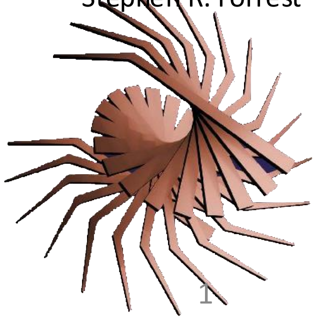
Introduction to Organic Electronics

Week 1

Chapter 1

Concepts in Organic Electronics
Stephen R. Forrest



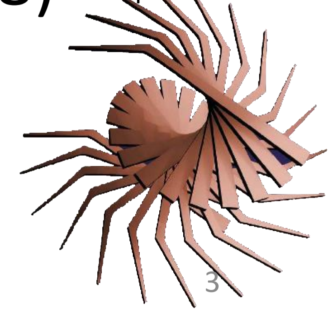
Objectives

- To introduce the basic promise and characteristics of organic materials and their electronic applications
  - What makes them different?
  - What makes them worth our time?
- To introduce the landmark advances in the field

Organic Materials: Definitions

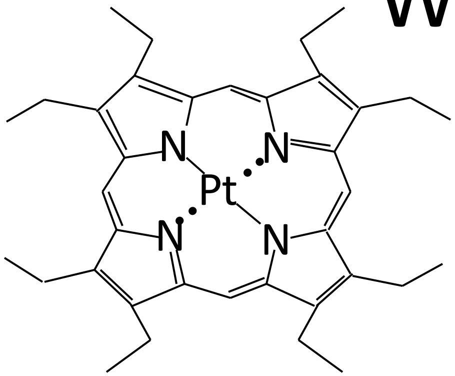
- Formally, a material containing one C-H bond known as an organic material
  - C_{60}, C_{70}, graphene, etc. by this definition are not organics
  - More frequently described as C-rich compounds
  - Can contain metals, any other element
- Extreme variety due to facile chemistry
  - Several million compounds synthesized
  - First synthetic molecule: urea (Wöhler, 1828)

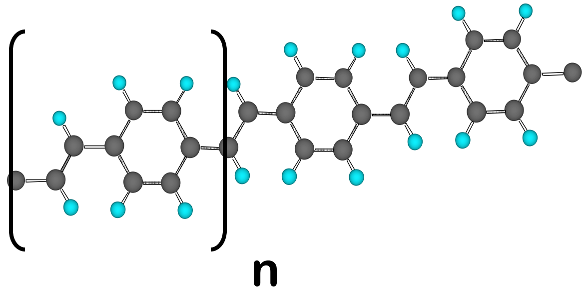
$$NH_4^+OCN^- \xrightarrow[\Delta]{heat} H_2N-\underset{\underset{O}{||}}{C}-NH_2$$

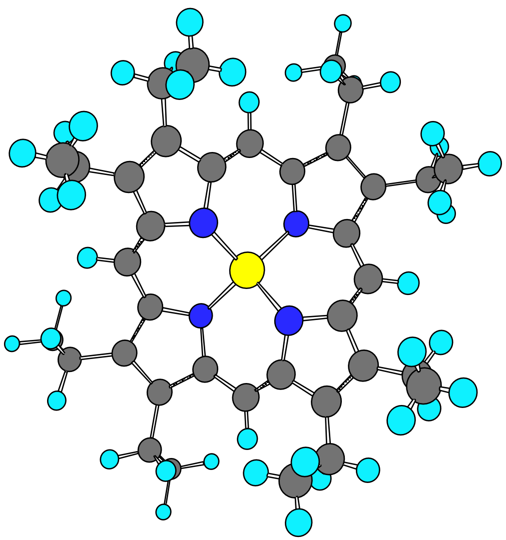


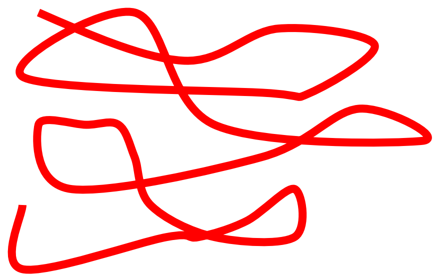
Organic (excitonic) materials:

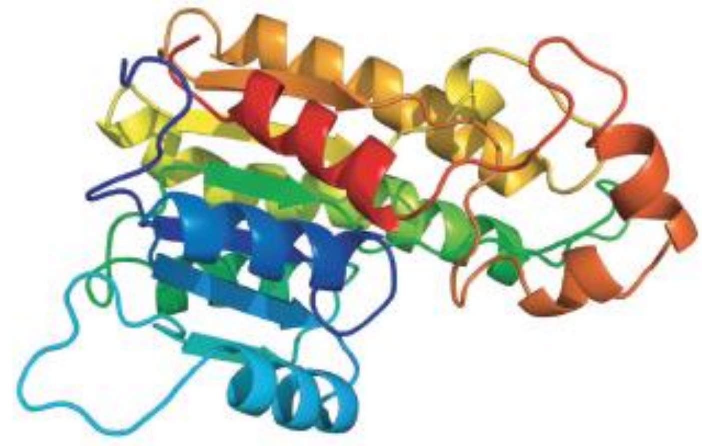
Where the scaling is easy





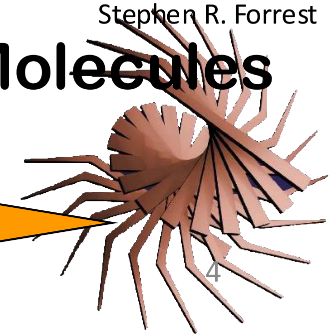






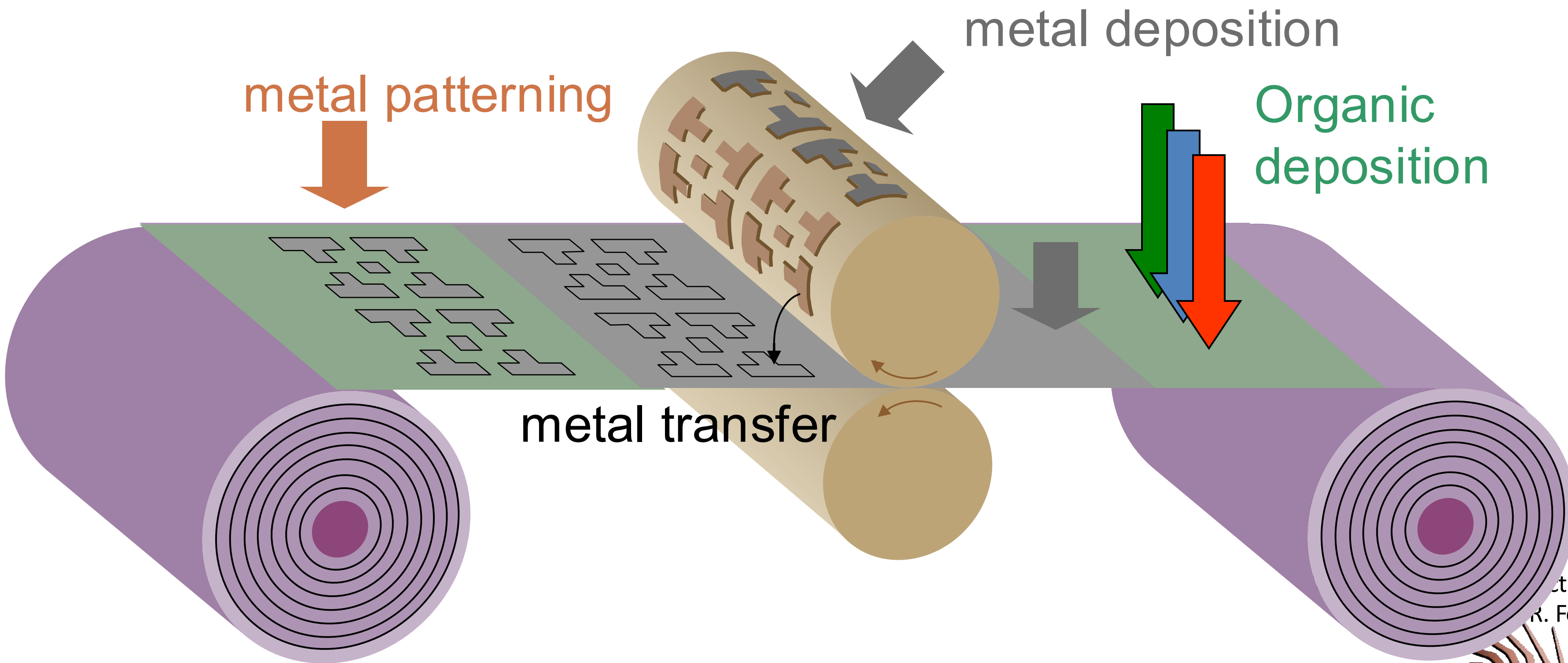
Monomers **Polymers** **Biological Molecules**

Increasing Complexity



The Promise of Organics

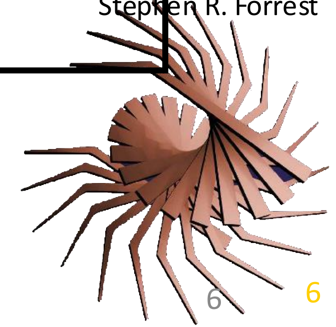
Making Large Area Electronics "By the Mile"



R2R-processing of organic devices

Organic & Inorganic Semiconductors: What makes them different?

Property	Organics	Inorganics
Bonding	van der Waals	Covalent/Ionic
Charge Transport	Polaron Hopping	Band Transport
Mobility	~1 cm^2/V·s	~1000 cm^2/V·s
Absorption	10^5-10^6 cm^{-1}	10^4-10^5 cm^{-1}
Excitons	Frenkel	Wannier-Mott
Binding Energy	~500-800 meV	~10-100 meV
Exciton Radius	~10 Å	~100 Å

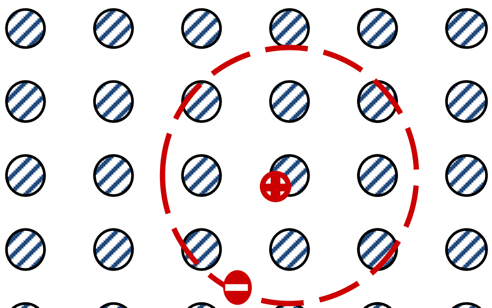


Organic Semiconductors are Excitonic Materials

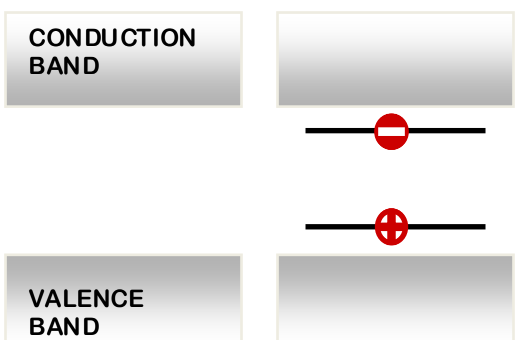
Inorganics ←→ **Organics**

Wannier exciton

Inorganic semiconductors



SEMICONDUCTOR PICTURE

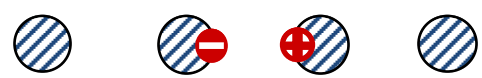


GROUND STATE WANNIER EXCITON

Dielectric constant ~15
binding energy ~10meV (unstable at RT)
radius ~100Å

Charge Transfer (CT) Exciton

(bridge between W and F)

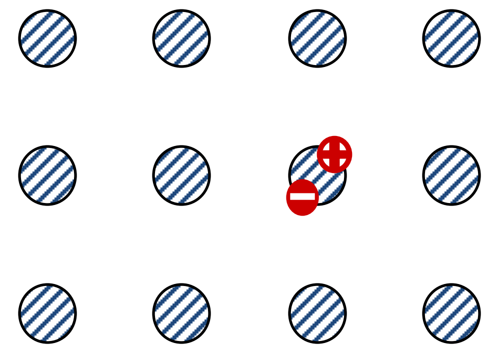


treat excitons as chargeless particles capable of diffusion.

