be by a factor of 2.7. Homo- and co-polymers are very stable thermally³⁸ with $> 400^\circ\text{C}$ decomposition temperature for many materials. Several PF materials, including PFO and PFO copolymers show liquid crystalline behaviour, opening the possibility for polarised

LEDs³⁹. PFO or 'F8' is the most liquid crystalline and most studied of the PFs. Nanoscale crystallinity has been observed for PFO in XRD. In PFO the octyl chains are believed to intercalate⁴⁰ (90 degrees to backbone), resulting in monodomain structures. Also as a result of ordering, PFs show well-resolved structural features, with respect to PPVs, in emission spectra of spincoated films. PFO emission is characterised by intrachain singlet features with maxima at 420, 445, 475 nm corresponding to 0-0, 0-1, and 0-2 peaks⁴¹. Due to some longer wavelength tail emission, PFs are typically bright sky-blue in colour. The solid film PLQY ranges between 40 – 80 %⁴² depending on film morphology, where due to the high tendency to order, solvent choice has a strong effect on the morphology and photophysical properties. From oligomer studies, the effective conjugation length in PDHF, a dialkyl PF similar structurally to PFO, is found to be about 11.8 fluorene units⁴³.

Although cyclic voltametry is often used to obtain HOMO and LUMO data, results should be interpreted with care since diffusion of ions may have an effect on the polymer structure⁴⁴. UPS data can also provide a value for the HOMO and for PFO the ionisation potential is found to be $-5.6 \pm .05$ eV. The band gap was found to be $3.1 \pm .1$ eV, in close agreement with the optical gap, implying an electron affinity of 2.5 eV. Generally the deeper blue the PF emission is, the deeper the HOMO level is and so the use of PEDOT:PSS (or even higher workfunction materials) are needed as an HTL to achieve efficient hole injection.

Apart from being good blue emitters, PFs show excellent charge transport properties. Non-dispersive transport of holes with a weakly field dependent mobility of $4 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, a factor of 10 – 100 times better than that typically found in PPVs, is found in many PF materials. As with PPV, unsubstituted PF⁴⁵ is insoluble. The first substituted PFs, made via oxidative coupling, resulted in low M_w materials with a lot of residual impurities and defects. The Yamamoto method⁴⁶ minimises mislinking and crosslinking but a lot of metal catalyst is used and so the polymer produced needs careful purifying. Suzuki coupling can minimise the problem of metal impurities.

One of the main issues with application of blue PFs in PLEDs is colour stability. Despite polyfluorenes exhibiting blue peaks, often the pure blue emission is contaminated upon annealing in air or during device operation by a green emission band centered

around 530 nm. In other words the colour purity is temperature dependent, being pure blue at low temperatures and often turquoise or green at elevated temperatures. Initially this was thought to be due to aggregates and or excimers⁴⁷ which act as energy and or charge traps. The green emission is not observed in dilute solutions⁴⁸ of PFs. Initial attempts to determine the origin of this green component focused on using bulky sidechains or main chain moieties in order to help separate chains in thin films. It has been shown recently that although the latter approach stabilised blue emission in some cases, the real cause of the green emission is due to fluorene-9-one defects in the chain. This was confirmed⁴⁹ for PL spectra of films annealed in air and in nitrogen, and by IR (infrared) spectroscopy where C=O peaks were observed in the spectra. Less than 1 % fluorenone of these *keto*-defects can quench the blue emission⁵⁰ and these defects may form during synthesis and or photooxidation during device operation.

Dense packing of PF molecules facilitates energy transfer onto fluorenone defects, and hence the defect originated emission is reduced in solutions⁵¹. The intensity of keto-defect green emission in EL is worse than PL since the keto defects act as electron traps increasing the probability of recombination there. The green emission has been proposed to be due to monomeric fluorenone by some⁵² and to be due to fluorenone excimers (interchain effect) by others based on work with matrix-isolated PF chains⁵³. The mechanism of fluorenone formation is thought to be related to monoalkylated fluorene moieties, present as impurity or defect sites in dialkylated PFs like PFO, since these sites are the most sensitive to oxidation⁵⁴. Unsurprisingly, monomer purity is crucial in reducing keto-emission in PFs and it has been found that deprotonation of the monoalkylated impurity reduces green emission⁴⁵.

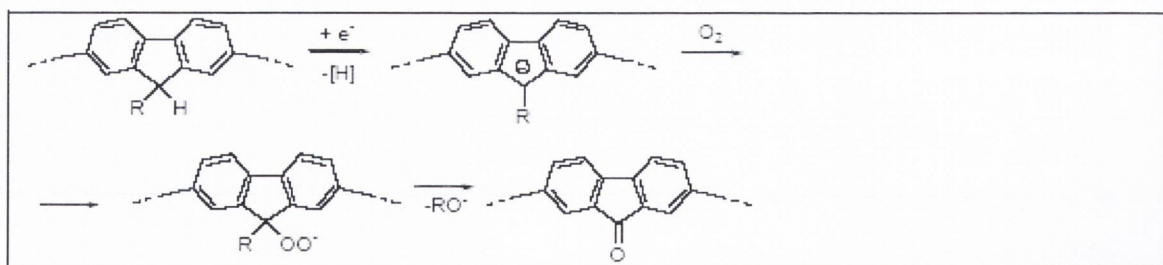


Fig. 53 Mechanism proposed for the formation of keto defects in polyfluorenes.

The first diaryl-substituted PFs were blue emitters with PL at 417 , 439 and 473 nm in solution. A PL maximum of 430 nm⁴⁵ was achieved with no green emission and excellent colour stability during annealing (2 hrs at 180 C in air with no C=O peaks seen in FTIR after that). Random copolymers have also exhibited similar colour stability and PL maxima but lower luminous efficiency and increased turn on voltage⁴⁵.

The use of dendrons in substituted PFs and PF copolymers has been employed where the bulky side groups reduce aggregation. These materials can suffer, though, from oxidation at benzyl linkages and at CH₂ groups. Dendrons⁴⁷ do suppress the green emission, completely in some cases, without altering the emission with respect to PFO much. A spiro-anthracene-fluorene polymer also exhibited stable blue emission at 418 nm as did cross-linked PF copolymers with siloxane bridges⁴⁷. Hyperbranched PFs lead to blue emission without a green component and $\eta_{\text{ext}} = 1\%$ ⁵⁵

As with PPVs blending PFs with transport layers like triarylaminines increases device efficiency.⁴⁸ However, in both cases, phase separation is likely when small molecules are used. Blending with polymers can reduce this problem⁴⁹. Another approach to improving charge transport is to put an HTL moiety such as TPA in the polymer backbone of PF or, as a sidegroup⁵⁰, resulting in increased hole mobility. It was found that the PLQY was less than half that of PFO but turn on voltage was low and green emission was well suppressed. This highlights the problem of using the same moieties to shift emission and tailor the charge transport.

End-capping can replace reactive end-groups in PFs. Both HTL and ETL⁵¹ end-capping has been used to improve efficiency and green emission (competitive recombination on HTL units) with respect to uncapped polymers. End-capping, which does not shift the emission significantly, can also be used to cross-link polymers to provide an insoluble layer for further spincoating⁵². Interestingly an end-capped (alkyl-substituted) PF, with no alkyl side-groups in the main chain, exhibited no green emission, confirming the fluorenone origin of green emission⁵³. As with PPVs, copolymers offer the opportunity to tune EL and transport properties of PFs. Both ETL⁵⁴ and HTL⁵⁵ comonomers were used to improve efficiency. A statistical copolymer with both ETL and HTL comonomers⁵⁶ resulted in a stable blue emitter with $\eta_{\text{ext}} = 1.21$. A binaphthyl PF

LED with a copper-phthalocyanine (CuPc) transport layer and Ca as the cathode gives $\eta_{\text{ext}} = 0.82\%$ and blue EL peaks at 420 and 446 nm with a PL efficiency of 44%.

Other colours are possible from PFs using the co-polymer approach. A green (545 nm) LED with $\eta_{\text{ext}} = 3.86\%$ (using a TPD HTL and an Al cathode) was made using a fluorene-benzothiadiazole copolymer (F8BT)⁵⁷ PF-benzothiadiazole randomers with electron deficient and electron rich units for balanced transport⁵⁸ resulted in LEDs (PEDOT:PSS HTL and Ca electrode) with $\eta_{\text{ext}} = 6.5\%$ at 540 nm where the BT unit dominates the EL. The best efficiency was for a material with the greatest electron-deficient BT content, indicating the importance of improving electron transport for PFs. Also, using the copolymer approach, UV (395 nm)⁵⁹ and NIR $1.035\ \mu\text{m}$ ⁶⁰ PLEDs were demonstrated. Almost monochromatic light can be achieved by energy transfer to Eu^{3+} emitters for red emission with a FWHM of about 4 nm⁶¹. A PF-MEH-PPV copolymer was made⁶² with an emission maximum at 580 nm. Fluorene-thiophene random copolymers exhibit performance far greater than homo or alternating copolymers owing to fine tuning of the co-monomer ratio and⁶³ possess good suppression of the green keto-emission. A red randomer⁶⁴ with a $\eta_{\text{ext}} = 3.1\%$ was made using a PF-naphthalenanthiozole copolymer. Colour tuning in PFs is also achievable via down-conversion using efficient Förster energy transfer in PFs doped with phosphorescent (blue to red) and non phosphorescent (violet to blue) dye molecules⁶⁵. Interestingly inefficient Förster transfer can be used advantageously to produce white emitters⁶⁶.

4.9 A NEW POLY(PHENYLENE-VINYLENE)-POLY(FLUORENE) COPOLYMER

Use of PPV-fluorene copolymers which had high PLQY of 81 % and 24 % in film have been produced with emission maxima of 495 nm and 473 nm respectively. An MEH-PPV-fluorene copolymer was made with a PL maximum of 503 nm and HOMO - 5.16 eV and LUMO of -2.6 eV. A dialkyl PF-PPV random alternating copolymer was produced previously and showed the same properties as the corresponding fluorene-vinylene homopolymer. This material had a HOMO of -5.73 eV and a LUMO of 3.13 eV with EL peaks at 465, 500, and 530 nm⁶⁷. Good performance (brightness of 870

cd/m² at 16 cd/A for a PEDOT/polymer/Ca/Al device was achieved.) Flourenyl-substituted PPV has been produced by Gilch polycondensation and has fluorene as a side group. This polymer had a hole-mobility of $4.5 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, two orders of magnitude higher than that for MEH-PPV. The PPV backbone determined the optical properties though. An LED (ITO/PEDOT:PSS/Polymer/Ca) with $\eta_{\text{ext}} = 0.53 \%$ with emission maximum at 500 nm and a shoulder at 532 nm was produced.

The PFO-PPV copolymer studied in this thesis is similar to some of the PF0-PPV copolymers synthesised previously with the aim creating a bluer emitting PPV type material. The polymerizations of the rigid fluorene monomers, in which two phenyl rings are locked into a plane via the C-9 carbon of the fluorene-units, can be realized through Stille, Heck, Wittig, Yamamoto, Grignard and Suzuki coupling reactions. The facile functionalization at the C-9 position of the fluorene unit may offer an opportunity to reduce the interchain interactions thereby improving the NLO response and optoelectronic properties of the resulting polymers. Recently Chou and Shu⁶⁸ developed a simple way to introduce 4-hydroxyphenyl functionality to the C-9 position of fluorene.

4.9.1 Chemical Structure, Absorption and Photoluminescence

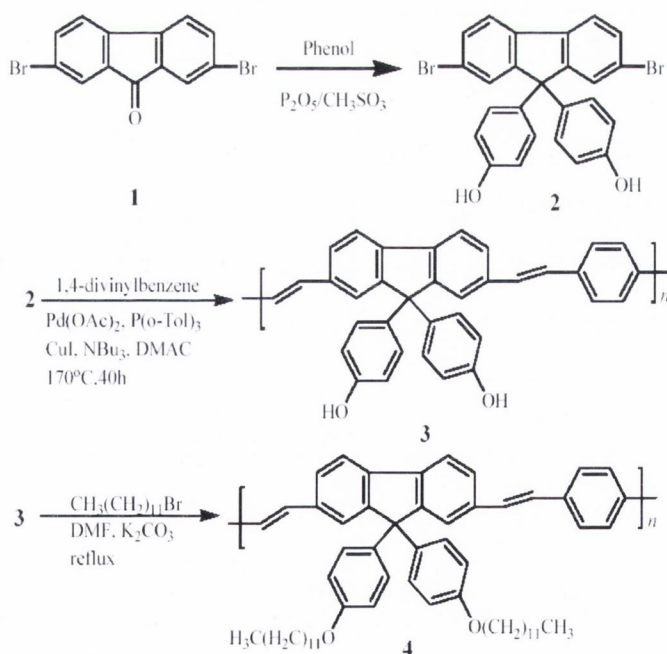


Fig. 54 Chemical structure and synthesis route for PFO-PPV

The full name of the polymer is Poly(di-4-dodecyloxyphenyl-7-fluorene). The M_w is 4.28×10^5 for this polymer, giving it good film-forming properties. The glass-transition temperature (T_g) is about 95°C , which is higher than those of poly(9,9-dioctylfluorene) ($\sim 51^\circ\text{C}$)²¹ and poly(9,9-dihexylfluorene) ($\sim 55^\circ$)⁶⁹ due to the attachment of two 4-dodecyloxyphenyl groups onto the C-9 position of every fluorene unit. The objective in using an extended 9,9-bis(4-hydroxyphenyl)fluorenyl core in the polymerization reaction is that insertion of a rigid phenylene spacer between the large side chain and the polymer backbone would increase shielding of the polyfluorene main chain, resulting in reduced aggregates/excimer formation, while not blocking the reaction sites of the macromonomer from the palladium-catalyzed polymerization reaction. Furthermore the C9 position may now be less susceptible to oxidation. In previous PFO-PPV copolymers the C9 position is unphenylated with alkoxy chains attached directly at the C9 position. The TGA thermogram exhibits two weight-loss plateaus. At lower temperatures almost no weight loss was observed. The 4-dodecyloxy-side chain in PFO-PPV decomposed first at $160\text{--}320^\circ\text{C}$, with an onset temperature for the thermal bond cleavage of 210°C , then the main chain decomposed with an onset temperature for thermal bond cleavage of 404°C . These findings indicated that the resultant polymer has good thermal stability.

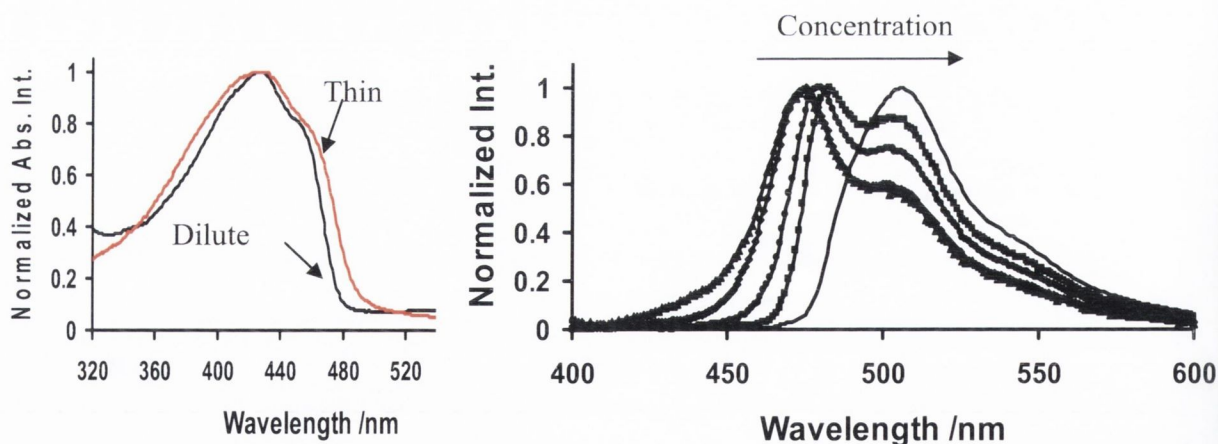


Fig. 55 Left: UV/Vis absorption spectra of PFO-PPV in dilute benzonitrile solution (2.6×10^{-4} mM) and in thin film. Right: PL of PFO-PPV in solution. The bluest PL is for the most dilute solution and the PL redshifts as concentration increases (2.1×10^{-6} , 2.6×10^{-4} , 8.7×10^{-3} , 2.6×10^{-2} , and 0.5 M).

The main absorption peak in the UV-vis spectrum is located at 427 nm, followed by a shoulder peak at 450 nm. The peaks are attributed to the π - π^* transition of the polymer. Intermolecular interaction makes the solid absorption broader than the solution. As expected, the polymer exhibits very strong photoluminescence (PL) with maximum emission centered at 474 nm in dilute benzonitrile solution. The maximum PL peak is shifted gradually to the longer wavelengths with the increase of the polymer concentration from 2.1×10^{-6} to 0.5 M, suggesting the formation of aggregates (leading to excimers) in solution. The fluorescence decay monitored at 474 nm ($\lambda_{\text{exc}} = 410$ nm) in deoxygenated dry benonitrile showed two exponential-decay processes. From the initial fast decay part of the decay, the lifetime (τ_{f1}) of the single excited state was found to be 584 ps⁷⁰ (fraction of this component: 88%). From the slow decay component, the lifetime (τ_{f2}) is 1.38 ns (fraction of this component: 12%). The value of the latter is quite close to the fluorescence lifetime of typical PPV polymer (about 1.27ns). The excited triplet-state maximum of polymer occurs in the region of 460-540 nm with a lifetime of 65.8 μ s. The nanosecond transient absorption spectrum was obtained by the excitation of the polymer with 355 nm laser light in deaerated benzonitrile solution, in which the rapid and slow decay components were observed; both components showed the same absorption band at 500 nm. On addition of O₂, the transient absorption band showing slow decay at 500 nm, attributed to triplet-triplet (T-T) absorption of this polymer, disappeared⁷⁰, suggesting that the energy transfer takes place from the triplet excited states of to O₂, probably yielding ¹O₂.

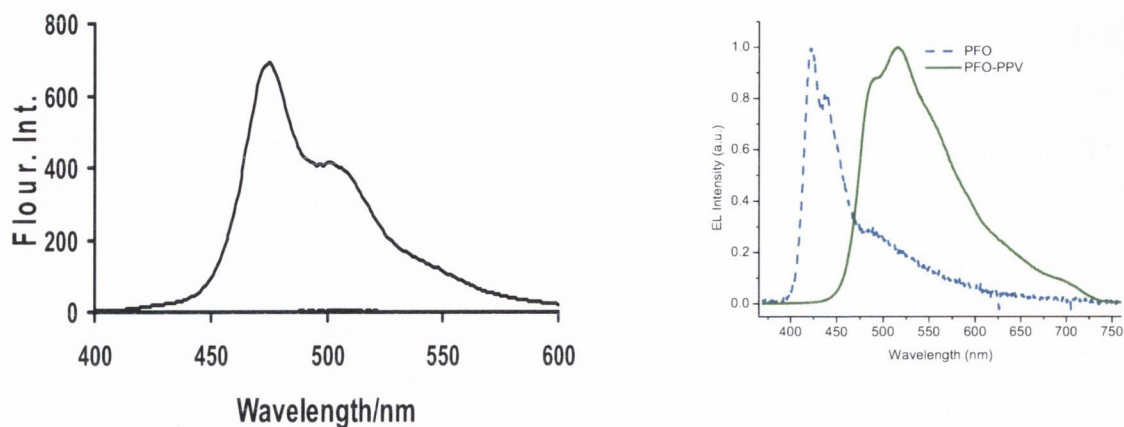


Fig. 56 Left: Quenching of photoluminescence from that observed in dilute solution (main plot,) to that observed (weak signal around 500 nm) for thin film. Right: EL spectrum of multilayer PFO-PPV (solid line) LED. The EL spectrum of a similar PFO multilayer LED is included (dashed line) for comparison.

As part of this thesis work PLEDs with the structure ITO/Au(1nm)/PFO-PPV/LiF/Al were made. A 100 nm thick film of PFO-PPV was spincoated onto a ITO substrate from a 5 g/l chloroform solution at 900 rpm. The stable electroluminescent (EL) spectrum obtained is shown in Fig. 56 (right), with a peak wavelength of 515 nm and a shoulder at 490 nm. This was compared with the EL from a similar control device made with a common polyfluorene material (poly(9,9-di-*n*-octylfluorenyl-2,7'-diyl) obtained from American Dye Source Ltd. From the PL data in Fig. 56 is clear that the bright green emission observed over the whole active area of the PFO-PPV PLED resembles the PL of the highest concentration solution (0.5M) most. This suggests that despite the use of phenyl spacers, chain-stacking in the solid state is responsible for the observed green EL. This suggests that bulkier sidegroups are required to reduce aggregation effects. The most dilute solution of PFO-PPV is still much greener than PFO EL. It is worth noting that on their first run the EL from the PFO-PPV PLEDs initially appeared bluish to the eye but was not stable enough to obtain a spectrum as it rapidly became green. The fact that the change to green emission was permanent suggests that it may be linked to keto-type defect formation occurring upon exciton generation. Initially a the keto-related emission may not be detected by eye but within a couple of seconds the number of keto-defect sites is such that you can already tell the colour is changing.

The peak brightness at 10 mA was just 8.6 cd/m² which corresponds to an external efficiency of 0.012 %. Due to the small amount of PFO-PPV at our disposal, the emissive layer had to be spin-coated at low rpm from a dilute solution in order to get a uniform thin film. The resulting emissive layer was measured to be 30 nm thick using AFM. Typically a more concentrated solution (e.g. 15 mg/l) and a higher spin speed (e.g. 1500 rpm) would result in an emissive layer thickness between 100 nm and 150 nm. The thinness of the emissive layer combined with the fact that the PFO-PPV device was a single layer device contributed to the low efficiency of this particular device. Furthermore, the fluorescence of the thin-film spin-coated onto indium-tin oxide (ITO)-coated glass substrate has been shown to be almost completely quenched due to possible energy transfer to ITO, but the emission peak at around 500 nm in the PL spectrum was still clearly resolved. Similar observation on the quenching of PL of poly(*p*-phenylenevinylene)(PPV) spin-coated onto ITO was reported by Herold *et al.*⁷¹ The quenching of PL means that the electroluminescence (EL) efficiency is also quenched. To overcome this problem, fluorene-doped tin dioxide (FTO) instead of the ITO substrate has been used and also thin polymer interlayers between the ITO and LEP, intended for hole transport only, might help reduce the quenching. In any case this is only a problem for single layer devices.

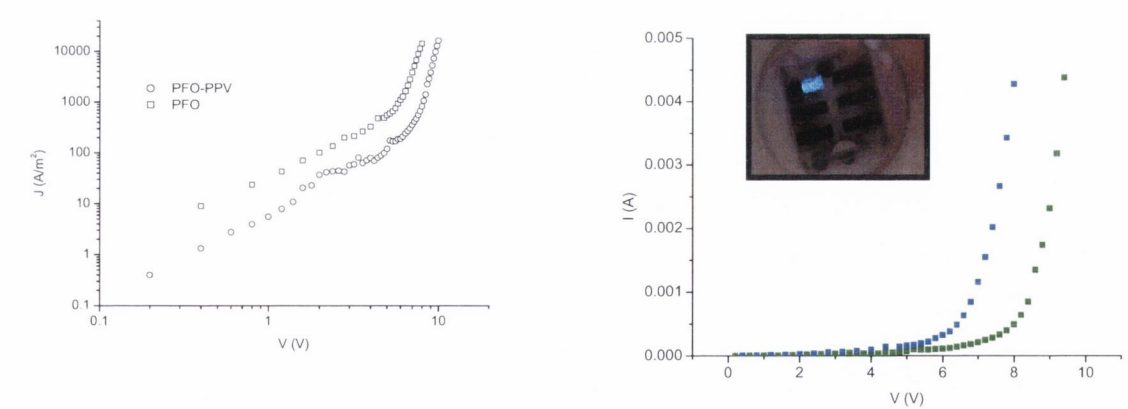


Fig. 57 Left: Current density versus voltage for single-layer PFO (open squares) and PFO-PPV (open circles) LEDs. Right: Current-voltage characteristics for PFO-PPV and PFO multilayer LEDs. The inset shows the blue electroluminescence from the PFO LED.

The I-V curves in Fig. 57 are very similar, with the PFO having a slightly lower operating voltage of 6.2 V compared with 6.8 V for the copolymer PFO-PPV at a current

density of 167 Am^{-2} , suggesting that there is more balanced charge transport in the PFO device and or that the pure PFO homopolymer has a higher mobility than the copolymer. Note the magnitude of the current density at equivalent operating voltages is considerable higher in both PFO-containing polymers than that seen in the MEH-PPV derivatives again suggesting the mobility of PFO materials is greater than PPV materials (given the efficiency is poor for both).

4.10 A NEW BLUE-EMITTING 9,9-BIS[4-(DIPHENYLAMINO)-PHENYL]FLUORENE SMALL MOLECULE

Aswell as polymers, part of this thesis work involved fabricating SMOLEDs using the small molecule 9,9-bis[4-(diphenylamino)-phenyl]fluorene (DPA-F), which, like PFO-PPV, is based on the fluorene structure. The motivation for making this material is two-fold i) it is expected to have high PLQY and possibly be bluer than PFO, if this were the case it could be a good candidate monomer to produce a deeper blue LEP than PFO and ii) it may be a good small molecule emitter for use in SMOLEDs. Achieving more efficient, deeper blue (lower CIEy value) EL is a major priority area of research for all OLED types.

4.10.1 Chemical Structure, Absorption and Photoluminescence

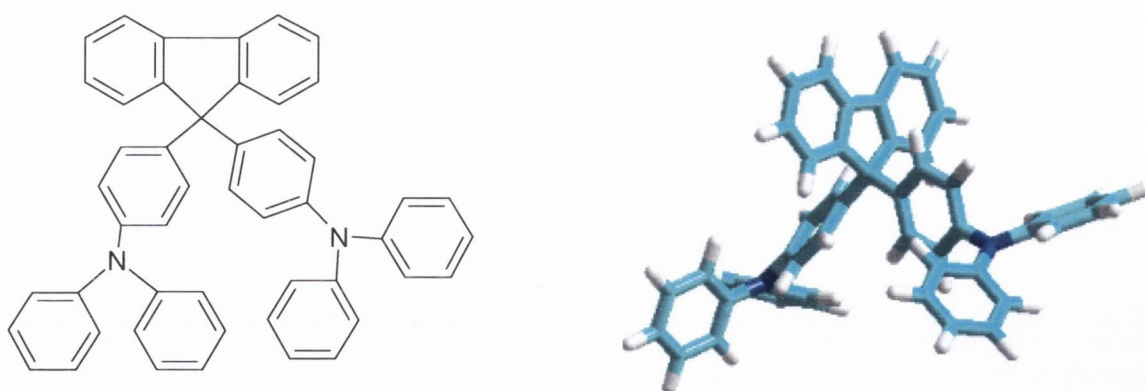


Fig. 58 Left: Chemical structure of DPA-F small molecule. Right: Geometry-optimised structure using Hyperchem_{TM} and a Fletcher-Reeves convergence algorithm.

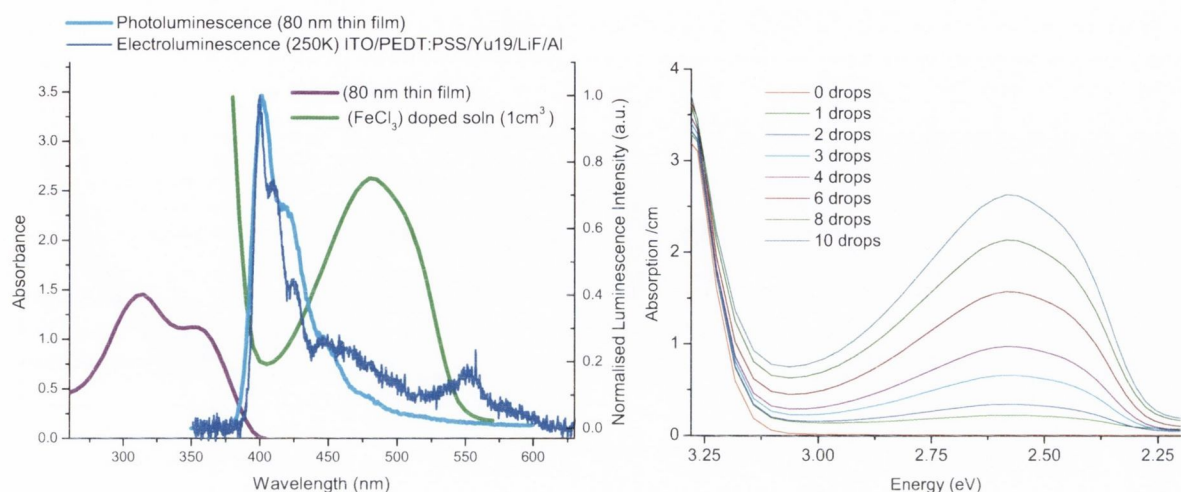


Fig. 59 Left: Absorbance thin film (purple line), Polaron absorption due to FeCl_3 doped DPA-F solution (green line), PL thin film (light blue line), EL DL DPA-F LED (dark blue line). Right: 0.25 M FeCl_3 doping-induced absorption of a 9 g/l toluene solution of DPA-F.

