C|D|T

Polymer-OLED Technology:
Improvements in Device and Materials Performance

Jeremy Burroughes
CTO

FPD International 2004 -Displaying the future-

October 2004

- Introduction
- Understanding PLEDs
- Tri Layer PLEDs
- Singlet:Triplet Ratio
- Conclusions

New or Modified

Introduction

Understanding PLEDs

Tri Layer PLEDs

Singlet:Triplet Ratio

Conclusions

Polymer LED Devices

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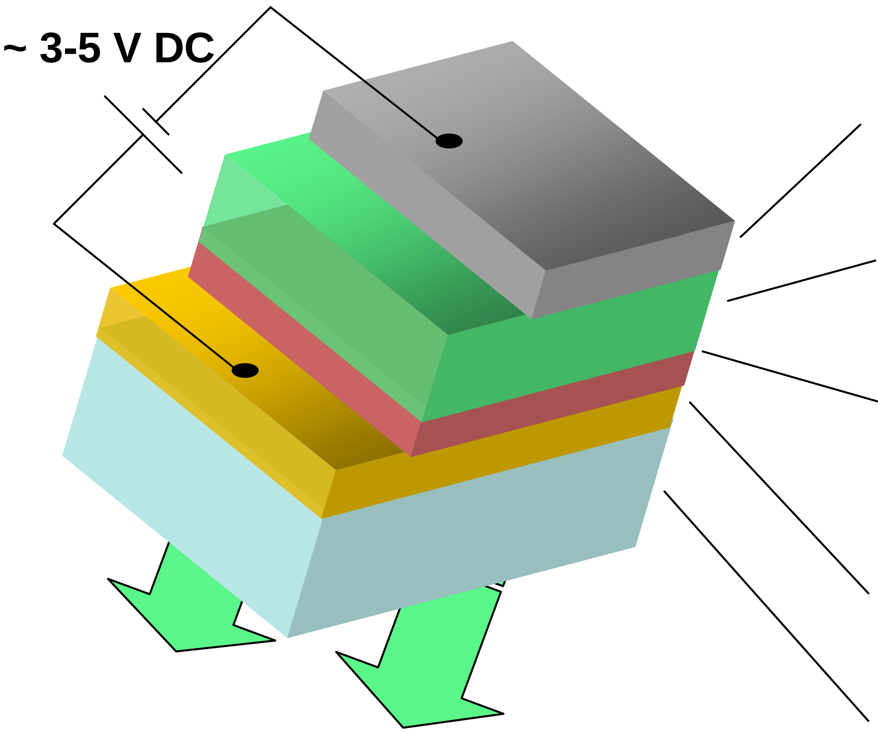
- Simple device structure
- Uniform, area Emitter
- Flexible devices possible



Low workfunction metallic cathode

Thin (<100 nm) emissive layer of polymer (LEP)

Transparent hole transporting layer (PEDOT/PSS) (70 – 200 nm)

Transparent anode (e.g. ITO)

Glass/Plastic substrate

PLED Materials and Fabrication

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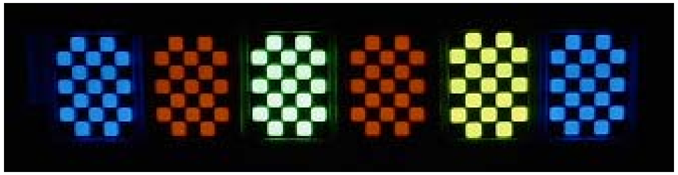
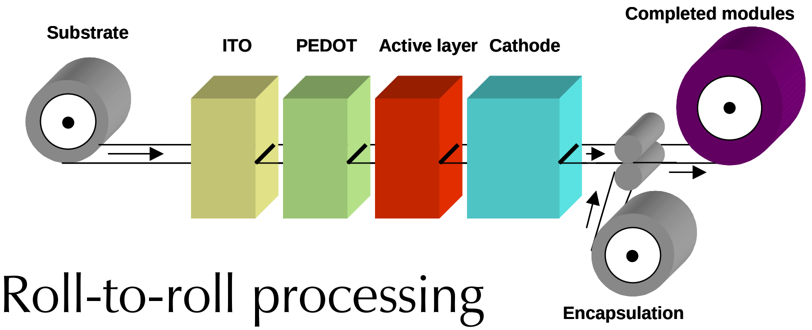
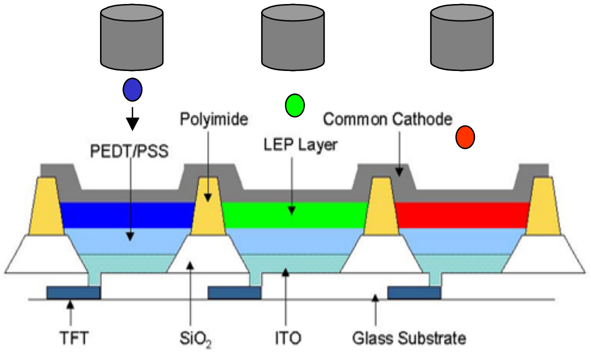
- Polymer semiconductors are solution processable materials
- Colour tuning through molecular design
- Wide range of deposition processes feasible
- Low manufacturing and plant cost
- Efficient materials utilisation
- Compatible with flexible substrates





Roll-to-roll processing

Ink-Jet Printing



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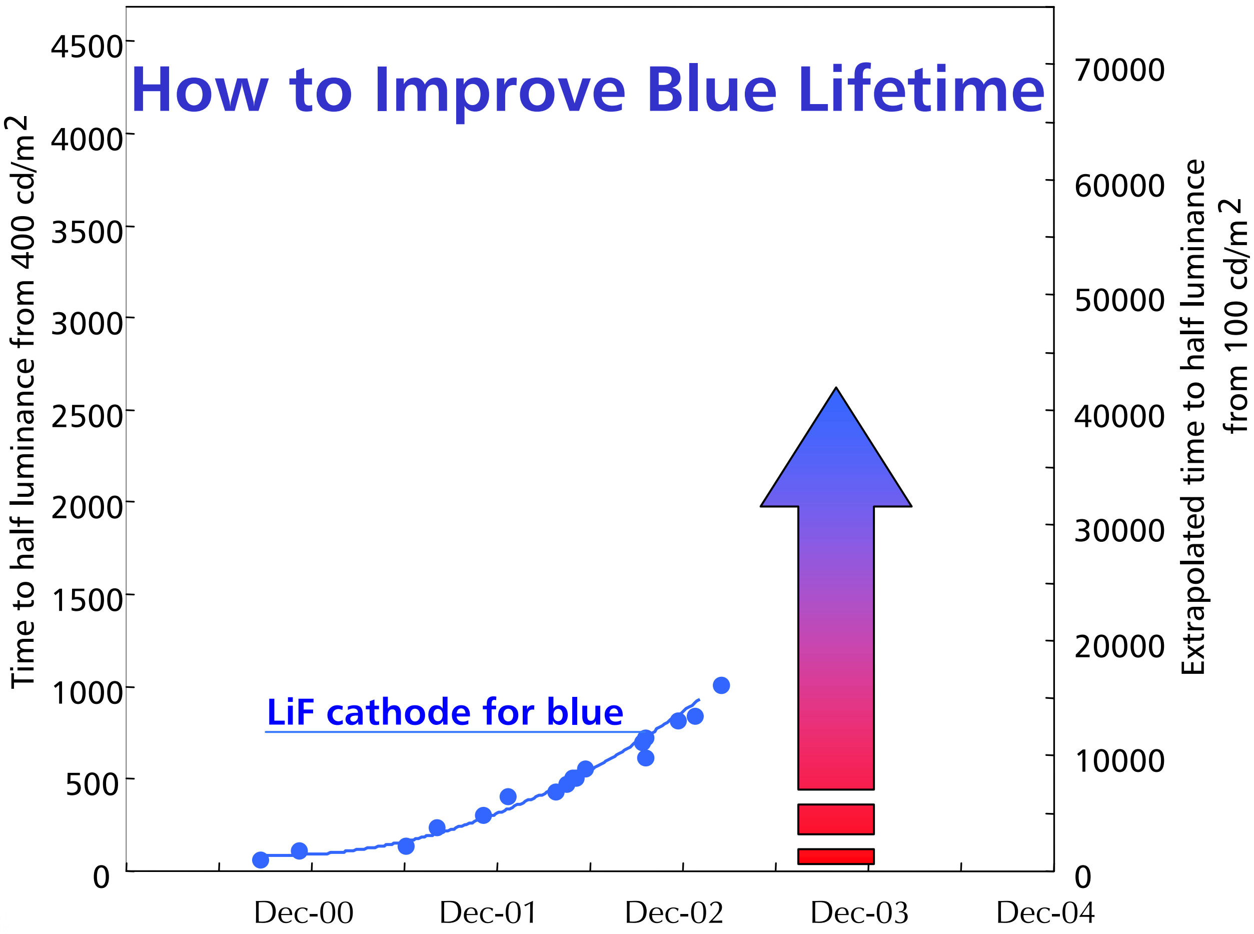
- Introduction
- **Understanding PLEDs**
- Tri Layer PLEDs
- Singlet:Triplet Ratio
- Conclusions

Blue Lifetime Progress



Basic Device Structure

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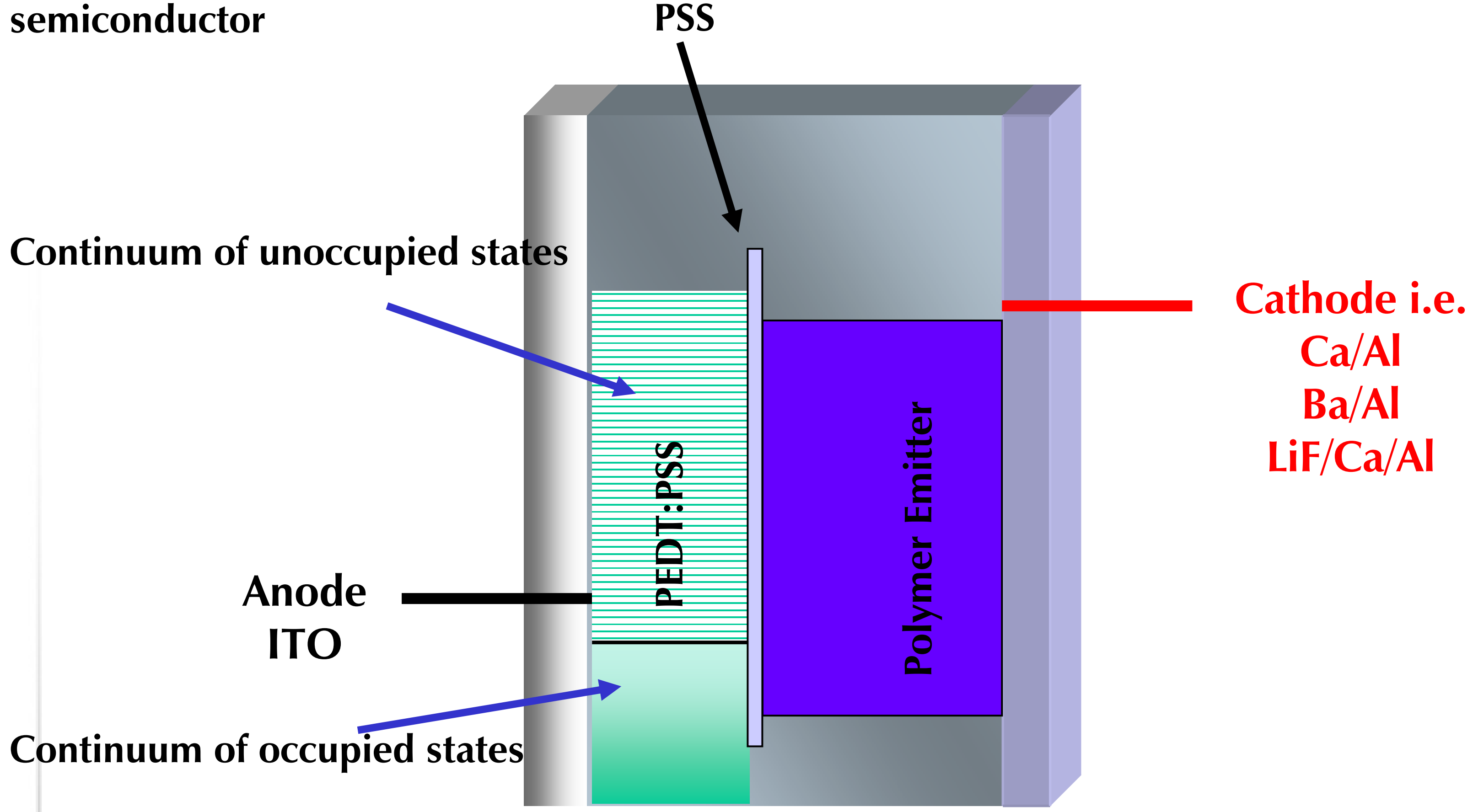
Note: PEDT:PSS is disordered metal with ~ 0.3 charges per PEDT unit, it is not a semiconductor



Neutron Scattering on deuterated PEDT:PSS shows that the surface is PSS rich, Circa 5 - 10 nm thick

Ideal Device Operation

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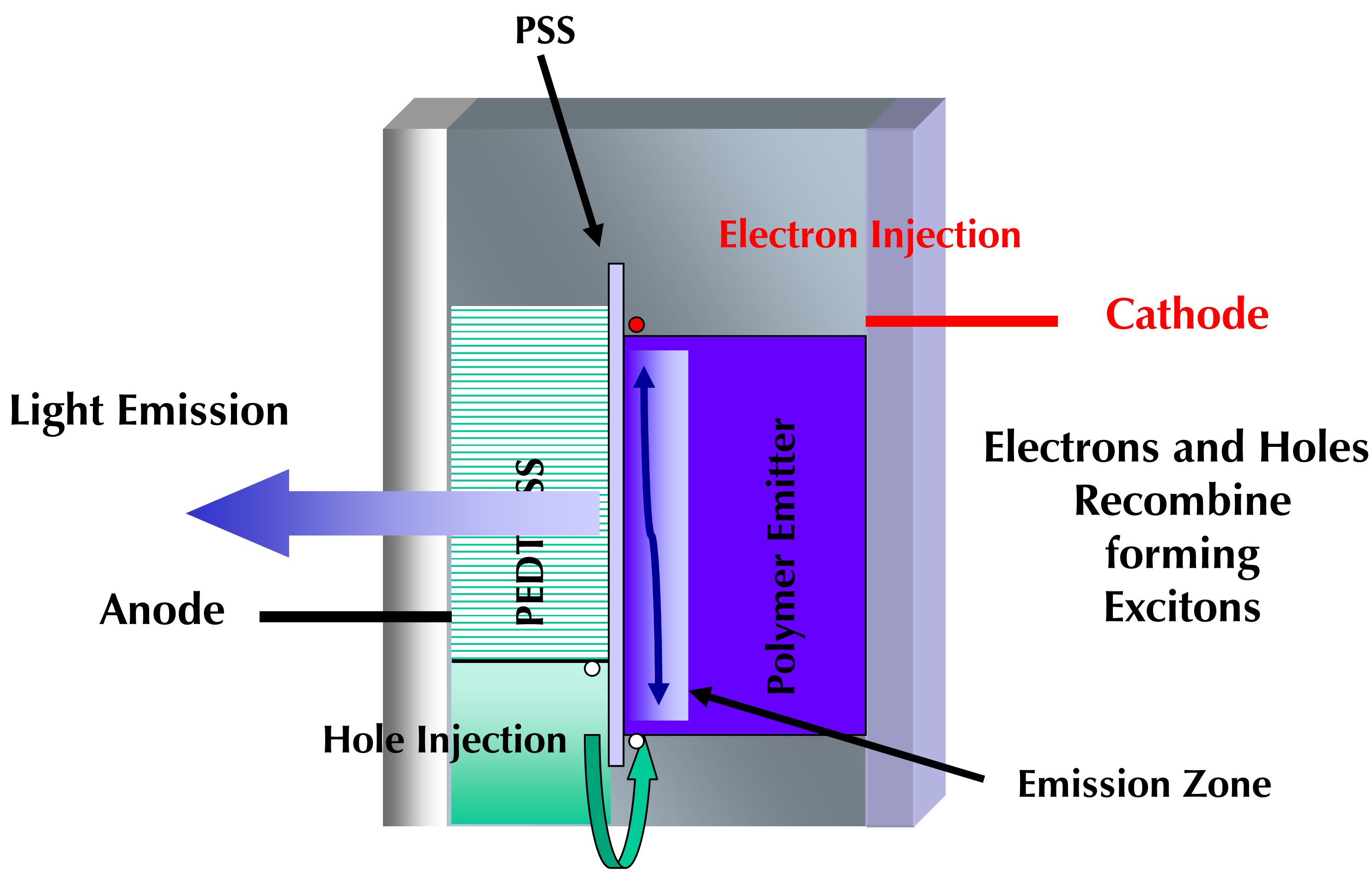

