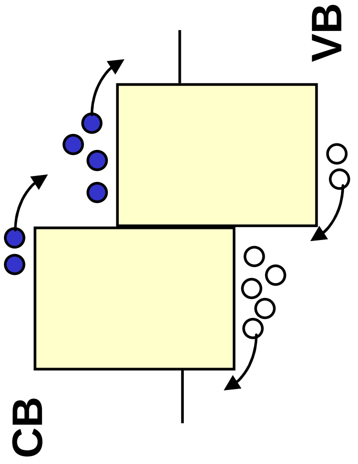
Photovoltaics and Photodetectors - part II

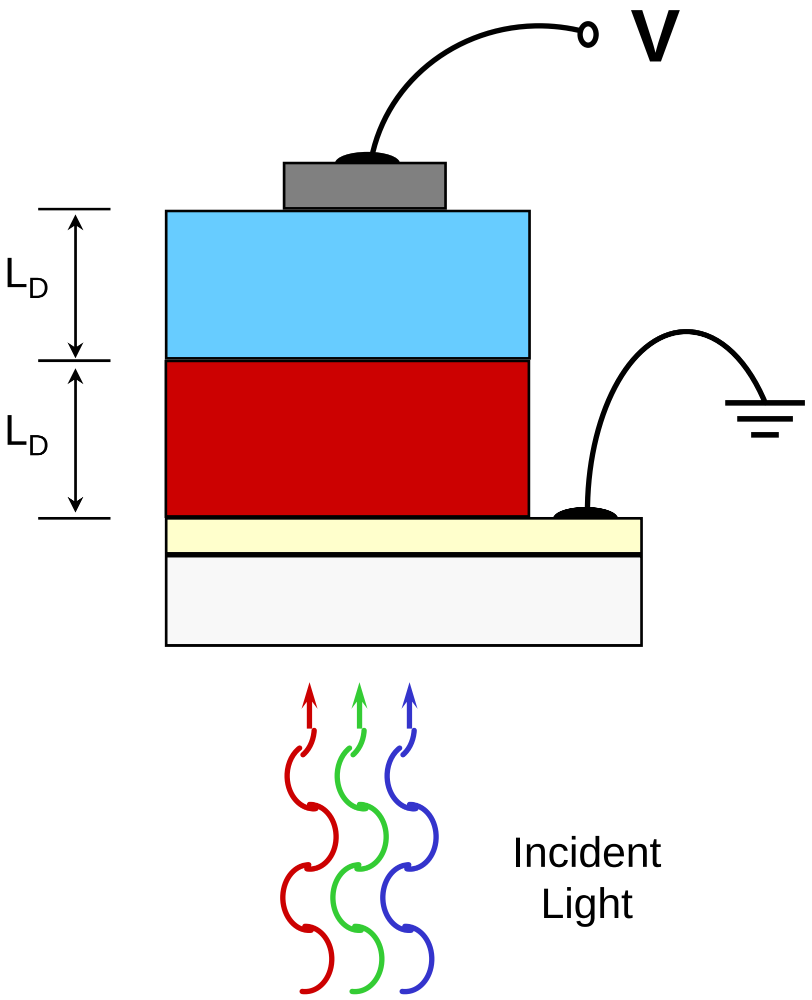
- Organic Heterojunction Photovoltaic Cell
- Organic Multilayer Photodetector

Data on Solar Cells and Photodetectors taken from

Peumans, Bulovic, and Forrest.,
Appl. Phys. Lett. 76, 2650 (2000) – solar cell
Appl. Phys. Lett. 76, 3855 (2000) - photodetector

Organic Heterojunction PVs





Photovoltaics

Optical power ⇒ electrical power

FIGURES OF MERRIT:

Power conversion efficiency
Full solar intensities
Reliability

Photodetectors

Consume power to detect a signal

FIGURES OF MERRIT:

High external quantum efficiency
High bandwidth
Low noise, low power consumption

Solid state organic solar cells

- high absorbtion in the visible spectrum
- have **relaxed deposition requirements**

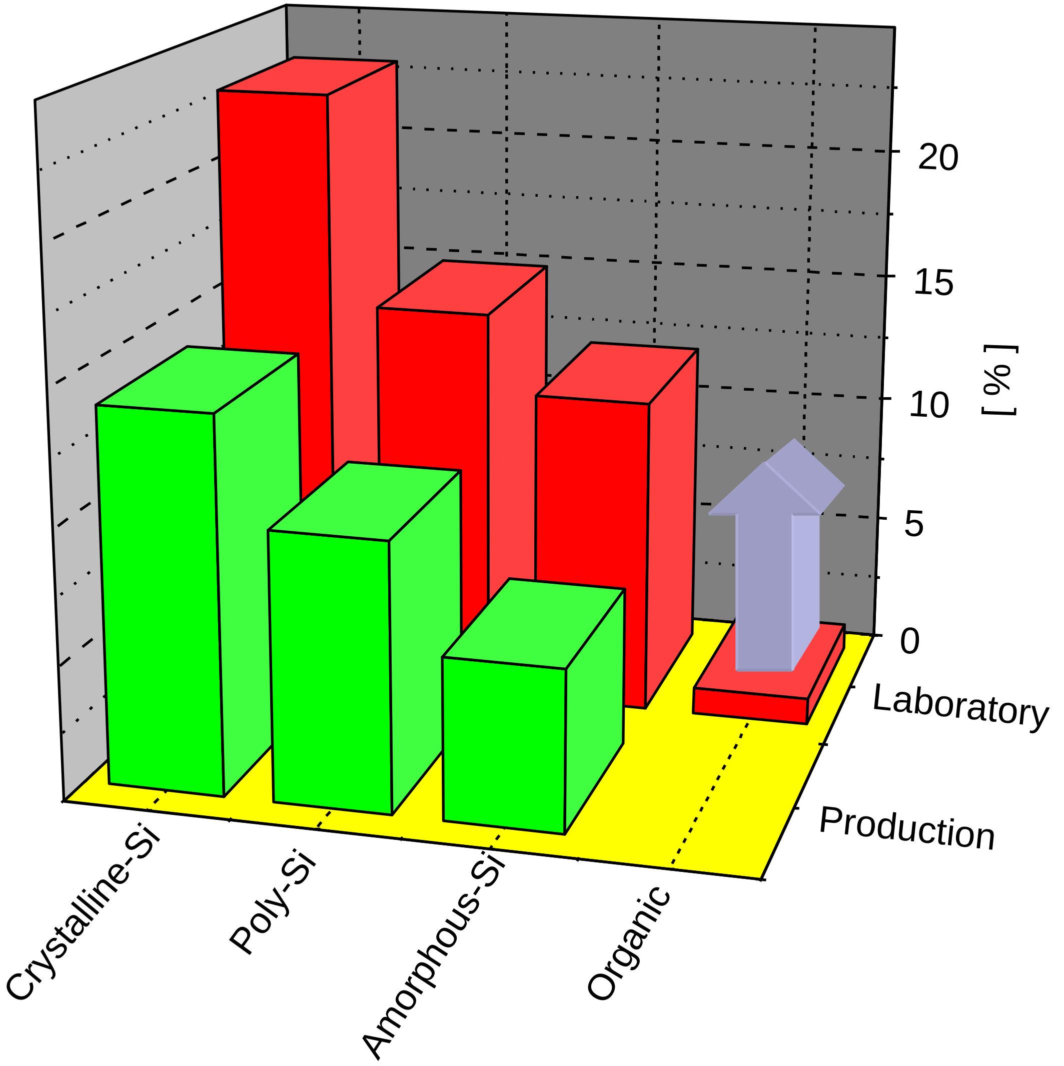
⇩

- can be manufactured in a **low cost** process
  (roll-to-roll, web-processing, etc.)
- can be grown on thin, flexible substrates → **light weight**
- can **add value** to existing products (window coatings, etc.)

CHALLENGE!

Current power conversion **efficiencies are too low** for commercial implementation (especially at full solar intensities)

Solar Cell Power Efficiency



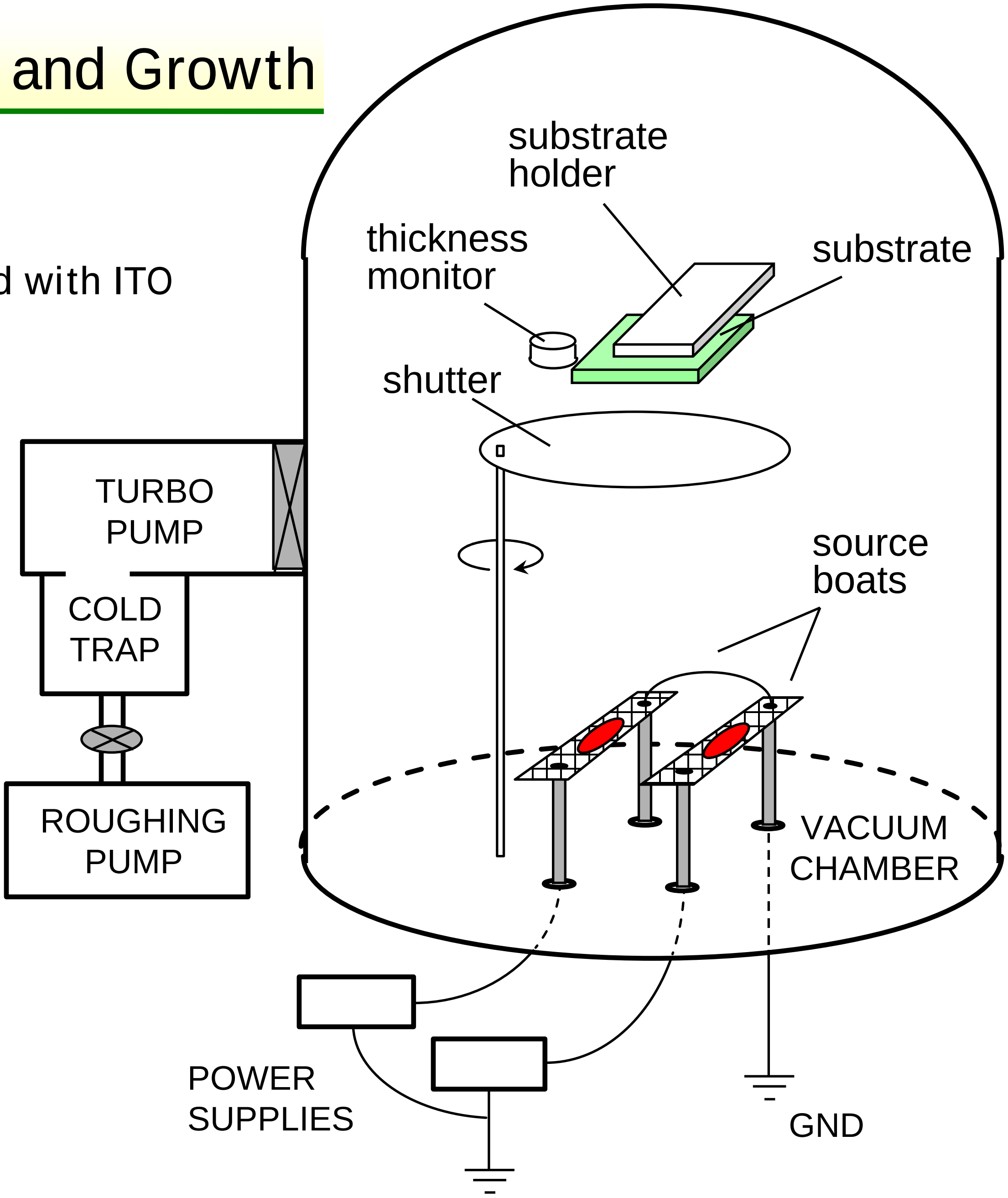
Device Preparation and Growth

- Glass substrates precoated with ITO
  - 94% transparent
  - 15 Ω/square

- Precleaning
  Tergitol, TCE
  Acetone, 2-Propanol

- Growth
  - 5 x 10^{-7} Torr
  - Room T

  - 20 to 2000 Å
    layer thickness



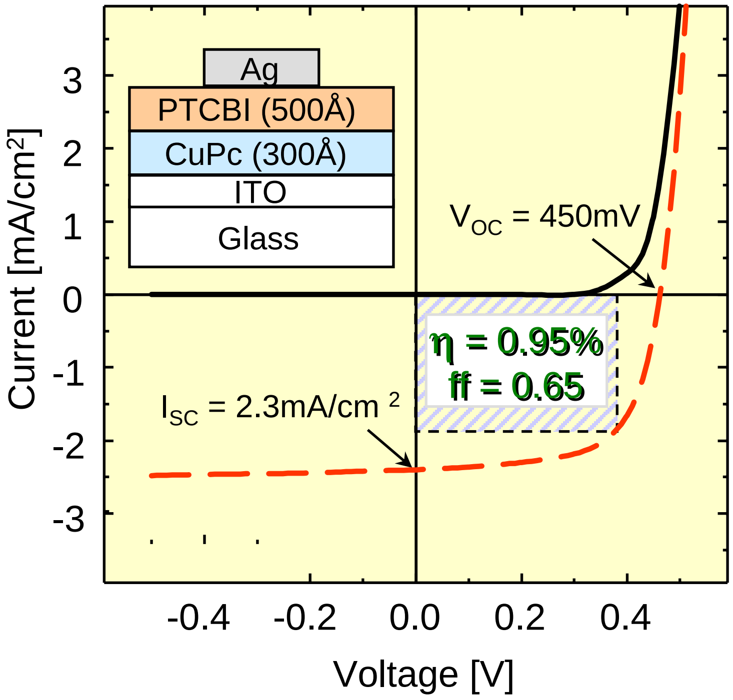
History and Progress

‘86: Heterojunction Solar Cell

C.W. Tang

- first **heterojunction** for efficient charge generation
- ~**0.95%** conversion efficiency
- nearly ideal IVs (FF~0.65)
- under **full solar illumination** (1 sun)

Tang, *Appl Phys Lett.* **48**, 183 (1986).



‘90s: Polymer Networks

➡ G. Yu *et al.*, Science **270**, 1789 (1995).

