C|D|T

The Route from Organic Materials Synthesis to High Performance Processable Electro-optical Devices

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Organic Materials: New Opportunities for Synthetic Chemists

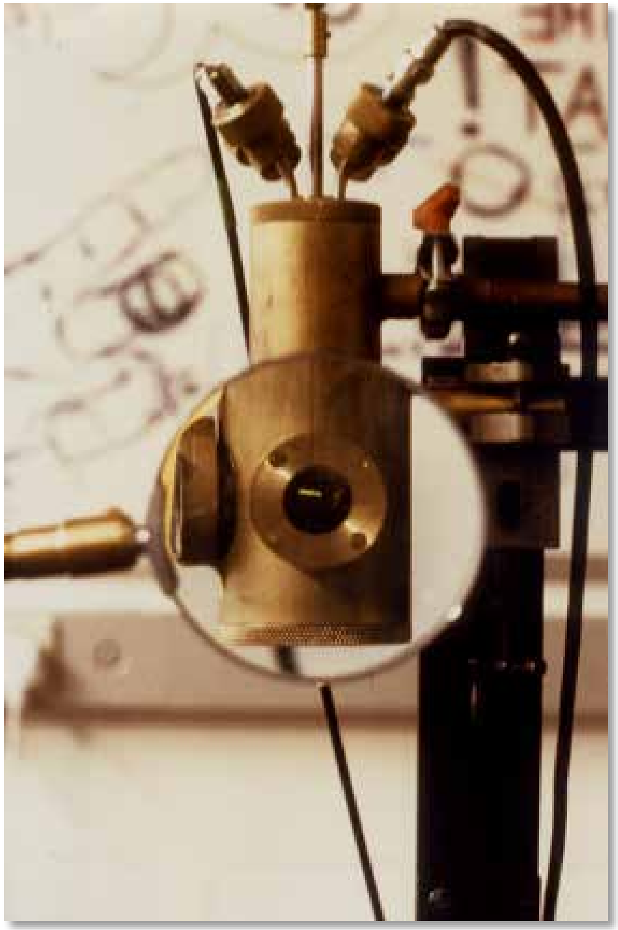
- Introduction to Solution Processable OLEDs
- Synthesis of Conjugated Polymers for Blue OLEDs
  - Summary of Synthetic Schemes
  - Impact of Purification on Performance
  - Maximising RGB Efficiency
- OLED Applications
- Other Solution Processed Devices
  - Thin Film Transistors
  - All-Printed OLEDs
  - Solar Cells
- Summary

Introduction to Solution Processable OLEDs

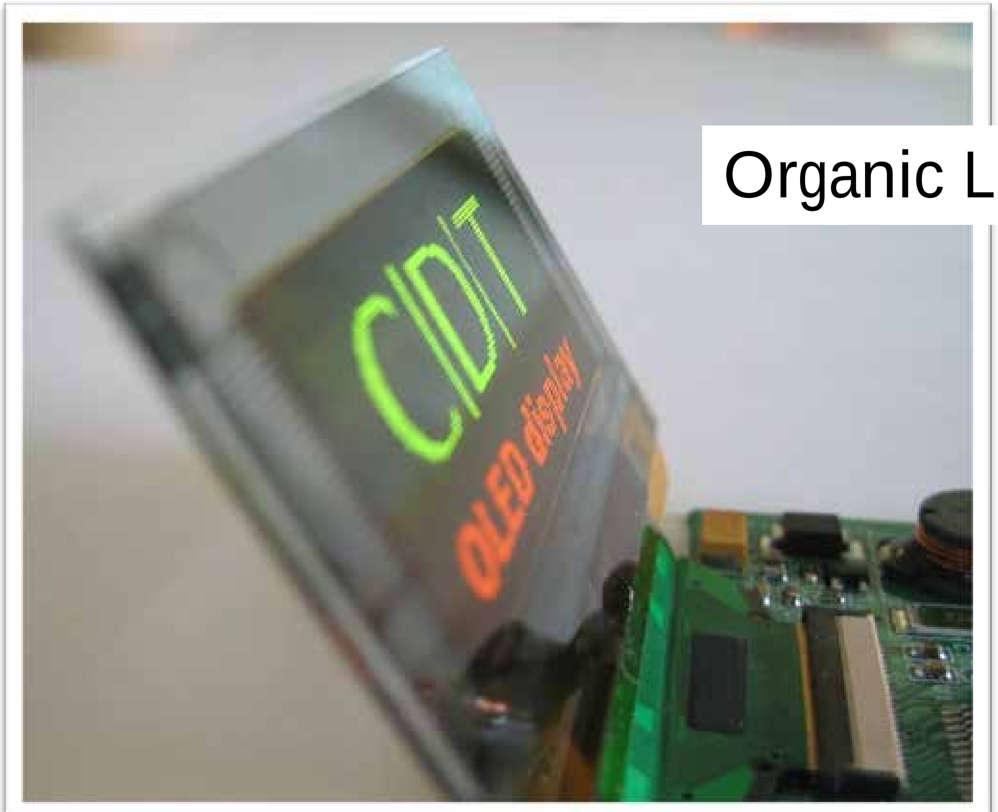
1989 – First Polymer Generated Light

CDT

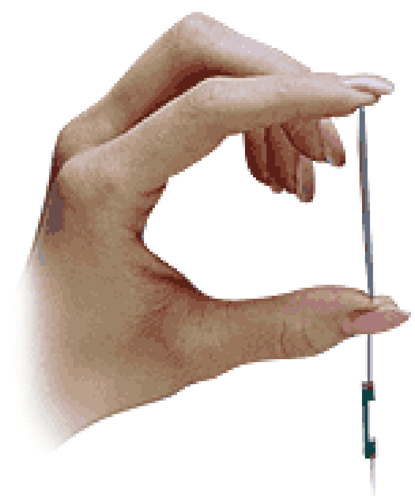
- CDT originated from work at the Cavendish Laboratory, Cambridge
- In 1989, an investigation of the breakdown voltage of Poly(p-phenylene vinylene) found the device emitted green light!
- The research teams quickly focused on the commercial potential of this effect



What is OLED?



Organic Light Emitting Diode

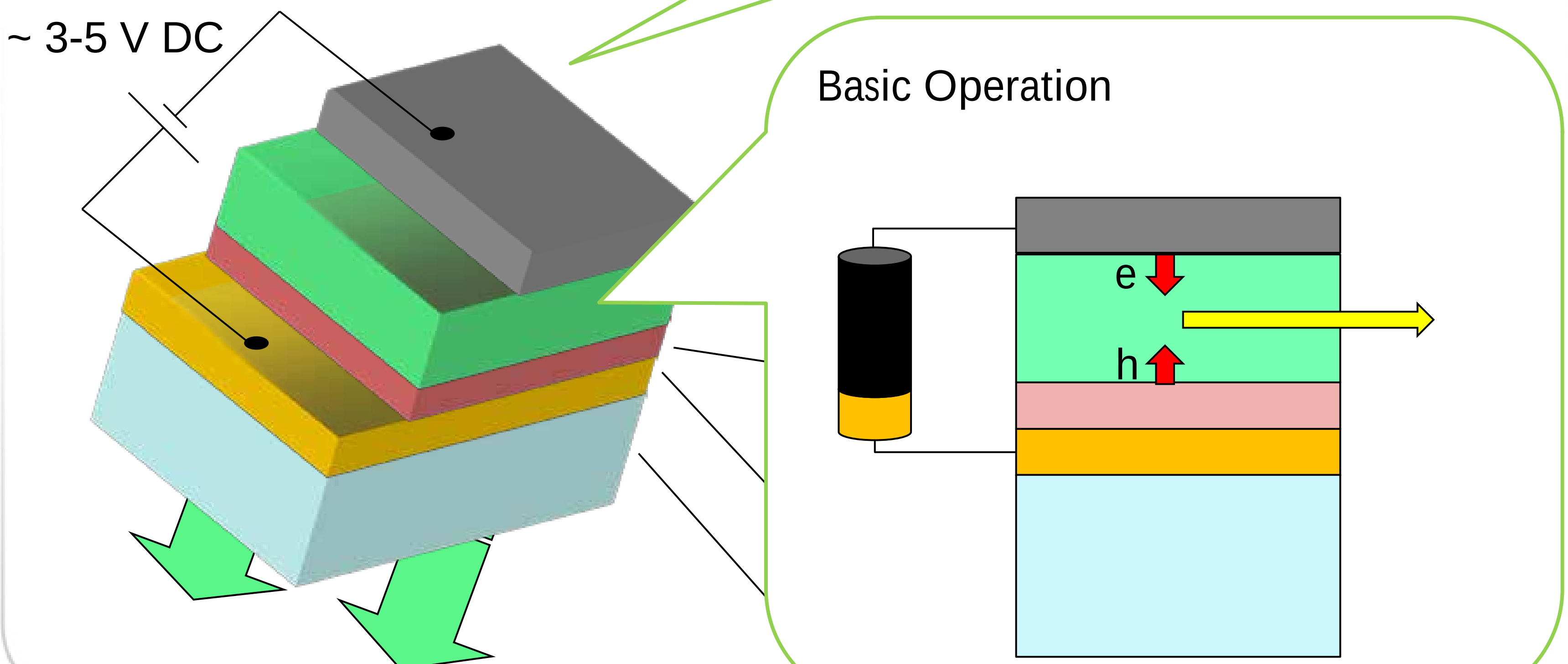


… The next generation display and solid state lighting technology

How OLED works

- Simple device structure
  - No backlight required
  - Thin active layers

More layers may be incorporated to improve performance .



Bottom Emission structure

Semiconducting Polymers

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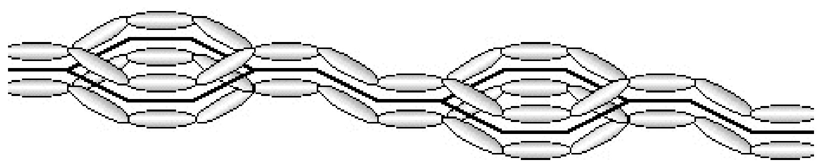
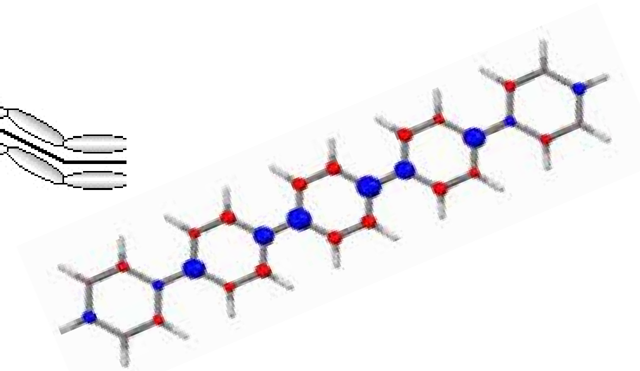
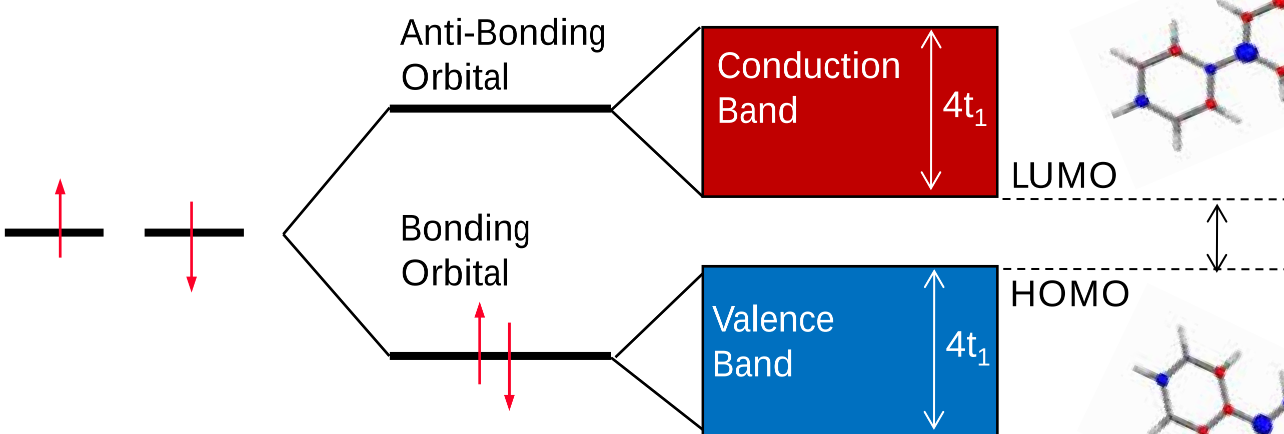
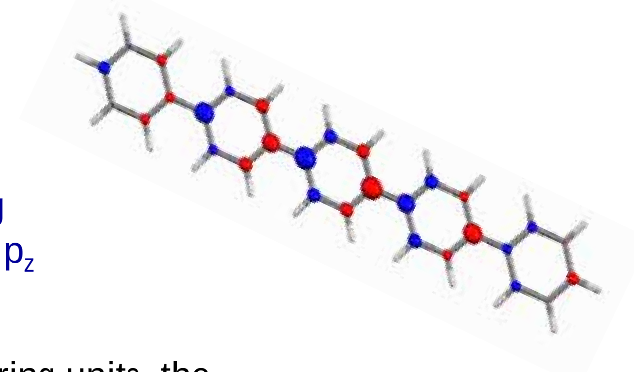
- Semiconducting properties arise from overlap of delocalised pi-orbitals









Degenerate p_z levels

Non-degenerate molecular orbital levels

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

The stronger the interaction between neighbouring units, the smaller the HOMO-LUMO energy gap

Light Emission from Organic Polymers

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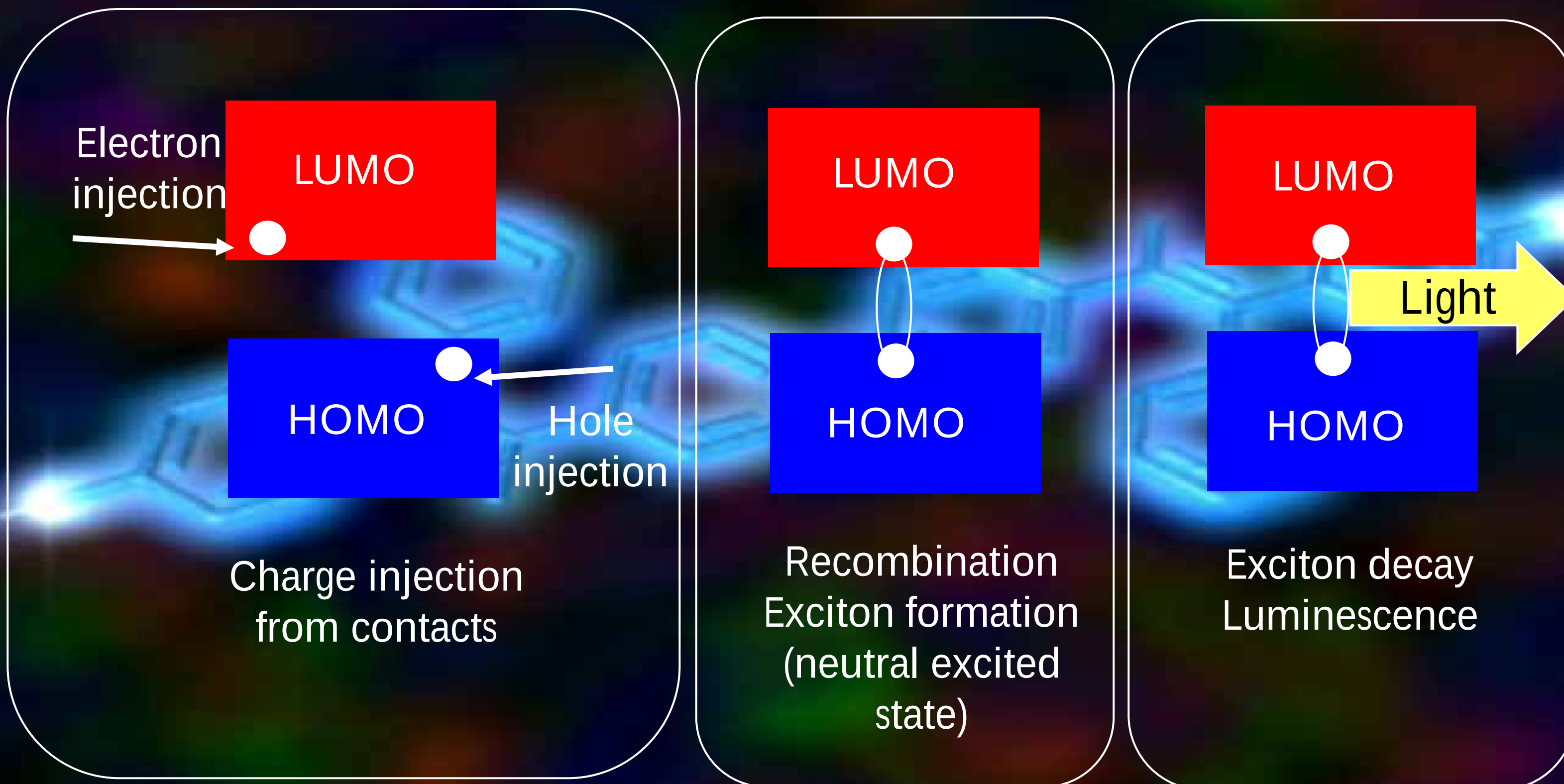
- Light emission results from recombination of injected charges



Device structure of Polymer-OLED (PLED)

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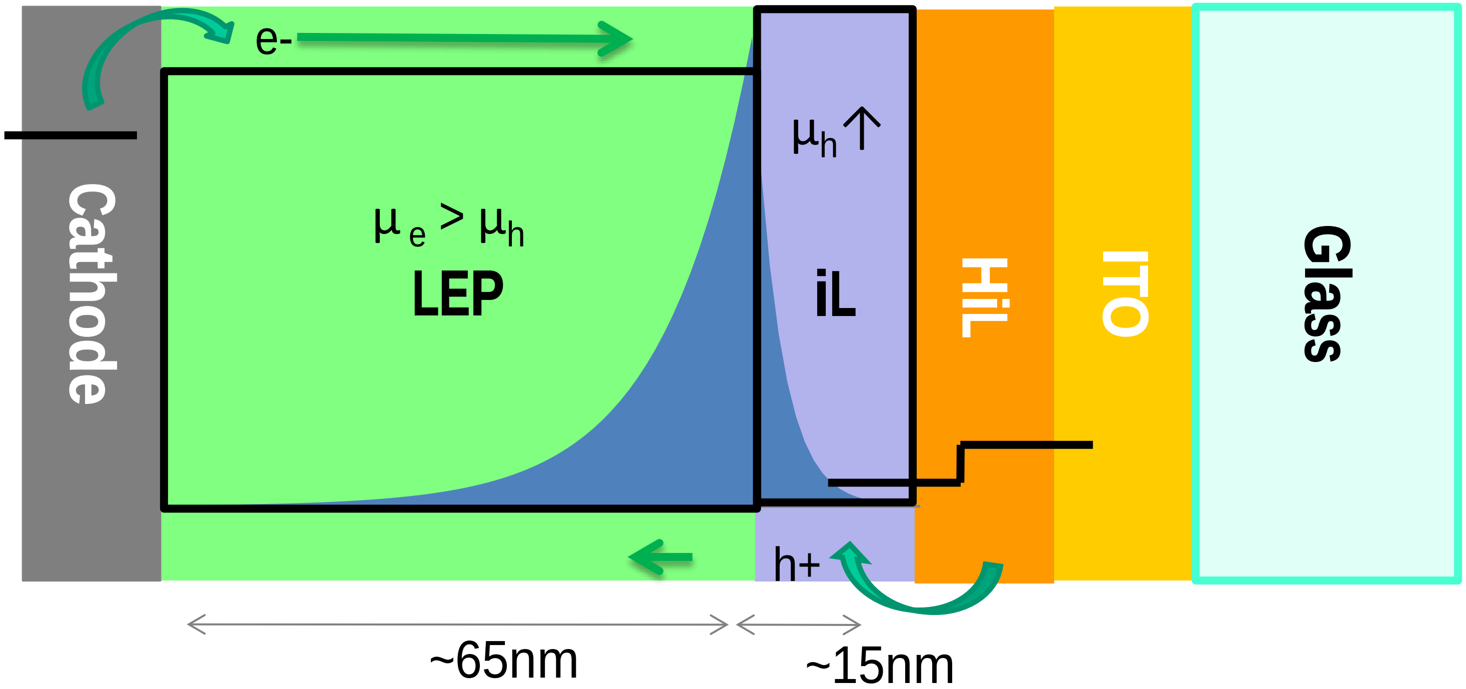
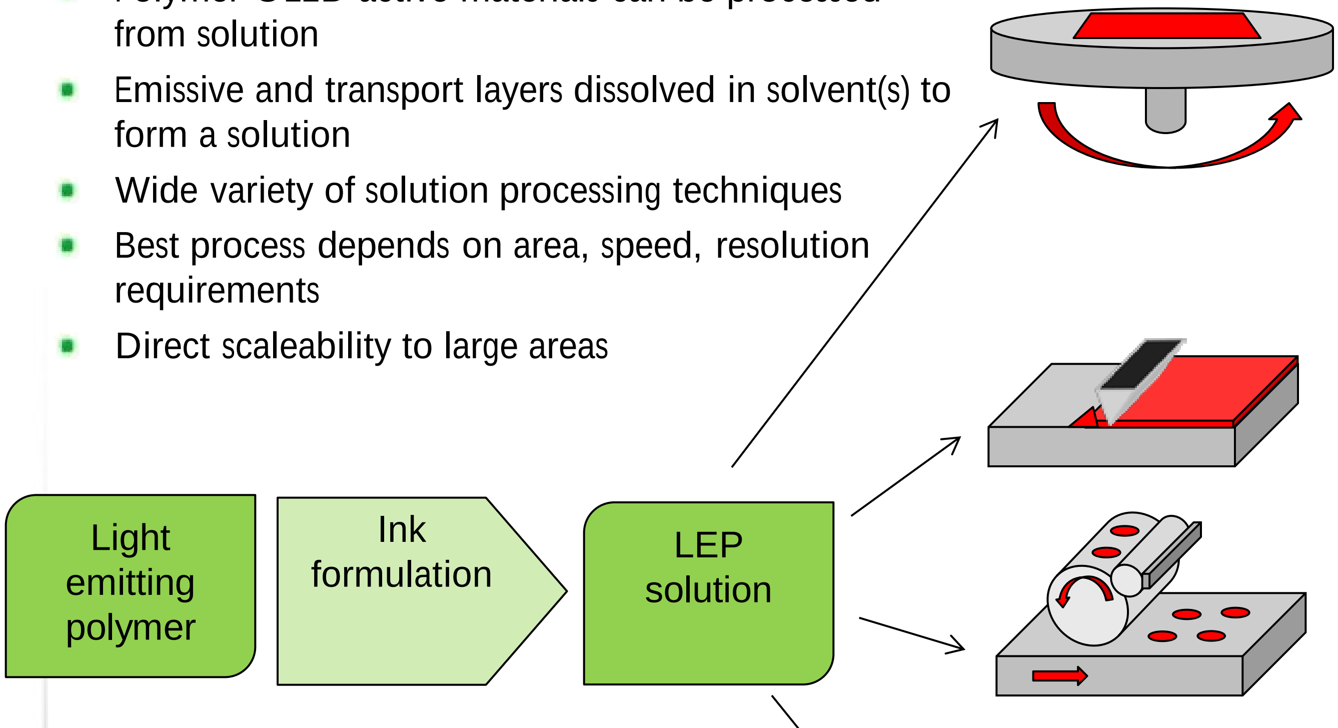
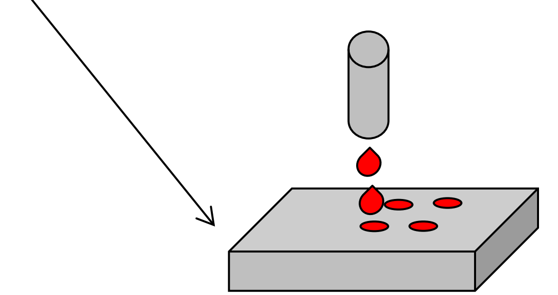


1. LEP thickness and carrier mobilities à Optimum RZ and outcoupling
2. Introduction of iL à Hole injection, efficiency and lifetime
3. HIL and ITO thicknesses à Colour and outcoupling
4. Electrodes / charge injection layers à Stable electron/hole injection

P-OLED Solution Processability

- Polymer OLED active materials can be processed from solution
- Emissive and transport layers dissolved in solvent(s) to form a solution
- Wide variety of solution processing techniques
- Best process depends on area, speed, resolution requirements
- Direct scaleability to large areas





Spin coating
+ Uniform films
+ Simple R&D process
- High wastage

Blade coating
+ Uniform films
- Efficient utilisation

Roller Printing (flexographic, gravure etc)
+ Large Area
+ High speed
+ High resolution

Ink Jet printing
+ High resolution
+ Large area

Synthesis of Conjugated Polymers for Blue OLEDs
Summary of Synthetic Schemes

Polymer History & Options

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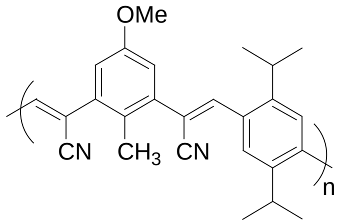
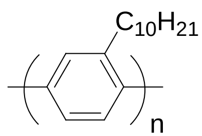
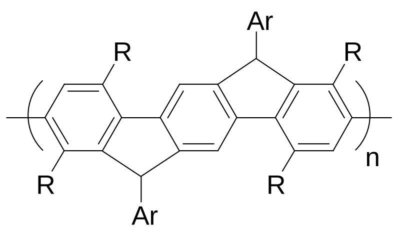
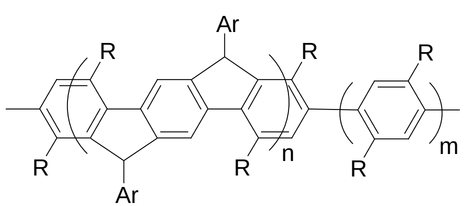
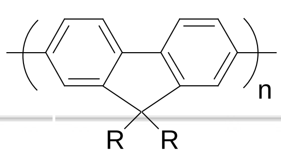
Type	Structure	Disadvantage
PPVs		Emission from more conjugated segments, broadening and red-shifting emission – energy gap not big enough for blue
PPPs		Addition of solubilising substituents twist backbone, disrupt π-electron system and decrease PLQY
LPPPs		Large Stokes shift after annealing (yellow) attributed to polymer stacking (formation of excimers)
"Step-ladder" PPP-LPPPs		Blue emission – low internal efficiencies (0.1%)
Polyfluorenes		Good efficiencies but homopolymers show short lifetime