The absorption and photoluminescence of a sublimed layer of DPA-F on a quartz (spectrosil B) substrate are shown in Fig. 59. The fact that several strong peaks other than the 0-0 peak are visible is a good indication of strong electron-lattice coupling as expected for a small molecule. Further evidence of this is the fact that the peak for the 0-0 transition is not the strongest peak in the spectrum. The DPA-F was deposited from a quartz boat using an Edwards Auto-306 evaporator at a vacuum of $< 2 \times 10^{-6}$ mbar and at a rate of 2.5 nm/sec. The film quality appeared very uniform and of very good quality to the eye. Also shown in Fig. 59 is the polaron absorption data from and the EL taken from a double layer LED at 250K (room temp spectra was rather noisy). Like the polymers, there is significant overlap of polaron absorption and EL spectra.

4.10.2 I-V and EL Spectra of Single and Multi-Layer Devices

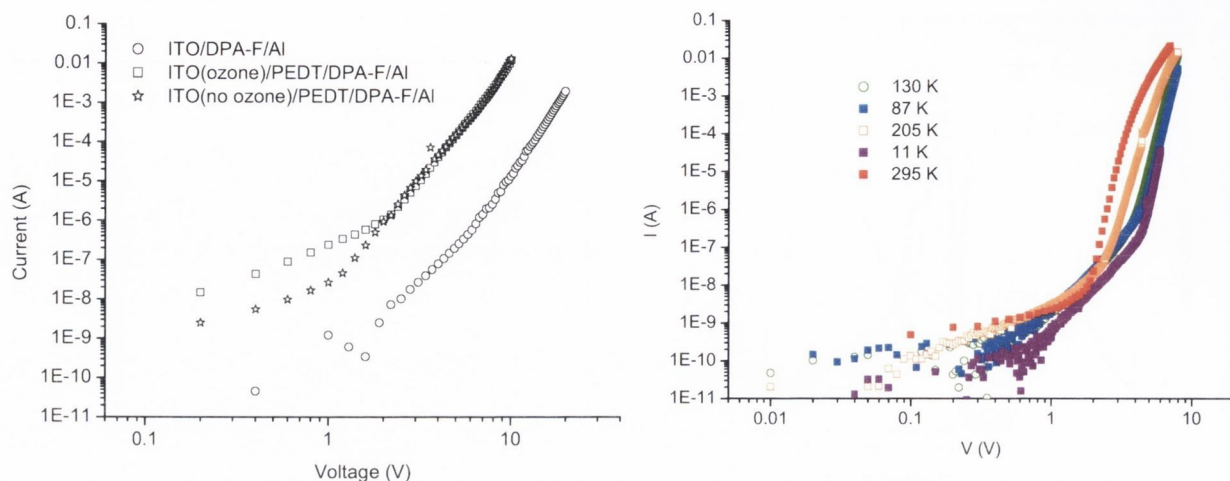


Fig. 60 Left: Current versus voltage for DPA-F devices (80 nm) with Right : Temperature dependent I-V data for a ITO/(ozone)PEDOT/DPA-F (110)/LiF/Al device.

The thickness of the sublimed layer was $80 \text{ nm} \pm 5 \text{ nm}$ using a Digital Instruments Nanoscope IIIa AFM in tapping mode and applying a stepheight analysis to a cut made in the film using a blade. Care was taken to measure away from the region where material builds up as a result of the cut.

Generally the top aluminium electrode does not seem to adhere very well to the DPA-F layer as evidenced by rather rapid electrode destruction at moderate current densities. Despite this it was possible to perform some device characterization. Fig. 61 right shows that PEDOT used as a HTL significantly lowers the operating voltage of the device. Using ozone treated PFO (1min exposure) was sufficient to modify the ITO surface. Though this only resulted in a slight reduction in hole injection barrier as seen in Fig. 61, the stability of the device was improved as evidenced by the longer emitting lifetime observed with respect to the untreated device and the single layer device.

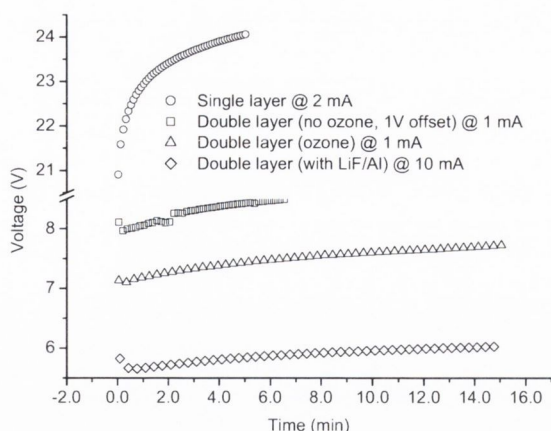


Fig. 61 Emitting lifetime at constant current for DPA-F devices. Clearly the ozone treatment of ITO improves the stability of the treated devices which exhibit a lower voltage drift for a constant current density, than the single layer device or the double layer device without any ozone treatment.

Using a 60 nm thick DPA-F layer, ozone treated ITO with PEDOT, and LiF/Al as as the cathode resulted in a low operating voltage device with similar stability (similar increase in drive voltage with time) to the treated devices with just an Al cathode (Fig. 61: diamonds). This device structure was used to obtain EL spectra. For this structure EL was seen at 5 – 7 V. The other devices did emit but at a very low level intensity

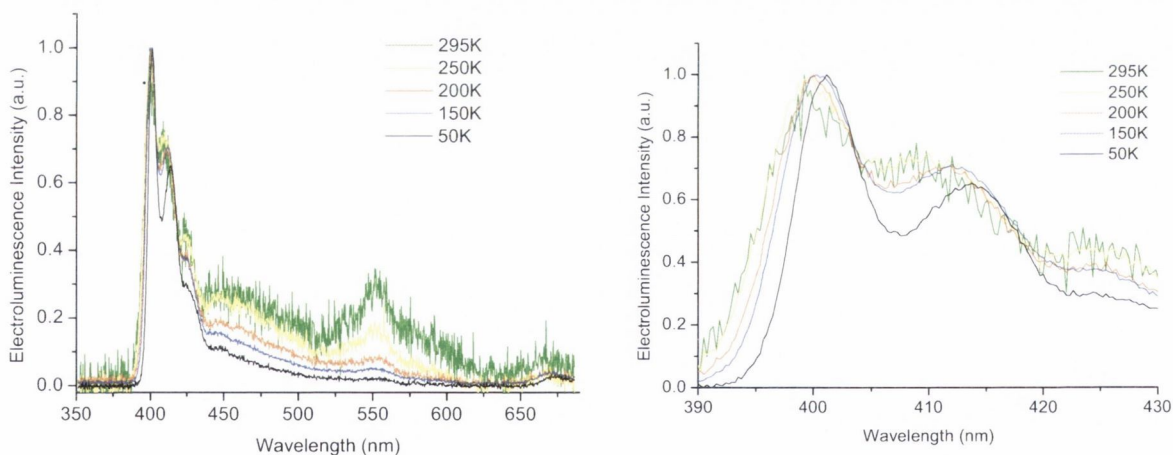


Fig. 62 Left: Temperature dependent EL spectra of an ITO(ozone)PEDOT/DPA-F/LiF/Al device. **Right:** Close-up for the same temperature dependent EL data, of the the blue spectral region.

With regard to the EL, the main peak is at 401 nm. There is not too much parasitic green emission at low temperature which is often a problem with fluorene-based blue emitters. The PL and EL main peaks are the same (both due to singlet exciton emission) but the EL contains more features in the green region of the spectrum, albeit at a lower intensity than the blue features. This is possibly because the sites

responsible for the green emission are good charge trapping sites. The origin of the green emission is likely to be due to keto-defects as discussed earlier. The formation of these defects and the quenching in the spectrum are most likely linked to oxidation effects. The oxygen molecule, dioxygen, has a triplet ground state, denoted by T_1 ($^3\Sigma_g^-$), with the symbol 3O_2 . The lowest energy excited states are singlet states denoted by $S_1(^1\Delta_g)$ and $S_2(^1\Sigma_g^+)$; singlet states have long lifetimes since the singlet-triplet transitions are forbidden. The energy levels of singlet oxygen, 1O_2 , 1.63 eV and 0.98 eV. Singlet oxygen formed by excitation is by excitation of dioxygen and Dexter energy transfer from a photosynthesiser, in this case the blue emitting molecule in question, DPA-F. The long-lived triplet state energy in DPA-F, is probably sufficient to produce singlet oxygen which is electrophilic in nature and undergoes 'two-electron' reactions and is thus highly reactive. Carbon double bonds are electron rich areas, very susceptible to attack from singlet oxygen which is noted for resulting in chain scission and the formation of carbonyl groups at these sites on the backbone and at alkoxy substituent points in fluorenes and also PPVs. The breaking of conjugation due to scission and carbonyl formation caused by photooxidation in devices results in blue shifted electroluminescence spectra and a reduction in intensity. It can be seen that the peaks at 401 and 414 nm shift to slightly higher energy as the T increases from 50 K to 295 K, opposite to what is normally observed for organic emitters and it is not clear why this is observed. The green peak in the EL in Fig. 62 centered at 550 nm is not seen in the PL and, it can be seen that the associated transition increases in oscillator strength as the temperature is increased. This increase in the intensity of the 550 nm emission is slow at first (50K – 150 K) and then increases more rapidly (150 K – 295 K) and appears to be in line with a reduction in the overall EL emission intensity in this temperature range. In other words, the green component of the EL increases with increasing T relative to the blue component. This peak is probably associated with a keto-type defect and the quenching of intensity is due to photooxidation of DPA-F which is very unstable in air.

4.10.3 General Conclusions on the Red, Green and Blue Emitters Tested

The electroluminescence from six new materials was studied. Given identical device preparation conditions, it is clear that the blue small molecule was the most unstable, closely followed by the PFO-copolymer. This is a universal problem, most of the best blue materials current available have much shorter lifetimes than the best red and green ones (by 1- 2 orders of magnitude). If oxidation degradation was minimised by encapsulation it would be possible to achieve much longer lifetimes for all the devices tested, particularly the blue small molecule which appears to be most sensitive to oxidation. However, even for encapsulated devices, blue lifetimes lag behind the rest. The PF based materials operate at lower voltages and have higher mobilities than the PPV type materials. This is possibly due to the fact that there are effectively two routes for charge to travel between phenyls in the fluorene unit so that if one pathway is defective charge may still flow along the chain. Optimisation of all the devices tested would involve knowing the ionization potentials obtained from UPS measurement for each material rather than inferring what electrodes will suffice from previous work on similar materials, also optimising HTL and ETL and optical outcoupling. This would allow estimates for the electron affinities and choice of the best electrodes to use. A full thickness dependent analysis of single-carrier devices would help elucidate details of the transport in each material.

Finally it has been noted that from electrical pulsing experiments (PPV), that the device efficiency and not the ultimate brightness limits laser action. At high exciton density quenching due to excited state absorption is a problem. Therefore, although some very high PL solid state efficiencies have been achieved for both types of materials PF and PPV, this does not always translate to high EL efficiency or long device lifetime. Separation of transport and emission functions in a material does seem like the best approach to achieve efficient devices. This may be achieved by using dendrimer structures or by using careful choice of blends of an emitter and a transport material, for example. It may also be possible to have transport and emitter functions better separated on a given backbone. For the PPV materials studied, blending with an electron transport layer is likely to be a good, easy route to take given that the materials in this thesis are all

predominantly hole-transporting. In order to learn more about what limits the fluorescence yields in the materials studied, photoinduced absorption and FTIR spectroscopies of the materials studied would be interesting and would help to assign structure property relationships in this series of related chemical structures.

References

1. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, *Nature* **347**, (6293), 539-541 (1990).
2. Askari, S. H.; Rughooputh, S. D.; Wudl, F., "Soluble Substituted PPV Conducting Polymers - Spectroscopic Studies". *Synthetic Metals* **1989**, 29, (1), E129-E134.
3. Deng, X. Y.; Lau, W. M.; Wong, K. Y.; Low, K. H.; Chow, H. F.; Cao, Y., "High efficiency low operating voltage polymer light-emitting diodes with aluminum cathode". *Applied Physics Letters* **2004**, 84, (18), 3522-3524.
4. Spreitzer, H.; Becker, H.; Kluge, E.; Kreuder, W.; Schenk, H.; Demandt, R.; Schoo, H., "Soluble phenyl-substituted PPVs - New materials for highly efficient polymer LEDs". *Advanced Materials* **1998**, 10, (16), 1340-+.
5. R. A. Wessling, R. G. Zimmerman, "Polyelectrolytes from bis-sulfonium salts" U.S. Patent No. 3401152 1968
6. Staring, E. G. J.; Braun, D.; Rikken, G.; Demandt, R.; Kessener, Y.; Bouwmans, M.; Broer, D., "Chemical-Vapor-Deposition of Poly(1,4-Phenylenevinylene) Films". *Synthetic Metals* **1994**, 67, (1-3), 71-75.
7. Gilch, H. G.; Wheelwright, W., "Polymerization of Alpha-Halogenated P-Xylenes with Base". *Journal of Polymer Science Part A-1-Polymer Chemistry* **1966**, 4, (6PA1), 1337-&.
8. L. Smilowitz, A. Hays, *Synth. Met.* **1993** 55
9. Hsieh, B. R.; Yu, Y.; VanLaeken, A. C.; Lee, H., "General methodology toward soluble poly(p-phenylenevinylene) derivatives". *Macromolecules* **1997**, 30, (25), 8094-8095.
10. Neef, C. J.; Ferraris, J. P., MEH-PPV: "Improved synthetic procedure and molecular weight control". *Macromolecules* **2000**, 33, (7), 2311-2314.
11. Burn, P. L.; Grice, A. W.; Tajbakhsh, A.; Bradley, D. D. C.; Thomas, A. C., "Insoluble poly 2-(2'-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene for use in multilayer light-emitting diodes". *Advanced Materials* **1997**, 9, (15), 1171-&.
12. a) Hsieh, B. R.; Yu, Y.; Forsythe, E. W.; Schaaf, G. M.; Feld, W. A., "A new family of highly emissive soluble poly(p-phenylene vinylene) derivatives. A step toward fully conjugated blue-emitting poly(p-phenylene vinylenes)". *Journal of the American Chemical Society* **1998**, 120, (1), 231-232. b) Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W., "Chemical Tuning of Electroluminescent Copolymers to Improve Emission Efficiencies and Allow Patterning". *Nature* **1992**, 356, (6364), 47-49.
13. Becker, H.; Spreitzer, H.; Kreuder, W.; Kluge, E.; Schenk, H.; Parker, I.; Cao, Y., "Soluble PPVs with enhanced performance - A mechanistic approach". *Advanced Materials* **2000**, 12, (1), 42-+.
14. Hilberer, A.; Brouwer, H. J.; Vanderscheer, B. J.; Wildeman, J.; Hadziioannou, G., "Synthesis and Characterization of a New Efficient Blue-Light-Emitting Copolymer". *Macromolecules* **1995**, 28, (13), 4525-4529.
15. Ho, P. K. H.; Kim, J. S.; Burroughes, J. H.; Becker, H.; Li, S. F. Y.; Brown, T. M.; Cacialli, F.; Friend, R. H., "Molecular-scale interface engineering for polymer light-emitting diodes". *Nature* **2000**, 404, (6777), 481-484.
16. Zheng, L. X.; Urian, R. C.; Liu, Y. Q.; Jen, A. K. Y.; Pu, L., "A binaphthyl-based conjugated polymer for light-emitting diodes". *Chemistry of Materials* **2000**, 12, (1), 13-+.
17. Leung, L. M.; Chik, G. L., "Phase-Transfer-Catalyzed Synthesis of Disubstituted Poly(Phenylene Vinylene)". *Polymer* **1993**, 34, (24), 5174-5179.
18. Sarker, A. M.; Ding, L. M.; Lahti, P. M.; Karasz, F. E., "Synthesis and luminescent studies of poly(phenylenevinylene)s containing a biphenyl moiety". *Macromolecules* **2002**, 35, (1), 223-230.
19. Yang, Z.; Sokolik, I.; Karasz, F. E., "A Soluble Blue-Light-Emitting Polymer". *Macromolecules* **1993**, 26, (5), 1188-1190.
20. Ahn, T.; Jang, M. S.; Shim, H. K.; Hwang, D. H.; Zyung, T., "Blue electroluminescent polymers: Control of conjugation length by kink linkages and substituents in the poly(p-phenylenevinylene)-related copolymers". *Macromolecules* **1999**, 32, (10), 3279-3285.
21. Kim, J. H.; Park, J. H.; Lee, H., "Highly efficient novel poly(p-phenylenevinylene) derivative with 1,3,4-oxadiazole pendant on a vinylene unit". *Chemistry of Materials* **2003**, 15, (18), 3414-3416.

22. Yu, L. S.; Chen, S. A., "Full-range tunability of electron and hole carrier mobilities and density ratios via incorporation of highly electron-deficient moieties in poly(phenylene vinylene) side chains". *Advanced Materials* **2004**, 16, (8), 744-+.
23. H.-H. Horhold, H. Tillmann, "MEH-PPV and dialkoxy phenylene vinylene copolymers. Synthesis and lasing characterisation". *Synth. Met.* 2001 119
24. Y.Cao, I.D. Parker, "Improved quantum efficiency for electroluminescence in semiconducting polymers" *Nature*, 1999, 397
25. W. Holzer, A. Penzkofer, "Photo-physical characterisation and travelling-wave lasing of some TPD-based polymer neat films", *Opt. Mater.* 2002 19
26. Y.Liu, M.S.Liu, and A.K.-Y Jen, *Acta Polym.* **1999**, 50
27. Kraft, A.; Burn, P. L.; Holmes, A. B.; Bradley, D. D. C.; Friend, R. H.; Martens, J. H. F., "Hole-Transporting Compounds for Multilayer Polymer Light-Emitting-Diodes". *Synthetic Metals* **1993**, 57, (1), 4163-4167
28. W. Holzer, A. Penzkofer, "Travelling-wave lasing of triphenylamine-based poly(phenylene vinylene)" *Synth. Met.* **2001** 124
- 29 Y. Liu, M.S. Liu, A.K.-Y. Jen, *Acta Polymerica*, **1999**, 50
30. W. Holzer, A. Penzkofer, "Photo-physical characterisation and travelling-wave lasing of some TPD-based polymer neat films," *Opt. Mater.* **2002** 19
31. Redecker, M.; Bradley, D. D. C.; Inbasekaran, M.; Wu, W. W.; Woo, E. P., "High mobility hole transport fluorene-triarylamine copolymers". *Advanced Materials* **1999**, 11, (3), 241-+. b) Hertel, D.; Scherf, U.; Bassler, H., "Charge carrier mobility in a ladder-type conjugated polymer". *Advanced Materials* **1998**, 10, (14), 1119-+.
32. Y.Cao, I.D. Parker, "Improved quantum efficiency for electroluminescence in semiconducting polymers" *Nature*, 1999, 397.
33. I. D. Rees, K. L. Robinson, "Recent developments in light-emitting polymers", *MRS Bulletin*, **2002** pp451 – 455.
34. Lee, J. K.; Schrock, R. R.; Baigent, D. R.; Friend, R. H., "A New-Type of Blue-Light-Emitting Electroluminescent Polymer". *Macromolecules* **1995**, 28, (6), 1966-1971.
35. Kim, J. J.; Kim, K. S.; Baek, S.; Kim, H. C.; Ree, M., "Synthesis and properties of photoluminescent polymers bearing electron-facilitating oxadiazole derivative side groups". *Journal of Polymer Science Part a-Polymer Chemistry* **2002**, 40, (8), 1173-1183.
- 36
37. Fukuda, M.; Sawada, K.; Yoshino, K., "Synthesis of Fusible and Soluble Conducting Polyfluorene Derivatives and Their Characteristics". *Journal of Polymer Science Part a-Polymer Chemistry* **1993**, 31, (10), 2465-2471.
38. Grell, M.; Bradley, D. D. C.; Long, X.; Chamberlain, T.; Inbasekaran, M.; Woo, E. P.; Soliman, M., "Chain geometry, solution aggregation and enhanced dichroism in the liquid-crystalline conjugated polymer poly(9,9-dioctylfluorene)". *Acta Polymerica* **1998**, 49, (8), 439-444.
39. Neher, D., "Polyfluorene homopolymers: Conjugated liquid-crystalline polymers for bright blue emission and polarized electroluminescence". *Macromolecular Rapid Communications* **2001**, 22, (17), 1366-1385.
40. Whitehead, K. S.; Grell, M.; Bradley, D. D. C.; Jandke, M.; Strohriegel, P., "Highly polarized blue electroluminescence from homogeneously aligned films of poly(9,9-dioctylfluorene)". *Applied Physics Letters* **2000**, 76, (20), 2946-2948.
41. Fukuda, M.; Sawada, K.; Yoshino, K., "Synthesis of Fusible and Soluble Conducting Polyfluorene Derivatives and Their Characteristics". *Journal of Polymer Science Part a-Polymer Chemistry* **1993**, 31, (10), 2465-2471.
42. Ariu, M.; Lidzey, D. G.; Sims, M.; Cadby, A. J.; Lane, P. A.; Bradley, D. D. C., "The effect of morphology on the temperature-dependent photoluminescence quantum efficiency of the conjugated polymer poly(9,9-dioctylfluorene)". *Journal of Physics-Condensed Matter* **2002**, 14, (42), 9975-9986.
43. Klaerner, G.; Miller, R. D., "Polyfluorene derivatives: Effective conjugation lengths from well-defined oligomers". *Macromolecules* **1998**, 31, (6), 2007-2009.
44. Janietz, S.; Bradley, D. D. C.; Grell, M.; Giebeler, C.; Inbasekaran, M.; Woo, E. P., "Electrochemical determination of the ionization potential and electron affinity of poly(9,9-dioctylfluorene)". *Applied Physics Letters* **1998**, 73, (17), 2453-2455.

45. Raultberthelot, J.; Simonet, J., "The Anodic-Oxidation of Fluorene and Some of Its Derivatives - Conditions for the Formation of a New Conducting Polymer". *Journal of Electroanalytical Chemistry* **1985**, 182, (1), 187-192.
46. Pei, Q. B.; Yang, Y., "Efficient photoluminescence and electroluminescence from a soluble polyfluorene". *Journal of the American Chemical Society* **1996**, 118, (31), 7416-7417.
47. Sims, M.; Bradley, D. D. C.; Ariu, M.; Koeberg, M.; Asimakis, A.; Grell, M.; Lidzey, D. G., Understanding the origin of the 535 nm emission band in oxidized poly(9,9-dioctylfluorene): The essential role of inter-chain/inter-segment interactions". *Advanced Functional Materials* **2004**, 14, (8), 765-781.
48. Scherf, U.; List, E. J. W., "Semiconducting polyfluorenes - Towards reliable structure-property relationships". *Advanced Materials* **2002**, 14, (7), 477-+.
49. Gong, X. O.; Iyer, P. K.; Moses, D.; Bazan, G. C.; Heeger, A. J.; Xiao, S. S., "Stabilized blue emission from polyfluorene-based light-emitting diodes: Elimination of fluorenone defects". *Advanced Functional Materials* **2003**, 13, (4), 325-330.
50. de Freitas, P. S.; Scherf, U.; Collon, M.; List, E. J. W., "(9,9-Dialkylfluorene-co-fluorenone) copolymers containing low fluorenone fractions as model systems for degradation-induced changes in polyfluorene-type semiconducting materials". *E-Polymers* **2002**.
51. Romaner, L.; Pogantsch, A.; de Freitas, P. S.; Scherf, U.; Gaal, M.; Zojer, E.; List, E. J. W., "The origin of green emission in polyfluorene-based conjugated polymers: On-chain defect fluorescence." *Advanced Functional Materials* **2003**, 13, (8), 597-601.
52. List, E. J. W.; Guentner, R.; de Freitas, P. S.; Scherf, U., "The effect of keto defect sites on the emission properties of polyfluorene-type materials". *Advanced Materials* **2002**, 14, (5), 374-378
53. Craig, M. R.; de Kok, M. M.; Hofstraat, J. W.; Schenning, A.; Meijer, E. W., "Improving color purity and stability in a blue emitting polyfluorene by monomer purification." *Journal of Materials Chemistry* **2003**, 13, (12), 2861-2862.
54. Hwang, D. H.; Park, M. J.; Lee, J. H., "EL properties of stable blue light-emitting polyfluorene copolymers." *Materials Science & Engineering C-Biomimetic and Supramolecular Systems* **2004**, 24, (1-2), 201-204.
55. Pogantsch, A.; Wenzl, F. P.; List, E. J. W.; Leising, G.; Grimsdale, A. C.; Mullen, K., "Polyfluorenes with dendron side chains as the active materials for polymer light-emitting devices." *Advanced Materials* **2002**, 14, (15), 1061-+.
56. Cho, H. J.; Jung, B. J.; Cho, N. S.; Lee, J.; Shim, H. K., "Synthesis and characterization of thermally stable blue light-emitting polyfluorenes containing siloxane bridges". *Macromolecules* **2003**, 36, (18), 6704-6710.
57. Sainova, D.; Miteva, T.; Nothofer, H. G.; Scherf, U.; Glowacki, I.; Ulanski, J.; Fujikawa, H.; Neher, D., "Control of color and efficiency of light-emitting diodes based on polyfluorenes blended with hole-transporting molecules". *Applied Physics Letters* **2000**, 76, (14), 1810-1812.
58. Brown, T. M.; Kim, J. S.; Friend, R. H.; Cacialli, F.; Daik, R.; Feast, W. J., "Built-in field electroabsorption spectroscopy of polymer light-emitting diodes incorporating a doped poly(3,4-ethylene dioxythiophene) hole injection layer". *Applied Physics Letters* **1999**, 75, (12), 1679-1681.
59. Ego, C.; Grimsdale, A. C.; Uckert, F.; Yu, G.; Srdanov, G.; Mullen, K., "Triphenylamine-substituted polyfluorene - A stable blue-emitter with improved charge injection for light-emitting diodes". *Advanced Materials* **2002**, 14, (11), 809-811.
60. Gong, X.; Ma, W. L.; Ostrowski, J. C.; Bechgaard, K.; Bazan, G. C.; Heeger, A. J.; Xiao, S.; Moses, D., End-capping as a method for improving carrier injection in electrophosphorescent light-emitting diodes." *Advanced Functional Materials* **2004**, 14, (4), 393-397.
61. Chen, J. P.; Klaerner, G.; Lee, J. I.; Markiewicz, D.; Lee, V. Y.; Miller, R. D.; Scott, J. C., "Efficient, blue light-emitting diodes using cross-linked layers of polymeric arylamine and fluorene". *Synthetic Metals* **1999**, 107, (2), 129-135.
62. Lee, J. I.; Klaerner, G.; Miller, R. D., "Oxidative stability and its effect on the photoluminescence of poly(fluorene) derivatives: End group effects". *Chemistry of Materials* **1999**, 11, (4), 1083-1088.
63. Wu, F. I.; Reddy, D. S.; Shu, C. F.; Liu, M. S.; Jen, A. K. Y., "Novel oxadiazole-containing polyfluorene with efficient blue electroluminescence". *Chemistry of Materials* **2003**, 15, (1), 269-274.
64. Jung, B. J.; Lee, J. I.; Chu, H. Y.; Do, L. M.; Shim, H. K., "Synthesis of novel fluorene-based poly(iminoarylene)s and their application to buffer layer in organic light-emitting diodes". *Macromolecules* **2002**, 35, (6), 2282-2287.