Holes are injected into the LEP Layer

Device Reverse Engineering

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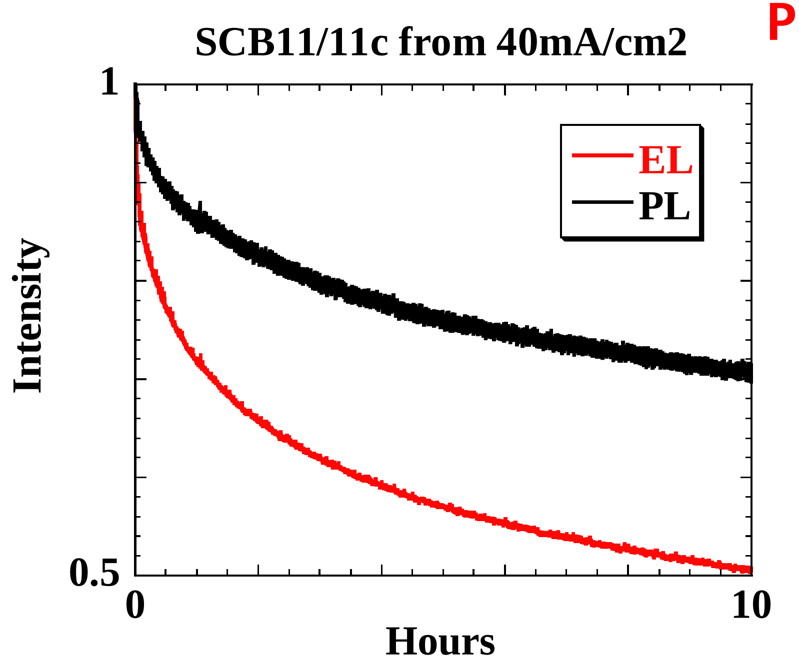
- CDT has developed techniques for reverse engineering PLED devices – layer by layer

  - The cathode is removed by an acid wash
    - Exposing the LEP surface
  - The soluble LEP is removed by solvent wash
    - Exposing PEDT:PSS surface for un-driven devices
    - Exposing insoluble LEP for driven devices
  - Insoluble and soluble LEP can be lifted off by dissolving PEDT
    - Thus LEP can be examined separately

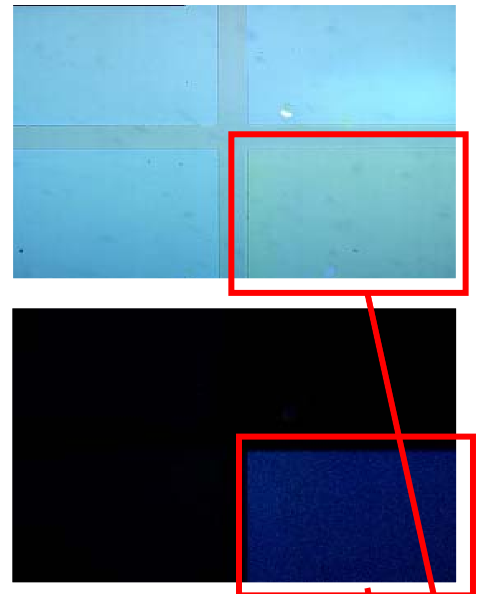
  - Reverse Engineering Helps CDT Understand Degradation

New or Modified

PL decay and insoluble layer



Photoluminescent Images



After acid rinse LEP Exposed

After solvent rinse PEDT exposed for un-driven devices

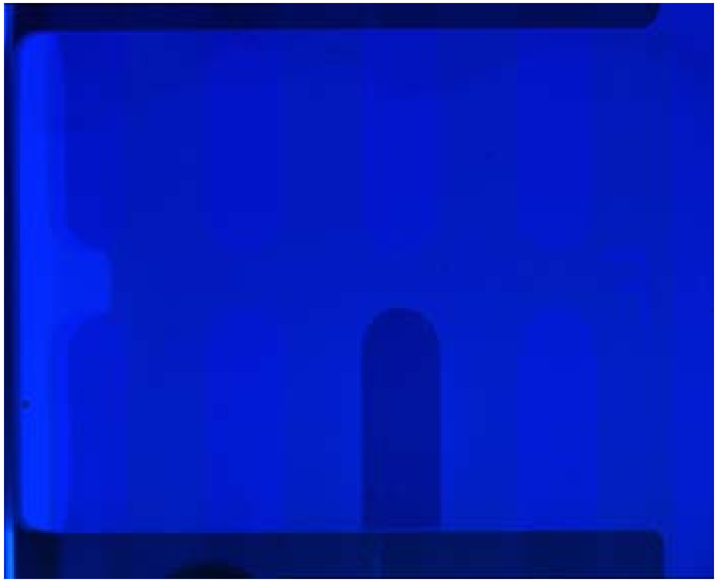
Driven Pixel

- PL intensity is reduced with driving
- Insoluble layer remains after cathode removal and solvent rinse

Photoluminescent Image of Driven and un-Driven Devices

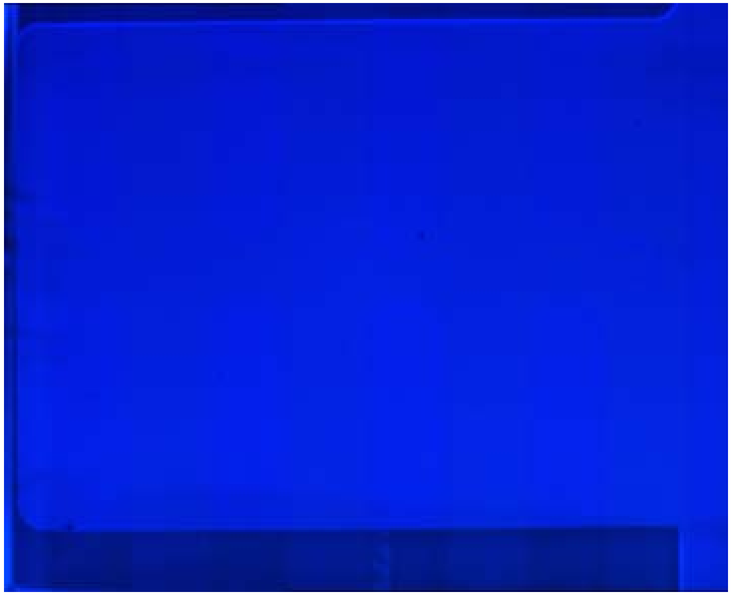
SCB bipolar

Pixel 2 - 960hrs at 4mA/cm2



SCB hole only device

Pixel 2 - 960hrs at 4mA/cm2 Pixel 3 - 290hrs at 32mA/cm2



- PL does not seem to decay in hole only devices despite 5 times charge fluence
- Results suggest no PL decay in electron only devices either

Insolable layer and EL decay

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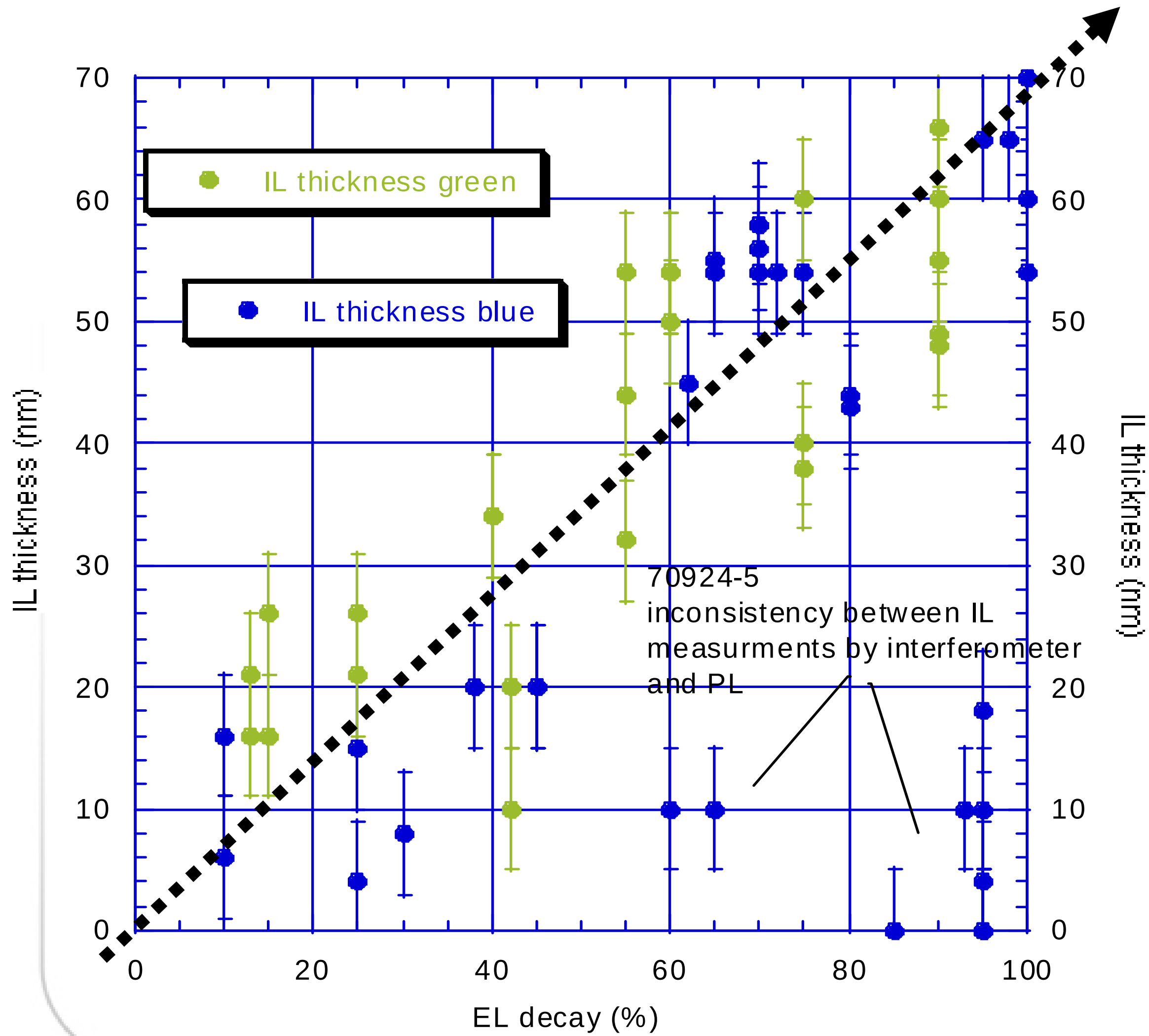

Results so far suggest insoluble layer thickness correlates with EL decay, but not with PL decay

Insoluble layer properties

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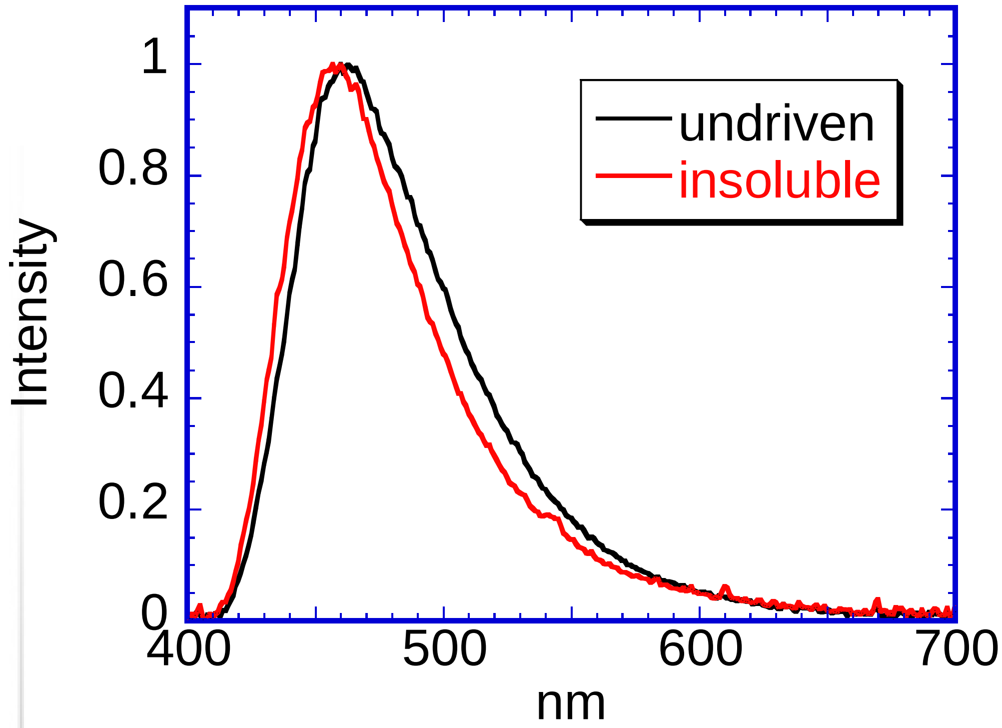
PL spectrum of Insoluble SCB11



- Lower PL yield than pristine films
- Spectral shifts – blue shift often observed, but looks like could be an artefact
- Solubility – insoluble in THF, MeOH, acetone, xylene – heated for 30mins

Time Resolved Spectroscopy

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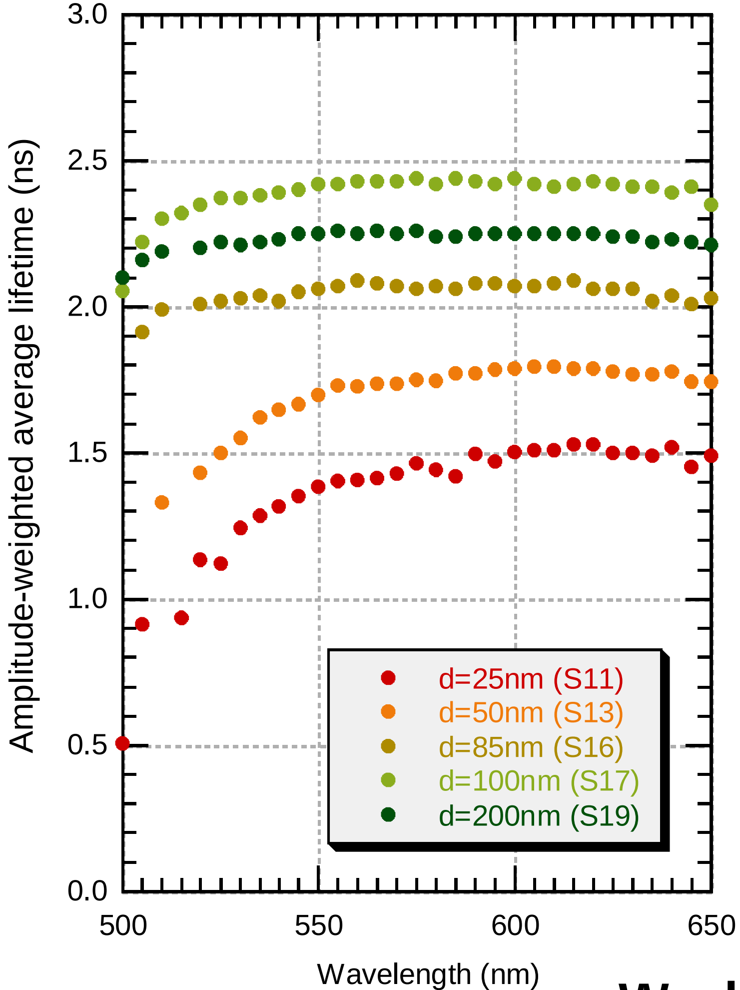

