OLED100 Summer School, 2011

Polymer OLED Materials and Device Operation

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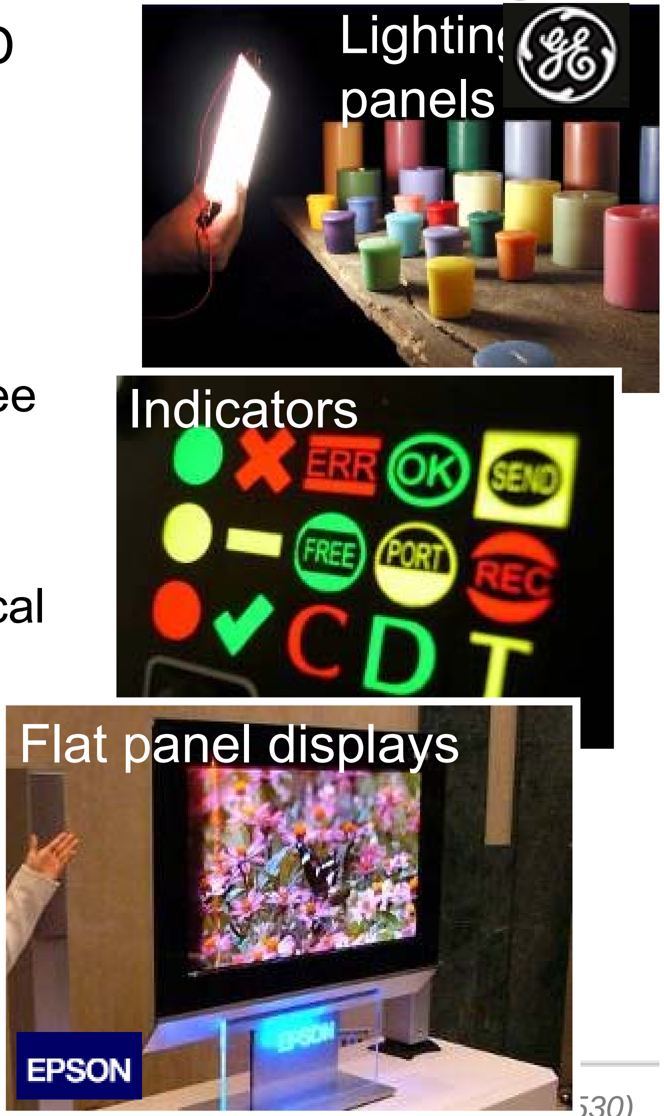
Outline

- Materials and Material Properties
- Device Operation
- Improving Device Performance
- Conclusions

Introduction to CDT

- CDT founded in 1992 to exploit Polymer-OLED technology technology for display applications
- CDT is now owned by Sumitomo Chemical Group
- 159 permanent staff
  - 105 scientific & technical employees with degree
  - 56% (59) – PhD
- Multidiciplinary scientific environment:
  - Analytical/Organic/Inorganic/Physical/Theoretical Chemistry
  - Materials Science & Polymer Chemistry
  - Electronics & Engineering
  - Device Physics, Optics, Modelling
  - Microscopy
  - Design (3D-CAD)
  - Formulation



Outline

Materials and Material Properties

Device Operation

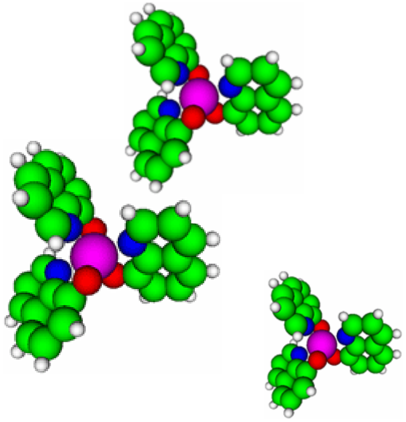
Improving Device Performance

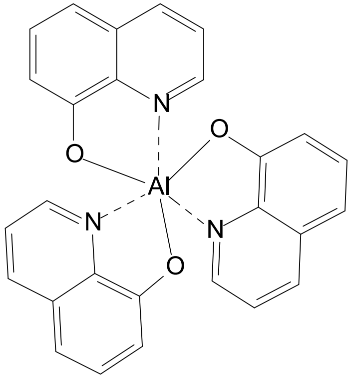
Conclusions

Overview - OLED materials

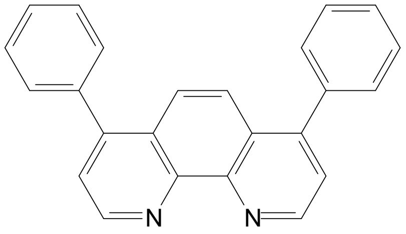
Small Molecule OLEDs (SM-OLEDs)

Invented 1985 by Tang, van Slyke (Kodak)





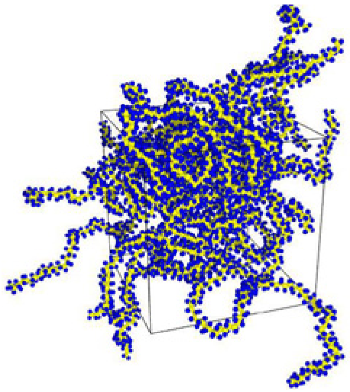
Alq3

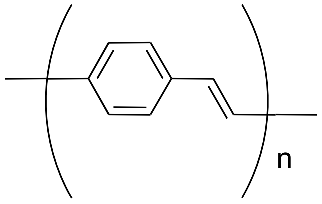


Biphen

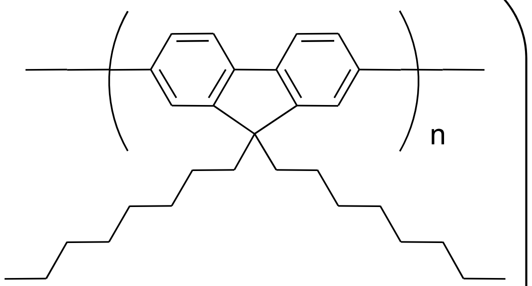
Polymer OLEDs (P-OLEDs)

Invented 1989 by Burroughes, Friend, and Bradley (Cambridge)





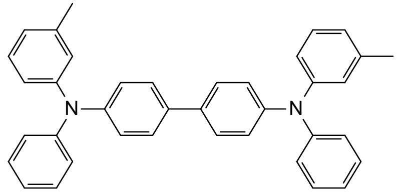
PPV



Poly(9,9’-dioctylfluorene)

Materials - examples

Small Molecules



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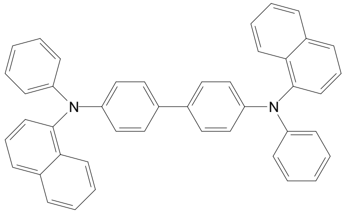

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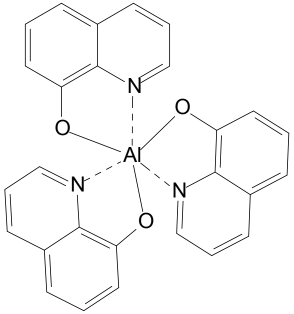
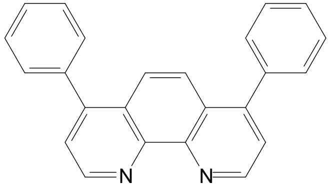
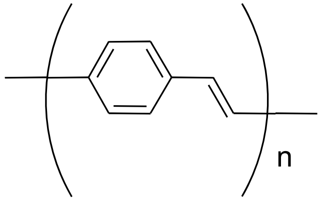


Alq3

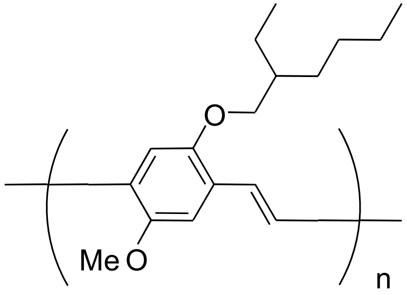


Biphen

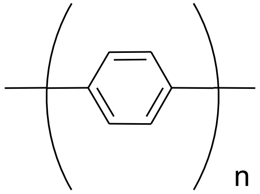
Polymers



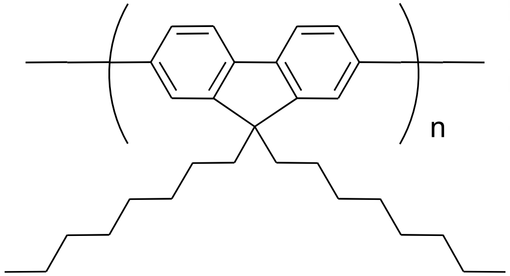
PPV



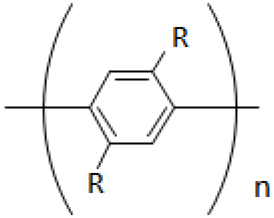
MEH-PPV



PPP



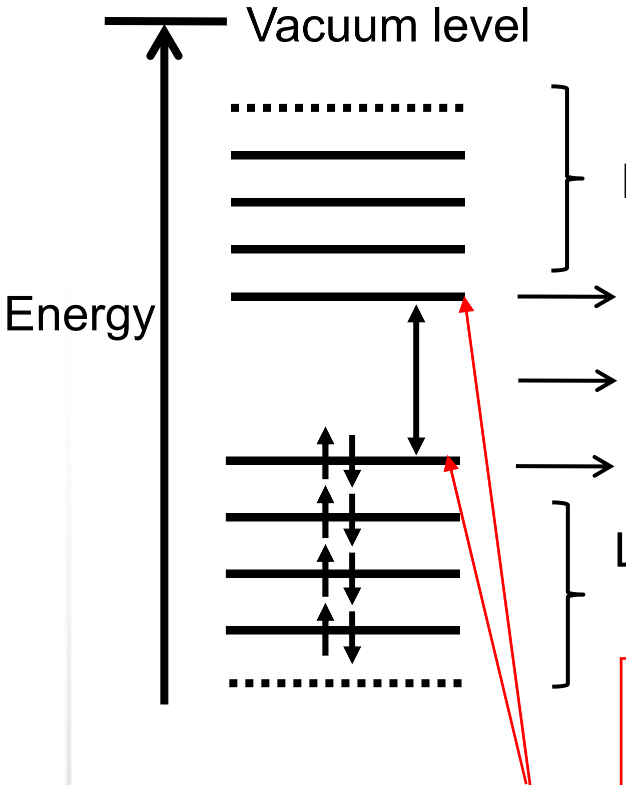
Poly(9,9'-dioctlyfluorene)



subsituted PPP

Molecular Orbitals & Energy Levels

C|D|T



Vacuum level

Energy

Higher unoccupied levels

LUMO (lowest unoccupied molecular orbital)

Eg (Bandgap) – determines colour of emitted light

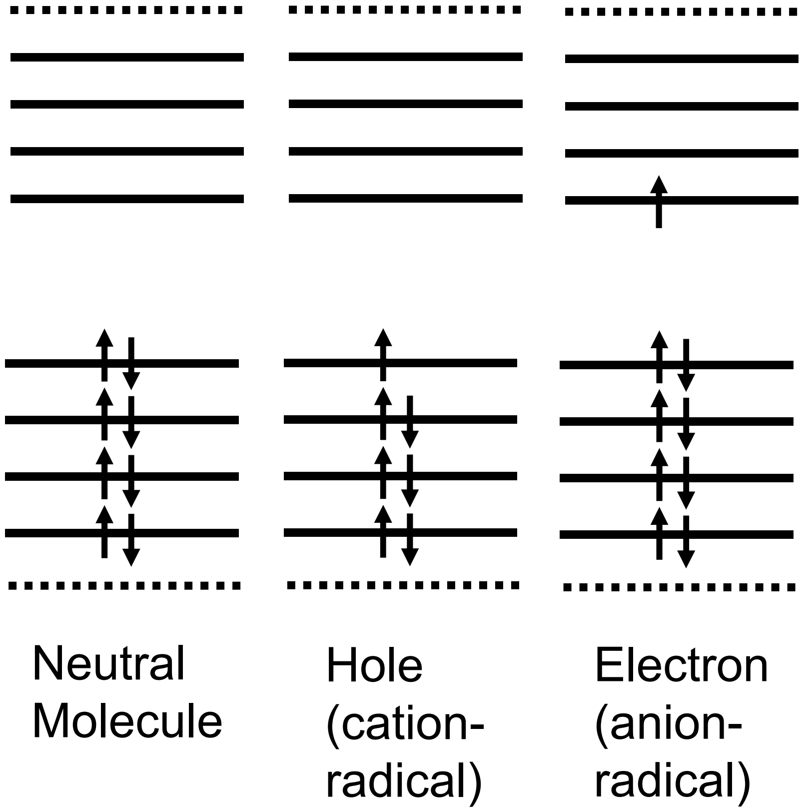
HOMO (highest occupied molecular orbital)

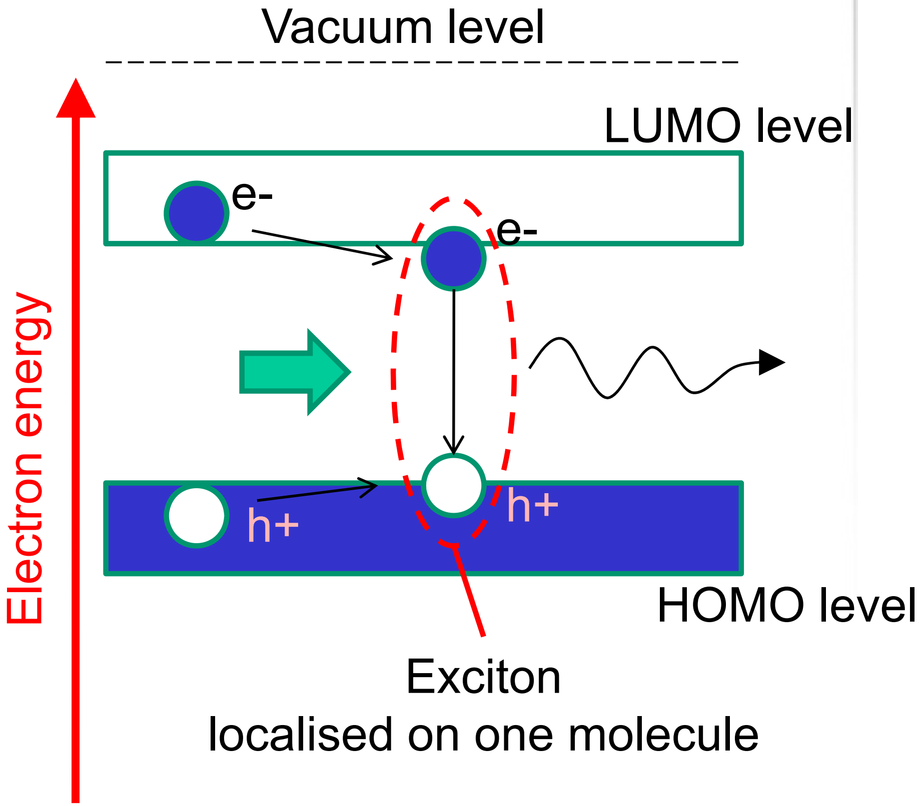
Lower occupied levels

Most important orbitals for OLED device physics

- Number of levels, energies, spacing, etc. determined by molecule ie. # and type of atoms.
- Number of electrons directly linked to molecular charge.
- 0, 1 or 2 electrons per level (opposite spins in case of 2 electrons).
- Energy is relative to vacuum level