65. Liu, X. M.; He, C. B.; Hao, X. T.; Tan, L. W.; Li, Y. Q.; Ong, K. S., "Hyperbranched blue-light-emitting alternating copolymers of tetrabromoarylmethane/silane and 9,9-dihexylfluorene-2,7-diboronic acid." *Macromolecules* **2004**, 37, (16), 5965-5970.
66. Herguch, P.; Jiang, X. Z.; Liu, M. S.; Jen, A. K. Y., "Highly efficient fluorene- and benzothiadiazole-based conjugated copolymers for polymer light-emitting diodes". *Macromolecules* **2002**, 35, (16), 6094-6100.
67. Lu, P.; Zhang, H. Q.; Shen, F. Z.; Yang, B.; Li, D.; Ma, Y. G.; Chen, X. F.; Li, J. H.; Tamai, N., A wide-bandgap semiconducting polymer for ultraviolet and blue light emitting diodes". *Macromolecular Chemistry and Physics* **2003**, 204, (18), 2274-2280.
68. Chen, M. X.; Perzon, E.; Andersson, M. R.; Marcinkevicius, S.; Jonsson, S. K. M.; Fahlman, M.; Berggren, M., "1 micron wavelength photo- and electroluminescence from a conjugated polymer". *Applied Physics Letters* **2004**, 84, (18), 3570-3572.
69. Pei, J.; Liu, X. L.; Yu, W. L.; Lai, Y. H.; Niu, Y. H.; Cao, Y., "Efficient energy transfer to achieve narrow bandwidth red emission from Eu³⁺-grafting conjugated polymers." *Macromolecules* **2002**, 35, (19), 7274-7280.
70. Jin, S. H.; Kang, S. Y.; Kim, M. Y.; Chan, Y. U.; Kim, J. Y.; Lee, K.; Gal, Y. S., "Synthesis and electroluminescence properties of poly(9,9-di-n-octylfluorenyl-2,7-vinylene) derivatives for light-emitting display." *Macromolecules* **2003**, 36, (11), 3841-3847.
71. Yang, W.; Hou, Q.; Liu, C. Z.; Niu, Y. H.; Huang, J.; Yang, R. Q.; Cao, Y., "Improvement of color purity in blue-emitting polyfluorene by copolymerization with dibenzothiophene". *Journal of Materials Chemistry* **2003**, 13, (6), 1351-1355. b) Yang, J.; Jiang, C. Y.; Zhang, Y.; Yang, R. Q.; Yang, W.; Hou, Q.; Cao, Y., "High-efficiency saturated red emitting polymers derived from fluorene and naphthoselenadiazole". *Macromolecules* **2004**, 37, (4), 1211-1218. c) Virgili, T.; Lidzey, D. G.; Bradley, D. D. C., "Efficient energy transfer from blue to red in tetraphenylporphyrin-doped poly(9,9-dioctylfluorene) light-emitting diodes". *Advanced Materials* **2000**, 12, (1), 58-+. d) Hwang, D. H.; Park, M. J.; Kim, S. K.; Lee, N. H.; Lee, C. H.; Kim, Y. B.; Shim, H. K., "Characterization of white electroluminescent devices fabricated using conjugated polymer blends". *Journal of Materials Research* **2004**, 19, (7), 2081-2086. e) Lee, S. H.; Yasuda, T.; Tsutsui, T., "Charge carrier mobility in blue-green emitting fluorenyl-substituted poly(p-phenylene vinylene)s". *Journal of Applied Physics* **2004**, 95, (7), 3825-3827. f). "Synthesis, Characterization, and Optoelectronic Properties of a Novel Polyfluorene/poly(p-phenylenevinylene) Copolymer": Y. Chen, Y. Araki, J. Doyle, A.E. Strevens, O. Ito, and W.J. Blau. *Chemistry of Materials* 17, 1661 (**2005**). g) R. D. Scurlock, B. Wang, "Singlet Oxygen as a Reactive Intermediate in the Photodegradation of an electroluminescent polymer". S.M. Lipson, "Optical and Electrical Properties of Modified Conjugated Polymer Thin Films", Trinity College Dublin, Ireland **2001** h) J. Am. Chem. Soc. 117 **1995** i) S.M. Fonseca, J.Pina, "Triplet and Singlet Oxygen Formation in Fluorene-Based Alternating Copolymers". *J. Phys. Chem. B* **2006**, 110.

Chapter 5

5 DEVICES WITH NOVEL NANODOT-ARRAY ANODES

5.1 INTRODUCTION

So far, organic light-emitting diodes have been discussed almost exclusively from the point of view of using different emissive media. However, device *architecture* plays an equally important role in determining device efficiency and performance.¹ In this context, architecture relates to the geometry (dimensions) or physical elements of all the layers (active and passive) involved. Device architecture can be used to maximize performance via improved carrier injection and transport² (with a view to bulk recombination), thermal management, and optical outcoupling³. Architecture can also be used to control the spatial distribution of the emitted light and the narrowness of the emission via the inclusion of diffractive elements. In this chapter the motivation is to see if using a nanodot array of metal contacts to inject charge in a PLED improves the thermal management in the device. The development of a nanodot metallic array produced via porous alumina templating to meet this objective is described. The physical grounds deemed responsible for the proposed benefits of such a structure are discussed. The feasibility of the idea was investigated initially using copper- (Cu) filled porous alumina. Subsequently, an improved version, based on a polished nickel (Ni)-filled array was made as this was more in line with the kind of quality of component required for a device application. Much of my research went into developing the nanodot electrode itself. However, preliminary characterization of the resulting device prototypes was done. Consequently, and possibly of greater interest, one can now envisage the possibilities in terms of new devices structures. Although, at present, the template used in our research and in the proposed future work is inorganic, there are already indications that it may be possible to switch to suitable organic templates materials in the not-too-distant future.

5.1.1 OLED Performance Limited by Joule Heating

Since the discovery of light-emitting polymers, there has been much progress⁴ in the field of OLEDs with ever increasing demands for more efficient and brighter devices. For example, passive matrix OLED displays need to be pulse driven at high currents to achieve reasonable average brightness. This means that maximising current density

levels will be very important as the technology goes forward. Also, any potential electrically pumped organic laser devices will require high current densities to achieve lasing. It is, therefore, clear that for these kinds of applications, good thermal management by minimizing Joule heating is crucial to achieve and maintain high current densities and useful operating lifetimes under such driving conditions. Apart from the issue of joule heat causing cathode degradation, it is reasonable to assume that trapped carriers may be mobilised, and similarly impurities may be more mobile in a heated environment. The combination of heat and electric field may cause an unfavourable redistribution of these defects which may adversely effect device performance and lifetime. Furthermore, increased heat will cause increased molecular vibration which may increase the number of non-radiative decay paths available directly or indirectly.



Fig. 63 An example of black spot formation which is due to localized electrode melting and is a major cause of early device failure.

In electronic devices, the elevated operating temperature of the active medium with respect to “standard” room temperature (21-23°C) is a direct result of Joule heating⁵ and acts as a limiter to device performance and lifetime. The carrier mobilities in polymers have been shown to be temperature dependent. The heat in a device is proportional to the electrical power of the device. Now, as the power scales with the square of current flow or current density J (J is proportional to the mobility), there is good potential for thermal runaway at elevated current densities when the device is not actively cooled.

Tessler *et al*⁶ have studied heating in devices which had a thick cathode (200 nm) in conjunction with a pressure contacted external heatsink. The devices which effectively had two-stage heatsinking were studied under direct current (DC) and pulsed driving. For 15 V pulses with a corresponding 25 mA current (high for a 1mm² active

area), the pulse width was varied while keeping the repetition rate constant. Below a 5% duty cycle, heating was not significant but, by 30%, the device temperature had already risen by 20 C. Below 5% the thick cathode has sufficient heat capacitance to dissipate the heat effectively. Based on a linear relationship between temperature increase and pulse width, a 20 C rise was higher than expected. This was attributed to the high contact resistance of the second stage heatsink which was lightly contacted to avoid film damage. In DC or continuous wave (CW) operation with heatsinking, the device temperature rose by 60 C. It has also been shown that pulsed drive schemes maximize device brightness. These, and other similar experiments, highlight that current heating in devices plays a critical role in determining device performance. It should be noted that the majority of the research was carried out for single pixel devices⁵ and that heatsinking is even more crucial in a display where temperature rise depends on the peak power determined by the number of pixels and the drive scheme.

As a corollary to the last observation, it is not unexpected that that electrode area, or more specifically pixel size, significantly affects device performance with smaller pixels resulting in improved heatsinking and reduced Joule heating. In the case of discrete devices, it has been shown that, as the active area was reduced the device becomes less susceptible to Joule heating⁵. In other words, smaller devices may be driven at higher current densities for a longer period of time than similar devices with a larger active area. This is important for electronic display applications where the display brightness is proportional to current density. In practice, for most applications, it is of more interest to see how the integrated emission from an array of nanoscale devices compares with that from a single device of the same area. So, although single molecule devices⁷, CNT devices and other nanowire devices have been made, they are typically difficult to position and require top-down patterning to assist in positioning and addressing them. Whether discrete nanoscale components or arrays of nanoscale components are of interest, clearly there is an overriding need for high resolution patterning over a range of areas. Given that Joule heating in OLEDs is related to pixel size, our aim was to see whether we could produce a nanodot array type electrode in order to create a nano-pixel OLED array and to characterize the array OLED electrically and optically. To do this first involved choosing a suitable patterning technique.

5.2 OLEDS FABRICATED BY HIGH-RESOLUTION PATTERNING

Patterning methodologies can be split into three main categories which are top-down, template guided and bottom-up patterning. Top-down patterning usually refers to patterning of a single continuous layer of material which is deposited prior to patterning.

5.2.1 Top-Down Patterning

Some of the top-down patterning techniques⁸ available are UV-crosslinking of polymers, ink-jet printing, OVPD (organic vapour phase deposition), CVD (chemical vapour deposition), evaporation, sputtering, focused ion beam, electron beam, ion beam, rubber stamping, nanoimprint lithography (NIL), UV-NIL, photoresist lithography, femtosecond laser ablation using upconverted light, maskless (interference) lithography, excimer laser ablation⁵, SNOM lithography (with or without aperture), reactive ion-etching, dip-pen lithography, cold welding.

Bottom-up typically refers to both manipulation (AFM, STM, microfluidics) or self-assembly of atoms or molecules to form ordered structures. Self assembly may occur during or post synthesis of the material. The growth of porous membranes is an example of the former and a self assembled monolayers (SAM) produced via the Langmuir Blodgett (LB) technique is an example of the latter. Molecular self-assembly may be initiated by surface functionalisation or by molecular design and is thus really only valid when one speaks of a layer (LB film or SAM) or complex molecule (e.g. hexabenzocoronene) self assembled from more simple components without the use of top-down patterning. Prepatterned catalysts on a substrate are used in many cases where it is wished to direct self assembly. Here the catalyst will be required to position molecules or molecular structures at a desired location. Although this is generally spatially limited by the top-down patterning method used to produce the catalyst pattern, it is, nonetheless, essentially a bottom-up approach.

Porous template guided patterning⁹ may be considered intermediate between top-down and bottom-up in many respects and refers to patterning materials using templates which are themselves produced by self-ordering processes. Although the templates

themselves develop via self assembly, their growth may be guided using top down imprinting methods.

5.2.2 Porous Templates

Porous templates¹⁰ and films include, porous alumina, track etched polycarbonate, self-assembled micro-bead arrays¹¹, porous films produced by micelle expansion, porous films produced by solvent condensation methods, self-assembled films of molecular cages, wet etched semiconductor films including porous silicon and indium phosphide, electrospun polymer films and inkjet deposited carbon nanotube mats.

5.2.3 The Proposed Nano-array-PLED Device Structure

Our approach to patterning involved an array-electrode made using a template which is customizable on the nanoscale. The aim was to demonstrate the operation of a device comprised of an organic light emitting material sandwiched between a metal-filled porous alumina membrane (PAM) and a planar metal electrode as depicted in Fig. 64. This device can be referred to as a nano-array-PLED or NA-PLED for convenience.

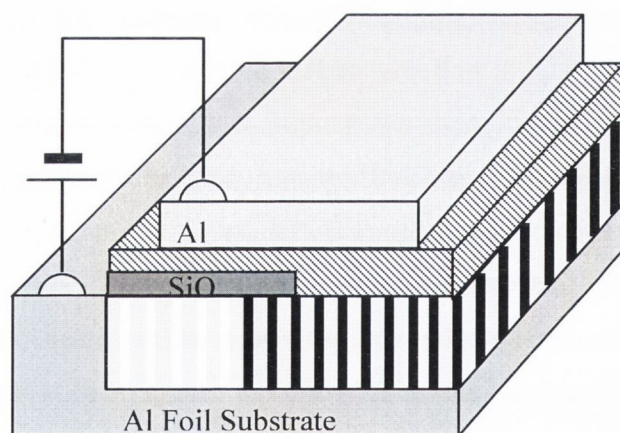


Fig. 64 Idealised nanowire array device schematic showing the device bias. The device structure is as follows: aluminium foil substrate (dark grey); filled and unfilled porous alumina regions (thick black and thick white, vertical lines respectively); SiO (dark grey horizontal bar); spin-coated light-emitting polymer TPD-MEH-PPV (shaded layer); evaporated aluminium top contact (uppermost light grey layer).

5.3 THE CHOSEN TEMPLATE: POROUS ALUMINA

Of all the patterning methods listed above, the one chosen to produce a metal nanodot array in line with our proposed device structure, was porous alumina templating. Anodically grown porous alumina (or porous aluminium oxide) was chosen as the template for two main reasons. Firstly, the pore depth and diameter can be easily controlled by varying the anodization time and voltage respectively. Secondly, PAMs can be filled with a range of metals to form an array of metal nanowires surrounded by an insulating matrix that could be used as an array electrode. Well ordered regions in porous alumina were first reported by Masuda *et al* in 1995¹² and since then the long range order has been further improved, resulting in highly uniform PAMs over large areas, which now makes this application worth investigating.¹³

Under appropriate conditions, Porous Alumina Membranes (PAMs) were produced by the anodisation of high purity aluminium foil, containing a regular hexagonal matrix of isolated cylindrical pores of uniform diameter, length and inter-pore distance. These parameters are highly manipulable by the variation of anodization voltage and time. Pore diameters between 5 nm and 250 nm¹⁴, pore densities between 10^9 and 10^{11}cm^{-2} and membrane thicknesses between 0.1 and 200 μm are obtainable. Porous alumina, or, to give it its correct chemical name, *aluminium oxide* (Al_2O_3), is an inorganic dielectric. It is electrically insulating with a bandgap of 7 – 9.5 eV. PAMs may be separated from the excess aluminium foil from which they are grown or they may be left as a chemically converted porous oxide region on the foil. Freestanding PAMs are chemically durable and transparent in the ultraviolet, visible, and infrared spectra. Freestanding PAMs in the < 20 micron thick are physically very brittle, however, and may hence need a support in practical application. Alternatively, they may need to be left on the original foil which, if thick enough, will provide good support. Apart from the excellent degree of dimensional control over PAMs, their versatility with respect to device fabrication is further enhanced by the wide range of materials – from metals to semiconductors that can be deposited in the pores by different means.

While our proposed structure involves the incorporation of metal nanowire arrays into a conventional OLED, the current and potential applications of PAMs¹⁵ and PAM-

based arrays are many. Some of these include the use of PAMs as photonic crystals, solution filters, lab-on-a-chip test arrays for biological samples, sensors, out-coupling elements for LEDs, templates for a wide range of nanowire, nanorod, and nanotube growth including magnetic and superconducting nanowire array templates, high density memory devices, and patterning masks for evaporation and dry etching.

5.3.1 Using Cu-filled PAMs for the Proposed Device Structure

In order to test the feasibility of our proposed structure, a prototypical electrode, comprised of a copper nanowire array fabricated by AC electrodeposition into a porous alumina membrane, was incorporated into a single-layer organic light-emitting device. The 48-nm-diameter copper nanowires effectively form an array of electrical nanocontacts. The following sections detail the formation and filling of the porous alumina membranes but, first, some information on the imaging techniques used to provide feedback at each stage of the development is given.

5.3.2 Imaging Techniques Used to Monitor PAMs

In order to monitor and optimize our development of PAMs for electrode applications, scanning electron microscopy (SEM), Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM) were used to image features in the 10 – 200 nm size range.

For SEM imaging, the surface of the PAMs was monitored using a Hitachi S-4300 SEM at the Centre for Microscopy and Analysis (CMA) at TCD and their cross-sections were imaged using a Philips XL30 SFEG SEM (AlCove GmbH). Sample preparation for surface imaging at the CMA involved cutting a section of the foil and mounting it on a metal stub with double sided conductive adhesive tape or with silver paint. For cross-sectional imaging the sample was set in an epoxy resin which was frozen, cut and mounted with the cut face and pores parallel to the surface of the metal stub. The samples were generally coated with about 10 nm of gold in a sputterer. The highly polished empty and metal-filled PAM samples did not actually require any gold coating although the empty samples did exhibit some charging effects during imaging. For metal-coated samples, the beam current was less than for uncoated samples since

coating reduces charging effects. The contrast in the SEM images was enhanced in some images by using the SEM in backscattered mode. The working distance (sample-gun distance) varied between 6 and 14 mm and images were generally taken at 20 keV, and for three magnifications (x 200, x 30K, x 200K) for each sample to get a good idea of the condition of the sample surface. The resolution of the instruments used was about 15 nm once astigmatism (image wobble) was reduced as much as possible.

Although the main interest was in the as-prepared metal-filled PAMs and therefore in SEM imaging, some TEM was also carried out in order to check the uniformity of the metal nanowires electrodeposited in the PAMs. The latter is difficult to achieve along the whole length of a single wire in cross sectional SEM since a perfect cleave is required. For TEM imaging, the alumina membrane was dissolved in NaOH, liberating the metal nanowires which were subsequently dropped from a suspension onto copper TEM grids for imaging. A JEOL Instruments TEM was used at 200 KeV for this purpose.

Finally, it is quite difficult to get topological information from a regular SEM or TEM instrument (with STEM this *is* possible), AFM was also used to image the surface of PAMs. The AFM used was a Nanoscope III A by Digital Instruments and had an E type scanner with a max scan area of 13 micron. After laser alignment by maximizing reflection of an image of the AFM cantilever onto a piece of white paper, tapping mode AFM was used, slightly off resonance and at a slow scan speed with low gains, to image some PAM samples. This provided information about the surface roughness of the samples.

5.3.3 Formation of PAMs

5.3.3.1 Theory of Pore Formation

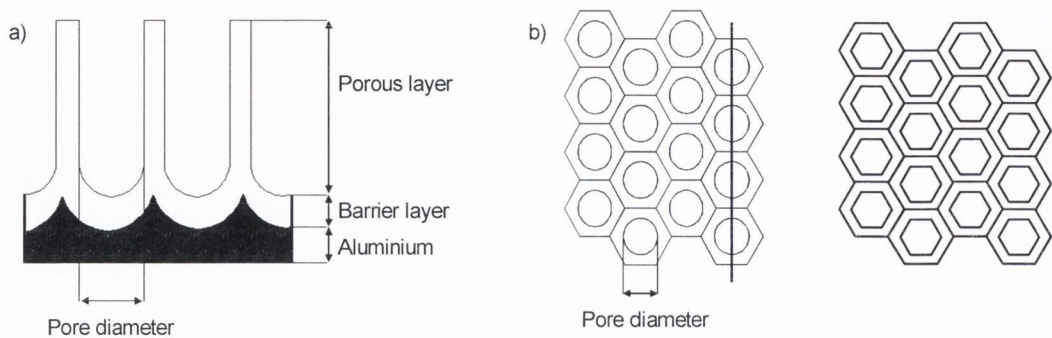


Fig. 65 Schematic of an anodized aluminium foil (a) depicting the aluminium foil (black substrate, the porous oxide layer on the surface, and a barrier oxide layer separating the two and top down view of the hexagonally ordered porous oxide surface (b). The pores are often illustrated as being hexagonally ordered cylindrical pores but they are in fact hexagonal in shape (c).

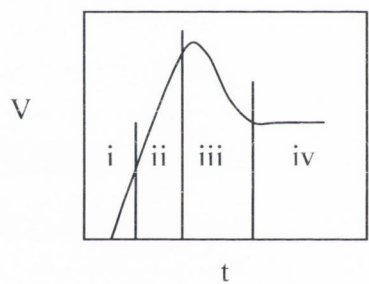


Fig. 66 Vertical lines represent the different stages during anodisation. i) barrier oxides starts to grow, ii) fine featured pathways form on outer oxide surface iii) the surface features start to propagate into barrier oxide, enlarging as they do so, iv) steady state pore structure is formed.

It is generally believed that pore growth is due to surface inhomogeneity which results in non-uniform Electric field at the surface when a foil sample is connected to a counter electrode in an anodisation rig. There are very few papers which detail the early stage of pore formation. McDonald suggests¹⁶ that voids which form at triple points between hexagonal crystallites in the anodic oxide shortly after anodising has commenced, are responsible for the initiation of a porous structure. Due to field enhanced ejection of metal cations without a fast enough vacancy annihilation mechanism, vacancies condense below the triple points in this point defect type model. Condensation of the cation and/or metal vacancies in localised decohesion of the barrier

oxide film from the substrate, restricting oxide growth in the regions directly below. This effectively creates metal protrusion in the barrier layer as surround regions of barrier oxide continue to grow in thickness. At this point mechanical forces due to a factor or two difference of aluminium in alumina and metallic aluminium come in to play. Since the oxidation takes place at the entire pore bottom simultaneously, expansion can only be vertically upwards from the foil, so that the ‘walls’ of the early stage depressions/pores in the oxide surface are pushed up. (In practice aluminium expansion is < 2 since Al^{3+} ions are mobile in the oxide under the anodising E field, so some of the oxidised aluminium does not contribute to oxide growth.) At an early stage pores are very disordered, however, self organisation kicks in over time to give pore arrays with uniform pore dimensions and spacings in some electrolytes. Pores of virtually tubular shape with hemispherical bottoms and a more or less hexagonal outside alumina cell are a logical consequence of expanding circles, evenly distributed over a surface in a (111) type arrangement (starting from e.g.triple points), and merging after their perimeters hit each other.

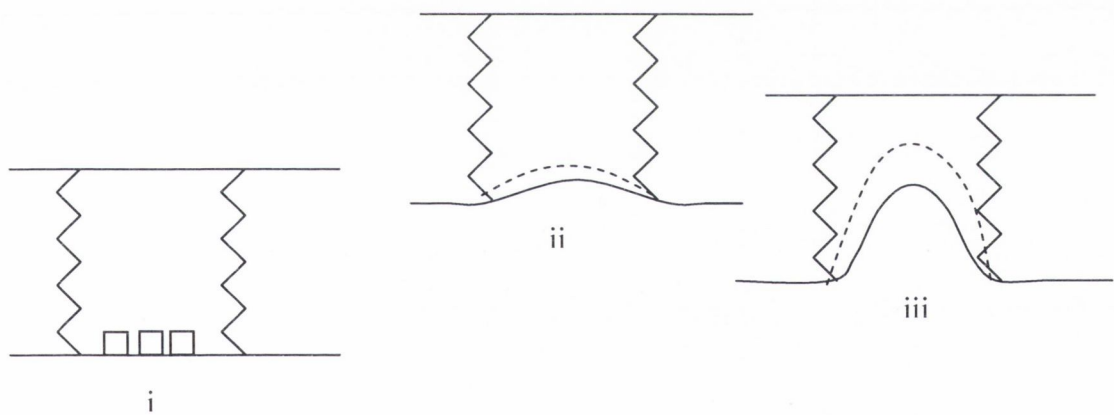


Fig. 67 Cartoon of vacancy condensation mechanism for void formation in anodic oxide films. i) vacancies condense at $\text{Al}/\text{Al}_2\text{O}_3$ interface, ii) Decohesion of oxide from metal film, iii) void formation. Clearly the field will be stronger in regions between voids on the film surface and hence that is where pore formation by anodisation occurs.

The elementary processes involved in porous oxide growth¹⁷ are:

- External oxide interface dissolution by interaction of electrolyte species with the oxide surface via a proton-assisted E-field enhanced mechanism. The dissolution

process is comprised of electrochemical (current assisted) and chemical (field assisted) mechanisms.

- Movement of oxygen anions and aluminium cations through the barrier by the field-stimulated mechanism
- Oxide growth at both internal and external oxide interfaces as a result of ionic species movement. The oxide grows at its external boundary as a result of outward migration of Al^{3+} ions and their reaction with oxygen-containing electrolyte species. At the same time the internal aluminium/oxide interface is shifted inwards in the sample due to interaction of moving oxygen species within the Al.

The most complete first principles model of anodic growth is given by Parkhutik et al¹⁷ and is applicable to porous alumina growth and other porous materials. Because of the inhomogeneity of the E-field laterally (max @ pore base, less at pore walls) and vertically in the film (due to space charge effects as a result of anodic growth process) a 3-D or at least 2D (space charge effect may be neglected) is required to model the growth. The internal and external oxide surfaces are used as boundary conditions, however, only the current at the oxide surface is considered as this is where the oxide growth rate-determining reaction takes place. The equation for the current density at this interface is:

$$\frac{dR_e}{dt} = [\alpha A \exp(k_d E_e) - \beta B \exp(k_0 E_e)] \cdot N_e$$

$$A = A_0 C_{H^+}^\eta = A_0 10^{-\eta pH}$$

The model ensures that the barrier layer thickness is constant and takes account of the curvature of oxide interfaces. The E field at the pore bottom remains practically unchanged during steady state growth. The ratio E_m/E_e is independent of temperature and electrolyte concentration.

The dependance of pore cell size R_m (and pore radius and oxide thickness) on anodisation conditions is given by :

$$R_m = \frac{U_a / E_{co}}{\kappa_3(1 - \kappa_3)}$$

Substituting eqn for concentration for A into eqn 25 gives the R_m dependance on electrolyte parameters:

$$R_m = \frac{R_{mo}}{1 - 2.3 pH \left[\ln \left(\frac{\alpha k_d A_o}{\beta k_o B} \right) \right]^{-1}}$$

Both the voltage and electrolyte dependances given by the model have been substantiated by experimental results.

With respect to the self organisation in porous alumina, it has been concluded that for both oxalic and sulfuric acid electrolytes, optimal conditions for the growth of ordered structures are accompanied by a moderate expansion of aluminium, where the expansion was found to increase strongly with anodisation voltage. This corresponds to an expansion factor of 1.2 - 1.4 independent of electrolyte as determined by the porosity rule which is governed by the porosity equation for a perfect hexagonal structure.¹⁸ The linear elastic strain at the interface is $(\sqrt[3]{V_R} - 1)$, V_R is expansion factor, and Young's modulus E_p can be related to porosity p , $E_p = E_{alo} (1-p)^2$, so knowing p and V_R one can get the stress in PA¹⁹.

5.3.3.2 Cleaning of Aluminium Foils

Before anodising the commercial aluminium foils (source: Goodfellow, purity: 99.999%, thickness: 0.25 mm) it is important to clean them. The thermal oxide layer, surface grease and debris were removed together by dipping in a hot chromic acid solution (48 g/l $K_2Cr_2O_7$ (potassium dichromate) in 10 % phosphoric acid at 80 °C) for 5 -10 minutes. Surface inhomogeneities and scratches were removed by electrochemical polishing at 15 V in a 11:7 (v/v) mixture of concentrated phosphoric and sulphuric acids at 70 – 75 °C. The setup was similar to the anodisation setup in fig 72.

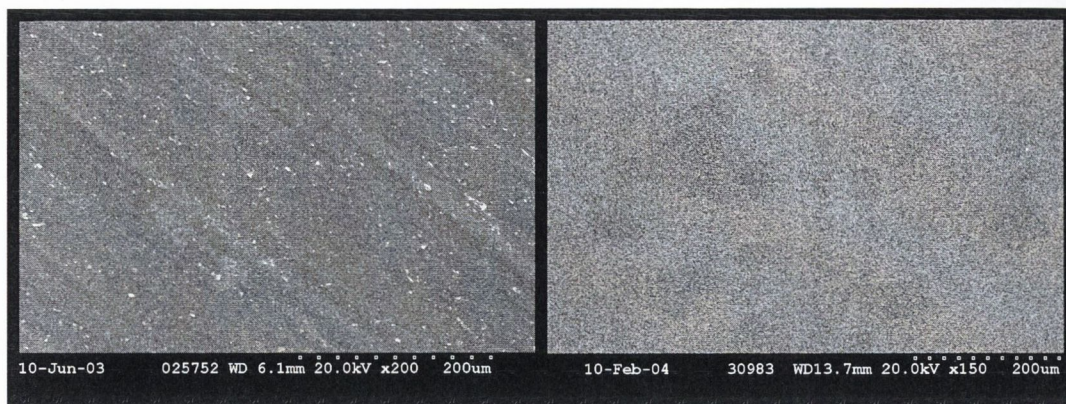


Fig. 68 Typical SEM images of an untreated aluminium foil x 200 (left) and a cleaned foil x 250 (right) where the scale is 200 μm .

From the SEM images above it is clear that the cleaning process is quite effective at removing most of the surface debris and the grains produced by rolling the sheets of aluminium during foil production. No gold coating was needed for imaging the foils as they are metallic.

5.3.3.3 Anodisation of Aluminium Foils

Anodisation of an aluminium²⁰ foil causes a hexagonally ordered aluminium oxide layer to grow on the aluminium. A schematic of the situation is shown in **Fig. 65**.

In order to anodize the foil, it is placed in a cold (0°C) acidic bath and anodised at a specific voltage for a specified time. It is important to keep the concentration and temperature of the solution as homogeneous as possible. This was done by stirring the solution constantly and by using an automated temperature controller. A schematic of the apparatus used is shown in **Fig. 69**.