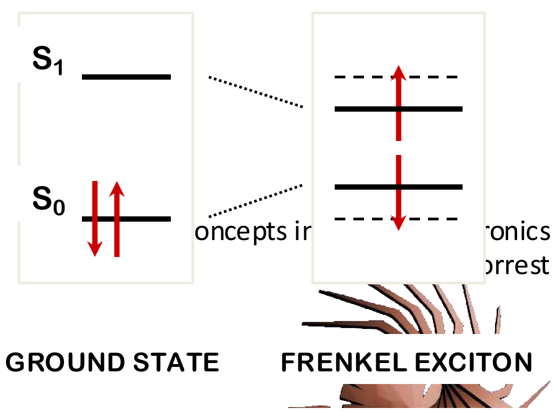
Transport of energy (not charge)

Frenkel exciton

Organic materials



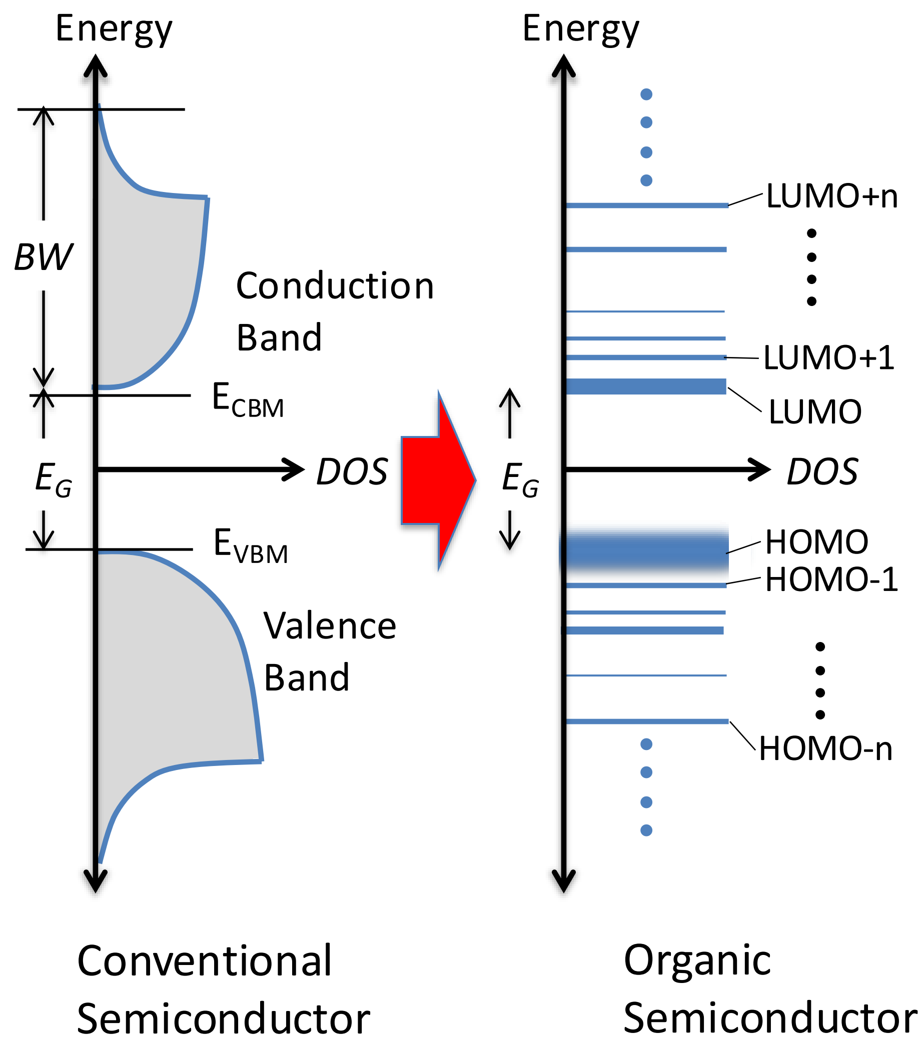
MOLECULAR PICTURE



GROUND STATE FRENKEL EXCITON

Dielectric constant ~2
binding energy ~1eV (stable at RT)
radius ~10Å

Band Structure is Replaced by ***Energy Levels***



LUMO: Lowest unoccupied molecular orbital

HOMO: Highest occupied molecular orbital

Concepts in Organic Electronics
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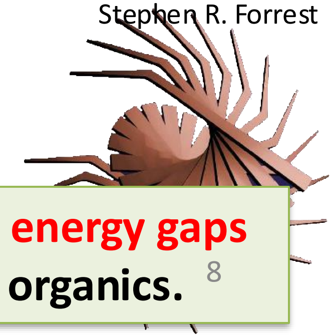


It is <u>essential</u> to keep your terminology clear: Band gaps exist in inorganics, energy gaps without extended bands are the rule (but with important exceptions) in organics.

Electronic Materials: A Comparison

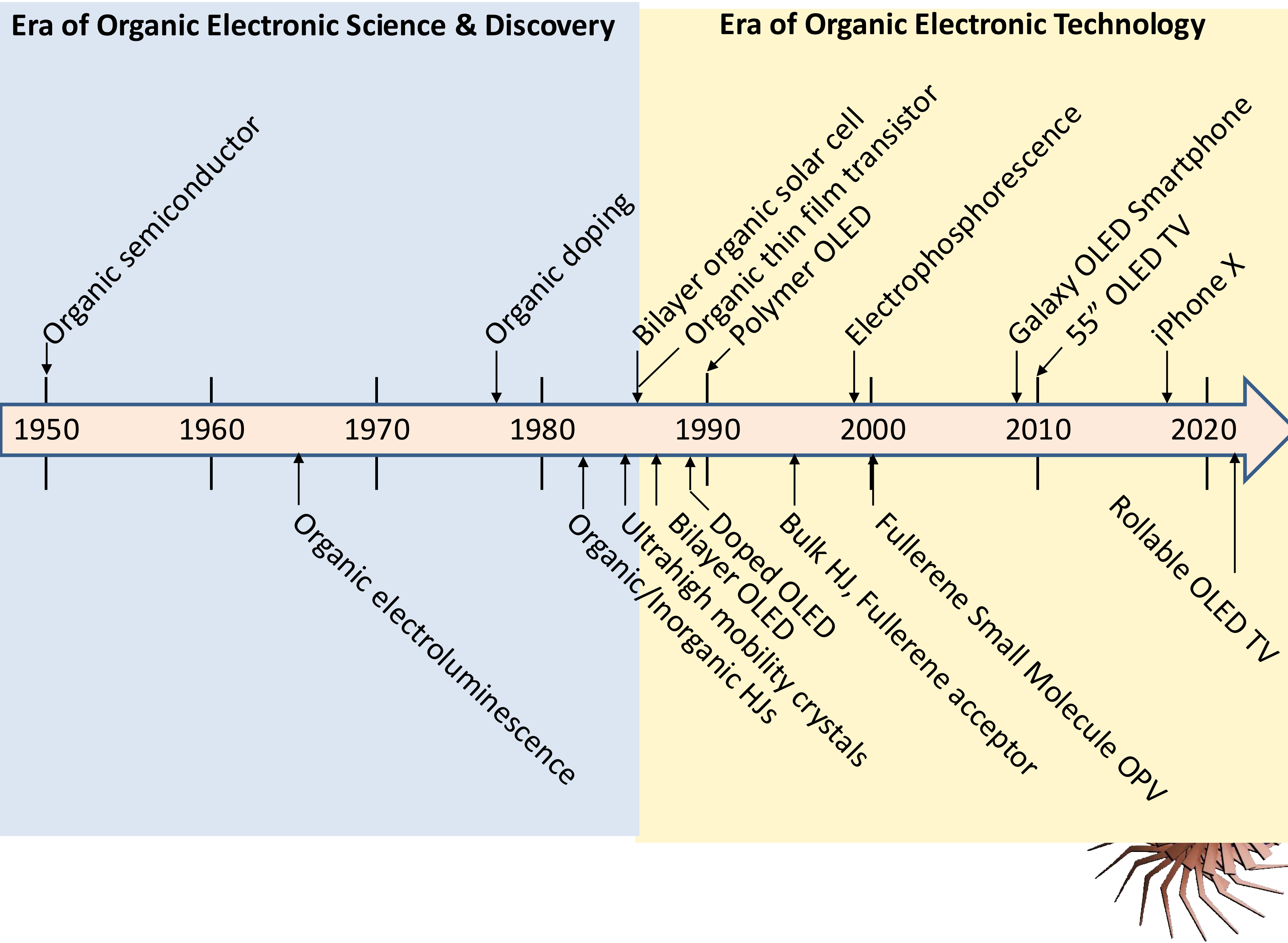
	Inorganics	Organics
Large area	---	+++
Cost	--	++
Green processing	--	+
Easy to pattern	+	0
Complexity	+	0
Tunable properties	0	++
Optical absorption	-/+	++
Optical emission	-/++	++
Low resistance	+	--
High reliability	++	-

Organic Materials are Interesting for Electronics Because…

- They are *potentially* inexpensive
- Their properties can be ”easily” modified through chemical synthesis
- They can be deposited on large area, flexible and/or conformable substrates
- They can be very lightweight
- They have excellent optical properties
- They can be manufactured “by the kilometer”

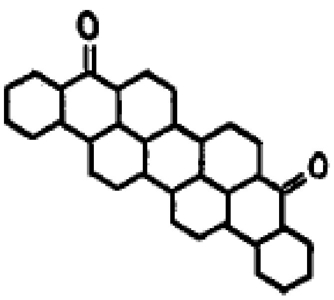
But remember…..

If you are competing with silicon, go home. You’ve already lost!

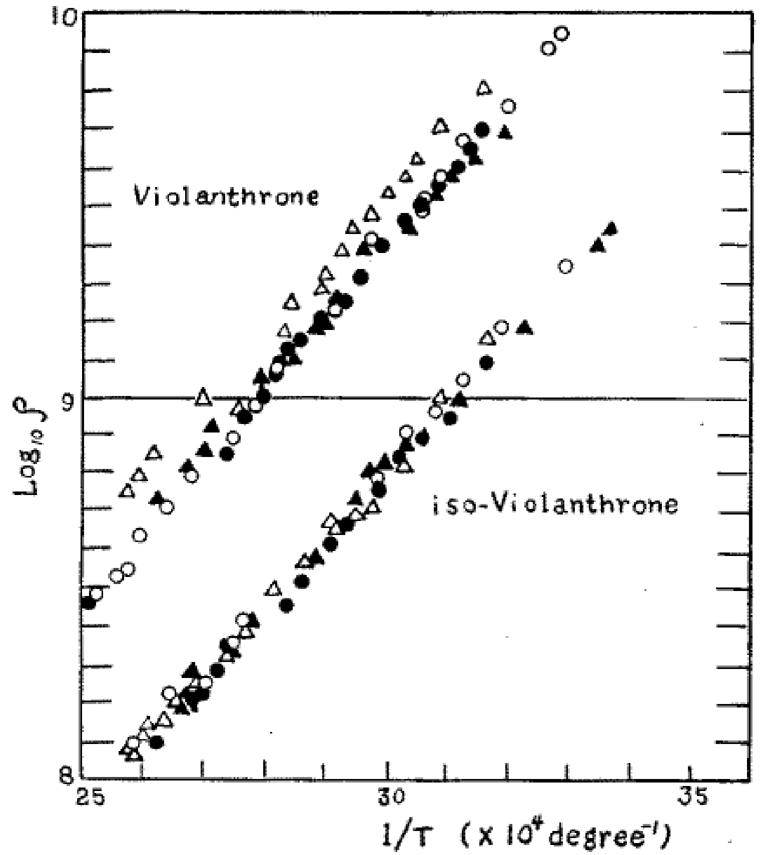

Era of Organic Electronic Science & Discovery
Era of Organic Electronic Technology
1950
1960
1970
1980
1990
2000
2010
2020
Organic semiconductor
Organic doping
Bilayer organic solar cell
Organic thin film transistor
Polymer OLED
Electrophosphorescence
Galaxy OLED Smartphone
55” OLED TV
iPhone X
Organic electroluminescence
Organic/Inorganic HJs
Ultrahigh mobility crystals
Bilayer OLED
Doped OLED
Bulk HJ, Fullerene acceptor
Fullerene Small Molecule OPV
Rollable OLED TV

Organics Can Be Semiconductors

H. Akamatu and H. Inokuchi, J. Chem. Phys., 18, 810 (1950)



Violanthrone

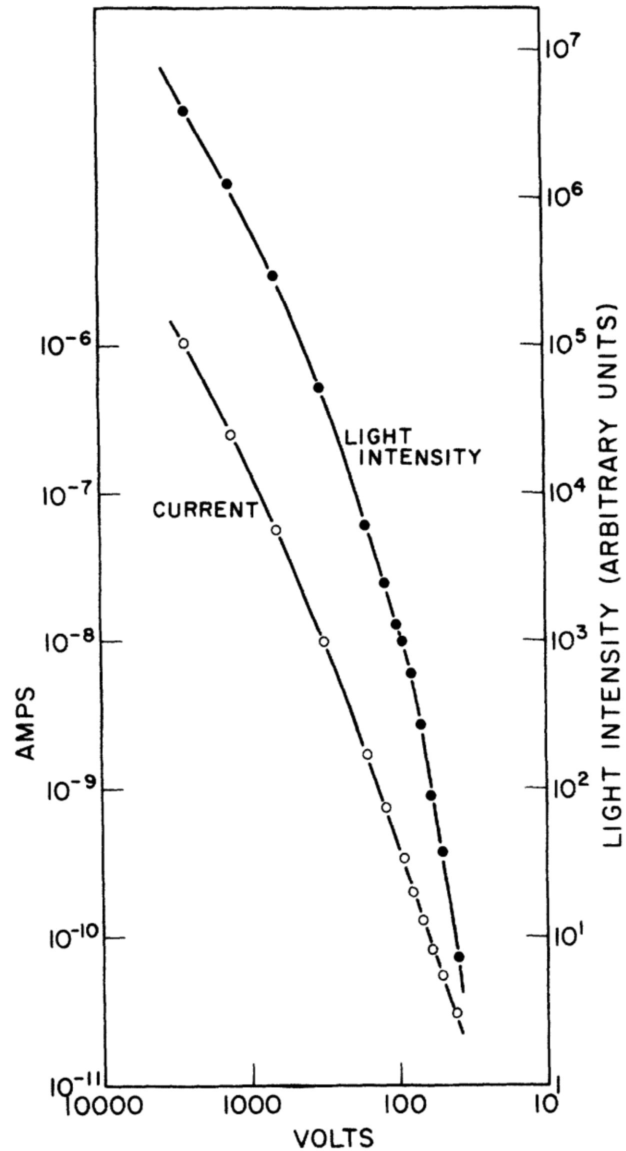


$$\sigma = \sigma_0 \exp(-\Delta\epsilon/2kT),$$

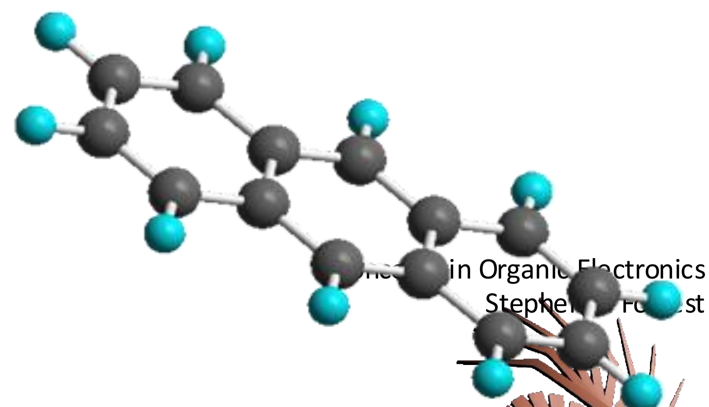
See also B. A. Bolto, R. McNeill and D. E. Weiss: Aust. J. Chem., 16, 1090 (1963) for similar data on polymers (polypyrroles)