Design of Polymers for R,G,B Emission

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- Quantum chemistry to look at trends in polymer properties
- Selection of the backbone monomer considering
  - Efficient charge transport.
  - Solubility
  - Rigidity
  - Twist of the chain
  - Aggregation
- Colour through selection of appropriate emitting monomer units
- Selection of functional groups
  - Limit number of trap site/ quenching
  - Tune the HOMO-LUMO for good injection and transport properties
  - Ensure good solubility polymer

Molecular Engineering

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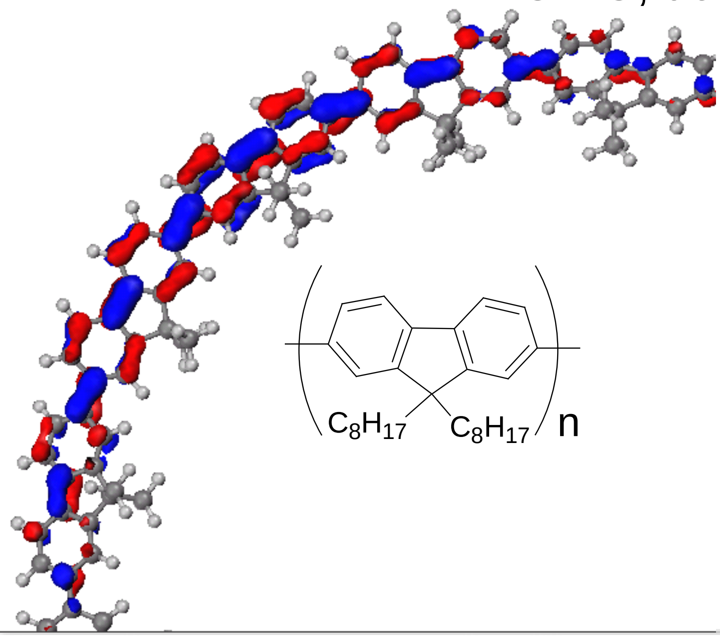
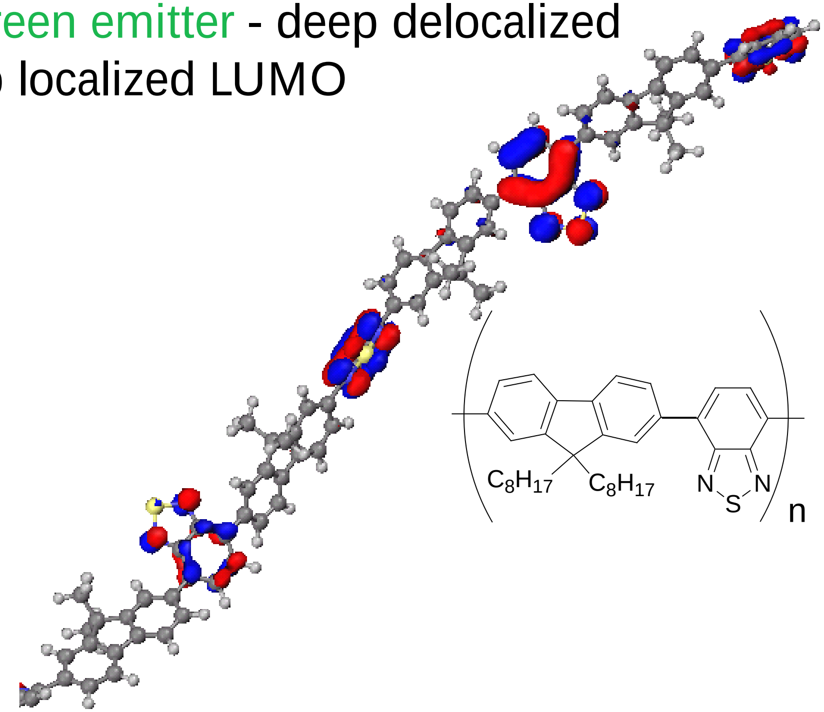
- Polyfluorene - blue emitter, deep delocalized HOMO and moderate delocalised LUMO – wide band gap
- Co-polymerise with benzothiodiazole, deep HOMO and deep LUMO – smaller band gap

- Emission localised on the green emitter - deep delocalized HOMO, deep localized LUMO





CIE 1931 Chromaticity Chart

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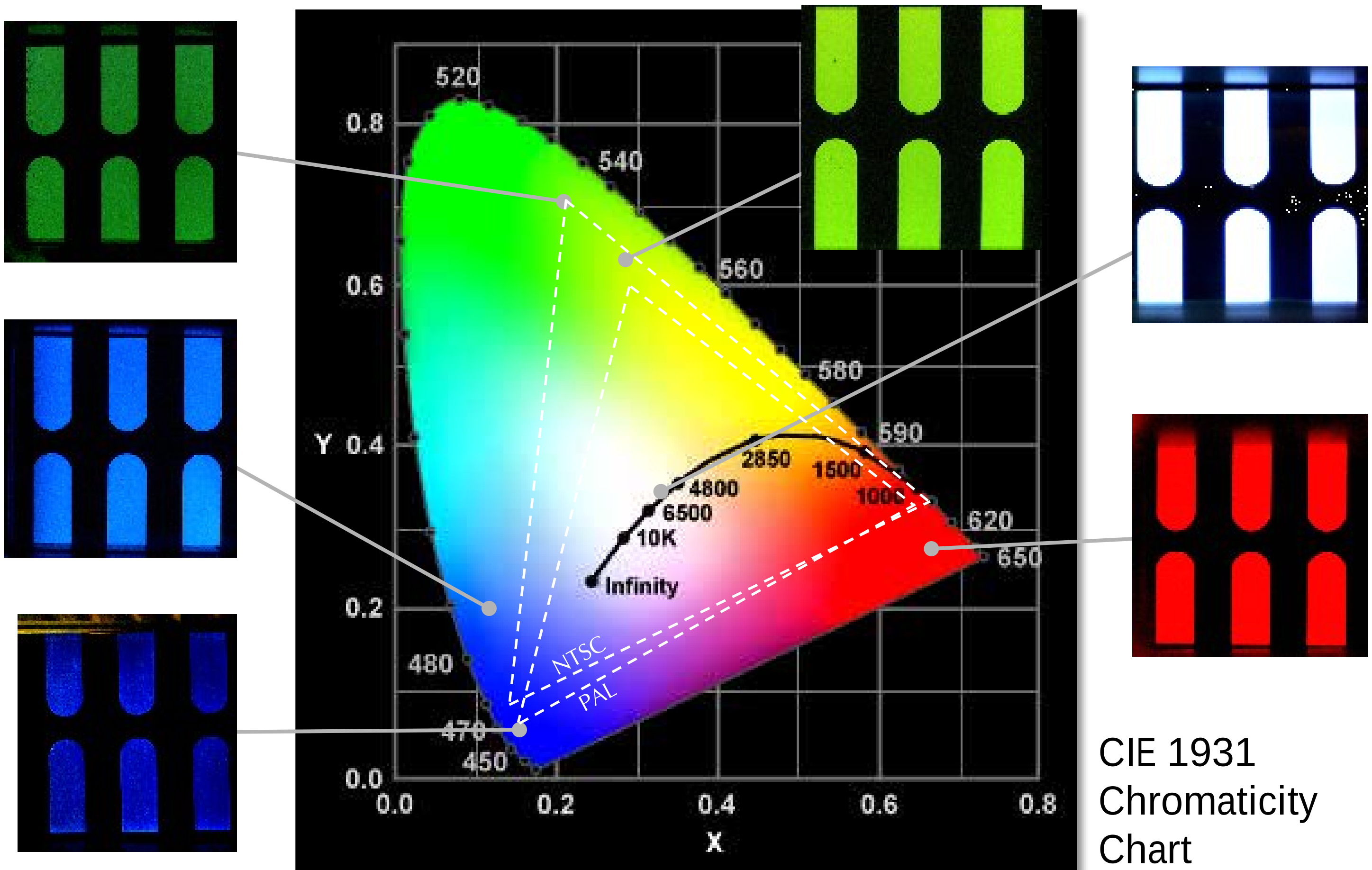

CIE 1931 Chromaticity Chart

PLEDs can be used to produce light of any visible hue

Single Component Polymers

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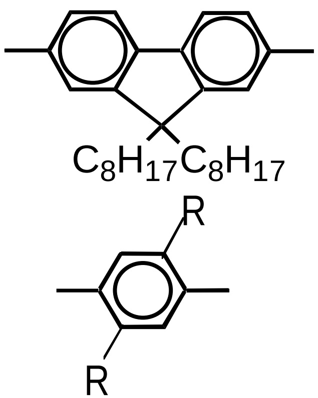
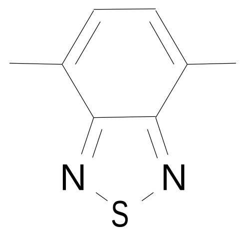
Integration of all functions using copolymer system

Copolymerization with each functional unit

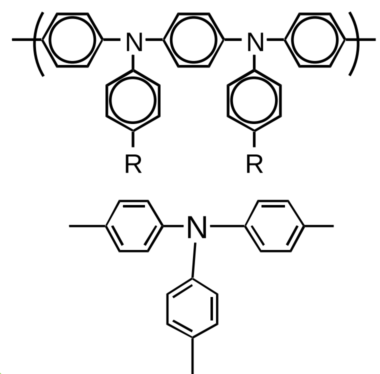
Backbone



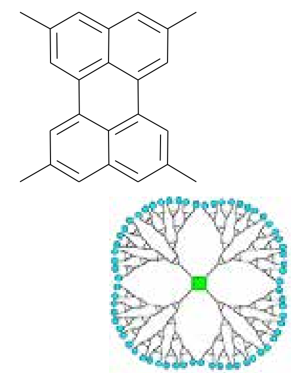
Electron affinitive



Hole affinitive



Emission



Optimize monomer ratio
- carrier-charge balance
- quantum yield

Controlled unit-sequence

Controlled molecular weight

Important Factors - Polymerisation Process

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- Robust process
- Availability of air stable catalysts for ease of handling
- Range of available monomers
  - Crystalline and air stable
  - A variety of functional groups are tolerated
- Control of polymer architecture
  - Control of monomer feed
- Control of molecular weight
  - Ability to synthesize a range of molecular weights for different solution processing methods with narrow Pd
- Reproducibility of polymerisation
  - Batch to batch reproducibility
- Produces high purity polymers
- Scalable (Research and Production scale)

Synthesis Methods for LEPs

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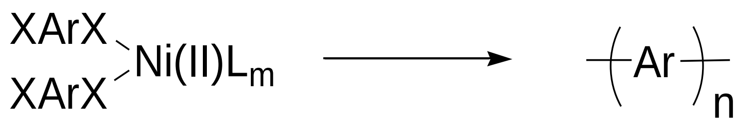
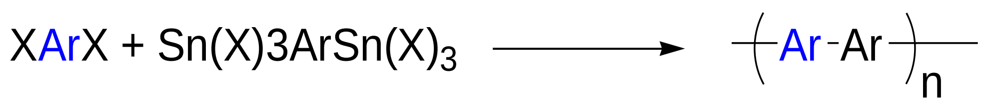
- Yamamoto Chemistry
  - Air and water sensitive reaction
  - Poor Pd



- Pd or Ni catalysed Coupling of Grignard reagents
  - Air and water sensitive reaction

- Stille Chemistry
  - Toxic
  - Air sensitive reaction



- Suzuki Chemistry
  - Air sensitive reaction
  - Water tolerant , versatile to a wise range of functional groups
  - High Mw & Good (low) Pd

Suzuki Advantages

- High molecular weight polymer produced
  - Mw > 1,000,000
  - Pd 2-3
- Good reaction control and therefore good batch to batch reproducibility
  - Also tailor Mp for deposition techniques
    - Spin coat, Ink jet etc
- Simple purification procedure
- Control over end capping process
- Several thousand different polymers have been prepared using this process

Synthesis of Conjugated Polymers for Blue OLEDs
Impact of Purification on Performance

Monomer Purification

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- Absolute monomer purity is critical for successful polymer synthesis
    - Impurities can have negative impact device performance

- >5 Recrystallisations is not unusual
- Repetitive chromatography or sublimation is often used for emitters
    - Development of “clean” robust chemistry is often required to facilitate scale-up
        - Might require purification after each synthesis step!

- Monomers must be stable & non-hygroscopic

Monomer Analysis & QC

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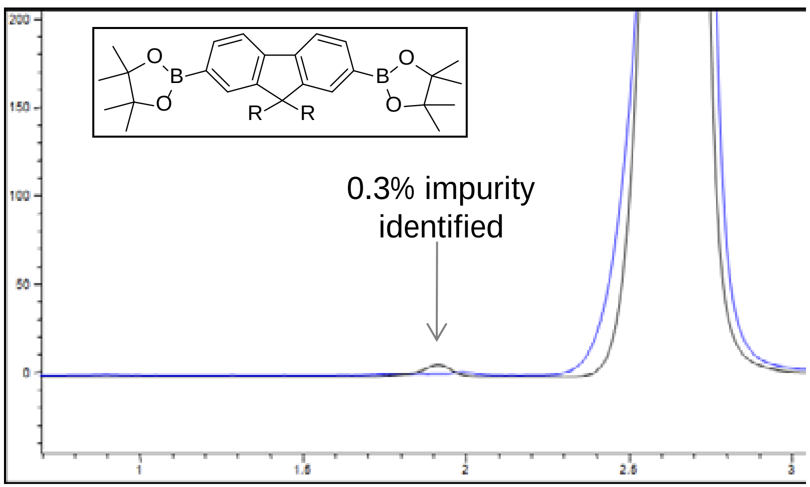
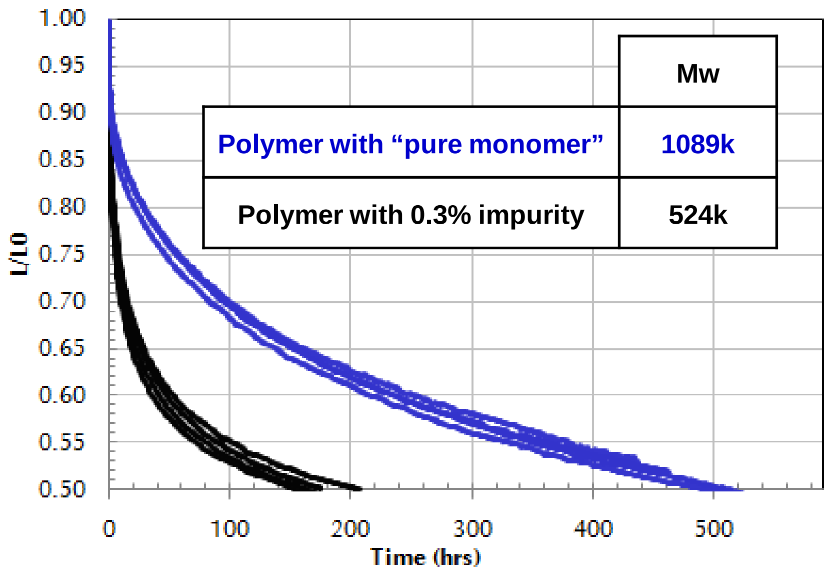
- CDT synthetic chemists have a “Love/Hate” relationship with our analysts
  - HPLC methods are optimised for each compound to give best sensitivity
  - New analytical methods are implemented whenever possible
  - Impurity profiling can identify “problematic” impurities
- QC includes HPLC, LCMS, GCMS, NMR, TGA, Mp, GPC, ICP, solution clarity
- Alignment of Chromatography methods is also required for outsourcing projects

Effects of Monomer Purity

- Method development on a nominally pure monomer identified a 0.3% impurity

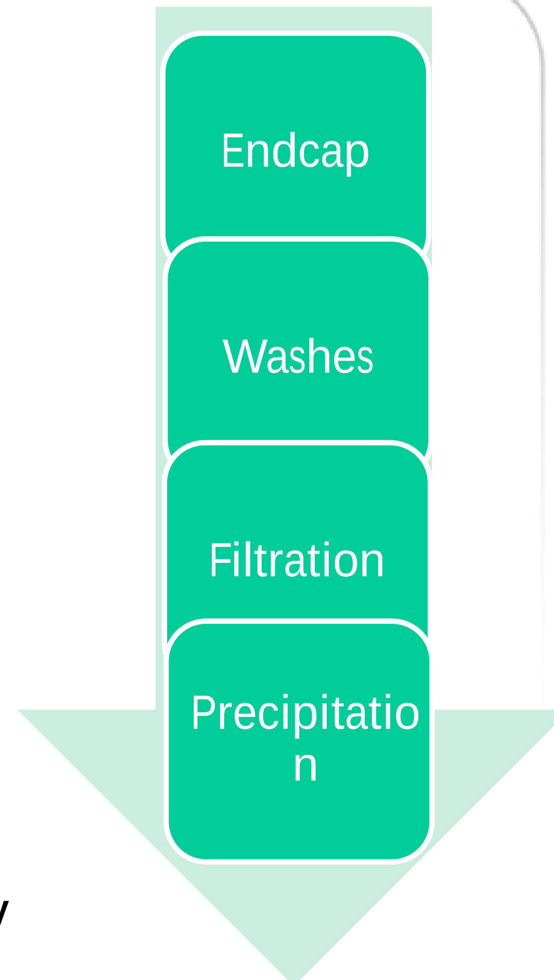




- Removal of the impurity has a dramatic effect on Mw & device lifetime

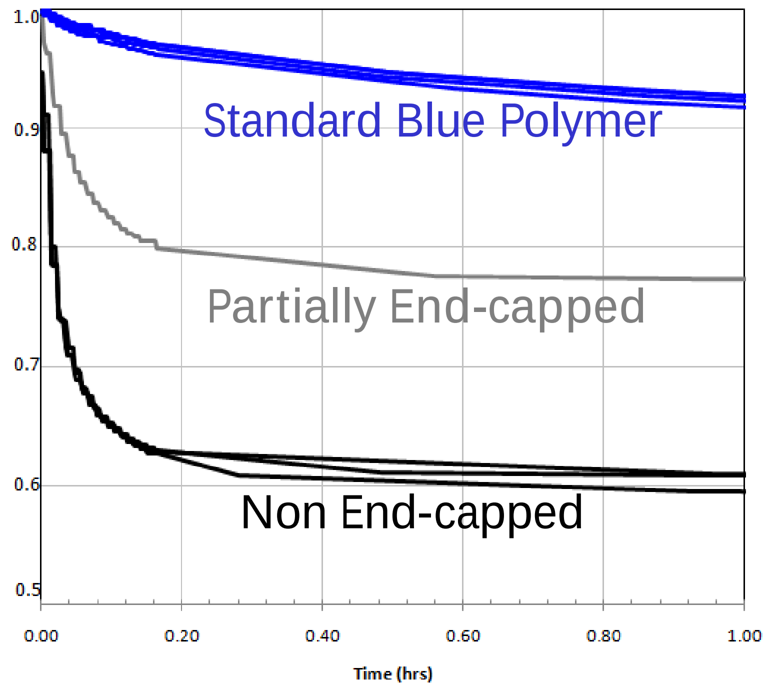
Termination & Isolation

- Polymer is end-capped to remove reactive terminal groups
  - ppm bromine levels
- Washes to remove inorganics & Pd
- Filtration for Pd(0) removal & clarification
  - ppm levels of metals & inorganics
- Precipitation into anti-solvent
  - Removal of organic impurities
- Processes complicated by solution viscosity



Halogen Effect

- High levels of bromine (& other halogens) have a catastrophic effect on device lifetime



- End-capping & removal of Bromine by-products must be effective

Routine Polymer Analysis Capability

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- GPC – absolute Mol. Wt. determination
- DSC – Tg
- PLQY – photoluminance quantum yield (emitter efficiency)
- UV – optical & band-gap properties
- Electrochemistry – HOMO/LUMO & bad-gap levels
- ICP – ppm metal analysis
- XRF – complimentary to ICP + halogen analysis
- FTIR – low resolution structural information
- 600MHz NMR – high resolution structural characterisation

Material QC – The Final Test

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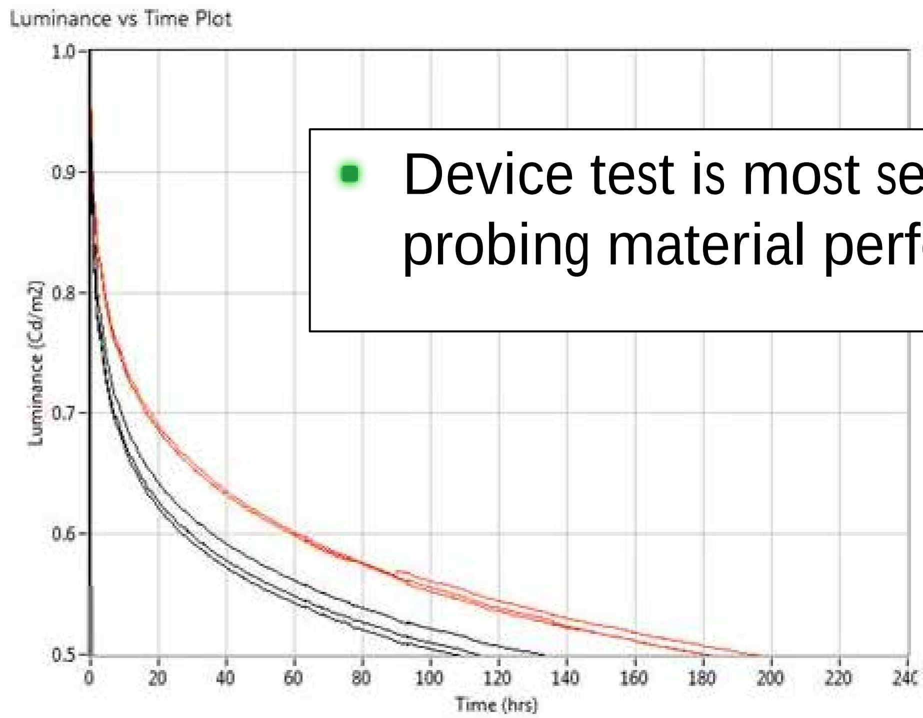
- After POLED has passed analytical QC, the material performance is assessed in a light emitting test cell.



- Device test is most sensitive tool for probing material performance

- Analytical and purification method development continues to improve baseline material performance!

Challenge Summary

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- Monomer purity > commonly required in other chemical industries

- Polymer defects must be carefully controlled

- Polymer impurities must be removed to ppm level
  - Or even ppb levels!

- Despite the challenges, tremendous progress has been made over the past 10 years ....

Synthesis of Conjugated Polymers for Blue OLEDs
Maximising Efficiency

P-OLED RGB efficiency

Key parameters

Materials improvements

mcavity performance

P-OLED RGB efficiency

CDT

Key parameters

Materials improvements

mcavity performance

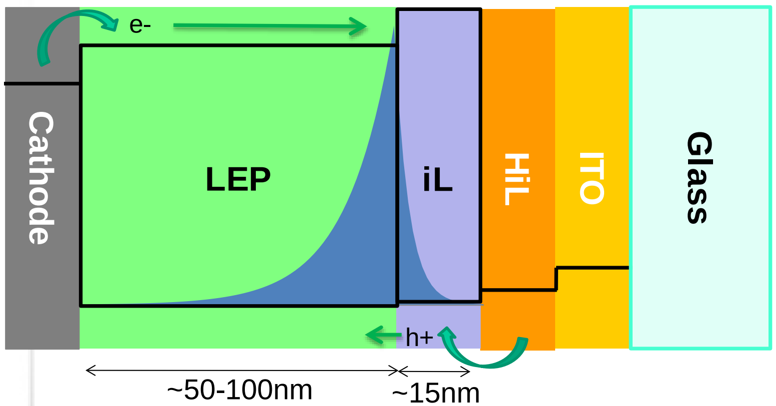
Key factors affecting efficiency

CDT

'charge balance' 'Singlet Yield' 'PLQE' 'outcoupling'

$$EQE = \eta_{exciton\ formation} \times \eta_{singlet\ formation} \times \eta_{photon\ emission} \times \eta_{photon\ escape}$$

Standard device structure



- Mobility / energy level offsets
- **Singlet Yield ($F_{s:t}$, χ_{TTA})**
- **PLQE at RZ (k_{rad}, k_{nrad})**
- **Recombination Zone profile**
- **Dipole orientation (k_x, k_y, k_z)**
- Optical constants (n, k)
- Layer thicknesses
- PL spectrum

à What can we measure to enable good estimates?