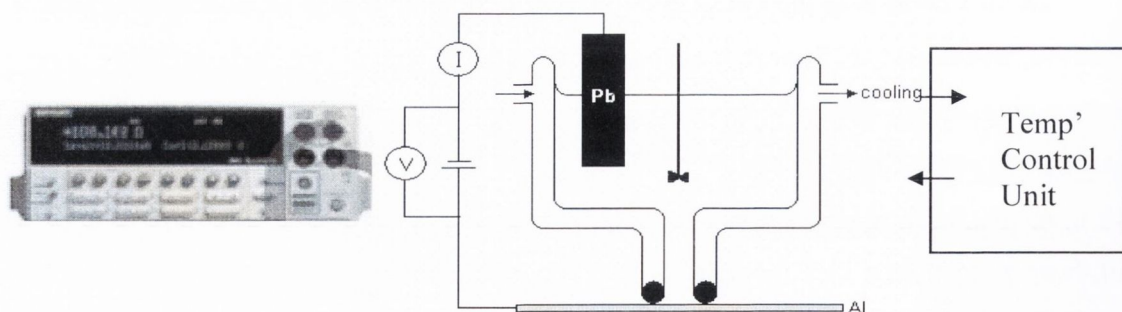


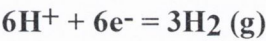
Fig. 69 Anodisation setup showing external circuit, aluminium foil (held in position using a rubber o-ring clamp fixture), glass container with water cooling, stirrer, and lead plate (holding clamp not shown). Left of the schematic is the power supply used and on the right is the temperature control unit.

Depending on the acid used (sulphuric: 4 – 30 nm, oxalic: 30 – 80 nm, phosphoric: 80 - 250 nm), a wide range of pore diameters is achievable. The pore diameter is directly related to the anodisation voltage (1.2 – 1.4 nm/V). The electrolytic reaction proceeds according to:

Oxidation Process at Anode:



Reduction Process at Cathode:



The number of electrons transferred therefore determines the total oxidised thickness which increases linearly with time until the anodisation is halted. Two step anodisation, which was introduced by Masuda *et al*¹² is the preferred way to achieve excellent pore order. The first step involves anodising a thick aluminium foil for a long time (e.g. overnight) and removing the resulting oxide using hot chromic acid (similar to the solution used in the degreasing step.) This leaves a regular hexagonal pattern on the aluminium surface to act as a template for a second, shorter time anodisation.

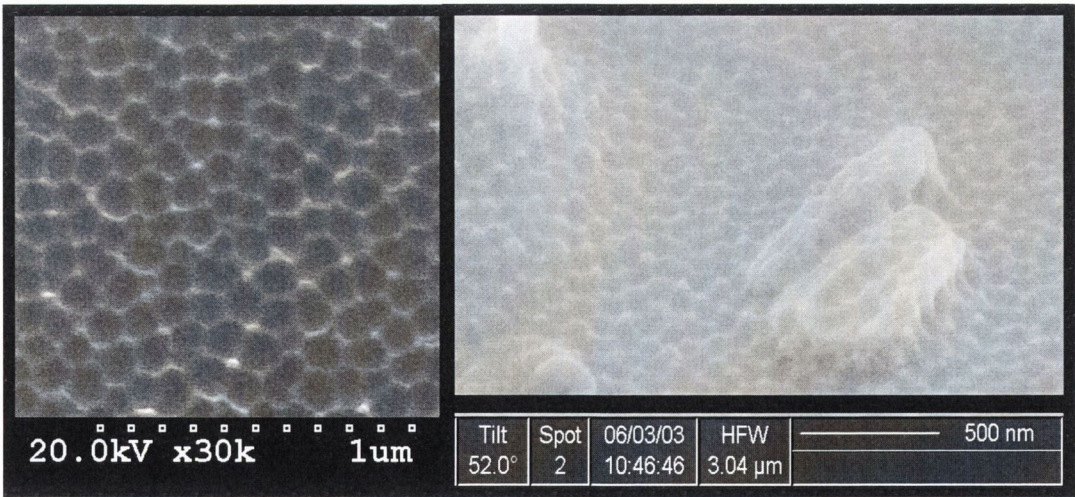


Fig. 70 Left: SEM image showing thin oxide walls of natively oxidized aluminium foil after removal of oxide from the first anodisation (80 V). Right: e-beam image taken with a dual beam FIB instrument , of the surface of PAM after second anodisation.

In Fig. 70 lumps on the surface which are also porous alumina are due to impurities. Note in Fig. 70 (right) that the porous alumina surface has considerable curvature around the defective regions.

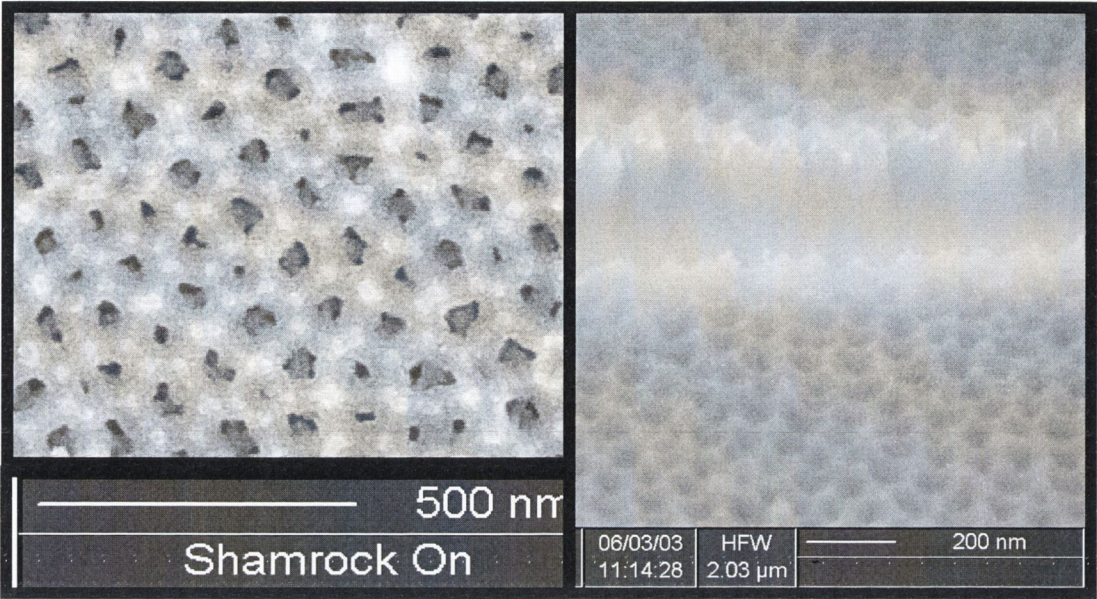


Fig. 71 Electron-beam images of the PAM surface (left) and of a crack in the PAM (right).

In Fig. 71 above it looks as though the edges of the pores must be above the plane of the pore mouths because the highest points (white dots in Fig. 71 (left image)) correspond to the corners of the hexagonal pore walls. This is further borne out in Fig. 71 (right) where the image of a crack in a PAM was fortuitously obtained and good use of beam tilt with respect to the sample provided an image which helps one appreciate what the topology of an unpolished or unmilled surface is really like. Clearly the PAM surface which could be compared to an egg-box topography.

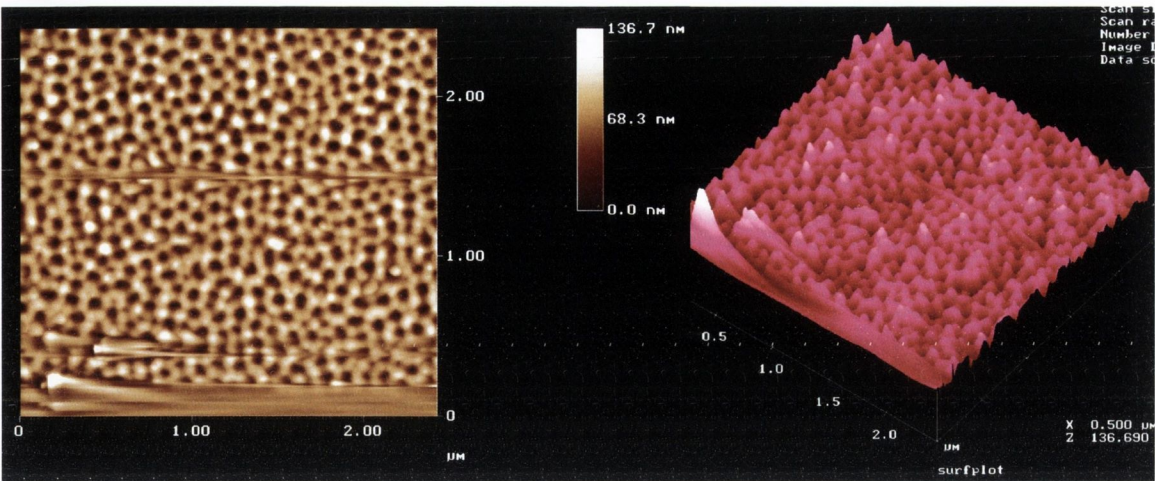


Fig. 72 False colour AFM images: standard tapping mode image (left) and surface plot corresponding to the AFM image on the left for the same sample (right).

As with the previous e-beam images for a similar sample, the AFM image (Fig. 72 - left) shows the white as high points again, a clearer idea of the topology is given by the surface plot.

Although in our work, double anodisation was used, further anodisation steps, much longer anodisation periods in the two step method, and better temperature control, should improve the pore ordering even more. The trade-off is between increased order at longer anodisation times for thick, expensive foils and shorter anodisation times and less well ordered PAMs on thinner, cheaper foils.

5.4 BARRIER LAYER FORMATION AT THE FOIL:POROUS ALUMINA INTERFACE

The schematic in Fig. 65 depicts the presence of a barrier layer at the aluminium foil:porous alumina interface. This barrier layer is central to the PAM formation (anodisation) process and also to some PAM-filling electrodeposition processes.

The whole PAM structure in fact consists of a duplex oxide layer²¹ made up of an inner oxide layer which is known to be pure alumina, and an outer oxide layer between the inner oxide and the pore wall which contains anionic impurities. Therefore, the barrier layer too is made of a duplex oxide layer. However, the inner oxide thickness in

the barrier layer at the centre of the hemisphere under a pore base is twice as thick as it is at the edges of the hemisphere where it equals the inner oxide thickness of the pore wall. This has been attributed to the electric field being concentrated at the pore center. Choi *et al*²² have shown that the inner oxide dielectric constant is 2.8 whereas for the outer oxide it varies between 2.4 – 2.7 and that the interface between the two oxide layers is hexagonal in shape.

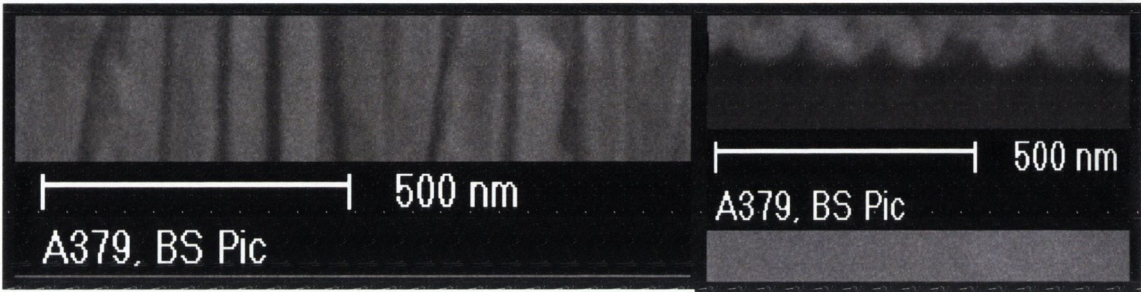


Fig. 73 A regularly prepatterned foil by way of a long first anodiation (left) helps to achieve well ordered straight, parallel pores (right). Note the interpore spacing is larger than the pore diameter (even allowing for asymmetrical cleaving).

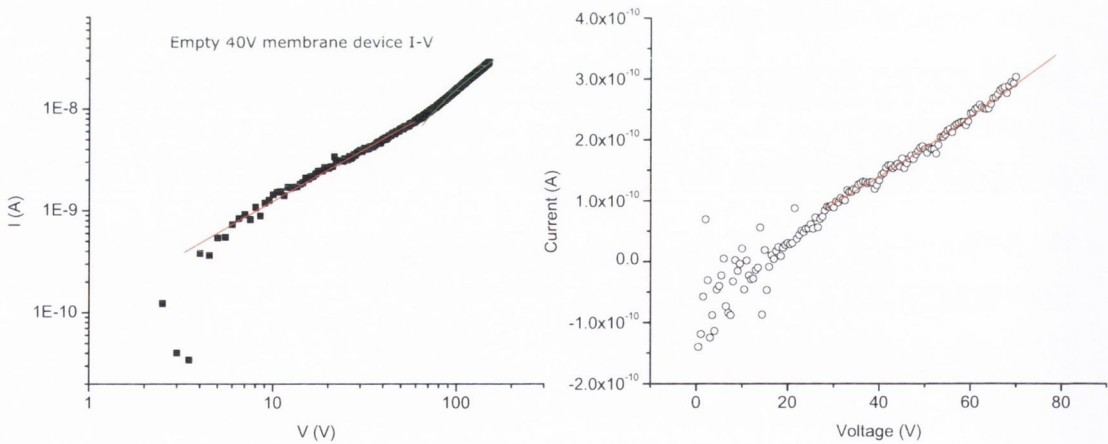


Fig. 74 Left: Al/barrier oxide/PA/Au Right: Al/barrier oxide/PA/SiO/Au .

As seen in Fig. 74 (left) by the extremely low currents at high applied voltages, the electrical insulation afforded by the PA itself is excellent. From Fig. 74 (left) it can be seen that the log-log plot has readily identifiable slope = 1 and slope = 2 regions and thus in the PAM the current may be described by the current flow equation for an

insulator with shallow traps. In Fig. 74 (right) the effect of the SiO layer is to suppress the current flow yielding so that only a low level ohmic response is observed.

5.4.1 Reduction of The Barrier Layer Thickness

In order to fill a PAM as uniformly as possible by electrodeposition it is beneficial to reduce the thickness²³ of the highly insulating barrier layer. Furthermore, the barrier oxide region in a metal-filled PAM, although less insulating than the barrier in an unfilled PAM, is still likely to result in a high contact resistance for a PAM based nanowire array electrode. Thus it is likely that in order to achieve current densities high enough to observe electroluminescence, a high applied voltage would be required. For these reasons barrier layer reduction for PAMs is often required.

To reduce the thickness of the barrier layer at the interface between the aluminium foil and the oxide, which inhibits anodic current in the electro-deposition process, a stepwise voltage reduction was carried out at the end of the second anodisation. The reduction process works by forcing the system into a non-equilibrium regime where the rate of oxide dissolution is greater than the oxide formation rate²⁴.

Note also that it is possible to alter the r/a (radius/interpore distance) ratio by isotropic wet chemical etching but this is a much slower process than the anodisation process. This is usually done using phosphoric acid (10 % at 30° C) and because the etching is isotropic the barrier layer will also be reduced.

5.4.2 Complete Removal of The Barrier Layer

It is possible to eliminate completely the barrier layer oxide and expose the pore bases (or nanowire ends in a filled PAM). For an empty PAM, this means that after barrier layer removal, a metal layer may then be evaporated or deposited onto to underside of the membrane in order to fill it using DC electrodeposition. For a filled PAM the metal layer would be deposited on the exposed nanowire array and would provide a good electrical contact with low contact resistance. Motivated by these issues, removal of the barrier layer in an empty membrane was attempted. Copper chloride solution was used to dissolve away the aluminium foil and the barrier layer beneath the porous oxide. It was found that, for the anodisation times used, the resultant free

standing transparent oxide membranes were much too brittle to handle for device fabrication with our current setup. Furthermore, SEM images showed the barrier layer removal to be quite patchy, being incomplete in many areas. Hence, it was decided to stay with the proposed device structure which includes the aluminum foil and use the voltage reduction process to reduce barrier layer thickness.

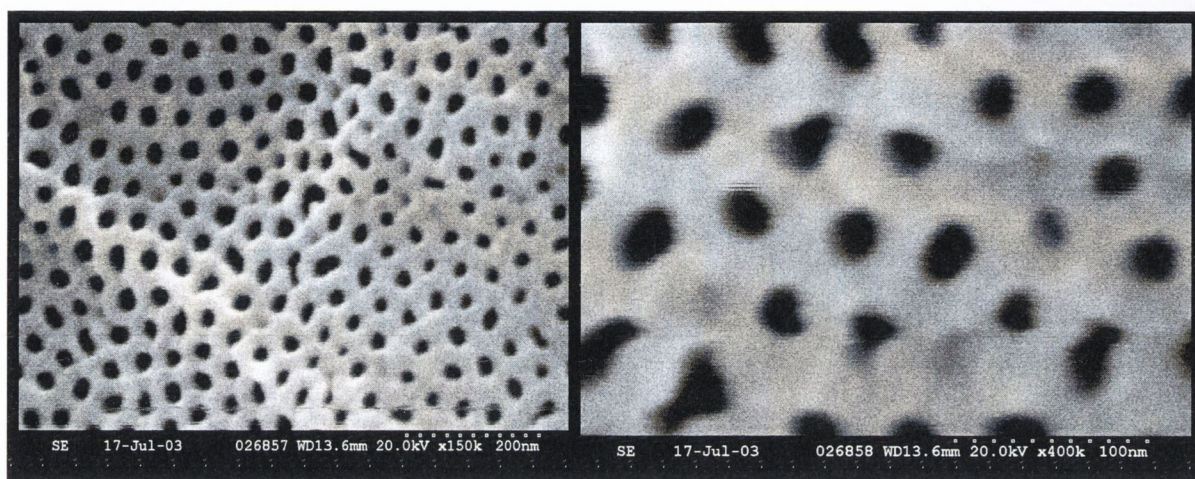


Fig. 75 Images after barrier layer removal for 25 nm pores (right: x 150k , left: x 400k). As expected, the order is better at the pore bases, which are the growth front, than at the pore mouths.

5.4.3 Electrodeposition Techniques Used to Fill Porous Alumina

The three main ways of electrochemically depositing a metallic or semiconducting material into PA are by direct current (DC), alternating current (AC) and pulsed current or pulsed electrodeposition (PED) as the latter is known. In all of these methods deposition is often continued until there is a drop in deposition potential which indicates that deposition has commenced on the outer surface of the PA.

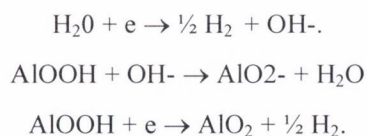
5.4.3.1 DC Electrodeposition

Electrodeposition by DC in the presence of a barrier layer is very unstable²⁵ and uniform pore filling is not achievable due to a cathodic side reaction which causes partial removal of the barrier layer and hence deposition is favoured individual pores. Hence, if DC is going to be used, the PA must be detached from the aluminium foil and the barrier layer dissolved away. If a metallic contact is then sputtered, evaporated or even pressure

contacted on one side of the PAM the pores may then be filled quite readily. The free-standing PAM must be > 20 micron thick for handling without the risk of it breaking. Hence most commercially available PAMs are very thick (several hundred microns) and already have the barrier layer removed. However, they are generally made using phosphoric acid and so the pore size is large (100 – 200 nm) and also the pore order is usually poor. Filling by DC is the fastest electrodeposition method but is quite rough and ready.

5.4.3.2 AC Electrodeposition

In the case of AC deposition²⁶, the PA remains on the foil substrate and metal is deposited on the barrier layer at the bottom of the pores. Deposition into the pores is not limited by the thickness and size of the barrier oxide and its rectifying contact allows metal deposition by an alternating current. It is thought that charge transfer across the barrier layer can occur because the metal ions in the electrolyte can migrate through the oxide. Once a current path is established, electrodeposition will start in the pores and they will be filled from the bottom up. However, the high cathodic potentials cause some hydrogen evolution which tends to inhibit deposition. Hydrogen evolution can occur at sufficiently negative potentials, as a result of the hydrous nature of the alumina. Charge passed through the oxide can therefore leave an excess of OH⁻ ions, which may dissolve the oxide layer locally as follows:



The overall reaction (third equation) shows that water is not consumed as the Boehmite (hydrate of alumina) becomes soluble which means the reaction proceeds until a hole is formed in the barrier layer and hence the plating solution may be in direct contact with the aluminium foil and hence lead to non-uniform filling of the pores. Buffering and stirring of the plating bath can reduce the increasing hydrogen evolution with time but

will not stop it completely. Oxide dissolution can also occur at the anodic side of the barrier layer but even if it does it is a much slower process than the one just described.

5.4.3.3 Pulsed Electrodeposition

The effect of hydrogen can be minimized best if the deposition interfaces are adequately supplied with metal ions during the course of deposition. This can be achieved by using pulsed electrodeposition (PED) which can compensate for the slow diffusion-driven transport of ions in the pores. This technique was first applied to filling a porous template (PA) in 2000²⁴. During a single deposition pulse the local ion concentration is exhausted and the overall ion concentration is reduced. Pulsed electrodeposition (PED) allows better control over the deposition parameters by optimizing the delay between pulses to allow the metal ions to diffuse into the pores bottoms between successive deposition pulses. Furthermore since the deposition current density is typically higher for PED than DC, the number of deposition centres in each pore should be higher too. For 100% current efficiency a negative pulse (deposition) of 8 ms was used followed by a short positive pulse (2ms) to discharge the capacitance of the barrier layer and interrupt the field at the deposition interface. By modulating the delay between deposition pulse signals in the microsecond range, Nielsch *et al*²⁴ have shown that the optimal delay time is about 1 s for filling into a 40 V membrane similar to the ones used in this thesis.

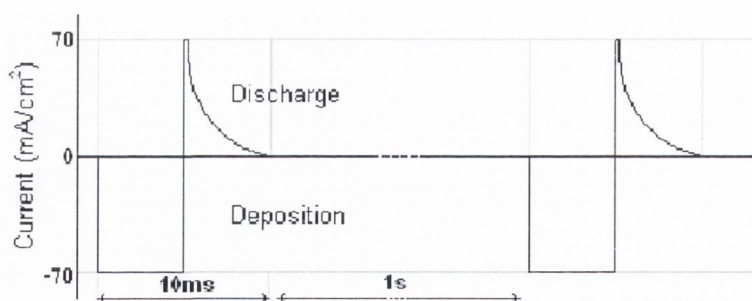


Fig. 76 Typical pulse-times and -currents for PED.

Shorter delays of 10 – 100 ms result in fluctuations in the metal growth rates in the pores due to the hydrogen evolution process described above. Consequently the formation of hydrogen bubbles on the membrane surfaces is visible during the PED process. If the delay time is too long ($> 2\text{s}$) macroscopic pieces of alumina peel off. Thus at optimised pulsing parameters, PED yields the most uniform deposition with greatest number of filled pores, with 100 % filling having been observed over 90% of a 1 micron deep PAM of area approx 1 cm^2 . Although the use of a 1 s delay renders the process slower than AC, this is compensated for somewhat by virtue of the fact that the filling is more efficient. For both AC and PED, reduction of the barrier layer will ensure lower electrodeposition fields and more uniform filling.

5.5 COPPER-FILLED PAM DEVICES

5.5.1 Production and Characterisation of Cu-filled Nanowire Arrays

Initially to become acquainted with anodisation and plating procedures, thin, cheap foils were anodised once using sulphuric acid at 20 V and AC-plated with copper. The AC deposition of copper was done at 13 V (AC, 50 Hz) for about 1 min (the actual plating time depends on the thickness of the PA) using a CuSO_4 electrolyte (35 g/l CuSO_4 , 20 g/l MgSO_4 , H_2SO_4 , pH 1.3). Thus this provided initial rough samples quite quickly. Since the anodisation was at a relatively low potential there was no need to do a voltage reduction. Having become familiar with the procedures necessary to produce and plate PA it was decided to focus on 40 V membranes for which considerable literature information is available. The foils used for the 40 V samples were purer and thicker and consequently a lot more expensive. They were plated using the same copper sulphate electrolyte as used for AC.

During our initial trials PAMs were anodized at various voltages including 10, 20, 50 and 80 V. However, for consistency, 40 V was used for the remainder of the work and for the device data discussed in this thesis. The reasons for this selection include the good order and relatively uniform pore size exhibited by PAMs formed using oxalic acid at this voltage, recent progress in achieving almost 100% metal filling by electrodeposition²⁴ using this system and the relative ease of imaging the features of a

40 V PAM. Therefore, well ordered PAMs were made using the double anodization method by anodizing at 40 V for 9 hours in oxalic acid and then re-anodising, after oxide removal, for 4 hours. This resulted in PAMs with a mean pore diameter of 48 nm, centre to centre pore spacing of 123 nm and a depth of approximately 8 μm (measured using image tool software on SEM cross-sectional images). The oxide growth rate is, therefore, about 2 micron/hr. The 8 micron thick oxide formed ensures electrical isolation of top and bottom contacts.

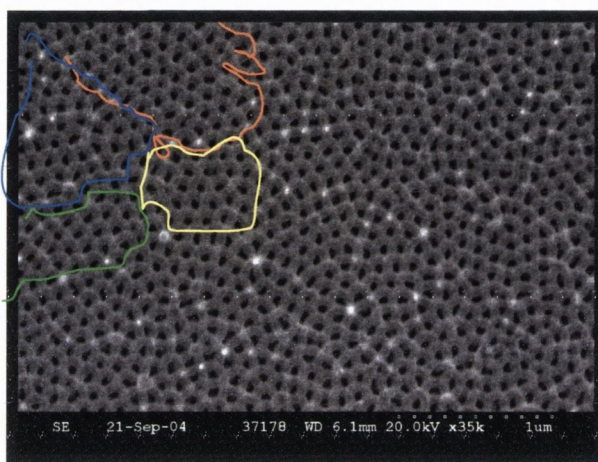


Fig. 77 Surface of an empty 40 V PAM (an underfilled PAM will also look the same) with the coloured lines roughly indicating the boundary of an ordered domain with pore orientation which differs from the surrounding regions. Thus, the PAMs used here are polycrystalline.

Perfect monodomain PAMs may be made by pretexturing the foil by e-beam lithography or by nano-imprinting methods.²⁷ In order to achieve monodomain PA with a high aspect ratio, the anodisation conditions must match the lattice constant of the prepattern. Using SiN pyramids as a master stamp, monodomain PA over an area 4 cm^2 has been achieved.²⁸

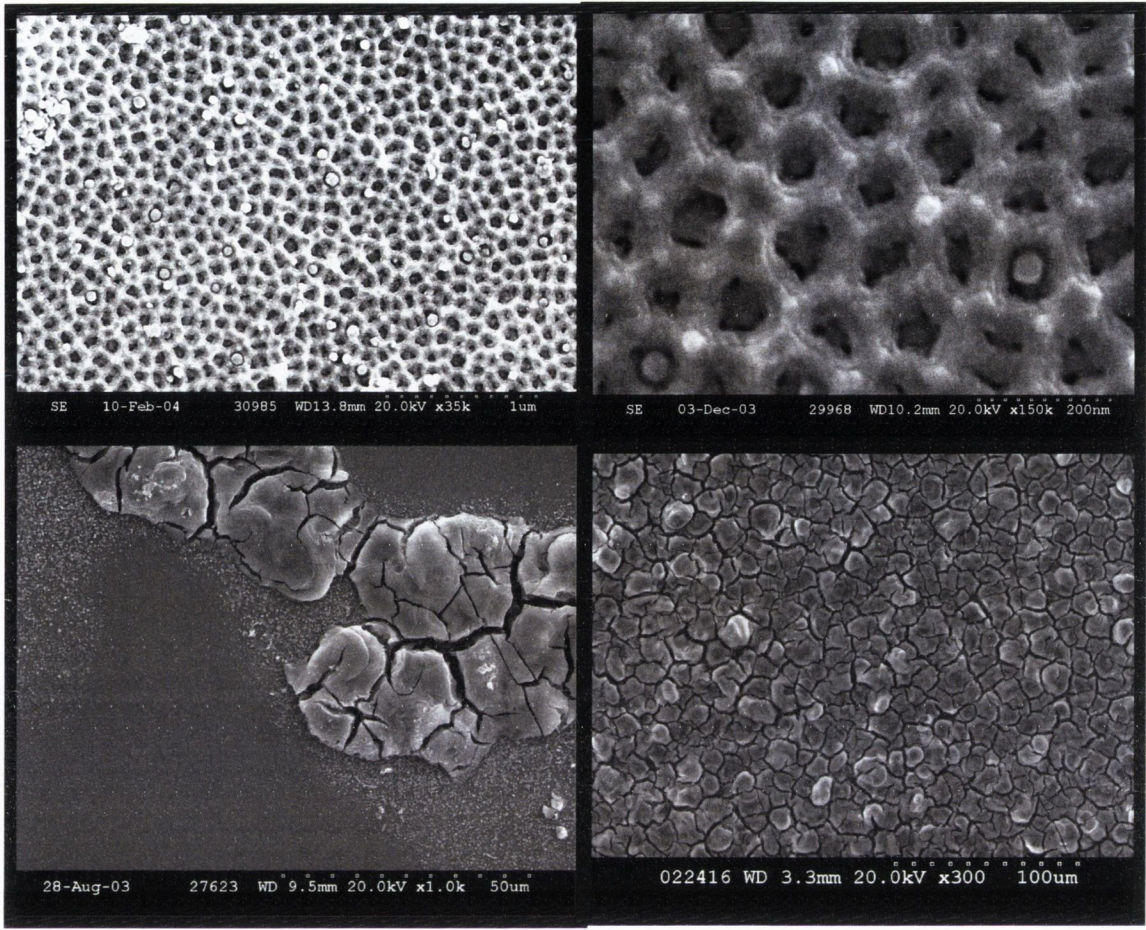


Fig. 78 Top left: SEM surface images showing filling of a PAM anodized at 40 V, filled with copper by AC electrodeposition., Top right: high resolution SEM of same sample. Bottom left: Non-uniform filling as only where some areas are heavily overplated. Bottom right: Extreme overplating where the whole surface is covered in copper /copper oxide.