Charge Carriers & Organic Semiconductor Band Diagram



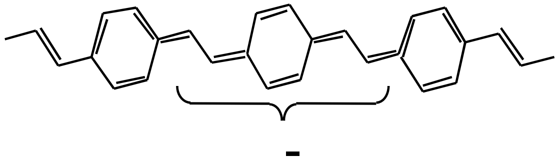


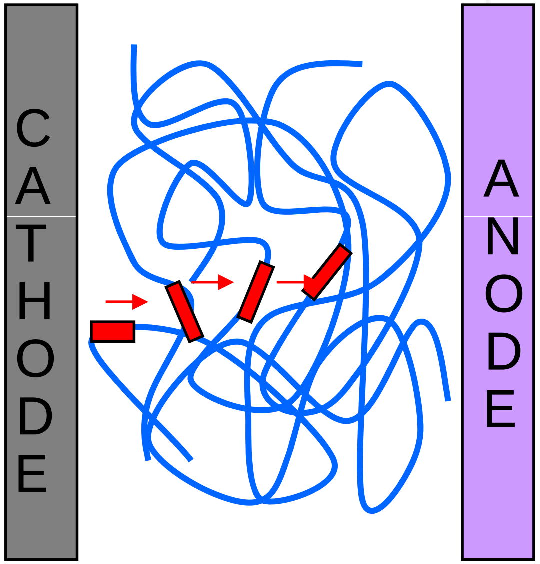
Charge Transport

Hopping transport

- charges hop from site to site along or between polymer chains
- there is a barrier to hopping between sites
- hopping probability depends on temperature, electric field, molecule separation and level of disorder in the film
- charges drift (under the influence of the electric field) and diffuse (as a result of density gradients)

- Localized carriers
- Nuclei relax around charge



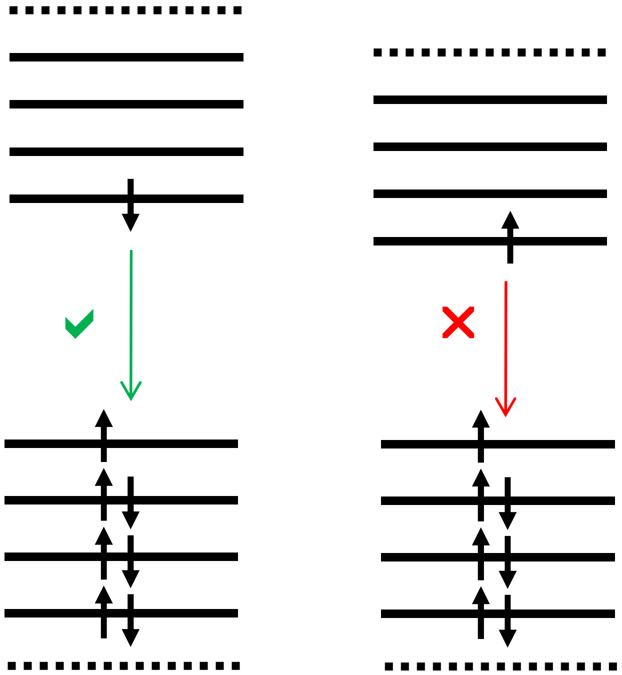


2 types of excitons are possible

SINGLET

The spin of the LUMO electron can pair with the spin of the HOMO electron.

Can recombine to emit light in any material (fast).



TRIPLET

The spin of the LUMO electron does not pair with the spin of the HOMO electron.

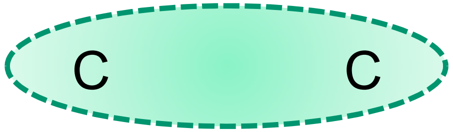
Can only recombine to emit light in a phosphorescent material (slow).

- Electrons and holes recombine forming either a triplet or singlet exciton
- Singlets can decay to emit light in fluorescent and phosphorescent materials.
- Triplets can only decay to emit light in phosphorescent materials (lower energy) Non-radiative (thermal) decay will be present in any material.
- Spin statistics suggests a 3:1 ratio of triplets:singlets - Not necessarily the case for all materials.

Organic Semiconducting Materials

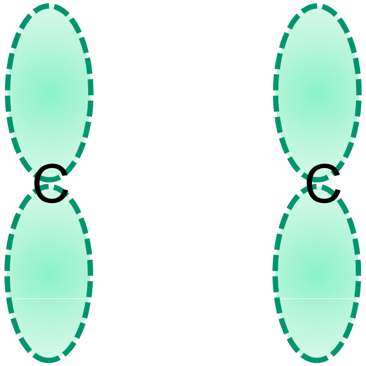
- What makes an organic material semiconducting?
- There are two basic types of covalent bond:

Sigma (σ) bond



- Strong
- Tightly bound
- Localised

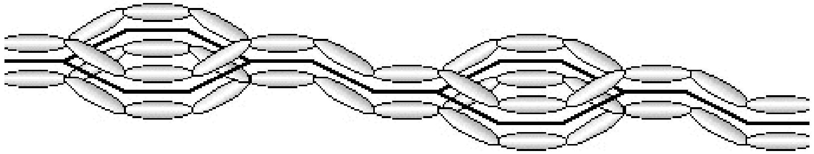
Pi (π) bond

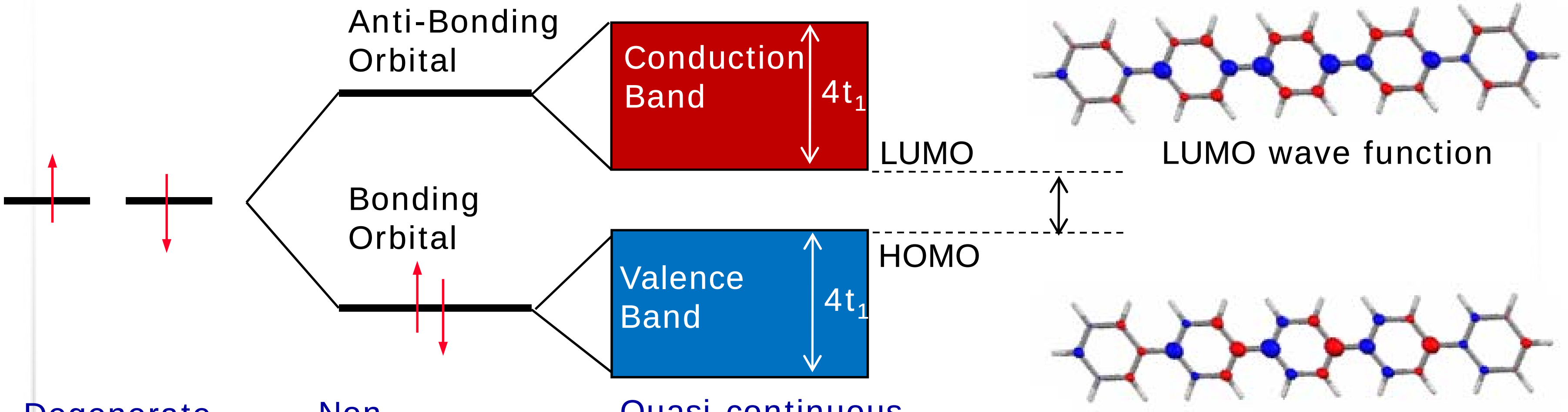


- Weak
- Loosely bound
- De-localised

Semiconducting Molecules and Polymers

- As the de-localised pi-orbitals form a bond they split into bonding (HOMO) energy levels and anti-bonding (LUMO) energy levels with semiconductor properties emerging as the delocalisation extends.





Degenerate pi levels

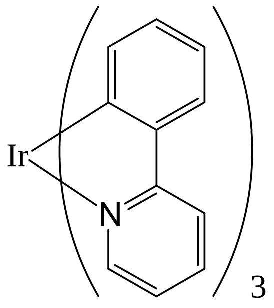
Non-degenerate molecular orbital levels

Quasi-continuous energy bands resulting from overlap of many pi orbitals

Molecular orbitals of poly(*para*-phenylene) (PPP)

Phosphorescent materials

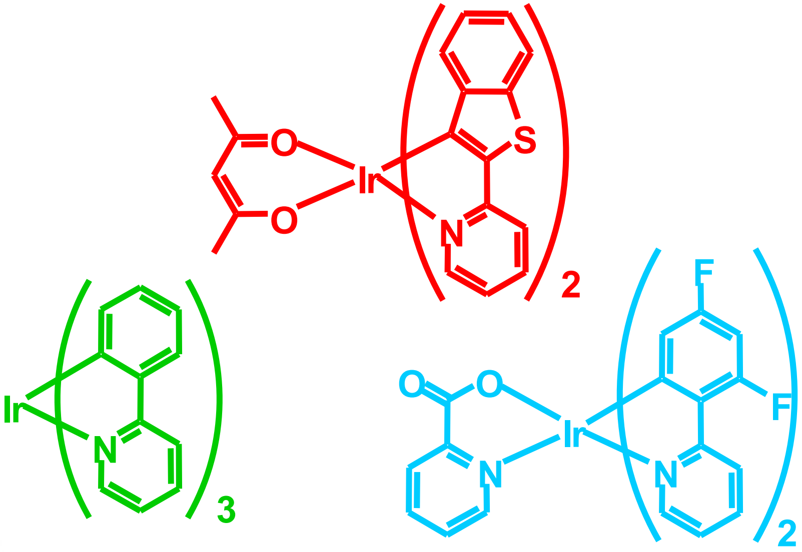
- In order for triplet excitons to emit, spin-orbit coupling is required.
  - Spin-orbit coupling is the interaction between the magnetic moments that arise from the spin and the orbital angular moments of an electron.
  - This effect is strong in heavy atoms.
- Transition metals are common candidates to enable phosphorescence from organic molecules.

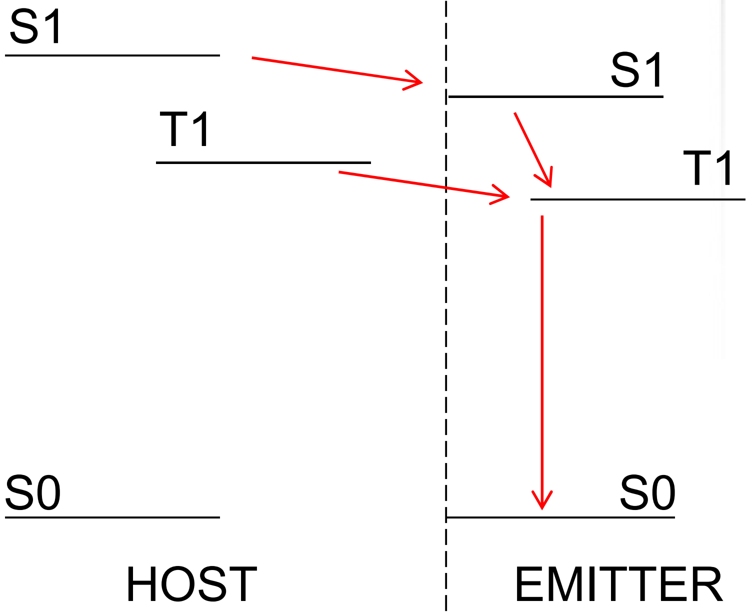


Iridium *tris*(phenylpyridine) aka. Ir(ppy)$_3$

Phosphorescent dopants

- Example Iridium-based phosphorescent dopants for RGB emitters
- To use phosphorescent materials, their exciton energy must be lower than the host triplet.
  - e.g. a red phosphorescent emitter needs a blue host





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- **Device Operation**
- Improving Device Performance
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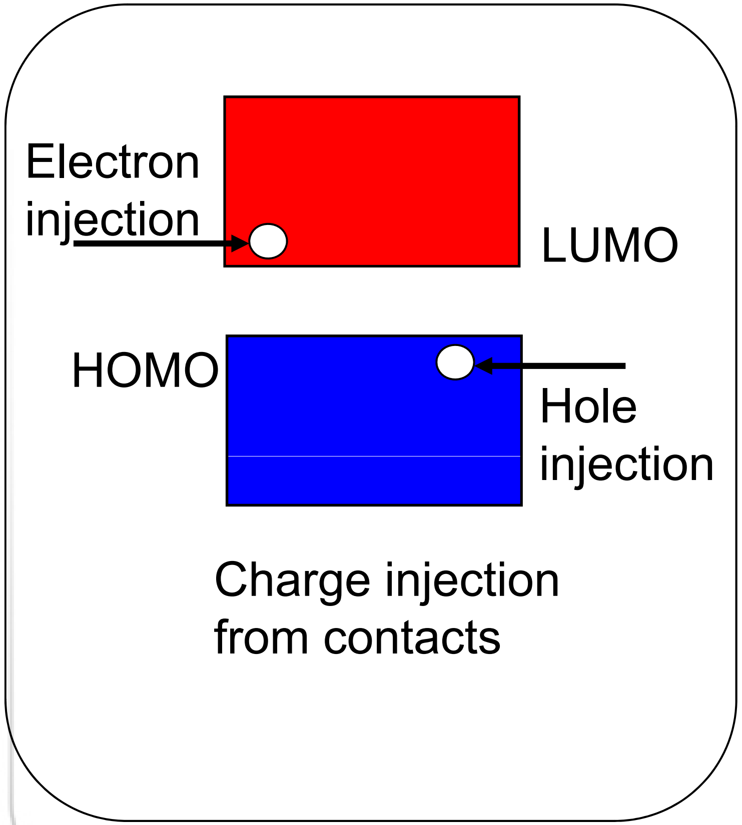
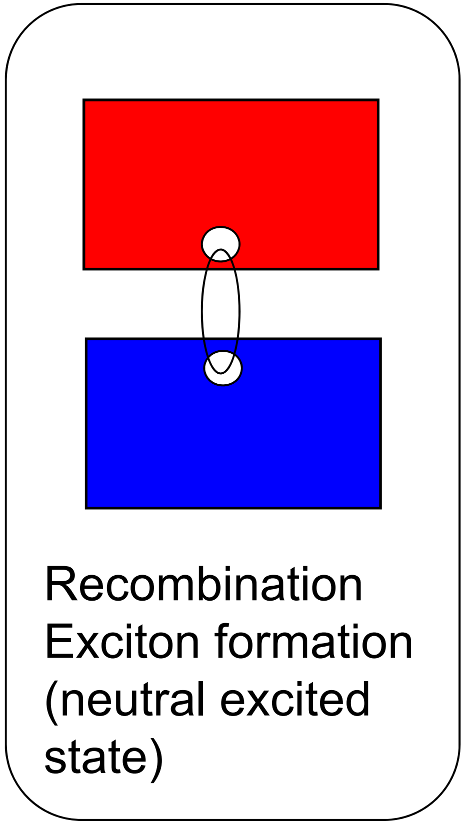
Light Emission from Organic Polymers