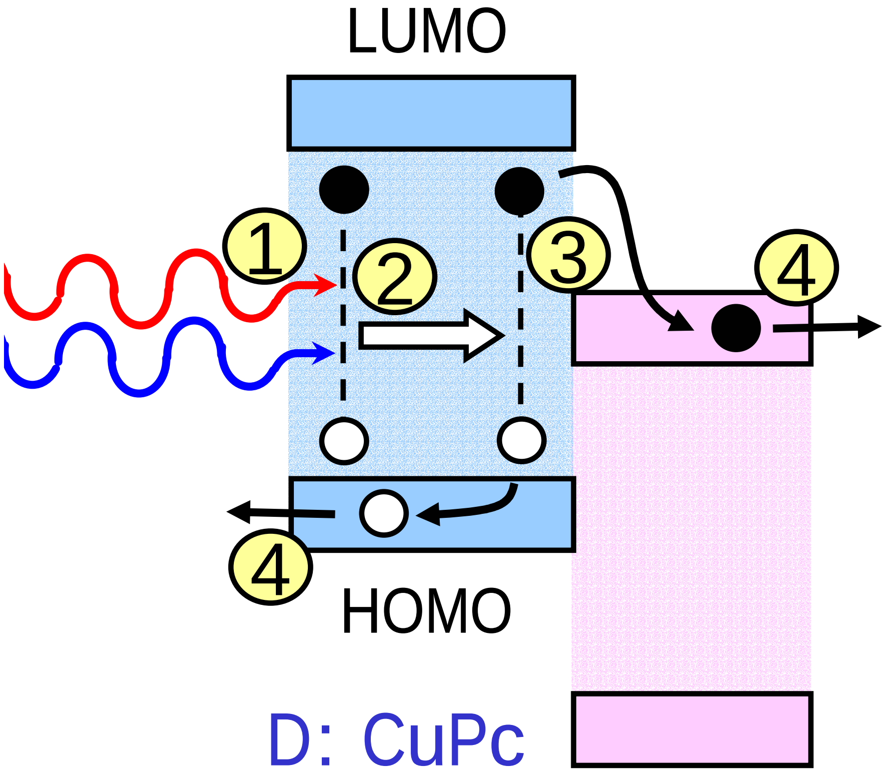
- series resistance problem (low FF)
- calculated power conversion efficiency of ~1.5%
- not well matched to solar spectrum

➡ Shaheen *et al.* , Appl. Phys. Lett. **78**, 841 (2001).

- power conversion efficiency ~2.5%
- not well matched to solar spectrum
- long term stability ?

Photoinduced Charge-Transfer

Processes occuring at a Donor-Acceptor heterojunction



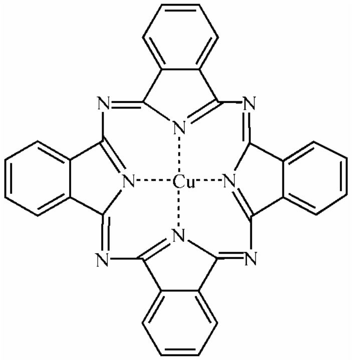
① Exciton generation by absorption of light

② Exciton diffusion over ~L_D

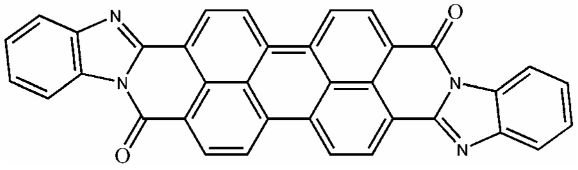
③ Exciton dissociation by rapid and efficient charge transfer

④ Charge extraction by the internal electric field

D: CuPc

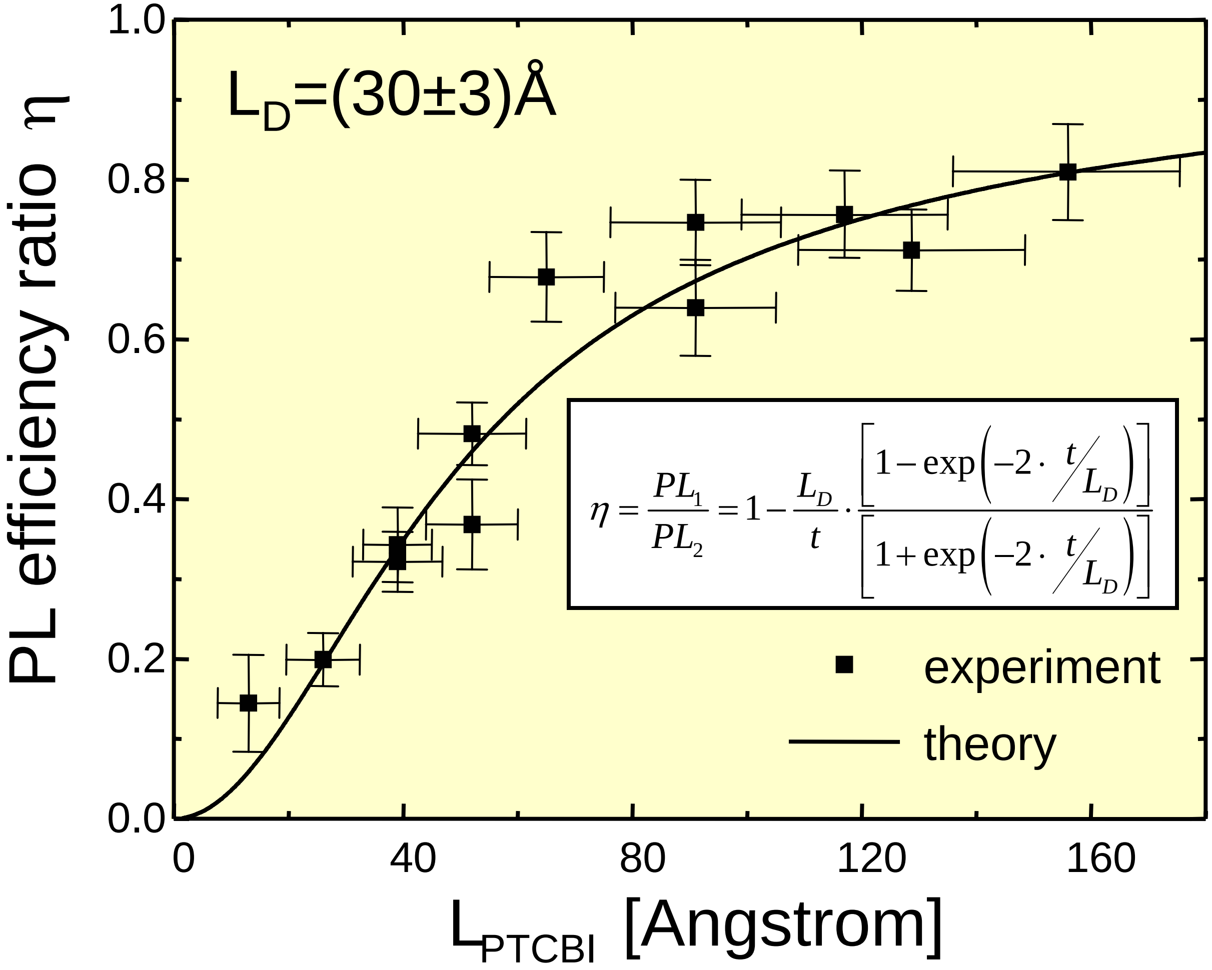


A: PTCBI

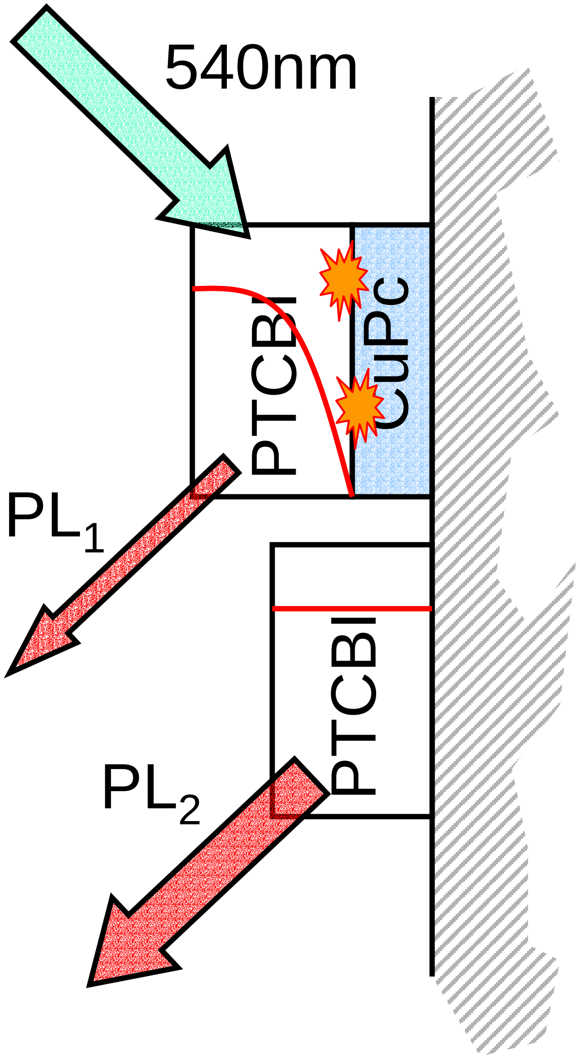


Exciton Diffusion: Experiment and Theory

- Photoluminescence (PL) probes the exciton lifetime
- Exciton lifetime depends on proximity of donor-acceptor interface

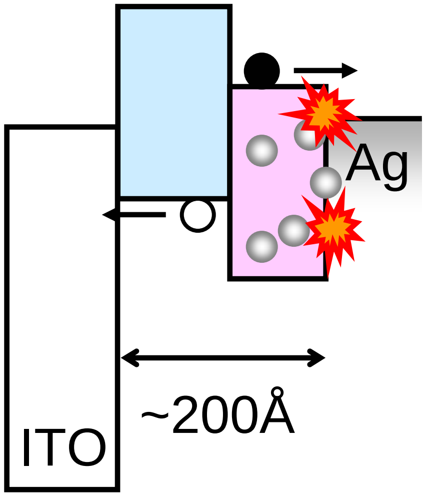


$$\eta=\frac{PL_1}{PL_2}=1-\frac{L_D}{t}\cdot\frac{\left[1-\exp\left(-2\cdot {}^{t}\!/_{L_D}\right)\right]}{\left[1+\exp\left(-2\cdot {}^{t}\!/_{L_D}\right)\right]}$$



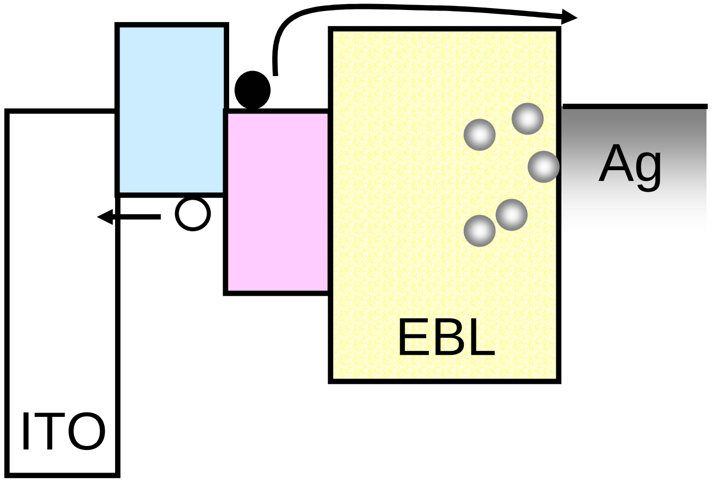
Double Heterojunction

Problem



- ● •cathode metal diffusion
- ✸ •deposition damage
- ✸ •exciton-plasmon interaction
- •vanishing optical field
- •electrical shorts

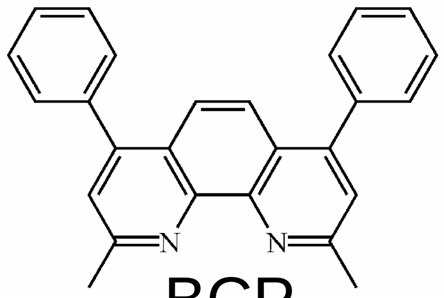
Solution



Introduce ‘Exciton Blocking Layer’ (EBL) to:

- •confine excitons to active region
- •act as a damage-absorber

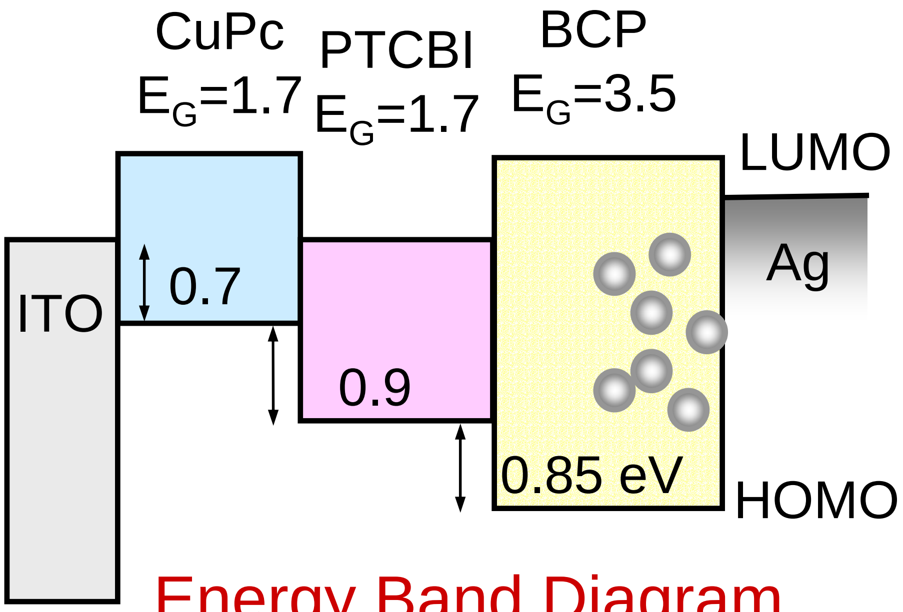
Exciton Blocking Layer (EBL)