Fluorescent or Phosphorescent

- For a fluorescent material, only singlet excitons are emissive
- Simple quantum mechanics suggests a 1:3 S:T ratio
- This would give a limit of 25% Internal QE

Singlet

Spin = 0

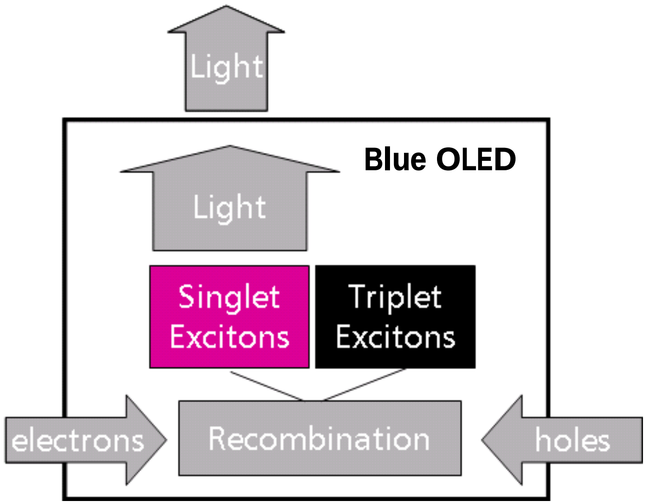
$$\frac{1}{\sqrt{2}}\left(|-\,^{-}\rangle - |^{-}\,-\rangle\right)$$

Triplet

$$\left\{\begin{array}{c} |-\,-\rangle \\ \frac{1}{\sqrt{2}}\left(|-\,^{-}\rangle + |^{-}\,-\rangle\right) \\ |^{-}\,^{-}\rangle \end{array}\right\}$$

Spin = 1

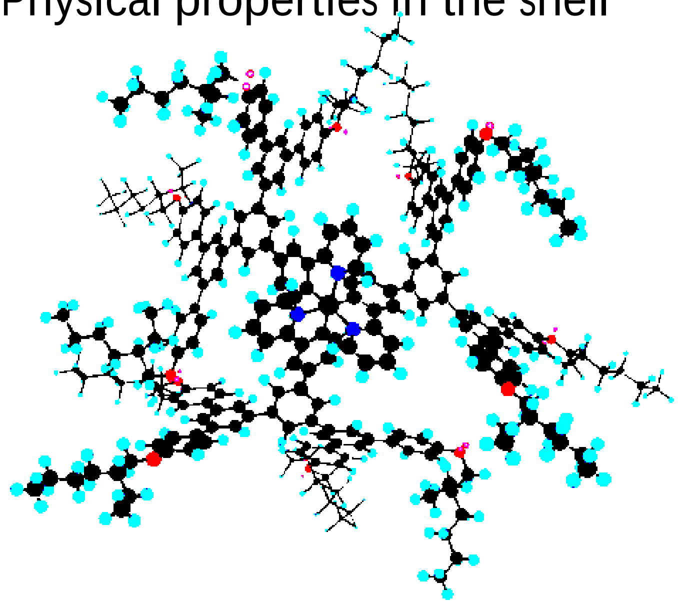
3 States

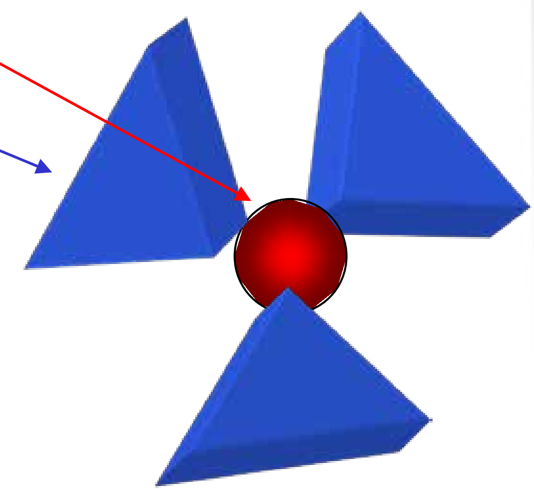


- Phosphorescent materials potentially have 100% Internal QE
- For displays require a deep blue emitter
  - Phosphorescent blues have much shorter operational lifetime than fluorescent materials
  - RG for displays is phosphorescent and RGB (White) for lighting is phosphorescent
  - Blue emission for displays is fluorescent
    - How to maximize fluorescent efficiency?

Solution Processable Phosphorescent Materials

- CDT Phosphoescent platform is built around dendrimer emitters blended into the polymer host matrix
- Dendrimers have complex structure allowing independent control of:
  - Optoelectronic properties in the core
  - Physical properties in the shell





Key parameter 1 - Singlet Yield

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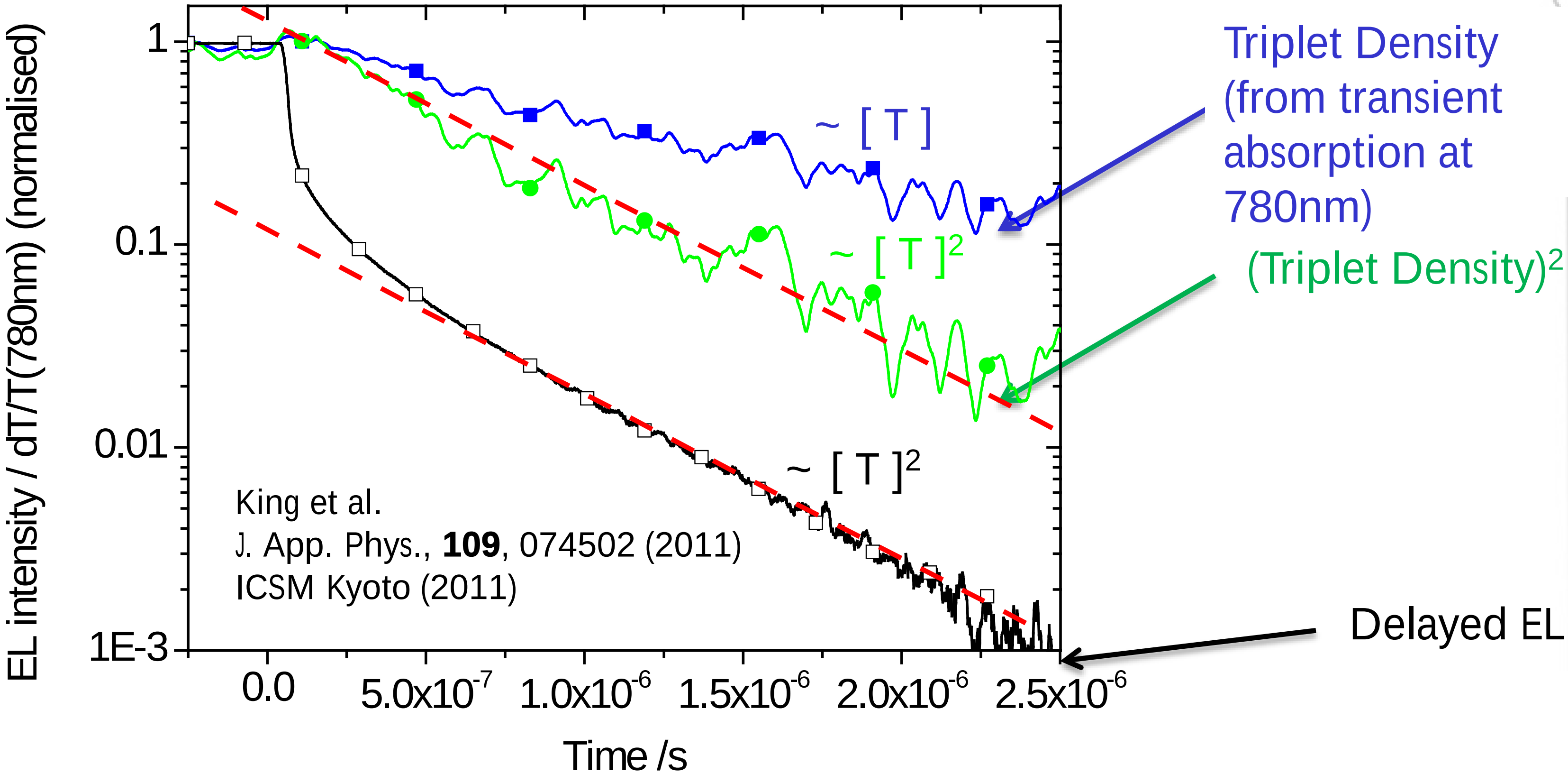

- Origin of delayed fluorescence is TTA : $T_1 + T_1$ à $S_1 + S_0$

à Key process in optimising the efficiency in fluorescent OLEDs

Key parameter 1 - Singlet Yield

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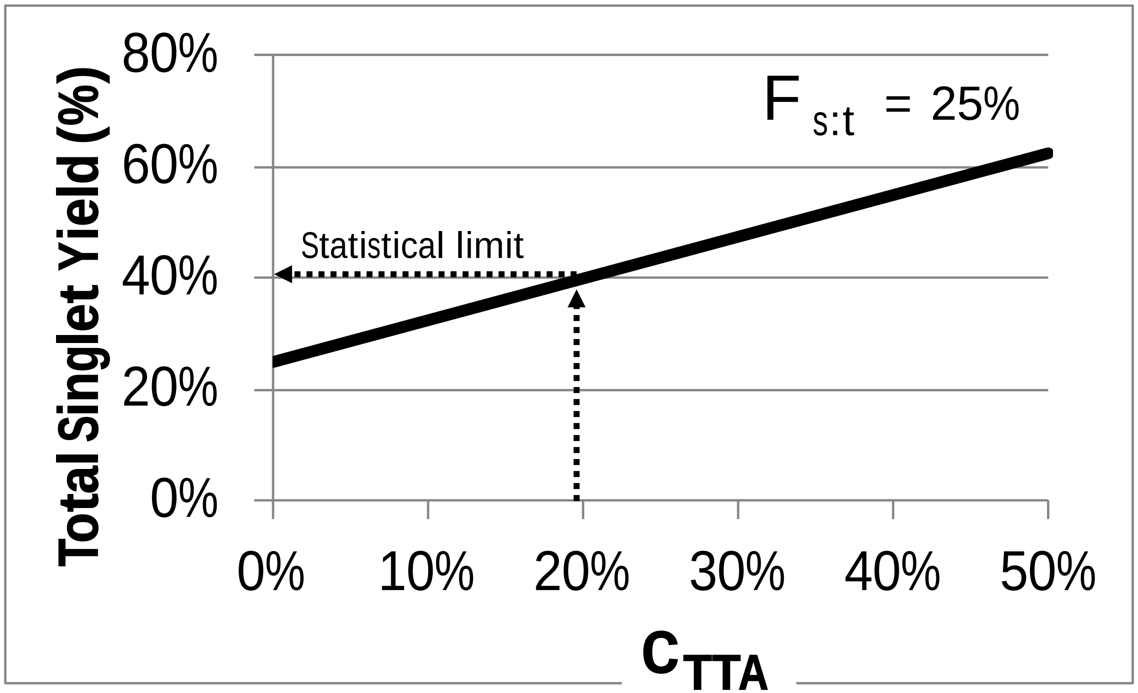
From charges — From TTA

$\text{Singlet Yield} = F_{s:t} + (1 - F_{s:t})\, c_{TTA}$

$F_{s:t}$ = S:T ratio

c_{TTA} = TTA Singlet Yield



TTA processes

$T_1 + T_1$ à **3** x $(S_0 + T_n)$
1 x $(S_0 + S_1)$

Statistical TTA Singlet Yield C_t

1/8 + 3/8x1/8 + 3/8x3/8x1/8 +… **~20%**

Singlet Yield

25%+0.2*75% = **40%**

Kondakov, J. Soc. Inf. Disp. 17, 137 (2009)

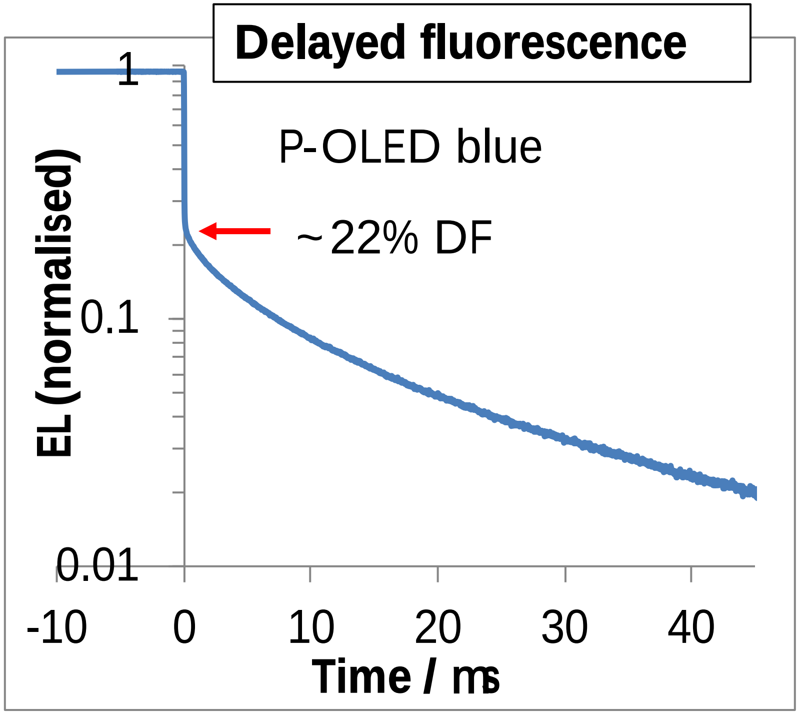
à Up to 40% Singlet Yield expected for standard spin statistics

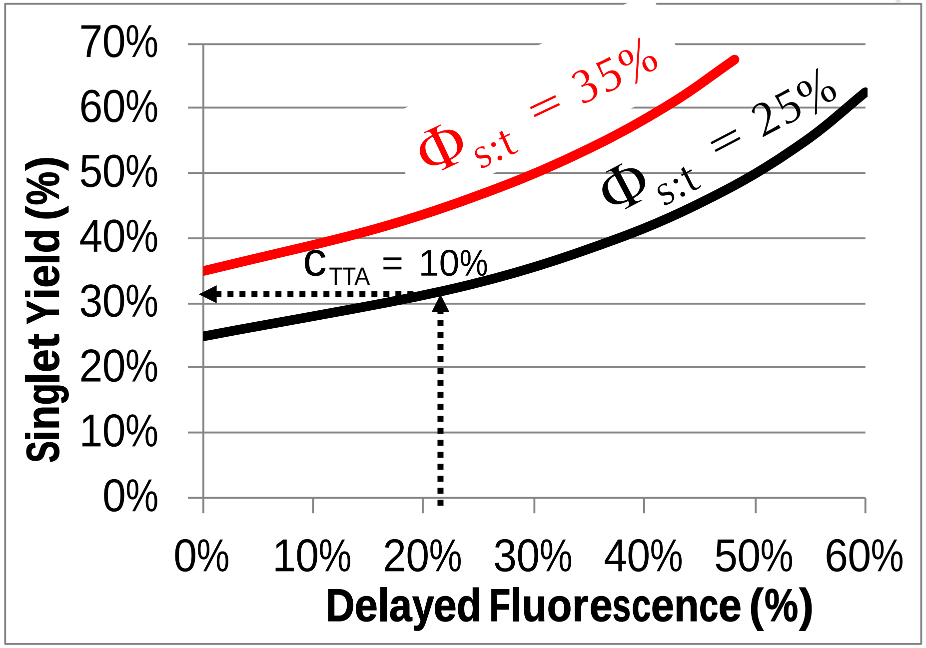
Key parameter 1 - Singlet Yield

From charges — From TTA

$$\text{Singlet Yield} = F_{s:t} + (1 - F_{s:t})\, c_{TTA}$$

$F_{s:t}$ = S:T ratio
c_{TTA} = TTA yield





à 32% lower limit to Singlet Yield
…some scope for improvement…

Key parameter 2 – PLQE at Recombination Zone

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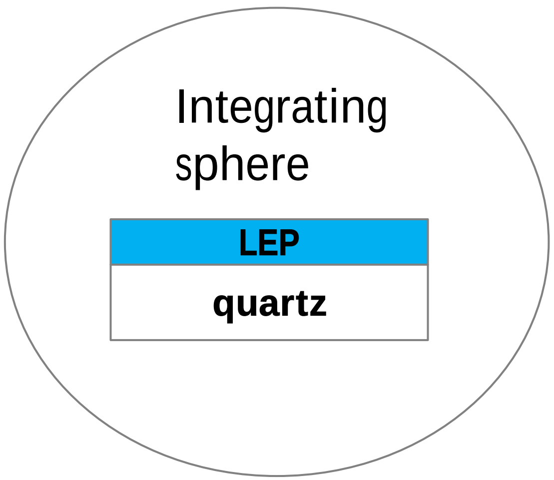
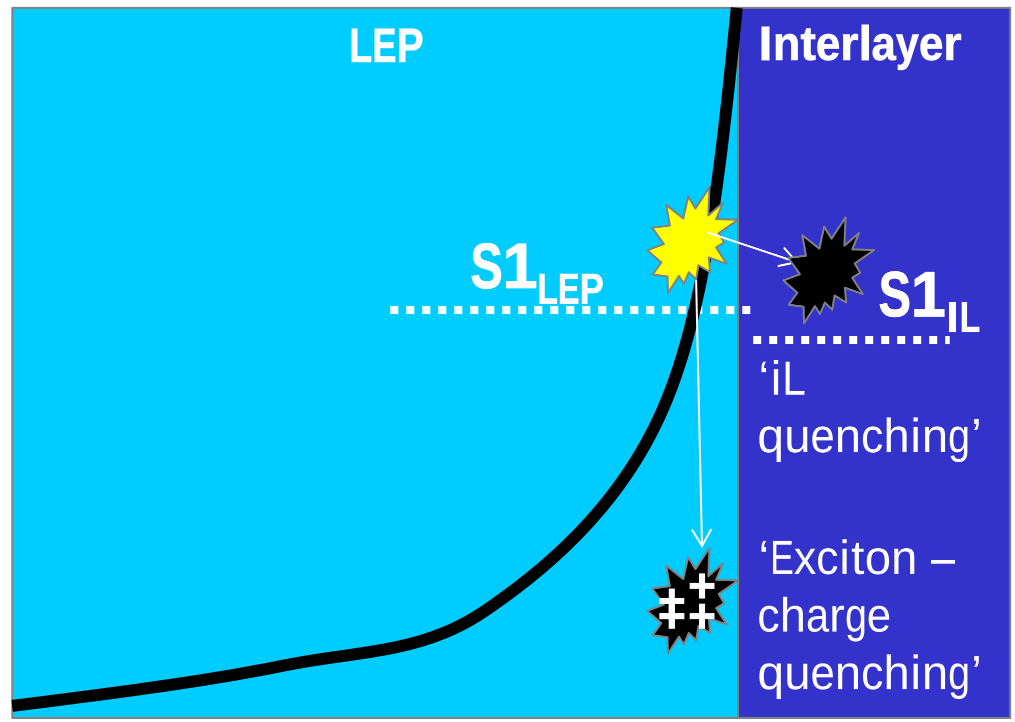
'Intrinsic PLQE'



'PLQE at RZ'



à In this analysis, all PL quenching effects are taken into account in the parameter 'PLQE@RZ'

Key parameter 3 - RZ profile

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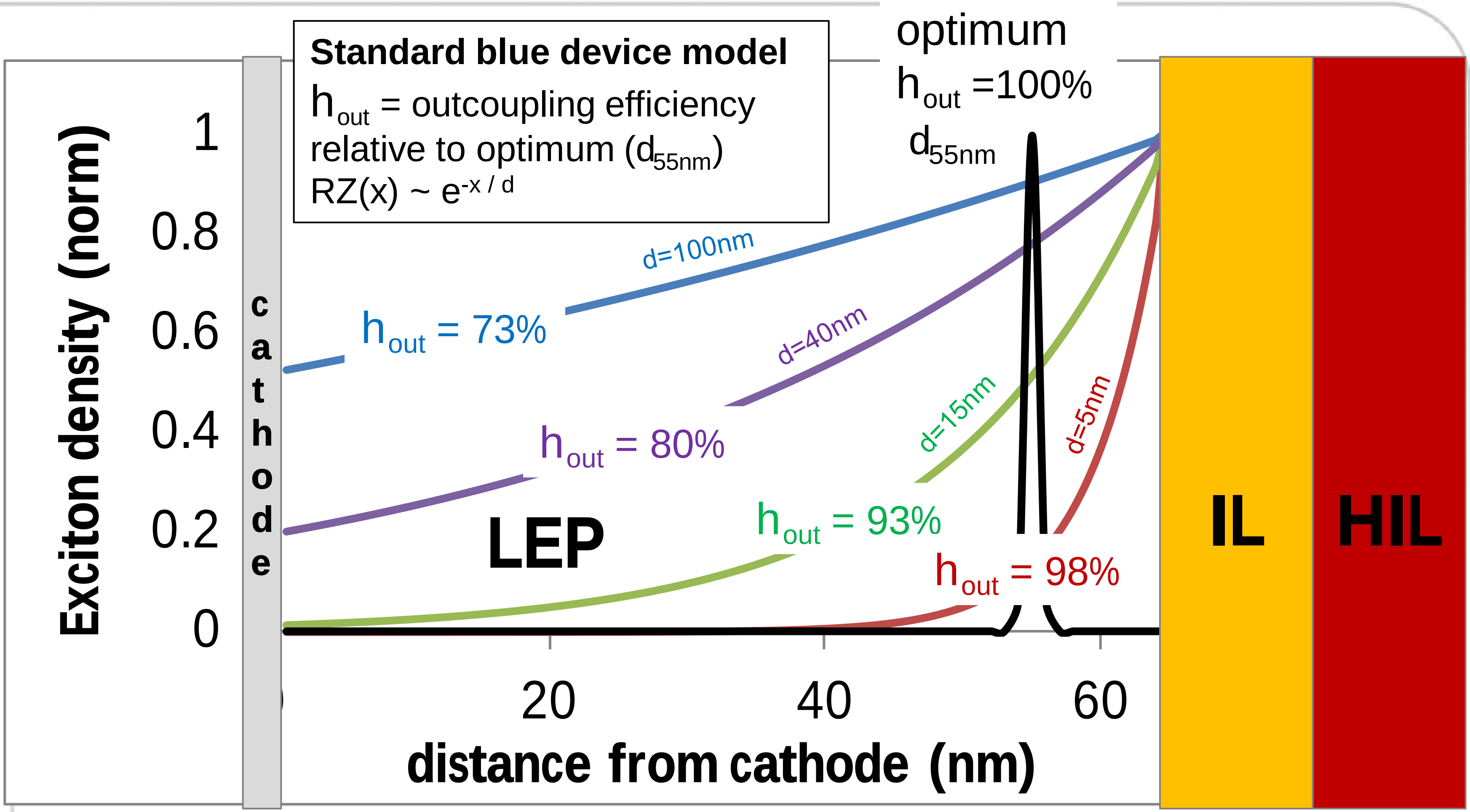
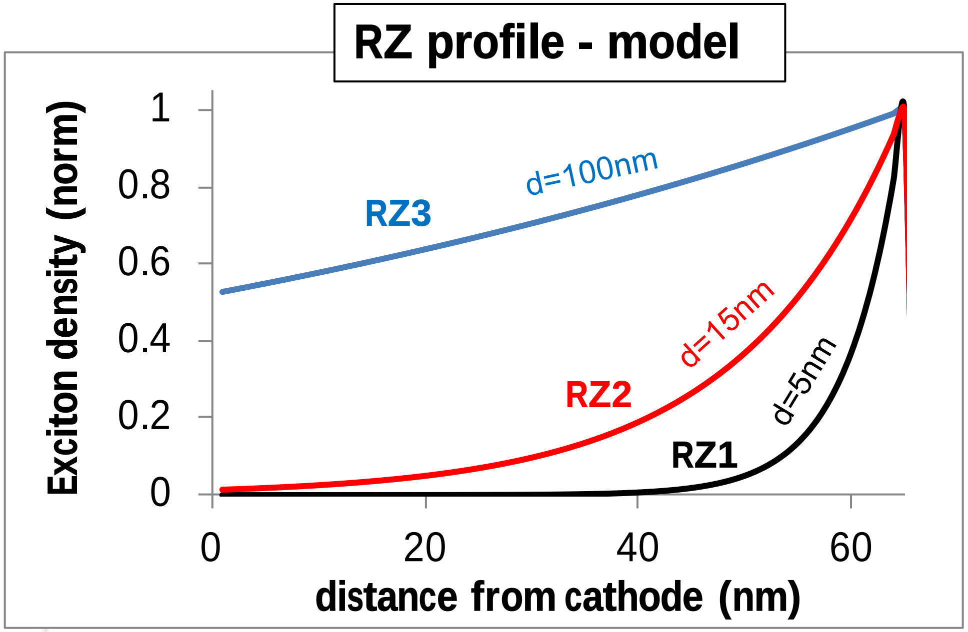
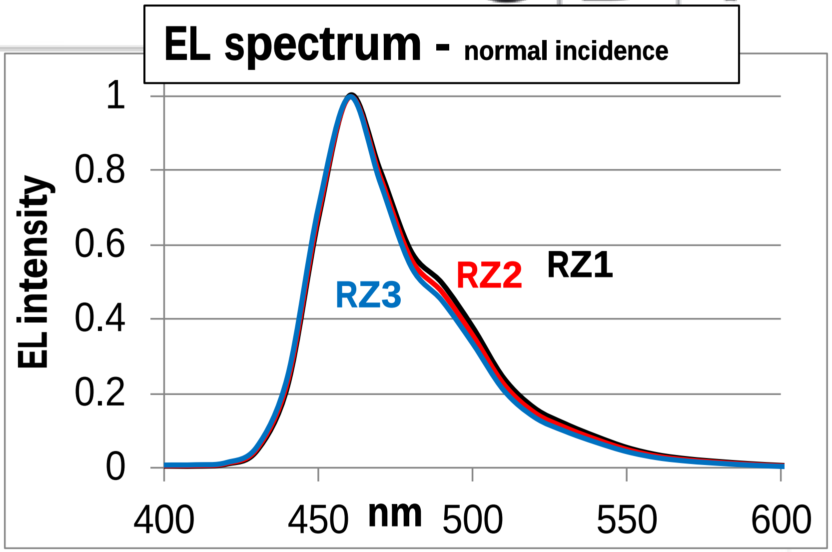


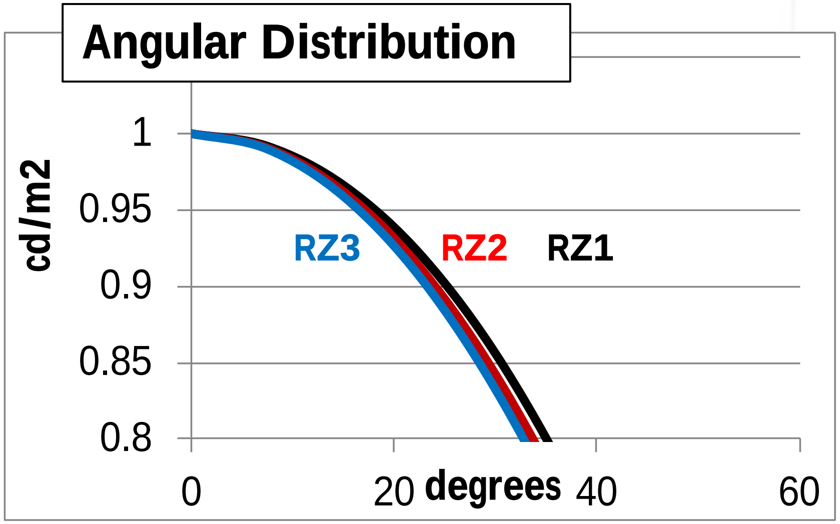
à RZ widths d < 20nm give efficiency within 90% theoretical max

Key parameter 3 - RZ profile

Standard blue device model







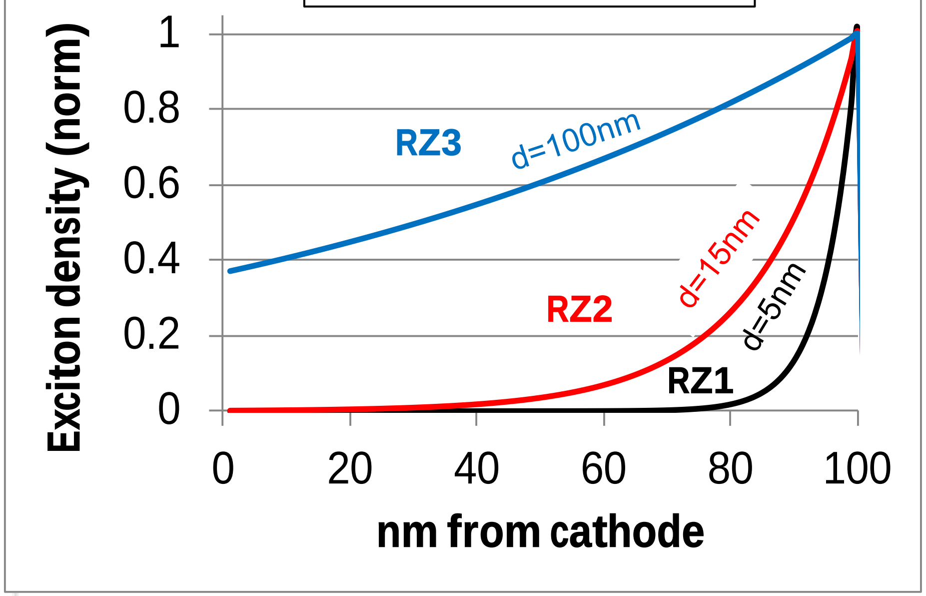
à RZ position impacts colour and angular distribution – but in standard structures these differences are quite small…..