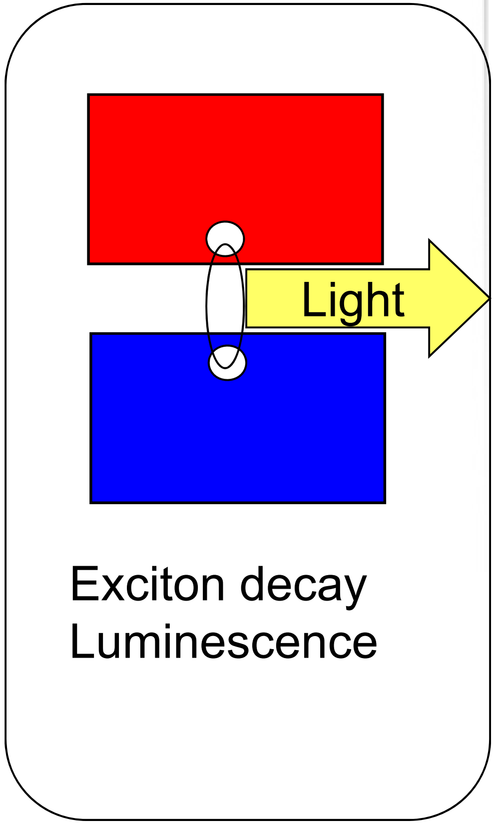
- Light emission results from recombination of injected charges
- Charges can be introduced optically by light absorption



Charge injection
from contacts

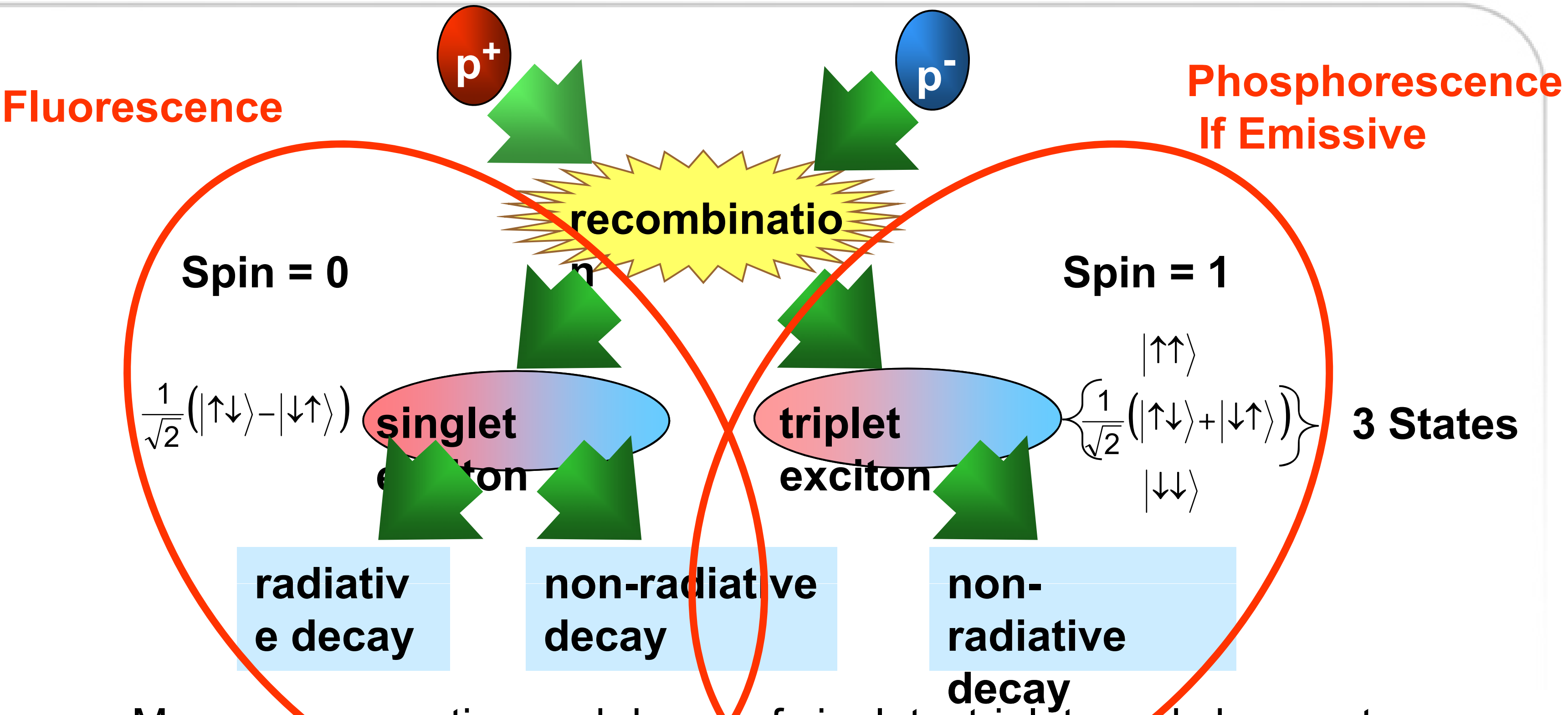


Recombination
Exciton formation
(neutral excited
state)



Exciton decay
Luminescence

Excited States in PLEDs



Fluorescence

Phosphorescence If Emissive

p^+

p^-

recombination

Spin = 0

$\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$

singlet exciton

radiative decay

non-radiative decay

Spin = 1

$|\uparrow\uparrow\rangle$

$\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right)$

$|\downarrow\downarrow\rangle$

3 States

triplet exciton

non-radiative decay

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**

- It is possible to generate a higher ratio of singlet states

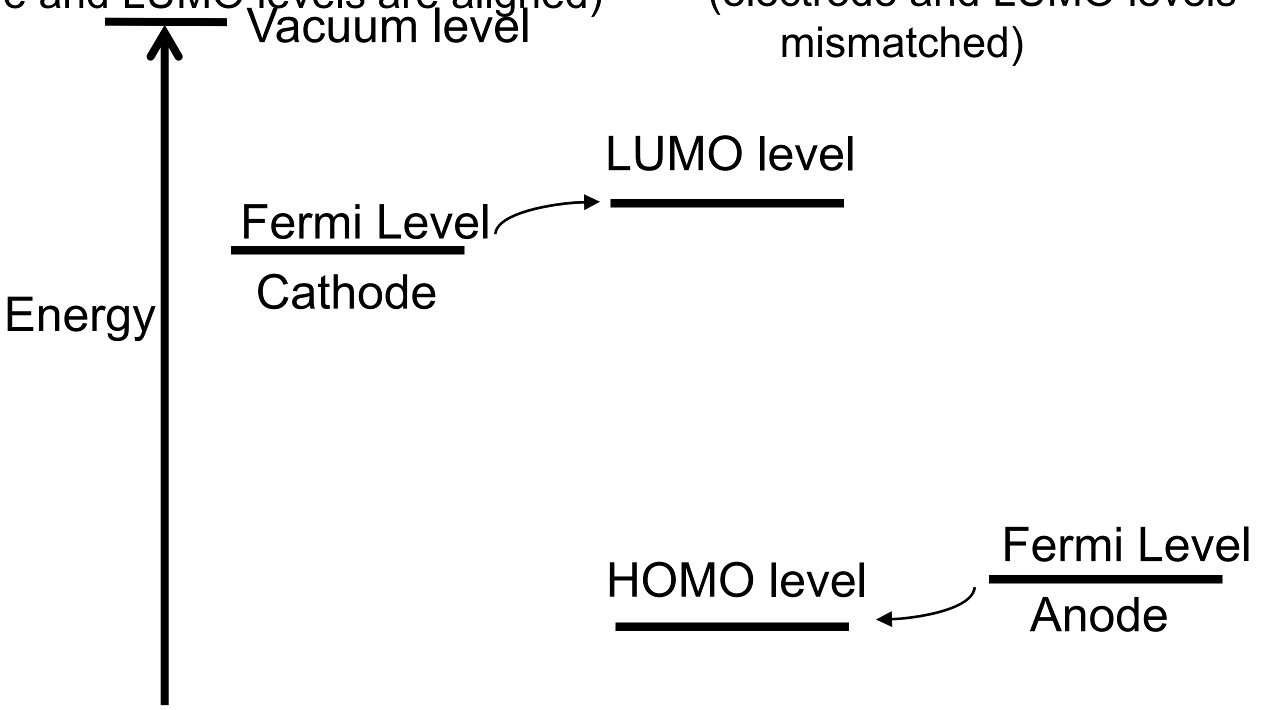
Completed OLED structure

Cathode: Small barrier for electron injection

(electrode and LUMO levels are aligned)

Anode: Large barrier for electron injection

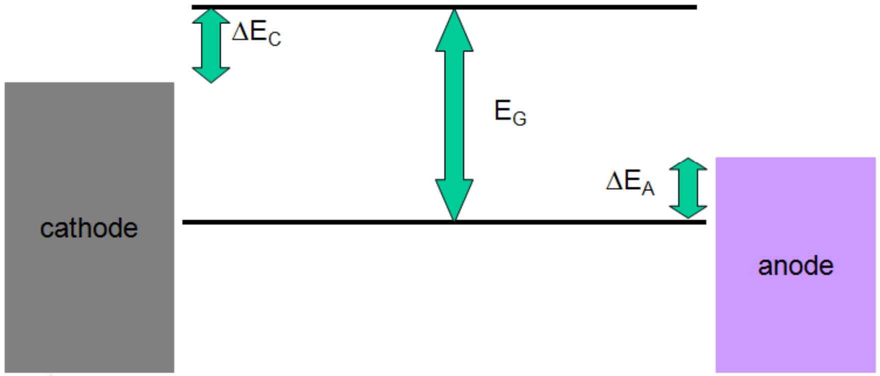
(electrode and LUMO levels mismatched)



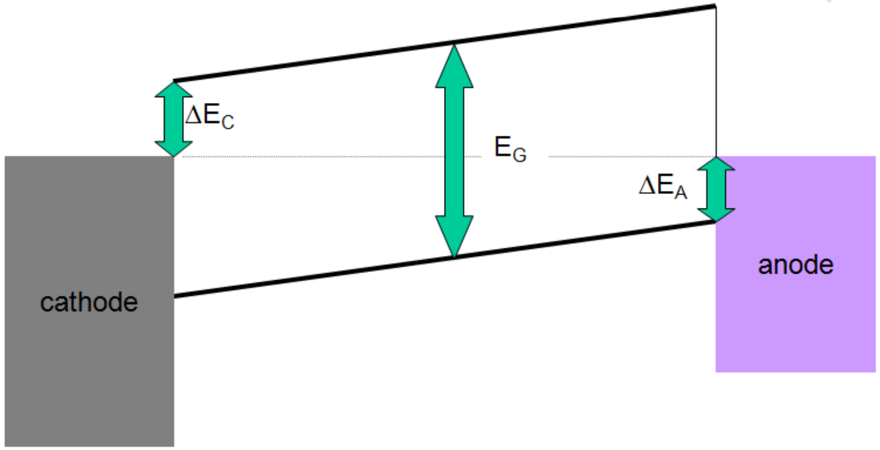
- HOMO-LUMO gap determined by desired wavelength (red ~2V, blue <3V)
- Anode and cathode Fermi levels must differ by few volts
- Typically, anode: ITO F=4.7 V; cathode: Mg F=3.7 V, Li F=2.9 V