Test Structure:
PEDT:PSS/Green LEP
Where LEP Thickness is 25 – 200 nm

Measure Exciton Lifetime

Observation:
Shorter Lifetime for thin LEP
I.E. PEDT Quenches Excitons

Work done at the Cavendish Laboratory

Electrical modelling: Blue Device

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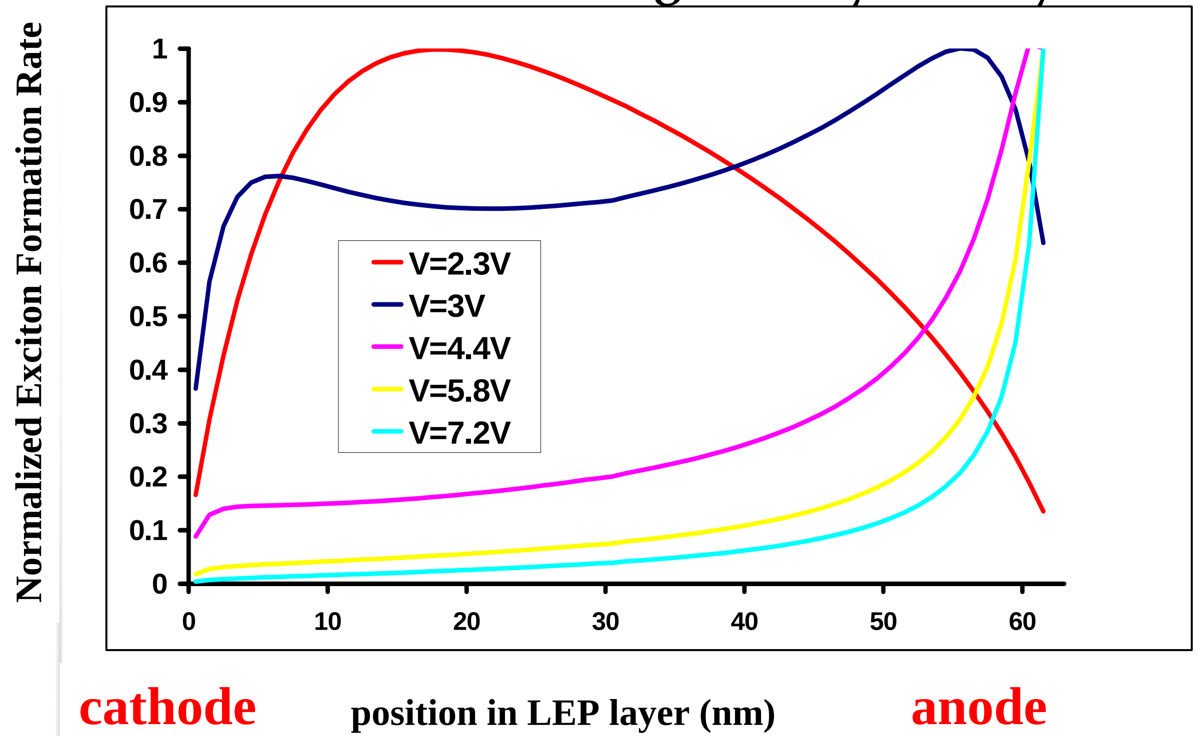
- Integrated with experiment – fit device I-V characteristics
- Determine injection mechanisms, charge balance & exciton formation zone profile
- As a function of device geometry and layer materials



At low voltage $m_h > m_e$
RZ towards cathode

$V > 2.8$, $m_e > m_h$
RZ towards anode

@ Operating Point exciton formation zone adjacent to PEDT

Possible Evidence for Electron Damage

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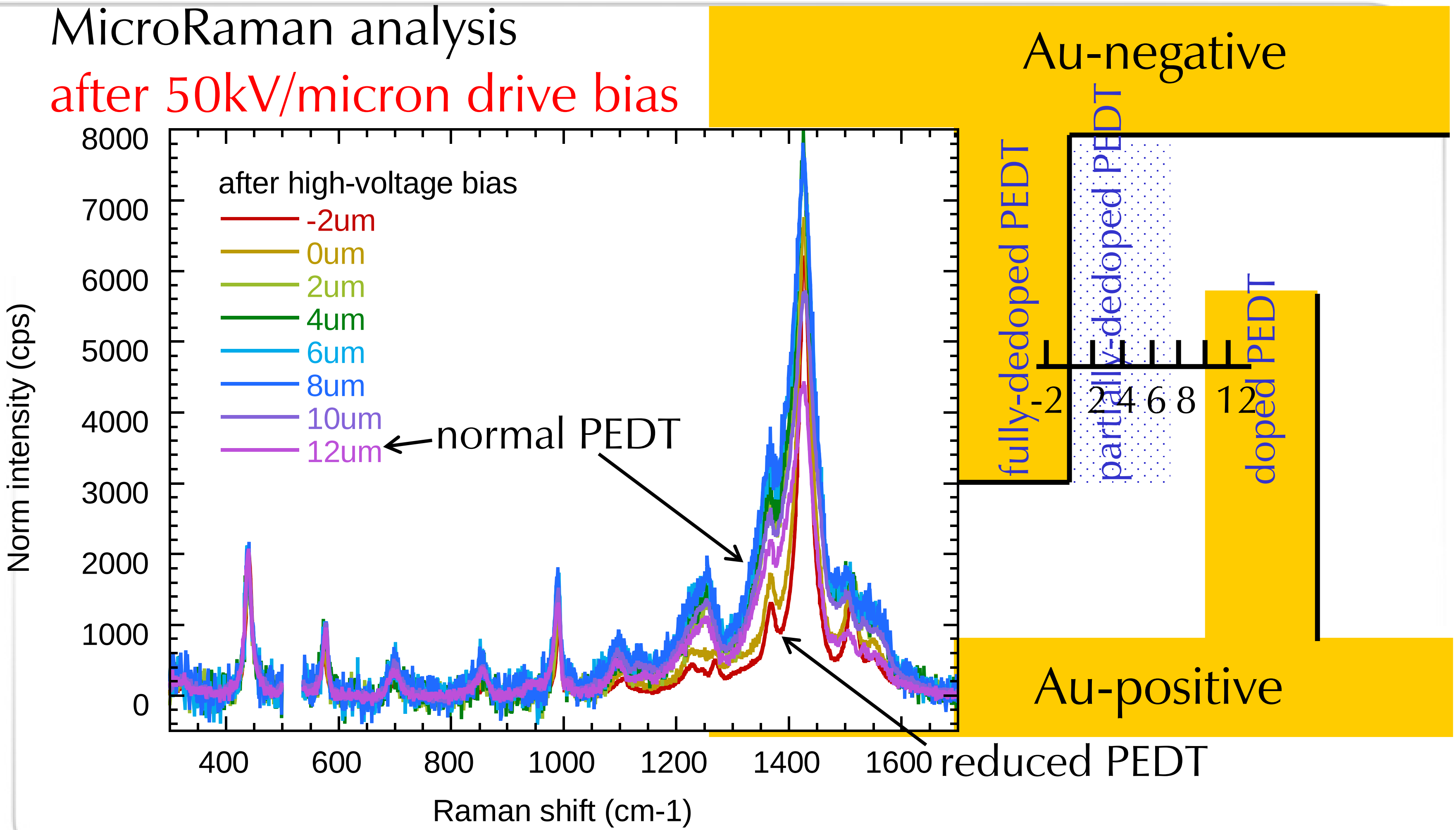
MicroRaman analysis

after 50kV/micron drive bias



Work done at the Cavendish Laboratory

Summary

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- Insoluble LEP layer forms with driving of device
  - Thickness correlates with EL decay very well
  - Growth from PEDT:LEP interface
- Holes show no evidence of degradation
  - LEP or PEDT
- Electrons show no evidence of degradation in LEP
- Insignificant PL spectrum change
- Exciton Formation near PEDT:LEP Interface
  - Therefore Electron Accumulation
- Significant Exciton Quenching at PEDT:LEP Interface
- Evidence for change in PEDT with Electron Injection

New or Modified

Proposed Device Decay Mechanism

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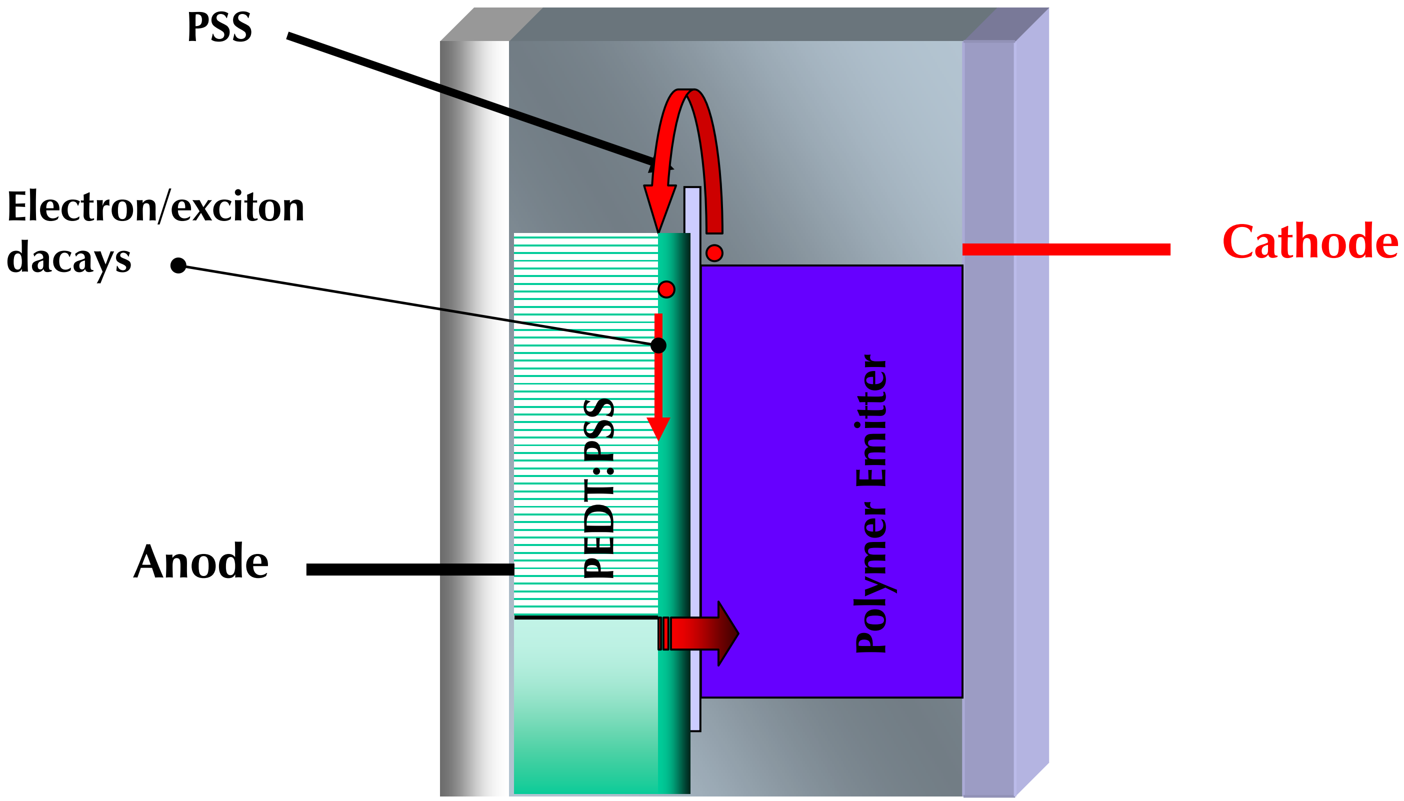
Some electrons/excitons injected into PEDT:PSS



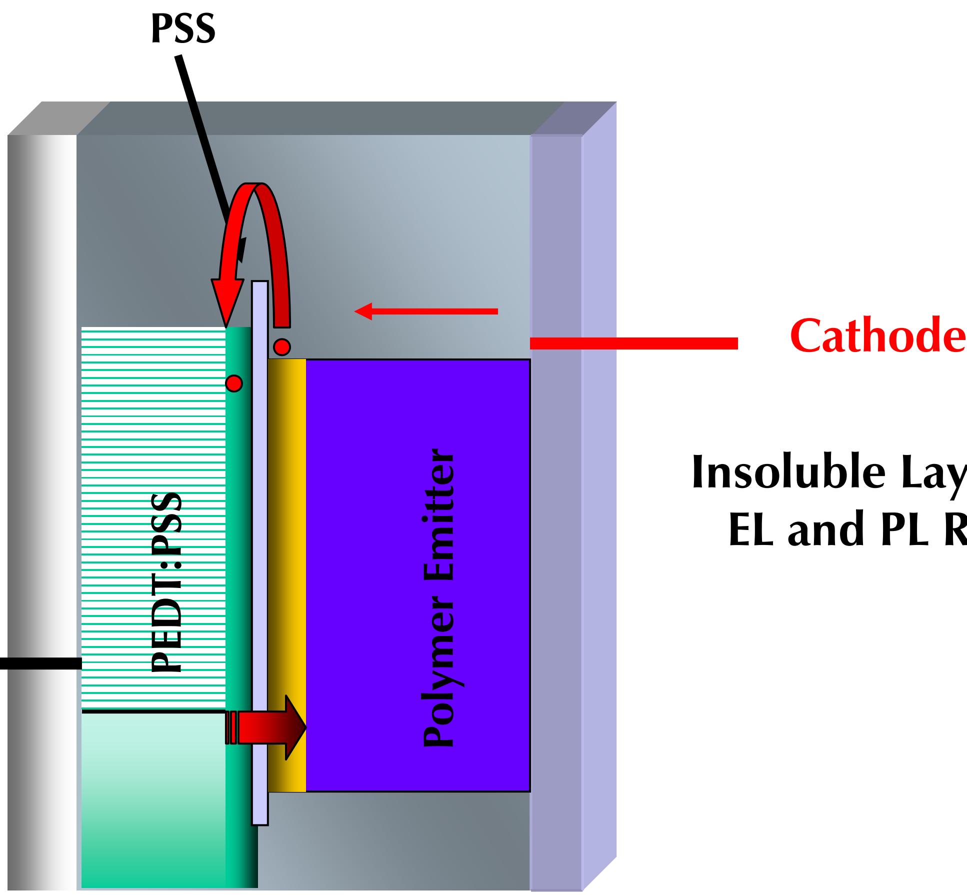
Resulting in damage to PEDT:PSS
Residues diffuse into the LEP Layer

Device Decay Mechanism

C|D|T

Some electrons/excitons injected into PEDT:PSS

As time passes insoluble Layer keeps on growing



Insoluble Layer Grows
EL and PL Reduced

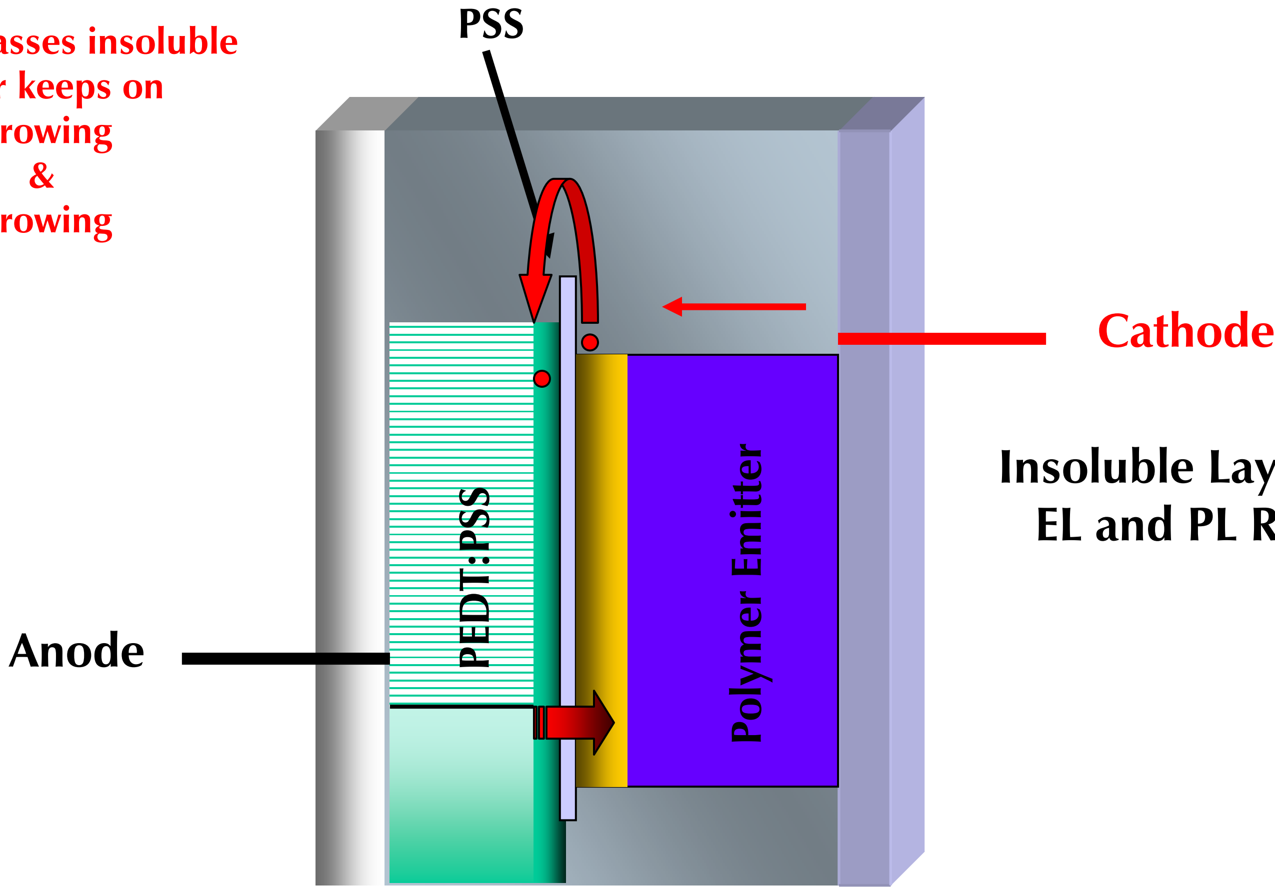
Resulting in damage to PEDT
Residues diffuse into the LEP Layer