Key parameter 3 - RZ profile

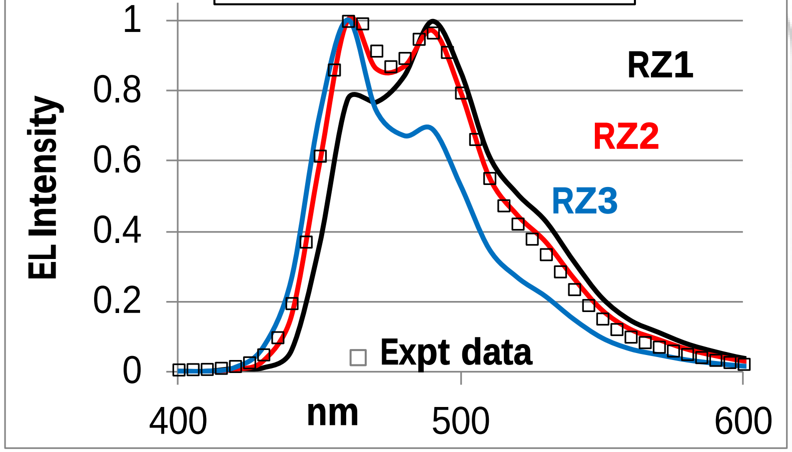
CDT

Detuned LEP thickness device - for improved RZ sensitivity

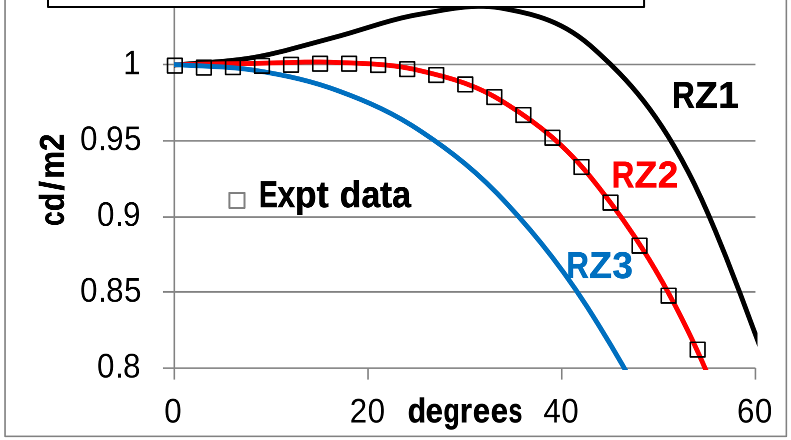
RZ profile - model



EL spectrum - fit



Angular Distribution - fit

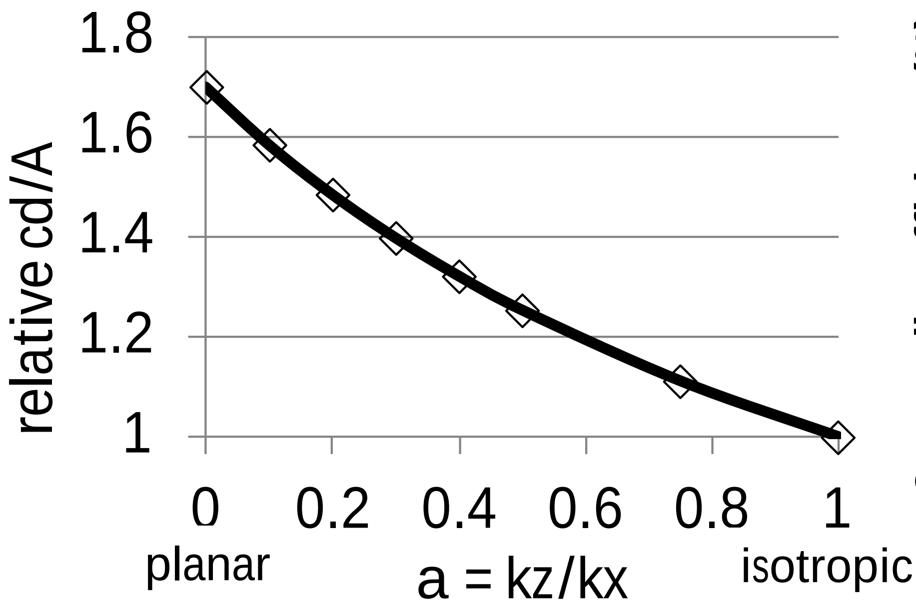


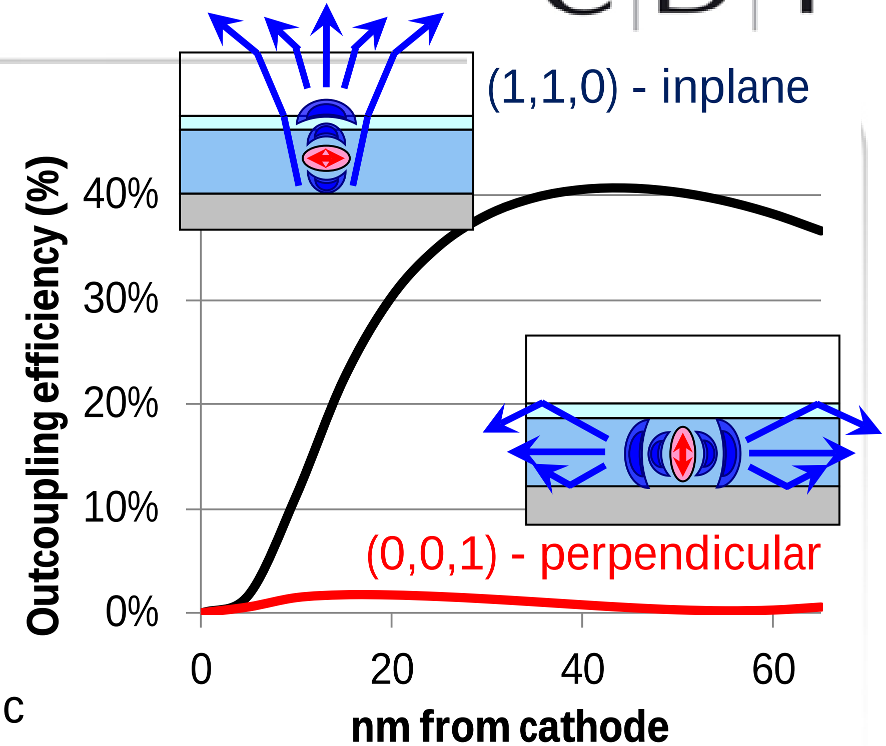
- RZ widths ~ 15nm typical
- cd/A typically >90% of single dipole theoretical maximum

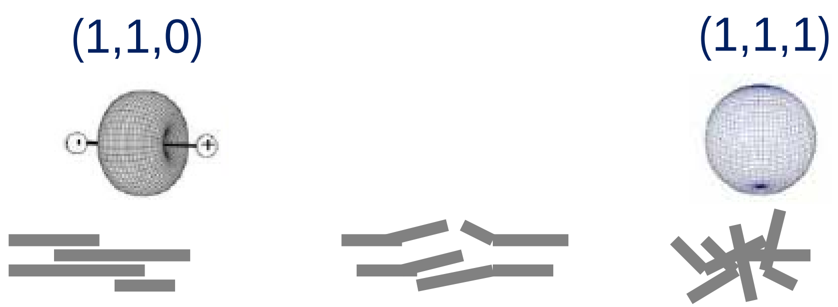
à RZ width of 15nm representative of optimised materials / devices

Key parameter 4 - Dipole orientation

C|D|T







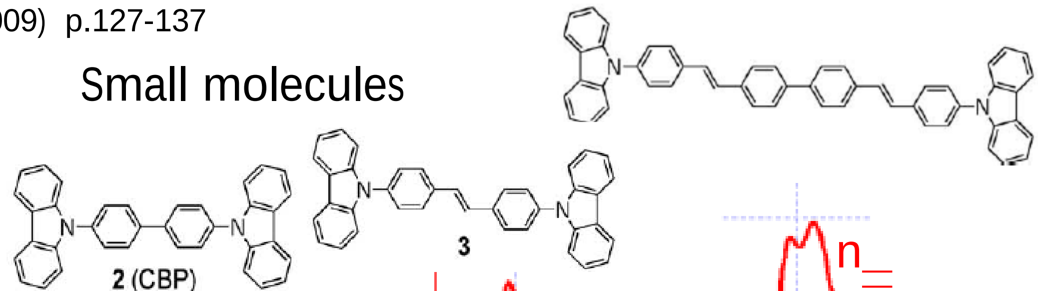
à Perpendicular dipole energy is absorbed by cathode, or channelled into waveguide modes

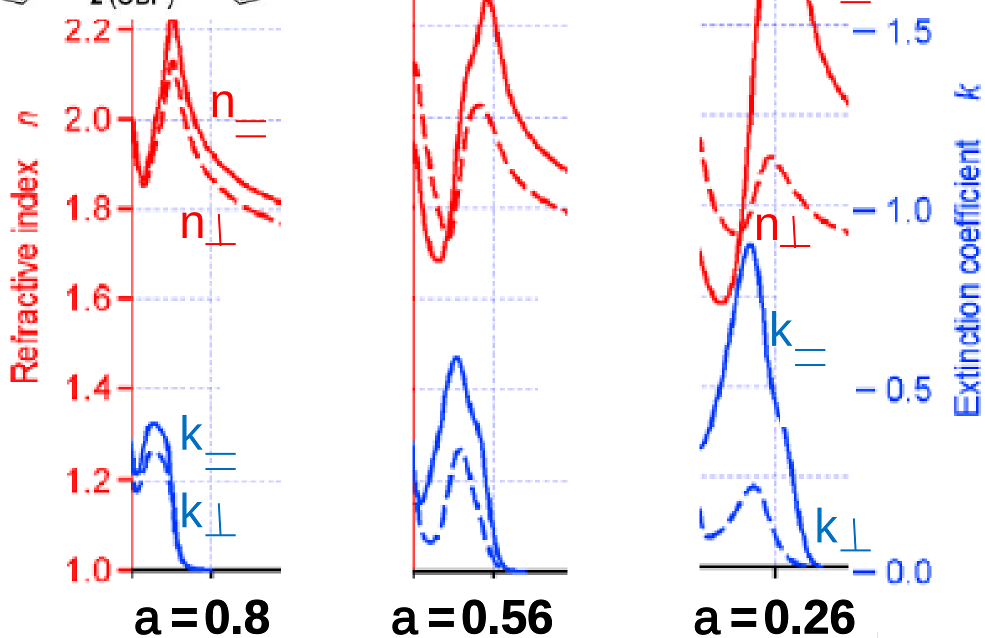
à Dipole orientation plays a key role in efficiency

Key parameter 4 - Dipole orientation

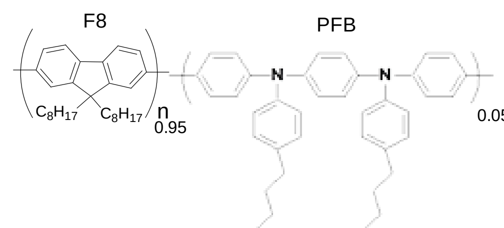
Spectroscopic ellipsometry - Yokoyama et al. Organic Electronics 10 (2009) p.127-137

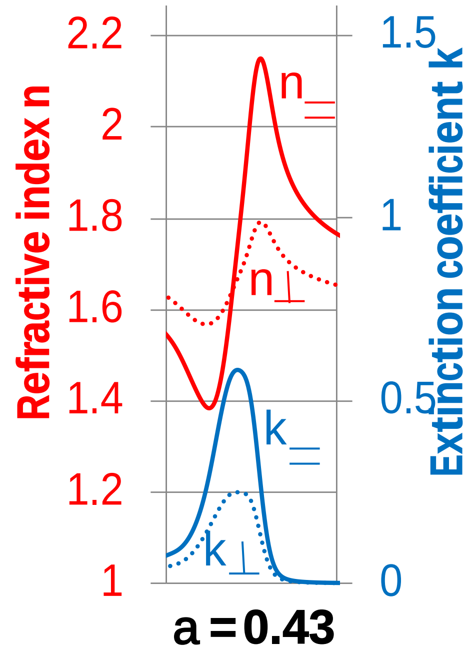
Small molecules





Model Polymer

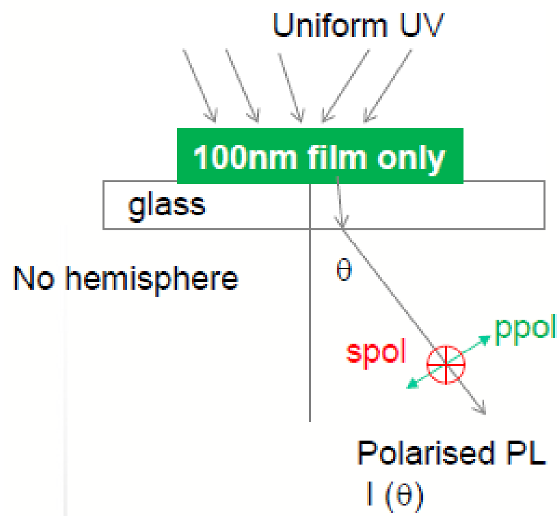


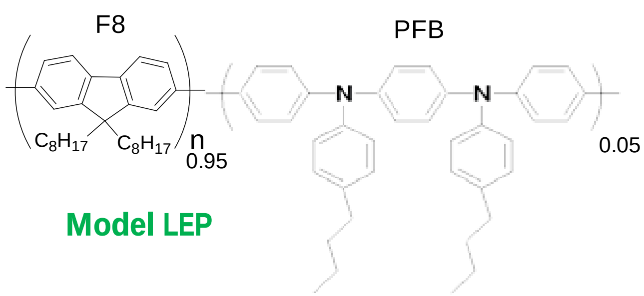


à Model blue PLEDs anisotropic…some scope for improvement..

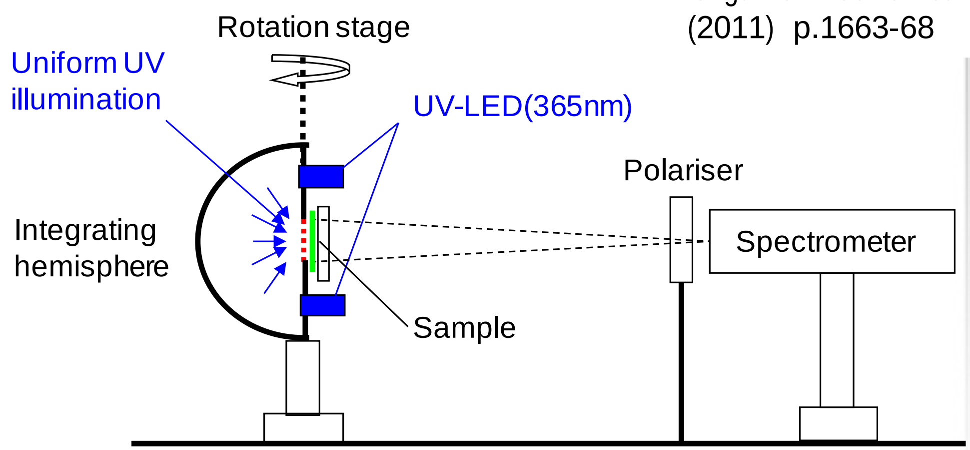
Key parameter 4 - Dipole orientation

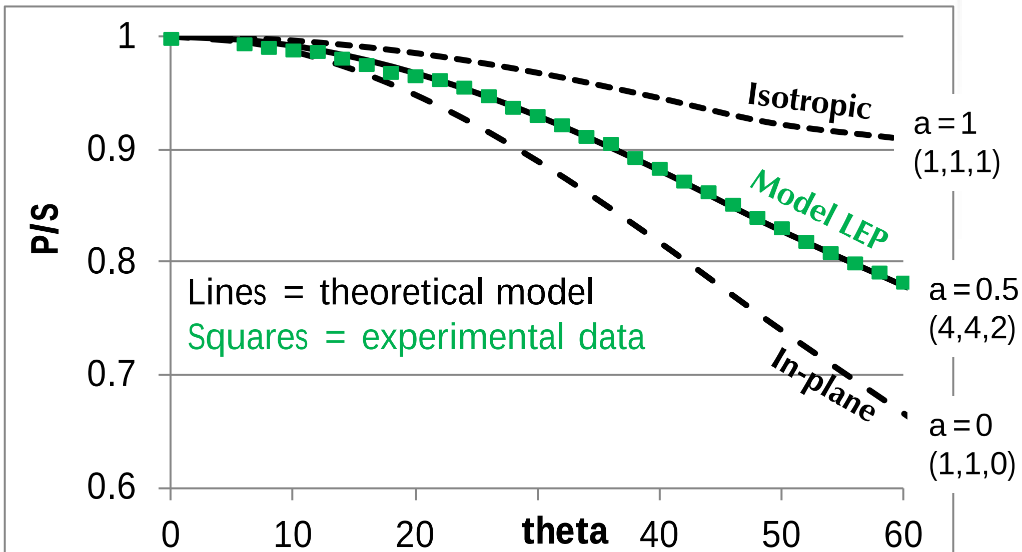
CDT





[1] Flammich et al. Organic Electronics 12 (2011) p.1663-68



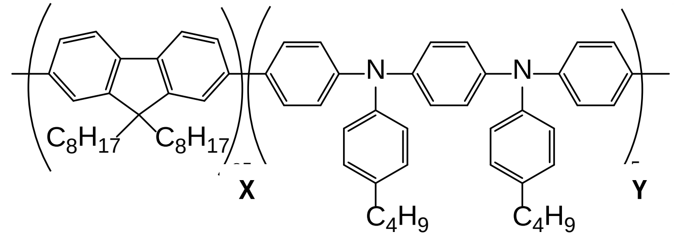


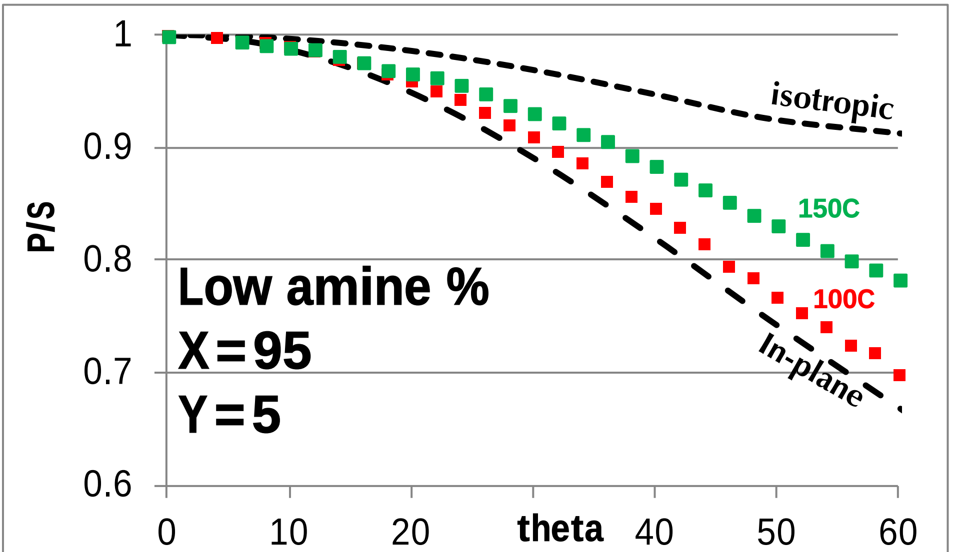
à Polarised angular PL[1] contains information on the anisotropy of emission

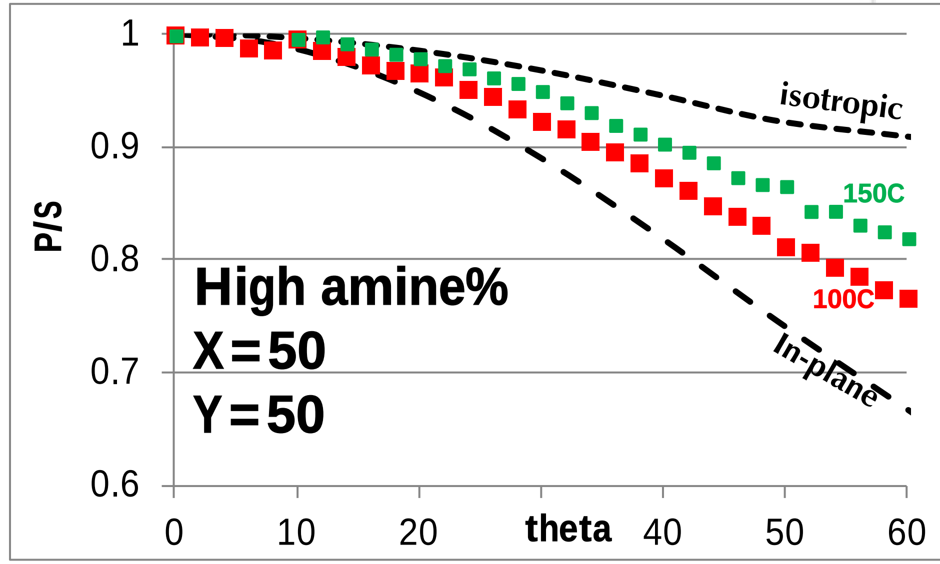
Key parameter 4 - Dipole orientation

C|D|T

Variations in materials (Amine%) and bake temperature (15mins in N_2)







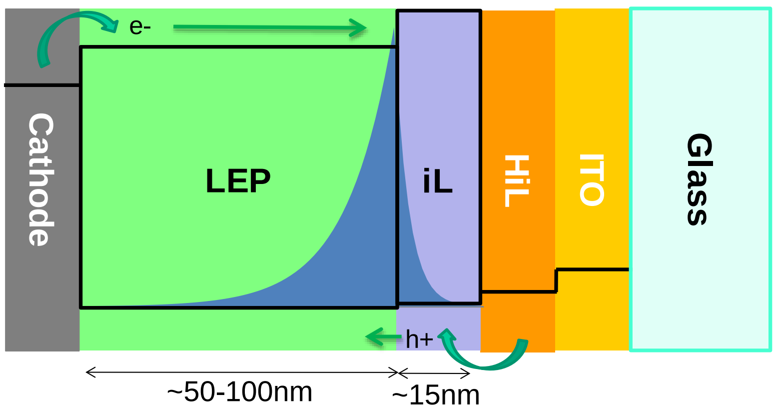
à Both materials design and processing are key to optimising emitter orientation

Key parameters - summary

C|D|T

'charge balance' 'S:T ratio' 'PLQE' 'outcoupling'

$$EQE = h_{\text{exciton formation}} \times h_{\text{singlet formation}} \times h_{\text{photon emission}} \times h_{\text{photon escape}}$$



- Singlet Yield ($F_{s:t}$, c_{TTA}) → Scope for increasing %DF
- PLQE at RZ (k_{rad}, k_{nrad}) → Consider IL quenching
- Recombination Zone profile → Within ~10% of optimum
- Dipole orientation (k_x, k_y, k_z) → Scope for increasing planarity

P-OLED RGB efficiency

C|D|T

Key parameters

Materials improvements

mcavity performance

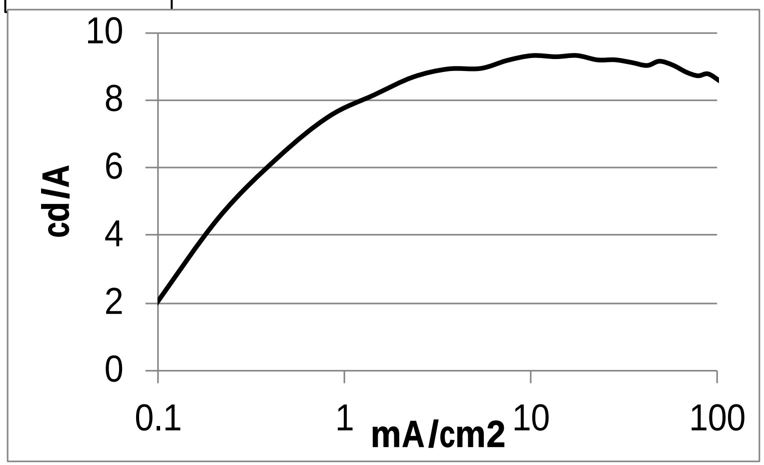
Blue – standard model

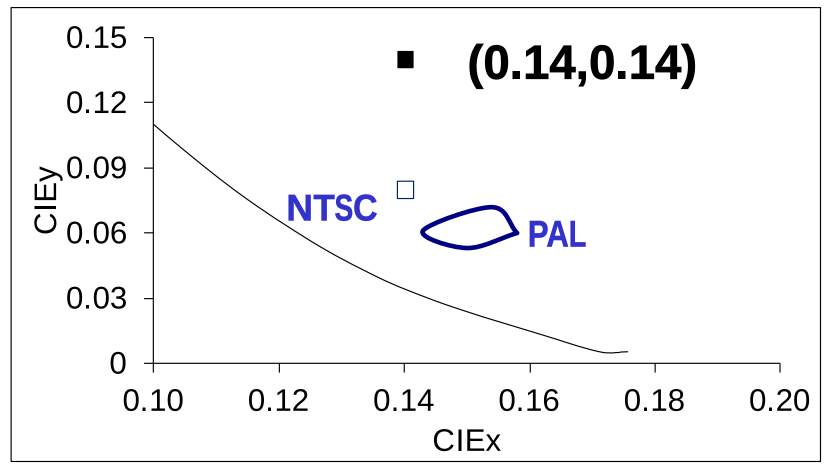
C|D|T

MODEL	à **9.4cd/A (0.14,0.14)**

PLQE@RZ = **65%** (Intrinsic PLQE = 80%)
Singlet Yield = **32%** (%DF = 22%)
RZ profile = **15nm** width near iL
Dipole orientation = k_z/k_x = **0.3**