Organic Electroluminescence

W. Helfrich and W. G. Schneider, Phys. Rev. Lett., **14** 229 (1965)

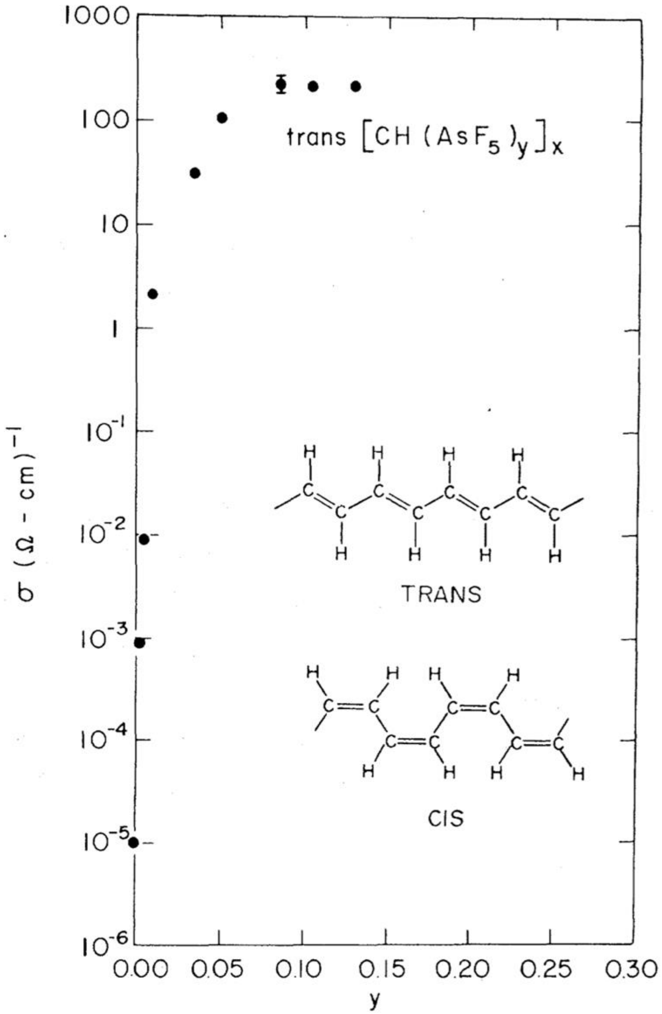


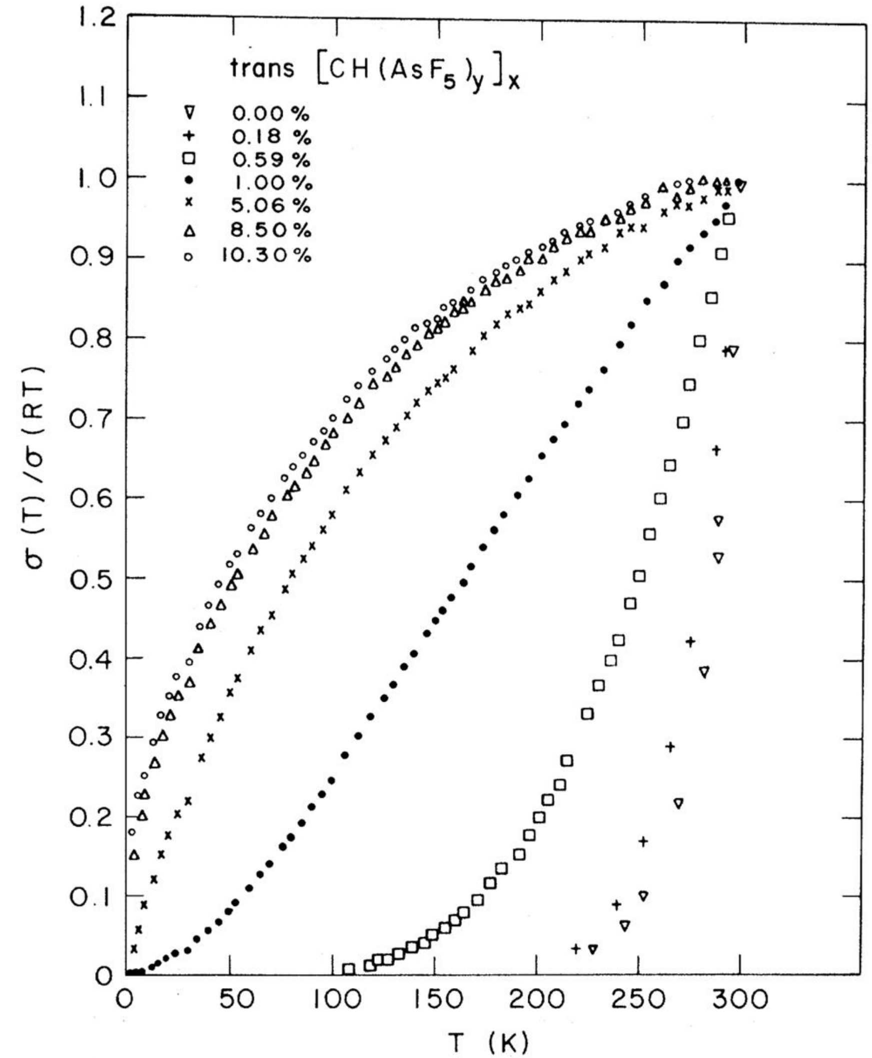
- Anthracene single crystal
- Several mm thick
- Aqueous ionic electrodes
- Blue glow



High Conductivity in Doped Polymers

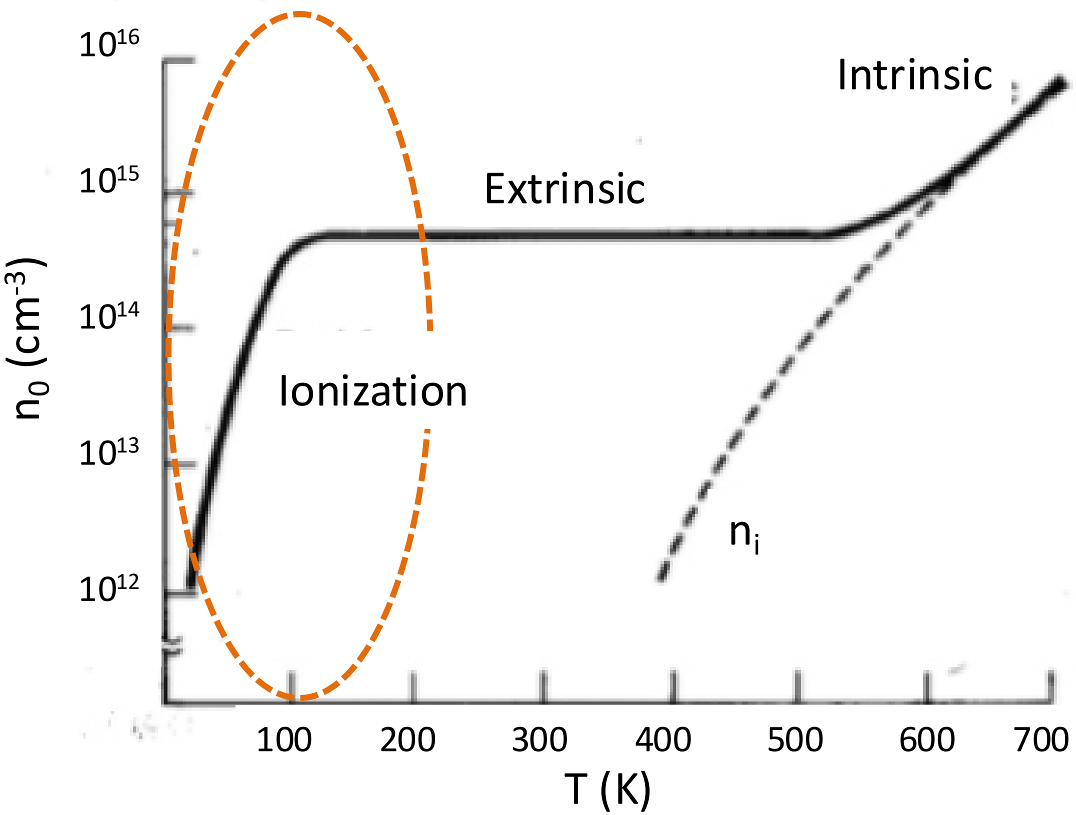
Heeger, Shirakawa, MacDiarmid, et al. Phys. Rev. Lett., **39** 1098 (1977)





Extrinsic Semiconductor (Extrinsic carrier concentration)

Electron density as a function of temperature



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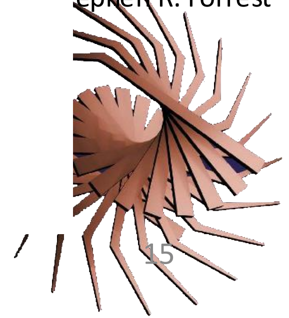
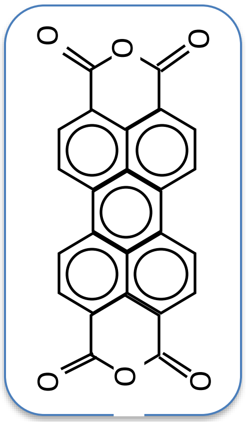
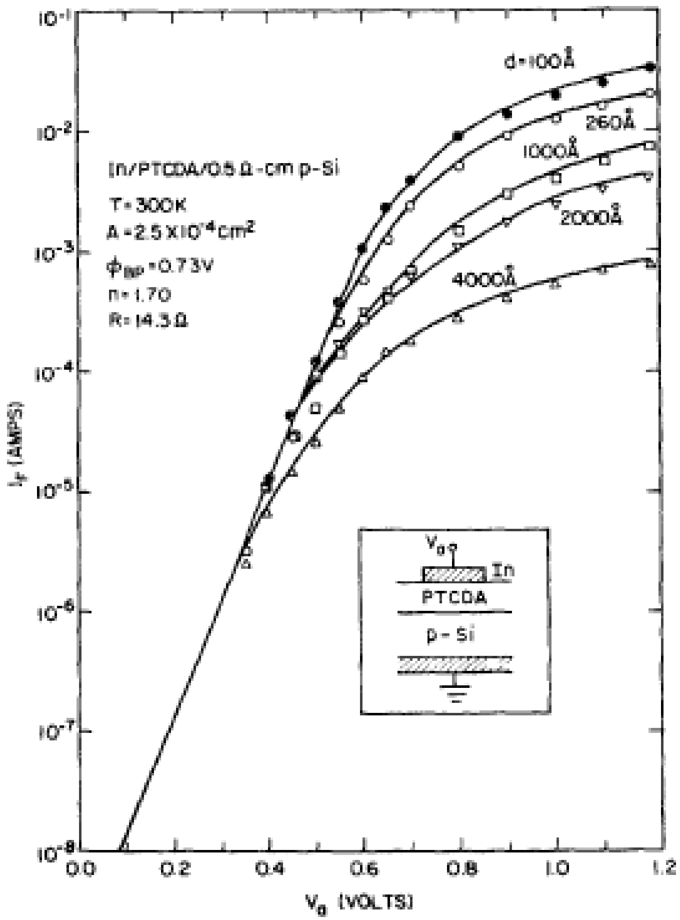
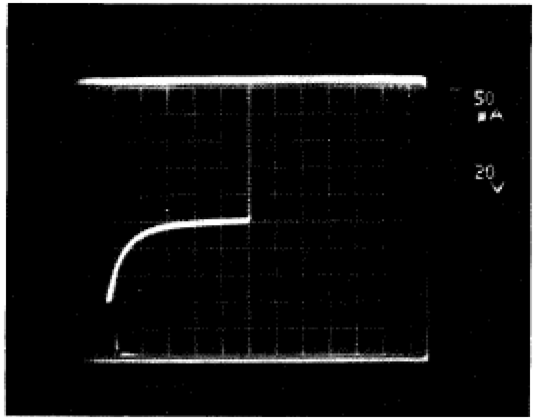


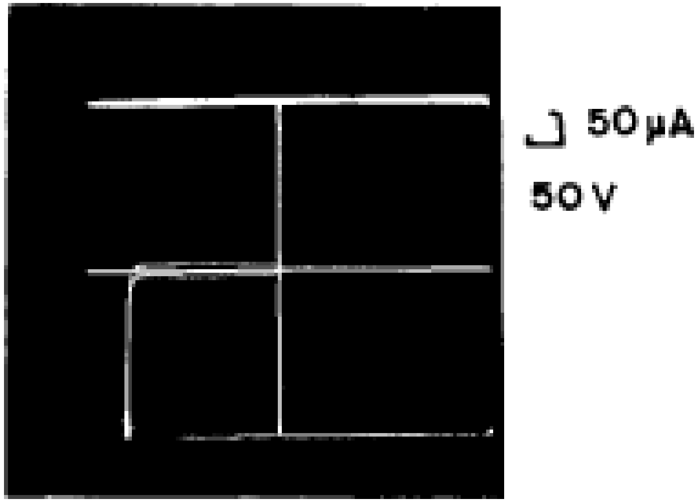
Organic/Inorganic Heterojunctions; PTCDA