BCP

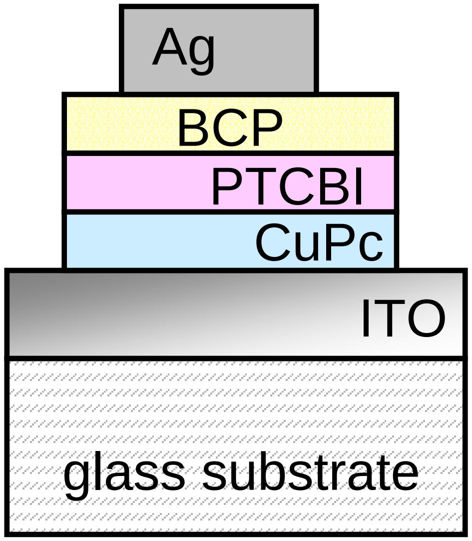
(2, 9-dimethyl, 4, 7-diphenyl, 1, 10-phenanthroline)
(aka bathocuproine)

- conducts electrons
- transparent
- effectively blocks excitons
- absorbs damage
- separates active layers from metal

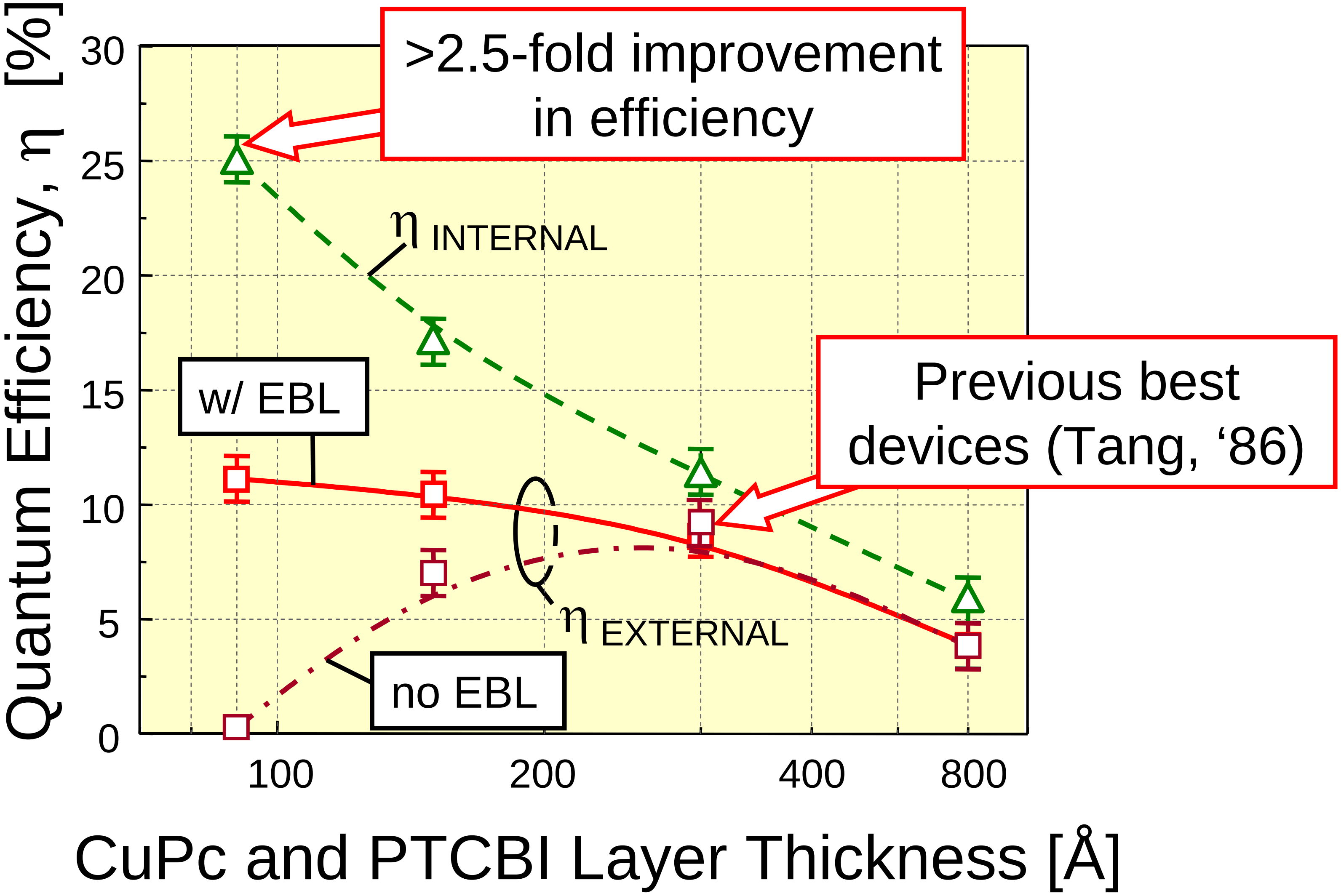


Energy Band Diagram

courtesy of I. Hill & A. Kahn



Exciton Blocking Layer (EBL) Improves Thin Cell Efficiency

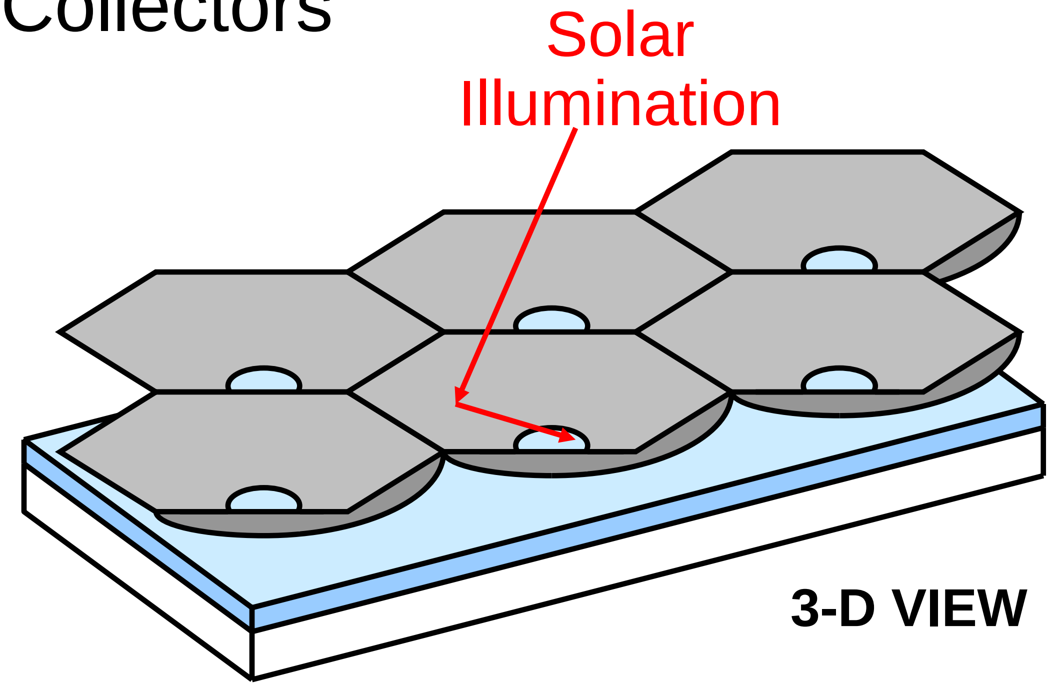


>2.5-fold improvement in efficiency

Previous best devices (Tang, '86)

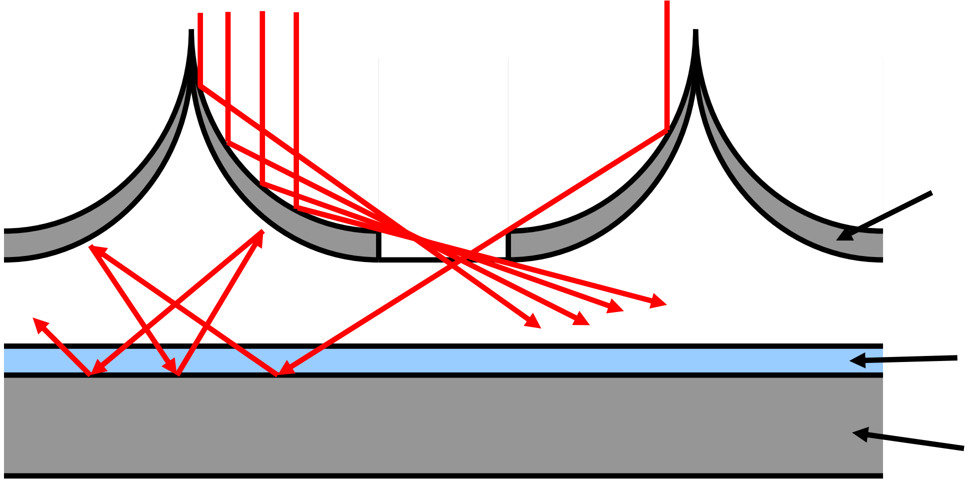
Practical Realization:

MicroMolded Winston Collectors



3-D VIEW

CROSS SECTION

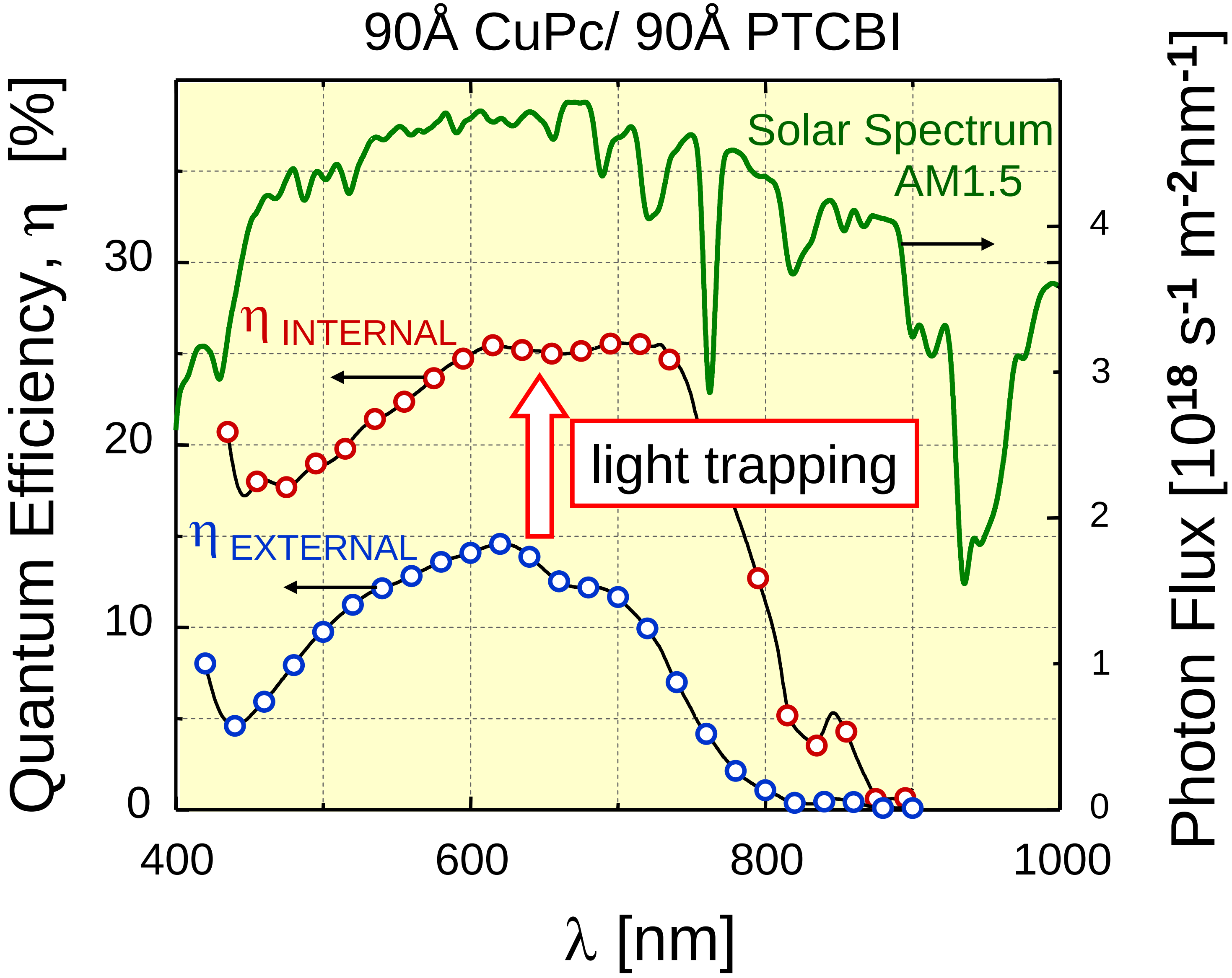


molded substrate
with collector profiles
and coated with Ag

organics + ITO (anode)