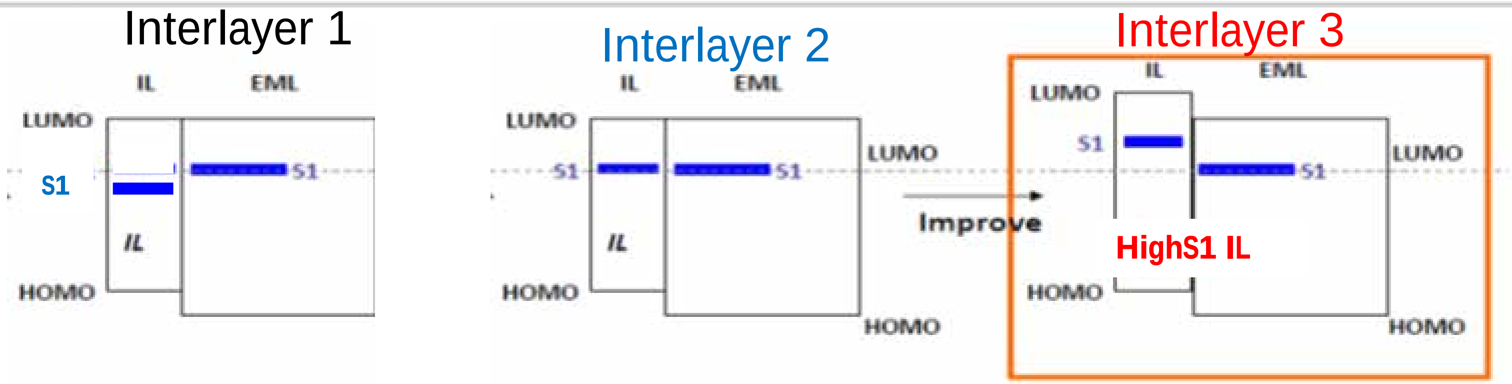
EXPT Previously published data – **9.4cd/A at 1000cd/m2 at (0.14,0.14)**

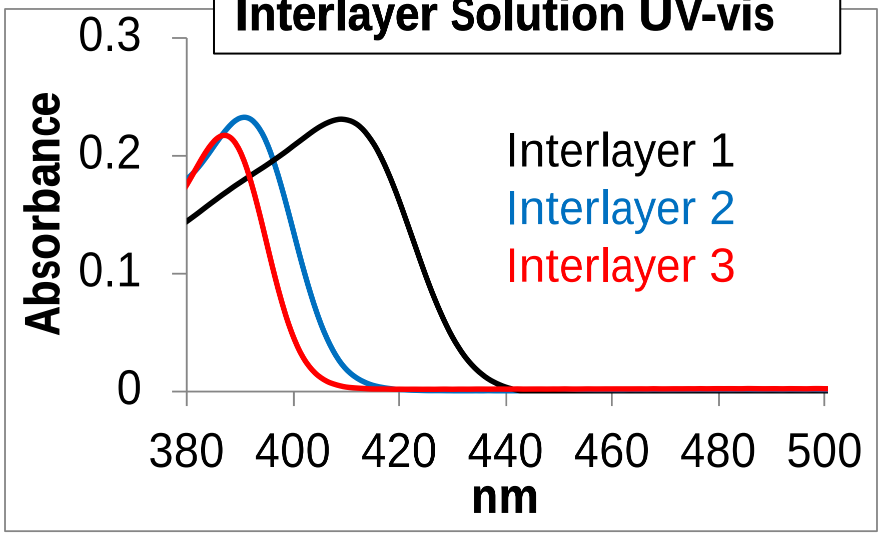


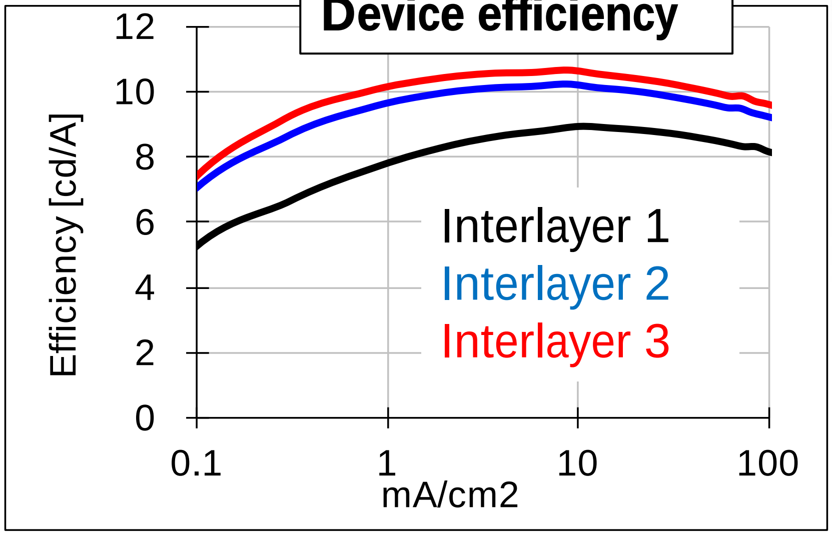


à Some scope for improvement in all areas

PLQE at RZ – reduced iL quenching



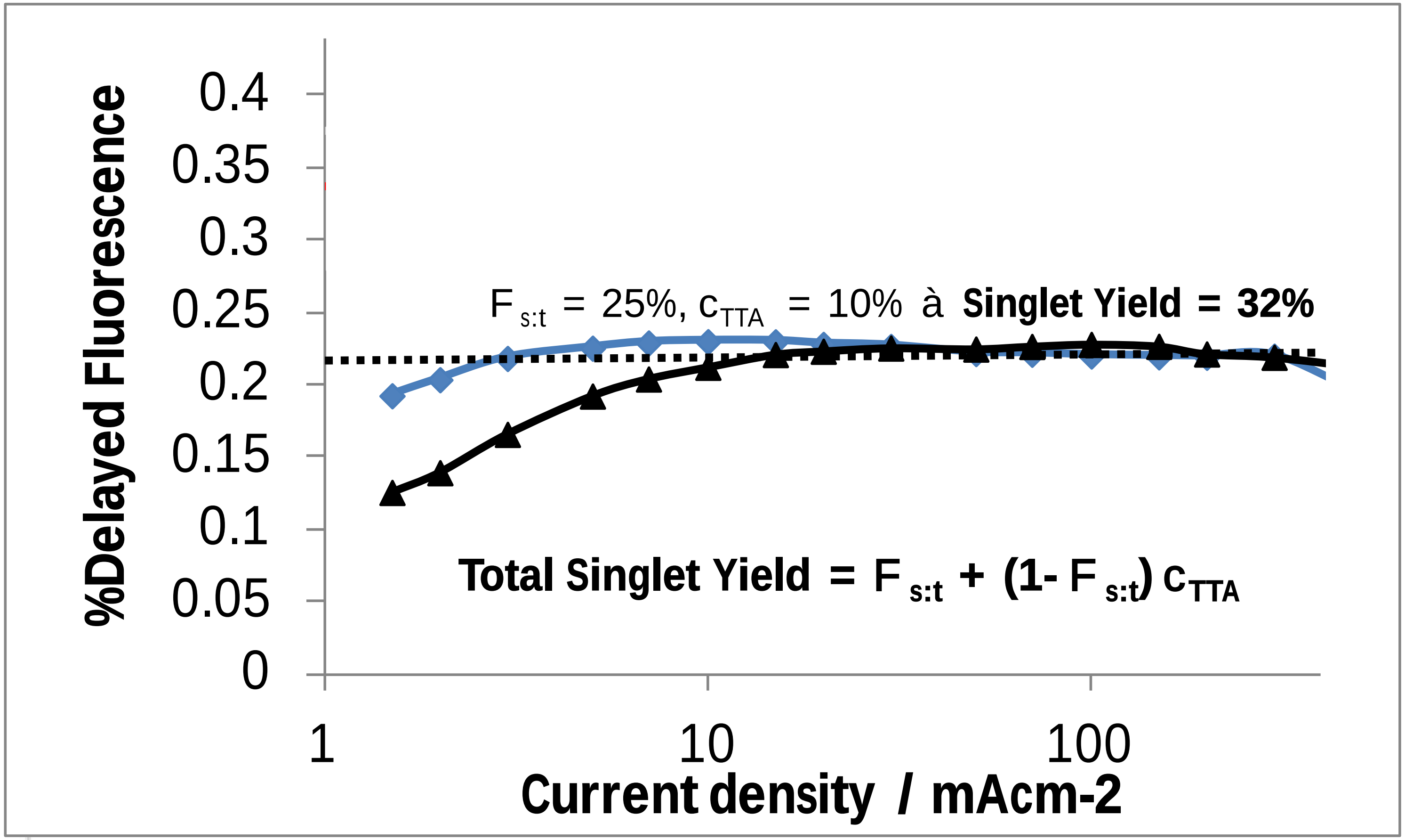




à Control of IL S1 can reduce PL quenching at emission zone

Singlet yield – improved TTA yield

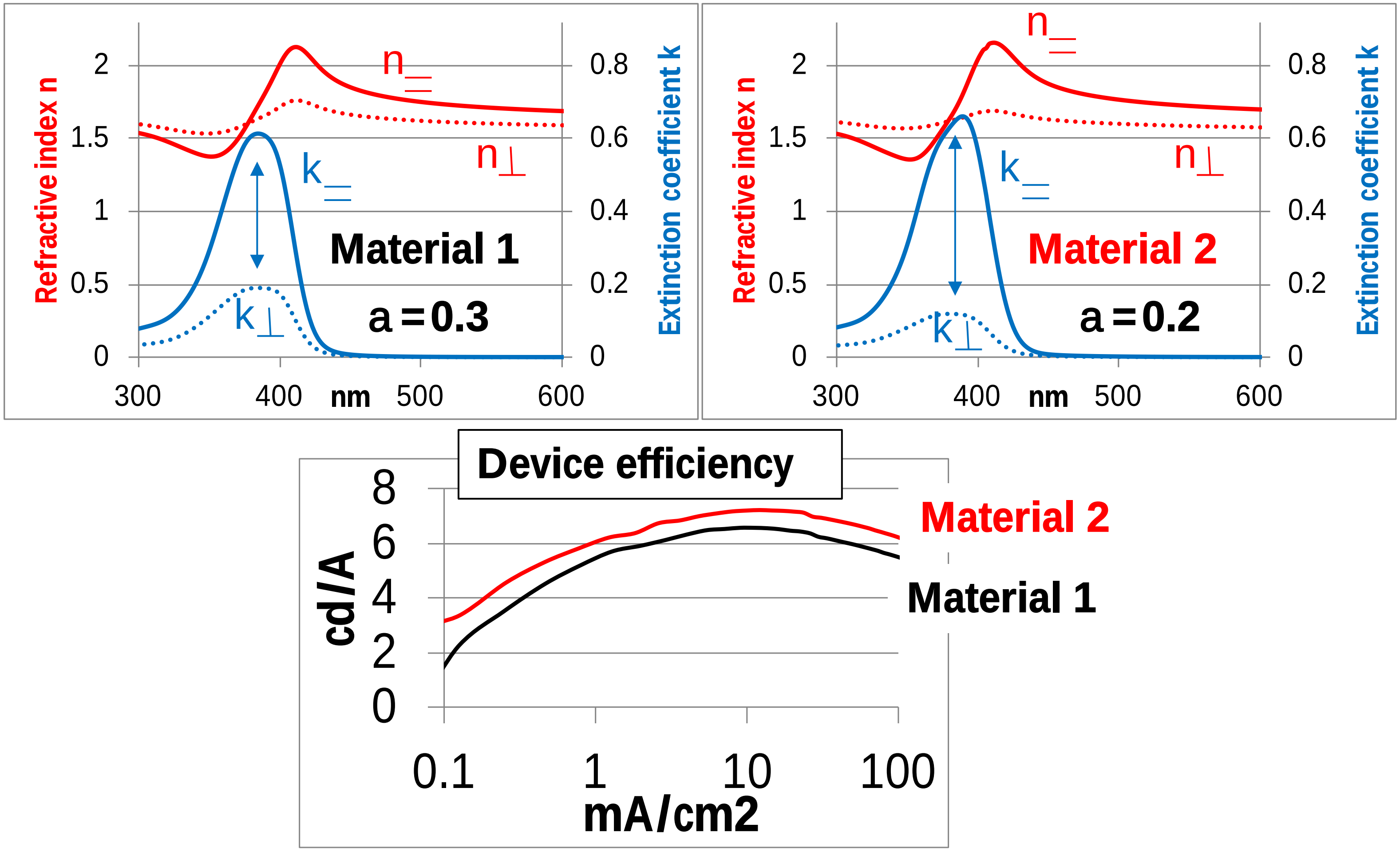
C D T



Older materials

à Improved materials give a higher Singlet Yield from TTA

Anisotropy – improved alignment



à Control of LEP morphology can improve efficiency

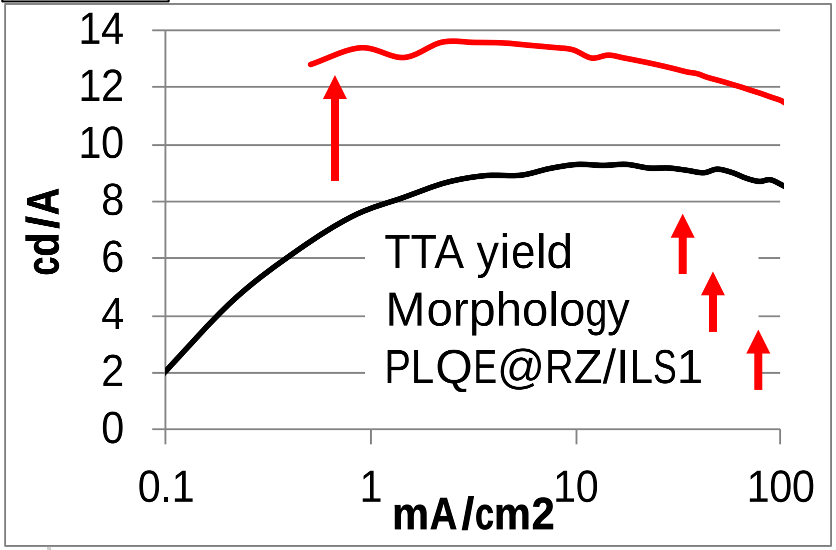
Blue – Improved efficiency

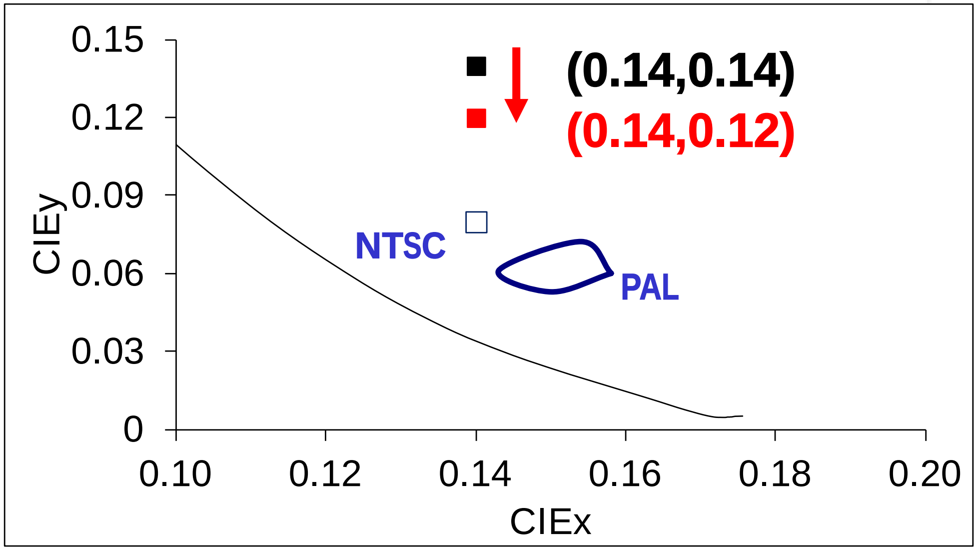
C|D|T

MODEL	à **9cd/A (0.14,0.14)**
PLQE@RZ = **65%** (Intrinsic PLQE = 80%) Singlet Yield = **32%** RZ profile = **15nm** width near iL Dipole orientation = k_z/k_x = **0.3**	

MODEL	à **13cd/A (0.14,0.12)**
PLQE@RZ = **80%** (=Intrinsic PLQE) Singlet Yield = **38%** RZ profile = **15nm** width near iL Dipole orientation = k_z/k_x = **0.2**	

EXPT **9.4cd/A (0.14,0.14)** à **13.4cd/A (0.14,0.12)**





à 13.4cd/A at 1000cd/m2 (0.14,0.12) achieved

Blue – Deep blue

C|D|T

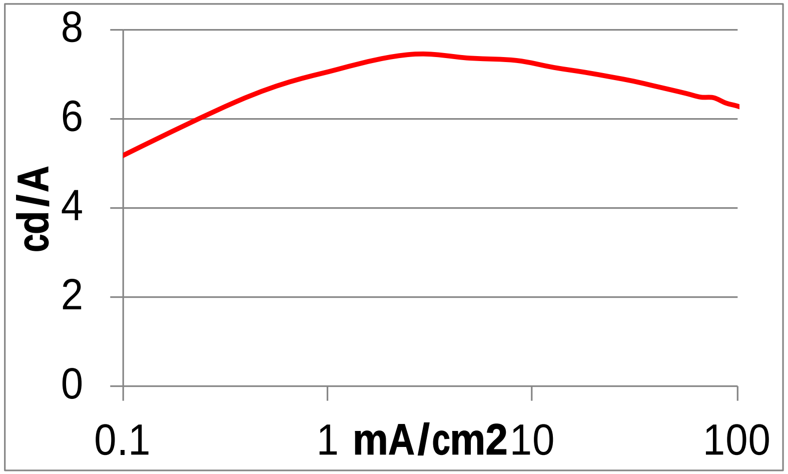
MODEL

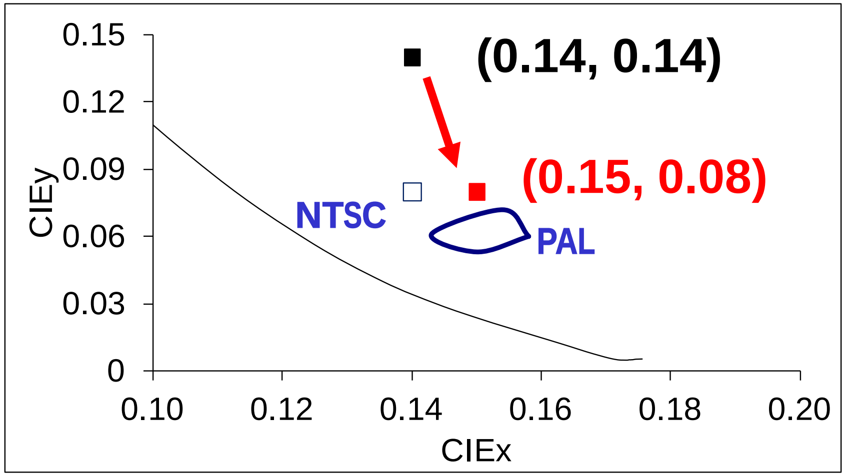
à **7cd/A (0.15,0.08)**

PLQE@RZ = **70%** (Intrinsic PLQE=80%)
Singlet Yield = **38%**
RZ profile = **15nm** width near iL
Dipole orientation = k_z/k_x = **0.2**

à emission spectrum only changed

EXPT **7.0cd/A (0.15, 0.08)**





à 7cd/A at 1000cd/m2 (0.15, 0.08) achieved

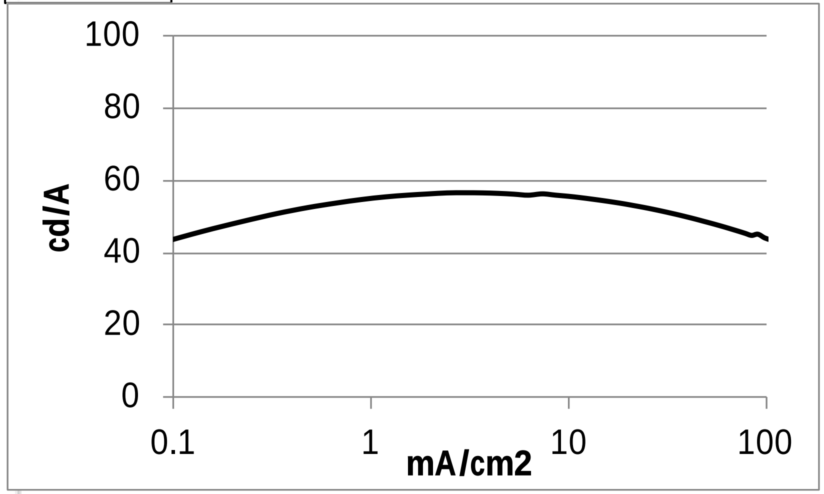
Green – std model

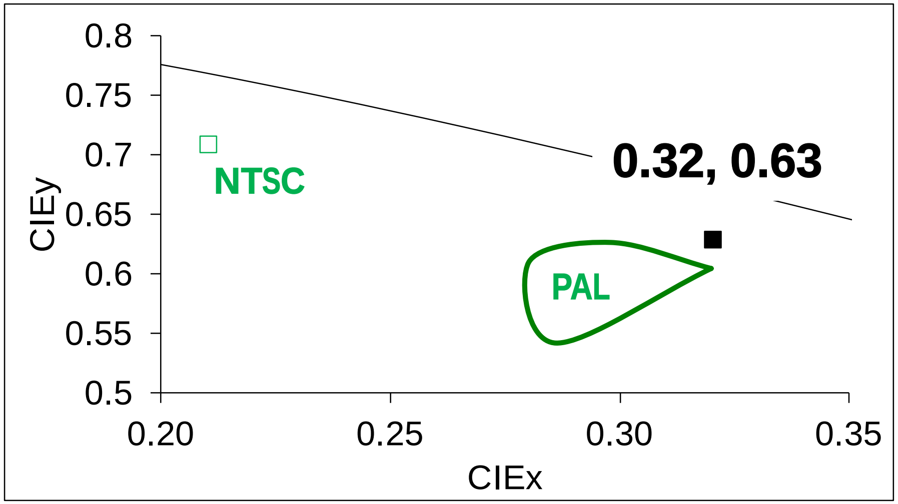
C|D|T

MODEL	à **56cd/A (0.32,0.63)**

PLQE@RZ = **44%** (Intrinsic PLQE = 75%)
Triplet Yield = **100%**
RZ profile = **15nm** width near iL
Dipole orientation = k_z/k_x = **1 (isotropic)**