Device Decay Mechanism

C|D|T

Some electrons/excitons injected into PEDT:PSS

As time passes insoluble Layer keeps on Growing & Growing



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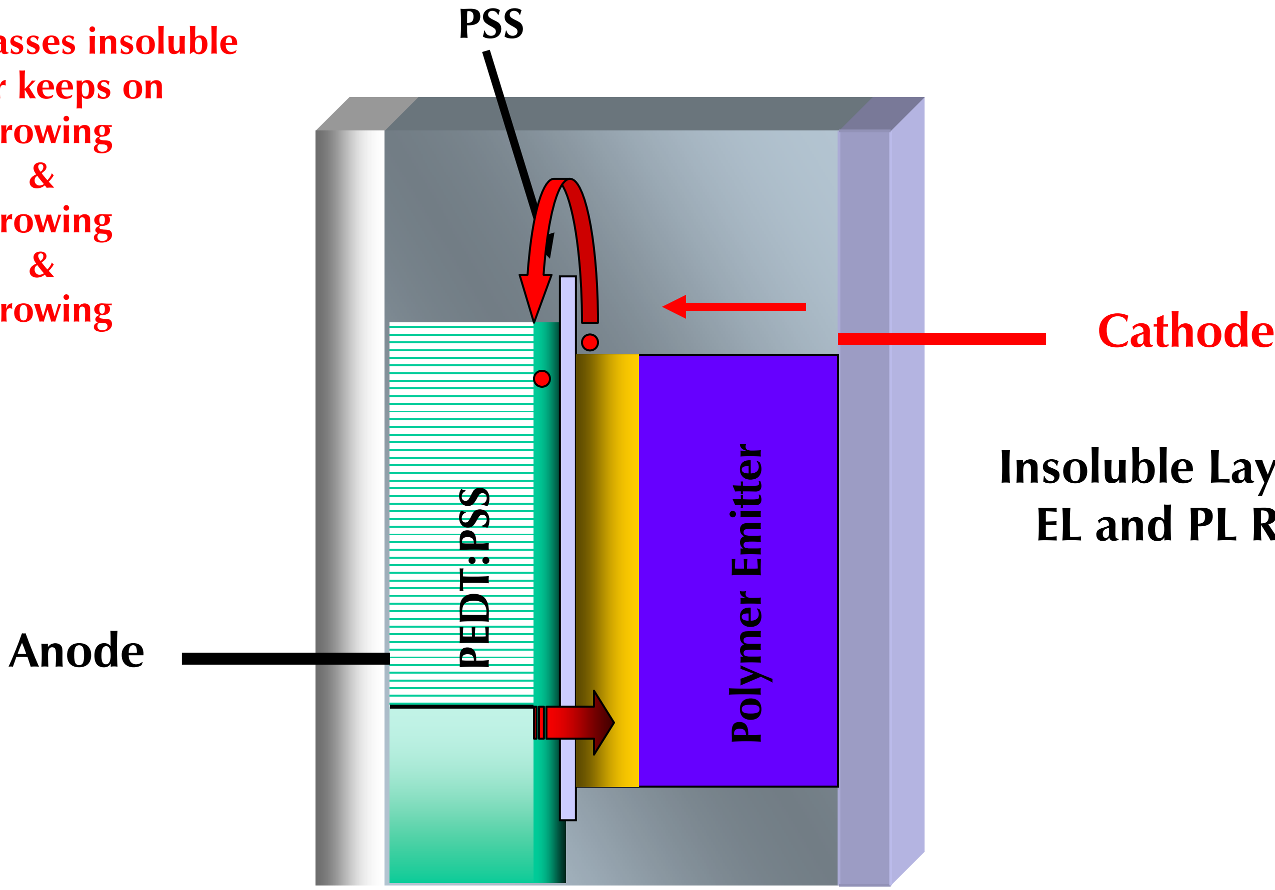

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As time passes insoluble
Layer keeps on
Growing
&
Growing
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&
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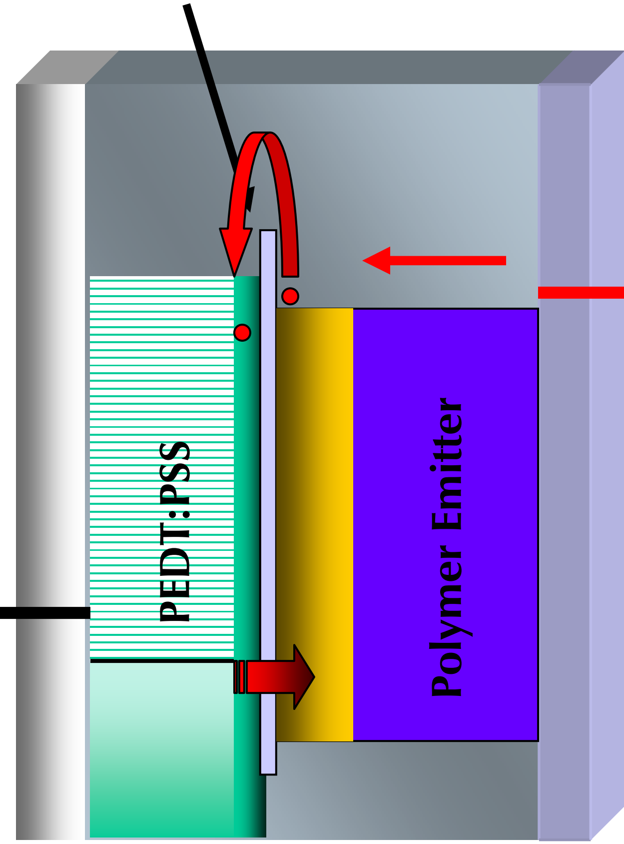

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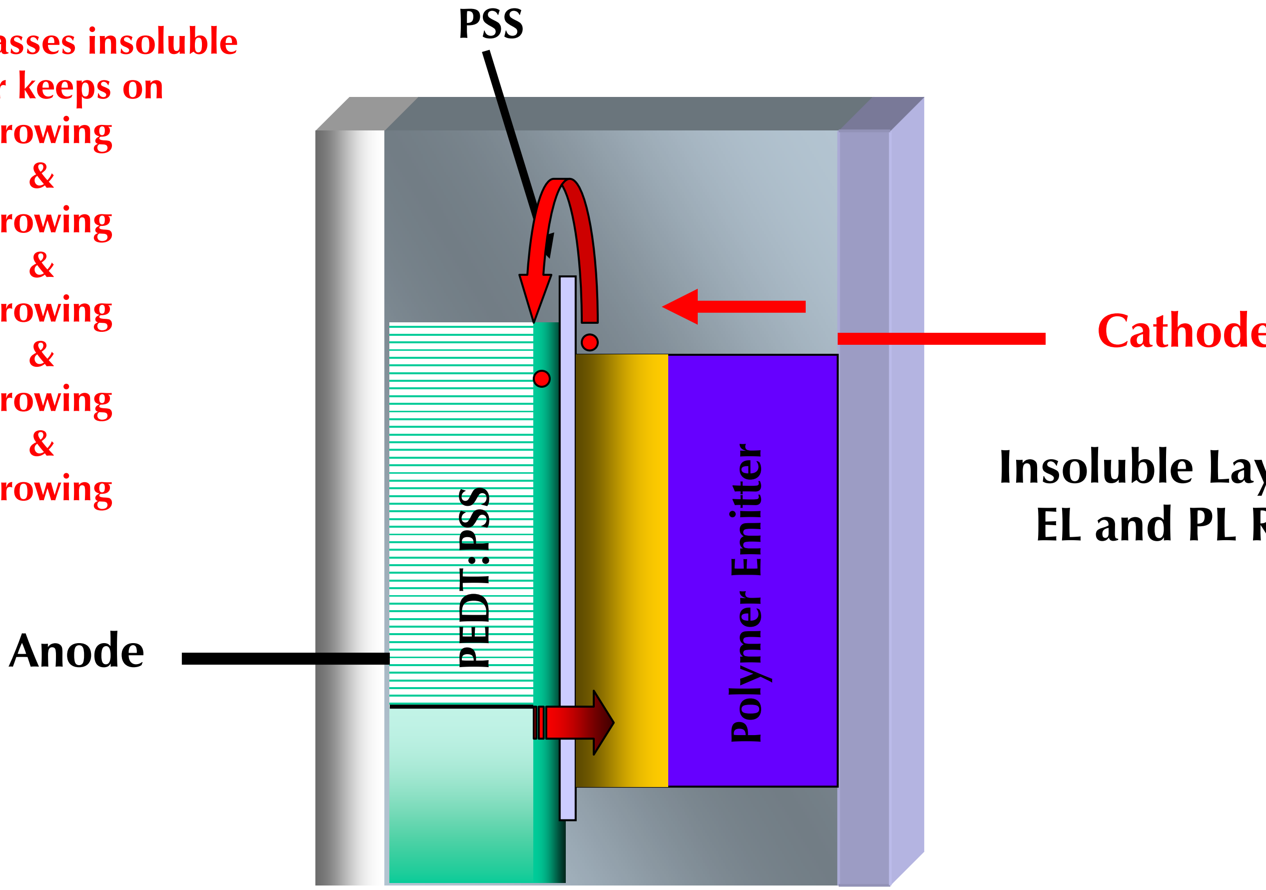
As time passes insoluble Layer keeps on Growing & Growing & Growing & Growing & Growing



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EL and PL Reduced

Resulting in damage to PEDT
Residues diffuse into the LEP Layer

Device Decay Mechanism

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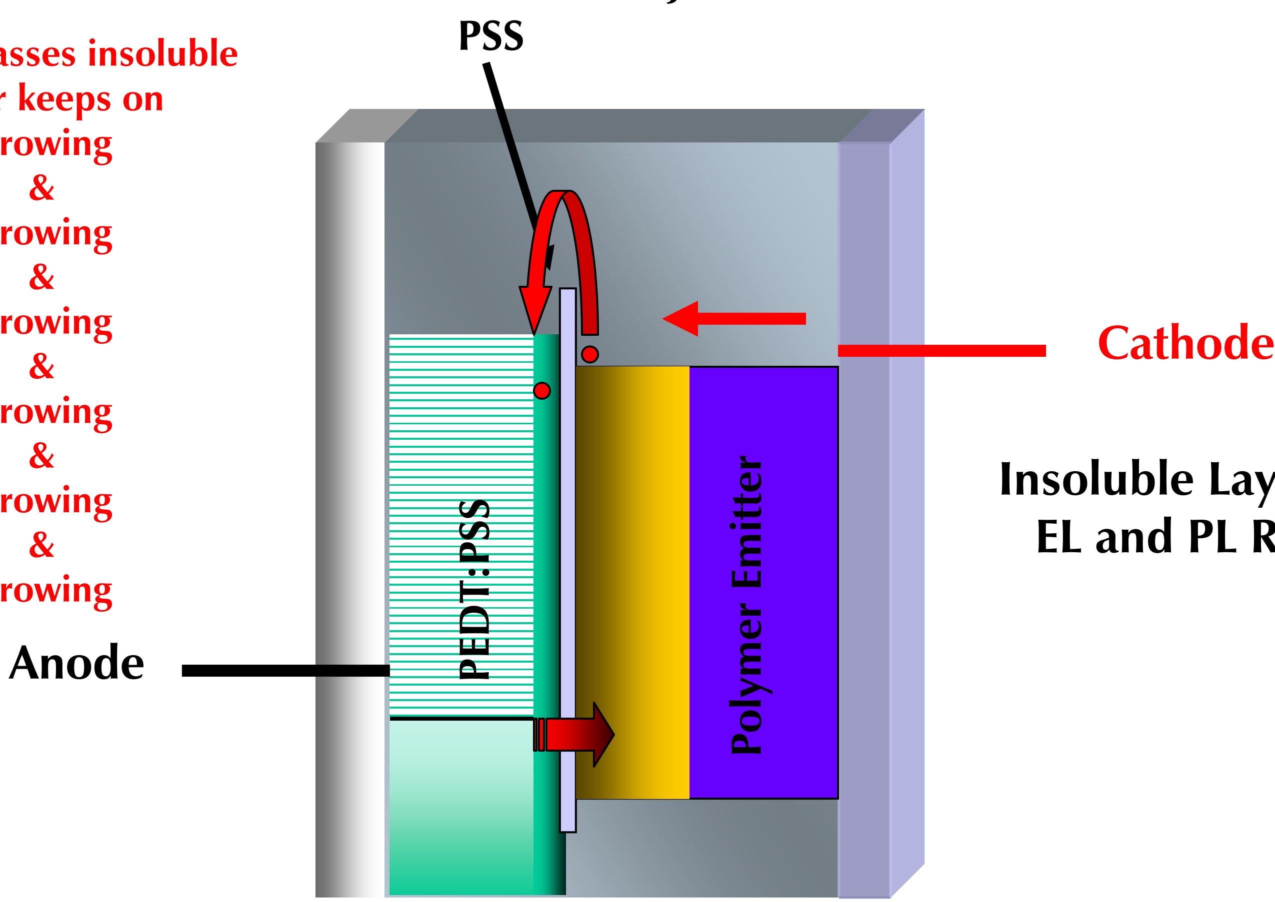
Some electrons/excitons injected into PEDT:PSS

As time passes insoluble Layer keeps on Growing & Growing & Growing & Growing & Growing & Growing



Insoluble Layer Grows
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Residues diffuse into the LEP Layer