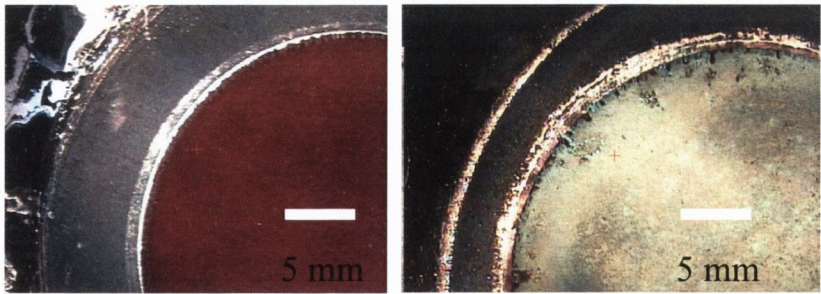


Fig. 79 Digital Camera Images of AC Cu- filled PAMs , left: empty anodized PAM, middle: underfilled PAM, right: completely overplated PAM.

Devices were made in accordance with the proposed device structure in Fig. 64. Firstly the nanowire array electrodes were produced. Each array was based on a 0.25 mm thick square sheet (50 mm²) of Al foil which was anodized at 40 V, giving pore diameters of 48 nm on average. The use of a rubber o-ring seal defined a centred, disk-shaped area (diameter 30 mm) of anodized portion of the foil. The 40 V PAMs were then filled with Copper (Cu) by AC electrodeposition where once again an o-ring seal defined the Cu-filled region, a disk-shaped area (diameter 20 mm) concentric with the anodized area. Overfilling is not desirable as uneven Cu domains form on the surface (see Fig. 78: bottom, left) that lead to electrical shorts. High resolution cross-sectional SEM images of the filled PAMs helped to determine the best filling time to ensure a good electrical contact at the polymer-Cu-filled PAM interface. Arrays were made with electrodeposition times of 4, 6, 7 and 8 minutes.

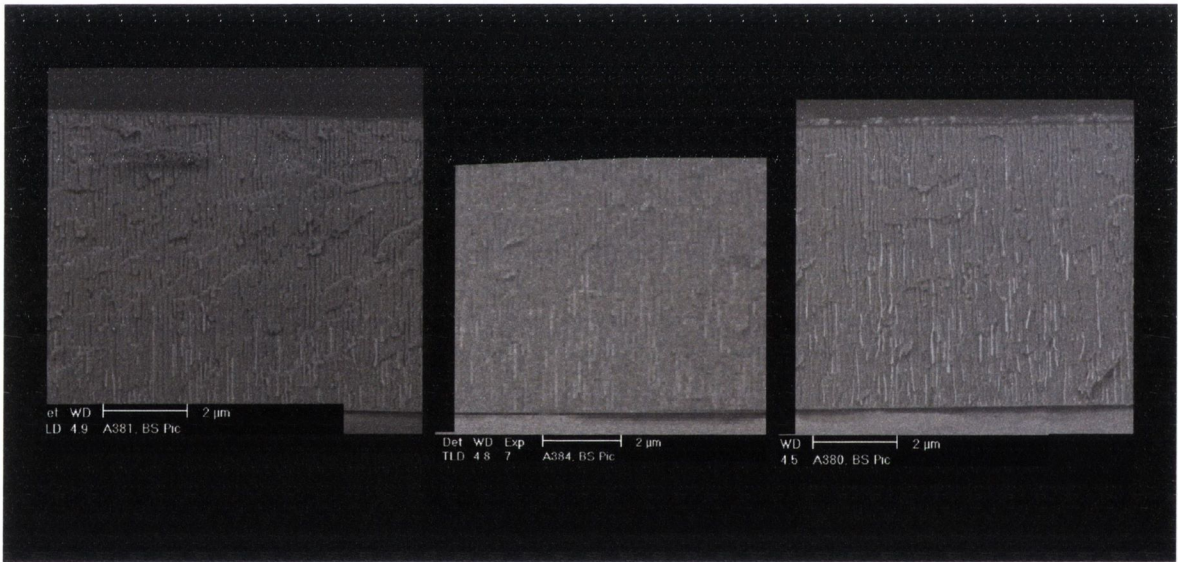


Fig. 80 Left to right: SEM of 4, 6, and 8 min AC filled Cu PAMs. Each PAM is anodized under the same conditions, barrier layer is 36 ± 3 nm. Oxide is 6 – 8 micron thick for each PAM.

Fig. 80 shows that, for similar PAMs, the average filling level is proportional to the filling time and that filling is non-uniform, with some pores being plated more easily than others.

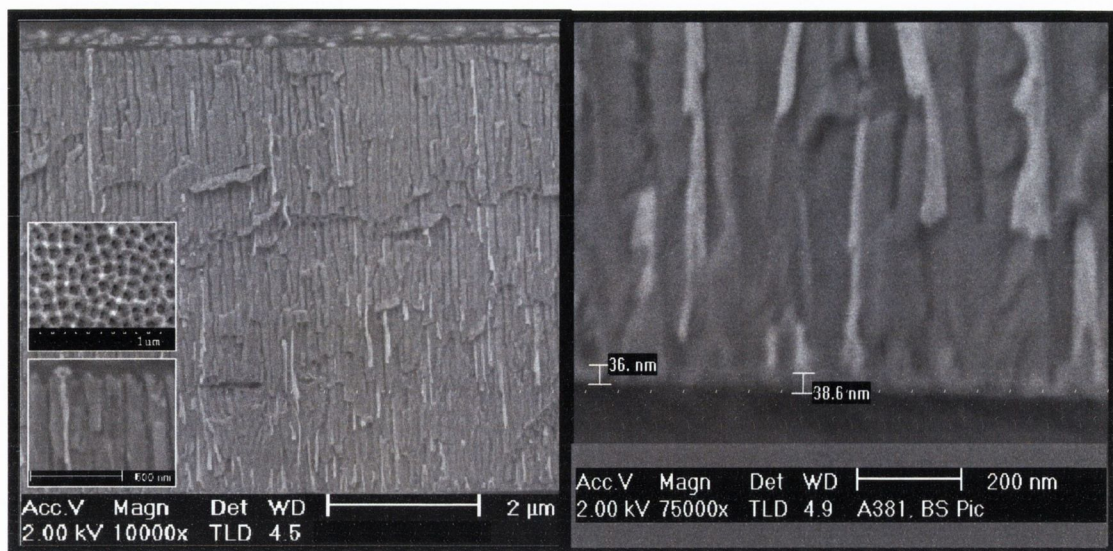


Fig. 81 Left: A cross-section SEM image of the 8 minute Cu-filled PAM. The upper inset shows a surface image of the PAM (scale bar 1 micrometer) and the lower inset shows a cross-section of an overfilled pore (scale bar 0.5 micrometer). Right: cross-section showing the 36 nm barrier layer and Cu-filling near the pore base.

After production of the arrays, the remaining OLED layers were deposited on top. First, a 200 nm thick layer of silicon monoxide (SiO) was thermally evaporated from a resistively heated tungsten boat at a vacuum of 2×10^{-6} mbar at a rate of 0.5-1.5 nm/s, onto the electroplated foil sheet through a shadow mask. The mask was designed to leave an uncovered central disk shaped area (diameter 15 mm), concentric with the first two disk areas, of the copper-plated alumina, and to leave some foil uncovered at the edge of the sheet to allow for an electrical contact with the aluminium. In this way the SiO distanced the active region from the boundary of the unfilled and metal-filled PAM which is prone to overfilling and defined a 6 mm^2 active area. The Cu-filled PAM was then spincoated with the polymer Poly[(4-methylphenyl) imino-4,4'-diphenylene-(4-methylphenyl)imino-1,4-phenylene-ethenylene-2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-ethenylene-1,4-phenylene)] (TPD-MEH-PPV) (Fig. 47) at 1500 rpm from a 15 g/l xylene solution. The thickness of the polymer layer was measured to be $100 \text{ nm} \pm 10 \text{ nm}$ using white light interferometry. Finally Al was thermally evaporated onto the polymer layer at a rate of 0.2 nm/s to form a 100 nm thick cathode.

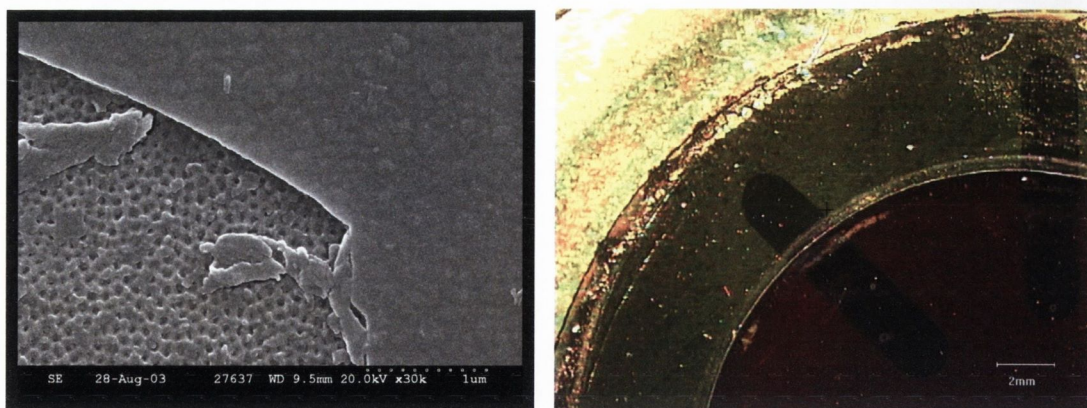


Fig. 82 Left: SEM of polymer on PAM at a crack in the dry polymer film. Right: actual AC plated (7 min) device.

From Fig. 82 it can be seen that the active area of the device is positioned within the electroplated section of the alumina layer and set in slightly (2 mm) from the interface between the Cu-filled and unfilled alumina sections. This was done to produce homogeneous device pixel areas because the interface region had a rougher topography than the rest of the plated membrane. The SiO layer not only defined the active area of the device but also isolated the top and bottom device contacts, reducing the risk of electrical shorts when making a mechanical contact to the top electrode. Additionally, in order to minimise the risk of electrical shorting, the top electrode was deposited so that it did not overlap the unanodised portion of the aluminium foil. Both the SiO and Al were deposited using an Edwards Autovac 306 evaporator fitted with a calibrated quartz crystal thickness monitor.

As can be seen in Fig. 82 (left), the filled PAM remains part of the Al foil from which it was grown allowing electrical contact to the metal nanowire array to be made by contacting the aluminium foil. Current can flow from the aluminium to the nanowire array via metal filaments, formed during the electrodeposition process, which span the 36 nm-thick barrier layer of alumina between the foil and the metal-filled PAM.

5.5.2 Current Voltage Characteristics of Cu-filled PAMs Devices

The direct current (DC) electrical characteristics of the devices were obtained at room temperature using a Keithly 2400 source-measure unit interfaced, using a Visual Basic programme, to a PC. Electrical contact to the device was by means of a solder

connection to the foil and a gold-plated point probe contact to a part of the top electrode over the unfilled membrane area.

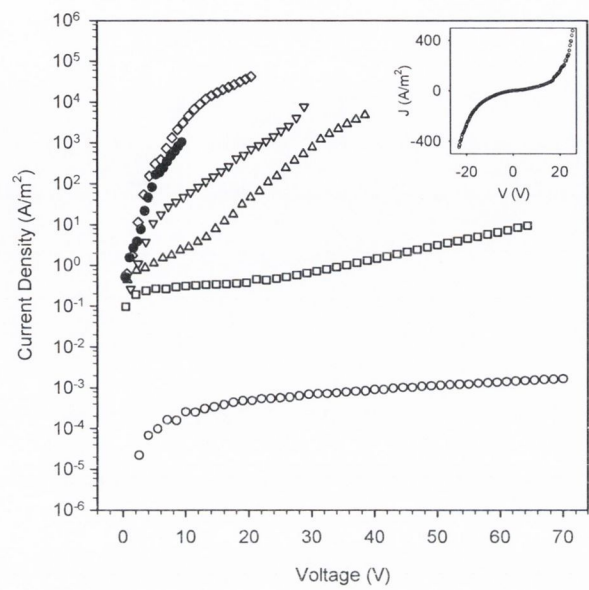


Fig. 83 Current Density vs Voltage for the unfilled PAM (open circles), four (open squares), six (open triangle), seven (inverted open triangle) and eight (open diamond) minute Cu-filled PAMs and the planar Cu-electrode device (solid circles). The inset shows the positive and negative bias characteristic for the 7 minute Cu-filled PAM device.

Fig. 83 shows a plot of Current Density (J) vs. Voltage (V) for Cu-filled PAM devices with filling times of 4, 6, 7 and 8 minutes with estimated maximum J values of 9.6 A/m², 4.8x10³ A/m², 7.6 x10³ A/m² and 4.7x10⁴ A/m² respectively. The current density was estimated using a pore density of 10.9 x 10¹³ m⁻² and assuming 10% of pores are filled to the surface of the PAM. The pore density was calculated based on previous work done by the Nielsch group where a relationship between pore density and anodisation voltage was found using HRTEM.

$$A_{eff} = \rho_{HRTEM} \times \pi (d/2)^2 \times A_p \times \theta$$

where ρ_{HRTEM} is the pore density as measured using High Resolution Transmission Electron Microscopy²⁷, d is the pore diameter, A_p is the total contact area and Θ is the filling fraction.

The current flow in the under-filled 4 and 6-minute devices may result from partial impregnation of the polymer into the pores due to wetting of the inner pore walls by polymer solution prior to spincoating. In addition, there may also be some unusually long wires that provide a conductive path through the PAM. The best filling time was found to be 7 minutes as 8 minutes resulted in overfilled regions on the PAM surface. Thus although the highest J value recorded was for the 8 minute device, this device was very unstable since the use of an overfilled PAM caused electrical shorting. This shorting was observed on the surface of the device and was across the polymer layer which was probably very thin in places due to the very rough surface of the overplated PAM.

The inset in Fig. 83 shows J-V data for the 7 minute device in forward and reverse bias. It is clear that there is essentially no rectification, which is attributed to the small difference (~ 0.4 eV) between the workfunctions of Al and Cu. Also shown in Fig. 83 is the J-V data for an unfilled PAM which clearly shows there is no conductive path through the unfilled PAM which was where contact was made to the top electrode.

The J-V data for an equivalent planar Cu anode device on a glass substrate is also shown in figure 3 with a maximum J of 1.2×10^3 A/m². It can be seen that up to a value of $J = 6$ A/m² the J-V curves of the planar and the 7 minute PAM devices overlap. However, beyond this point, J rises more steeply in the planar device and reaches a final J value lower than that attained by the filled PAM device prior to breakdown. Although the filled PAM devices attained a higher J, this was at a higher operating voltage. The latter is probably due to non-uniform metal-filling of the pores and partial impregnation of polymer into the pores.

It is proposed that the higher current density levels attained in the PAM device prior to failure suggest that it possesses better heat dissipating properties than a planar contact. Although the thermal conductivity of the metal-filled barrier layer was not measured, it is expected there will be some benefit from having the device built on this metal array electrode with attached to a metal foil. This is discussed in more detail in section 5.6.4.

5.5.3 Electroluminescence of a Cu-filled PAM Device

PL and EL measurements were made using an Oriel Multispec CCD spectrometer coupled to a liquid light-guide. The devices were tested in air owing to the difference in device structure compared with a conventional device. The light-guide was simply placed and held as close to the emitting region on the PAM -OLED as possible.

Before building an LED, the PL of an empty membrane was taken and is shown below:

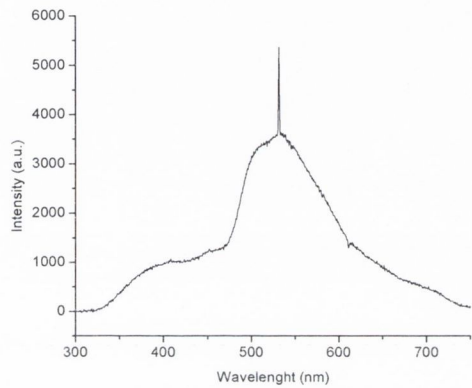


Fig. 84 PL of empty PAM with the laser harmonic of the pulsed mini-Yag laser used to excite the PA at 266 nm.

The PL spectrum of PA has quite a broad peak from 500 to 550 nm. In general the PL of PA is very sensitive to preparation conditions. For similar oxalic acid anodized membranes to the one above (i.e. 40 V high purity membranes), a peak of 470 nm was seen using a fluorimeter with a Xe lamp source. Gao *et al* ²⁹ attributed this fluorescence to the incorporation of oxalic acid compounds in PA during anodisation.

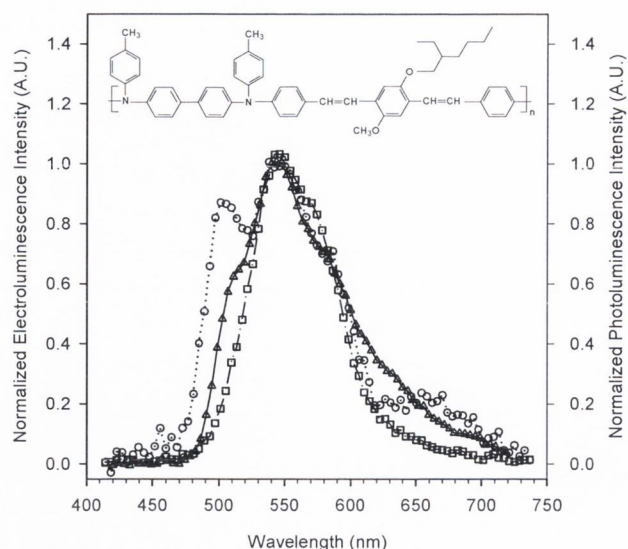


Fig. 85 Electroluminescence spectra for the 7 minute Cu-filled PAM (open circle and dotted line) and the Cu planar electrode device (open square and dash dot dot line). Photoluminescence spectrum for the emissive material (open triangle and solid line). The inset shows the chemical structure of the emissive polymer.

Although the devices presented in Fig. 83 (inset) showed virtually no rectification, when a semi-transparent Al cathode (30 nm) was used, green EL was visible over the entire predefined pixel area.

Fig. 85 shows the smoothed EL spectrum of the filled 7 min PAM device and of the equivalent planar electrode device. Also shown is the PL for a thin film of the LEP. The difference in oscillator strength observed between the devices may be due to differences in polymer film morphology, different electrode reflectance characteristics, and/or differences in J between the two device types.

Though the signal to noise ratio was quite high, the nanowire and planar EL main peaks are clearly similar to that of the PL from a film excited by a 370 nm UV diode which is at 542 nm. Allowing for graph scaling, the high energy shoulder or secondary peak is also similar in the film PL and nanowire EL device and is at about 505 nm. This secondary peak is suppressed in the Cu planar device. The very noisy hump centered around 640 nm in the nanowire EL is due to shorting across the polymer layer. At 30 nm the aluminium cathode is not very stable and furthermore is not very transparent which makes obtaining good quality EL spectra quite difficult.

Due to the nanowire array it is expected that, owing to the typical exciton diffusion lengths (6- 15 nm)³⁰ in PPV resulting from the short lifetimes of the excited states and the amorphous nature of PPV-type conjugated polymers, only the polymer

film directly above the metallic regions in the Cu-filled PAM is excited. This, coupled with the fact that recombination occurs near the cathode due to the imbalance of the electron and hole mobilities, means that there is an array of nanodots emitting corresponding to the positions of the ends of the nanowires in the PAM. However, the emission appeared uniform and not as a series of dots because the spacing between the filled pores is much smaller than the resolution of the human eye. It should be possible to resolve the emission at the plane of the device surface using techniques such as confocal microscopy. Previously, highly localized EL has been investigated via scanning tunneling microscopy tip-induced EL experiments,³¹ however, this is not a practical device configuration as the electrical contacts are not permanent.

5.5.4 Synopsis of Devices Using Cu-filled Porous Alumina Arrays

A working device based on the proposed device structure in Fig. 64 using a Cu-filled PAM as an array-electrode to inject charge into an organic sandwich-type device was demonstrated. Higher DC current densities prior to device failure were observed in the PAM devices compared with equivalent planar devices. This is attributed to improved thermal management in the PAM devices. The EL spectrum is largely unaffected by using a nanostructured electrode. With optimization and appropriate patterning and addressing, the structure demonstrated may be useful for producing stable display pixels consisting of arrays of nanosized light sources. As well as optoelectronic applications, this type of device could be useful for fundamental investigations of electrode-organic semiconductor interfaces. For any further research, however, several significant modifications to the demonstrated device structure are required before the device can approach performance similar to conventional OLEDs and before a more accurate analysis of electrical or optical properties can be carried out. The main improvements required are:

- Surface planarization of the filled PAMs.
- Use of PED to increase uniformity and degree of metal-filling.
- Reduction or complete removal of the barrier layer to reduce operating voltage.
- Use of more suitable electrode materials to improve device efficiency.

- Use of electron-transport layers to improve device efficiency.
- Use of a high transparency electrode to improve EL brightness.

5.6 NICKEL-FILLED PAMS FOR OLEDs

In order to implement some of the recommendations made at the end of the last section with regard to improving nanowire array devices, the PED method was used to electrodeposit Ni into PAMs. The use of Nickel which has a higher workfunction than copper³², makes it better at matching the HOMO of the polymer, and should therefore improve hole injection and increase rectification.

First of all, 50 mm² aluminium foils were doubly anodized at 40 V (as was done for the Cu-filled devices previously described. This resulted in PAMs with pores 48 nm in diameter on average and with a pore density of 10¹⁰ cm⁻². The barrier layer thickness was reduced from that in the copper devices by carrying out a voltage reduction at the end of the second anodisation which left a 20 nm thick barrier layer. Nickel was then electrodeposited into the pores by PED. The area of the anodized and metal-filled regions was the same as for the copper devices.

The PED process used to fill nickel into the PAMs involved placing the PAM in a Watt's bath containing 300g/l NiSO₄·6H₂O, 45g/l NiCl₂·6H₂O and 45g/l H₃BO₃ at 35°C with a graphite rod as counter electrode. The use of a highly concentrated electrolyte like this maximises the concentration of metal ions at the bottoms of the pores. The pH of the electrolyte was adjusted to 5 to prevent corrosive attack of the aluminium substrate. The pulse times used were 8 ms and 2 ms for deposition (foil biased negative with respect to graphite rod) and discharge (foil positive) respectively. An overfilled PAM with nickel aggregated on the surface was required to guarantee a uniform, densely filled PAM after mechanical polishing – the process used, in this instance, to planarise the metal-filled PAMs. As with the Cu-filled devices, the filling of PAMs with nickel by PED was again monitored predominantly using surface and cross-section SEM.

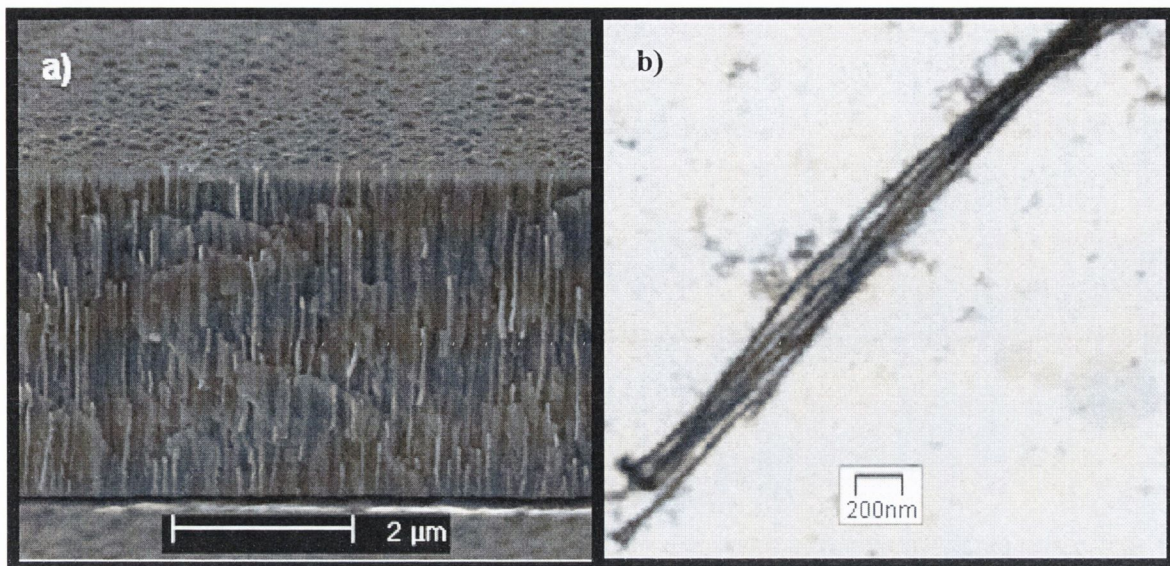


Fig. 86 a) Left: cross section SEM image Ni-filled PAM. Note that tilt of the sample belies actual membrane depth here. b) Right: TEM image of a bundle of Ni nanowires liberated from the filled PAM in fig xx a.

SEM cross section imaging (Fig. 86, left) shows improved uniformity of filling of the Nickel into the pores. Though filling uniformity and the percentage of filled pores are greater for these PED-filled PAMs than for the AC-filled PAMs, (albeit with a different metal) there is still considerable variation in pore-filling levels. It was also observed that hydrogen evolution was occurring which may, perhaps, indicate that the delay (1s) was still too short. TEM imaging (Fig. 86, right), demonstrates the integrity of the wires even without the support of the alumina matrix and, also, their structural uniformity with respect to length, diameter and straightness. In order to prepare samples for TEM, the aluminium substrate foil was removed by a solution of 0.2 mM CuCl_2 in 3 M HCl. The remaining, thin layer of alumina that exists between the substrate and the nanowires (barrier layer) was removed using 10% H_3PO_4 and the nanowires were extracted by shaking in a solution of 0.1 M NaOH and 30g/l PVP. The free nanowires were found to be approximately 45 nm in diameter, in agreement with estimates made from SEM images.

5.6.1 Planarisation of Ni-filled PAMs

For device fabrication involving thin films, it is desirable to have the films or layers in a device as flat as possible to promote the formation of clean, smooth interfaces and to avoid shorting. In order to improve the nano-array devices by planarising the array surface, several methods of achieving this were considered. Argon-ion-milling was tried but was found to be too slow. It also results in quite different etch rates for metal and oxide. Furthermore, dishing occurs – even with rotation of the sample. Similarly, reactive ion etching is quite a selective method. Neither of these methods is suitable for planarising a large area. Chemical mechanical polishing (CMP) is the method used to polish silicon wafers in the semiconductor industry and is a highly developed technique. For the purposes of our work, it was decided to use a simpler version of this method which is, for example, the one used to polish rock samples to a thinness suitable for TEM imaging - in other words mechanical polishing without the assistance of chemical etchants. This approach would not be expected to compromise the degree of planarisation achieved significantly. PAMs were mechanically polished with an aqueous slurry of alumina particles 0.3 μm in diameter, using a Beuhler Petrolpol polishing system. PAMs were mounted on leveled glass substrates using acetone soluble superglue while trying to ensure a zero bond was achieved with no bubbles present. These mounted samples were placed on a metal block which was in turn placed face down on a rotating cloth turntable and held in position under spring pressure. As the table turned, the polishing block with its mounted sample was also free to rotate. This helped to polish the sample evenly. A continuous drip feed of the polishing slurry was fed to the turntable during polishing. For our purposes, this process was initially developed and tested with empty PAMs and was monitored by SEM. Polishing successfully planarised the PAMs evenly (Fig. 87), leaving smooth surfaces suitable for device applications. Polished metal foils of similar thickness are also now of considerable interest for making flexible displays where polishing quality is critical for flexible TFT performance – in principle the polishing processes they use could be used to polish porous alumina or sheet Al over large areas³⁴

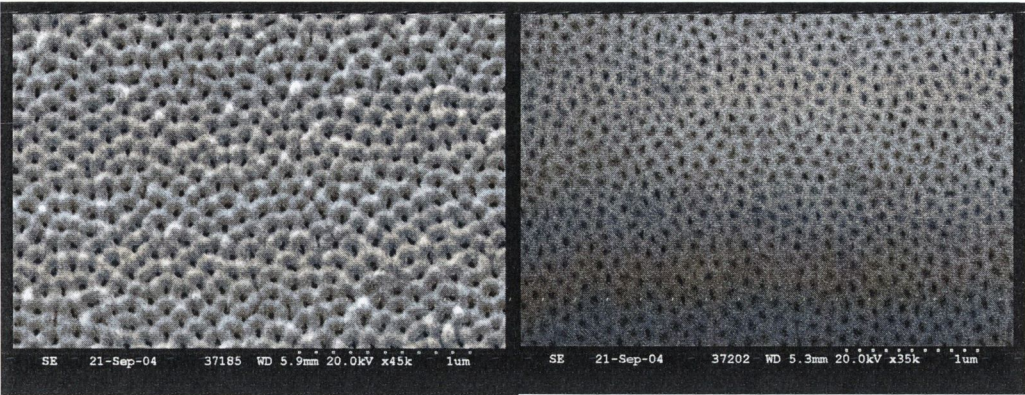


Fig. 87 Unpolished (left) and polished (right) SEM surface images of empty 40 V PAMs.