S. R. Forrest, M. L. Kaplan, P. H. Schmidt, et al., E. 1982. *Appl. Phys. Lett.*, **41,** 90.







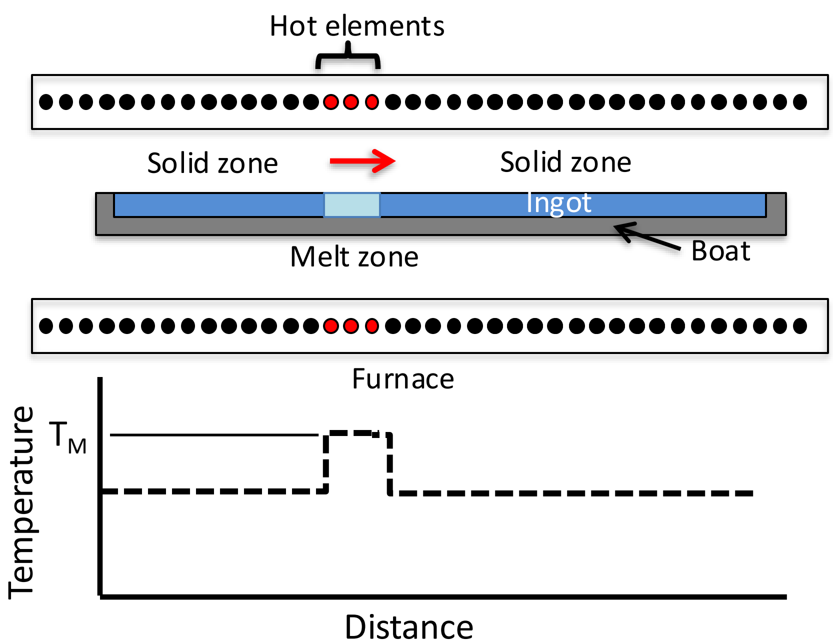


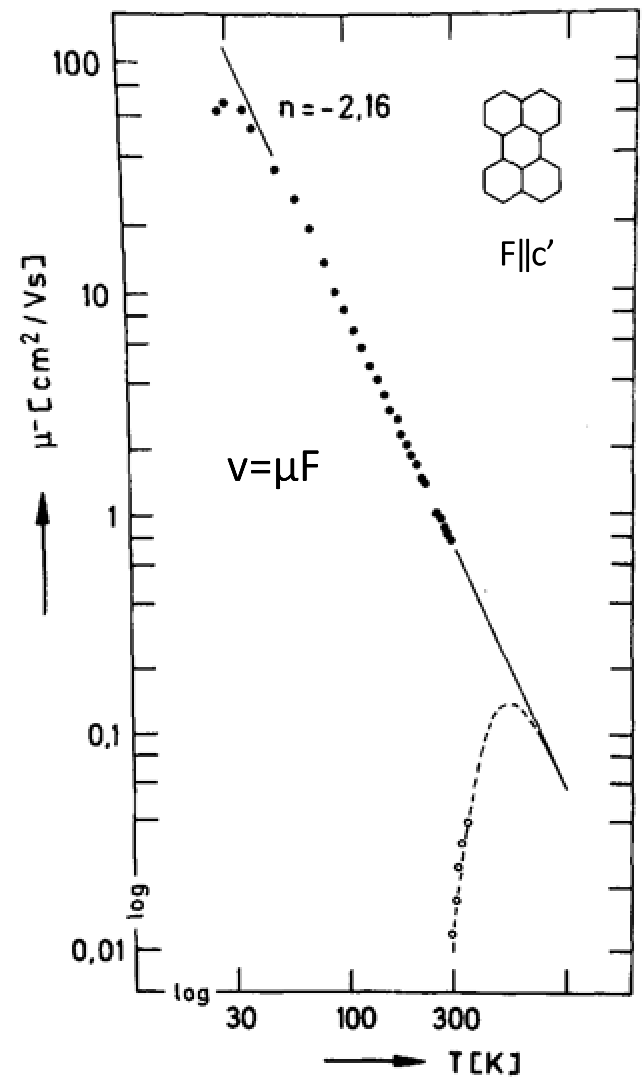
(a) In/PTCDA/10Ω-cm p-Si

PTCDA: An organic electronic archetype

High Mobility in Ultrapure Organics

W. Warta, R. Stehle & N.Karl, 1985. *Appl. Phys. A,* **36,** 163.

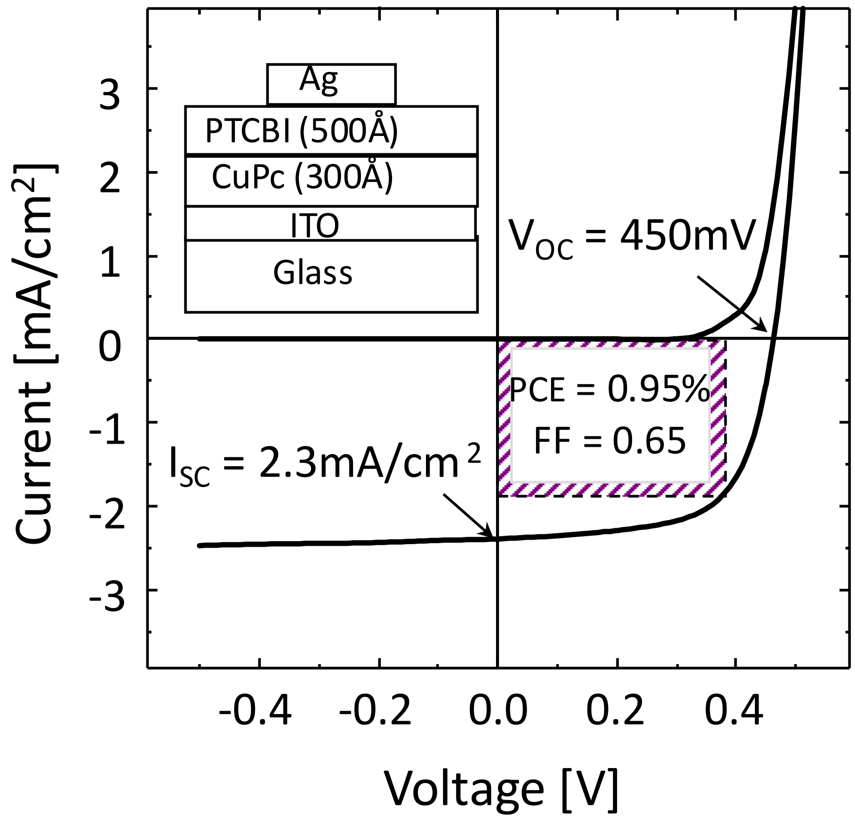




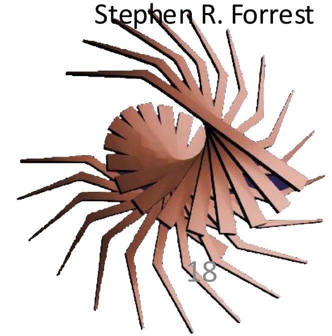
Thin Film Organic Solar Cells

Single Heterojunction Solar Cell

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

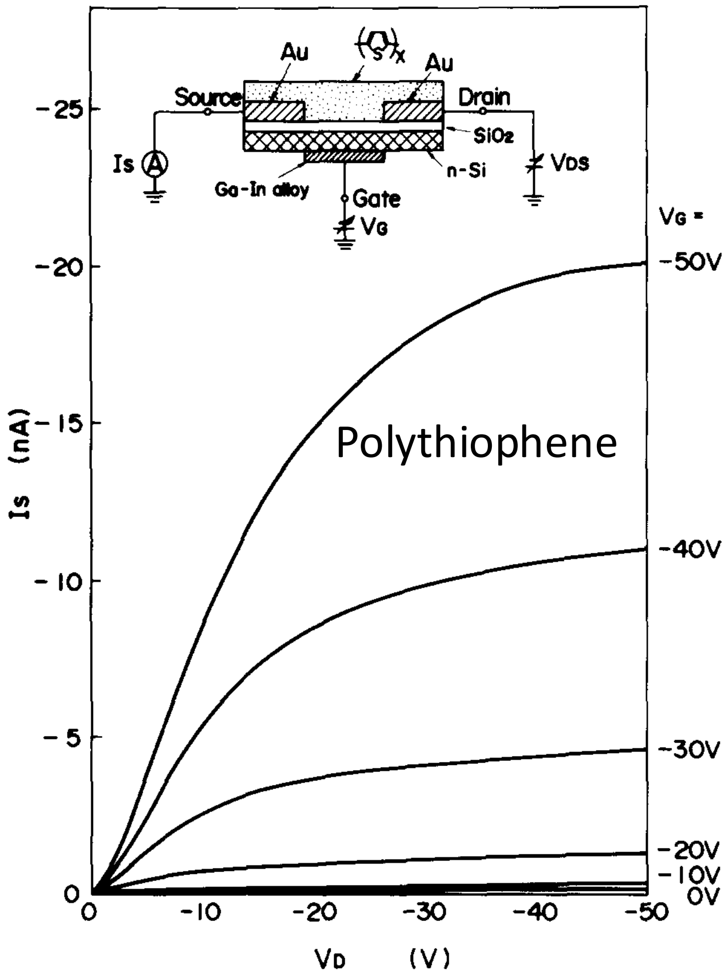


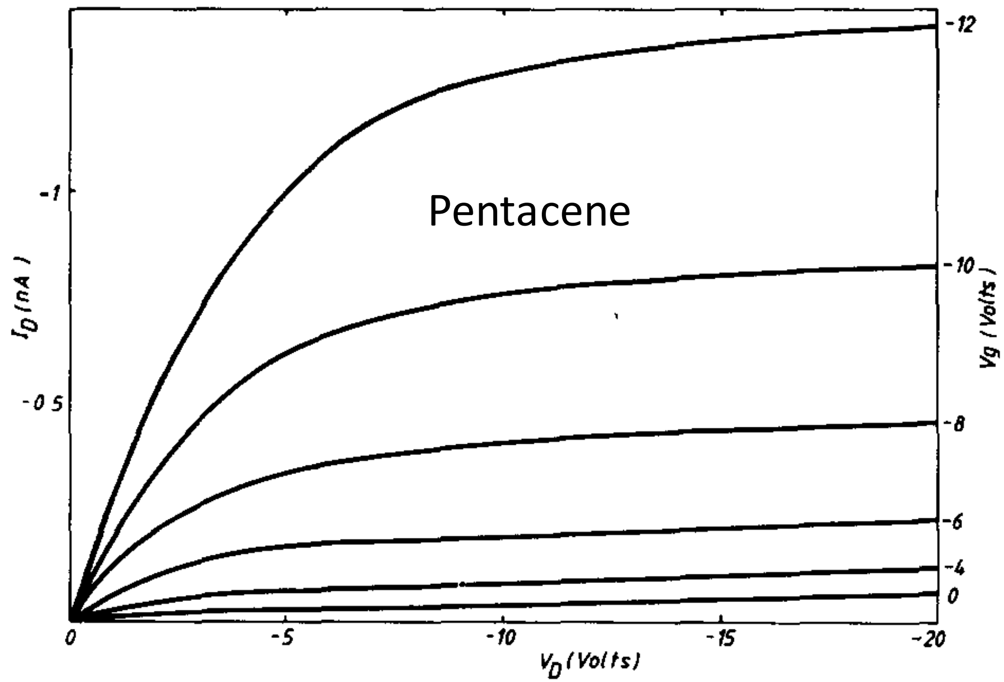
- first **heterojunction** for efficient charge generation
- ~**0.95%** conversion efficiency
- nearly ideal IVs (FF~0.65)
- **full solar illumination** (1 sun)



Organic Thin Film Transistors

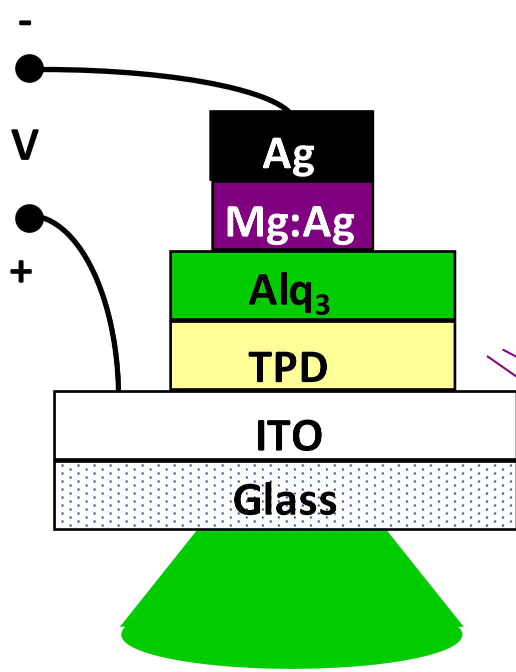
A. Tsumura, H. Koezuka, T. Ando, Appl. Phys. Lett., **49,** 1210 (1986)