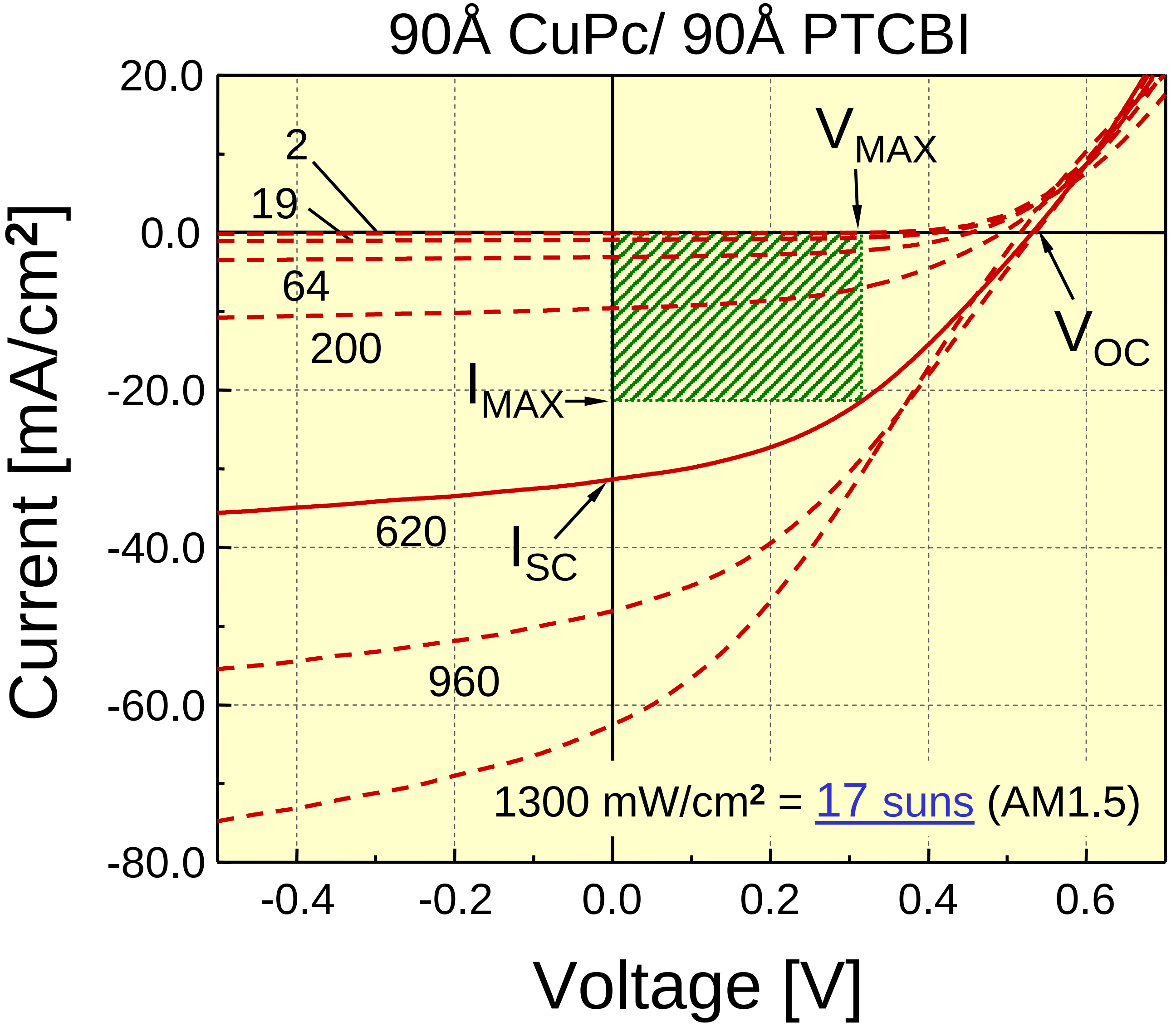
Ag mirror / cathode

Broad Spectral Response Matches Solar Spectrum

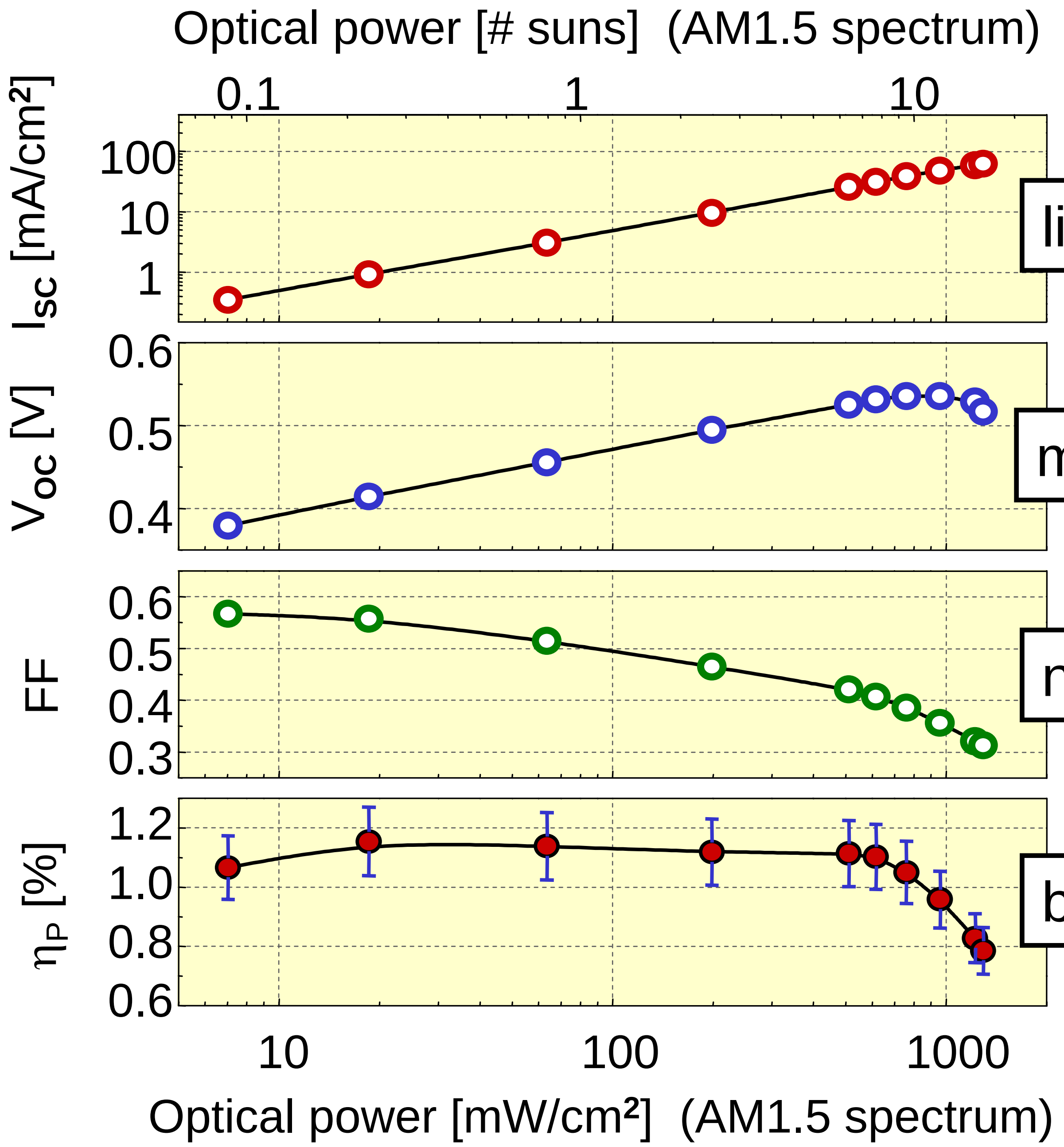


I-V Response under Solar Illumination

- Highest illumination levels to date
- Record-high short circuit currents



I-V Response under Varying Solar Illumination Intensity



linear

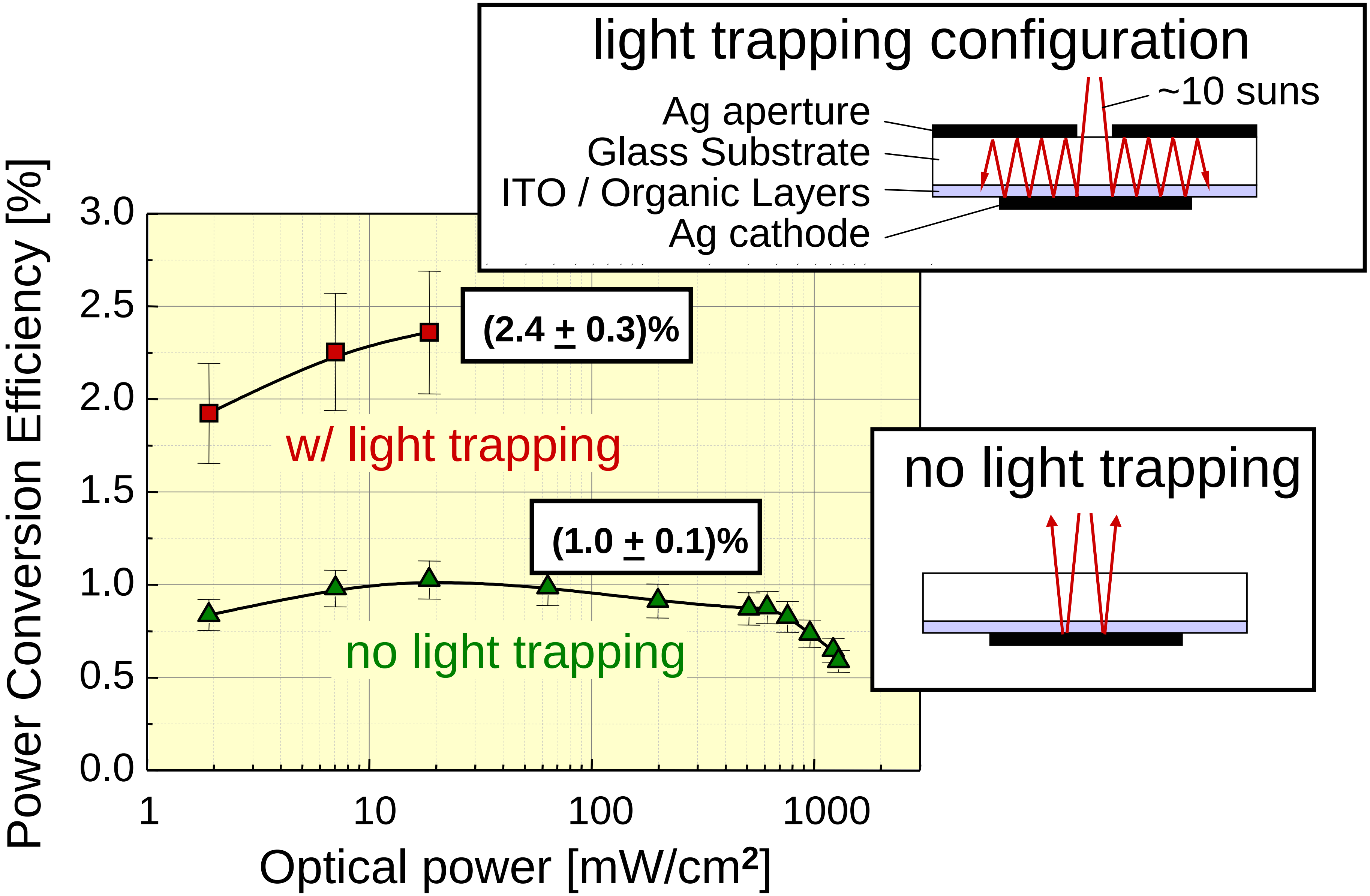
monotonic increase

no drastic decrease

broad plateau

Light Trapping Improves PV Efficiency ~2.5 Fold

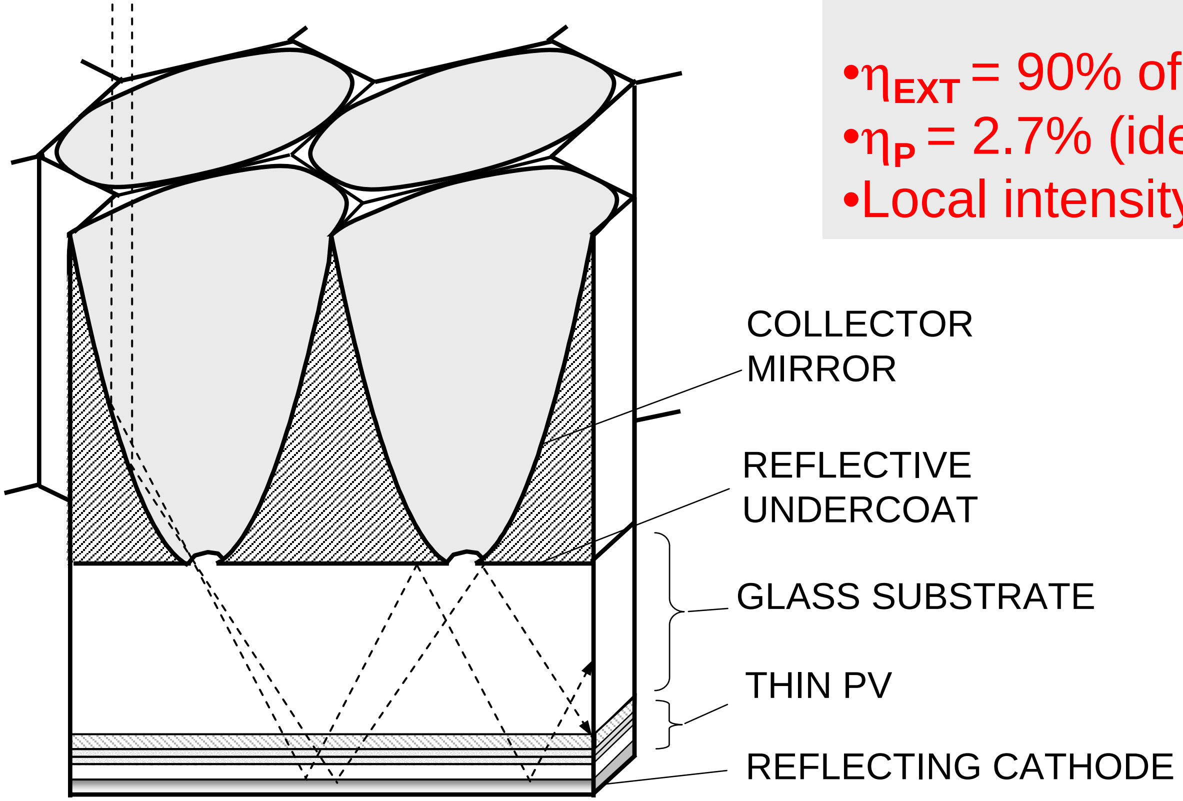
60Å CuPc/ 60Å PTCBI



Practical Realization:
MicroMolded Winston Collectors

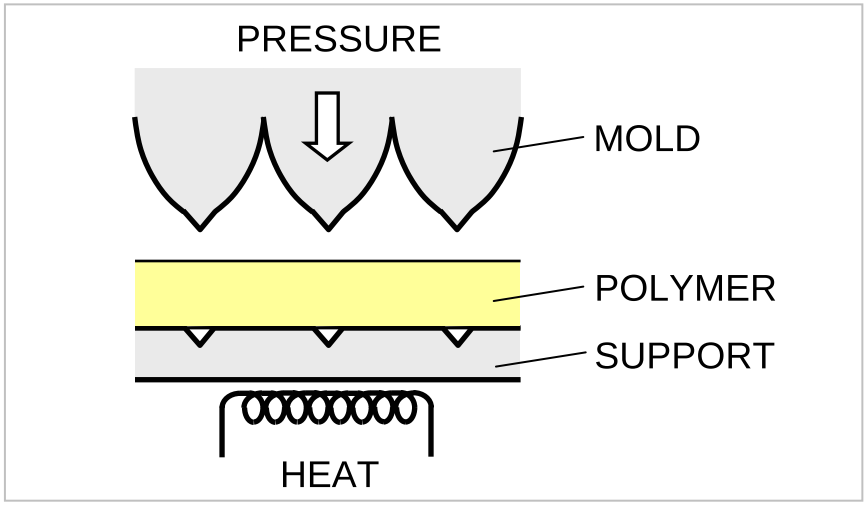
- Raytracing calculations
- Microcavity effects ignored
- 1D geometry
- Mirror/cathode reflectivity: 95%
- Cell absorption: 30%