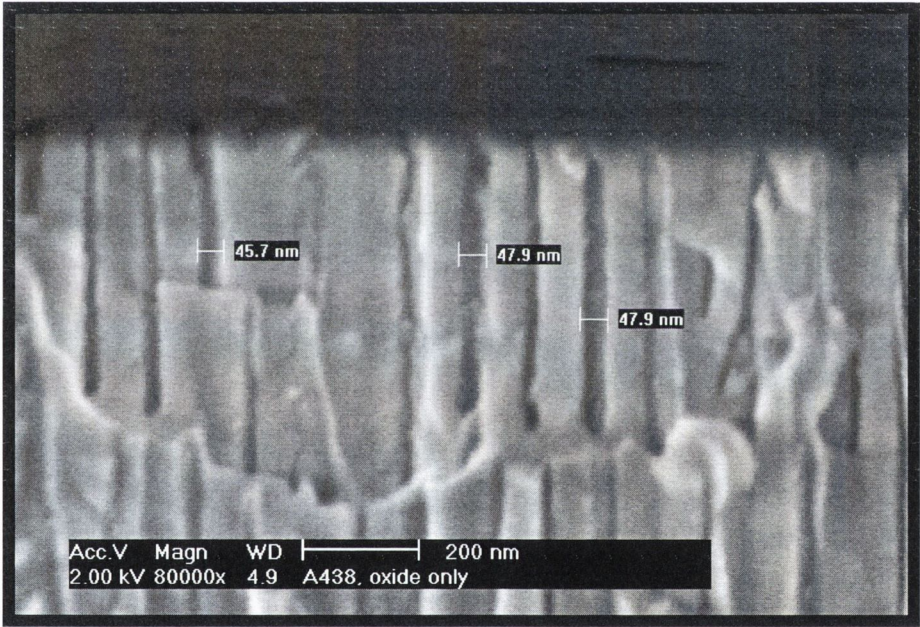


Fig. 88 SEM cross-section image of a polished, empty 40 V PAM.

Note in Fig. 88 above how pore width has only been measured for the channels which appear widest due to the fact that a pore may, necessarily, be cleaved across its widest point. Thus, for the same reason, a pore may appear to be very thin or even ‘missing’. Similarly, a single cleave can make it look as though a pore is ‘missing’ or cut. The diameter is best given by that of a circle of diameter d which, when placed within a hexagon, will touch each side. For this reason and the fact that pores in the

PAMs produced in our experiments were not perfectly hexagonal, the diameter referred to above is an estimate. The inter-pore distance is the distance between the centres of adjacent pores. Again, the centre is that of a circle of diameter d as defined above and the inter-pore distance is 73 nm for the sample above.

In order to obtain a similar level of planarisation with a Ni-filled PAM, polishing was done on an over-filled Ni-filled PAM. In Fig. 89, it can be seen that this degree of polishing was, indeed, achieved and that polishing of such a PAM results in metal nanodot arrays where the nickel is filled exactly to the surface of the PAMs (Fig. 96, left).

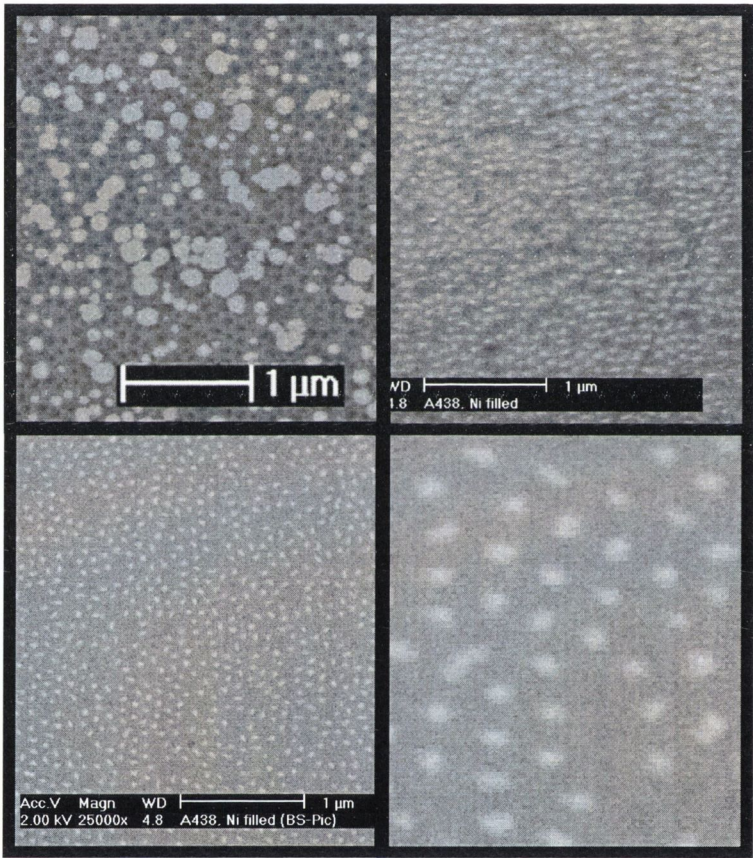


Fig. 89 Top left: unpolished PAM Left: Surface SEM image (2 kV, x 25k) of a Ni-filled PAM. Right: Surface SEM image (2 kV, x 25,000) of the same sample using BS (backscattered mode). Inset: cropped section from the BS-Mode image revealing good short range hexagonal ordering of metal nanodots with a diameter of about 48 nm and interpore spacing of 73 nm.

The SEM images in Fig. 89 show that the filling fraction is close to 90% across the plated surface. Unlike unpolished metal PAMs, the surface fraction of metal is well defined in

Fig. 89 as a result of planarisation, and the contact area can be quite reliably determined. This enables a more accurate estimate of the current density in the array-electrode device to be made. Note that the effect of using backscattered SEM mode in Fig. 89 (bottom left) improves dot imaging somewhat. Also notice the lines in Fig. 89 (top right) which are most likely due to handling the sample but it is also possible they are remnants of the polishing process which, though effective, is rather crude.

Without polishing a similarly over-filled Cu-PAM produced by AC electrodeposition, it is not possible to compare directly the efficacy of the AC and PED techniques. However, as discussed in section 5.9.2, AC filling is only uniform at the very start of electro-deposition and then rapidly deteriorates. This is why the PED method is preferred.

SEM images taken of polished, filled and empty PAMs over the maximum scan area at which the instrument can adequately resolve the template features are presented in Fig. 90 below.

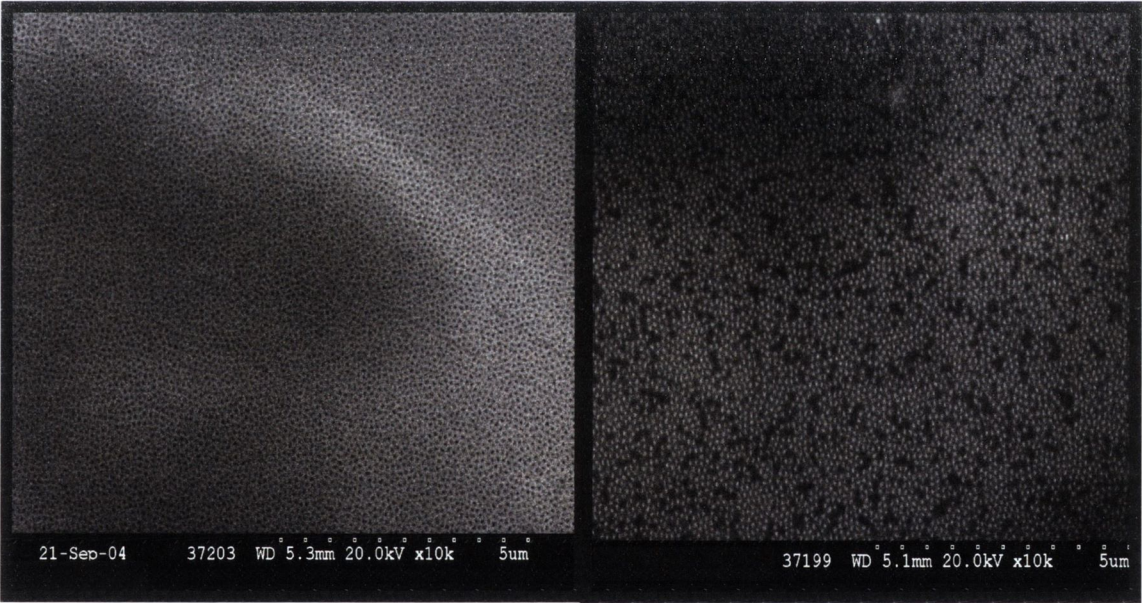


Fig. 90 Left: Surface SEM image of an empty polished 40 V PAM. Right: Surface SEM image of an equivalent, polished, Ni-filled PAM. Some charging is evidenced as these samples were not gold-coated.

Over an SEM scan area of about 10 micron, planarisation and high % filling levels are observed. Different regions on the disk shaped Ni-filled region (approx. 1.5 cm diameter) of the sample yielded similar images and the whole process should be

scaleable to diameters in the 50 – 100 nm range. By using a lower accelerating voltage in SEM imaging, both the PA template and the filled pores were resolved simultaneously as shown in Fig. 91 below.

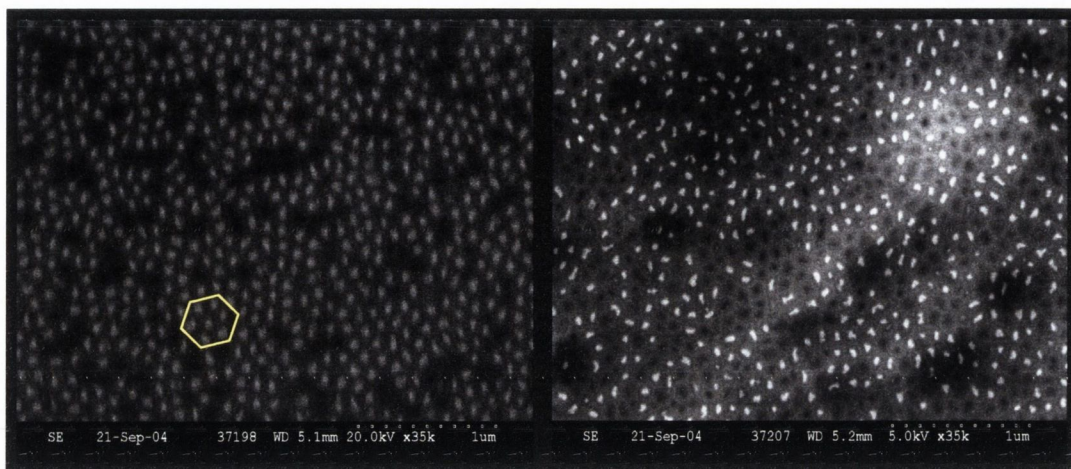


Fig. 91 Left: SEM surface image (20 kV, x 35k) of a polished Ni-filled PAM. Right: SEM surface image (5 kV, x 35k) of the same sample. In yellow is an example of six nanodots which are hexagonally distributed.

Also quite noticeable from Fig. 91 is that there is a distribution of nanodot sizes and shapes but the average size is approximately 48 nm and the shape is, in general, roughly hexagonal. The order is very short range with only a few nanodots distributed perfectly hexagonally. A visual summary of the effect of planarisation by polishing is given below in Fig. 92 where high resolution SEM images contrasting unpolished and polished membranes are presented.

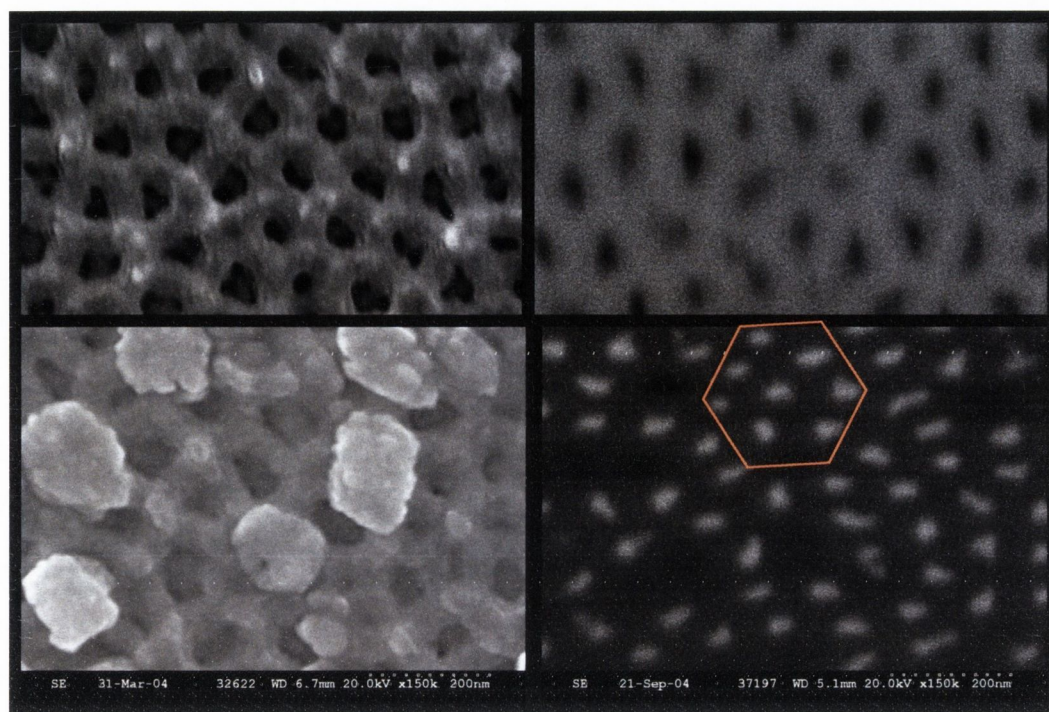


Fig. 92 Surface SEM images (20 kV, x 150k) of 40 V PAMs. Top left: Empty unpolished PAM. Top right: Empty, polished PAM. Bottom left: Ni-filled unpolished PAM with some overplating. Bottom right: Filled polished Ni-filled PAM

Note that in Fig. 92 (bottom left), although there is some overplating, most pores do appear to be almost full. This indicates yet again that uniformity is actually quite good over several microns with PED filling. The polished and unpolished images cannot correspond exactly to the same region on the samples. This makes feature size comparison difficult. Furthermore, the focus and contrast at this magnification in the polished samples is not good because all the features are coplanar. The smaller-than-average size distribution observed in Fig. 92 (bottom right) may be localized, or, be due to the fact pore regularity improves with polishing as the original growth front at the barrier layer is approached. A reduction in the average pore size results as there is less pore coalescence.

AFM was used to quantitatively measure and compare the surface roughness of polished and unpolished samples as shown in Fig. 93 below.

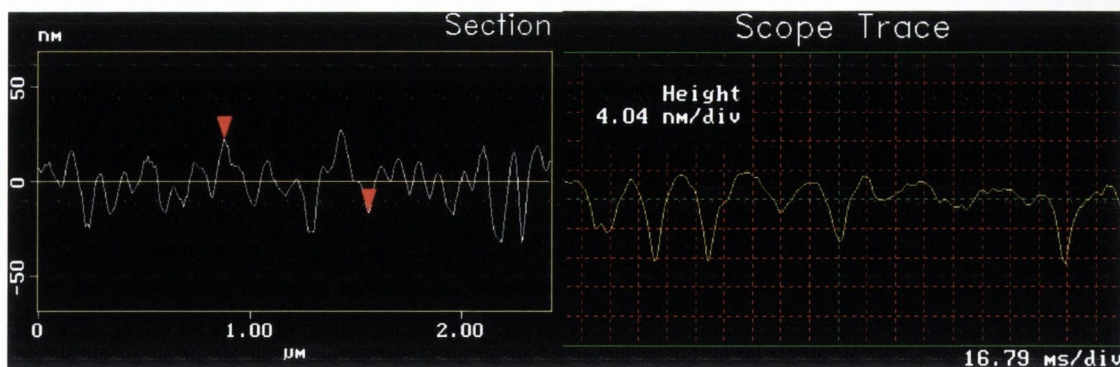


Fig. 93 Left: AFM section of empty unpolished PAM. Right: AFM section on empty polished PAM.

The AFM cross-section images suggest that an unpolished membrane over $2\ \mu\text{m}^2$ area has a surface roughness of at least 30 nm. However, this was for an area which could be imaged. Many areas were too rough to be imaged since they contained features hundreds of nanometers high, thereby causing damage to the AFM tip. The polished membrane over a similar area has a surface roughness of less than 5 nm and this is found over the entire sample area of $1.5\ \text{cm}^2$.

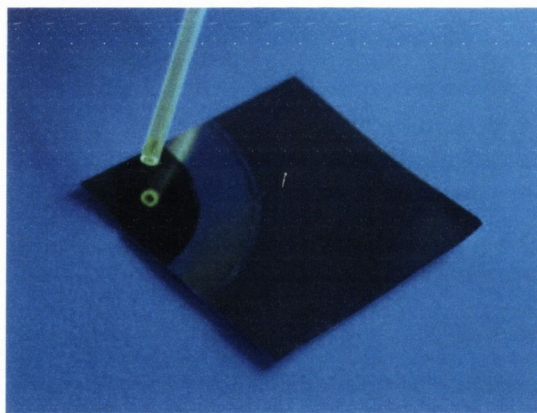


Fig. 94 A polished Ni-filled PAM reflecting the light from a micropipette which was dipped in light-emitting polymer solution.

The flatness over macroscopic dimensions can be illustrated by virtue of the fact that a polished metal-filled membrane acts as a good quality mirror as shown in Fig. 94, The polymer coated micropipette was excited using a UV lamp.

For polished samples, it is possible to confirm the presence of Ni in the pores by EDX (Energy Dispersive X-ray) analysis (Fig. 95). The sulphur signal is probably from the electrolyte, the carbon from oxalic acid and the aluminium and oxygen from the porous alumina.

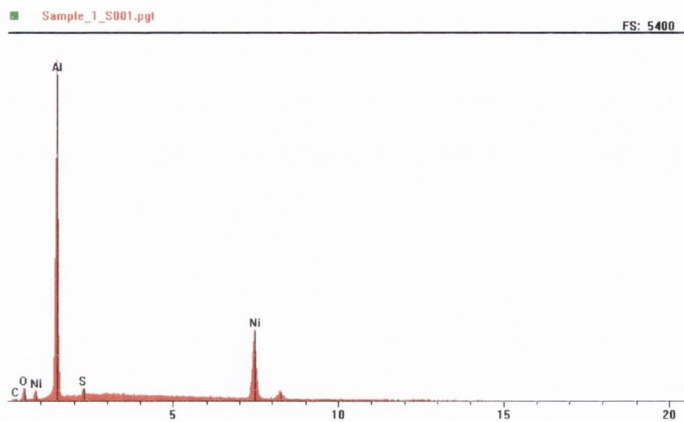


Fig. 95 EDX of a polished Ni foil with the main peaks being Al and Ni and also showing O and S.

5.6.2 Electrical Resistance of a 20 nm Thick Barrier Layer

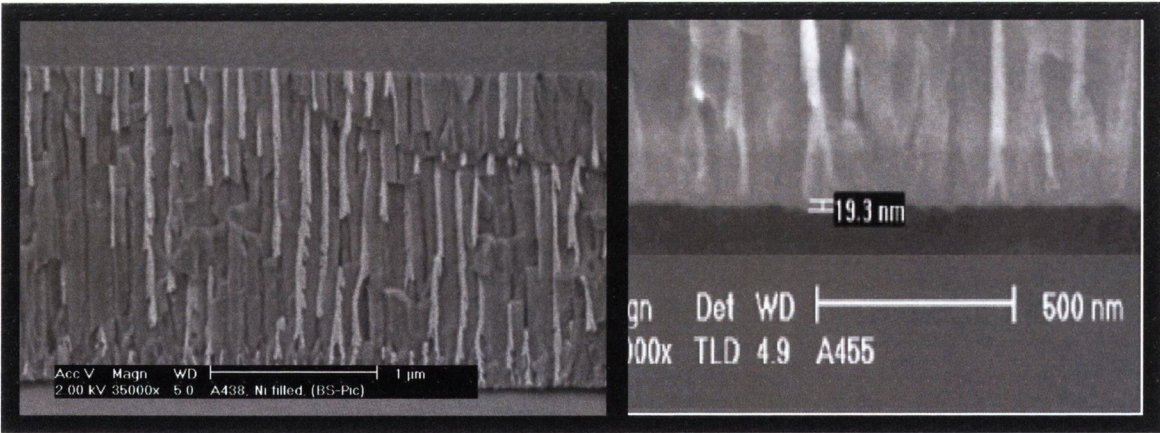


Fig. 96 Left: SEM cross section image of a polished Ni-filled PAM which is about 2 micron thick. Right: High resolution 5kV cross section image of the same sample clearing showing branching of the pores at the barrier layer and a barrier layer thickness of approx. 20 nm after a voltage reduction was performed.

Having characterized the foils structurally, it is now important to turn to the electrical characteristics of the polished Ni-filled PAM itself. The images in Fig. 96 show a polished nickel-filled PAM and its barrier layer.

It can be seen in Fig. 96 (right) that at the base of some wires, the main part of the filled pore or ‘trunk’ splits into a number of narrowing “dendritic” branches. The pores branch out at the formation front because the equilibrium number of pores cm^{-2} is inversely proportional to the square of the anodising potential. The pores in Fig. 96 (right) appear to stop at the surface of the barrier layer and so the electrical properties of the metal-filled PAM are expected to be dominated by the electrical resistance of the barrier layer.

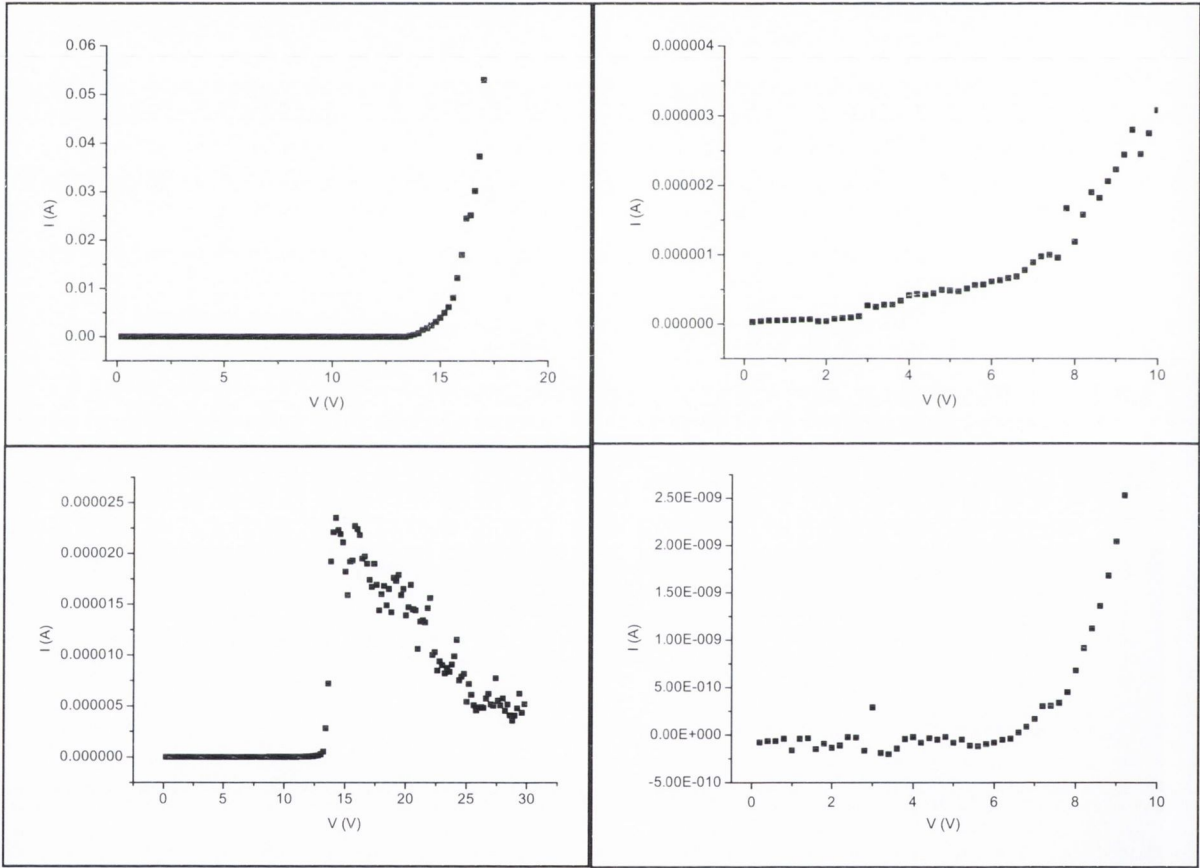


Fig. 97 I-V of an over plated 40 V Ni PED filled PAM. Top left: Using Ag to contact area = 6 mm². (right: low voltage region). Bottom left: Using point probe to contact surface (right: low voltage region).

In terms of device structure notation, the barrier layer device is: Al/barrier layer/Ni. From the I-V data in Fig. 97 (bottom), it is apparent that there is much less current when a point contact is used than is the case when a macroscopic contact using silver paint is made. This is to be expected as, in the former case, only one or, at most, a small bundle of nanowires is likely to be in good contact with the probe. It is also apparent that the barrier layers are not behaving like a macroscopic metal wire in that the I-V is non-linear. Furthermore, it appears to be the case that there is a threshold voltage beyond which there is a dramatic increase in current as shown in Fig. 97 (top right, bottom right). Though this is evident using both macroscopic and point probe contacts, it is better defined using the probe contact, and is roughly between 7.5 and 8 V for the sample in Fig. 97 (bottom right). Below this threshold voltage, based on the current flowing in actual LEDs below this value (fig. 101), the array contact would be expected to limit current in a PLED and to behave as a blocking contact. Above the threshold, the array device should in that case switch from being electrode-limited to being bulk-limited with respect to current flow in the device. However the data in Fig. 98 suggests that the barrier layer is not limiting the Nanodot array LED at any point, as the current density in these devices is comparable to the film electrode LEDs over most of the operating range.

It is known that the barrier layer beneath the metal-filled pore bottom is a duplex oxide of pure oxide and that if the pure portion near the foil base extends about 25% of the way into the barrier layer at which point an impurity containing phase is encountered. This means that most of the potential drop is over a thickness of about 5 nm for a 20 nm thick barrier layer. The metal-filled array with barrier layer was found to be slightly rectifying, which may be due to the fact that on one side we have Al and on the other Ni. However, it is known that the oxide itself is intrinsically rectifying by virtue of its structural composition.

One must ask how charge transfer can occur across the barrier layer both during the electro-deposition process and during array-electrode device operation. Since the electrical conductivity of the pure oxide is very low, it is unlikely that the magnitude of the current in a metal-filled PAM barrier oxide layer below the thresholds observed in Fig. 97 is due to some space charge limited conduction process in the barrier layer oxide.

It is possible that there is some tunnelling barrier (or barriers in the case of multiple tunnelling events) which must first be overcome in order to observe current flow. The lack of a threshold in the Nanodot array LEDs would possibly be due to the pure oxide layer being thin enough to tunnel through at very low voltage and then assumes conduction in the remainder of the barrier layer is high enough for it not to limit the LED current. Alternatively perhaps dielectric breakdown of the pure oxide component results in a current such that the device current is not array-electrode limited. It would be interesting to compare the current flow across a non-porous alumina layer on aluminium (like an extra thick native oxide) with that flowing across the barrier layer after metal deposition.

Having fabricated and characterised the polished Ni-filled PAMs, the next steps in the OLED fabrication process are the same as for those used in conventional devices. Unlike the case with the unpolished Cu-filled devices, there was no actual need to use a SiO layer to prevent shorting across the polymer layer but it was used to define the device area. As with the Cu-based devices, a conventional planar type device was made for comparison purposes. This was done by evaporating nickel onto a 12 mm x 12 mm glass substrate, spincoating the substrate with polymer and evaporating aluminium contacts on top to give an active pixel area of 0.06 cm^2 . In order to obtain the I-V characteristics of both kinds of device, the aluminium top contact was negatively biased with respect to the nickel contact.