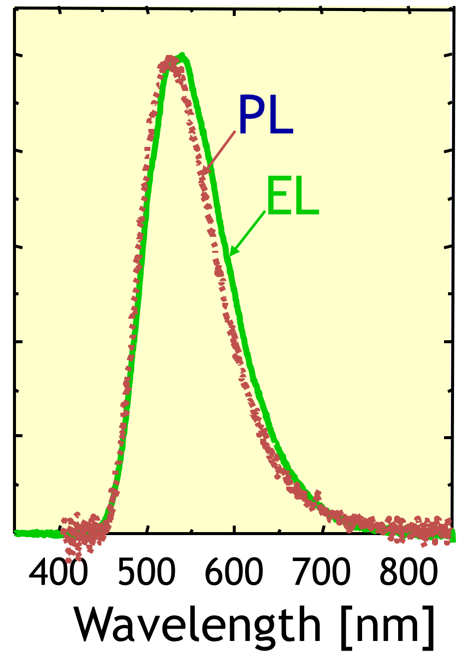




G. Horowitz, et al., Solid State Commun., **72** 381 (1989)

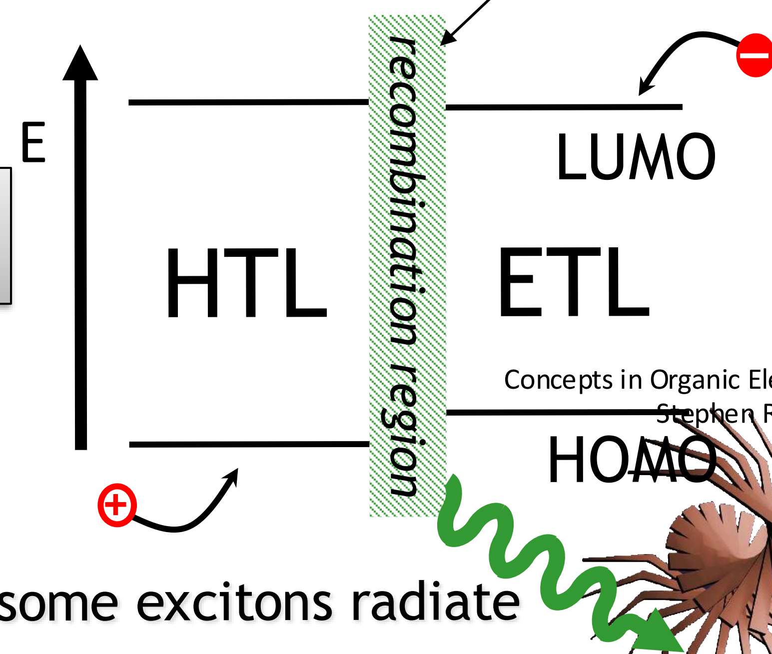
Organic Light Emitting Diode (OLED)



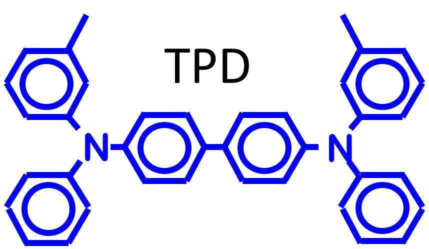


electrons and holes form ***excitons*** (bound e^--h^+ pairs)

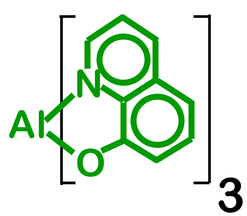
Low voltage
EQE=1%



TPD



Alq_3

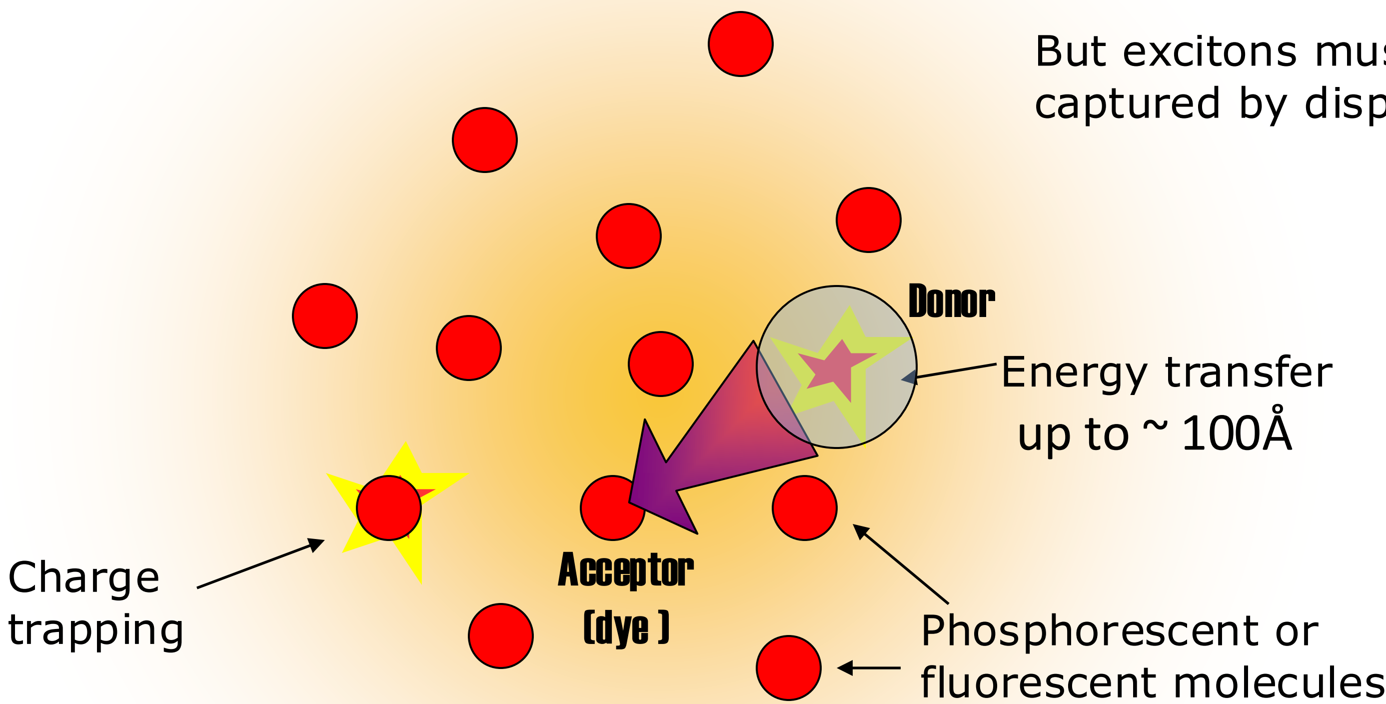


Tang & van Slyke, Appl. Phys. Lett., **51**, 913 (1987)

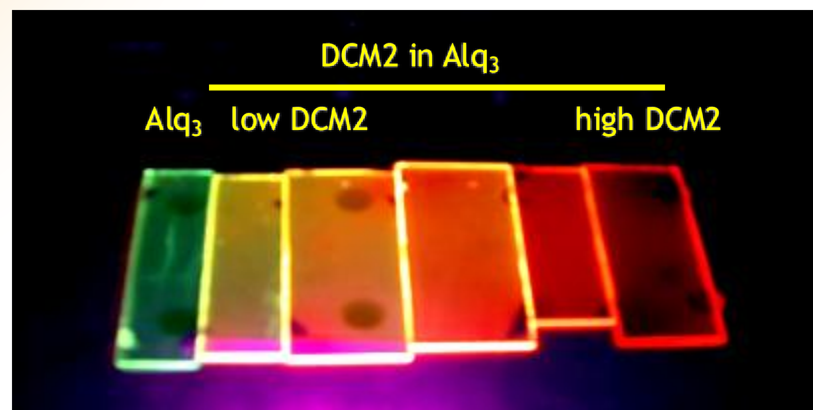
Luminescence of dye improves if dispersed in host material

C. W. Tang, S. A. Van Slyke, C. H. Chen, C. H. *J. Appl. Phys.*, **65,** 3610 (1989).

But excitons must be captured by dispersed dye

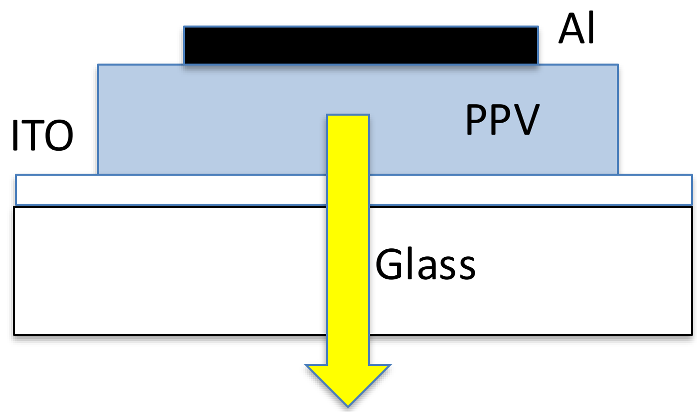


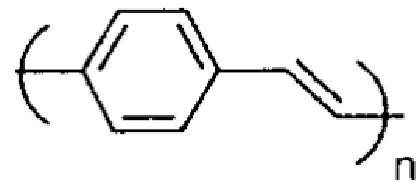
1. Charges trapped on dye molecules
2. Energy transferred from host
3. Effect used to increase color range and efficiency of OLEDs
4. Separates functions of conduction and luminescence



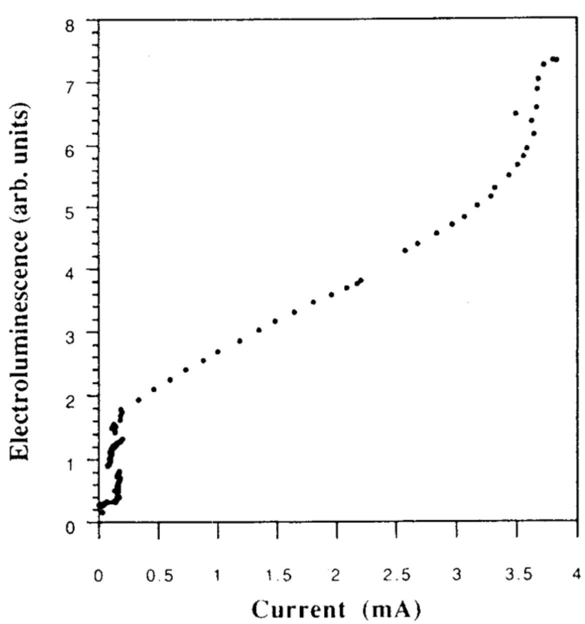
Polymer OLED

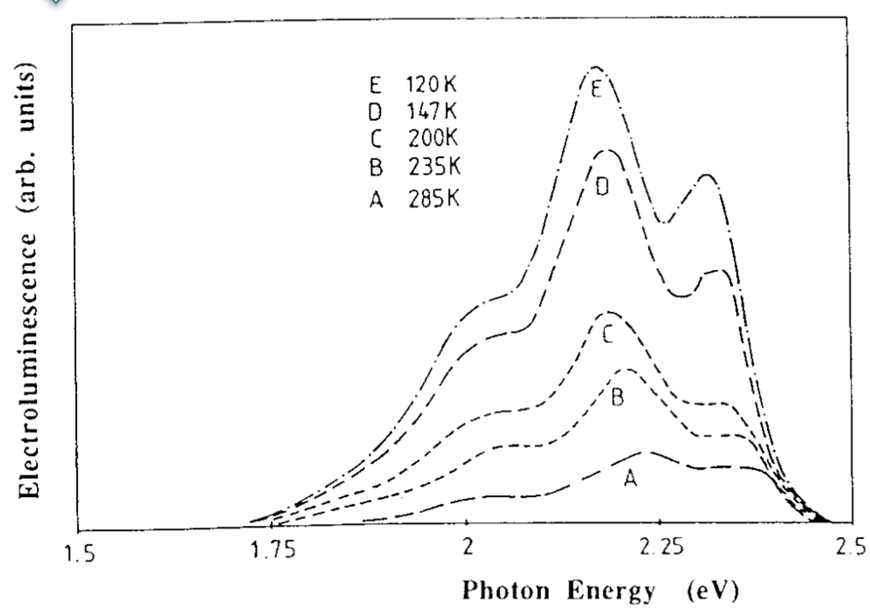
Burroughs, Bradley, Friend et al., *Nature* **347** 539 (1990)





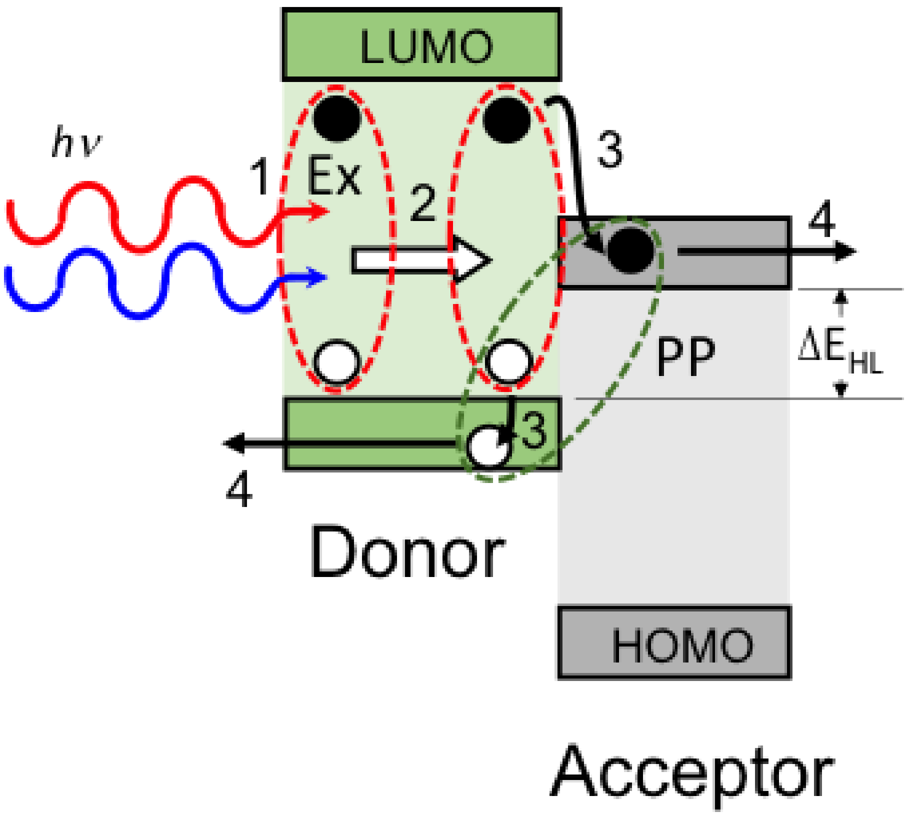
EQE ~ 0.05%





Photogeneration in organics

Processes occuring at a Donor-Acceptor Heterojunction

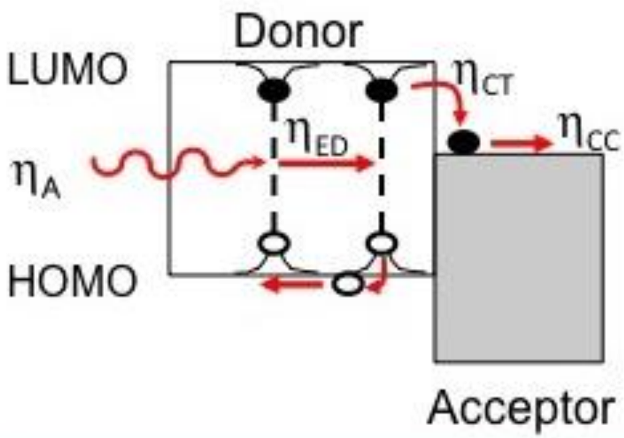


1. Exciton generation by absorption of light
2. Exciton diffusion over ~L_D
3. Exciton dissociation by rapid and efficient charge transfer
4. Charge extraction by the internal electric field