EXPT Previously published data **56cd/A at 1000cd/m2 (0.32,0.63)**

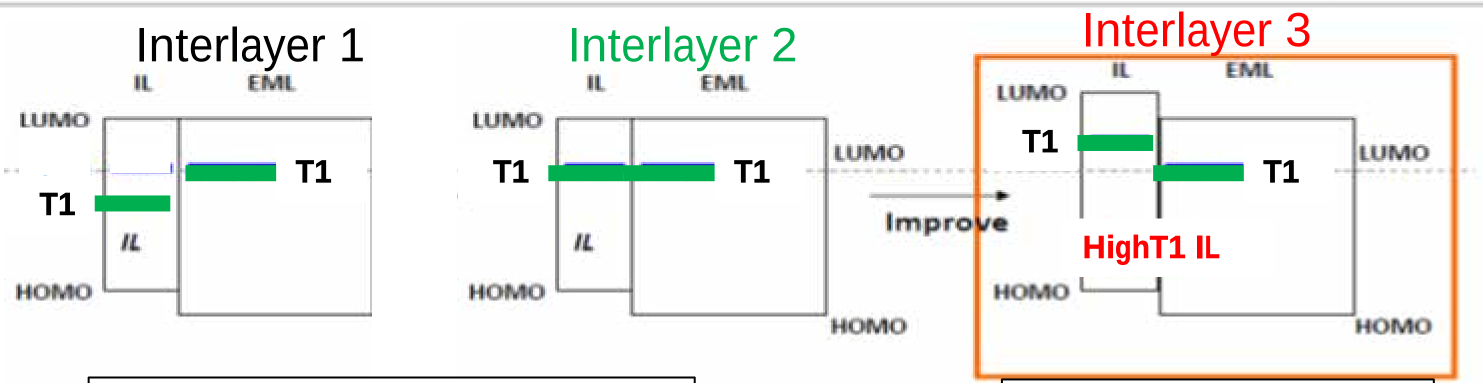


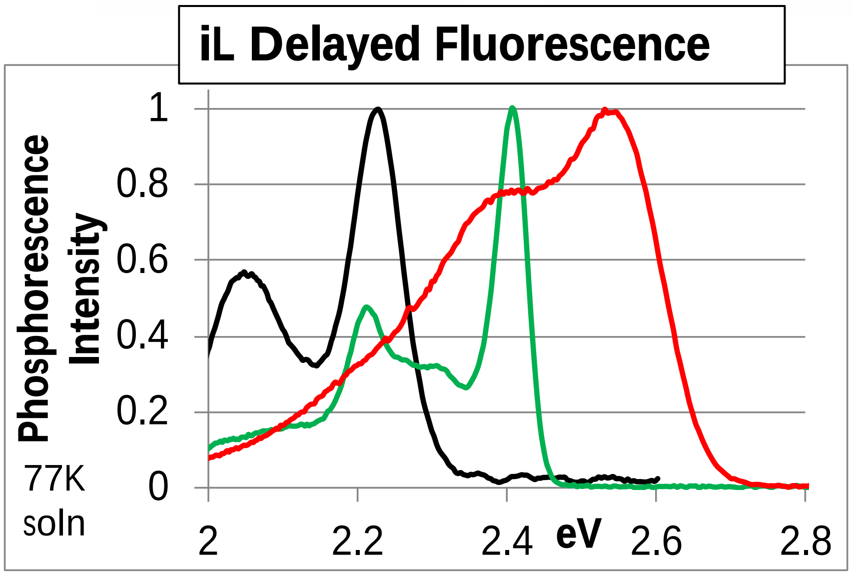


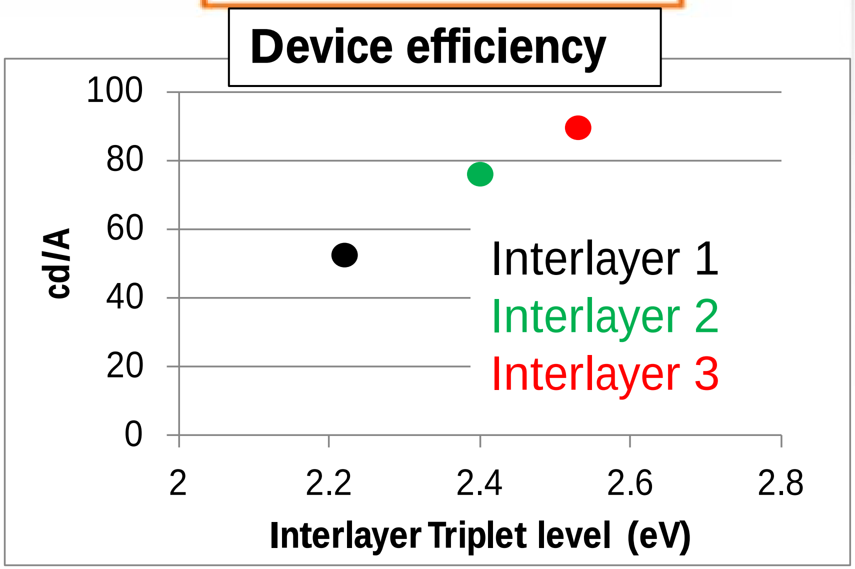
à PLQE@RZ is limiting efficiency…

PLQE at RZ – reduced iL quenching

C|D|T







à Reducing iL quenching is key to high green efficiency

Green – improved efficiency

C|D|T

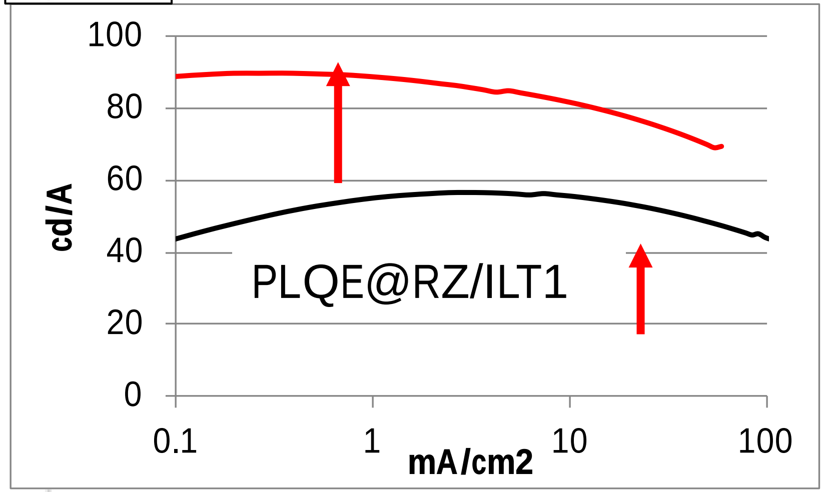
MODEL	à 56cd/A (0.32,0.63)

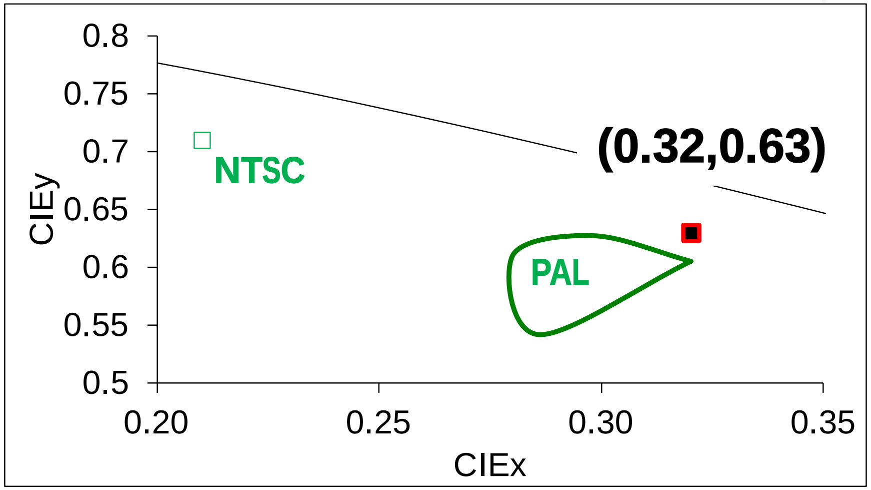
PLQE@RZ = **44%** (Intrinsic PLQE =75%)
Triplet Yield = **100%**
RZ profile = **15nm** width near iL
Dipole orientation = k_z/k_x = **1 (isotropic)**

MODEL	à 88cd/A (0.32,0.63)

PLQE@RZ = **75%** (=Intrinsic PLQE)
Triplet Yield = **100%**
RZ profile = **15nm** width near iL
Dipole orientation = k_z/k_x = **1 (isotropic)**

EXPT **56cd/A (0.32,0.63)** à **88cd/A (0.32,0.63)**





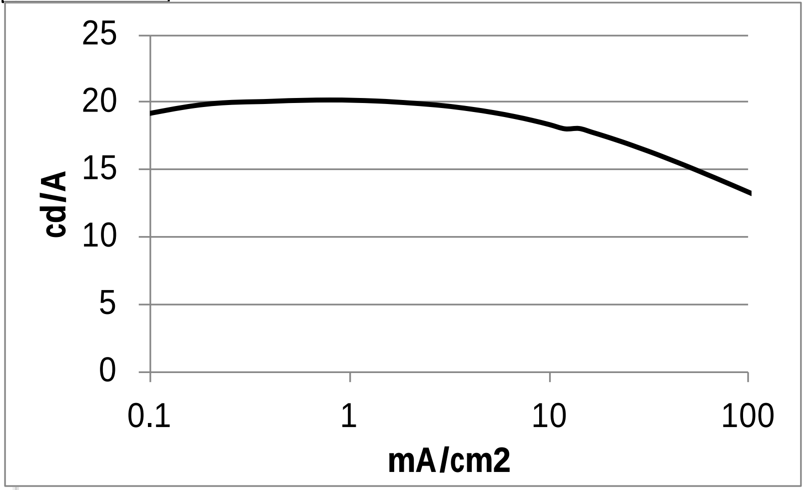
à 88cd/A at 1000cd/m2 (0.32, 0.63) achieved

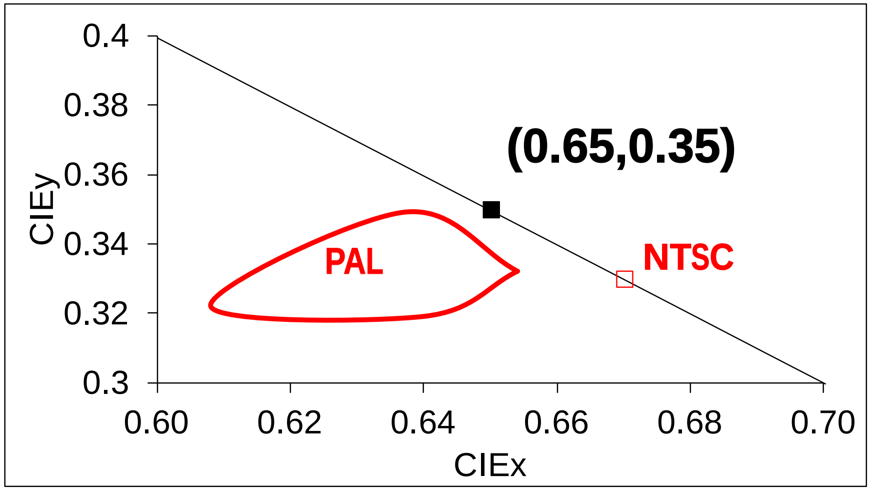
Red – standard model

MODEL	à 19cd/A (0.65,0.35)

PLQE@RZ = **55%** (=Intrinsic PLQE)
Triplet Yield = **100%**
RZ profile = **15nm** width near iL
Dipole orientation = k_z/k_x = **1 (isotropic)**

EXPT — Previously published data – **19.2cd/A at 1000cd/m2 (0.65,0.35)**





à Efficiency limited by Intrinsic PLQE

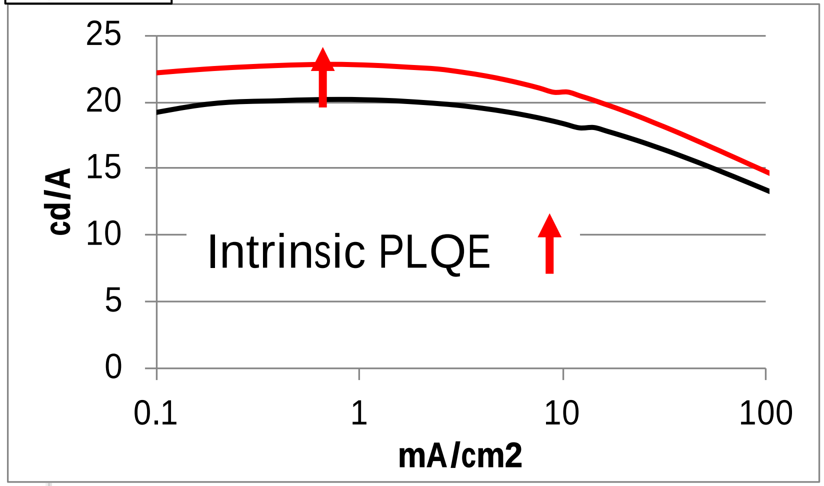
Red – improved efficiency

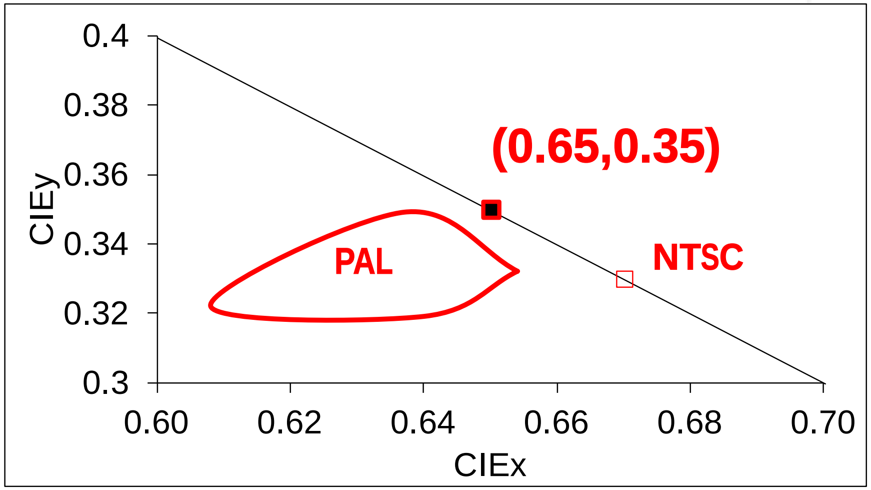
C|D|T

MODEL	à 19cd/A (0.65,0.35)
PLQE@RZ = **55%** (=Intrinsic PLQE) Triplet Yield = **100%** RZ profile = **15nm** width near iL Dipole orientation = k_z/k_x= **1 (isotropic)**	

MODEL	à **21cd/A (0.65,0.35)**
PLQE@RZ = **61%** (=Intrinsic PLQE) Triplet Yield = **100%** RZ profile = **15nm** width near iL Dipole orientation = k_z/k_x= **1 (isotropic)**	

EXPT **19.2cd/A (0.65,0.35) à 21.8cd/A (0.65, 0.35)**





à 21.8cd/A at 1000cd/m2 (0.65,0.35) achieved

Efficiency improvement summary for weak cavity devices

C|D|T

Previous efficiency	Improved performance	Origins of improvements
9.4cd/A (0.14,0.14)	13.4cd/A (0.14, 0.12) 7cd/A (0.15, 0.08)	TTA Yield Dipole orientation iL Singlet energy Deep blue Emitter
56cd/A (0.32, 0.63)	88cd/A (0.32, 0.63)	iL Triplet energy
19.2cd/A (0.65, 0.35)	21.8cd/A (0.65,0.35)	Material PLQE

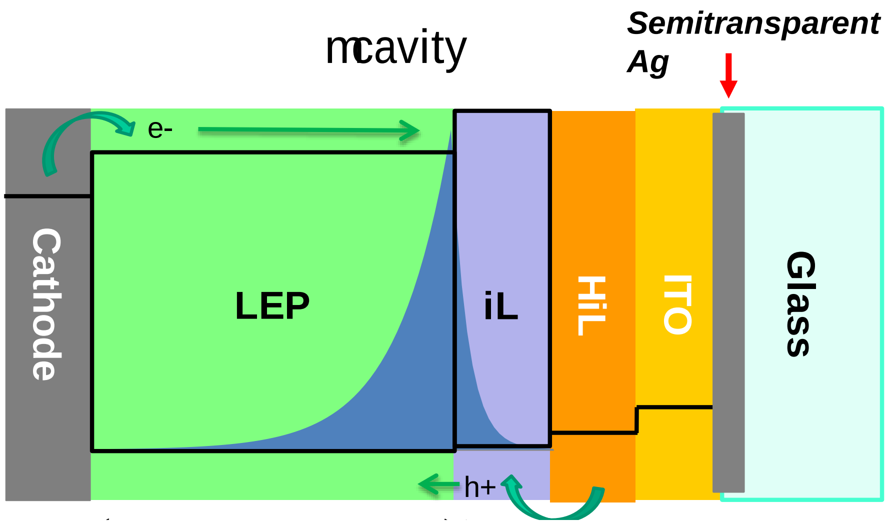
P-OLED RGB efficiency

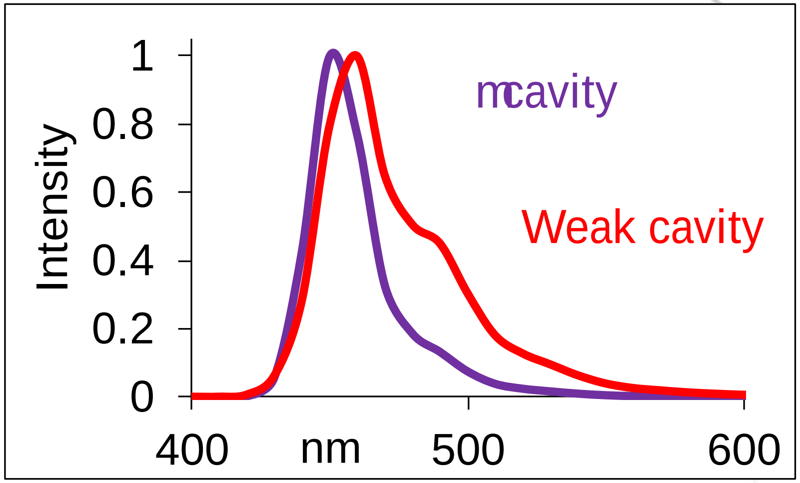
Key parameters

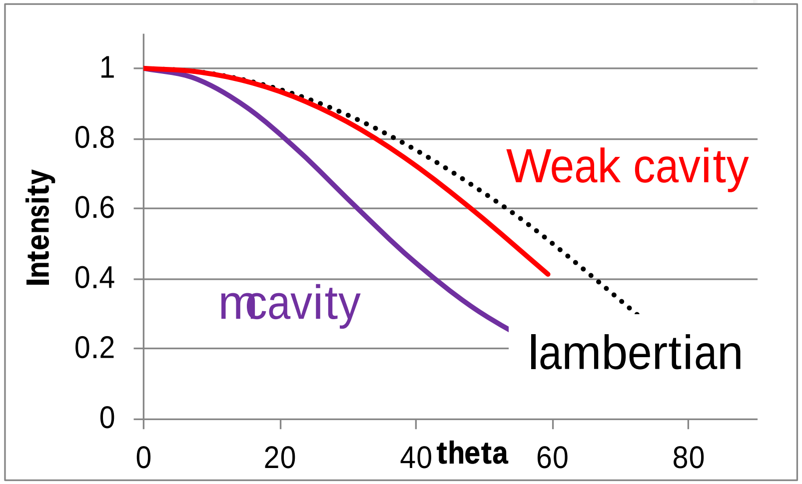
Materials improvements

mcavity performance

mcavity devices – MODEL







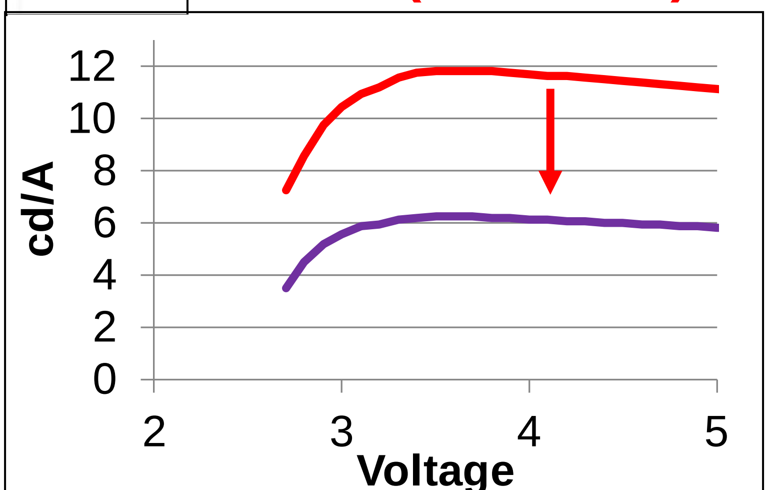
à mcavity device structures can significantly improve colour

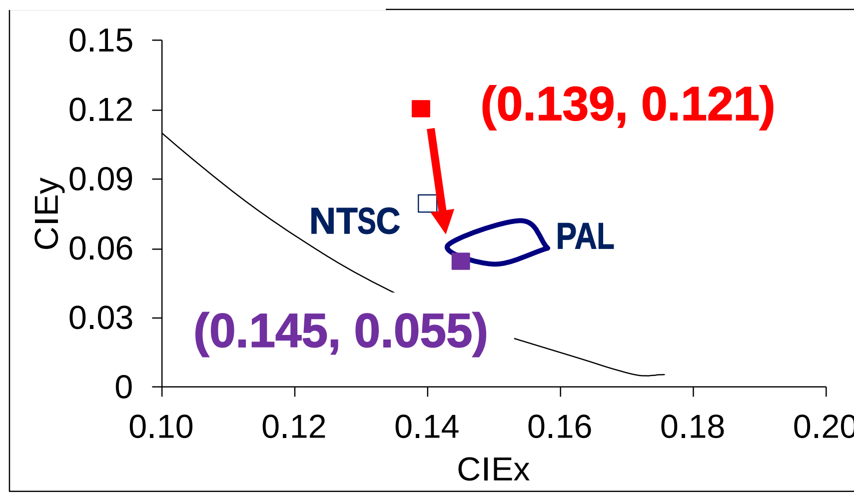
Blue – mcavity

C|D|T

Weak cavity device ITO/HIL/IL/LEP/Al	mcavity device ITO/**Ag**/HIL/IL/LEP/Al
MODEL à **12cd/A (0.14,0.12)**	MODEL à **6cd/A (0.15,0.05)**
PLQE@RZ = **75%** (Intrinsic=80%) Singlet Yield = **38%** RZ profile = **15nm** width near iL Dipole orientation = k_z/k_x = **0.2**	PLQE@RZ = **75%** (Intrinsic=80%) Singlet Yield = **38%** RZ profile = **15nm** width near iL Dipole orientation = k_z/k_x = **0.2**

EXPT **11.8cd/A (0.139,0.121)** à **6.3cd/A (0.145, 0.055)**





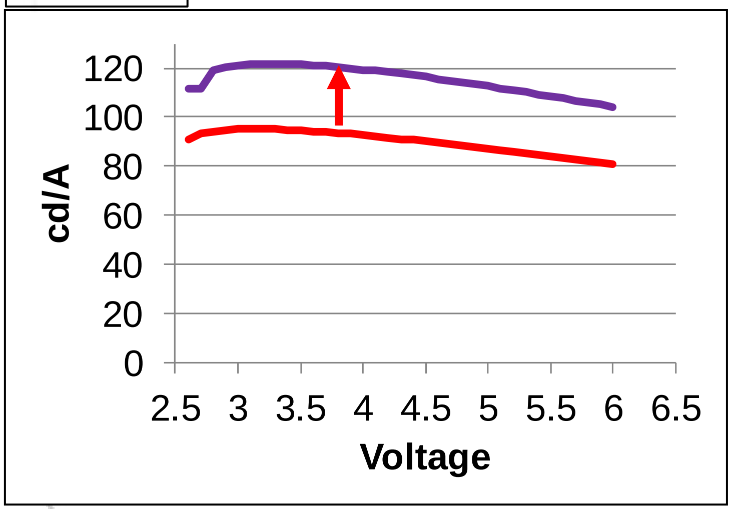
à 6.3cd/A at 1000cd/m2 (0.145,0.055) achieved

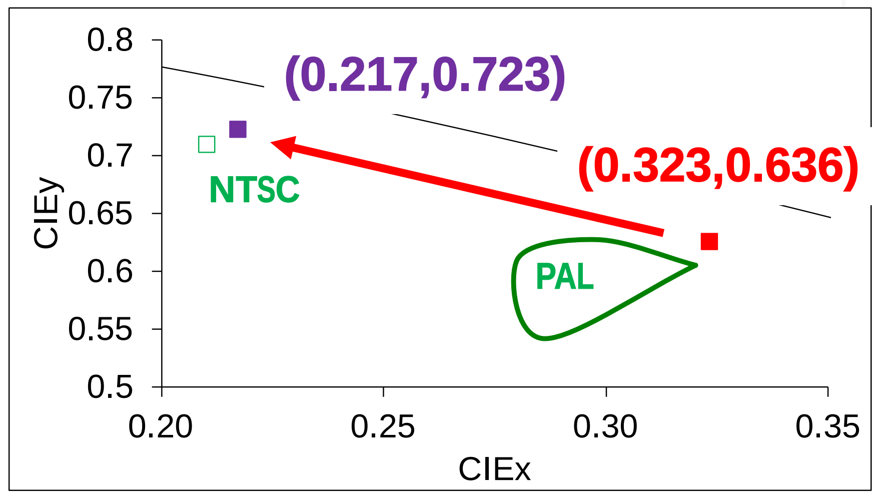
Green – mcavity

C|D|T

Weak cavity device ITO/HIL/IL/LEP/Al	mcavity device ITO/**Ag**/HIL/IL/LEP/Al
MODEL **à *88cd/A at (0.32, 0.63)***	MODEL **à *118cd/A at (0.22, 0.72)***
PLQE@RZ = **75%** (=Intrinsic PLQE) Triplet Yield = **100%** RZ profile = **15nm** width near iL Dipole orientation = k_z/k_x = **1 (isotropic)**	PLQE@RZ = **75%** (=Intrinsic PLQE) Triplet Yield = **100%** RZ profile = **15nm** width near iL Dipole orientation = k_z/k_x = **1 (isotropic)**

EXPT **90.0cd/A (0.323,0.636)** *à* **120cd/A (0.217, 0.723)**





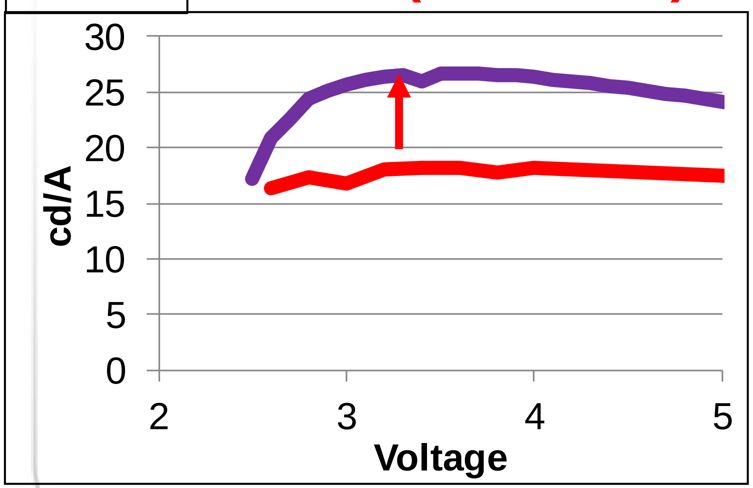
à 120cd/A at 1000cd/m2 (0.217,0.723) achieved

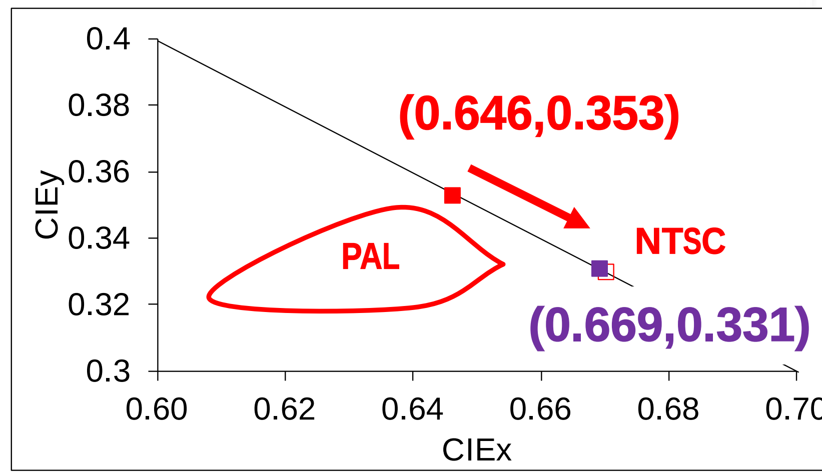
Red – mcavity

C|D|T

Weak cavity device ITO/HIL/IL/LEP/Al		mcavity device ITO/**Ag**/HIL/IL/LEP/Al	
MODEL	à ***19cd/A at (0.65, 0.35)***	MODEL	à ***25cd/A at (0.67,0.33)***
PLQE@RZ = **55%** (=Intrinsic PLQE) Triplet Yield = **100%** RZ profile = **15nm** width near iL Dipole orientation = k_z/k_x = **1 (isotropic)**		PLQE@RZ = **55%** (=Intrinsic PLQE) Triplet Yield = **100%** RZ profile = **15nm** width near iL Dipole orientation = k_z/k_x = **1 (isotropic)**	