LEDs – device function

before contact

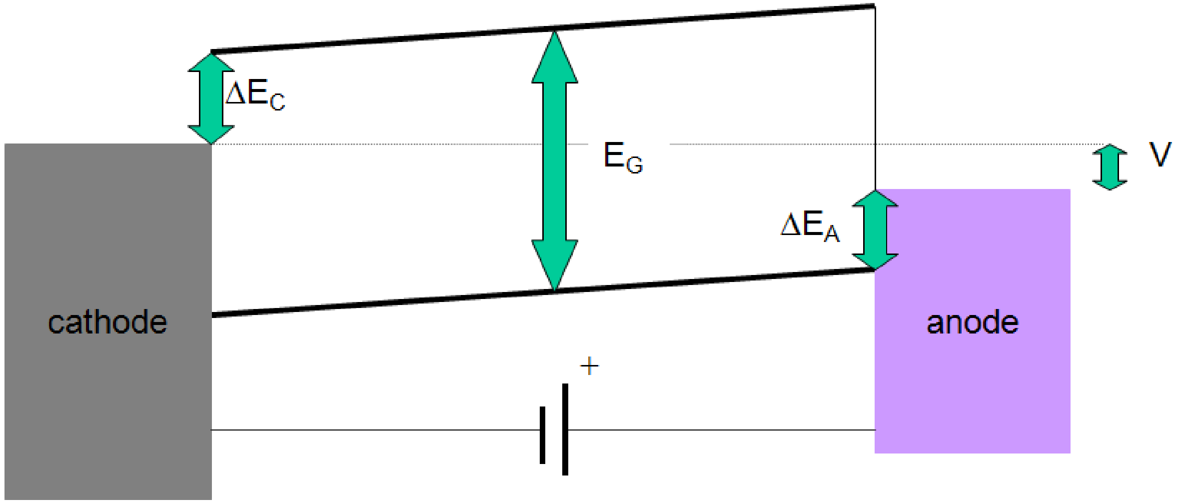


after contact
V=0



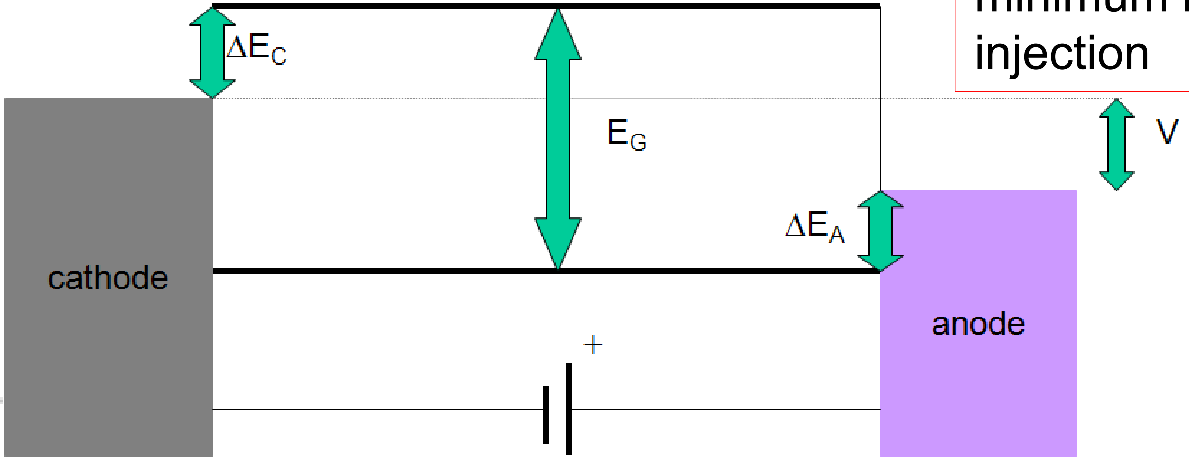
- fermi levels (workfunctions) align
- thermal equilibrium
- no charge inside the LEP layer
- no ‘band bending’

Forward bias to Flat Band Voltage



V = Vbi =~ f(cathode)-f(anode)

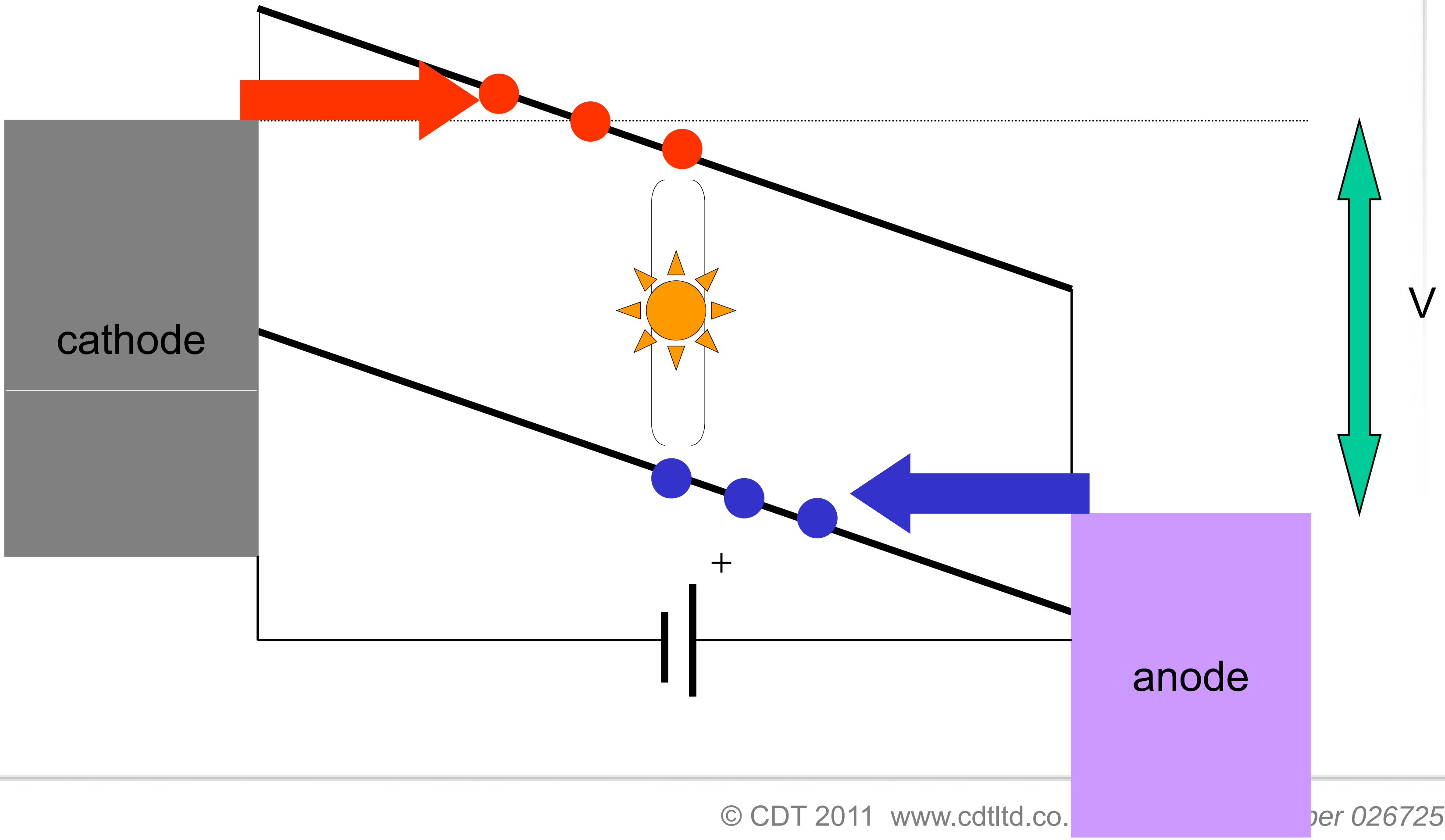
Flat band Voltage = minimum bias for charge injection



Forward Bias → light emission

Occurs for all V > Vbi

Space Charge Limited Current



Problems with simple structures

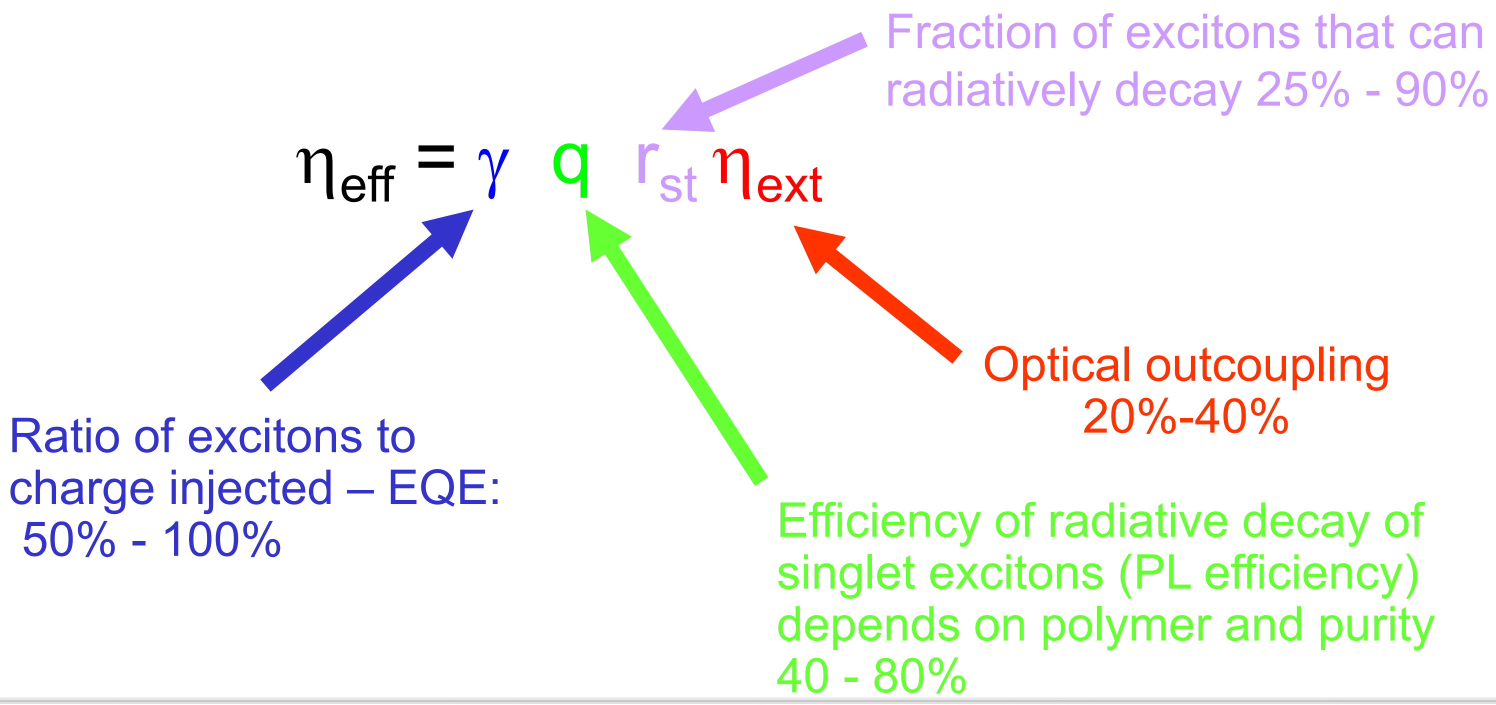
C|D|T

- A single organic layer OLED has a number of drawbacks
  - If the charge recombination occurs at either electrode the emission can be quenched.
  - The charges must be balanced to ensure recombination always towards the middle.
  - Charge balance typically changes with drive level, and often with age, so maintaining this balance is virtually impossible.

Efficiency Relationship

- Relationship between efficiency and controlling factors

Quantum efficiency $= \eta_{eff} = \dfrac{\text{photons out}}{\text{charges flowing in circuit}}$



$$\eta_{eff} = \gamma \;\; q \;\; r_{st} \; \eta_{ext}$$

Fraction of excitons that can radiatively decay 25% - 90%

Ratio of excitons to charge injected – EQE: 50% - 100%

Efficiency of radiative decay of singlet excitons (PL efficiency) depends on polymer and purity 40 - 80%

Optical outcoupling 20%-40%

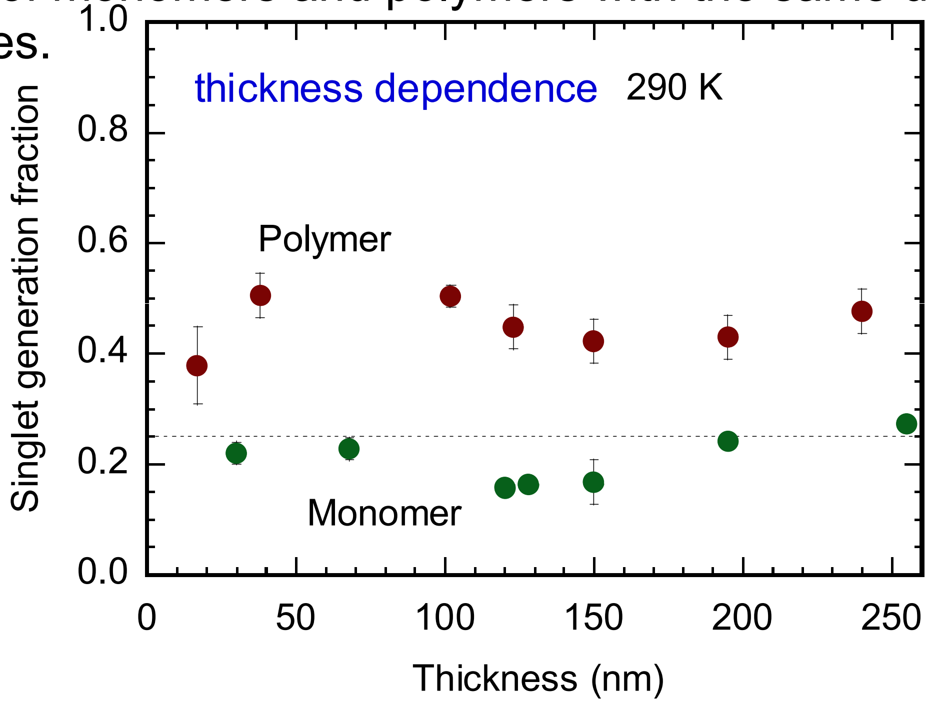
Maximising Singlet:Triplet Ratio

CDT

- For a fluorescent material, only singlet excitons are emissive.
- Simple quantum mechanics suggests a 1:3 S:T ratio and a 25% QE limit.
- Work at Cavendish Lab, Cambridge suggests ratio is ~1:1 for polymers (1:3 for small molecules)
- These are measurements of monomers and polymers with the same unit cell and identical techniques.

Polymers
ST Ratio~0.5

Monomers
ST Ratio~0.25

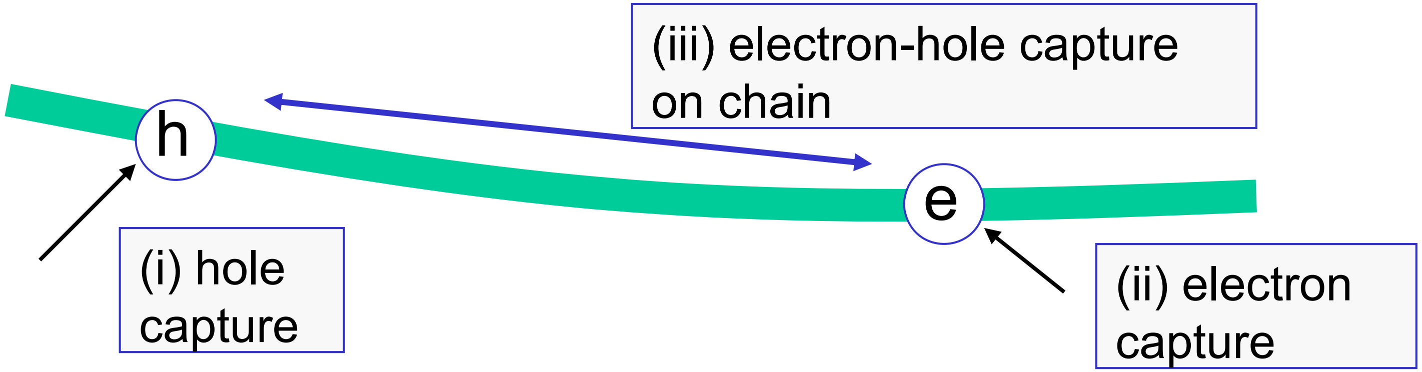


Wilson et al, Nature 413, 828 (2001)

- A reason for the increased S:T ratio will be shown later.