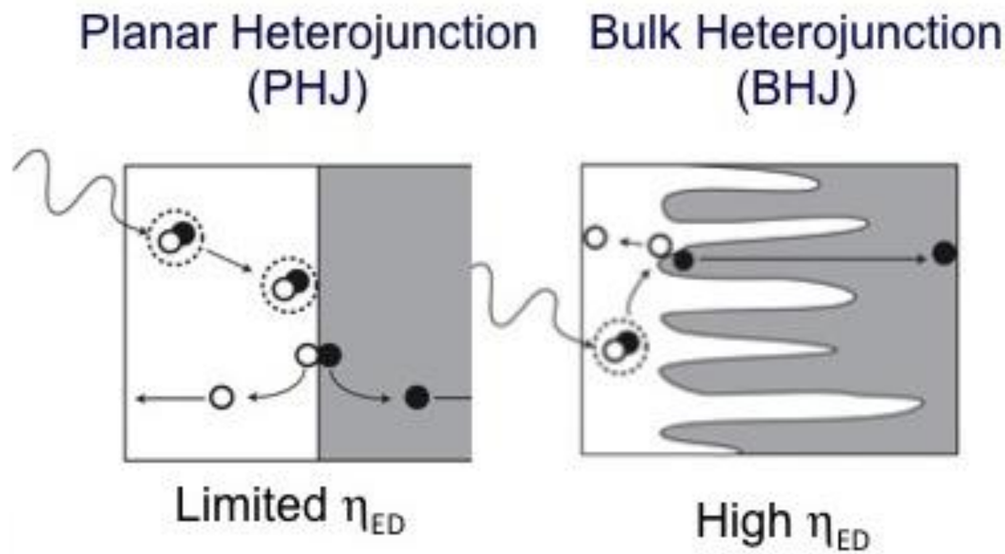
Typically: $L_D \ll 1/\alpha$

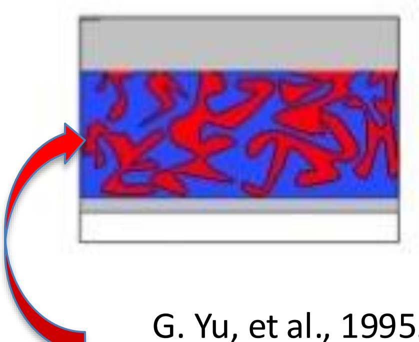
Bulk Heterojunctions Increase OPV Efficiency

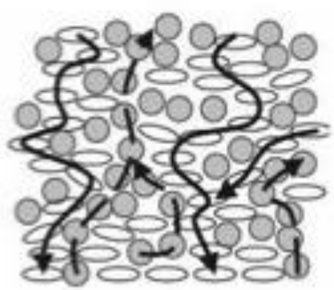
Function follows (nano)structure

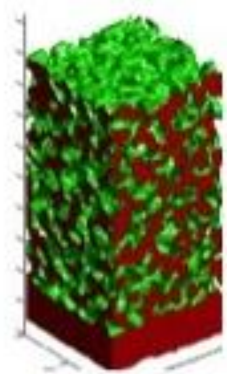


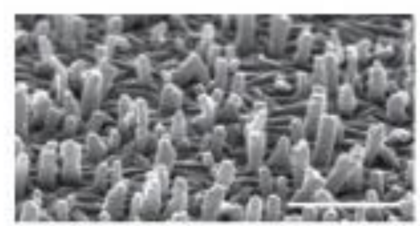
$$\eta_{ext} = \eta_A \eta_{int} = \eta_A \eta_{ED} \eta_{CT} \eta_{CC}$$

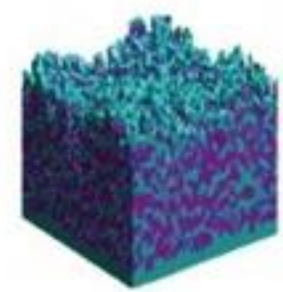












G. Yu, et al., 1995. *Science,* 270**,** 1789.
Halls, J. J. M. et al., (1995) Nature, 376, 498.

100% Internal Efficiency via Spin-Orbit Coupling

Heavy metal induced electrophosphorescence ~100% QE

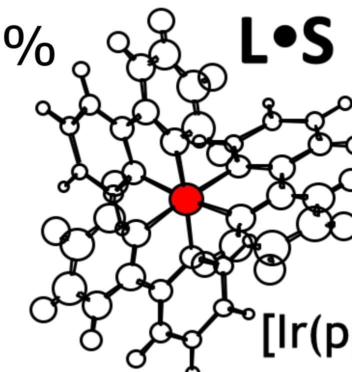
Baldo, et al., Nature **395**, 151 (1998)

MOLECULAR EXCITED STATES AFTER ELECTRICAL EXCITATION

Singlet 25%
spin anti-symmetric

75% **Triplet**
spin symmetric

100% **L•S**



$[Ir(ppy)_3]$

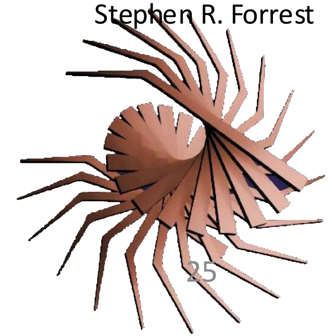
Relaxation allowed
fast, efficient
'**Fluorescence**'

Relaxation disallowed
slow, inefficient
'Phosphorescence'

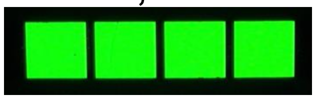
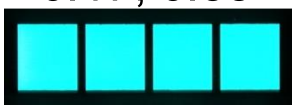
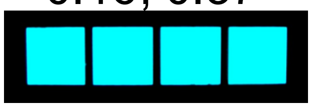
Phosphorescence enhanced by mixing S+T eg: spin-orbit coupling via heavy metal atom

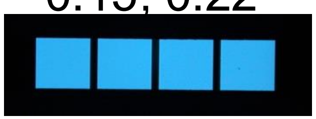
Relaxation allowed
not so slow, efficient
'**Phosphorescence**'

GROUND STATE
spin anti-symmetric



PHOLEDs Cover the CIE and Super CIE Gamuts

0.33, 0.63

0.17, 0.38

0.16, 0.37

0.16, 0.29

0.15, 0.22

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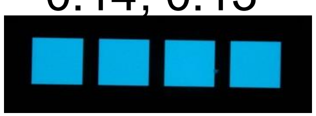
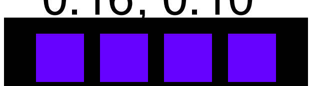
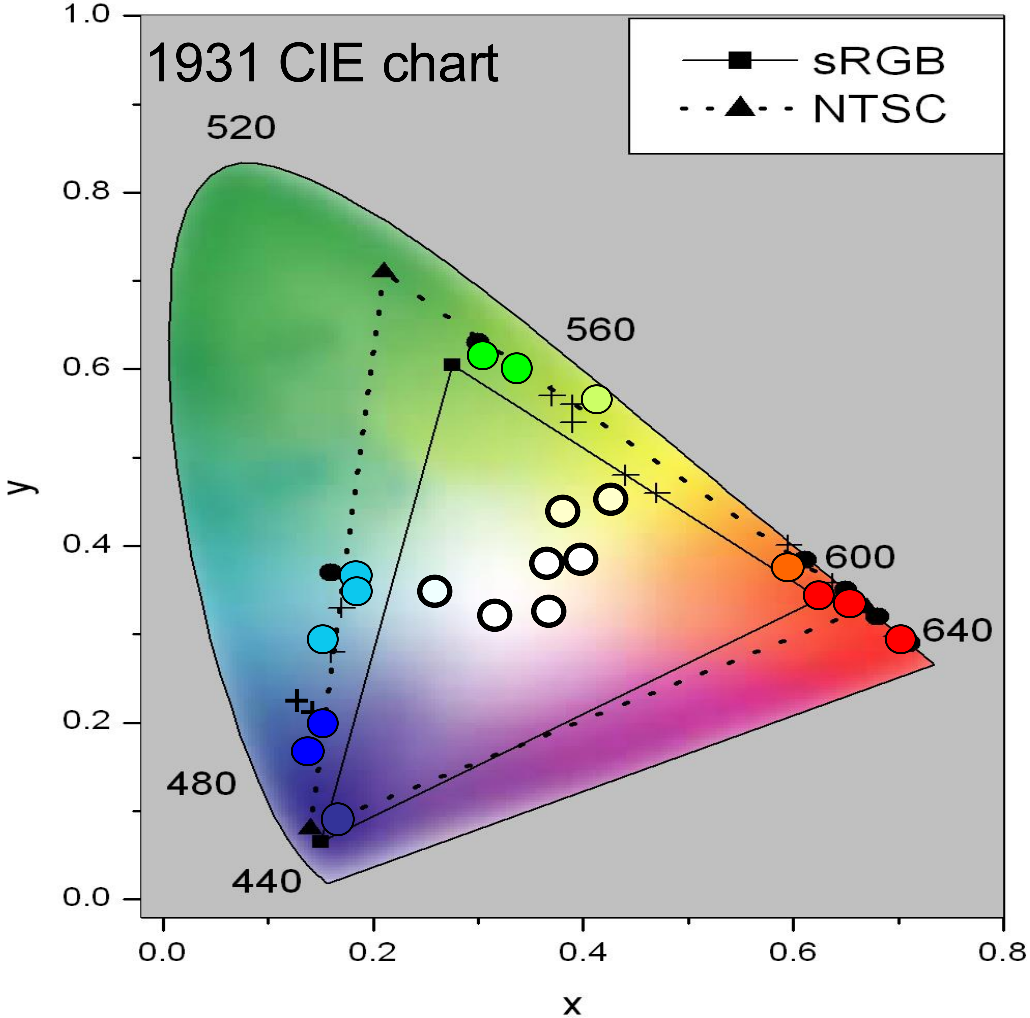
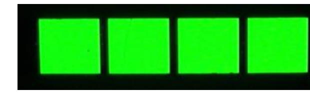
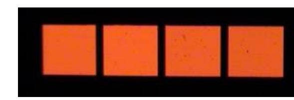
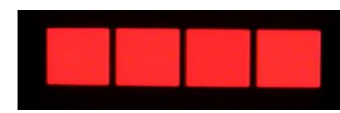

0.16, 0.10




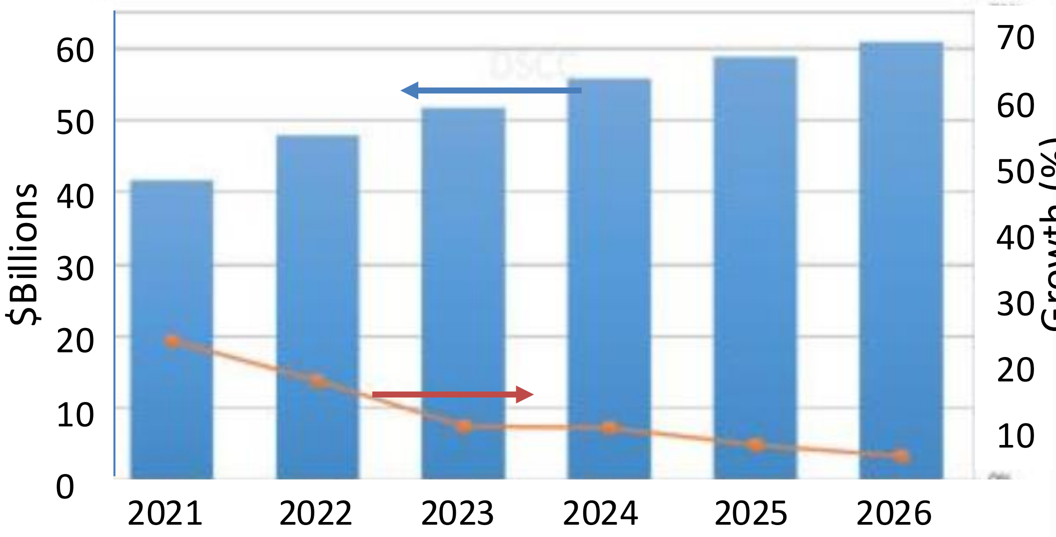
0.35, 0.61

0.42, 0.57

0.62, 0.38

0.65, 0.35

0.67, 0.33

0.68, 0.32


AMOLED Displays: Driving the Technology

Today: ~$50B market



2010: Galaxy Phones
Phosphorescent R,G
>3 Billion sold!
(Samsung Q321 report: 125M displays)