5.6.3 Characterisation of Ni-filled Array Electrode PLEDs

5.6.3.1 Current Densities Under Forward Bias

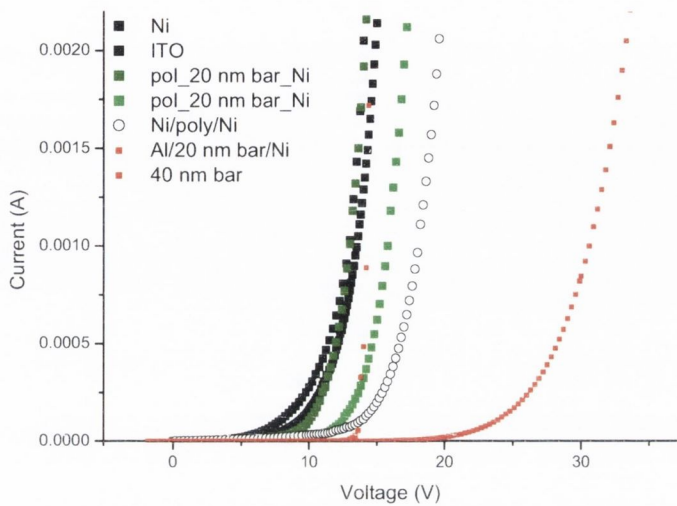


Fig. 98 The structure of all the above devices is X/poly/Al where X is the anode – the structures are listed in the plot legend.

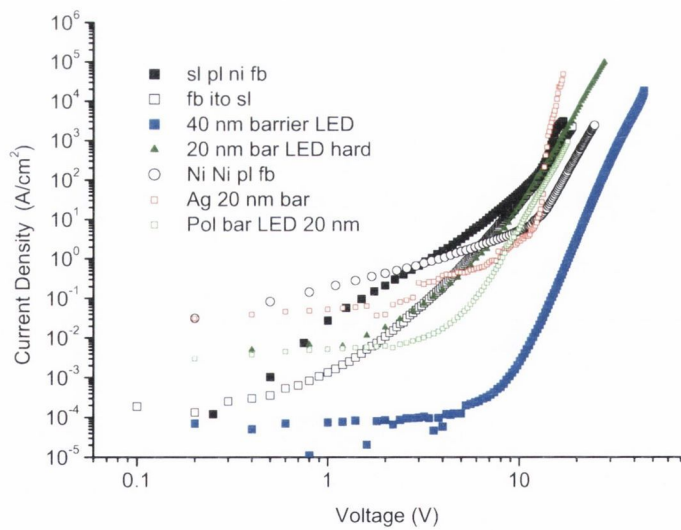


Fig. 99 Log-log plot of I-V for planar and nanowire array devices.

Based on fact that the slope is similar in Fig. 99 for voltages > ~10 V, the trapping distributions are therefore similar in the conventional and the nanodot array devices.

However, in Fowler-Nordheim (F-N) plots (Fig. 100), the nanodot array devices appear to be linear over a larger field range. The barrier extracted for the 20 and 40 nm barrier devices was 0.48 ± 0.09 and 0.8 ± 0.1 eV which is larger than the energy offset at the interface since the workfunction of nickel is 5.1 eV and the ionization potential of the polymer is expected to be 5.1 ± 0.2 eV. This may be due to backflow of current at the interface.

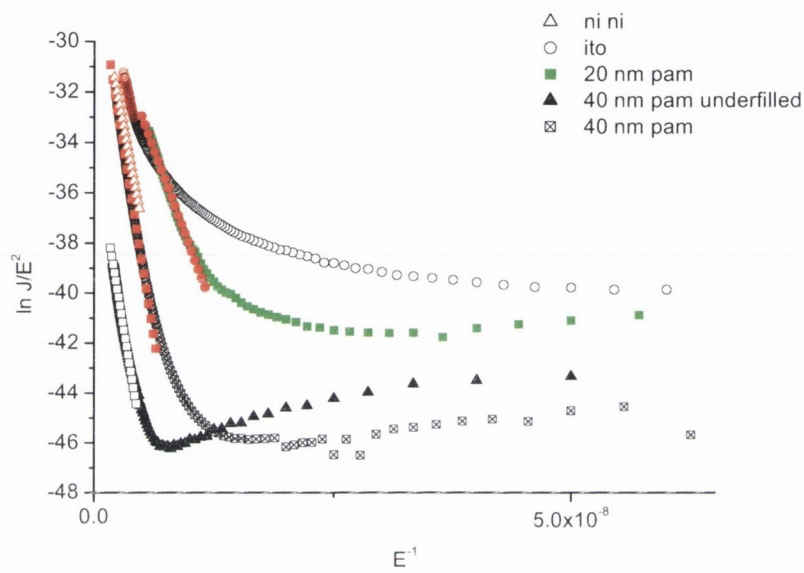


Fig. 100 Fowler-Nordheim plots for all the devices.

The plots are linear over a limited high field range in the case of the nanowire devices. However the applicability of tunneling theory does seem to be more suited to the nanowire devices than to the planar LEDs since the latter exhibit curvature throughout the plot. There is too much curvature for a linear fit to be made for the planar devices. The nanowire array LEDs yield barriers which seem to depend on barrier thickness. In order to check further the validity of an FN analysis, F-N plots at different temperatures for a Ni nanowire device were made and are shown below.

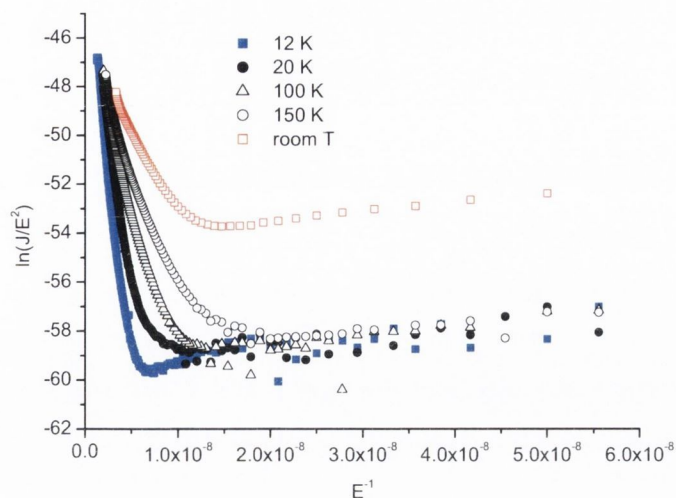


Fig. 101 Temperature dependence of FN tunneling for a 40 nm barrier Ni nanodot array device.

The FN equation predicts virtually no dependence on temperature and from Fig. 101 it is clear that this is only the case at very high fields where the FN plots for the same device at different temperatures converge. In many OLEDs this overlap is not seen at any field and modeling the current flow using the FN equation is not appropriate.

5.6.3.2 Rectification Ratios

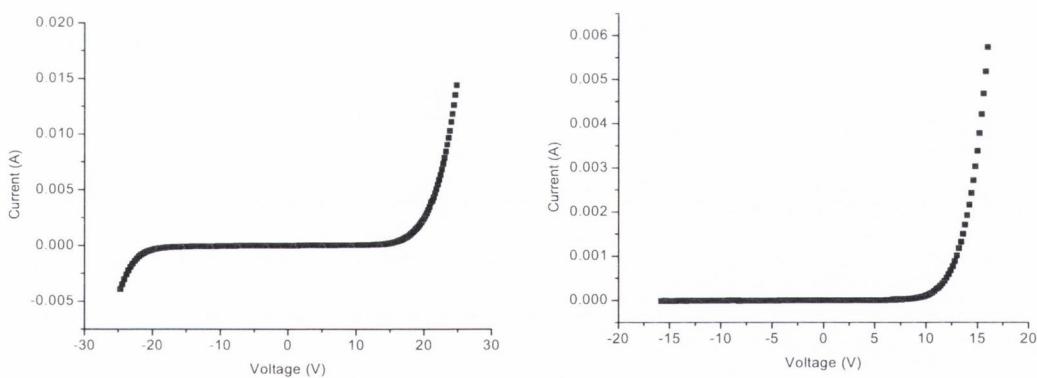


Fig. 102 Negative and positive bias I-V data for Ni-Ni sheet electrodes (left) and Ni nanowire array electrode (right) showing rectification.

The Ni-Ni data from a conventional planar device shows that nickel is a good ohmic hole-injector and that there is some rectification which is most likely due to differences in interfaces. The bottom interface is evaporated *Ni:spin-coated polymer* and the top interface is *polymer:evaporated Ni* and ,therefore, differences in injection

barriers are to be expected. This would apply to all metals in such a nominally symmetric device structure.

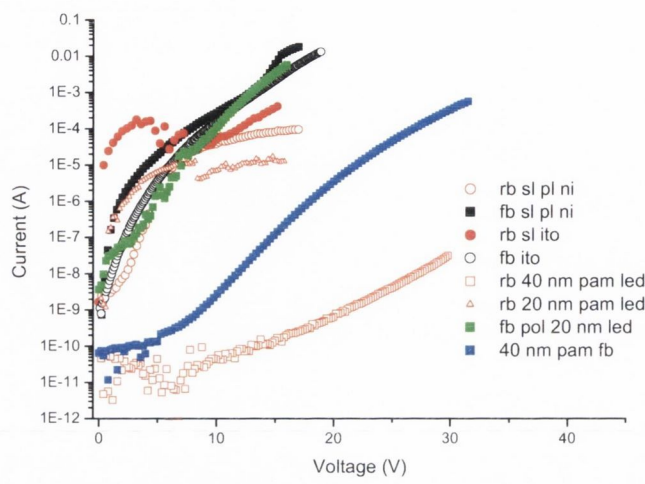


Fig. 103 Semilog plot showing rectification in thick barrier layer, unpolished devices, thin barrier layer, polished devices and planar devices.

Rectification, it should be noted, is generally better at high voltages, possibly due to small shorting pathways (which cause a vertical leakage current) being burned out more effectively and not being as dominant at high fields. Planar devices have rectification of $(10$ at 16 V for ITO and 10^2 at 16 V for Ni), polished, thin barrier devices have rectification (3×10^2 at 15 V) and those with thick barriers have the best rectification ($\sim 10^4$ at 30 V).

It should be noted that after several runs at a very high voltage, it may be possible to short out the barrier layer (thereby causing dielectric breakdown of the barrier layer oxide) and to have a normal Ohmic response from the array. In the future, this may be a way of effectively removing the barrier layer resistance of a metal-filled array prior to building an OLED or other device on top of it.

5.6.3.3 EL Spectra and Estimated Light Output

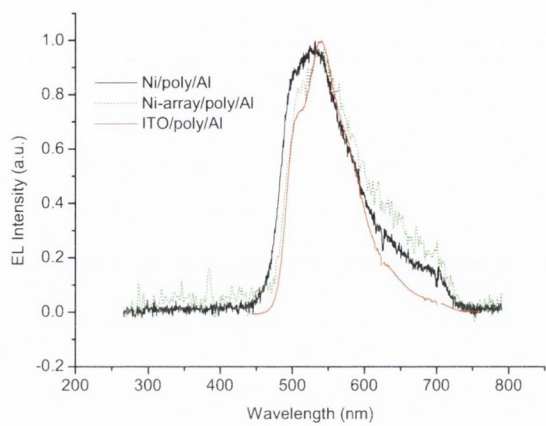


Fig. 104 EL spectra of nanowire-array and sheet-electrode devices.

Peaks at 544 nm and 512 nm and a shoulder at 598 nm are observed for the EL spectra of sheet and nanodot array devices. The higher intensity of the high energy peak compared with the main peak (at 544 nm) in the Ni planar device gives the impression that the EL is blue-shifted with respect to the other devices. The change in peak intensity ratios may be due to different reflectance characteristics of the electrodes. The noise in the EL spectra was due to shorting across the polymer film. No major spectral shifts were seen as expected for nano-pixelation where the emissive layer is not confined or affected by the electrode interface morphologically. These observations are in line with results from a nanopixelated OLED made using microbead arrays.²⁸ Note that were the polymer confined within the pores, one would expect to see some confinement effects in spectra. However, confinement here is not of the same origin as for inorganic confinement of, say silicon, which can cause silicon to luminesce. For silicon, quantum confinement is due to electron energy levels becoming spaced further apart for silicon nanoparticles but does not involve physical alteration of the silicon bonding. In the case of organic chromophores confined in pores, confinement will alter the packing of the organic material, possible also altering its physical structure in the process. This in turn will modify the PL and EL spectra. It has already been shown that confinement of organic materials in AA0 (anodic aluminium oxide) can produce some very specific types of packing and coiling of polymer chains²⁹. It is possible to incorporate light-

emitting polymers like PPV and other fluorescent organic materials in AAO³ although very little detailed work has been published on this topic to date.

The spectrum for the nanodot array device was collected through a semitransparent aluminium electrode, 70nm in thickness. Significantly, the intensity was sufficient to collect a reasonable signal. The EL spectra are normalised to the peak wavelength of 544 nm to see if there was a spectral shift. The un-normalised spectra, taking the active area into account, indicate that the brightness of the array devices is significantly better than the planar devices, particularly considering the poor outcoupling of light in the array devices. Further development of the array device structure will include the replacement of semitransparent aluminium electrodes with vacuum sublimed copper phthalocyanine and conductive ITO deposited by plasma sputtering. To this end, a conventional device with this structure was made but it had poor stability and due to time constraints involved in optimising the structure further work was not carried out.

5.6.4 A Thermal Model for OLEDs

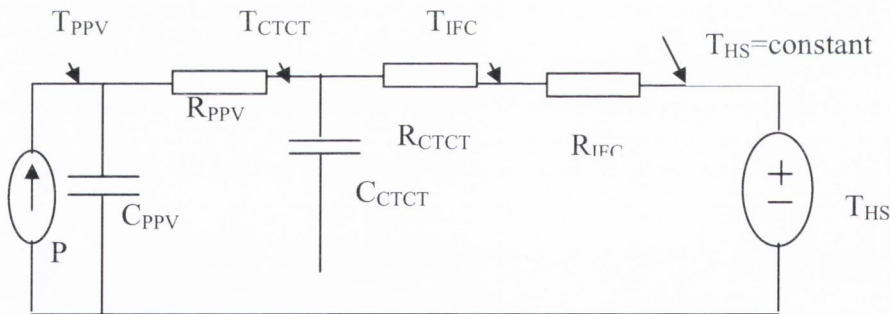


Fig. 105 Generic model for a thermal equivalence circuit describing heat flow in a Polymer LED.

In Fig. 105 an equivalent heat circuit³⁵ which models the heat flow in an OLED is provided where T_{HS} is heatsink temperature and is the analogue of an electrical voltage source. The power, P , dissipated in the LED is the analogue of an electrical current source where $P = R_T I^2$ and R_T is the thermal resistance. R_T has the components $R_{Polymer}$ (in this case R_{PPV}), R_{CTCT} , and R_{IFC} which are the thermal resistances of the polymer layers, the cathodic contacts, and the interfacial contact between the contacts and the heatsink. $C_{Polymer}$ and C_{CTCT} are the thermal capacitances of the polymer and of the

contacts, respectively. The heat capacitance, C_{PPV} , of a PPV film was found to be 5.6×10^{-8} J/K and R_{PPV} to be 375×10^{-3} K/W. The contact parameters obtained were: $C_{CTCT} = 380 \times 10^{-8}$ and $R_{CTCT} = 2.4 \times 10^{-3}$ K/W. The heat resistance of 1mm^3 glass is 110 K/W. R_{IFC} has been estimated to be 100 – 1000 K/W.

In the model, the mobility in the single carrier space charge limited current described by the Mott-Gurney square law is given by:

$$\mu = \mu_0 \exp\left(-\frac{\Delta}{kT}\right) \exp\left(\gamma\sqrt{E}\right)$$

$$\text{where } \gamma = B\left(\frac{1}{kT} - \frac{1}{kT_0}\right) \text{ and } T = T_{HS} + IVR_T$$

, where μ_0 is the zero-field mobility, E is the electric field and T is the device temperature, T_{HS} is the heatsink temperature, I is the current and R_T is the thermal resistance. It should be possible to calculate R_{IFC} for the NA-OLEDs in future once an effective way of measuring temperature rise in the device is possible. This requires a transparent top electrode so that the electroluminescence spectrum can be used as a thermometer to gauge the device temperature. Reducing device size and using substrates with a high thermal conductivity are both practical methods which have been demonstrated to improve heatsinking in OLEDs. Thus, in the nanodot array OLEDs (NA-OLEDs) the combination of small pixel size and improved thermal conductivity of alumina with respect to glass (46 versus 1.1 W/mK) act to improve heatsinking. The heat circuit model and equations clearly predict reducing heatsink temperature and/or thermal resistance of the polymer substrate interface delays the onset of thermal-runaway in a device.

Although the maximum current density and brightness have been shown to be better for smaller devices, the L-I curves are the same - i.e. EL efficiency is independent of device size.⁵ EL spectra were not presented in the literature. This would be interesting information to have since the whole PLED was confined in a plasma-etched hole in silicon nitride on ITO defined by patterned photoresist.

5.7 CONCLUSIONS AND IDEAS FOR FUTURE DIRECTIONS OF RESEARCH

5.7.1 Synopsis of Devices Incorporating Nanowire Array Electrodes

- OLEDs were made using both copper and nickel nanodot arrays as a hole-injecting array electrode.
- Planarisation of devices provided a better defined interface, however, if the foils were flatter to start with, the PAM would polish a lot more evenly. As this was not the case, foils tended to wear through to the aluminium foil in places. The latter could be avoided in future, even without planarising the foils, by polishing considerably thicker PAMs (> 20 microns).
- From the point of view of hole-injection, the metal *nanowire array: polymer* interface obtained using the polished nickel arrays represented a considerable improvement on the unpolished copper devices. It also represents a PEDOT-free device architecture with dramatically reduced lateral leakage currents with respect to a standard ITO SL device without PEDOT. Our electrical characterisations show that the nickel nanodot array devices exhibit improved rectification from the copper ones and afford a higher maximum current density.
- Reduction of the barrier layer in nickel devices reduced the operating voltage to levels comparable with conventional planar structures, for a single layer device. This may partially be due to the reduced resistance of the barrier layer but also to the associated improved filling in thin barrier layer PAMs, which effectively reduces the average polymer thickness for PAMs which are almost 100% filled with the electrodeposited metal.

➤ Very high current densities were obtained in the polished Ni array devices with a 20 nm barrier layer. These are compared with other high values from the literature for different device types in the table below. In the literature used to compile this table, in most cases either DC or pulsed current densities were cited with values for both regimes for a given device only reported in a few instances.

Device	Area	J _{DC} (A/m ²)	J _{pulsed} (A/m ²)	EL max (Cd/m ²)
STM SMOLED	1 nm ²	10 ⁸ 5.1 x 10 ⁶		predicted
SL film PAM _{Cu} PAM _{Ni}	6 mm ² 0.14 mm ² 1.1 mm ²	2.2x 10 ³ ±0.2 5x 10 ⁴ ±3 1x 10 ⁵ ± 6		4 Cd/m2 400 cd/m2 or
SMOLED DL SMOLED DL Extreme	.03 mm ² 2x 10 ³ μm ²	 5x10 ⁶	3 x 10 ⁶	 1.5x10 ⁶
DL PLED	1 mm ²	2 x 10 ⁵		
PLED	1 mm ²		1 x 10 ⁷	5 x 10 ⁶
SL PLED DL PLED	< 1mm ² as above		10 ⁷ .6 x 10 ⁷	5 x 10 ⁶ 1 x 10 ⁶
DL PLED	4.5 mm ² 2x 10 ³ μm ²	1.3 x 10 ⁴ 1.5 x 10 ⁵	 8.6 x 10 ⁴ 5.1 x 10 ⁶	2.4 x 10 ⁴ 1.9 x 10 ⁵ 1.3 x 10 ⁵ 6.5 x 10 ⁶
PHOLED		10 ³		1.2 x 10 ⁴
TOLED		7.3 x 10 ³		1.4 x 10 ⁴
patterned	400 μm ²	3.7 x 10 ²		3 x 10 ²

Table 5 High J and brightness values reported in the literature³⁶⁻⁴⁰ for various OLEDs.

More often than not, the pixel area is not quoted but, generally, a standard device is of the order of 1 mm^2 . Note that the EL intensity often saturates at J below J_{max} above particularly in case of DC driven devices. J_{pulsed} starts to deviate⁴¹ from J_{DC} at 50 mA/cm^2 . ($.5 \times 10^3 \text{ A/m}^2$). This typically occurs between $10^3 - 10^4 \text{ Am}^{-2}$. The DC brightness results in the table above for PHOLEDs are therefore very impressive because PHOLEDs tend to suffer from triplet-triplet annihilation at high current densities. There is still considerable scope for further optimisation of PED and thinning of the barrier layer to be used to improve the nanodot array devices. Also, given that the materials used here had lower carrier mobilities ($\times 10^4 - 10^6$) than current state of the art materials, higher DC current densities should be attainable with these device structures. If a linear relationship between luminance and current density is assumed it is reasonable to assume the light output of the NA-PLED (Ni) could be about 100 times more than the standard SL LED which we made. Our SL LED has very poor luminance, so assuming a high performance SL material set is used, based on the data above a maximum luminance of $5 \times 10^8 \text{ cd/m}^2$ could be achieved in theory. Although this neglects excited state absorption effects which are important at high J , some improvement over the current best DC brightness can be expected provided the brightness does not saturate due to such effects. It must be stressed that although addressing the issue of joule heating in devices is important and will extend the lifetime and maximum performance of a less well-heatsunk device, it is device efficiency rather than maximum brightness which will determine whether lasing can be achieved in an organic laser diode.

Although most of the improvements necessary for better characterisation of OLEDs based on the array electrode structure have been addressed, the issue of improved light outcoupling remains and this is clearly evidenced by the low signal to noise ratio in EL spectra. An inverted reversed device structure, with a low workfunction metal such as calcium as the nanowire array material, would be ideal for an efficient top-emitting array. However, such metals are too unstable in liquid electrolyte to electrodeposit. The most probable solution is to replace the thermally evaporated semi-transparent aluminium top contacts⁴² with electron injection layers and sputtered ITO contacts. This has yet to be demonstrated for the NA-OLED. A possible structure would be: $< 10 \text{ nm}$ barrier layer/Ni nanowire array/ polymer/ AlQ₃/ LiF/ CuPc/ ITO.

Note that the diffusion length is given by $l^2 = D_t$ where t is the exciton lifetime and D the diffusion coefficient. D in molecular semiconductors is $1 \times 10^{-3} \text{ cm}^2\text{s}^{-1}$ and is not expected to exceed this in these conjugated polymers. Also, current spreading is not expected to cause a wider emission area than that defined by the individual nanodots since no conductive hole-transport layer was used in our tests. Therefore, to our knowledge, this is one of the smallest nanopixelated OLEDs to have been produced to date.

Although the PLEDs made here were single layer devices, multilayer devices could, of course, be made on the metal arrays also. Furthermore, there is no restriction to using polymers and it would also be interesting to build SMOLEDs on planarised arrays. OLEDs are seen as the natural predecessor to the organic laser diode. The loss of guided mode intensity due to metal electrode absorption is one major issue which will determine if lasing is possible and, if it is, at what power useful outputs can be achieved. One approach to reducing electrode losses is to inject using a FET structure⁴³. Another idea is to use a metallic array to nanodisc array to inject charge. Lemmer *et al*⁴⁴ have studied gold nanodisc arrays with a view to this application. Lasing threshold results published by this group, for films spun onto such an array, have shown a reduced threshold with respect to planar metal electrodes.^{45,46} Furthermore, the threshold was not much more than that for a film spun onto silicon. It is possible to electrodeposit gold⁴⁷ into PA and it would, therefore, be interesting to perform similar studies with a Au-filled PAM coated with polymer.

5.7.2 Inline Nanowire Device Arrays

Beyond the particular device structure used in this work, there are good prospects for using PAMs for novel structures in microelectronics and micro-optics. Multilayered nanowires could act as tiny heterojunctions, p-n junctions and Schottky diodes, for example, and addressed metal or semiconductor nanowire arrays could be used as part of high-density logic or memory-storage devices.⁴⁸ Also, given that pore diameters as small as 4 nm are feasible, and that emissive materials may be deposited into the pores, confinement of organic or inorganic materials in the pores may allow for the tuning of electroluminesced light. Ultimately, it is hoped to use a combination of electrode and

active material in pores in order to create in-line devices in which the device is essentially comprised of arrays of multilayered nanowires.

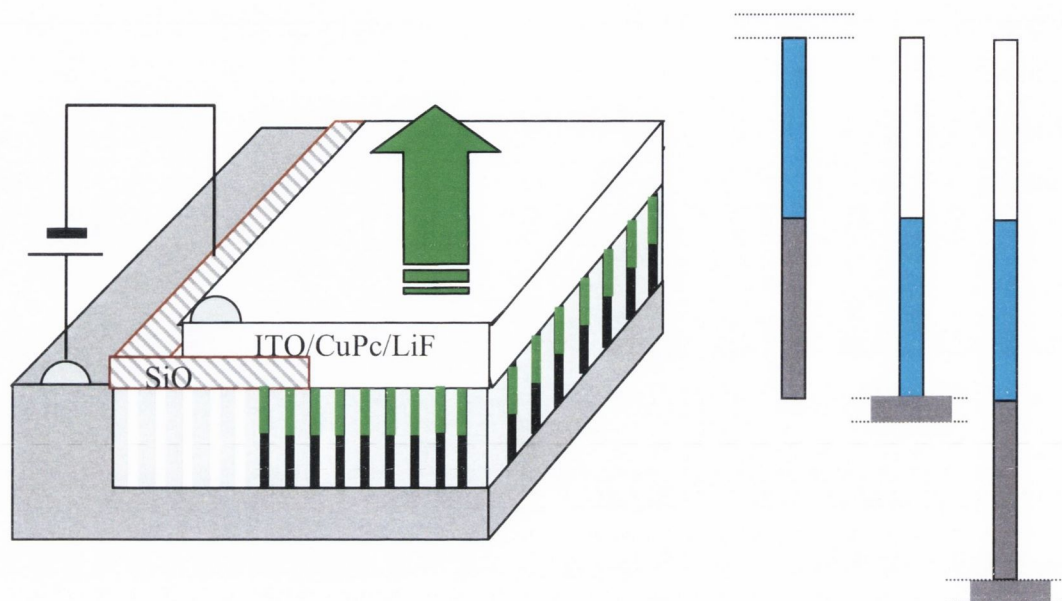


Fig. 106 Left: proposed structure for an in-line nanowire array device where the green represents the emissive organic material. Right: variations of the inline structures possible (blue: emissive material, grey: electrodeposited metal, white: transparent conducting oxide.)

One possible inline multilayer nanowire structure would be (Ni/PPV) with a thin film of ITO and electron transport layers on the array. If one wished to have better outcoupling from each nanowire device, a PPV/CdO or PPV/PANI arrangement might be feasible if the barrier layer were removed and an aluminium sheet cathode deposited in its place. With recombination and EL originating from material in the nanowire, such devices should exhibit altered optical characteristics with respect to conventional monolithic structures. The latter would be expected to be based on different packing of the chromophore molecules in a confined space compared with a film of chromophore molecules or even a patterned film of chromophore molecules. Some progress has been made with regard to filling organic chromophores into PA. This cannot be done by electrodeposition due to the low conductivity of the polymer. Techniques used to date include vacuum filtration, wetting of pore walls by polymer melt and capillary wetting from solution. PPV nanorods and nanowires have thus been made using PA templates⁴⁹. To the best of our knowledge, only a couple of groups attempted to make inline

structures similar to the above. However, the turn-on voltages were high because of the length of the polymer nanowires and the barrier layer. For a more satisfactory result, it would be necessary to have polymer nanowires of about 100 nm in length.

5.7.3 Bulk Heterojunction Solar Cells

Looking briefly to other organic electronic device applications which could benefit from the use of porous alumina templating, one might immediately think of solar cells.⁵⁰ In many respects a solar cell operates as the inverse of an OLED, with the separation of photogenerated excitons at an interface and their subsequent collection at opposing electrodes resulting in a photocurrent. This process is maximized for bulk heterojunction devices⁵¹. The use of polymer blends is one way of obtaining bulk heterojunctions. However, the best possible solar cell structure would involve a structure based on interdigitated bulk heterojunctions where each phase has excellent electrode connectivity.

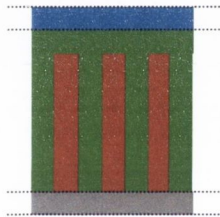


Fig. 107 An ideal solar heterojunction device with nanoposts of one semiconductor (brown) grown from metal-filled PA (grey), surrounded by another semiconductor (green) and capped with a transparent electrode (blue).