Why are polymers different from small molecules?

- Small Molecules : electron-hole capture at separation » 10 nm
- Polymers: electron and hole arrival on polymer chain, and subsequent recombination to exciton



(iii) electron-hole capture on chain

(i) hole capture

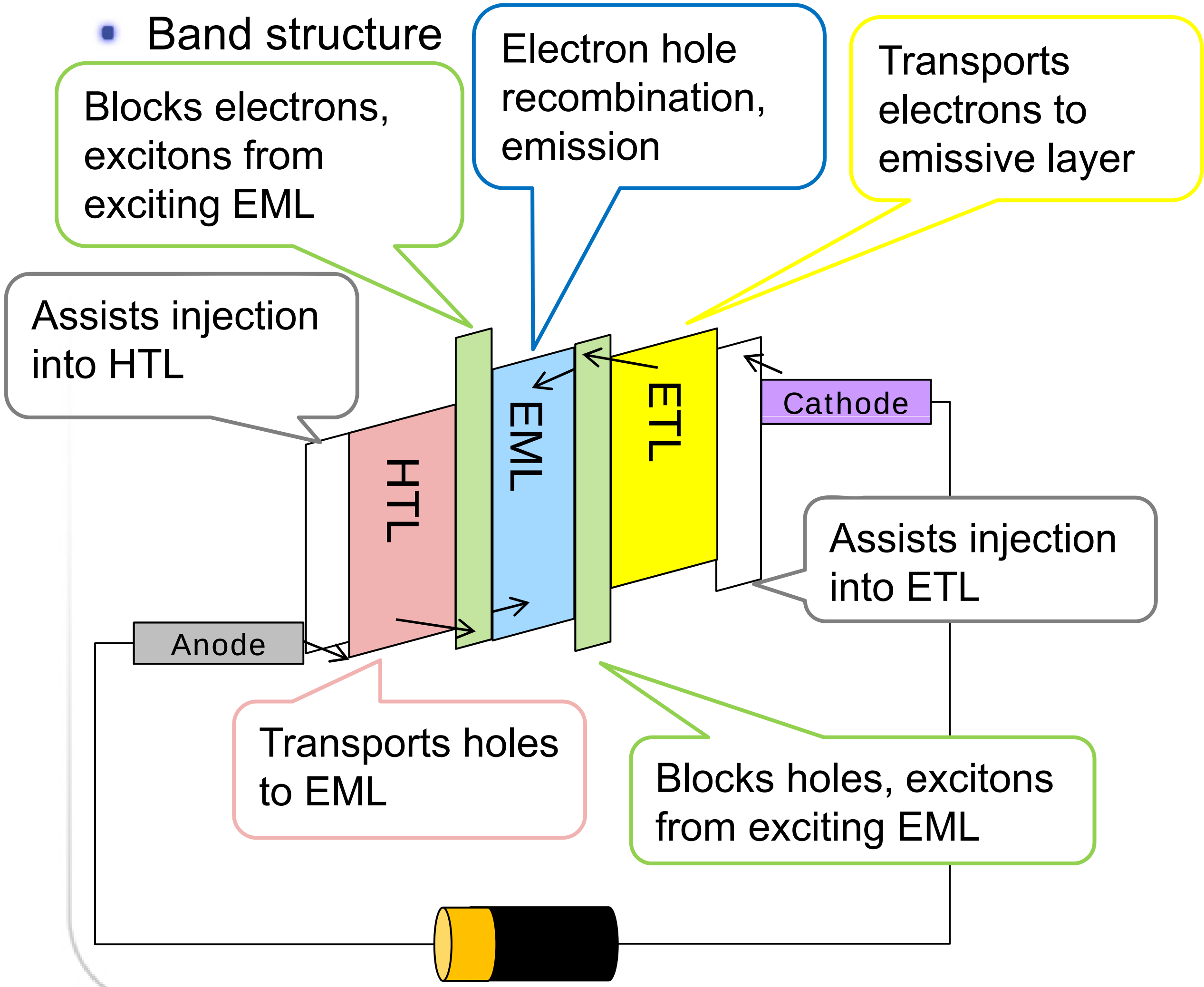
(ii) electron capture

- The singlet is higher energy and therefore larger. This is accentuated in 1D polymer systems.
- This favours singlet bound state at e-h capture (typical range 10 nm) *(Beljonne et al J. Chem. Phys. 102, 2042, 1995)*

SM-OLED Device Structure

C|D|T

- Band structure



Blocks electrons, excitons from exciting EML

Electron hole recombination, emission

Transports electrons to emissive layer

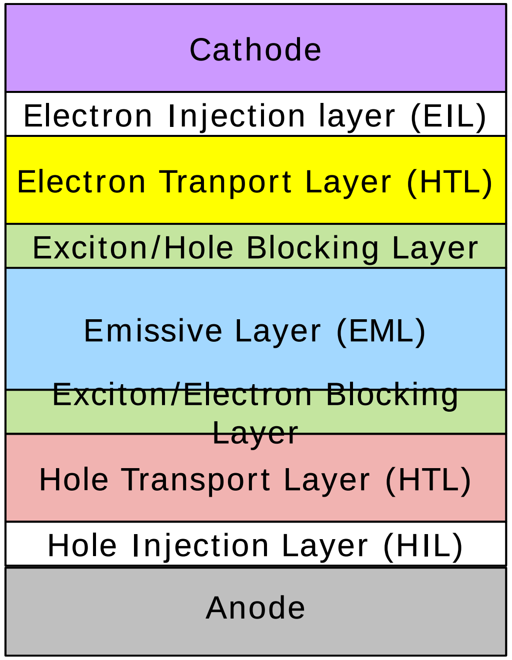
Assists injection into HTL

Assists injection into ETL

Transports holes to EML

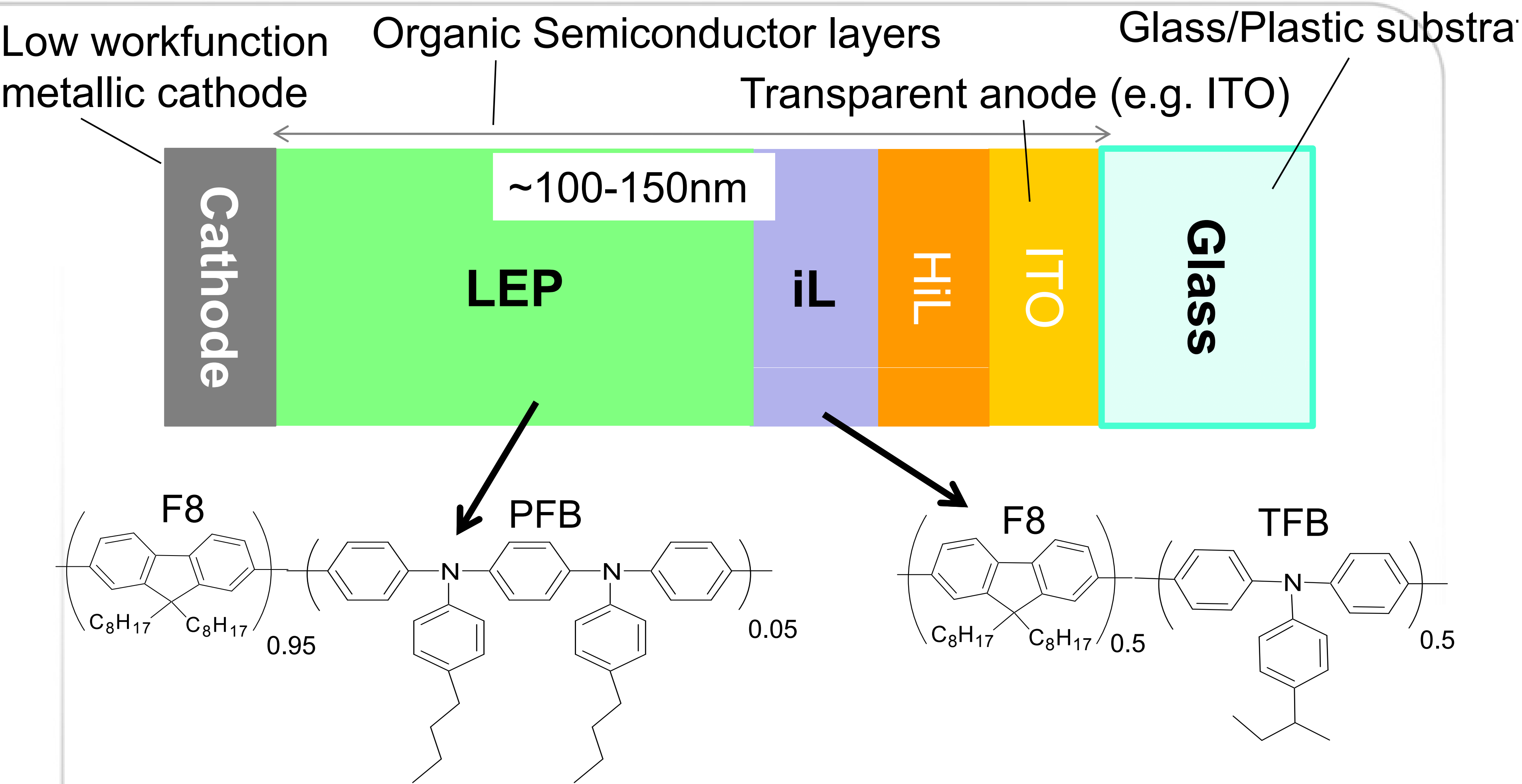
Blocks holes, excitons from exciting EML

Generic Structure



- Cathode
- Electron Injection layer (EIL)
- Electron Tranport Layer (HTL)
- Exciton/Hole Blocking Layer
- Emissive Layer (EML)
- Exciton/Electron Blocking Layer
- Hole Transport Layer (HTL)
- Hole Injection Layer (HIL)
- Anode

Materials and device structure



Low workfunction metallic cathode

Organic Semiconductor layers

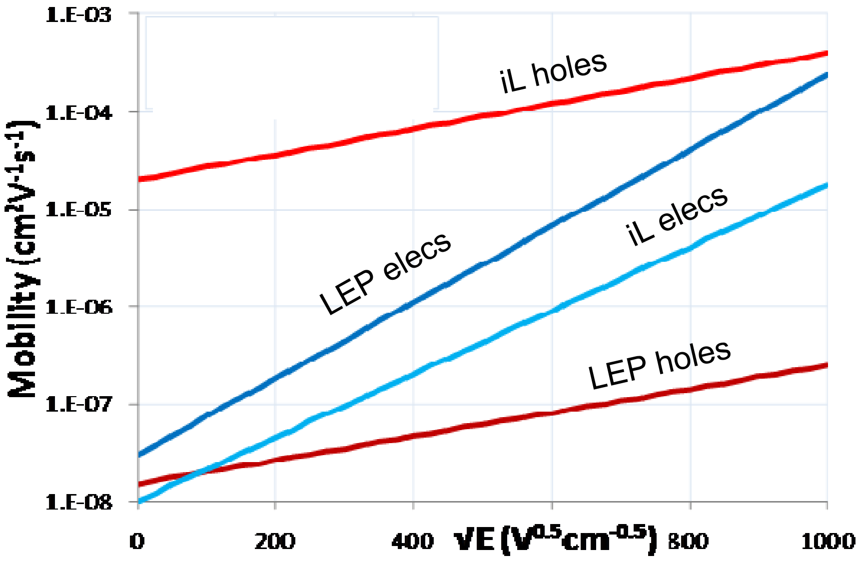
Glass/Plastic substra

Transparent anode (e.g. ITO)

Random copolymer
F8:PFB 95:5

A-B copolymer
F8:TFB 50:50

Charge Mobility

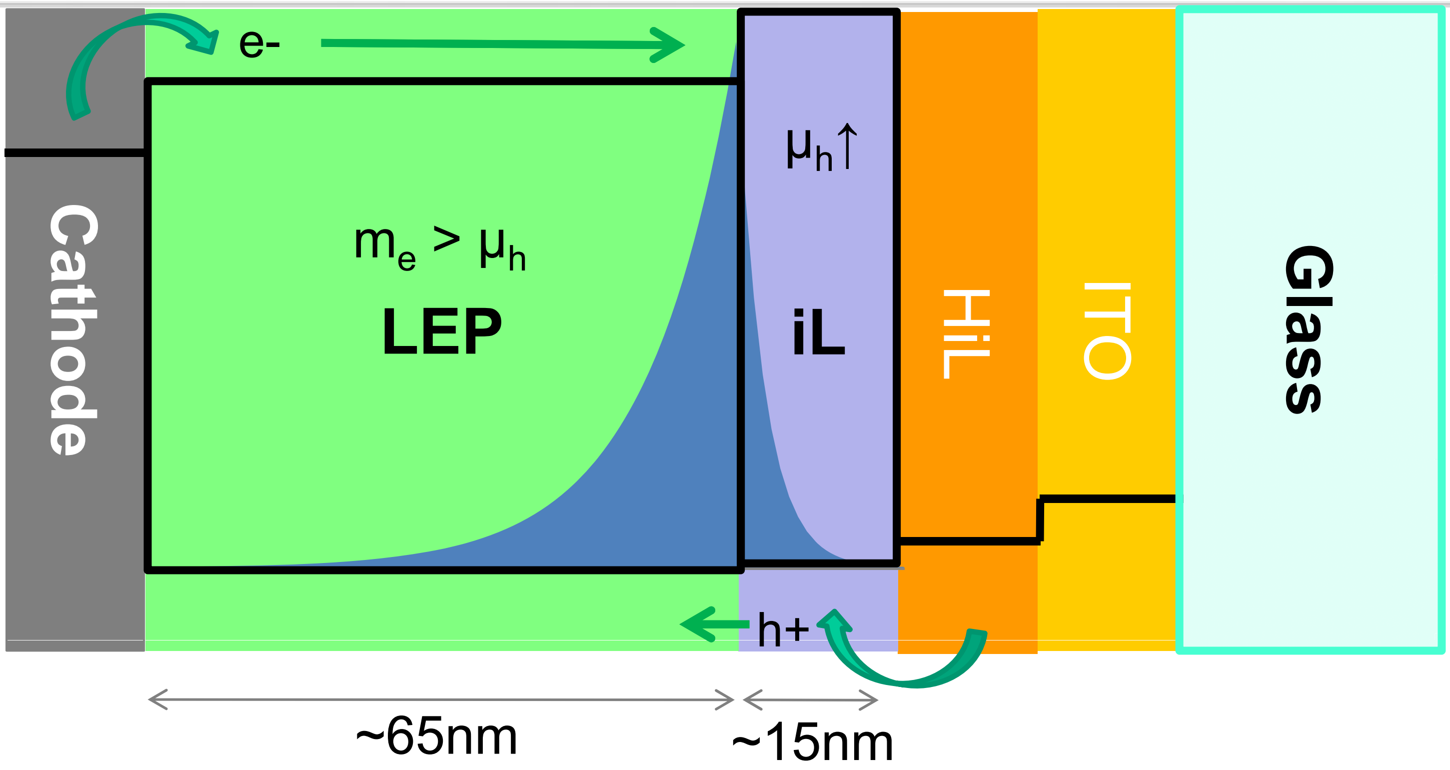


μ_h (LEP) < μ_e (iL) < μ_e (LEP) < μ_h (iL)