2012: LG 55" & Samsung
Phosphorescent TV, now $950
2017: iPhone X

2014-15: 65" and 77" OLED TVs
2016: 4K OLED TV
2022: 95" OLED TVs

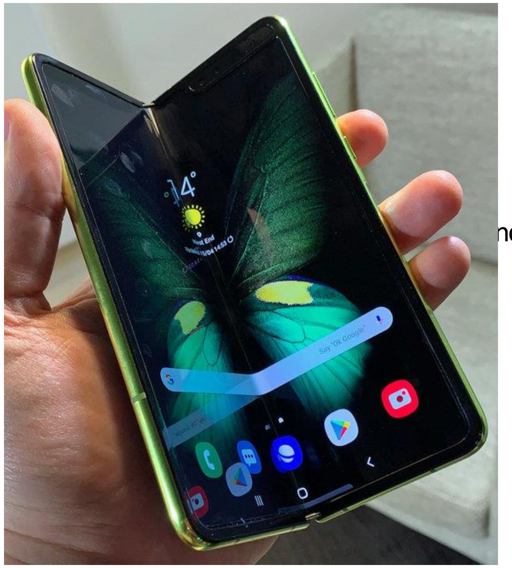
Panasonic, Sony, Toshiba…..(2017)

:tronics
Forrest

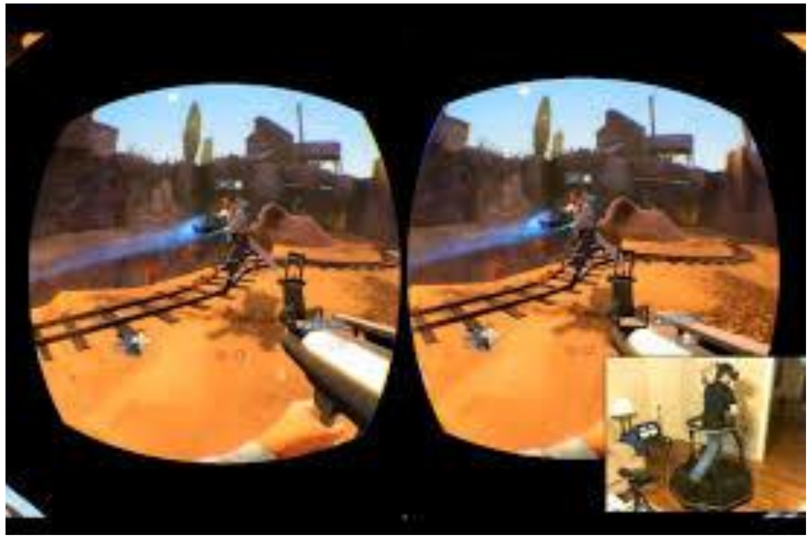
The Future is Flexible


Eluminati Compound Curved OLED TV


LG 65” Rollable OLED TV



Virtual and Augmented Reality Enabled by OLEDs



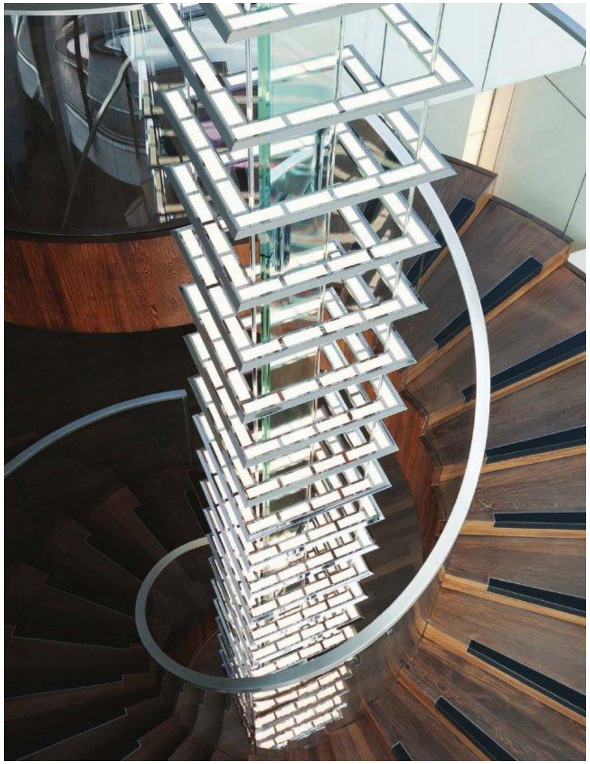
Requirements

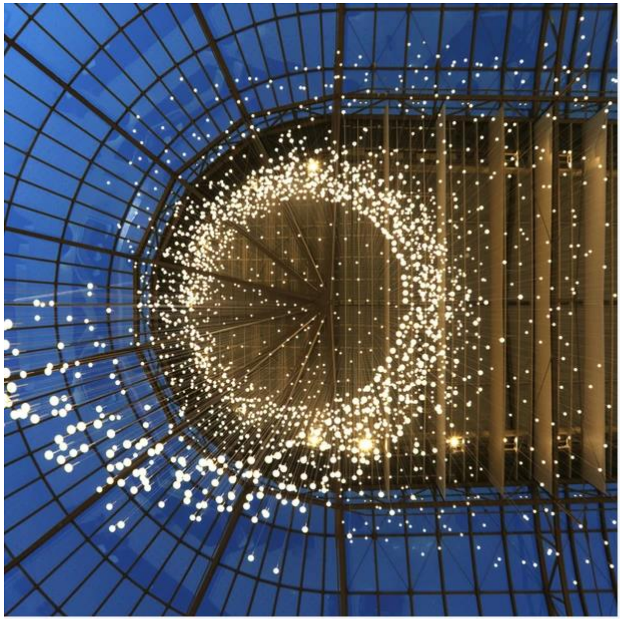
Fast

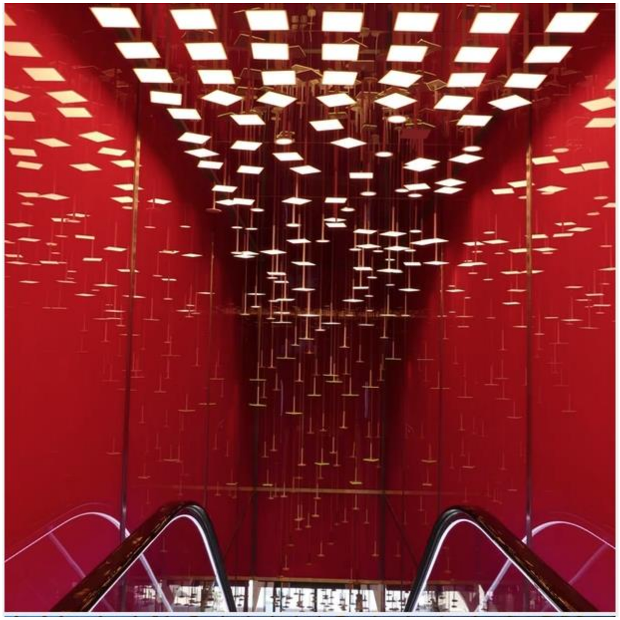
Bright

Ultrahigh resolution

White Lighting is Rapidly Becoming a Reality

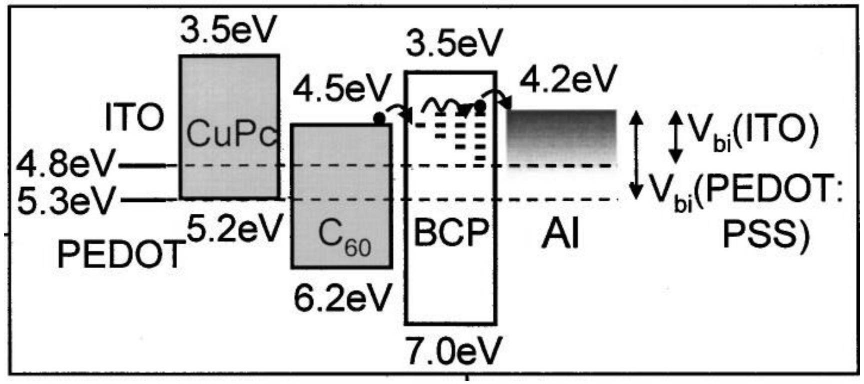




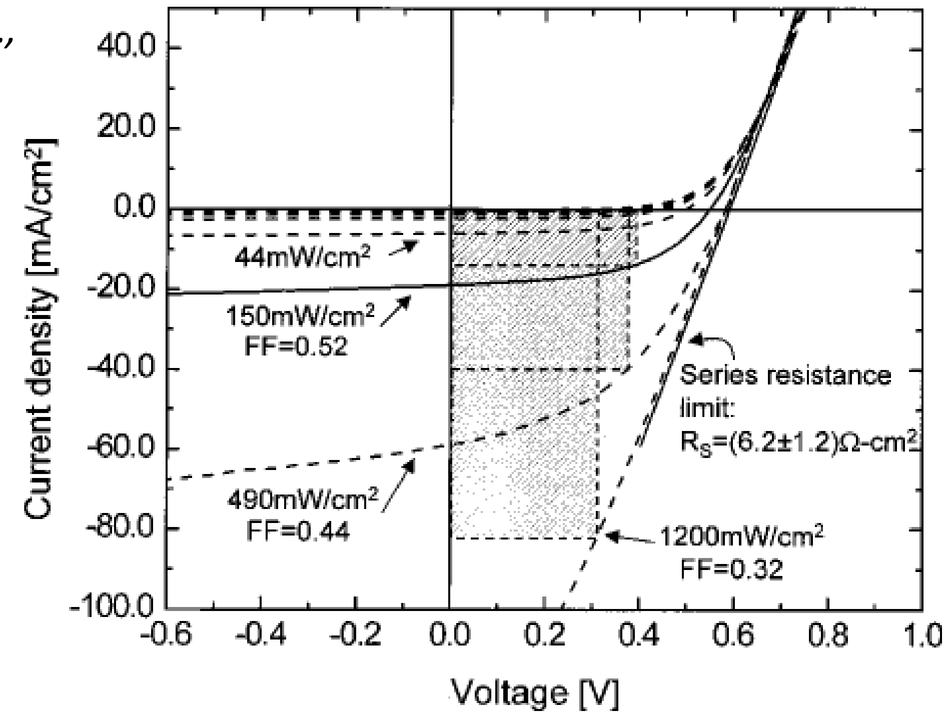


Efficiency Paced by New Materials

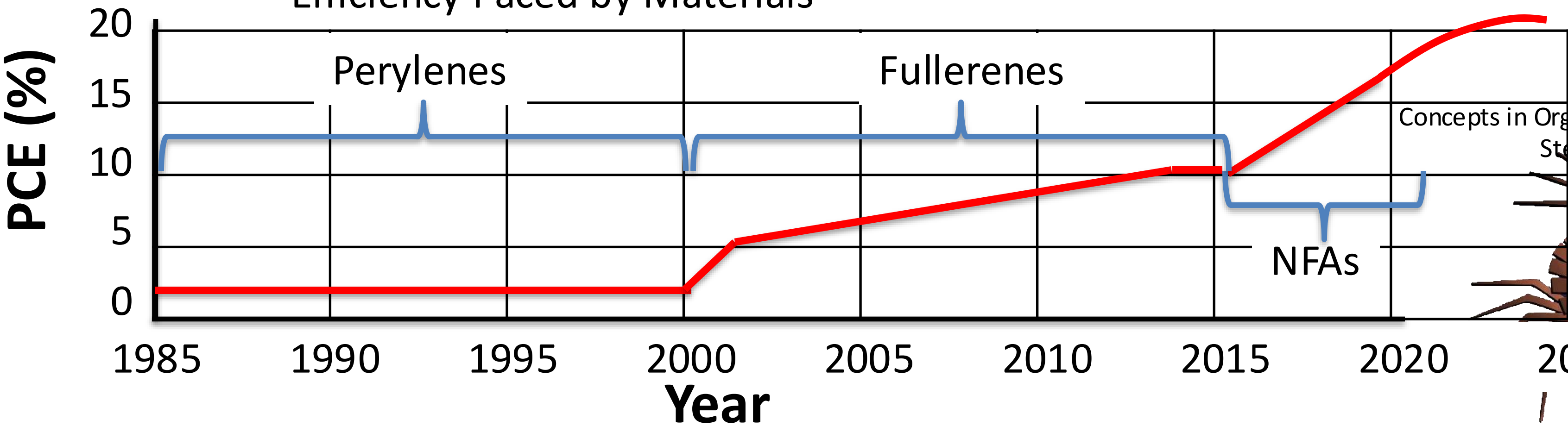
Peumans, P. & Forrest, S. R. 2001. *Appl. Phys. Lett.*,