Device Decay Mechanism

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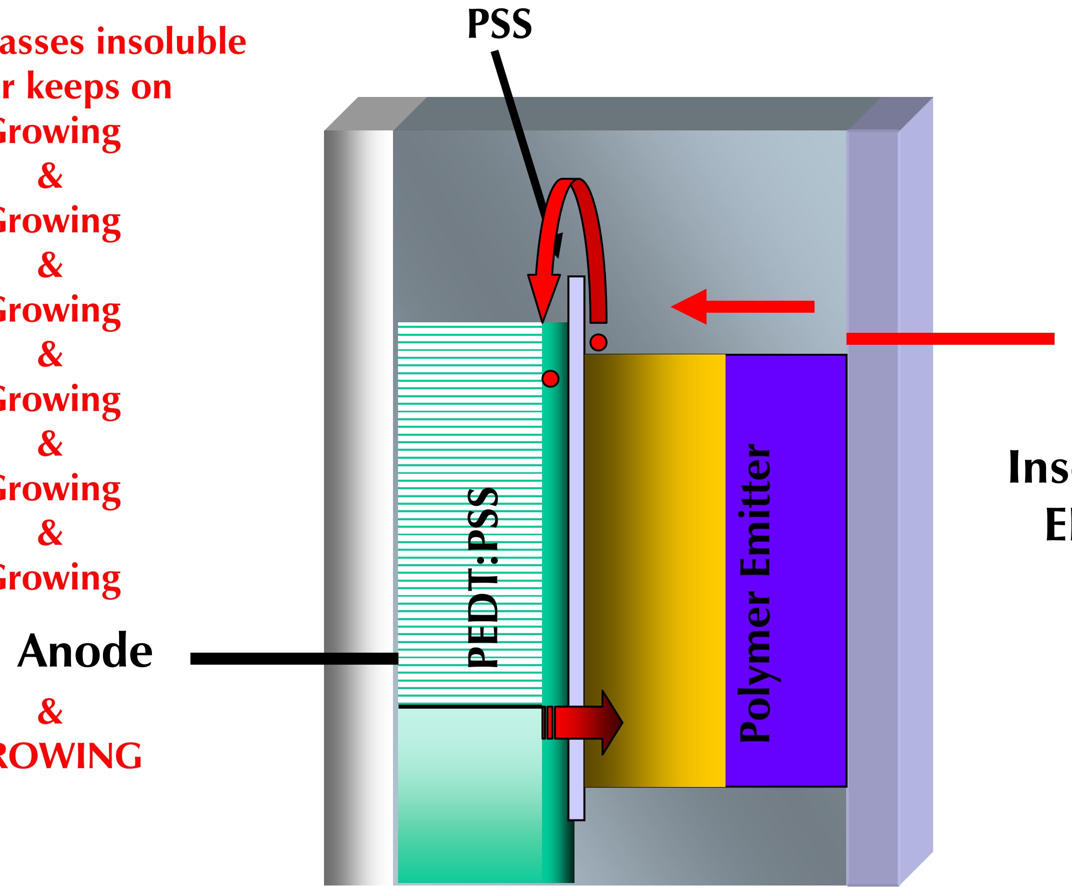
As time passes insoluble Layer keeps on Growing & Growing & Growing & Growing & Growing & Growing



& GROWING

Insoluble Layer Grows
EL and PL Reduced

Resulting in damage to PEDT
Residues diffuse into the LEP Layer

CDT

- Introduction
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- **Tri Layer PLEDs**
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PLED Progress-Blue Lifetime

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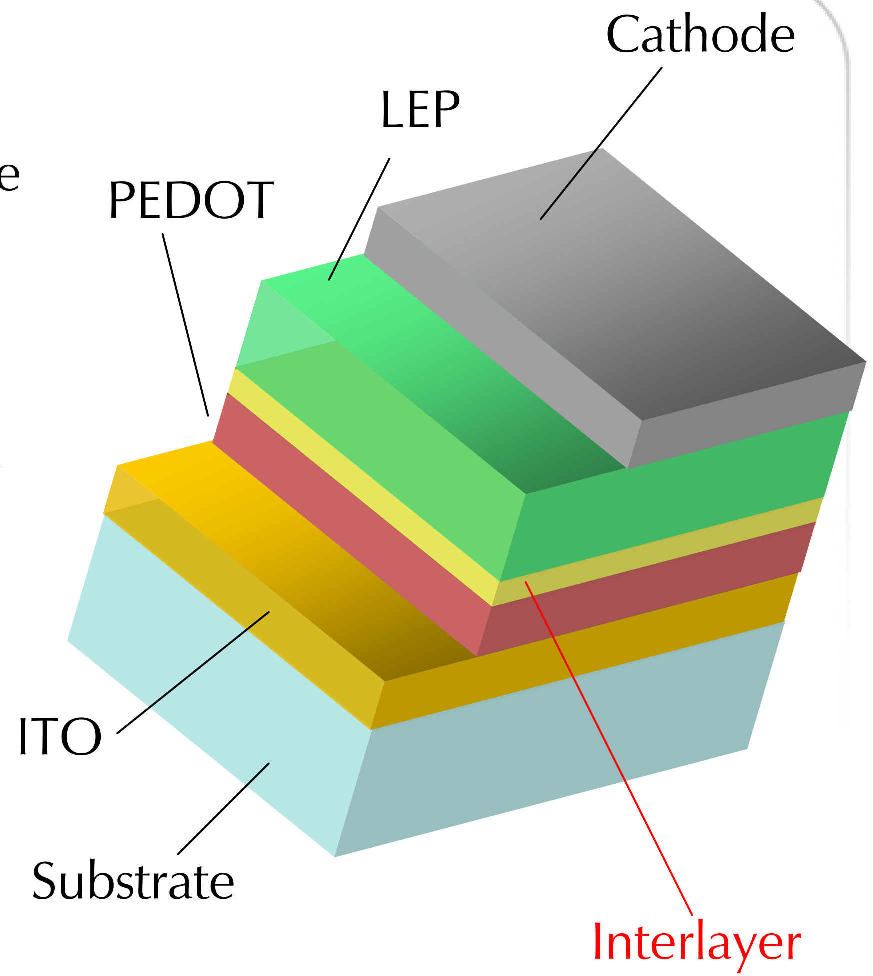
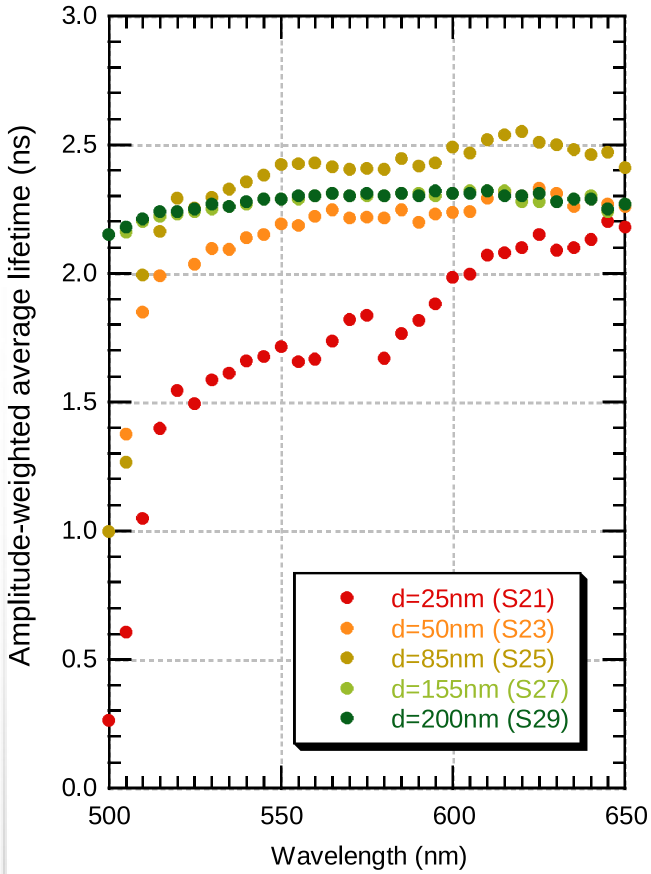
- Additional buffer layer inserted between PEDOT:PSS and emissive layer
  - Inhibit e- injection into PEDOT:PSS
  - Reduce exciton quenching at anode
- Interlayer is a polymer semiconductor deposited by solution processing
  - Compatible with ink jet printing



Time Resolved Spectroscopy

CDT



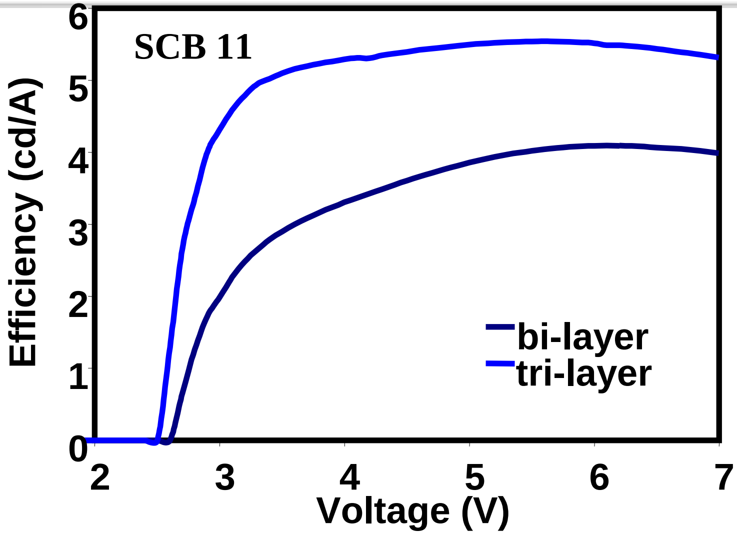
Test Structure:
PEDT:PSS/Interlayer/Green LEP
Where LEP Thickness is 25 – 200 nm

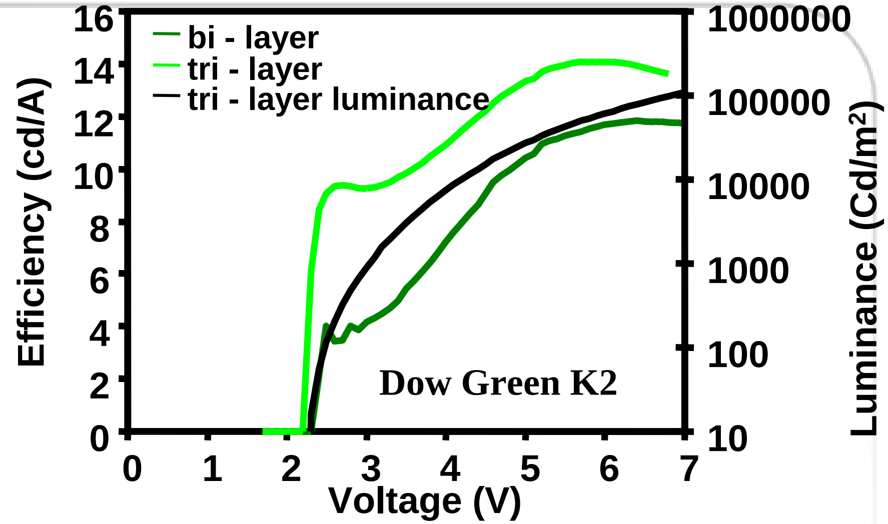
Observation:

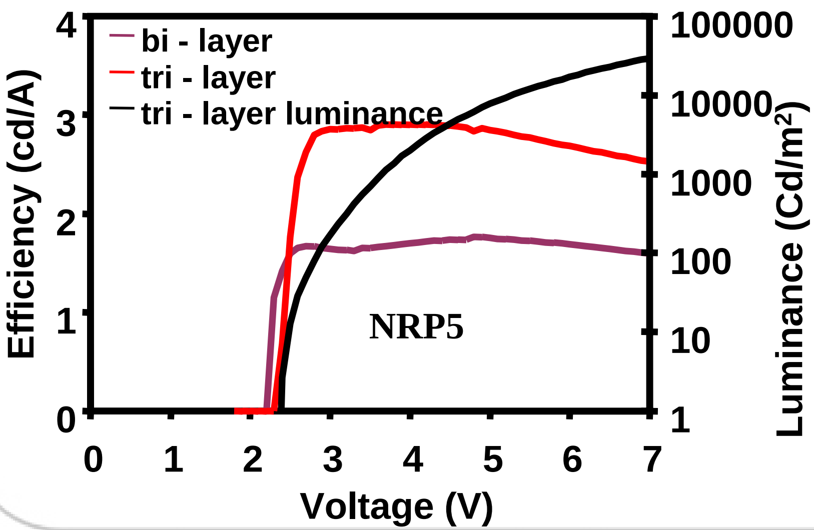
Reduced Quenching at PEDT

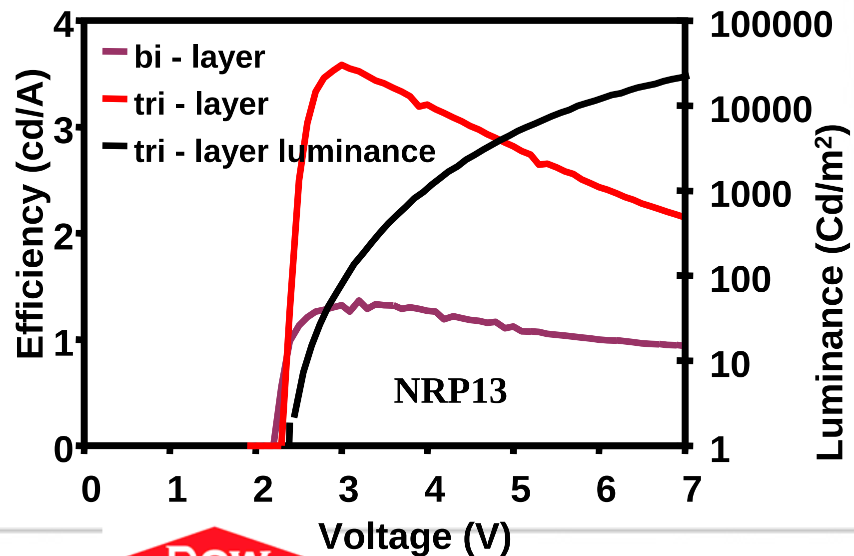
Work done at the Cavendish Laboratory

Dow LUMATION™ LEP Materials Efficiency Increases



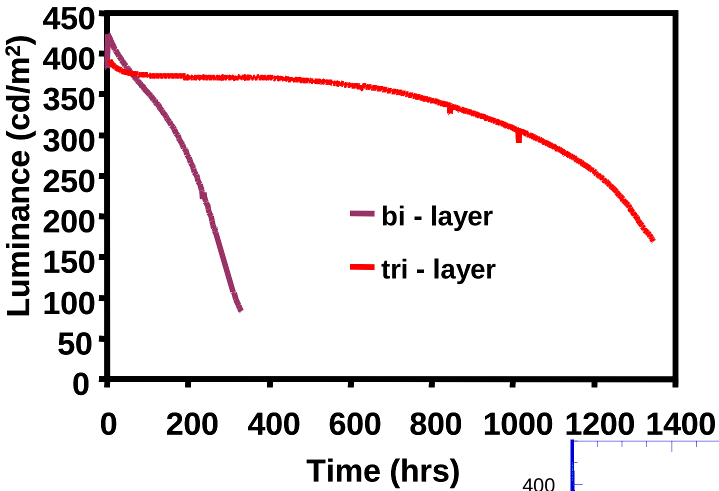




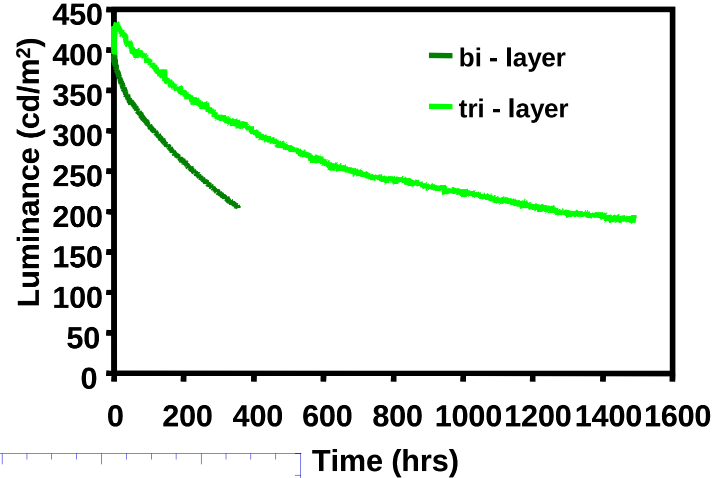


Lifetime Increases with interlayer

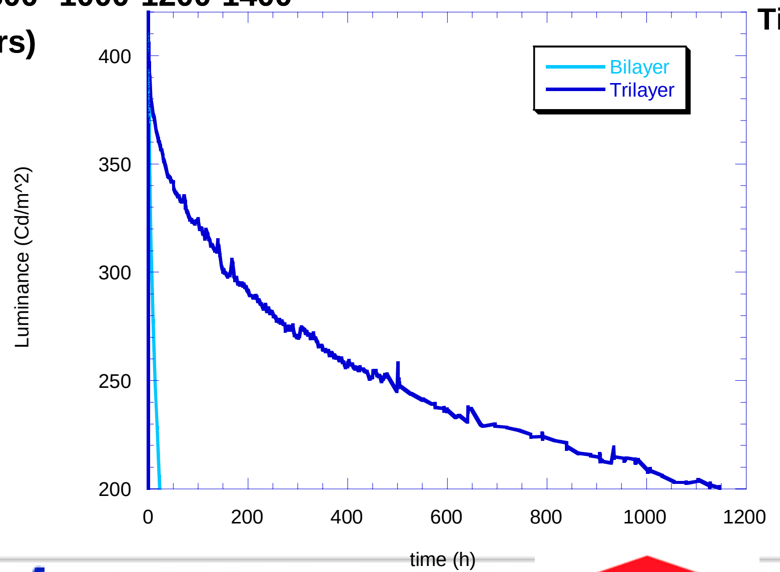
SCR2 Luminance Decay from 400Cd/m², 80C



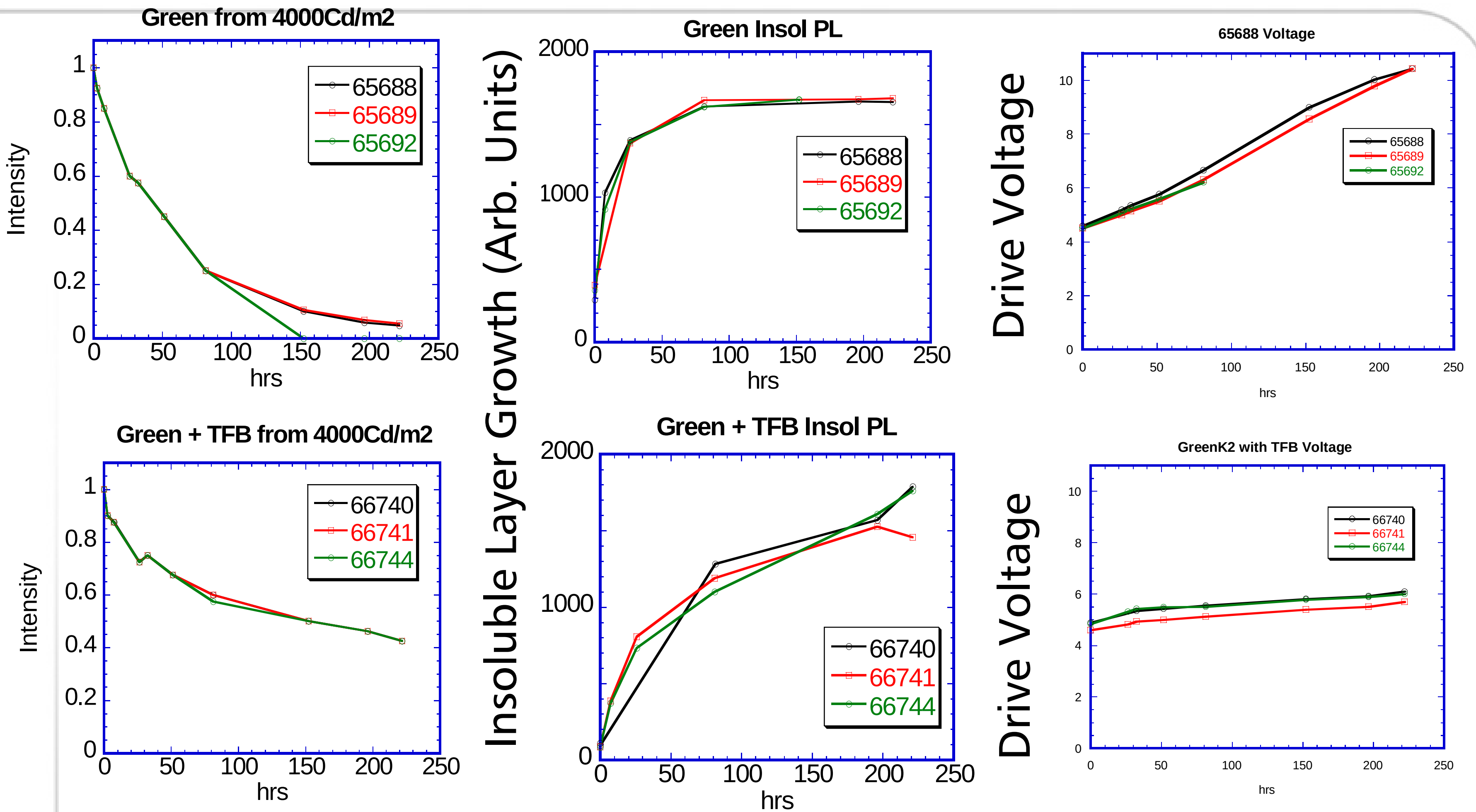
Dow Green K2 Luminance decay from 400Cd/m2, 80C



Blue Luminance Decay from 400Cd/m², RT



Insoluble layer – Kinetics



Interlayer Improves efficiency, lifetime, dV/dt and delays insol layer formation

Evidence for proposed mechanism

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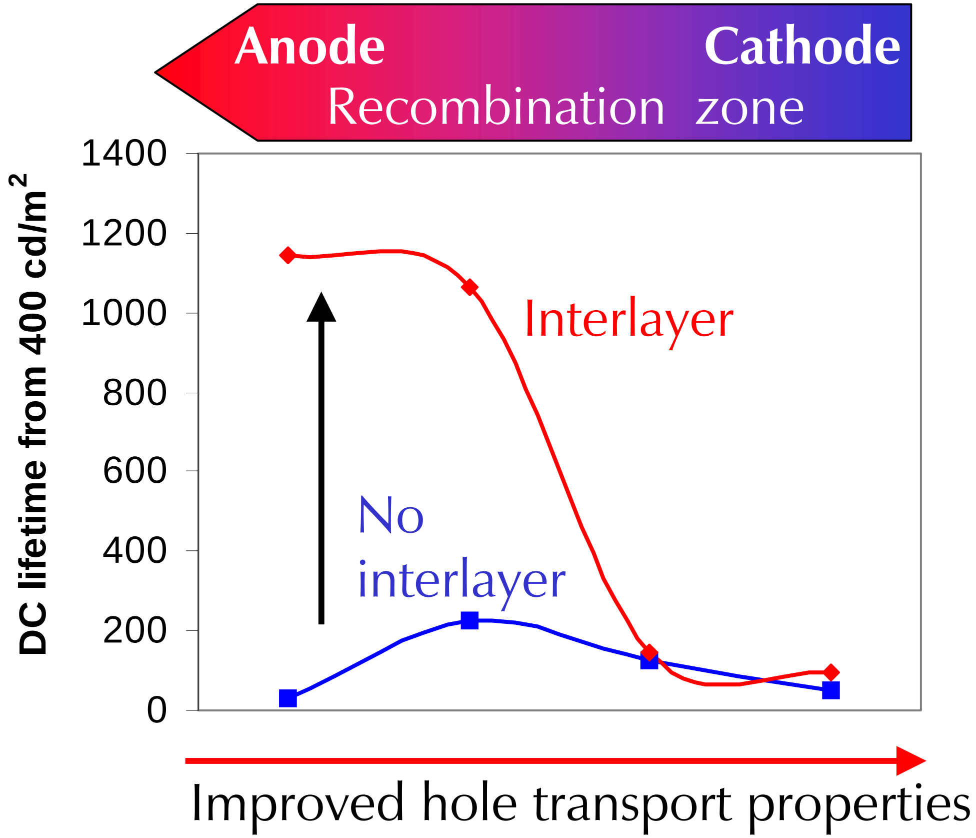
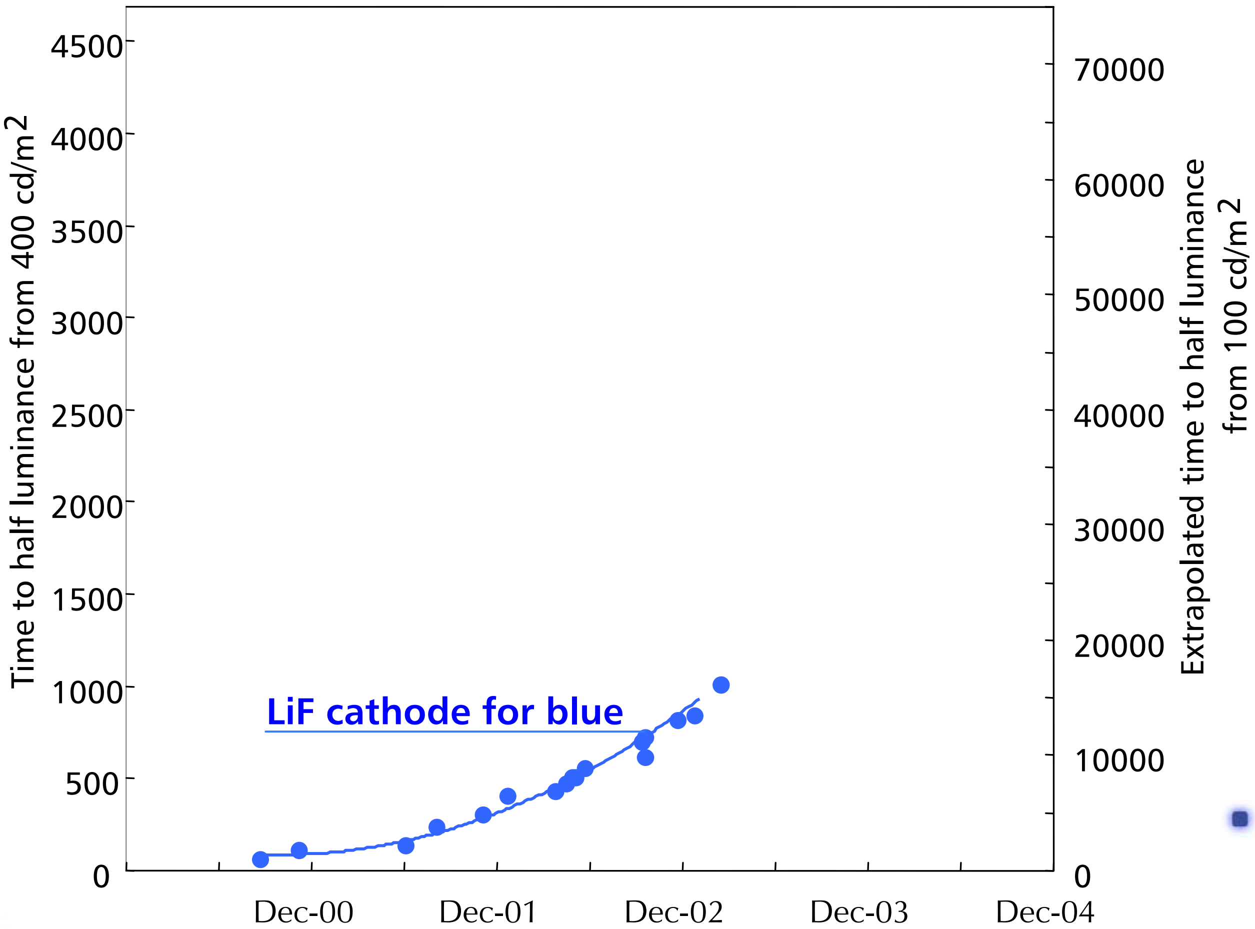
- Devices fabricated with emissive polymers with different hole transport properties
- Recombination zone moves towards anode as hole transporting properties are reduced
- Interlayer has biggest impact on lifetime when recombination zone is near anode
- Confirms possibility of exciton quenching and electron damage at the PEDOT interface



Blue Lifetime Progress

CDT



- *Mobile applications now feasible*

Blue Lifetime Progress

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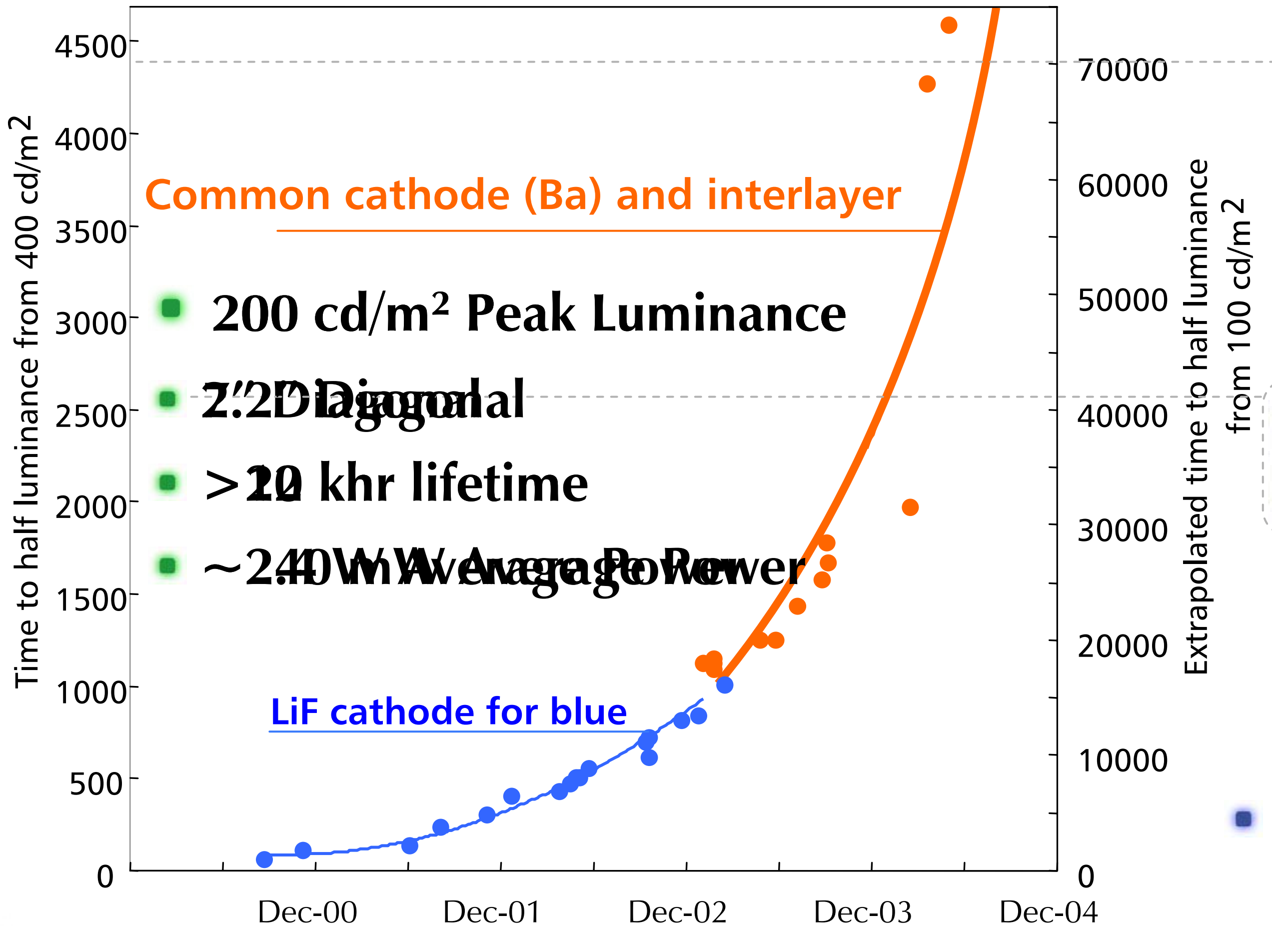

- *Mobile applications now feasible*

RGB Performance – DC Lifetime

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			At 100 cd/m²			Measured Lifetime (hrs at RT)	Extrapolated Lifetime at 100 cd/m², RT	Cathode	Interlayer	dV to half life (V)
	CIE-x	CIE-y	V	cd/A	Lm/W					
Red	0.68	0.32	3.6	1.7	1.5	1790 hrs at 2000 cd/m²	>210,000	Ba	Y	1.6
Green	0.43	0.55	3.4	7.7	7.0	2912 hrs at 2000 cd/m²	>190,000	Ba	Y	1.1
Blue	0.16	0.22	5.5	6.9	3.9	>1147 hrs at 800 cd/m²	>75,000	Ba	Y	1.0
Yellow	0.50	0.49	4.5	2.1	1.5	2420 hrs at 4000 cd/m²	>250,000	Ba	N	2.4
Orange	0.58	0.42	3.4	0.9	0.8	8138 hrs at 1000 cd/m²	>300,000	Ba	N	3.8