→ Model materials satisfy mobility requirements for ideal RZ

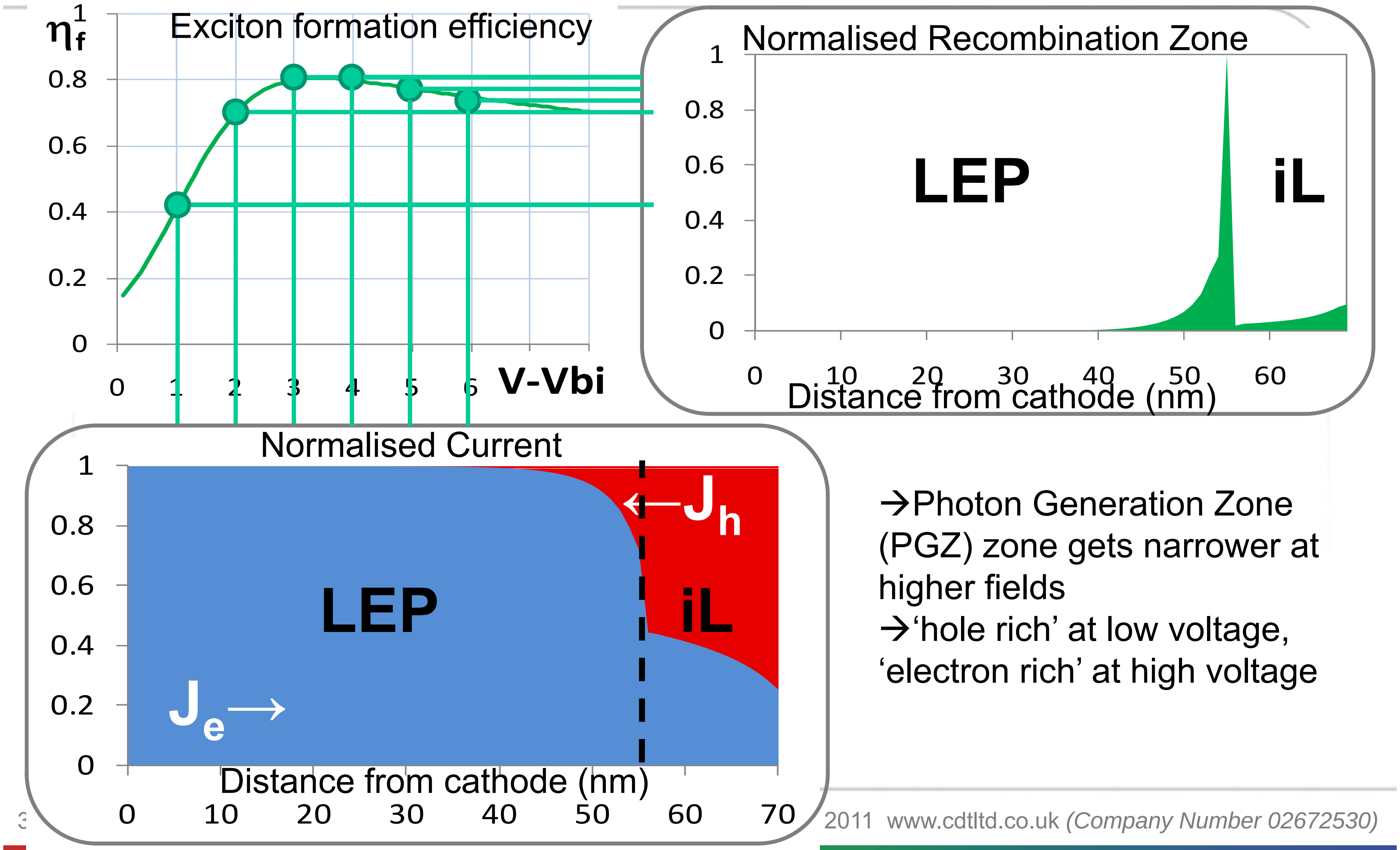
- Schematic and summary of optimized material mobility and thickness design rules.
- The model materials satisfy the mobility requirements for an ideal Recombination Zone (RZ)
- The RZ profile fits very well to exponential decay within LEP peaking at IL:LEP interface.

Device structure



- → LEP thickness and mobilities - Optimum RZ for outcoupling
- → iL - hole injection, efficiency and lifetime
- → HIL and ITO thicknesses – tuned for colour and outcoupling
- → Electrodes / charge injection layers - thermally stable

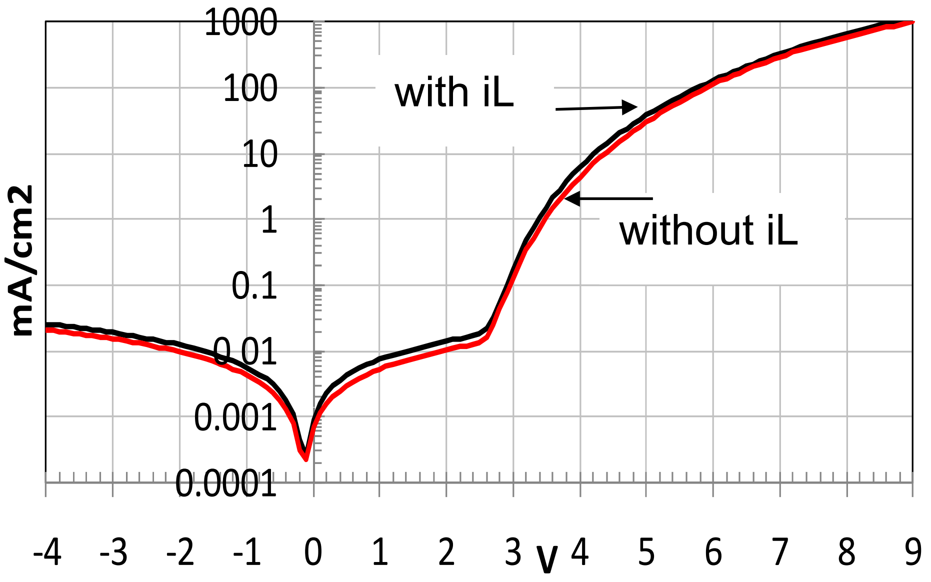
Simulation – RZ and IQE

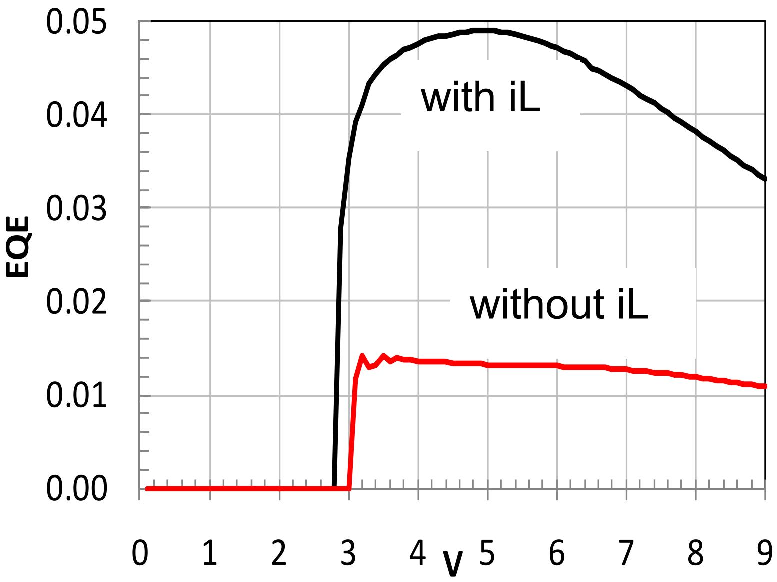


→Photon Generation Zone (PGZ) zone gets narrower at higher fields

→'hole rich' at low voltage, 'electron rich' at high voltage

Model materials – Device IVL





→ 5% EQE can be achieved with optimized device, at CIE-y ~0.13.

→In this optimized device structure, the importance of the interlayer in achieving this efficiency is clear and in agreement with the expectations from the simulations.