EXPT **18.0cd/A (0.646,0.353)** à **26.5cd/A (0.669, 0.331)**



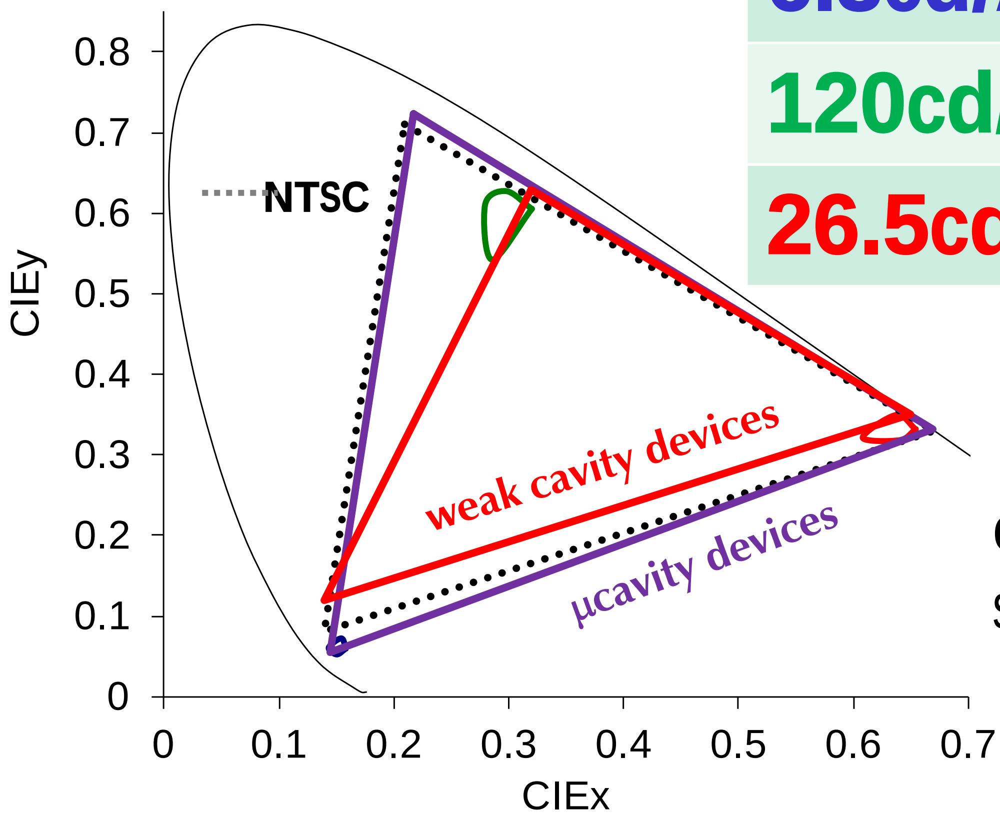


à 26.5cd/A at (0.67,0.33) achieved

Efficiency and colour achievement summary for mcavity devices

C|D|T

mcavity performance
6.3cd/A at (0.145,0.055)
120cd/A at (0.217,0.723)
26.5cd/A at (0.669,0.331)



à High efficiency near NTSC colour achieved for RGB in simple mcavity structure

OLED Applications

Displays


World's Largest
4K
World's Largest 4K OLED
created by Printing Technology
Panasonic

PLED performance 2013/Autumn

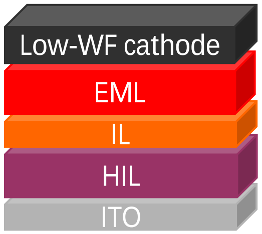
Non-cavity device

Spin/BE data @1000cd/m2	Red			Green		Blue		
Efficiency [cd/A]	31	22	17	75	75	12.4	8.6	7.3
Colour (C.I.E. x,y)	x=0.62 y=0.38	x=0.65 y=0.35	x=0.65 y=0.35	x=0.32 y=0.63	x=0.32 y=0.63	x=0.14 y=0.12	x=0.14 y=0.12	x=0.14 y=0.13
T50 lifetime [hrs]	350k	350k	>150k	>300k	190k	16k	-	-
T95 lifetime [hrs]	-	-	>3000	-	2100	-	150	700
Vd [V]	4.2	4.1	3.6	5.1	4.5	3.9	3.6	4.1

*Lifetime estimated from acceleration test.
*No electrical-ageing applied before lifetime test.

Device structure

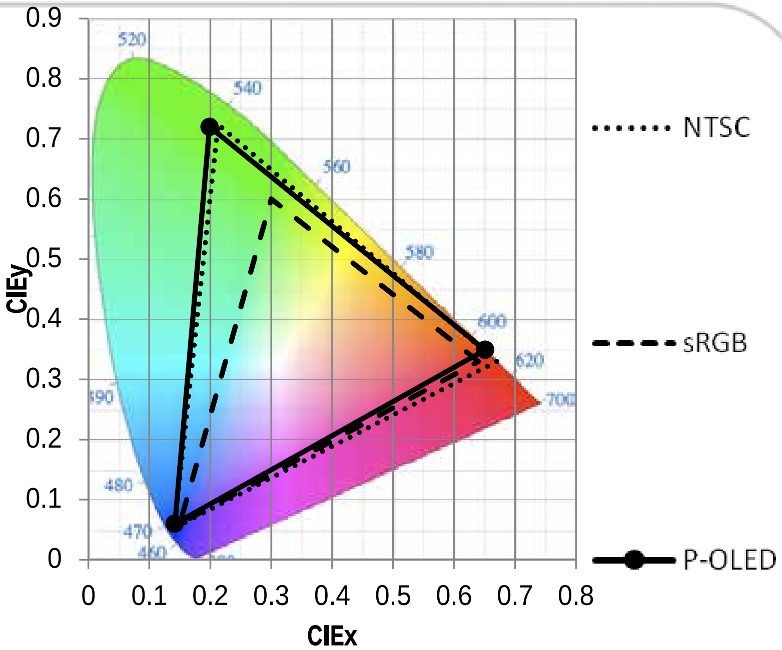
ITO (45nm)/ spin-coated HIL (30-65nm)/ Interlayer (20nm)/ LEP (60-75nm) / low-WF cathode



- RGB common and simple layer structure.
- Organics are fully solution-processed.

Materials for Display panels

- Good efficiency can be achieved with micro-cavity
- >100% s-RGB can be achieved with micro-cavity
- Forward direction cd/A efficiencies
- T95 lifetimes key to avoid image sticking
- **Display parameters:**
  - Average luminance 200 cd/m²
  - Circular polarizer transmittance 44%.
  - Aperture ratio 38%.



	Micro-cavity sub-pixel		
Colour	CIEx	CIEy	Luminance (cd/m²)
Red	0.651	0.349	1200
Green	0.199	0.720	2000
Blue	0.142	0.060	270

Materials Efficiency for Display panels

CDT

	Optical efficiency, cd/A		
	2011	2012	2013
Red	**25**	**25**	**31**
Green	**50**	**75**	**90**
Blue	**3.8**	**4.4**	**5.6**
Colour gamut - CIExy (1936) % of sRGB	135%	145%	140%
White point Optical efficiency (D65)	22.2cd/A	28.3cd/A	32.3cd/A
White point Power efficiency cd/W	4.0cd/W	6.4cd/W	8.8cd/W

Lighting

C|D|T

- OLEDs have great potential for creating large area, diffuse light sources
- General lighting requires **>80lm/W efficacy, large area tiles** and **low cost manufacturing**
- In a standard device structure, only ~25% (external QE) of the light is emitted

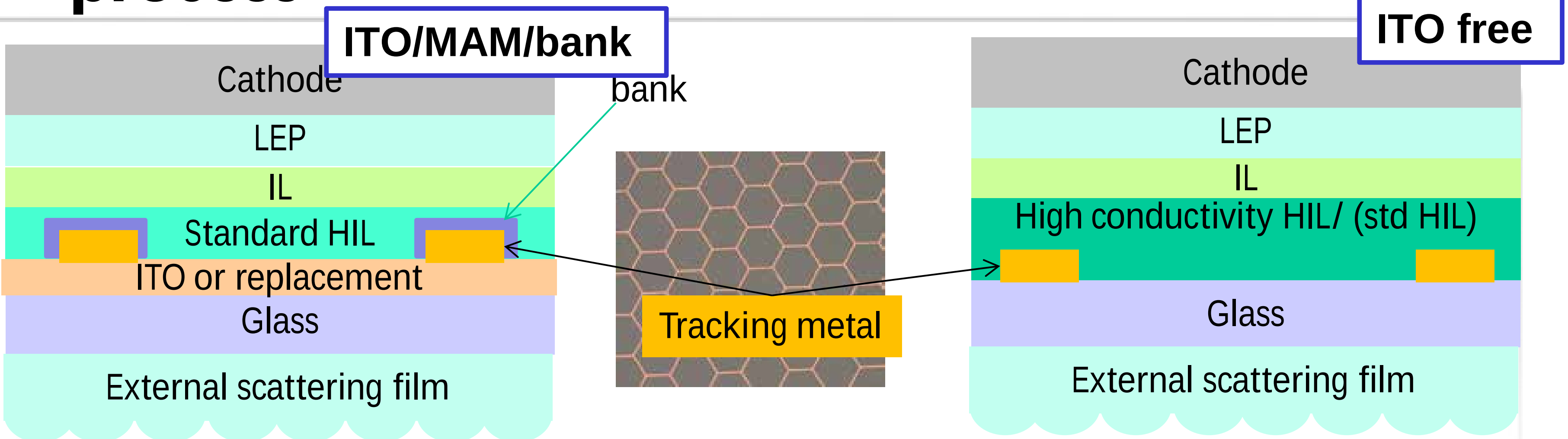
Þ **Technology challenges for lighting are not only materials related: device structure development is also key**

2014 Sumitomo Light and Build stand: Ink Jet Printed

The **Lighting Devices Project** at CDT tackles the **key device technology challenges:**
- Develop low cost structure and process => ITO free; low cost metal grid
- Extract trapped light out of the device to increase efficiency
- Develop a structure and process scalable to large area tiles (2" or 6")

Develop a low cost structure and process

C|D|T



Anode structure: ITO free is current development structure

Þ Removes potentially expensive ITO from structure

Þ Improved compatibility with low cost R2R process

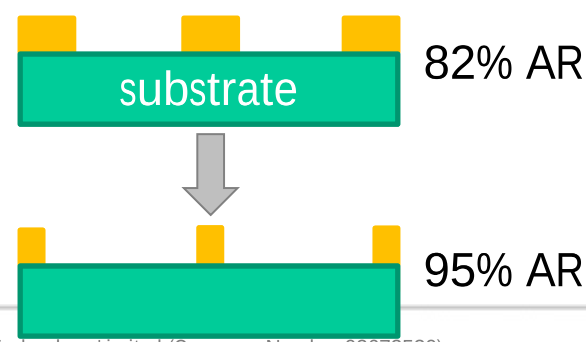
Þ Optical properties give more light extraction than ITO with external scattering film

Tracking metal grid: Metal grid required for both ITO or ITO free. Requirements:

Þ Optimise grid design for minimal loss (higher AR)

Þ Low cost metal

Þ Low cost deposition process for R2R

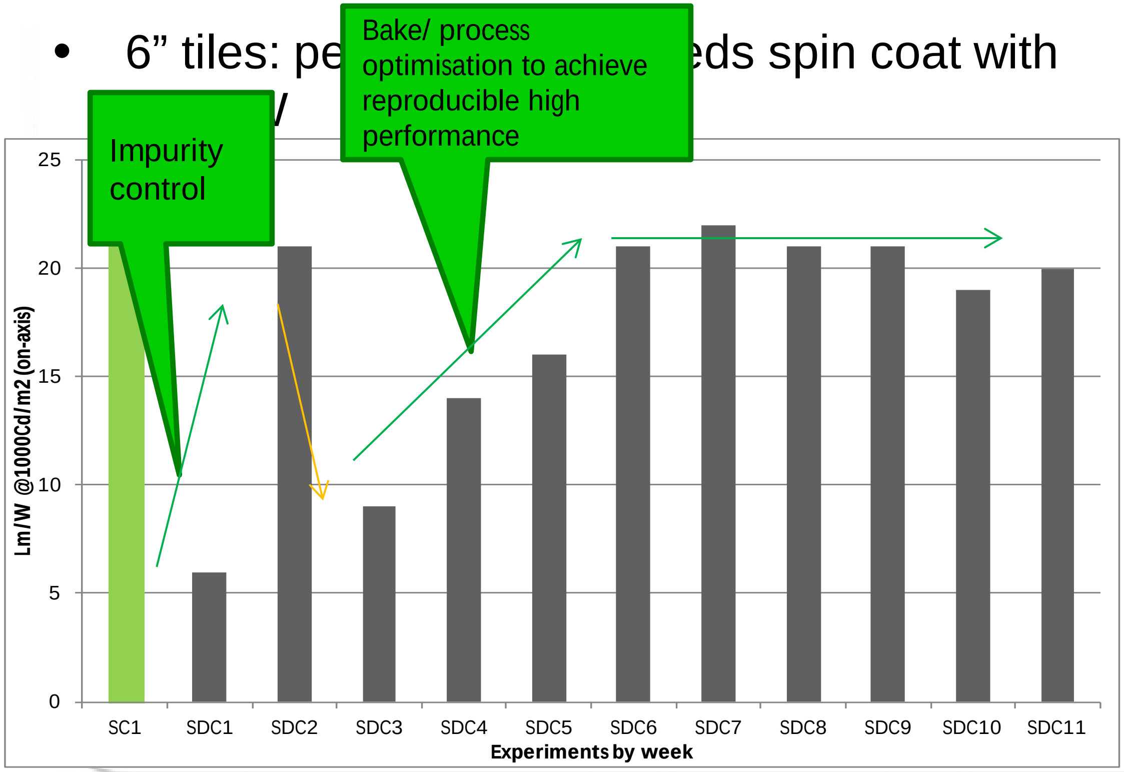


Deposition of solution processed layers (HIL/IL/LEP):
Developing low cost slot die coater process

Þ Reduced material loss and R2R compatible

High efficiency 6" tiles by spin coat and low cost slot die coater process

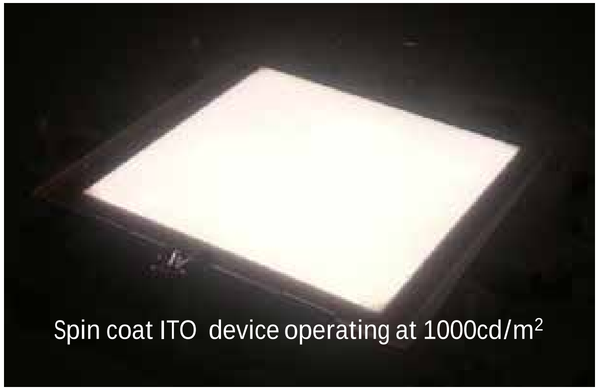
- Performance of tiles with slot die coater
  - Process and impurity control critical for good performance with high efficiency materials
  - Optimised process similar/ better lm/W to spin coat
  - 6" tiles: pe[...]eds spin coat with [...]/



SDC test pixel Lm/W over time

Best performance on 6" tiles using ext + internal scatter

	Spin coat LEP	Slot die coat LEP
Lm/W	40	42



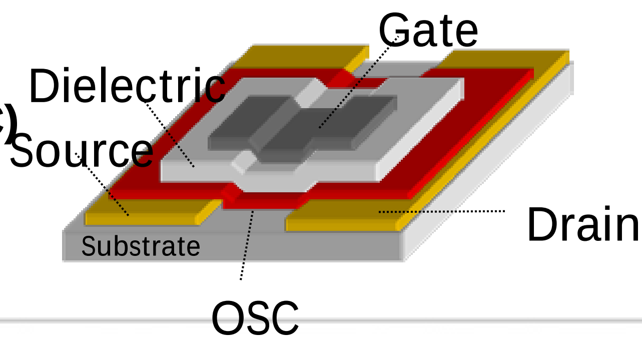
Automotive Engineering Exposition 2013

- Sumitomo Chemical demonstrates conformable solution processed lighting panels.
  - Fabricated using a glass substrate carrier
  - Red and White organic materials are printed by Ink Jet Printing
  - Layer thickness is designed so as to light the panel at the same voltage.
  - Electrodes are designed to achieve the uniform emission across the panel.

Other Solution Processed Devices: Organic Thin Film Transistors

Introduction

- We are developing “3rd generation” semiconductors in collaboration with Sumitomo Chemical OSC Team
- OTFT development focus:
  - Material development: High mobility semiconductors
    - Single component and blend systems
  - Device platform development: Improved uniformity
  - Customer support: Material sampling & sales
- Device performance requirements:
  - Mobility >$0.5cm^2V^{-1}s^{-1}$ with ≤10μm channel length
  - On/off current ratio ³ 10^5
  - Compatible with plastic substrates
- Material processing requirements:
  - Compatible with low temperature process (<100ºC)
  - Air stability:
    - Materials processable in air
    - Devices operational in air

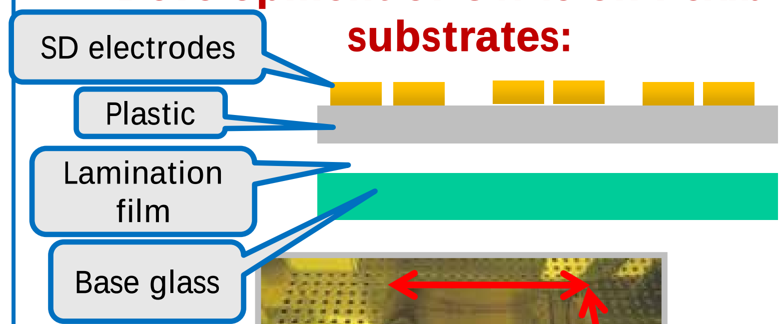


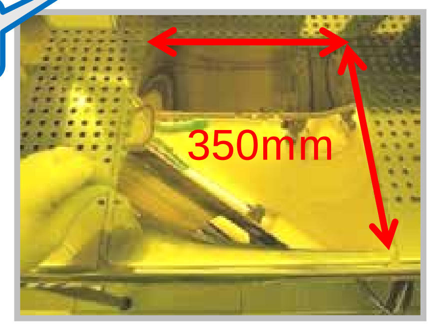
OTFT Development: Platform Development

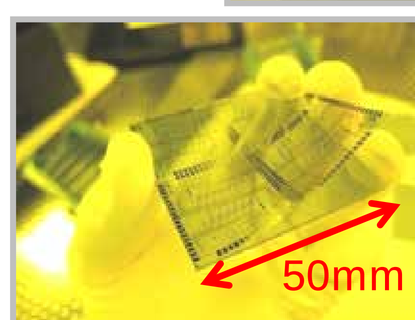
- **Device fabrication:**
  - OTFT devices are fabricated & testing in air
  - No encapsulation
- **Plastic substrates:**
  - OTFT technology shifted to plastic/flexible substrates
  - Developed lithography on plastic substrates at 350mm size with 5µm channel resolution
  - High performance demonstrated
- **Interface engineering & control:**
  - More efficient devices by controlling metal-semiconductor interfaces
  - Improved control of OSC morphology

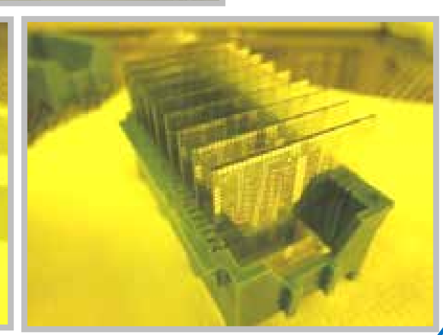
OTFT Device Platform Development

Development of OTFTs on flexible substrates:







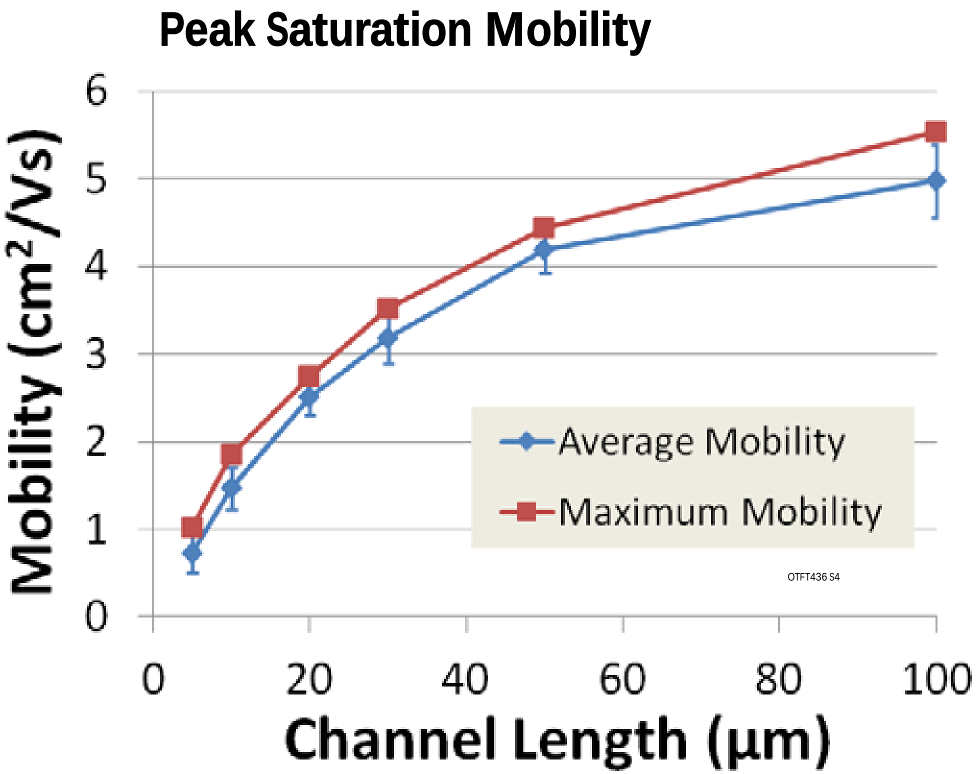


2nd Generation Device Performance

CDT

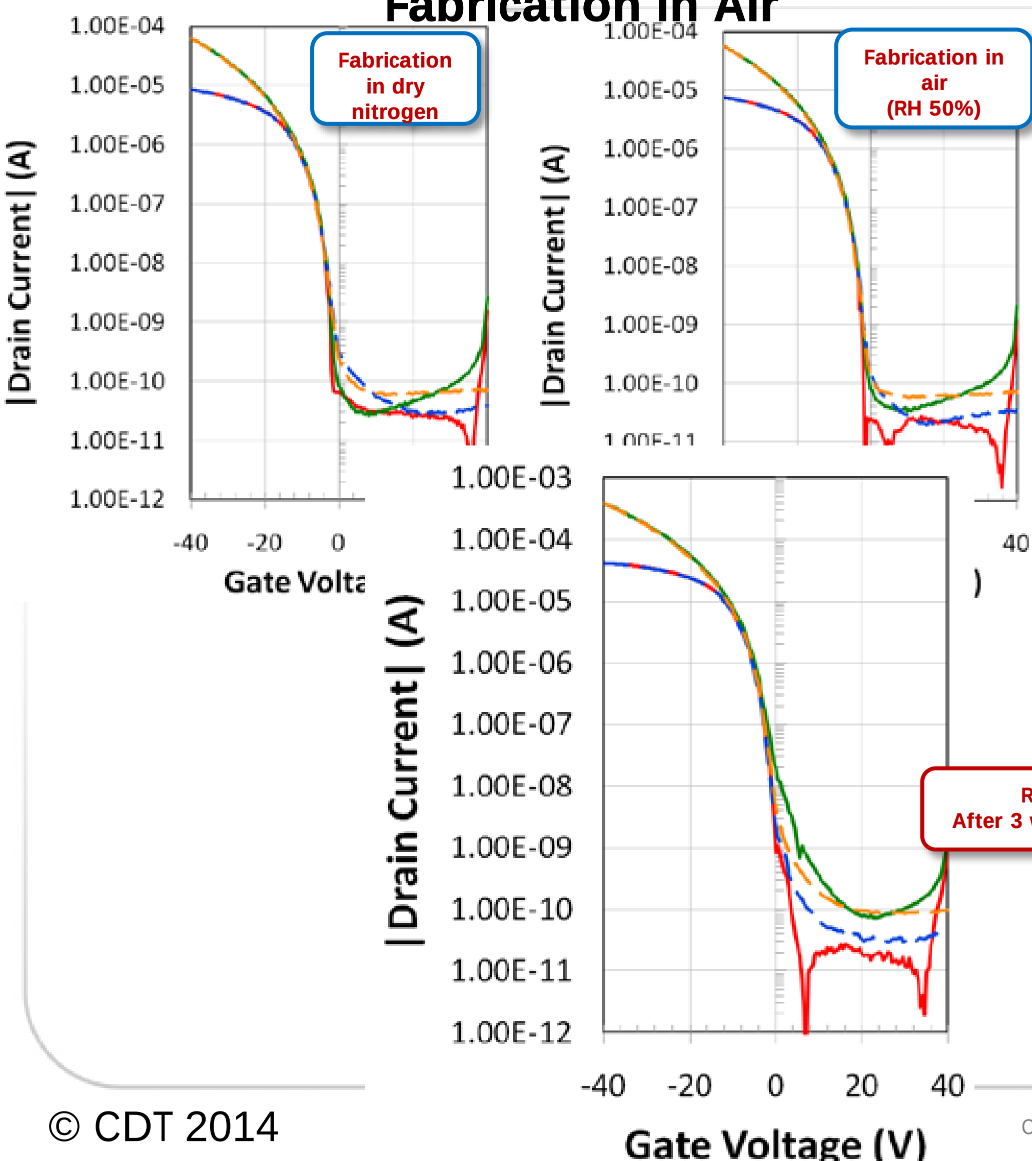
- Device improvements focussed to increase mobility for short channel devices
- Low contact resistance 4kWcm
- Low spread in mobility:

Devices fabricated in air. Upper process temp 100°C.