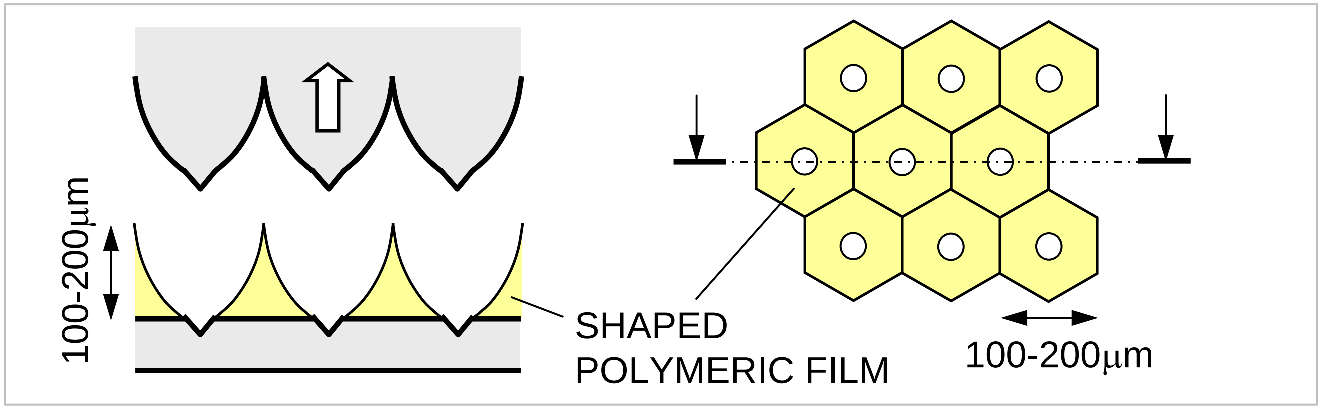
- η_{EXT} = 90% of η_{INT}
- η_{P} = 2.7% (ideal = 3.0%)
- Local intensity never exceeds 3 suns