RGB Performance – DC Lifetime

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			At 100 cd/m²			Measured Lifetime (hrs at RT)	Luminance for 10,000hrs Lifetime (DC)	Cathode	Interlayer	dV to half life (V)
	CIE-x	CIE-y	V	cd/A	Lm/W					
Red	0.68	0.32	3.6	1.7	1.5	1790 hrs at 2000 cd/m²	~700 cd/m²	Ba	Y	1.6
Green	0.43	0.55	3.4	7.7	7.0	2912 hrs at 2000 cd/m²	~900 cd/m²	Ba	Y	1.1
Blue	0.16	0.22	5.5	6.9	3.9	>1147 hrs at 800 cd/m²	>300 cd/m²	Ba	Y	1.0
Yellow	0.50	0.49	4.5	2.1	1.5	2420 hrs at 4000 cd/m²	~1300 cd/m²	Ba	N	2.4
Orange	0.58	0.42	3.4	0.9	0.8	8138 hrs at 1000 cd/m²	~900 cd/m²	Ba	N	3.8

Introduction

Understanding PLEDs

Tri Layer PLEDs

Singlet:Triplet Ratio

Conclusions

Excited states in polymer LEDs

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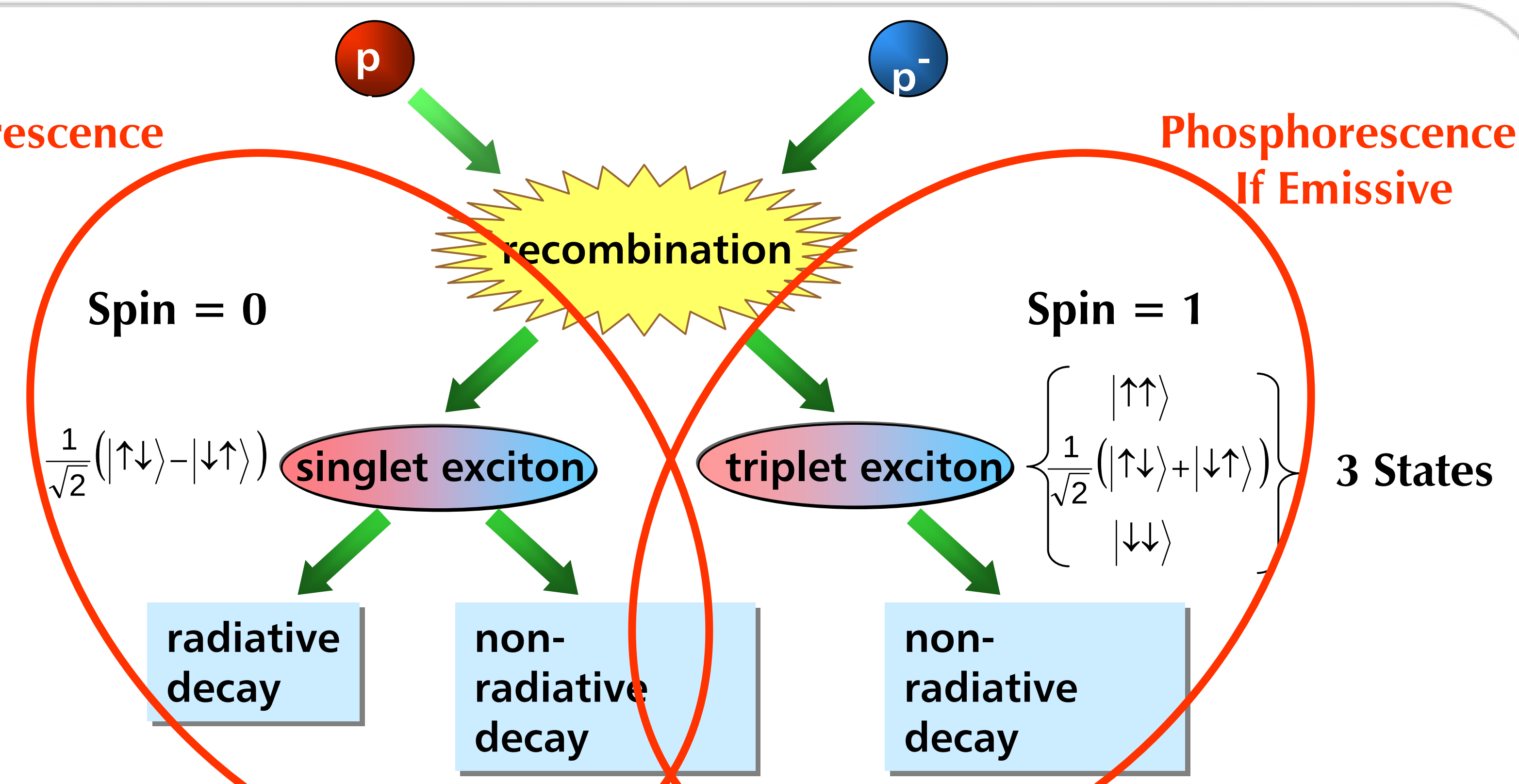

Measure generation and decay of singlets, triplets and charges to determine singlet:triplet ratio

IF formation probability of singlet and triplet states is identical then expect singlet:triplet ratio to be **1:3**

Calculation of the singlet-triplet ratio in OC1C10 LEDs

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Measure triplet induced absorption → Triplet generation rate

Measure EL output → Singlet generation rate

- Several LEPS measured
- All have high singlet ratios
- Small molecules have only 25% singlets as expected

Much Higher Than Expected

Singlet formation probability

$$r_{st} = \frac{g_s}{g_s + g_t} = 0.83 \pm 0.07$$

Note: Work carried at the Cavendish Laboratory

Polyfluorene devices - F8BT

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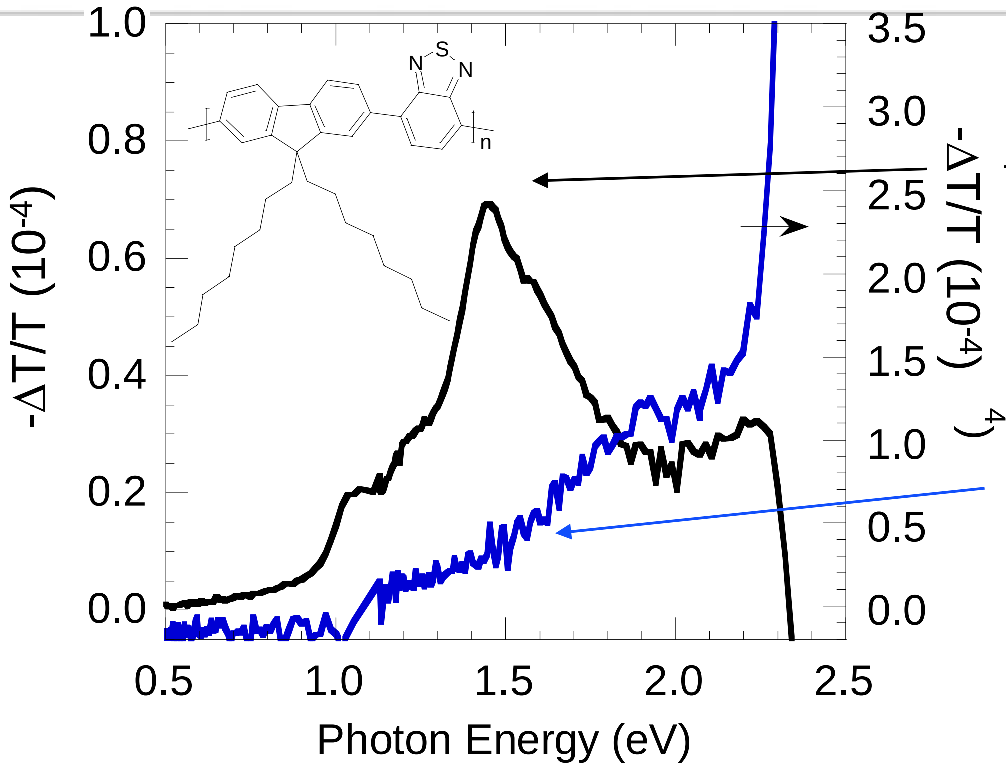

- No obvious triplet signal in device
- If we assume lifetime = 0.57 ms (as in PIA), and $s_t > 2 \times 10^{-16}$ cm^2
  - < 6% of excitons formed as triplets! Even less if s_t larger.
- lifetime should be confirmed

Singlet-triplet ratio

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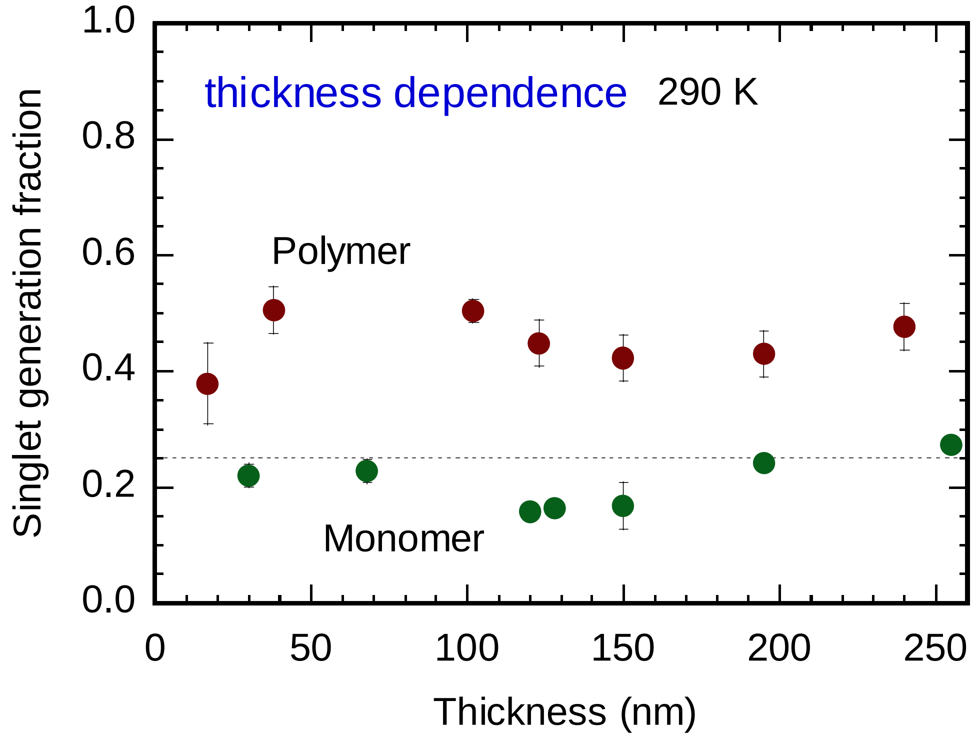
Direct comparison of monomers and polymers

- Recent work from Cavendish published in Nature
- Measurements of monomers and polymers with the same unit cell and identical techniques
- Monomers
  - Rst ~ 0.25
- Polymers
  - Rst ~ 0.5



Jo Wilson, Anna Köhler, Nature 413, 828 (2001)

Why are polymers different from small molecules?

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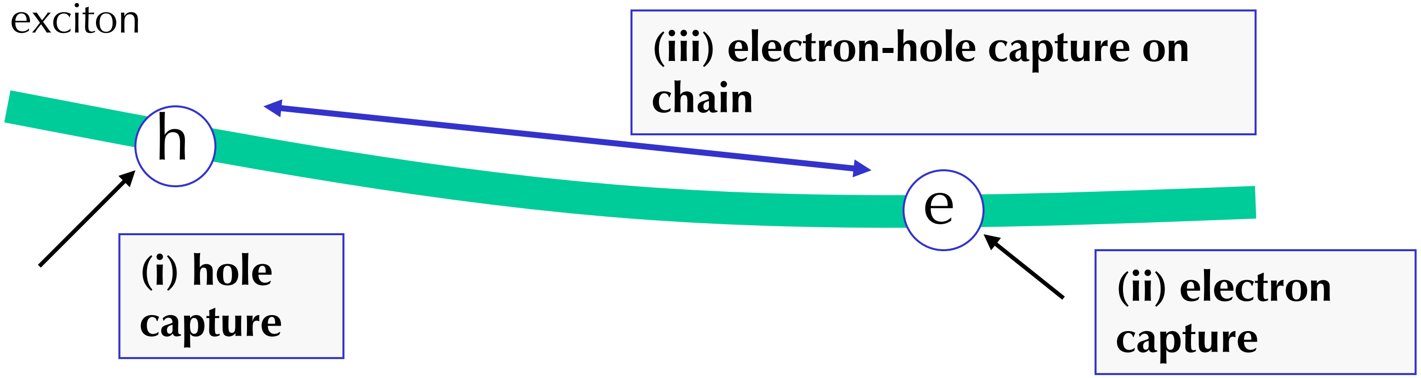
Small Molecules: **electron-hole capture at separation » 10 nm (Langevin recombination: Coulomb energy » thermal energy) weak inter-molecular e-h delocalisation, so only Coulomb interaction involved in e-h capture cross-section**

Polymers: electron and hole arrival on polymer chain, and subsequent recombination to exciton

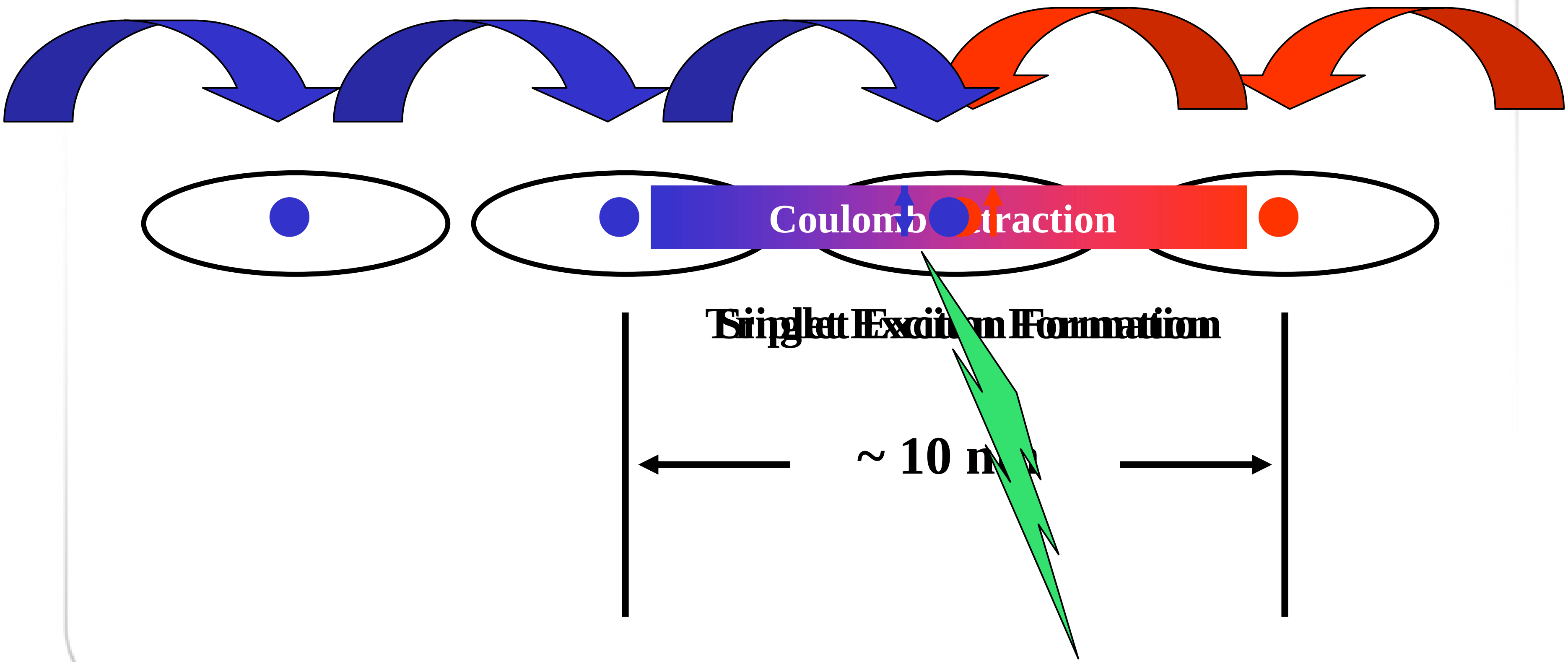


step (iii) spin-dependent?