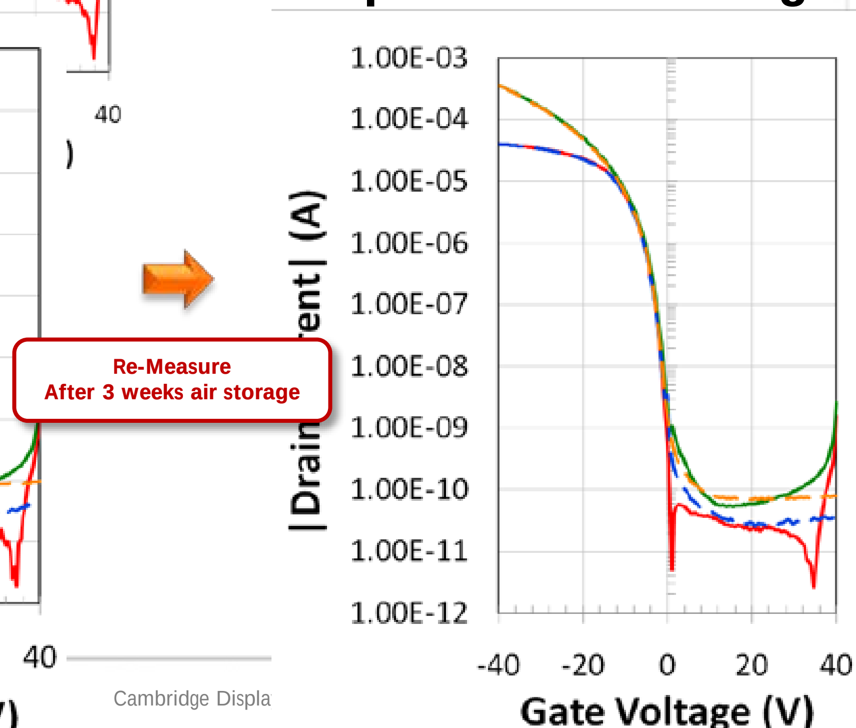
Semiconductor Performance:

Fabrication in Air



No difference in initial performance due to device fabrication environment

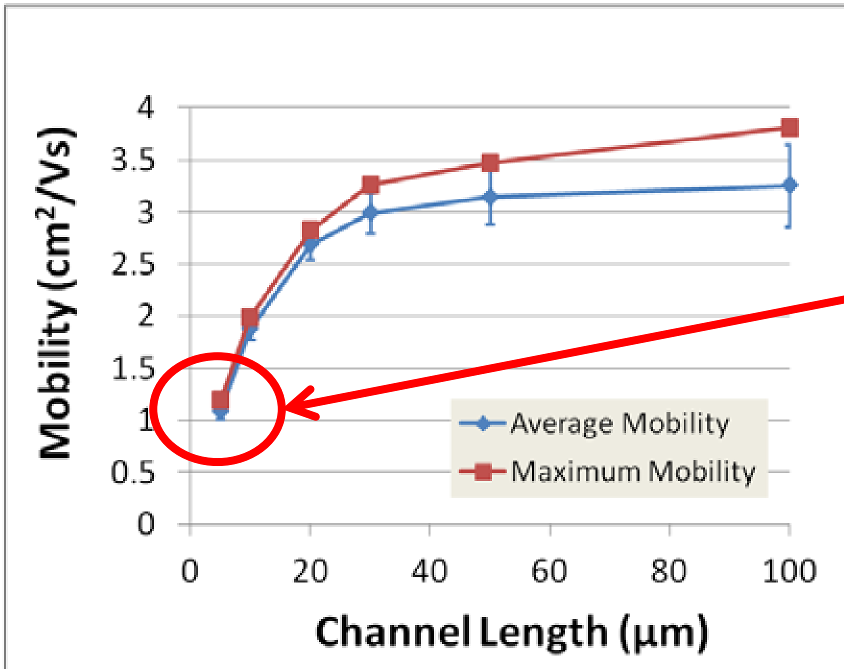
Un-encapsulated Air Storage



3rd Generation OSC

CDT

- **New Formulation:**
  - **Modifying HOMO levels between components**
  - **Rc reduced from 4-5 kWcm to < 2 kWcm**
  - **Long channel mobility suppressed**
  - **Short Channel performance improved**
    - **@ 10 mm channel length mobility > 1.8 cm^2/Vs**
    - **@ 5 mm channel length mobility > 1 cm^2/Vs**



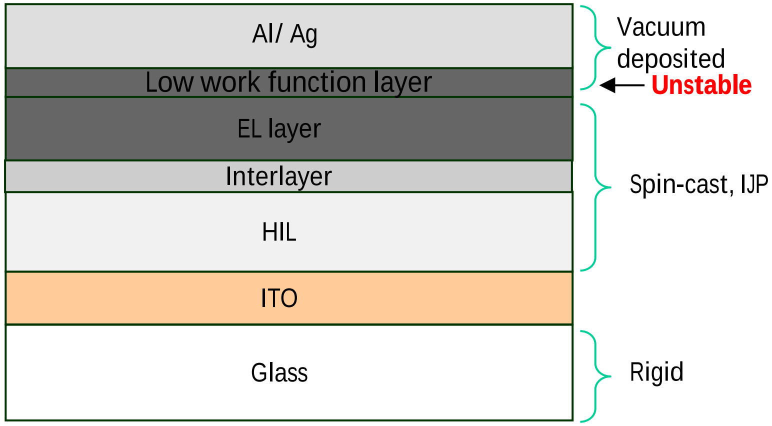
Note short channel data spread is small

Other Solution Processed Devices: All Printed OLED

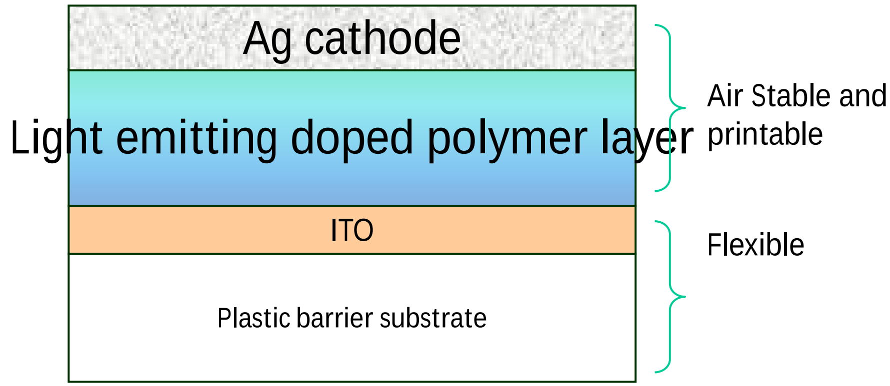
LEC Technology

CDT

Standard POLED



LEC POLED

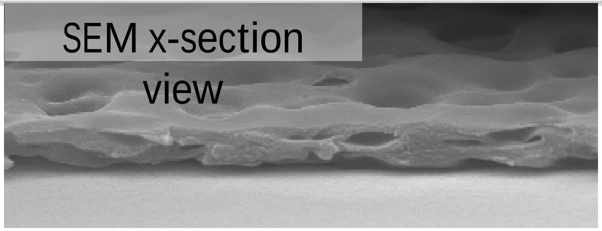


- High specification – best lifetime device structure
- High cost – suitable for high information content displays – HDTV
- Rigid substrate – because of high barrier property of glass

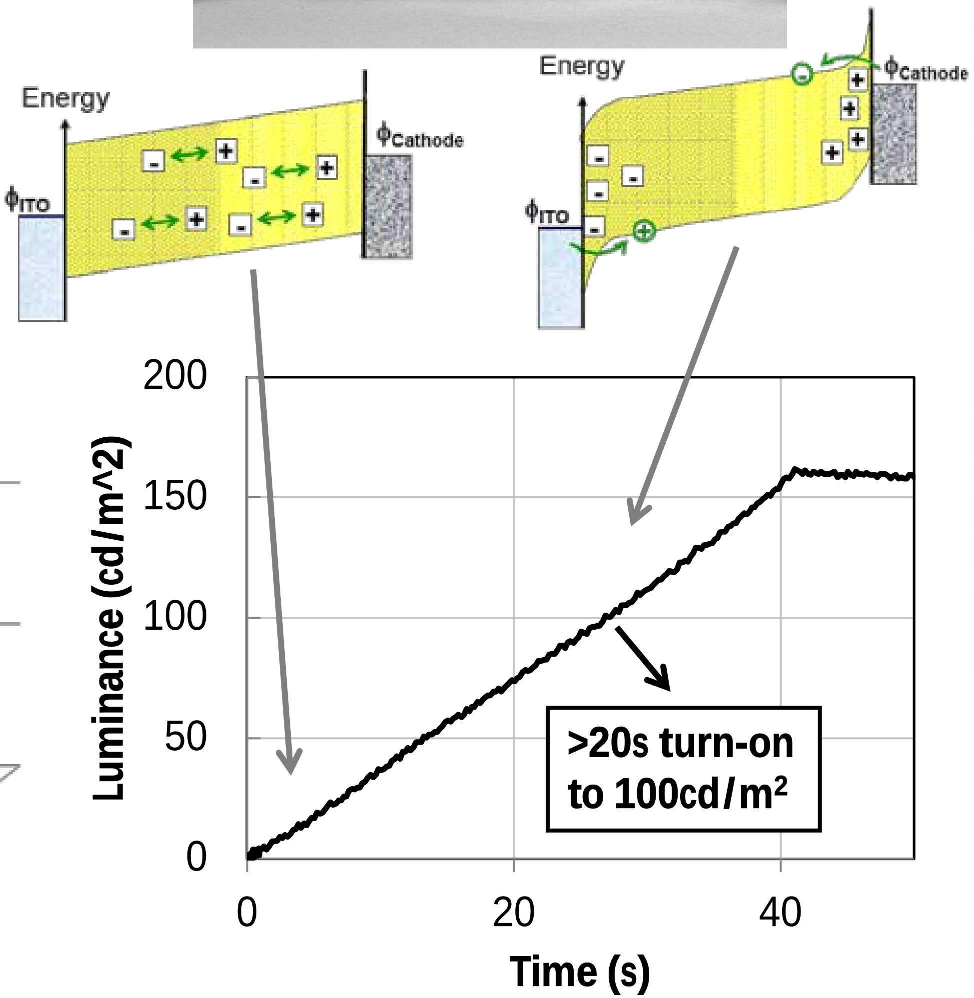
- Reduce number of process steps
- Reduce tool set cost
- Improve air stability à plastic flexible substrate

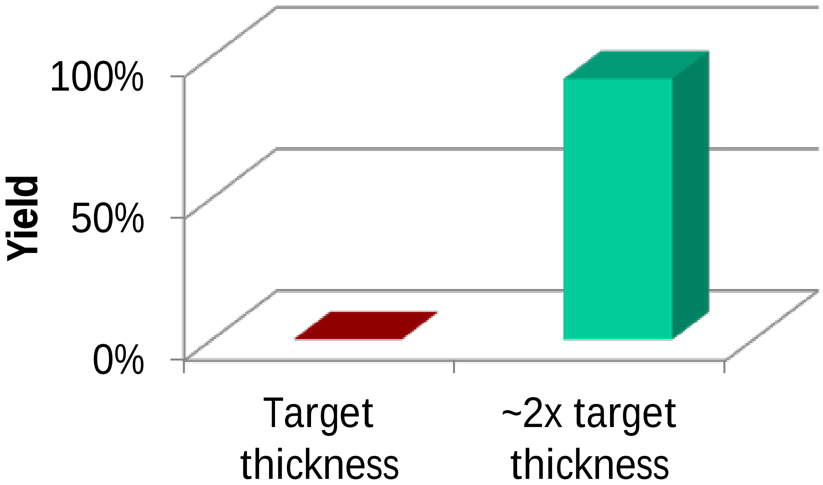
Initial Performance Limitations

- Standard LEPs incompatible with polyelectrolyte causing phase separation
  - Poor yield at target thickness



- But increased thickness impacts turn-on time
  - ØThicker film
  - ØSmaller electrical field
  - ØIons slow to reach electrodes





Compatible LEP

C|D|T

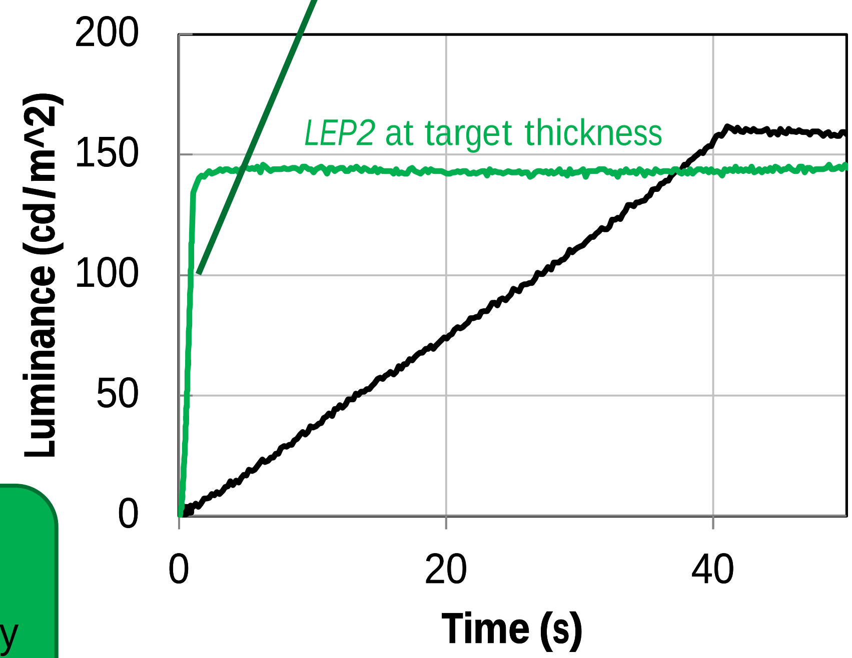
- Solving the problem by materials design
- Developing an LEP that is compatible with polyelectrolyte
  - ØReduced phase separation
  - ØSmoother films
  - ØYielding devices at target thickness

LEP1
- Standard white light-emitting LEP
- Ra roughness 55nm

Materials development

LEP2
- Modified monomer units for increased compatibility
- Ra roughness <20nm

<1s turn-on to 100cd/m²



Improvement of visual appearance

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- Increasing contrast display:
  - Improved visual appearance à **Improved user experience**
  - Operation at lower brightness   à **Better stability**
- Standard device has white background (outside of pixel area) and reflective cathode.
- High contrast device has dark background and non-reflective cathode.
  - Efficiency loss due to reduced out-coupling. But this is acceptable since device can be run at lower absolute brightness for same apparent clarity.

High brightness device
Suitable for applications where high brightness is important but contrast is less important

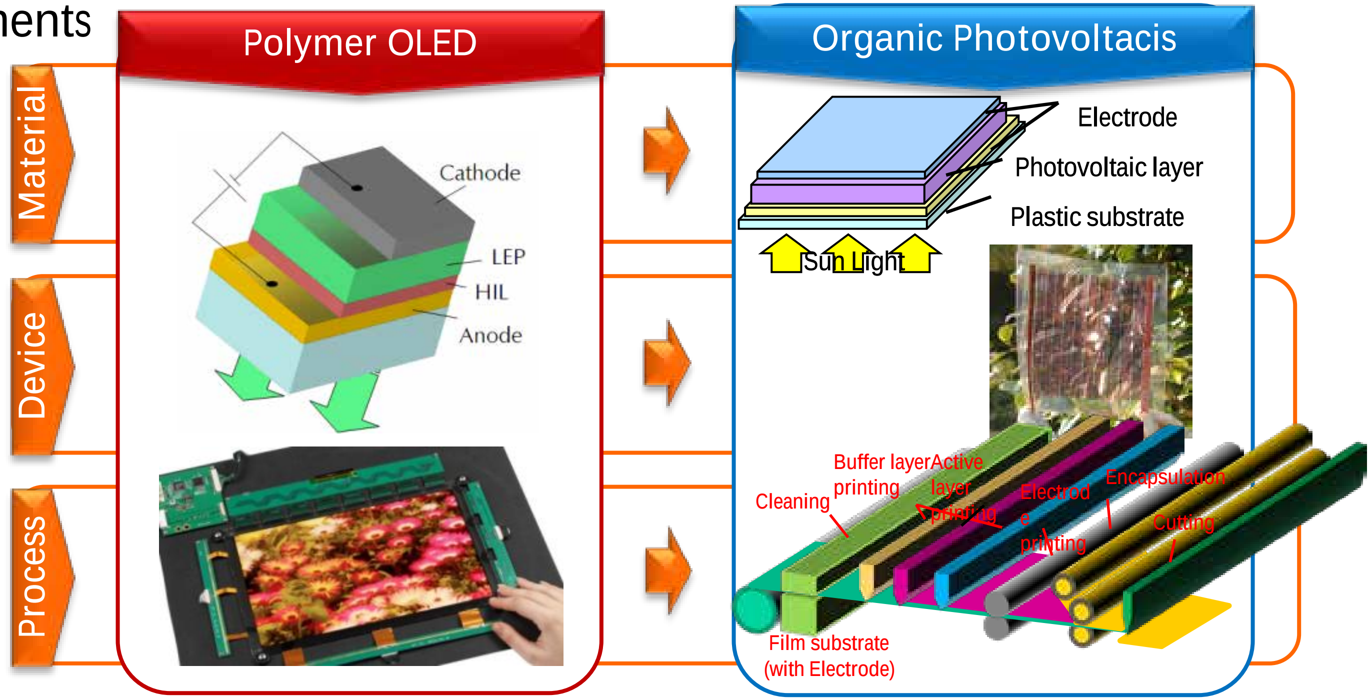
High contrast device
+ Favourable visual appearance
+ Improved stability
Additionally
Observe improved lifetime

Other Solution Processed Devices: Solar Cells

OPV Introduction

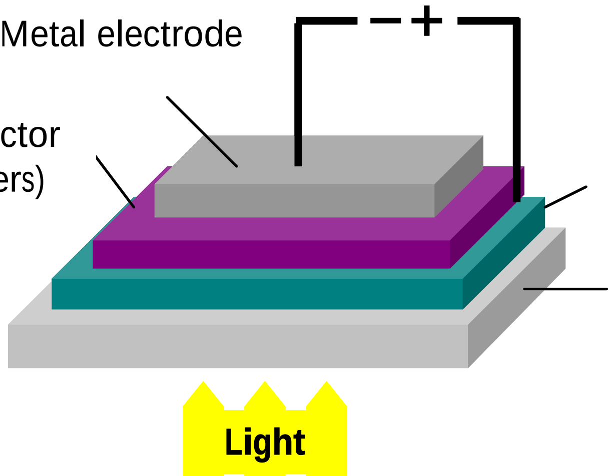
C|D|T

- OPV research started in order to develop photovoltaic materials into new business areas beyond our core P-OLED technology
- Sumitomo Chemical & CDT jointly developing high performance, solution processable photovoltaic materials for OPV
- OPV programme encompasses material & device & process platform developments

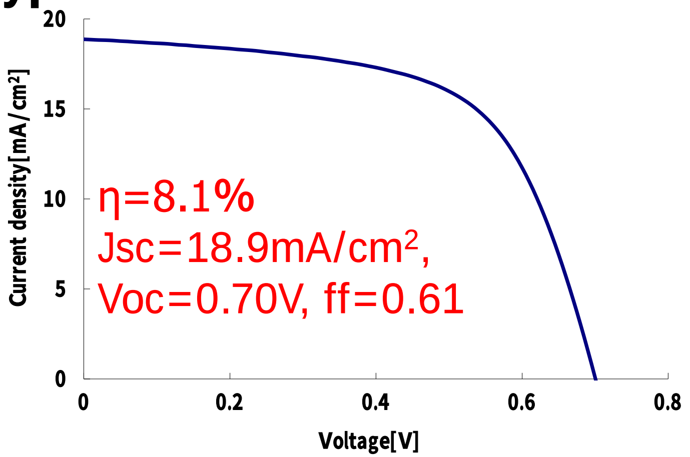


Organic photovoltaic cell activities in SCC

Basic Device structure

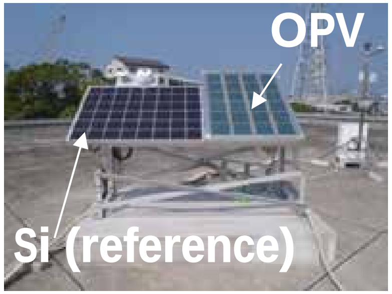


Typical I-V characteristics



200 x 200mm

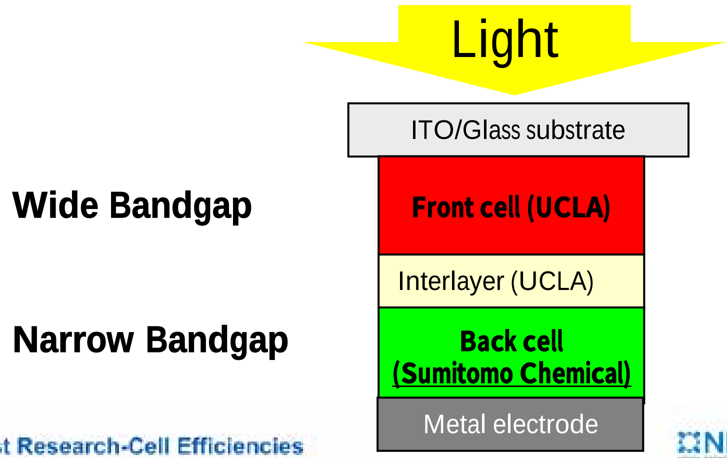
Flexible type



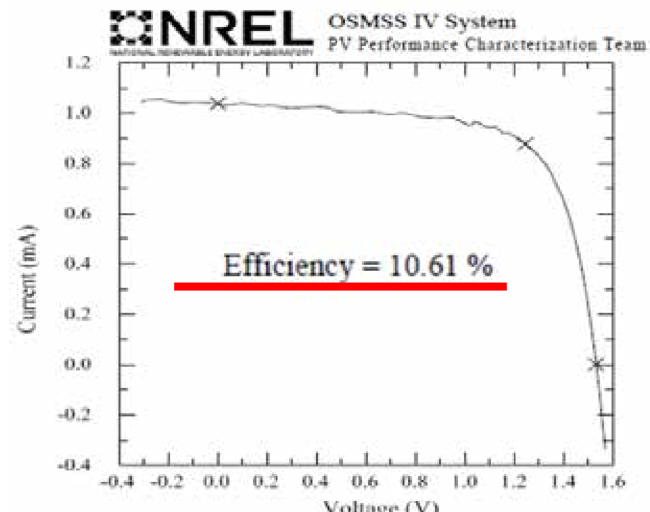
Field test

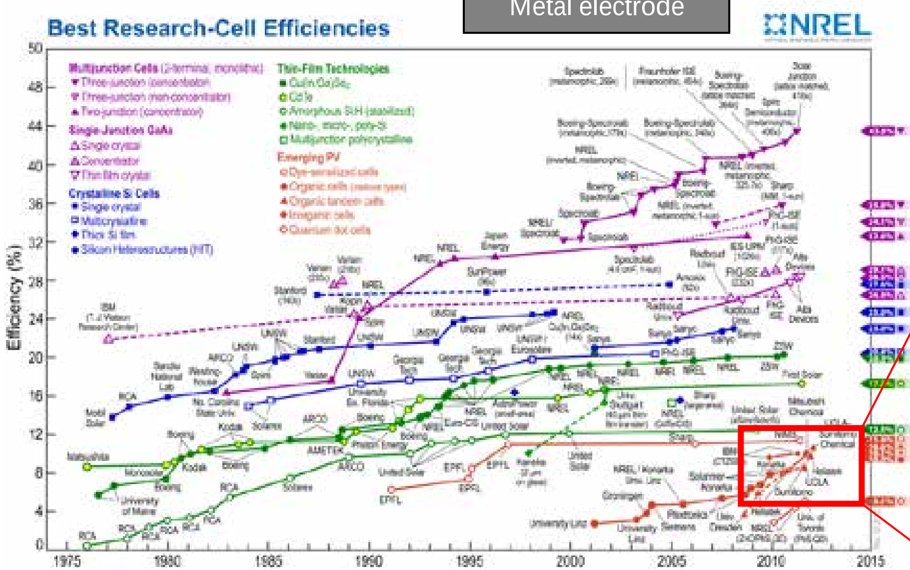
Tandem Polymer Solar Cell

CDT

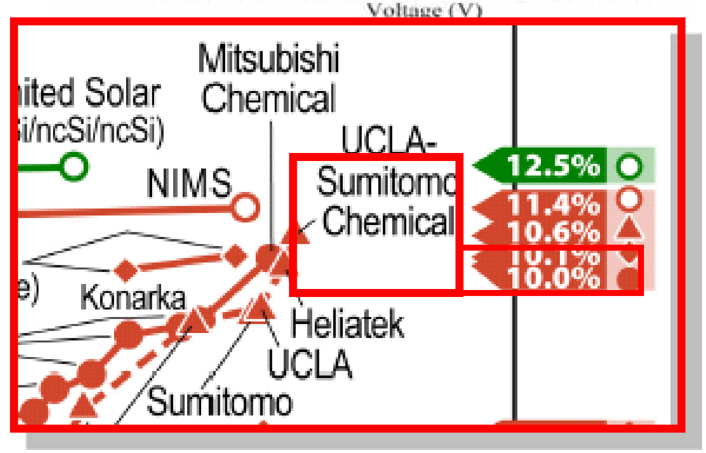


Collaboration with UCLA)





http://www.nrel.gov/ncpv/images/efficiency_chart.jpg



Summary

Organic Electronics

C|D|T

- Chemists and Physicists required to work together in order to understand the fundamentals of device operation.
- Detailed knowledge of the impact of material design and synthesis required to maximise the intrinsic material performance
  - Purification to levels not normally required in order to achieve application requirements
- Device operation is the only way to measure the material performance
  - Device degradation understanding allows new materials development
- Analytical procedures require continual improvement
  - Impurities and defects < ppm levels required!