Such a structure may be possible by using PA templating to plate Nickel into the pores followed by CdS. Preferential etching of the oxide may reveal nanoposts of CdS upon which an organic material may be deposited. It has been shown that polymer/C₆₀ interfaces are good for solar cells⁵² and it is possible to produce arrays of Cds (carbon nanotubes) using PA templating. Accordingly, an alternative structure might be CNT posts coated with polymer. Incidentally, CNTs have been used in OLEDs as hole injecting electrodes, HBLs and ETLs. This suggests that CNT arrays could, potentially, replace Ni in the nanowire devices as produced in this thesis. Many of the ideas discussed in this section represent a move away from traditional monolithic type

structures to dense array type structures which are now feasible with an increasing number of nanotechnologies.

References

1. Brown, T. M.; Friend, R. H.; Millard, I. S.; Lacey, D. J.; Burroughes, J. H.; Cacialli, F., "LiF/Al cathodes and the effect of LiF thickness on the device characteristics and built-in potential of polymer light-emitting diodes". *Applied Physics Letters* **2000**, 77, (19), 3096-3098.
2. C. I. Wilkinson, D. G. Lidzey, L. C. Palilis, R. B. Fletcher, S. J. Martin, X. H. Wang and D. D. C. Bradley, *Appl. Phys. Lett.* 79, 171 (2001).
3. B.J. Matterson, J. M. Lupton, "Increased efficiency and controlled output from a micro-structured light-emitting diode". *Adv. Mat.* **2001** 13 b) Smith, L. H.; Wasey, J. A. E.; Barnes, W. L., "Light outcoupling efficiency of top-emitting organic light-emitting diodes". *Applied Physics Letters* **2004**, 84, (16), 2986-2988.
4. Thompson, M. E.; Forrest, S. R., Enhancing the efficiencies, color purities and lifetimes of organic light emitting diodes. *Abstracts of Papers of the American Chemical Society* **2001**, 221, U481-U481
5. C. I. Wilkinson, D. G. Lidzey, L. C. Palilis, R. B. Fletcher, S. J. Martin, X. H. Wang and D. D. C. Bradley, *Appl. Phys. Lett.* 79, 171 (2001).
- 6 N. Tessler, N. T. Harrison, D. S. Thomas and R. H. Friend, *Appl. Phys. Lett.* 73, 732 (1998).
7. Jackman, R. J.; Wilbur, J. L.; Whitesides, G. M., "Fabrication of Submicrometer Features on Curved Substrates by Microcontact Printing". *Science* **1995**, 269, (5224), 664-666.
- Jackman, R. J.; Brittain, S. T.; Adams, A.; Prentiss, M. G.; Whitesides, G. M., "Design and fabrication of topologically complex, three-dimensional microstructures". *Science* **1998**, 280, (5372), 2089-2091.
- Ozin, G. A., "Nanochemistry - Synthesis in Diminishing Dimensions". *Advanced Materials* **1992**, 4, (10), 612-649.
- Schollhorn, R., "Intercalation systems as nanostructured functional materials". *Chemistry of Materials* **1996**, 8, (8), 1747-1757.
- Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L., "A New Family of Mesoporous Molecular-Sieves Prepared with Liquid-Crystal Templates". *Journal of the American Chemical Society* **1992**, 114, (27), 10834-10843.
8. Wise, K. D.; Najafi, K., "Microfabrication Techniques for Integrated Sensors and Microsystems." *Science* **1991**, 254, (5036), 1335-1342.
9. Hultheen, J. C.; Martin, C. R., "A general template-based method for the preparation of nanomaterials." *Journal of Materials Chemistry* **1997**, 7, (7), 1075-1087.
10. Cepak, V. M.; Hultheen, J. C.; Che, G. L.; Jirage, K. B.; Lakshmi, B. B.; Fisher, E. R.; Martin, C. R.; Yoneyama, H., "Chemical strategies for template syntheses of composite micro- and nanostructures." *Chemistry of Materials* **1997**, 9, (5), 1065-&.
- 11 T. J. Marks, J. G. C. Veinot, J. Cui, H. Yan, A. Wang, N. L. Edleman, J. Ni, Q. Huang, P. Lee and R. Armstrong, *Synth. Met.* 127, 29 (2002).
12. Masuda, H.; Fukuda, K., "Ordered Metal Nanohole Arrays Made by a 2-Step Replication of Honeycomb Structures of Anodic Alumina." *Science* **1995**, 268, (5216), 1466-1468.
13. Lee, W.; Ji, R.; Ross, C. A.; Gosele, U.; Nielsch, K., "Wafer-scale Ni imprint stamps for porous alumina membranes based on interference lithography." *Small* **2006**, 2, (8-9), 978-982.
14. Li, A. P.; Muller, F.; Birner, A.; Nielsch, K.; Gosele, U., "Hexagonal pore arrays with a 50-420 nm interpore distance formed by self-organization in anodic alumina." *Journal of Applied Physics* **1998**, 84, (11), 6023-6026.
- 15 S. Shingubara, "Fabrication of nanomaterials using porous alumina templates", *J. Nanopart. Res.* **2003** 5 b) J. Choi, Y. Luo, R. B. Wehrspohn, R. Hillebrand, J. Schilling and U. Gösele, *J. Appl. Phys.* 94, 4757 (2003). c) O.K. Varghese, D. Gong, M. Paulose, K. G. Ong, C. A. Grimes and E. C. Dickey, *J. Mater. Res.* 17, 1162 (2002). d) M. Sun, G. Zangari, M. Shamsuzzoha and R. M. Metzger, *Appl. Phys. Lett.* 78, 2964 (2001). e) G. Sauer, G. Brehm, S. Schneider, K. Nielsch, R. B. Wehrspohn, J. Choi, H. Hofmeister and U. Gösele, *J. Appl. Phys.* 91, 3243 (2002). f) Menon, V. P.; Martin, C. R., "Fabrication and Evaluation of Nanoelectrode Ensembles". *Analytical Chemistry* **1995**, 67, (13), 1920-1928. f) Nielsch, K.; Wehrspohn, R. B.; Barthel, J.; Kirschner, J.; Fischer, S. F.; Kronmüller, H.; Schweinböck, T.; Weiss, D.; Gosele, U., "High density hexagonal nickel nanowire array". *Journal of Magnetism and Magnetic Materials* **2002**, 249, (1-2),

234-240. g) Nielsch, K.; Wehrspohn, R. B.; Barthel, J.; Kirschner, J.; Gosele, U.; Fischer, S. F.; Kronmüller, H., "Hexagonally ordered 100 nm period nickel nanowire arrays". *Applied Physics Letters* **2001**, 79, (9), 1360-1362. h) Choi, J. S.; Sauer, G.; Goring, P.; Nielsch, K.; Wehrspohn, R. B.; Gosele, U., "Monodisperse metal nanowire arrays on Si by integration of template synthesis with silicon technology". *Journal of Materials Chemistry* **2003**, 13, (5), 1100-1103. i) Sauer, G.; Brehm, G.; Schneider, S.; Nielsch, K.; Wehrspohn, R. B.; Choi, J.; Hofmeister, H.; Gosele, U., "Highly ordered monocrystalline silver nanowire arrays". *Journal of Applied Physics* **2002**, 91, (5), 3243-3247. j) Schultze, J. W.; Macagno, V. A., "Electron-Transfer Reactions on Passive Tantalum Electrodes". *Electrochimica Acta* **1986**, 31, (3), 355-363. h) D. Routekevich, A. A. Tager, J. Haruyama, *IEEE Trans. On Elect. Dev.* **1996**, 43 i) S. Shingubara, "Fabrication of nanomaterials using porous alumina templates", *J. Nanopart. Res.* **2003** 5 j) T. Q.; Schwartz, B. J., "The nature of interchain excitations in conjugated polymers: Spatially-varying interfacial solvatochromism of annealed MEH-PPV films studied by near-field scanning optical microscopy (NSOM)". *Journal of Physical Chemistry B* **2002**, 106, (37), 9496-9506.

16 Macdonald, D. D., "On the Formation of Voids in Anodic Oxide-Films on Aluminum". *Journal of the Electrochemical Society* **1993**, 140, (3), L27-L30.

17 Parkhutik, V. P.; Shershulsky, V. I., "Theoretical Modeling of Porous Oxide-Growth on Aluminum". *Journal of Physics D-Applied Physics* **1992**, 25, (8), 1258-1263. b) Parkhutik, V. P.; Shershulskii, V. I., "The Modeling of Dc Conductivity of Thin Disordered Dielectrics". *Journal of Physics D-Applied Physics* **1986**, 19, (4), 623-641.

18 Nielsch, K.; Choi, J.; Schwirn, K.; Wehrspohn, R. B.; Gosele, U., "Self-ordering regimes of porous alumina: The 10% porosity rule". *Nano Letters* **2002**, 2, (7), 677-680.

19 Li et al, *J. Appl. Phys.* **1998** 84

20. Wood, G. C.; O' Sullivan, J. P., "Anodizing of Aluminium in Sulphate Solutions". *Electrochimica Acta* **1970**, 15, (12), b) Altenpohl, D., *I.R.E.* In **1954**. c) Wefers, H. G. a. K., *Metall* **1963**, 17, (202). d) Tertain, J. J. T. a. R., *Rev. Aluminium* **1949**, 26, (315). e) Wilsdorf, H. G. F., "Structure of Amorphous Aluminium Oxide Films". *Nature* **1951**, 168, (4275), 599-600. f) Mott, N. F., "The Theory of the Formation of Protective Oxide Films on Metals". *Transactions of the Faraday Society* **1947**, 43, (7), 429-434. g) Cabrera, N.; Mott, N. F., "Theory of the Oxidation of Metals". *Reports on Progress in Physics* **1948**, 12, 163-184. h) Dewald, J. F., "A Theory of the Kinetics of Formation of Anode Films at High Fields". *Journal of the Electrochemical Society* **1955**, 102, (1), 1-6. i) Dewald, J. F., "The Effects of Space Charge on the Rate of Formation of Anode Films". *Acta Metallurgica* **1954**, 2, (2), 340-341. j) Vermilyea, D. A., "On the Mechanism of Electrolytic Rectification". *Journal of Applied Physics* **1956**, 27, (8), 963-964. k) Sasaki, Y., P-I-N "Junction in the Anodic Oxide Film of Tantalum. *Journal of Physics and Chemistry of Solids* **1960**, 13, (3-4), 177-186. l) Vermilyea, D. A., "Stresses in Anodic Films". *Journal of the Electrochemical Society* **1963**, 110, (4), 345-346. m) Bradhurst, D. H.; Leach, J. S. L., "Stresses in Anodic Films". *Journal of the Electrochemical Society* **1963**, 110, (12), 1289-1291. n) Hunter, M. S.; Robinson, D. L., "Revealing the Subgrain Structure of Aluminum". *Transactions of the American Institute of Mining and Metallurgical Engineers* **1953**, 197, (5), 717-722. o) Paolini, G.; Masoero, M.; Sacchi, F.; Paganelli, M., "An Investigation of Porous Anodic Oxide Films on Aluminum by Comparative Adsorption Gravimetric and Electronoptical Measurements". *Journal of the Electrochemical Society* **1965**, 112, (1) p) Pinner, R.; Hunter, M. S.; Fowle, P., "Factors Affecting the Formation of Anodic Oxide Coatings". *Journal of the Electrochemical Society* **1955**, 102, (6), 359-360. q) Hoar, T. P.; Mott, N. F., "A Mechanism for the Formation of Porous Anodic Oxide Films on Aluminium". *Journal of Physics and Chemistry of Solids* **1959**, 9, (2), 97-99. r) Davies, J. A.; Domeij, B.; Pringle, J. P. S.; Brown, F., "Migration of Metal and Oxygen During Anodic Film Formation". *Journal of the Electrochemical Society* **1965**, 112, (7), 675 s) Thompson, G. E.; Furneaux, R. C.; Wood, G. C.; Richardson, J. A.; Goode, J. S., "Nucleation and Growth of Porous Anodic Films on Aluminum". *Nature* **1978**, 272, (5652), 433-435. t) Thompson, G. E.; Shimizu, K.; Wood, G. C., "Observation of Flaws in Anodic Films on Aluminum". *Nature* **1980**, 286, (5772), 471-472. u) Thompson, G. E.; Wood, G. C., "Porous Anodic Film Formation on Aluminum." *Nature* **1981**, 290, (5803), 230-232. v) Zhang, L.; Macdonald, D. D.; Sikora, E.; Sikora, J., "On the kinetics of growth of anodic oxide films." *Journal of the Electrochemical Society* **1998**, 145, (3), 898-905. w) Jessensky, O.; Muller, F.; Gosele, U., "Self-organized formation of hexagonal pore structures in anodic alumina". *Journal of the Electrochemical Society* **1998**, 145, (11), 3735-3740. x) Masuda, H.; Asoh, H.; Watanabe, M.; Nishio, K.; Nakao, M.; Tamamura, T., "Square and triangular nanohole array architectures in anodic alumina". *Advanced Materials* **2001**, 13, (3), 189-192. y) Masuda, H.; Yamada, H.; Satoh, M.; Asoh, H.; Nakao, M.; Tamamura,

- T., "Highly ordered nanochannel-array architecture in anodic alumina". *Applied Physics Letters* **1997**, 71, (19), 2770-2772.
21. Dorsey, G. A., "Characterization of Anodic Aluminas .3. Barrier Layer Composition and Structure". *Journal of the Electrochemical Society* **1966**, 113, (3), 284-
22. J. Choi, Y. Luo, "Perfect two-dimensional porous alumina photonic crystals with duplex oxide layers", *J. Appl. Phys.* **2003** 94.
23. Furneaux, R. C.; Rigby, W. R.; Davidson, A. P., "The Formation of Controlled-Porosity Membranes from Anodically Oxidized Aluminum". *Nature* **1989**, 337, (6203), 147-149.
24. Nielsch, K.; Muller, F.; Li, A. P.; Gosele, U., "Uniform nickel deposition into ordered alumina pores by pulsed electrodeposition". *Advanced Materials* **2000**, 12, (8), 582-586.
25. Pinner, R.; Hunter, M. S.; Fowle, P., "Factors Affecting the Formation of Anodic Oxide Coatings". *Journal of the Electrochemical Society* **1955**, 102, (6), 359-360
26. a) J. Gruberger and E. Gileadi, *Electrochim. Acta.* 31, 1531 (**1986**). b) W. Sautter, G. Ibe and J. Meier, *Aluminium* 50, 143 (**1974**).
27. Li, A. P.; Muller, F.; Birner, A.; Nielsch, K.; Gosele, U., "Fabrication and microstructuring of hexagonally ordered two-dimensional nanopore arrays in anodic alumina". *Advanced Materials* **1999**, 11, (6), 483-+.
28. J. Choi, Y. Luo, R. B. Wehrspohn, R. Hillebrand, J. Schilling and U. Gösele, *J. Appl. Phys.* 94, 4757 (**2003**).
29. T. Gao, G. Meng and L. Zhang, "Blue luminescence in porous anodic alumina, the role of the oxalic impurities". *J. Phys. Condens. Matter* 15 **2003**
30. J. J. M. Halls, K. Pichler, R. H. Friend, S. C. Moratti and A. B. Holmes, *Appl. Phys. Lett.* 68, 3120 (**1996**). b) T. Stübinger and W. Brütting, *J. Appl. Phys.* 90, 3632 (**2001**).
31. D. G. Lidzey, S. F. Alvarado, P. F. Seidler, S. F. Bleyer and D. D. C. Bradley, *Appl. Phys. Lett.* 71, 2008 (**1997**).
32. "Handbook of Chemistry and Physics, 72nd edition", Boston: CRC Press (**1991-1992** ed.)
33. CMP Methods, MRS Bulletin **2004** 11
34. Personal Communication from T. Maidron, LETI, 2006.
35. "Time-resolved transport in conjugated polymers". Pinner, D. J.; Friend, R. H.; Tessler, N., *Synthetic Metals* **2000**, 111, 257-261.
36. Yamamoto, H.; Kasajima, H.; Yokoyama, W.; Sasabe, H.; Adachi, C., "Extremely-high-density carrier injection and transport over 12000 A/cm(2) into organic thin films". *Applied Physics Letters* **2005**, 86, (8).
37. Tessler, N.; Harrison, N. T.; Friend, R. H., "High peak brightness polymer light-emitting diodes". *Advanced Materials* **1998**, 10, (1), 64-+. b) Nakanotani, H.; Oyamada, T.; Kawamura, Y.; Sasabe, H.; Adachi, C., "Injection and transport of high current density over 1000A/cm(2) in organic light emitting diodes under pulse excitation". *Japanese Journal of Applied Physics Part 1-Regular Papers Short Notes & Review Papers* **2005**, 44, (6A), 3659-3662.
38. Kozlov, V. G.; Burrows, P. E.; Parthasarathy, G.; Forrest, S. R., "Optical properties of molecular organic semiconductor thin films under intense electrical excitation". *Applied Physics Letters* **1999**, 74, (8), 1057-1059.
39. Kwong, R. C.; Nugent, M. R.; Michalski, L.; Ngo, T.; Rajan, K.; Tung, Y. J.; Weaver, M. S.; Zhou, T. X.; Hack, M.; Thompson, M. E.; Forrest, S. R.; Brown, J. J., "High operational stability of electrophosphorescent devices". *Applied Physics Letters*
40. Alvarado, S. F.; Riess, W.; Seidler, P. F.; Strohriegl, P., "STM-induced luminescence study of poly(p-phenylenevinylene) by conversion under ultraclean conditions". *Physical Review B* **1997**, 56, (3), 1269-1278. f) Suganuma, N.; Adachi, C.; Koyama, T.; Taniguchi, Y.; Shiraishi, H., "A 200nm x 2mm array of organic light-emitting diodes and their anisotropic electroluminescence". *Applied Physics Letters* **1999**, 74, (9), 1206-1208. g) S. Noach, E. Z. Faraggi, G. Cohen, Y. Avny, R. Neumann, D. Davidov and A. Lewis, *Appl. Phys. Lett.* 69, 3650 (**1996**). h) N. Suganuma, C. Adachi, T. Koyama, Y. Taniguchi and H. Shiraishi, *Appl. Phys. Lett.* 74, 1206 (**1999**). i) Granstrom, M.; Berggren, M.; Inganäs, O., "Micrometer-Sized and Nanometer-Sized Polymeric Light-Emitting-Diodes". *Science* **1995**, 267, (5203), 1479-1481. j) Alvarado, S. F.; Riess, W.; Seidler, P. F.; Strohriegl, P., "STM-induced luminescence study of poly(p-phenylenevinylene) by conversion under ultraclean conditions". *Physical Review B* **1997**, 56, (3), 1269-1278. k) Yamamoto, H.; Wilkinson, J.; Long, J. P.; Bussman, K.; Christodoulides, J. A.; Kafafi, Z. H., "Nanoscale organic light-emitting diodes". *Nano Letters* **2005**, 5, (12), 2485-2488. l) Kao, P. C.; Chu, S. Y.; Zhan, C. Y.; Hsu, L. C.; Liao, W. C., "Fabrication of organic light-emitting devices on flexible

- substrates using a combined roller imprinting and photolithography-patterning technique". *Journal of Vacuum Science & Technology B* **2006**, 24, (3), 1278-1282 m) Suh, D.; Lee, H. H., "Sub-100 nm organic light-emitting diodes patterned with room temperature imprint lithography". *Journal of Vacuum Science & Technology B* **2004**, 22, (3), 1123-1126. n) Veinot, J. G. C.; Yan, H.; Smith, S. M.; Cui, J.; Huang, Q. L.; Marks, T. J., "Fabrication and properties of organic light-emitting "nanodiode" arrays". *Nano Letters* **2002**, 2, (4), 333-335. o) Schaller, R. D.; Lee, L. F.; Johnson, J. C.; Haber, L. H.; Saykally, R. J.; Viececi, J.; Benjamin, I.; Nguyen,
- 41 Time-resolved transport in conjugated polymers. Pinner, D. J.; Friend, R. H.; Tessler, N., *Synthetic Metals* **2000**, 111, 257-261.
- 42 T. Dobbertin, M. Kroeger, D. Heithecker, D. Schneider, D. Metzdorf, H. Neuner, E. Becker, H.-H. Johannes and W. Kowalsky, *Appl. Phys. Lett.* 82, 284 (**2003**)
- 43 Pauchard, M.; Swensen, J.; Moses, D.; Heeger, A. J.; Perzon, E.; Andersson, M. R., "Light amplification in polymer field effect transistor structures". *Journal of Applied Physics* **2003**, 94, (5), 3543-3548. b) Swensen, J. S.; Soci, C.; Heeger, A. J., "Light emission from an ambipolar semiconducting polymer field-effect transistor". *Applied Physics Letters* **2005**, 87, (25) c) Swensen, J.; Moses, D.; Heeger, A. J., "Light emission in the channel region of a polymer thin-film transistor fabricated with gold and aluminum for the source and drain electrodes". *Synthetic Metals* **2005**, 153, (1-3), 53-56.
44. M. Reufer, S. Riechel, "Low-threshold polymeric distributed feedback lasers with metallic contacts", *Appl. Phys. Lett.* **2004** 84
45. M. Reufer, J. Feldmann, "Amplified spontaneous emission in an organic semiconductor multilayer waveguide structure including a highly conductive transparent electrode". *Appl. Phys. Lett.* **2005** 86
46. M. Reufer, J. Feldmann, "Amplified spontaneous emission in an organic semiconductor multilayer waveguide structure including a highly conductive transparent electrode". *Appl. Phys. Lett.* **2005** 86
47. J. Stehr, J. Crewett, *Adv. Mat.*, **2003**, 15
- 48 Dr. S. Parker, IBM, TCD Physics seminar 2006
- 49 Steinhart, M.; Wendorff, J. H.; Greiner, A.; Wehrspohn, R. B.; Nielsch, K.; Schilling, J.; Choi, J.; Gosele, U., "Polymer nanotubes by wetting of ordered porous templates". *Science* **2002**, 296, (5575), 1997-1997.
50. "Polymer-C60 transfer" P. Lane et al. *Phys.Rev.B.* 2005
- 51 Scharber, M. C.; Wuhlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. L., "Design rules for donors in bulk-heterojunction solar cells - Towards 10 % energy-conversion efficiency." *Advanced Materials* 2006, 18, (6), 789
52. Gershman, E.; Drori, T.; Herzog, C.; Eichen, Y.; Ehrenfreund, E., "Recombination kinetics of photoexcitations in films of MEH-PPV and MEH-PPV/C-60 mixtures".
53. Y. Wu, G. Cheng, "Composite mesostructures by nano-confinement", *Nature Mat.* **2004** 3.

Chapter 6

6 CONCLUSIONS

Four MEH-PPV light emitting polymers were used as the emissive layer in polymer light emitting diodes (PLEDs). Although single layer devices were very inefficient from an electroluminescence quantum yield and a power point of view, good efficiencies were achieved for double layer devices using an electron transporting layer. Devices of this structure fabricated using the light-emitting copolymers TPD-MEH PPV and TPA-MEH PPV resulted in external quantum efficiencies of 8.6×10^{-2} and 2.7×10^{-2} with peak electroluminescence wavelengths of 545.6 and 537.8 nm. OLEDs made using the light emitting homo- and ter-polymers MEHPPV and TPD-MEH M3EH PPV resulted in orange and red electroluminescence respectively. These materials had external quantum efficiencies of 6.7×10^{-3} and 1.2×10^{-1} with emission maxima at 576.7 and 584 nm, respectively. The electron and hole mobilities for these materials were generally quite low, being of the order of 7.0×10^{-16} V cm² s⁻¹ and 8.5×10^{-12} V cm² s⁻¹ respectively. The difference in magnitude between electron and hole mobilities was less for MEH-PPV than for the other MEH-PPV materials. Single carrier devices made using these materials indicate that current flow in these devices is best described by space charge conduction in the presence of an exponential energy distribution of traps with a characteristic trap energy ranging between .099 and .232 eV at 295K. Two new PFO-type materials were also used to make OLEDs. A turquoise coloured LED was made using the copolymer PFO-PPV which had an external efficiency of 0.1 % with an emission maximum of 514 nm. A multilayer blue LED with an emission maximum of 405 nm was made using the small molecule *9,9-bis[4-(diphenylamino)-phenyl]fluorene*. Although this device had a low operating voltage of 5 V, it proved to be very unstable even under high vacuum test conditions. The low levels of EL observed from this device are deemed to be due to transfer to triplet oxygen states which are non-radiative.

Suggested future work for this area would be to make blends of the MEHPPV materials with electron transporting materials and to use them as emissive layers in devices. It is also important to carry out, photo-induced absorption measurements in order to reveal how the excited state absorption varies in the solid state for the range of MEH-PPV chemical structures studied here. This would also be of interest for the green PFO-PPV copolymer and the blue small-molecule where such measurements would help to elucidate the origin of the rapid degradation of these materials during device testing.

In the second section of the work a new device structure was designed and successfully used to produce a PLED. This structure involved using TPD MEH PPV as the emissive layer in a single layer LED with a nanodot array anode. Two types of nanodot array were produced. The first was produced by using an alternating current to electro-deposit copper into a porous alumina membrane and the second using pulsed-electro-deposition to fill a porous alumina membrane with nickel. The LED made with a nickel nano-dot array exhibit greater rectification than a LED made using a copper array. This is due to the work function of nickel being closer matched to the polymer ionization potential. Both array type -LEDs exhibited similar electroluminescence features to those seen for a conventional sheet anode LED made with the same emissive layer. Both array type devices were capable of operating at higher current densities (10^5 A/m^2) than similar sheet-anode LEDs (10^4 A/m^2). This is because there is improved heat sinking in the array devices as the thermal resistances of the nickel-filled and copper-filled alumina anodes, which act as substrates for the LEDs, are lower than that of the glass substrate used for sheet-anode LEDs. Although current densities achieved are among the highest reported for direct current driving, it is possible that if high mobility materials were used, current densities in excess of 10^6 A/m^2 could be achievable with similar device structures.

Suggested future work for the nanodot-array devices includes further optimization of these structures via barrier layer reduction and the use of multilayer organic light emitting diode structures with a good top-emission cathode for efficient light outcoupling. Furthermore, it would be interesting to investigate the performance of optimised structures from a current density and brightness point of view by using a short pulse, low duty cycle, driving scheme. The issue of joule heating in devices is still a major problem affecting device lifetime is a barrier to achieving the high current densities that would be required for an electrically pumped organic laser. The array-electrode structures demonstrated a way of increasing the current densities sustainable in organic light emitting diodes.

Publications

“Hybrid Light-emitting Polymer Device Fabricated on a Metallic Nanowire Array”: **A.E. Strevens**, A. Drury, S.M. Lipson, W.J. Blau and H.H. Hörhold. *Applied Physics Letters* **86**, 143503 (2005).

“Synthesis, Characterization, and Optoelectronic Properties of a Novel Polyfluorene/poly(p-phenylenevinylene) Copolymer”: Y. Chen, Y. Araki, J. Doyle, **A.E. Strevens**, O. Ito, and W.J. Blau. *Chemistry of Materials* **17**, 1661 (2005).

“Hole Blocking in Carbon Nanotube-Polymer Composite Organic Light Emitting Diodes Based on Poly (m -phenylene vinylene-co-2, 5-dioctoxy- p-phenylene vinylene)” H.S. Woo, R. Czerw, S. Webster, D.L. Carroll, J. Ballato, **A.E. Strevens**, D. O’Brien and W.J. Blau. *Applied Physics Letters* **77**, 1393 (2000).

“A Composite from Poly(m-phenylenevinylene-co-2,5-dioctoxy-p-phenylenevinylene) and Carbon Nanotubes: A Novel Material for Molecular Optoelectronics” S. Curran, P.M. Ajayan, W. Blau, D.L. Carroll, J. Coleman, A. Dalton, A.P. Davey, B. McCarthy, and **A. Strevens**. *Advanced Materials*, **10**, 1091 (1998).

Conference Proceedings

“Nanowire Array Electrode Structure for Organic Light-emitting Diodes” **A.E. Strevens**, M. Kröll, S. Lipson, J.N. Coleman, W.J. Blau. OPTO-Ireland 2002; Optics and Photonics Technologies and Applications: Optoelectronic and Photonic Devices, *Proceedings SPIE (The International Society for Optical Engineering)*, **4876**, 168 (2003).

“Preparation and Nonlinear Optical Properties of Phthalocyanine Nanocrystals” C. Nitschke, S.M. O’Flaherty, M. Kroell, **A.E. Strevens**, S. Maier, M.G. Ruether, W.J. Blau. OPTO-Ireland, Galway, 2002: Organic Photonic Materials and Devices V; *Proceedings of SPIE*, **4991**, 124 (2003).

“Substrate Mediated Ordering in PmPV Thin Films” B. McCarthy, R. Czerw, **A.E. Strevens**, D.L. Carroll, and W. Blau. MRS Fall Meeting, Boston, U.S.A., 1999: Electrical, Optical, and Magnetic Properties of Organic Solid State Materials V, *Proceedings of MRS (The Materials Research Society)*, **598** (2000).