Peumans et al, US Patents #6440, 769, Aug 27, 2002

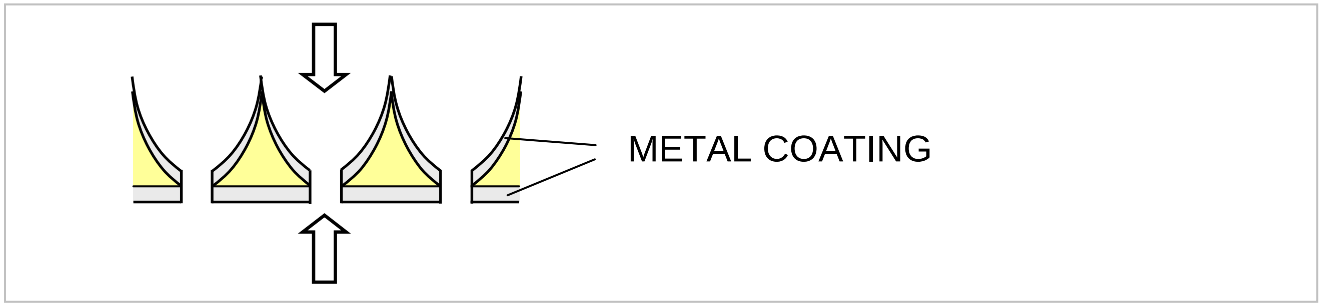
Collector Fabrication



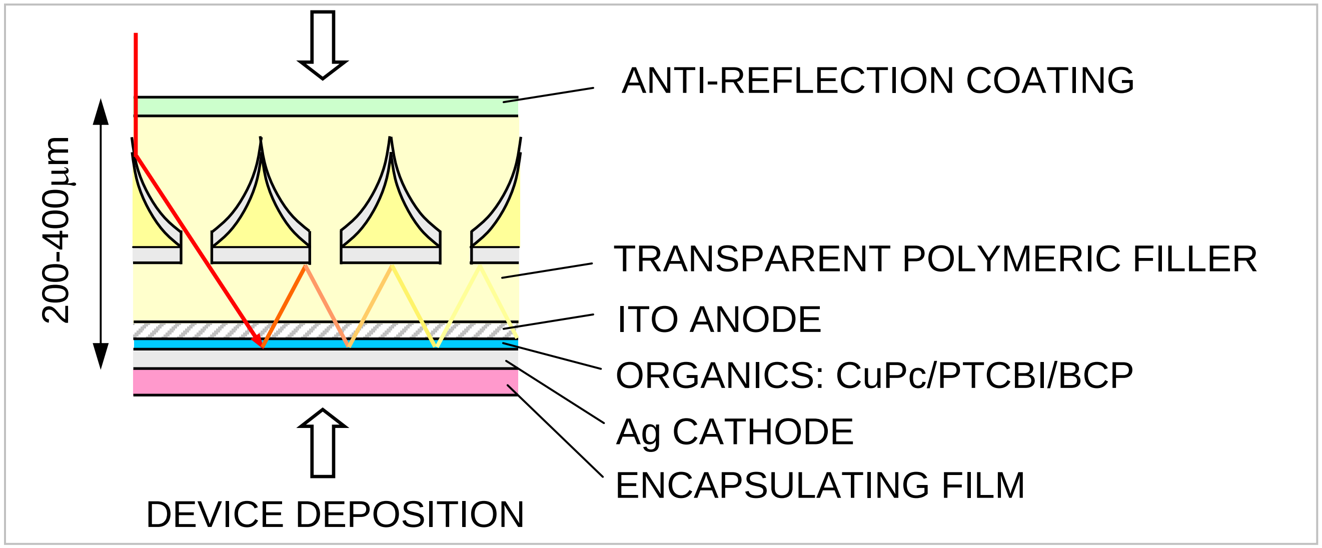


Peumans et al, US Patents #6440, 769, Aug 27, 2002

Collector Fabrication



METAL COATING



200-400μm

ANTI-REFLECTION COATING

TRANSPARENT POLYMERIC FILLER

ITO ANODE

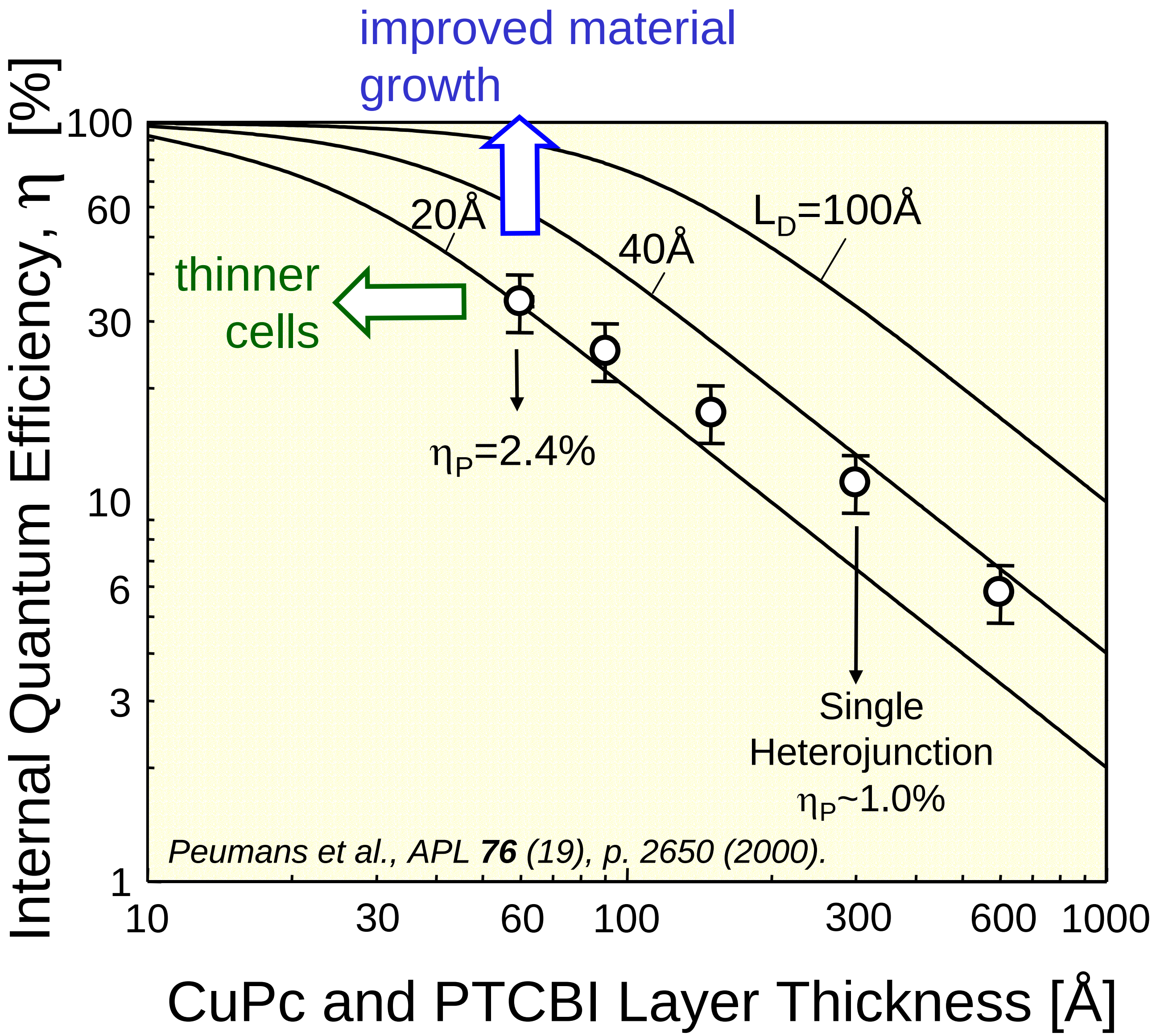
ORGANICS: CuPc/PTCBI/BCP

Ag CATHODE

ENCAPSULATING FILM

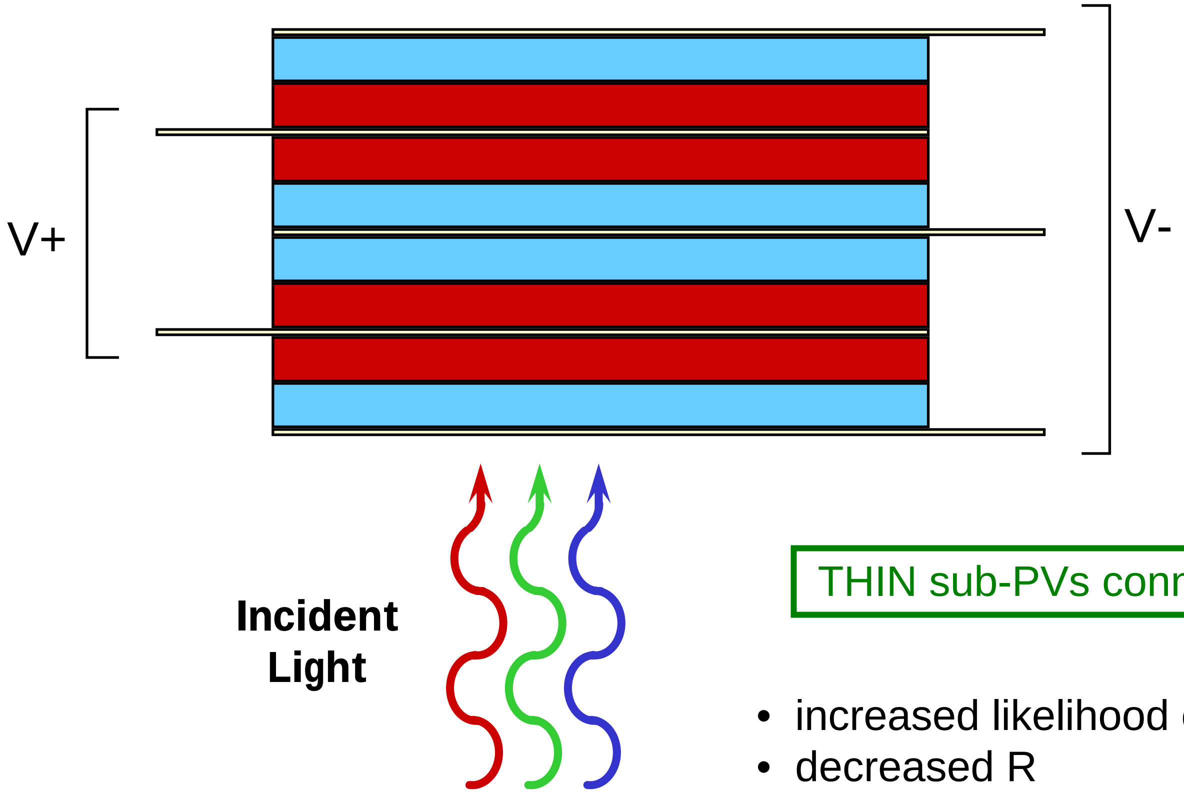
DEVICE DEPOSITION

Outlook – towards future PVs



Peumans et al., APL ***76*** *(19), p. 2650 (2000).*

Multilayer Organic PV

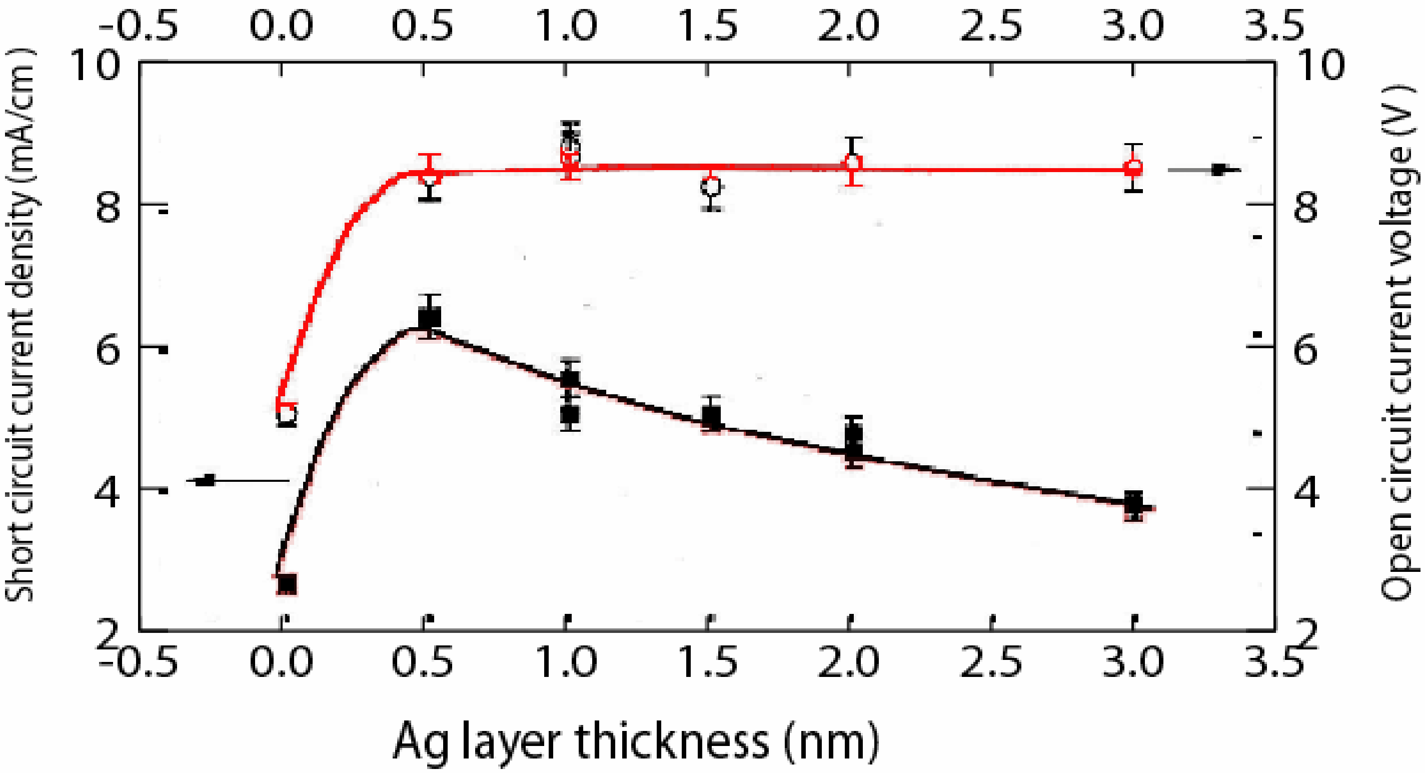


THIN sub-PVs connected in PARALLEL

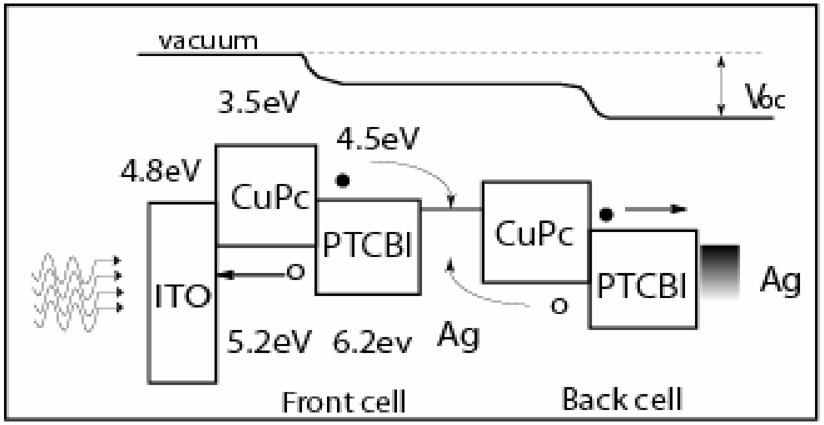
- increased likelihood of exciton dissociation
- decreased R

- I_{sc} of all sub-PVs add while V_{OC} ~constant

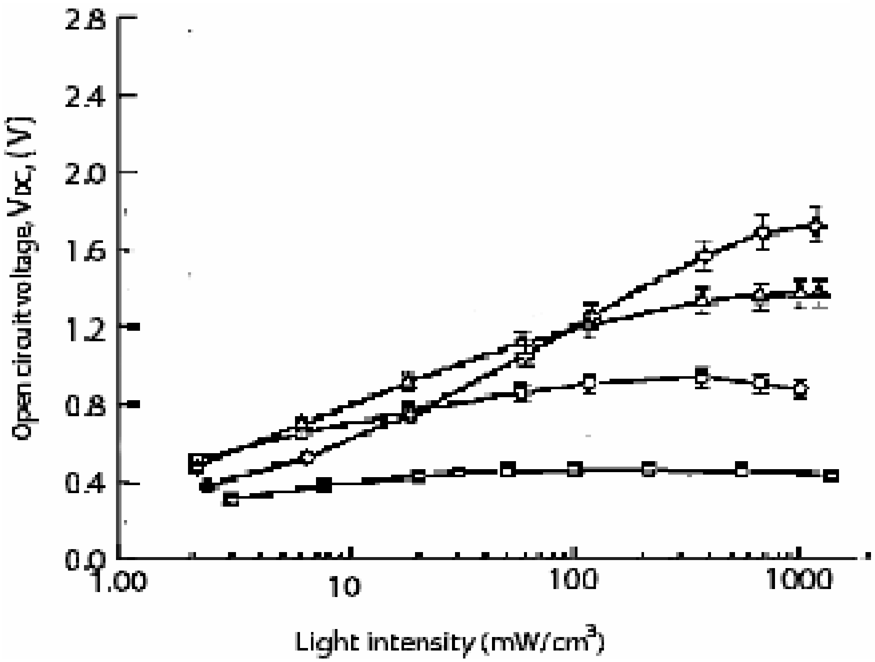
Bulović and Forrest, patents: US 6,198,091 (2001); US 6,198,092 (2001); US 6,278,055 (2001) .

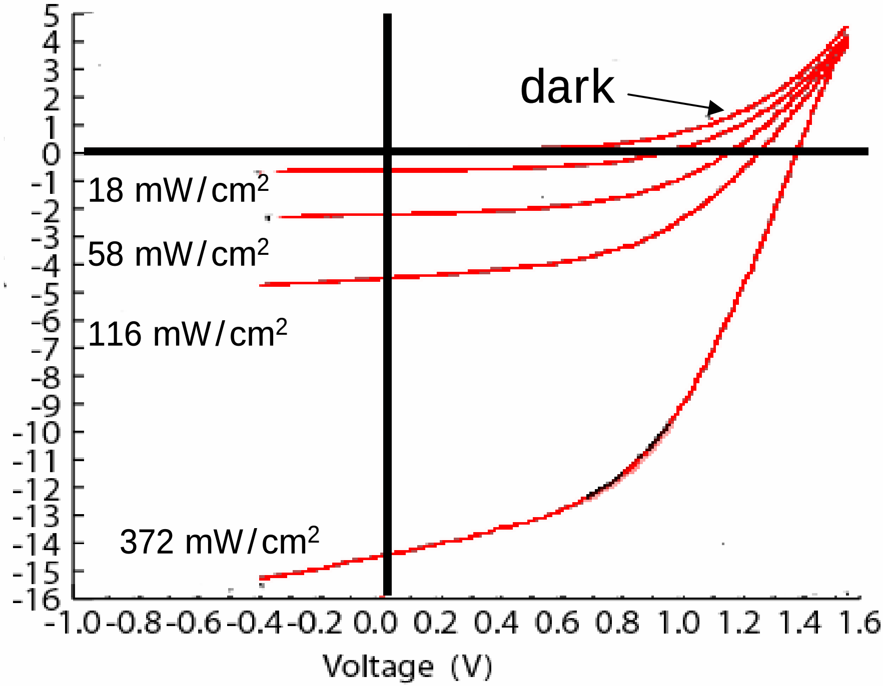


Short circuit current density (closed squares, left axis) and open circles, right axis) for dual cells having Ag interlayers of different average thickness. The measurements were performed under AM 1.5, 100mW/cm2 (1 sun) illumination. Also shown is the proposed energy level diagram of the dual-HJ device.



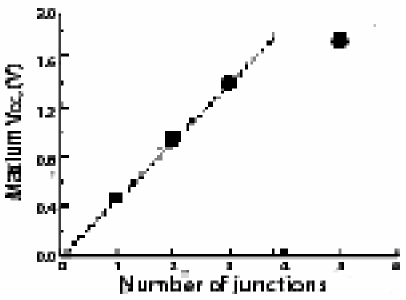
Adapted from *A. Yakimov and S. R. Forrest, Appl. Phys. Lett., 80, 1667 (2002).*





Open circuit voltage dependence on the incident light intensity for single (squares), dual (circles), triple (triangles), and fivefold (diamonds) HJ photovoltaic cells. The inset shows the maximum open circuit voltage achievable vs. the number of heterojunctions in the stacked devices.

Current density-voltage characteristics of a triple-H cell at different incident light intensities with an AM 1.5 solar spectrum. Here ~100 mW/cm^2 correspond to 1 sun intensity.



Power efficiencies (η_P) and open circuit voltages (V_{OC}) under AM 1.5 illumination:

Single HJ cell	$\eta_P = 1.1 \pm 0.1\%$	$V_{OC} = 0.43$ V
Double HJ cell	$\eta_P = 2.5 \pm 0.1\%$	$V_{OC} = 0.93$ V
Triple HJ cell	$\eta_P = 2.3 \pm 0.1\%$	$V_{OC} = 1.2$ V

A. Yakimov and S. R. Forrest, Appl. Phys. Lett., 80, 1667 (2002).

Photodetectors - Motivation

Applications

Molecular Organic Photonic Integrated Circuits (MOPICs) - Organic LEDs, transistors, photovoltaic cells demonstrated. There is a need for efficient, high-bandwidth photodetectors.

Large Area Photodetection - Solid-state scanner, solid-state X-Ray plate (in conjunction with scinitillator downconverter), very large area imaging arrays, etc.

Photodetectors on any Substrate - Organic photodetectors can be deposited on a variety of substrates, including low-cost, flexible foil.

Physics

Exciton Dynamics in Organic (Ultra)Thin Films - Organic donor-acceptor multilayers as probes for exciton dynamics.

Carrier Dynamics in Organic Heterostructures - Information about carrier transport across heterojunction barriers.

Organic PDs: Status

Yu et al.,

Synth. Metal **102** (1-3) 904 (1999), Science **270** 1789 (1995)

- operates over visible + near UV
- η_{EXT}=45% @ -10V, $I_{DARK}=1\times10^{-8}$A/cm^2 @ -5V
- functional 1D array
- response time?

Halls et al.,

Nature **395** 6699 (1998)

- operates over visible + near UV
- η_{EXT}=58%, I_{DARK}=? (RR=10^3) @ -2V
- response time?

- **Polymeric**
- $\mu\sim10^{-6}$-10^{-3}cm^2/Vs
- τ_{TR}>50ns

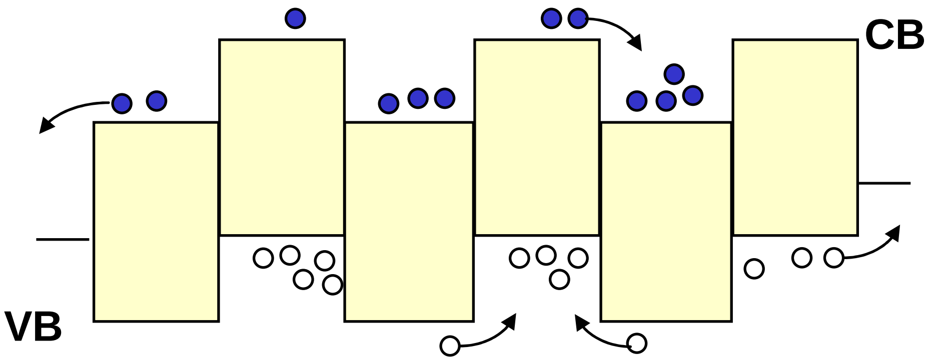
So et al.,

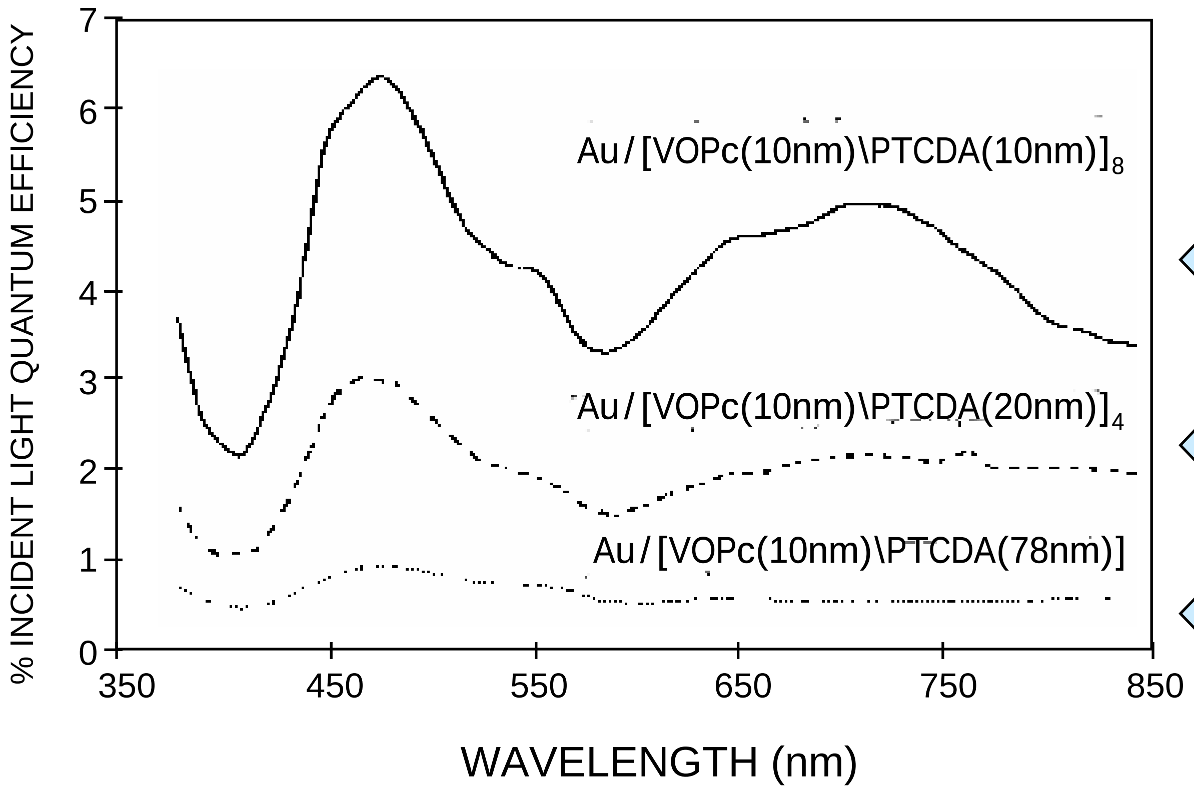
IEEE TED **36** (1) 66 (1989)