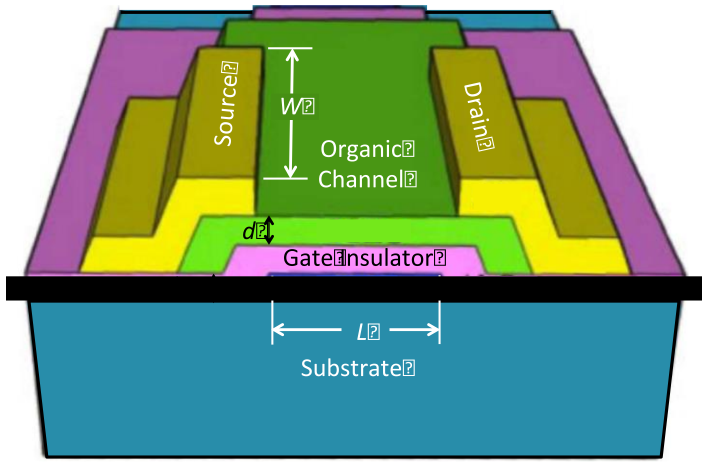
Double Heterojunction confines excitons

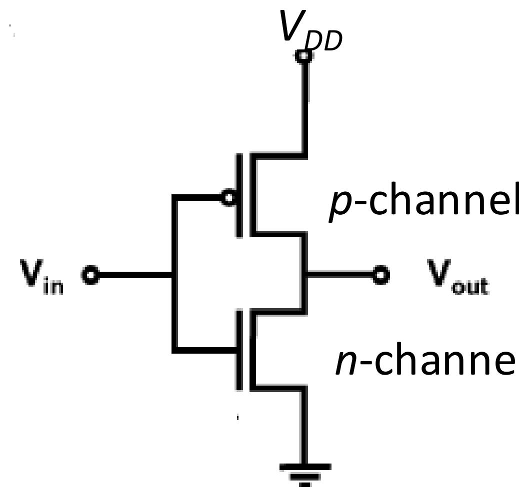


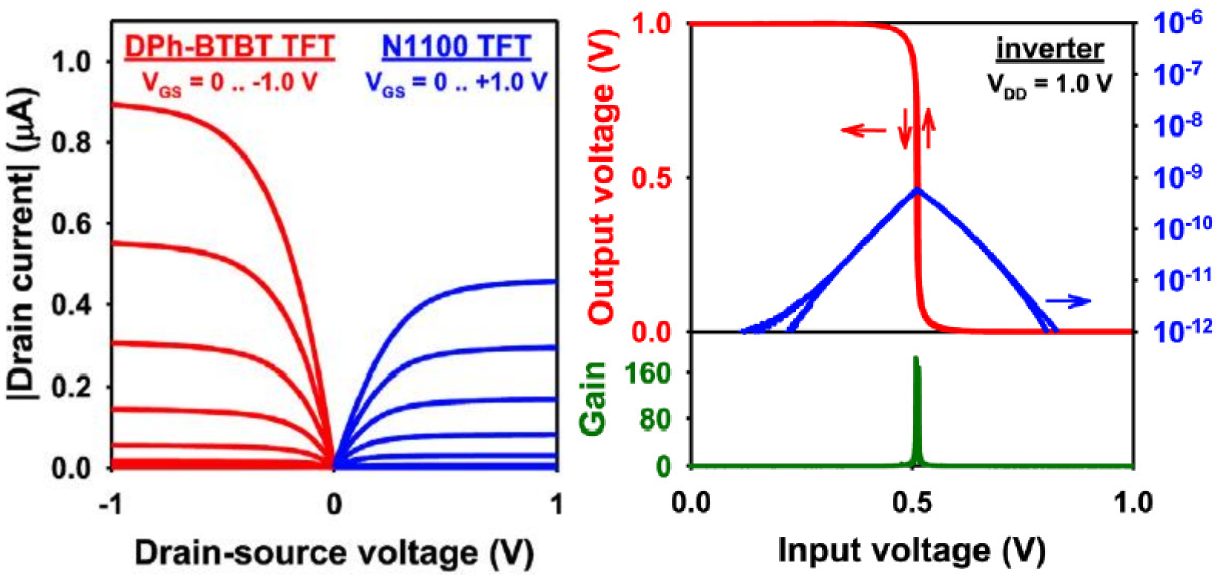
Efficiency Paced by Materials



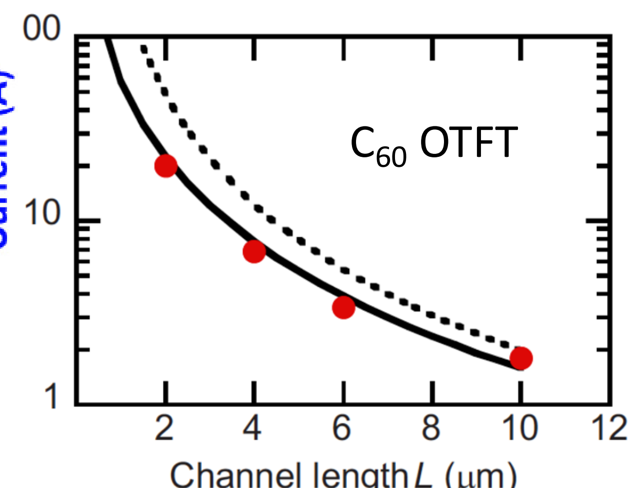
Transistors have come a long way





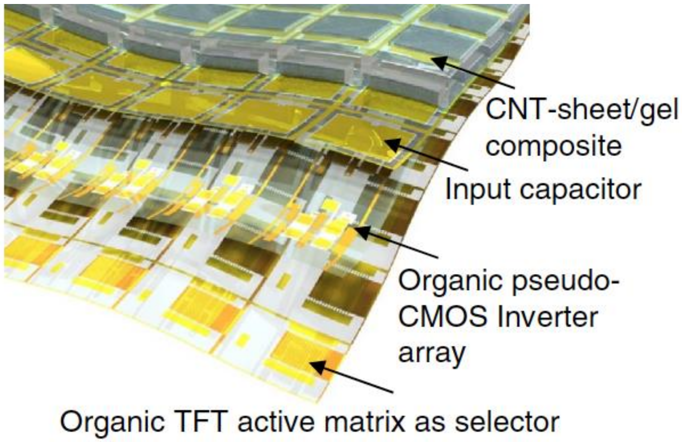


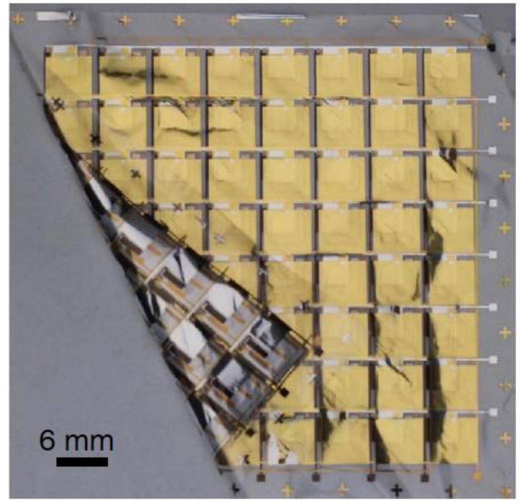
Zschieschang *Organic Electronics*, **49,** 179 (2017).

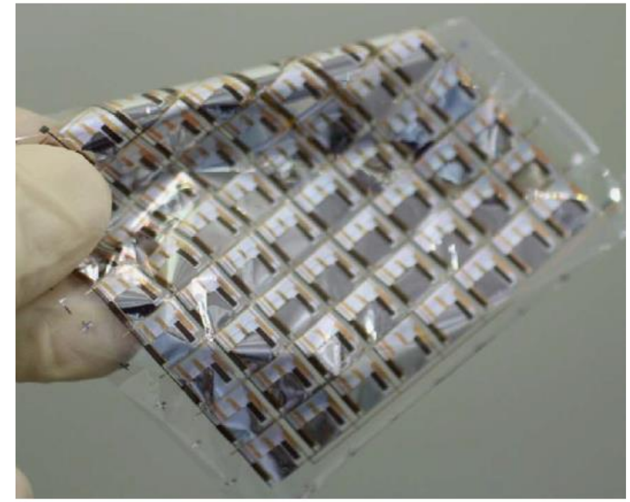


Kitamura, *Appl. Phys. Lett.*, **95,** 023503 (2009).

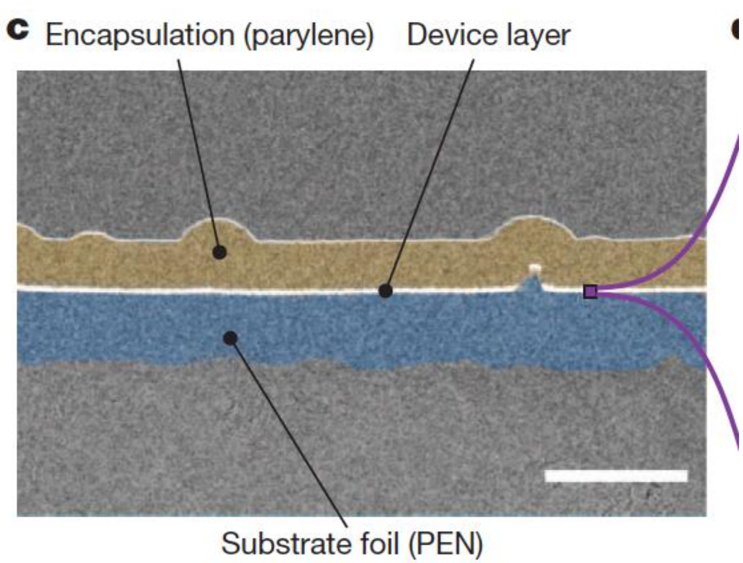
“Imperceptible” Electronics

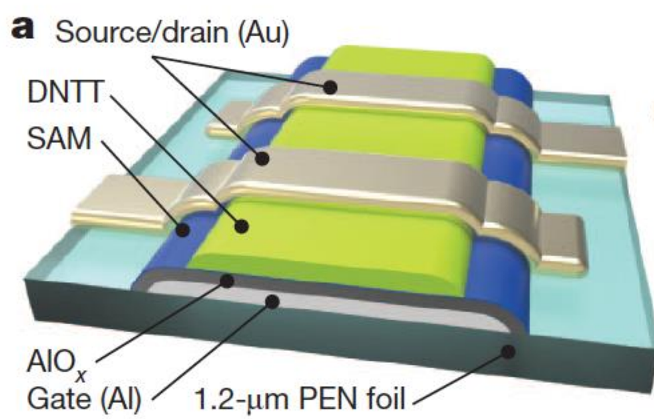






Substrates are 1 μm thick!





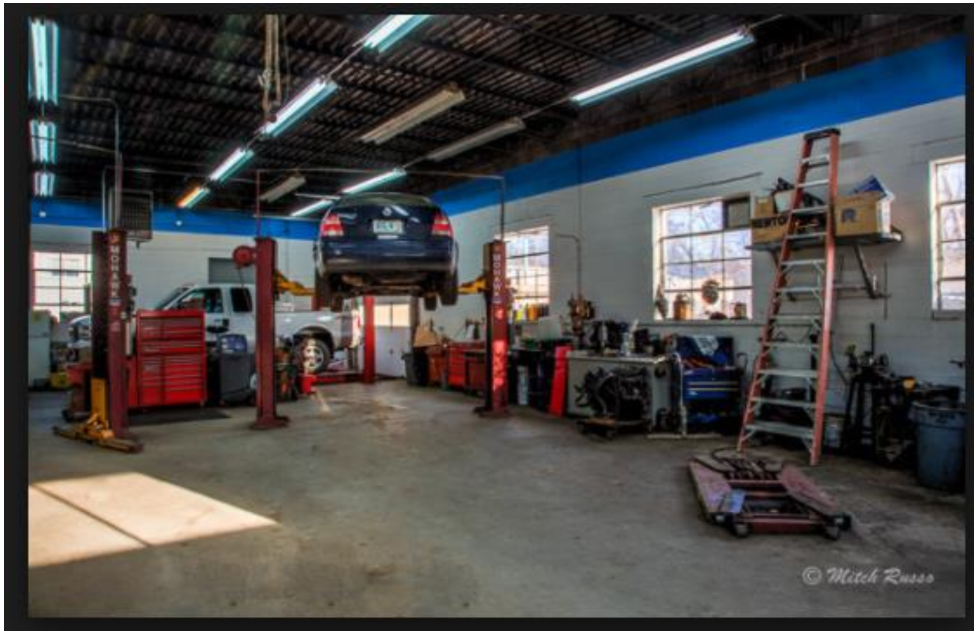
Kaltenbrunner, et al., *Nature*, **499**, 458 (2013).

Plastics: A Brief History

- *Plastic* (noun): an organic polymeric solid that often is lightweight, pliable, moldable
- *Plastic* (adj.): Pliable and easily shaped. Can undergo a permanent change in shape when strained beyond a certain point

- History
  - Natural plastics have been around, well, forever
    - ✓ Rubber
    - ✓ Cellulose (plants)
    - ✓ Collagen (cartilage, ligaments…)
  - First man-made plastics based on cellulose
    - ✓ Parkesine (Alexander Parkes, Birmingham UK, 1856, cellulosic)
    - ✓ John Wesley Hyatt, 1869 (1st synthetic plastic, substitute for ivory)
  - First fully synthetic plastic: Bakelite (Leo Baekeland, 1907)
  - Then all kinds of plastics:
    - ✓ Nylon (Wallace Carothers, 1935): synthetic silk for parachutes, ropes, stockings…
    - ✓ Polystyrene (BASF, 1930s): cups, insulators, insulation
    - ✓ Polyethylene, polypropylene, and on and on
  - Conjugated polymers for electronics (Heeger, Shirakawa, MacDiarmid, 1977): Doped polyethylene

We are in the age of plastics



- Plastic have changed the look of everything
- Today, 20% of the car itself is plastic
- Global plastics industry: $1,000,000,000,000 (I guess there is a great future in plastics!)
- A major source of pollution: Great Pacific Garbage Patch (size of Texas)
- And now they are demanded in all electronic appliances

But not all organic electronic materials are polymers

We are in the age of plastics

- Plastics have changed the look of everything

Plastic Types

- They can be amorphous or polycrystalline or a combination
- Thermoplastics: Can be repeatedly molded due to low glass transition temperature (T_g) – a temperature at which point the material begins to flow
- Thermosets: Can be molded once when heated – undergoes a chemical reaction/cross-linking. MW$\rightarrow\infty$
- Conducting polymers: conjugated backbone