Outline

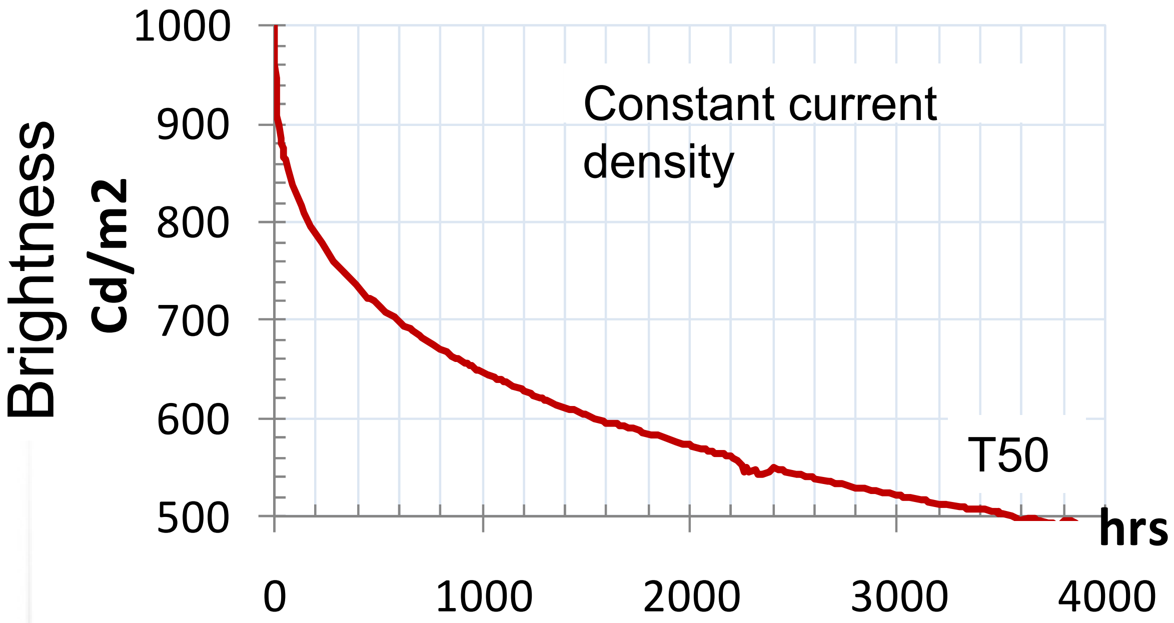
Materials and Material Properties

Device Operation

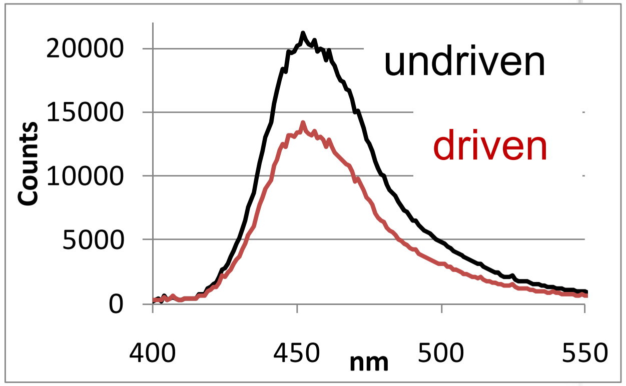
Improving Device Performance

Conclusions

Case Study 1: Fluorescence quench sites



PL intensity

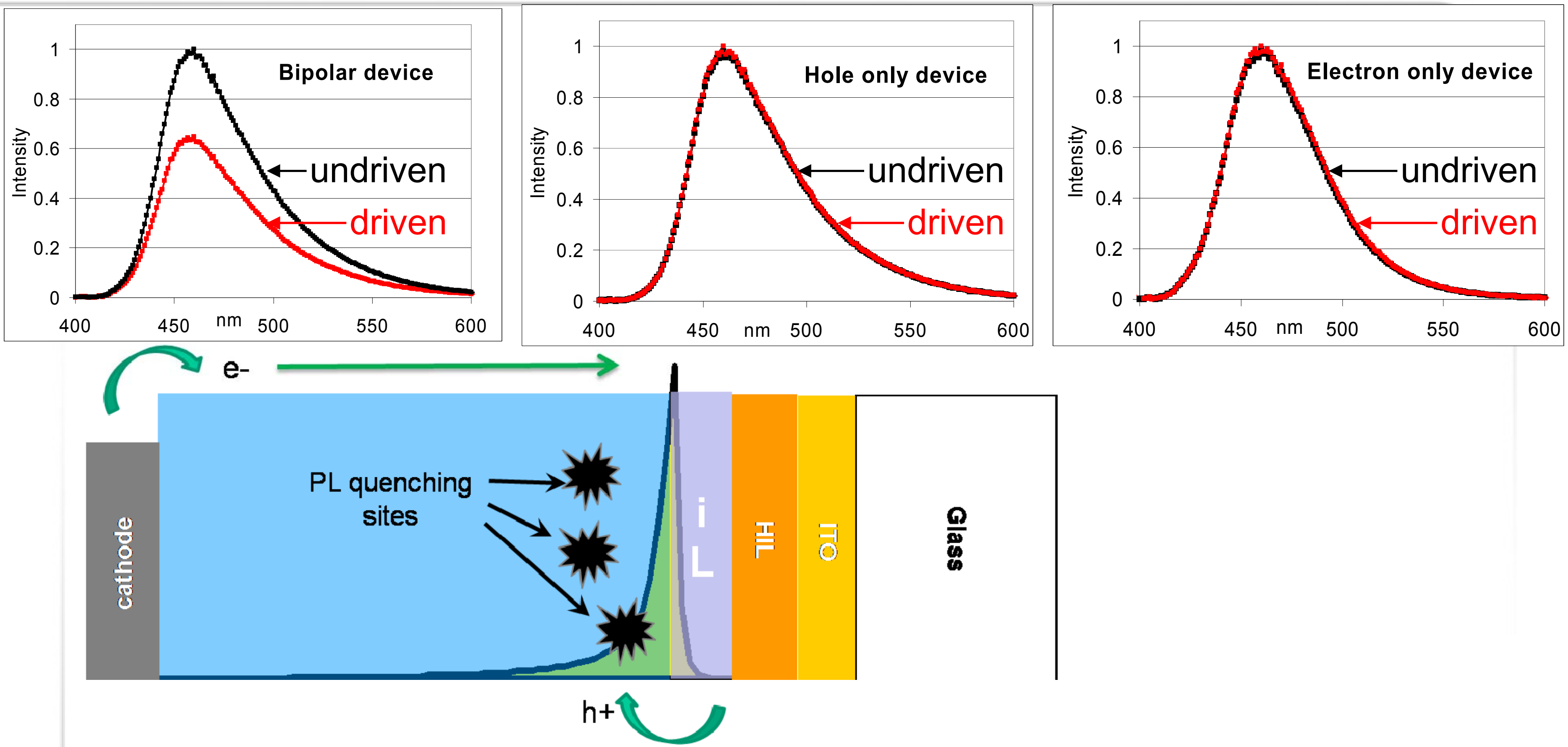


No change in colour

- Key challenge for P-OLED is extending lifetime.
- Analysis of PL of device driven to 50% of initial brightness reveals a 30% drop in PL intensity and is a real change in the material PLQE

→ PL quenching site formation is dominant degradation mechanism

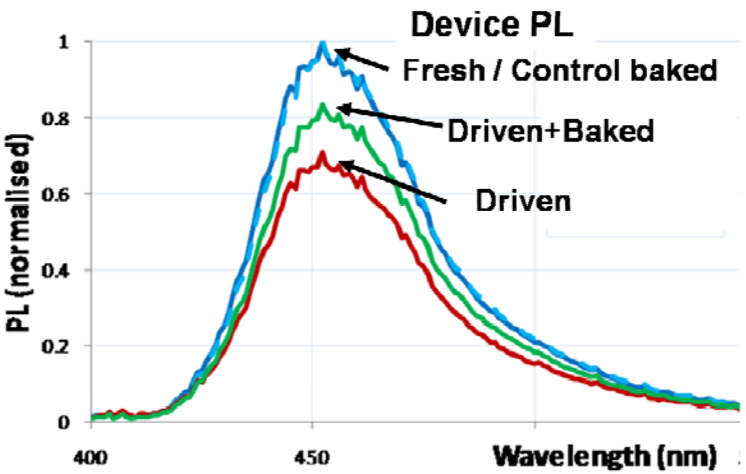
Cause of PL decay

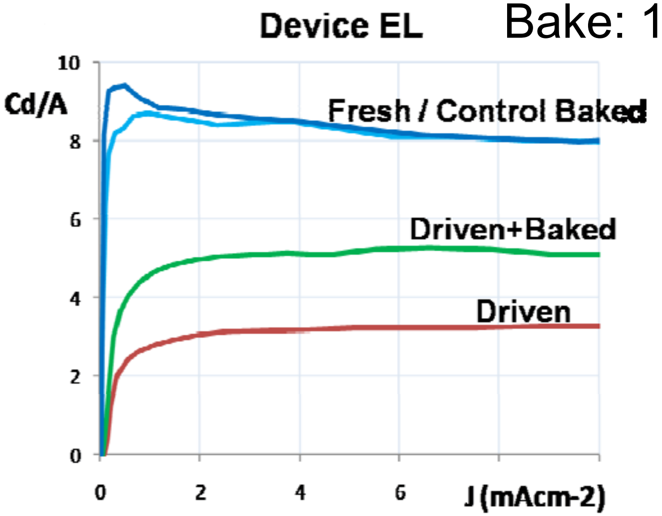


- PL quenching site formation is dominant degradation mechanism.
- The PL decay from single carrier devices is shown to be remarkably stable.
- This strongly suggests that excitons are required to generate PL quenching sites.

PL recovery matched by EL recovery

- PL decay can be split into ‘permanent’ and ‘recoverable’ components.
- The recovery in the optically excited PL efficiency is matched by a recovery in the electrically driven EL efficiency as shown below:

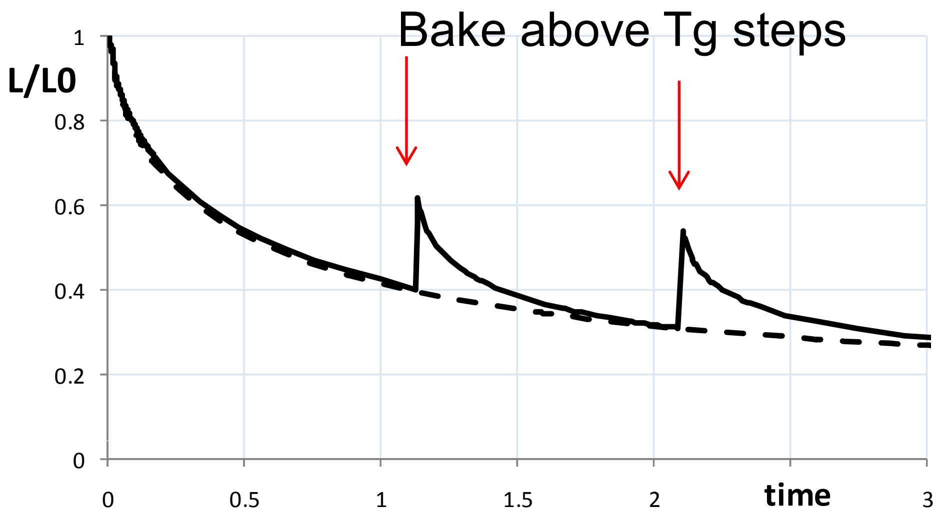




Bake: 120C 30mins

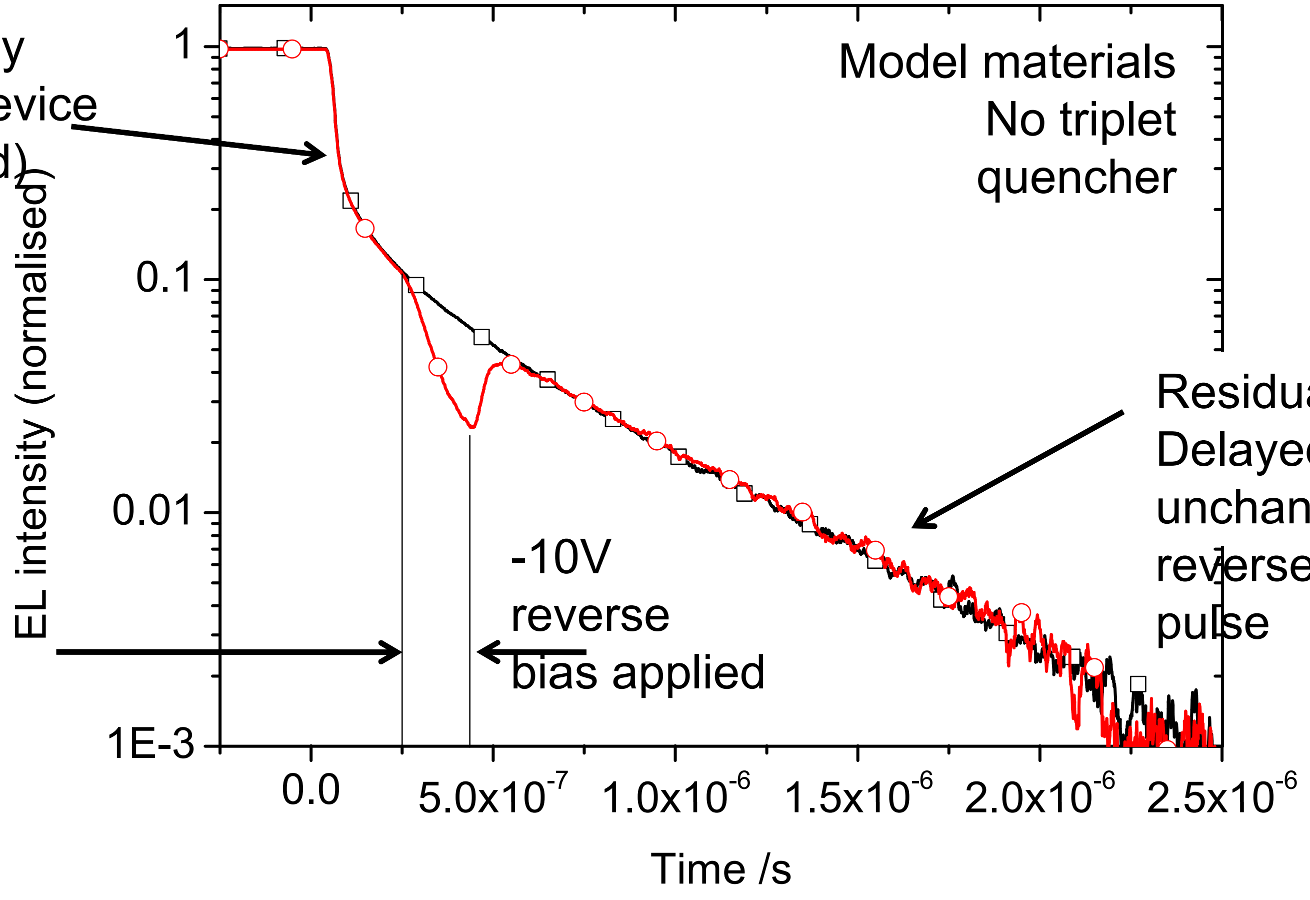
→ PL decay can be split into ‘permanent’ and ‘recoverable’ components
→ 40-50% of EL and PL decay at T50 can be recovered by baking!!
→ The threshold temperature for PL recovery is the LEP Tg and the recoverable component of decay can by cycled many times.

Reversible portion of degradation



- The characteristic lifetime of the recoverable degradation is similar after first and second bakes, suggesting that intrinsic stability of the recoverable portion of degradation indeed reverts back to it's pristine condition and not to some weakened intermediate state.
- Improved LEP materials are more stable to excitons, such that the recoverable PL dominates, with >95% PL recovery.
- Tackling the recoverable PL quenching sites is the key to P-OLED stability.

Case study 2 – loss of triplet yield



Fast decay ~24ns (Device RC limited)

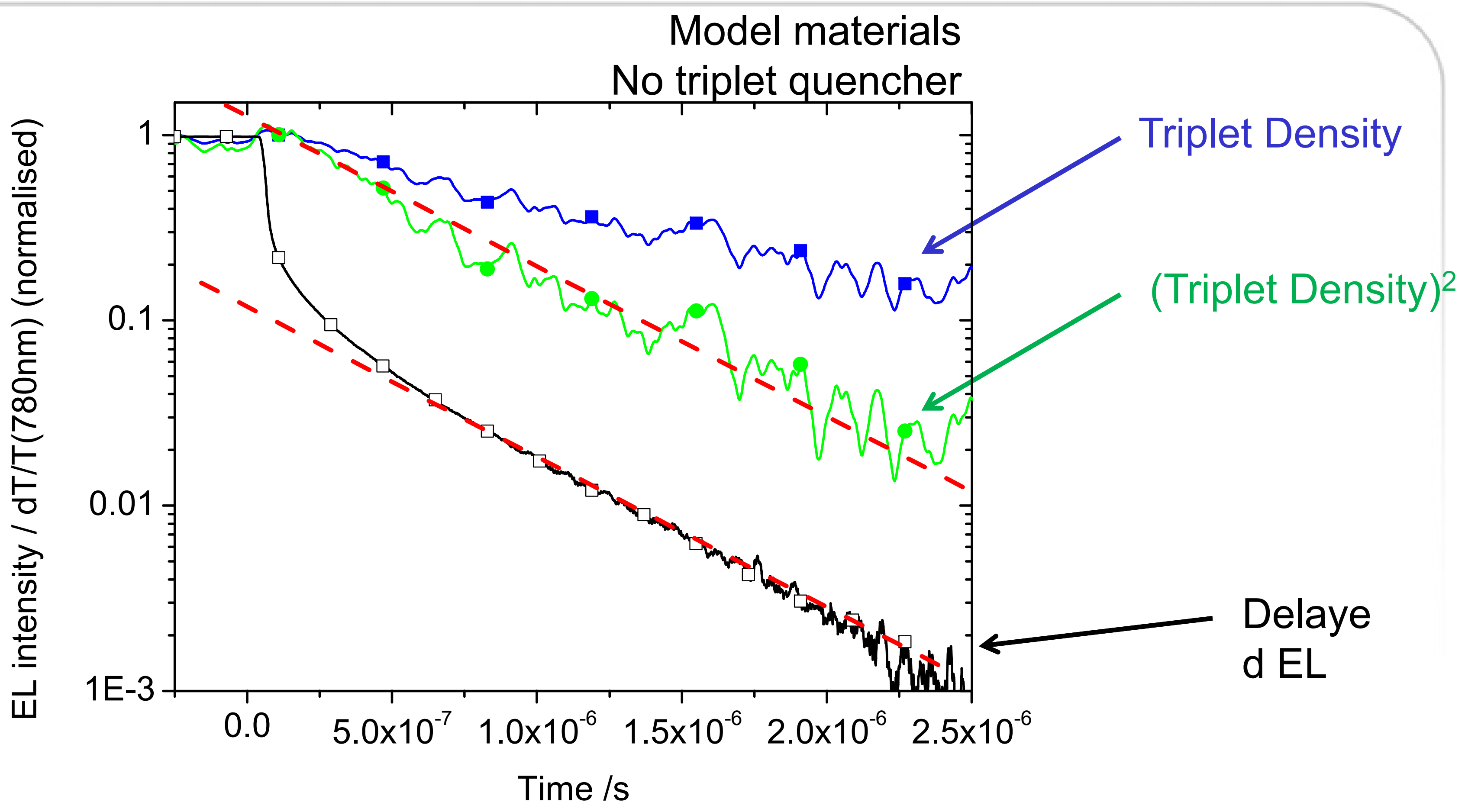
Model materials
No triplet
quencher

-10V reverse bias applied

Residual Delayed EL unchanged by reverse bias pulse

- ~20% of luminescence has a very long lifetime (msecs)
- Delayed electroluminescence does not originate from trapped charges