- PTCDA, CuPc, ... on Si
- 500MHz possible for t<500Å

- **Crystalline layers**
- $\mu\sim$1cm^2/Vs
- $\tau_{TR}\sim$1ns

VOPc/PTCDA Multilayers





# of interfaces

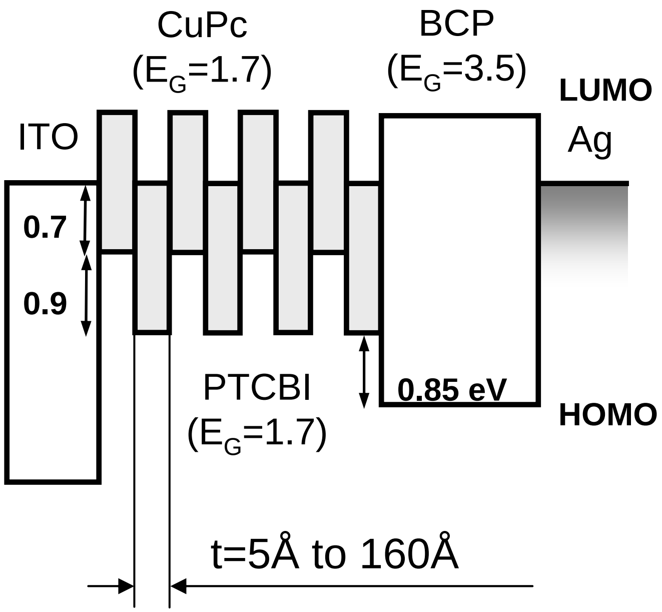
15

7

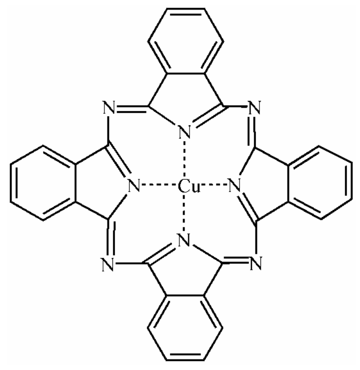
1

Adapted from: Arbour, et al., *Mol. Cryst. Liq. Cryst. 183, 307 (1990).*

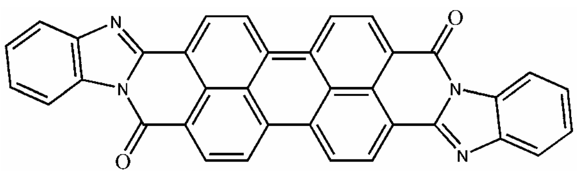
Donor-Acceptor **Multilayer** Structure



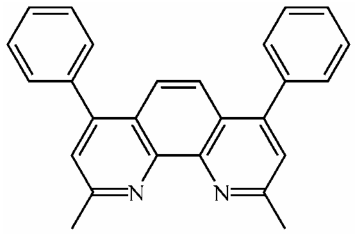
- **Growth**:
- Anode=ITO (ρ_{sheet}~40Ω/□)
- Growth: UHV (p_{base}~1×10^{-10}Torr)
- 320Å thick multilayer (2×160Å to 64×5Å) or codeposited (mixed) layer.
- ~300Å BCP cap
- Cathode=Ag (p_{base}~1×10^{-6}Torr)



CuPc
copper phthalocyanine



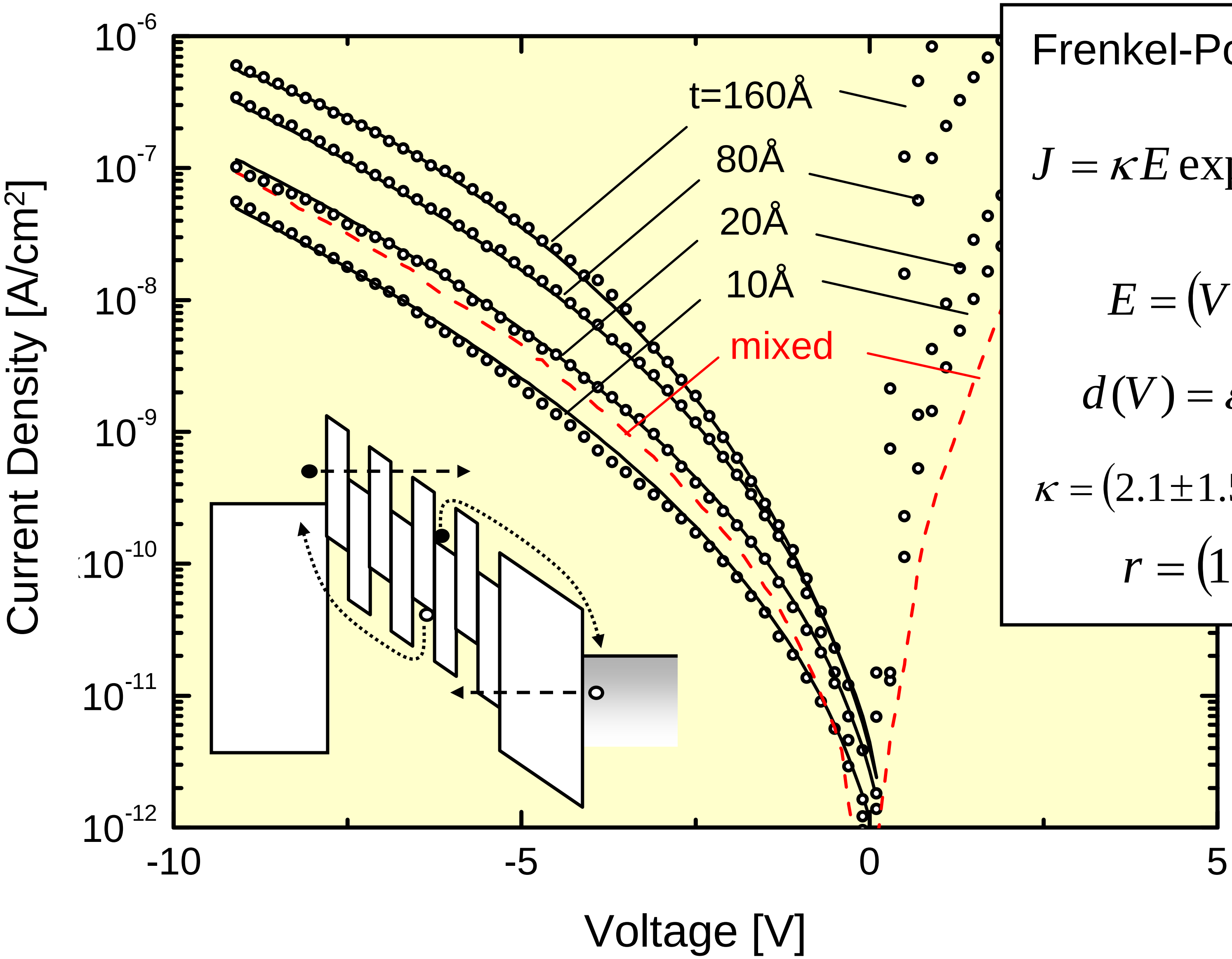
PTCBI
3,4,9,10-perylenetetracarboxylic bis-benzimidazole



BCP
bathocuproine

Dark Current

Dark current shows Frenkel-Poole dependence.



Frenkel-Poole Emission

$$J = \kappa E \exp\left(\frac{q}{rkT} \sqrt{\frac{qE}{\pi \varepsilon_i}} \right)$$