- delocalisation of electron and hole wavefunctions along chain allows exchange interaction at long range for charges on same chain this favours singlet bound state at e-h capture (typical range 10 nm)

(Beljonne et al J. Chem. Phys. **102**, 2042, 1995)

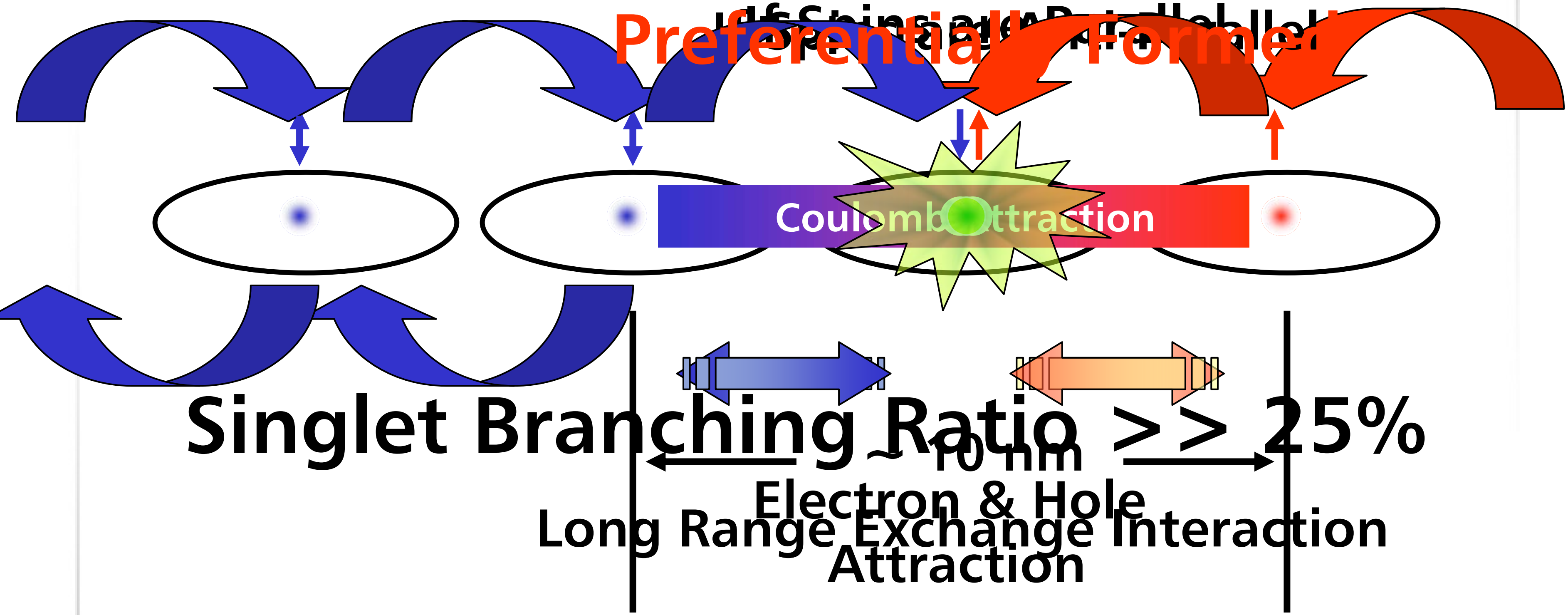
Small Molecules



Light Emitting Polymers

Couple Monomers Conjugatively

Excitons with S=0 Preferentially Formed



Singlet Branching Ratio >> 25%

To Make a Light Emitting Polymer

Why is the LEP device Efficiency not Higher ?

CDT

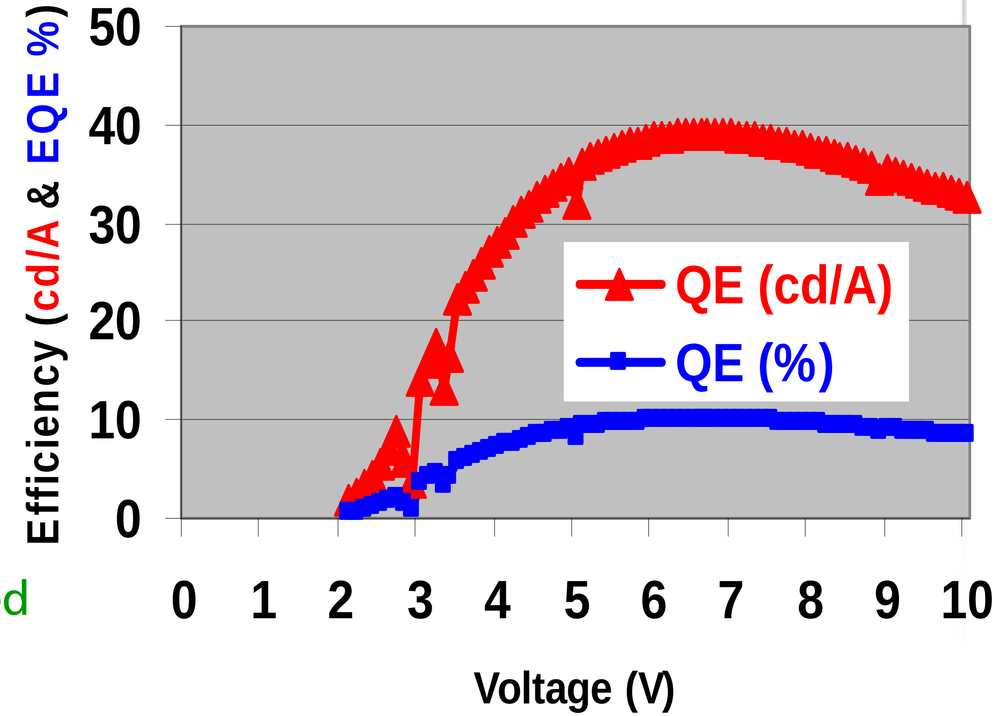
Because there are other loss mechanisms in the device

- Electrons or Holes passing through the device
- Exciton quenching at
  - PEDT/LEP Interface
    - i.e. Exciton Quenching occurs at PEDT/LEP Interface
  - Cathode

Ad-Vision Results on Thick Green/Yellow LEP

C|D|T

- Device Structure: ITO/PEDT:PSS (20-30 nm)/LEP (250 nm)/ Ca/Al
  - Recombination removed from quenching sites such as the cathode and PEDT:PSS
  - EQE > 10 %
  - IQE > 33 %
  - PL Efficiency 61 %
  - Singlet Ratio ~ 50+ %



  - Note 33 Cd/A (8% EQE) reported by TDK, Yamagata University, UCLA
- This supports the work at the University of Cambridge and suggests significant efficiency gains are still possible with optimised device design

Data supplied by Dr Melissa Kreger & Professor Sue Carter

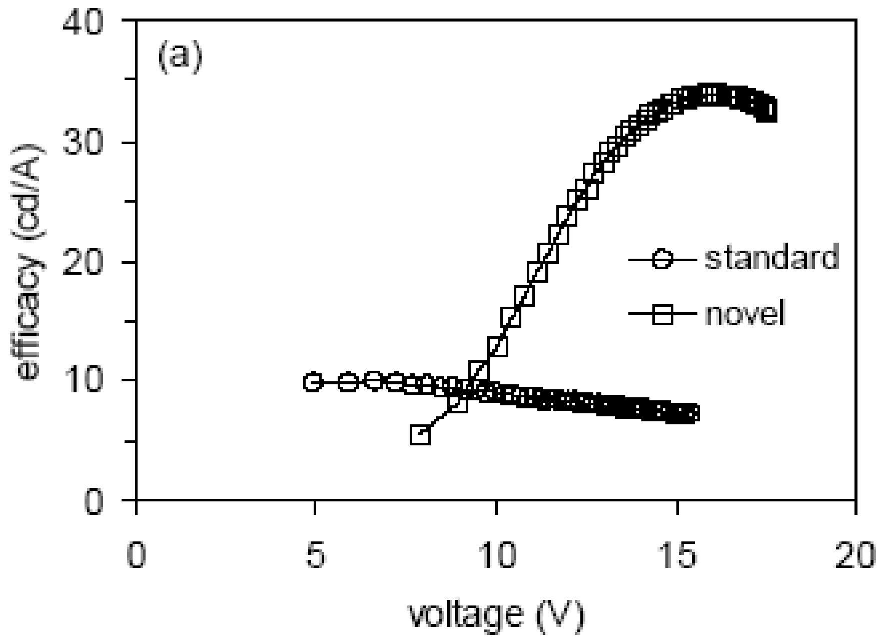
Philips Results

C|D|T

- **Device Structure: ITO/New HTL/Covion Super Yellow/Ba/Al**

  - **Recombination removed from quenching sites such as the cathode and PEDT:PSS**

  - **EQE > 12 %**
  - **IQE > 35 %**
    - **Assuming only observe 34% of generated light**
  - **PL Efficiency 41 %**
  - **Singlet Ratio close to 100 %**



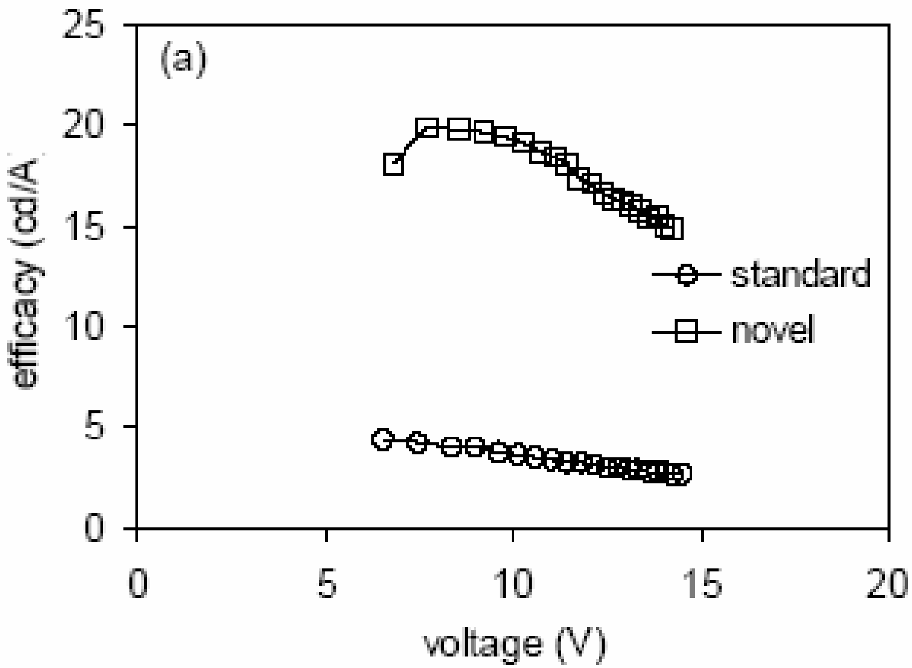
E A Meulenkamp et al
Philips, Eindhoven, 2004

Philips Results:Blue Emission

C|D|T

- Device Structure: ITO/New HTL/Covion Spiro PF/Ba/Al

- **Recombination removed from quenching sites such as the cathode and PEDT:PSS**
- **EQE > 12.5 %**
- **IQE > 36 %**
  - **Assuming only observe 34% of generated light**
- **PL Efficiency 38 %**
- **Singlet Ratio close to 100 %**



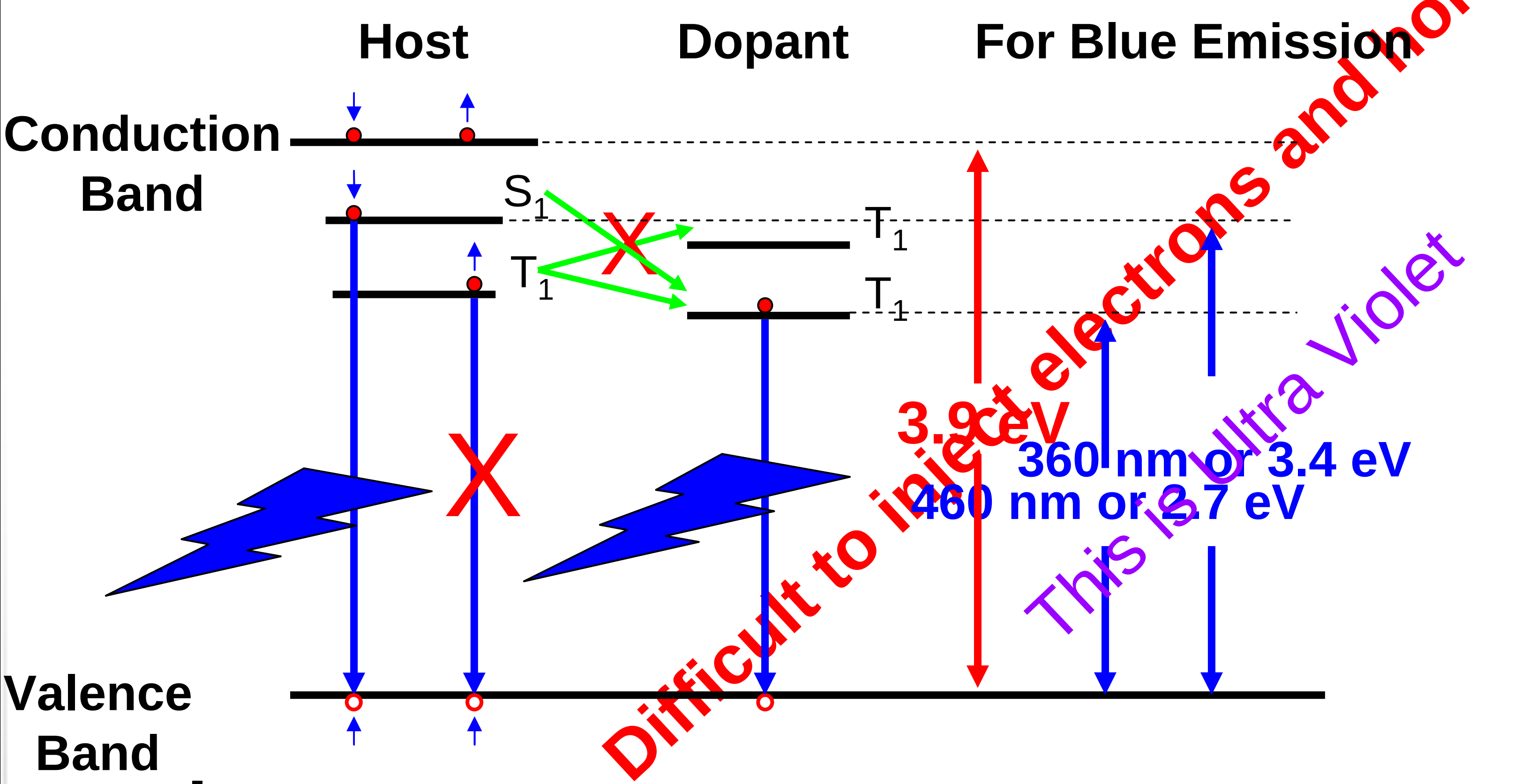
E A Meulenkamp et al
Philips, Eindhoven, 2004

Singlet:Triplet Ratio Summary

- More singlets than expected in polymer LEDs
- Understanding loss mechanisms results in significant efficiency improvements in LEP diodes
  - >25% singlet generation probability demonstrated in real diodes
  - For blue: Is this the only way to high efficiency?

Why is Blue Phosphorescent Emission Difficult?

CDT



Issues:

Need Stable UV Emitter

Very Large Barriers to Electron and Hole Injection

Singlet:Triplet Ratio Summary

C|D|T

- More singlets than expected in polymer LEDs
- Understanding loss mechanisms results in significant efficiency improvements in LEP diodes
  - >25% singlet generation probability demonstrated in real diodes
  - For blue: Is this the only way to high efficiency?

- MAYBE

- Introduction
- Understanding PLEDs
- Tri Layer PLEDs
- Singlet:Triplet Ratio
- Conclusions

Conclusion

- Blue lifetime increasing rapidly
  - > 70,000 hours
- Singlet:Triplet Ratio
  - SMF ~ 25%
  - P-OLED >> 25%

- PLED technology is gathering momentum

- CDT is established as the technology leader in this space

www.cdtltd.co.uk

jburroughes@cdtltd.co.uk