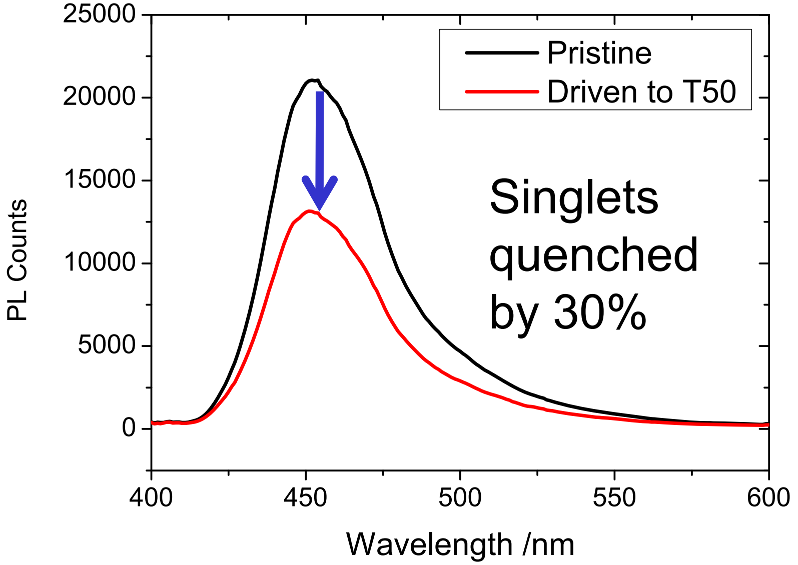
Delayed Electroluminescence



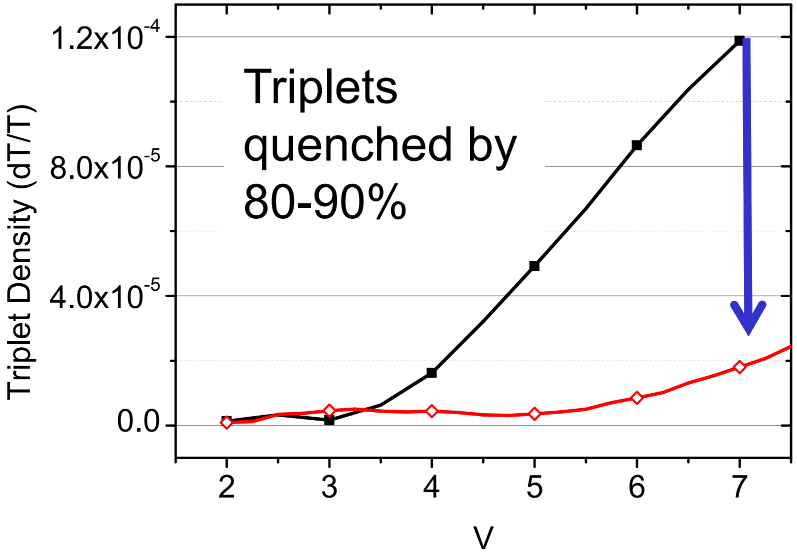
Origin of delayed fluorescence is TTA : $T_1 + T_1 \rightarrow S_1 + S_0$

Driving Effect on Triplet Density

Model materials, No triplet quencher



Singlets quenched by 30%

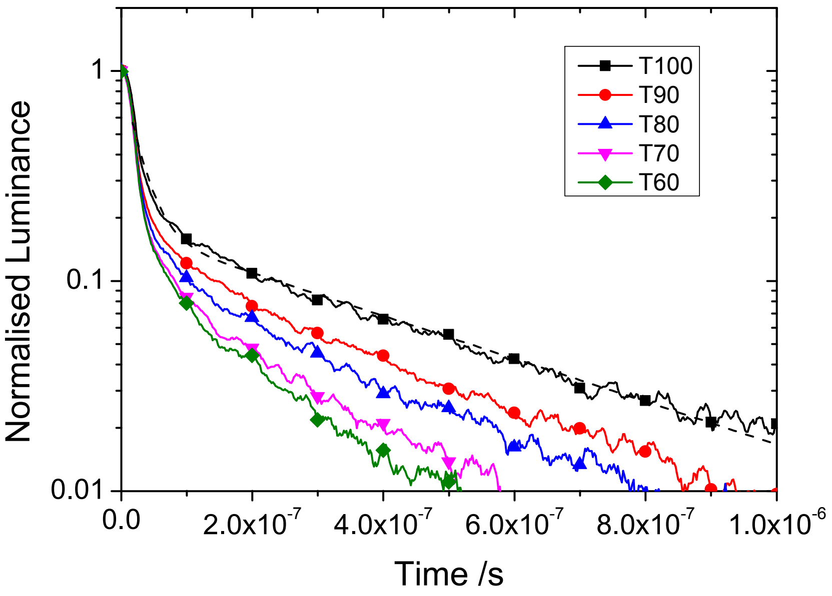


Triplets quenched by 80-90%

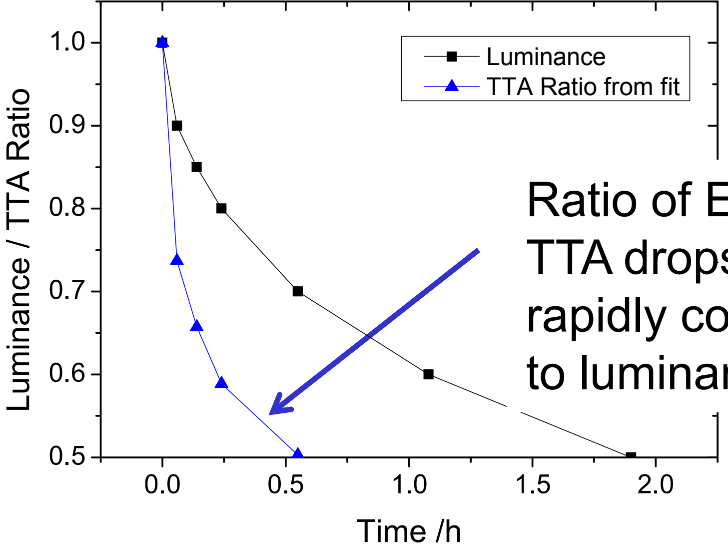
- Triplets are quenched very effectively in a driven device

Rapid loss of TTA during driving

Model materials, No triplet quencher



Device Lifetest from 5000Cdm^{-2}

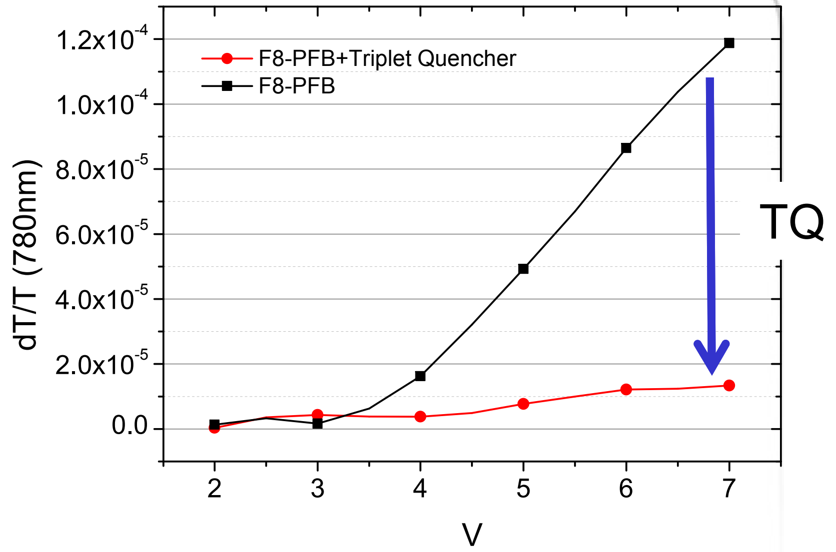


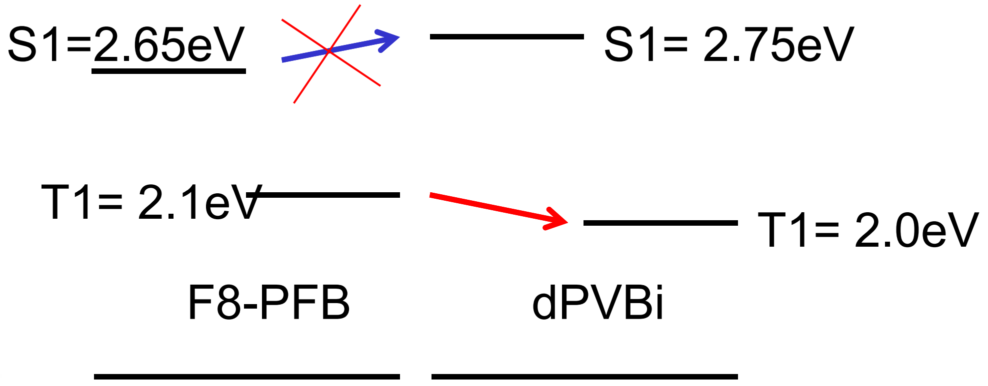
Ratio of EL from TTA drops rapidly compared to luminance

- Delayed fluorescence lost during early stages of lifetest

Effect of Triplet Quenching Additive

- Effective reduction of triplet density when device is doped with triplet quenching additive.
- No change of emission spectrum indicates that there is no singlet energy transfer
- 20% drop in EQE with TQ consistent with loss of TTA contribution





S1=2.65eV

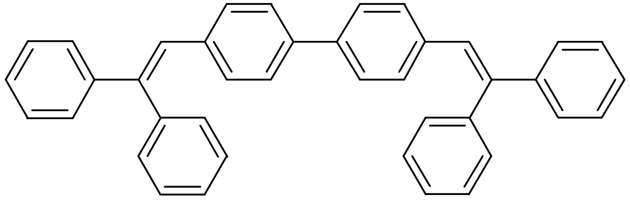
S1= 2.75eV

T1= 2.1eV

T1= 2.0eV

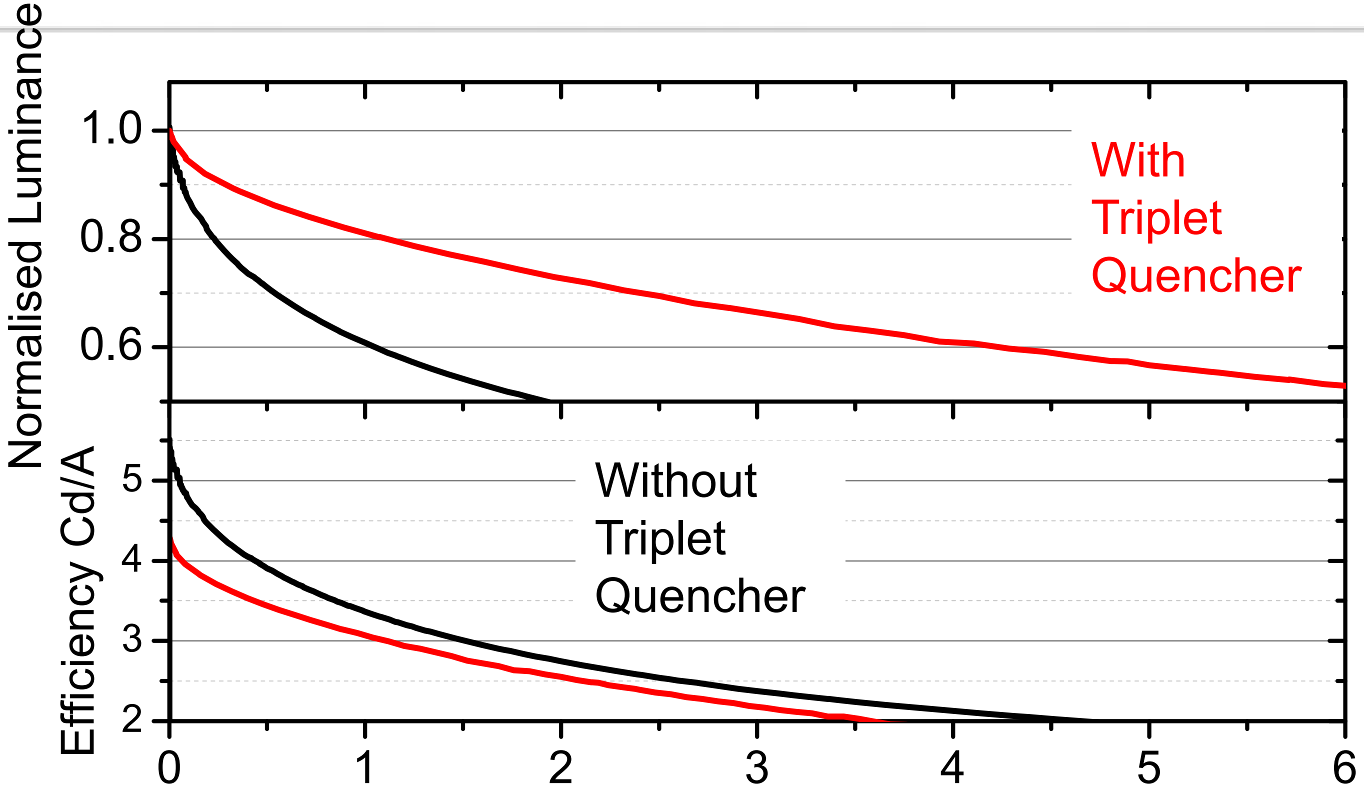
F8-PFB

dPVBi



Triplet Quenching Additive:
dPVBi (1% mol ratio)

Lifetime with Triplet Quencher



- Removing triplets reduces the rapid initial decay in lifetrace and gives substantial improvements in stability
- Loss of TTA contribution to efficiency during early stages contributes significantly to the steep intitial slope of lifetrace
- Control of triplet interactions is key for device efficiency and lifetime