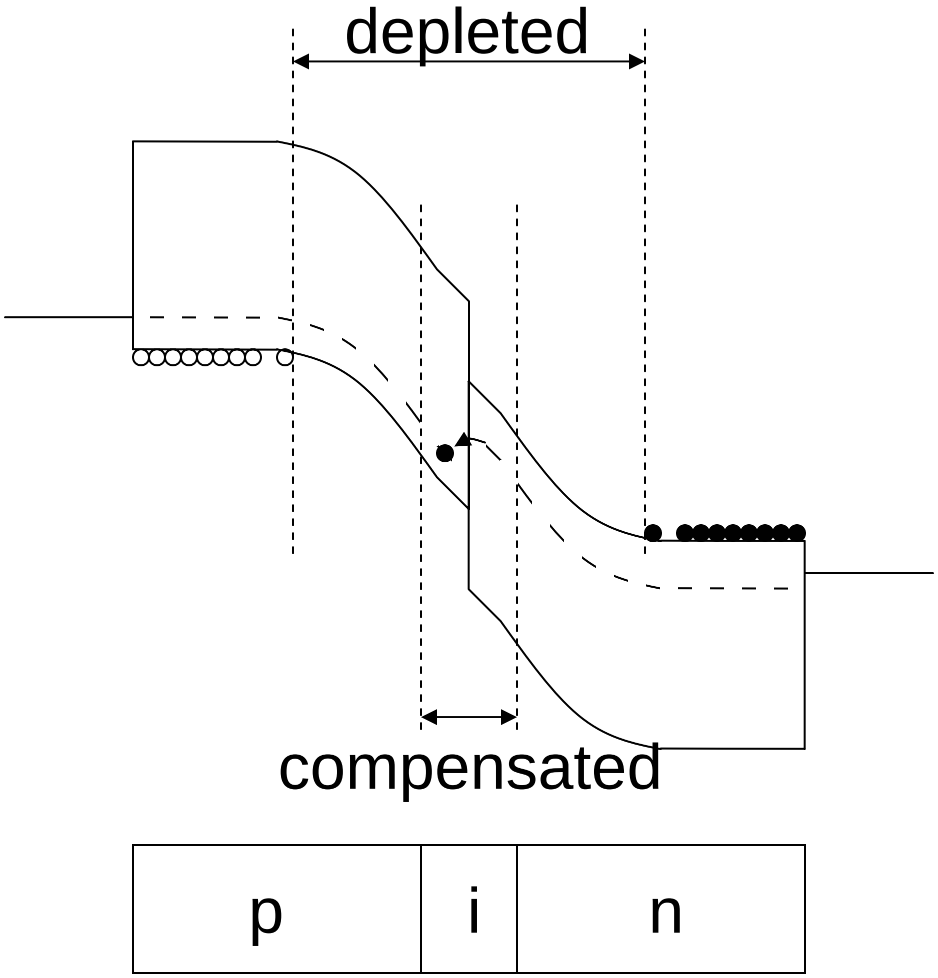
$$E = \left(V - V_{bi}\right)/d$$

$$d(V) = \varepsilon_i A / C(V)$$

$$\kappa = \left(2.1 \pm 1.5\right) \times 10^{18}\, A/Vcm$$

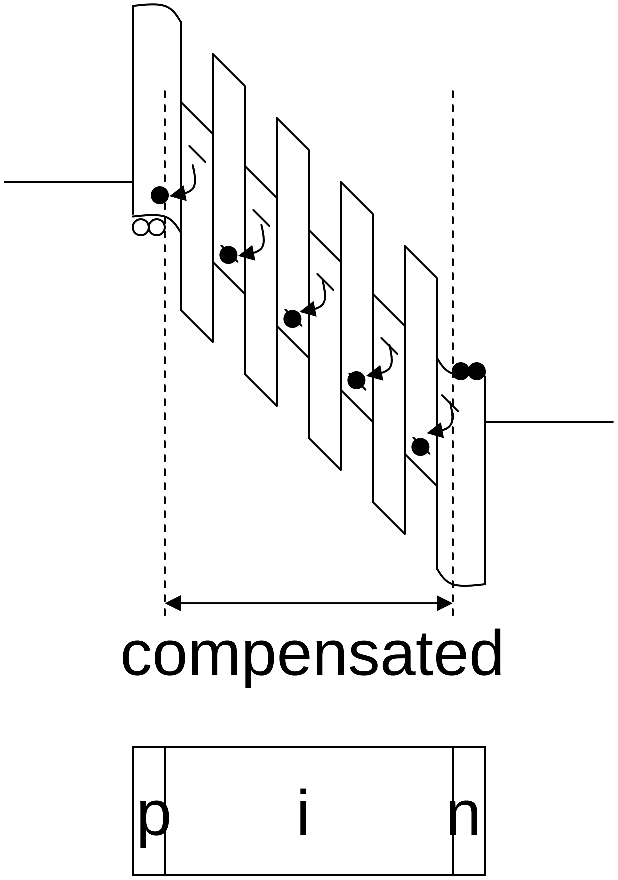
$$r = \left(1.8 \pm 0.1\right)$$

Electrical Characteristics



= p-n junction diode

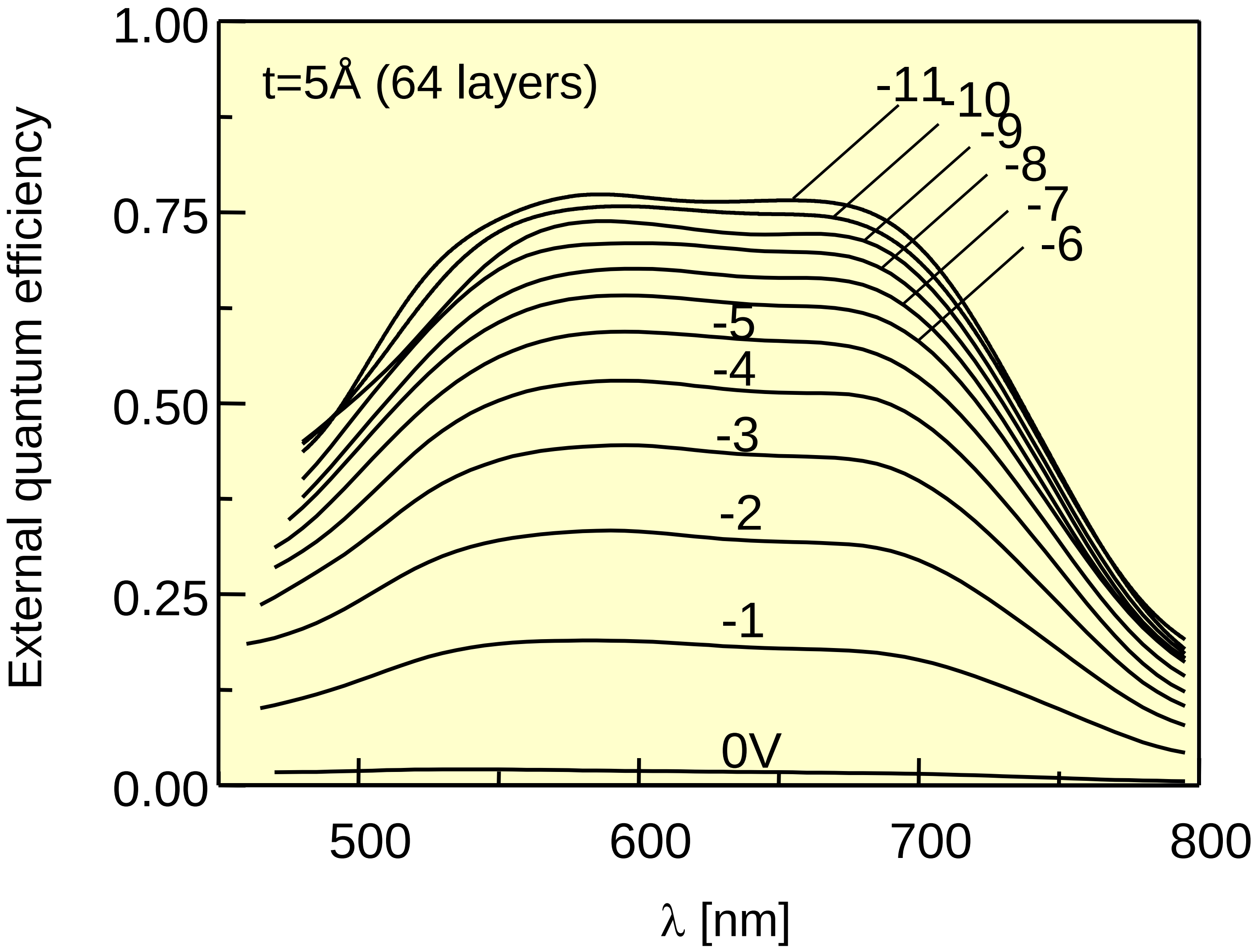
A possible origin for the compensating traps are O_2^- centers which act as deep acceptor levels in CuPc.



= p-i-n junction diode

Spectral + Voltage Dependence of the EQE

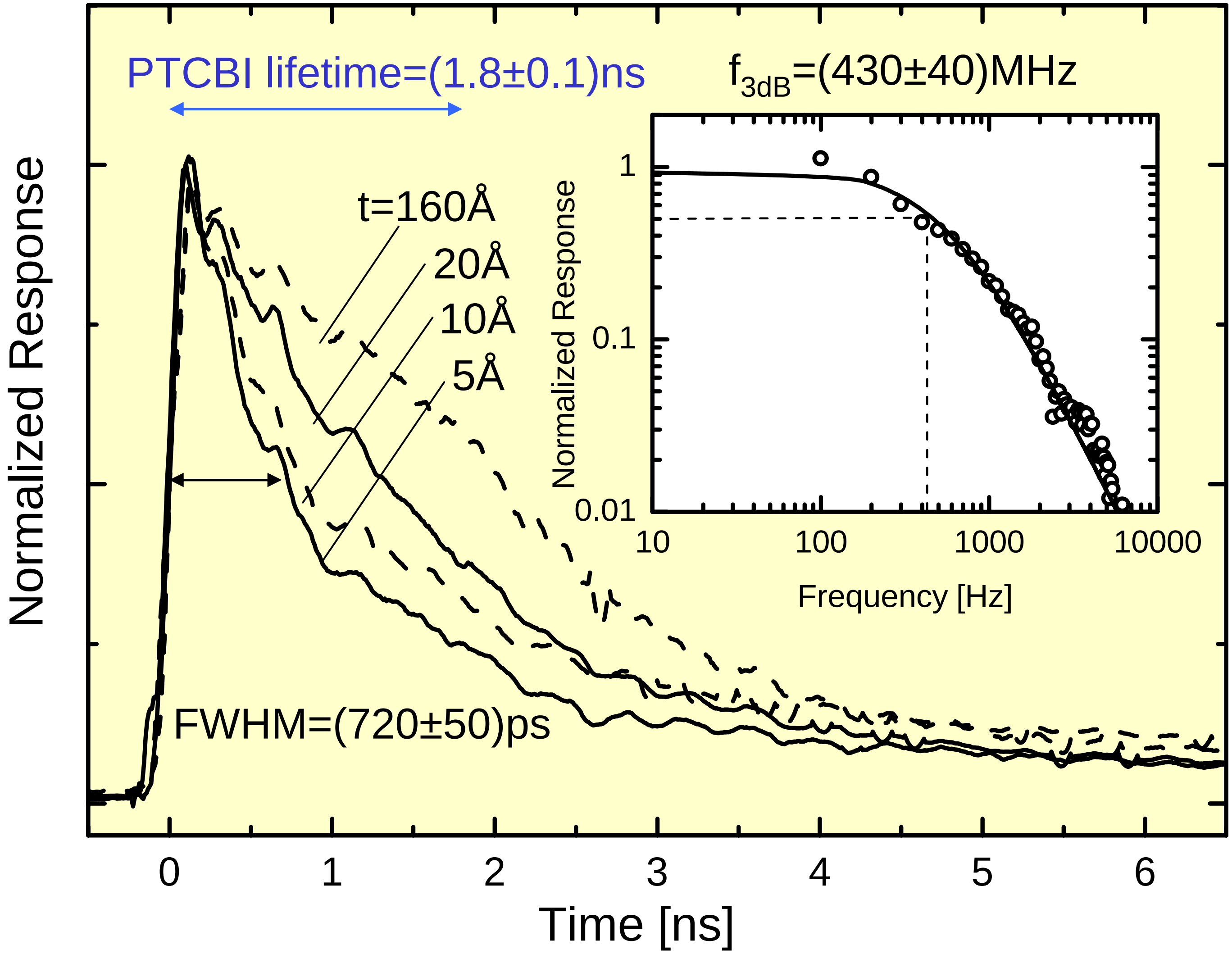
- Sensitive to visible + NIR wavelengths
- Strong dependence on bias: EQE~75% @ -10V



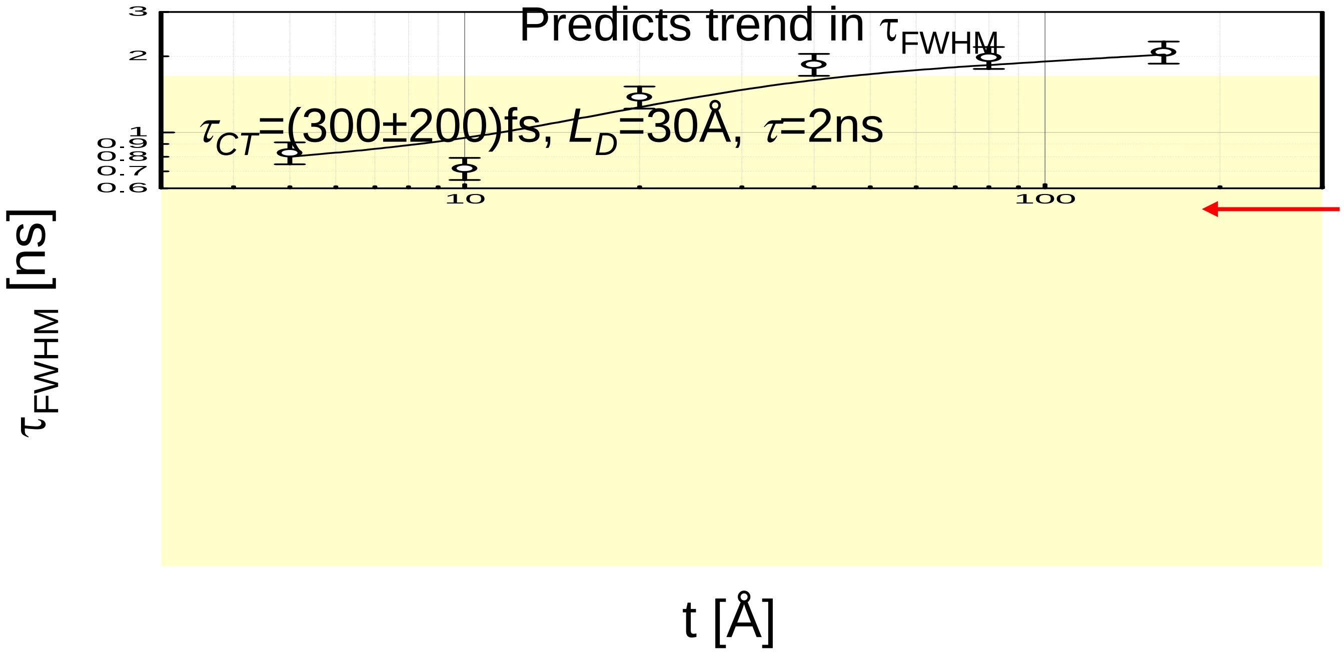
Response Time

Thinner individual layers makes faster devices due to a reduced exciton lifetime

100μm diameter, -9V, 1.4ps excitation @ 670nm under an average optical power of (1.0±0.3)W/cm². Estimated carrier velocities: $v = d/\tau = (1.1 \pm 0.1) \times 10^4\ cm/s$



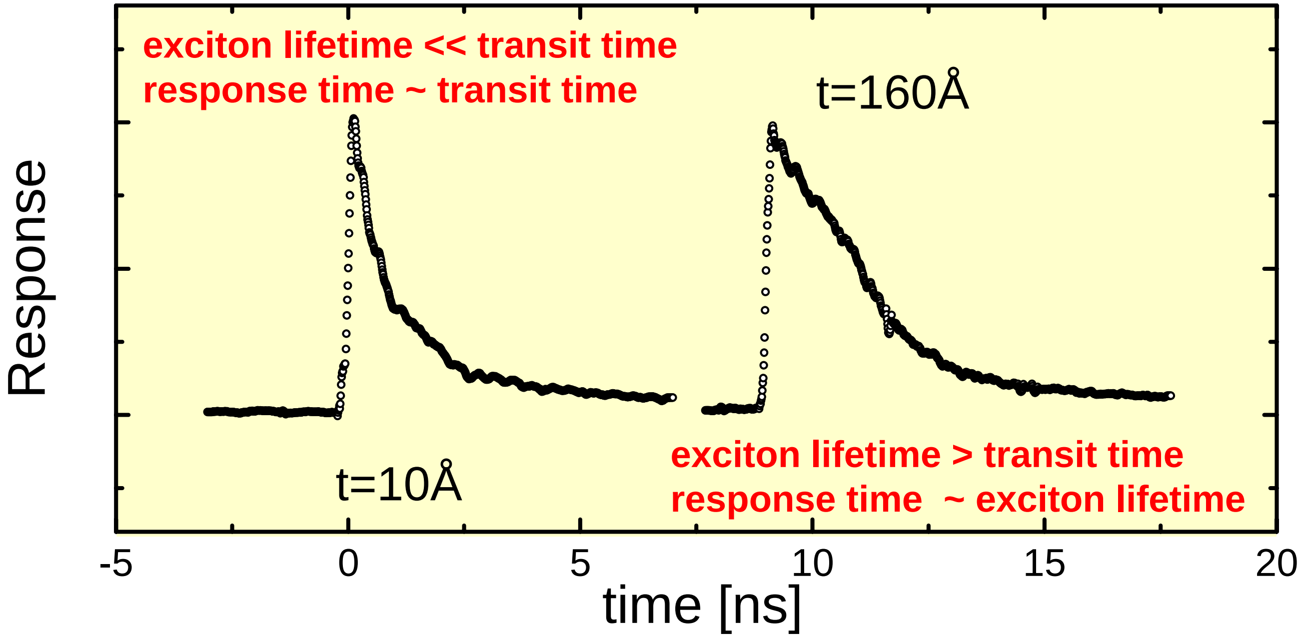
Model



Predicts trend in τ_{FWHM}

τ_{CT}=(300±200)fs, L_D=30Å, τ=2ns

PL lifetime of pristine PTCBI



exciton lifetime << transit time
response time ~ transit time

exciton lifetime > transit time
response time ~ exciton lifetime