Organic Electronics: Foundations to Applications

This course is divided into two semesters with the following objectives:

- **Semester 1-Foundations topics:** Crystal structure and binding, Optical and electronic properties of organics, and materials growth and patterning. This semester covers material in Chapters 1-5.
- **Semester 2-Applications topics:** Light emitters, light detectors, transistors (including phototransistors), and selected other topics. This semester covers material in Chapters 1-9.

Week 1-1

Introduction to Organic Electronics

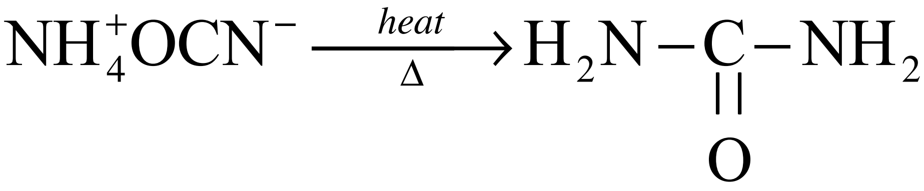
Chapter 1.1 – 1.3

Objectives of Week 1

- 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

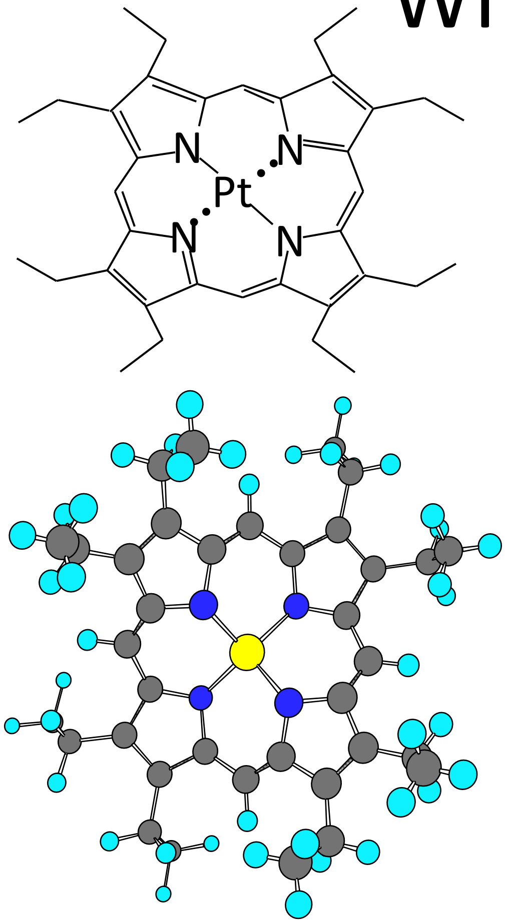
- Formally, a material containing one C-H bond known as an organic material
  - C_{60}, C_{70}, graphene, etc. by this definition are not organics
  - More frequently described as C-rich compounds
  - Can contain metals, any other element
- Extreme variety due to facile chemistry
  - Several million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



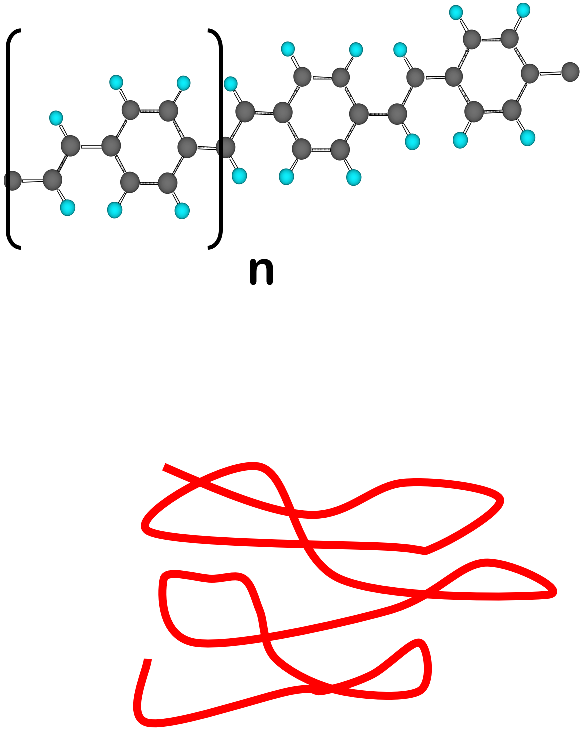
$$\mathrm{NH_4^+OCN^-} \xrightarrow[\Delta]{heat} \mathrm{H_2N-\underset{\underset{O}{||}}{C}-NH_2}$$

Organic (excitonic) materials:

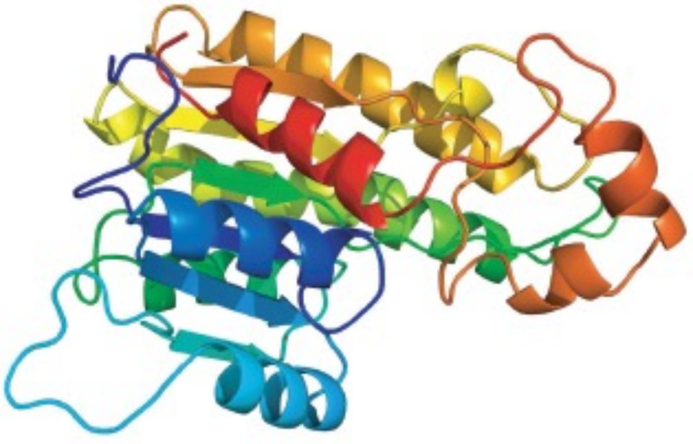
Where the scaling is easy



Monomers



Polymers

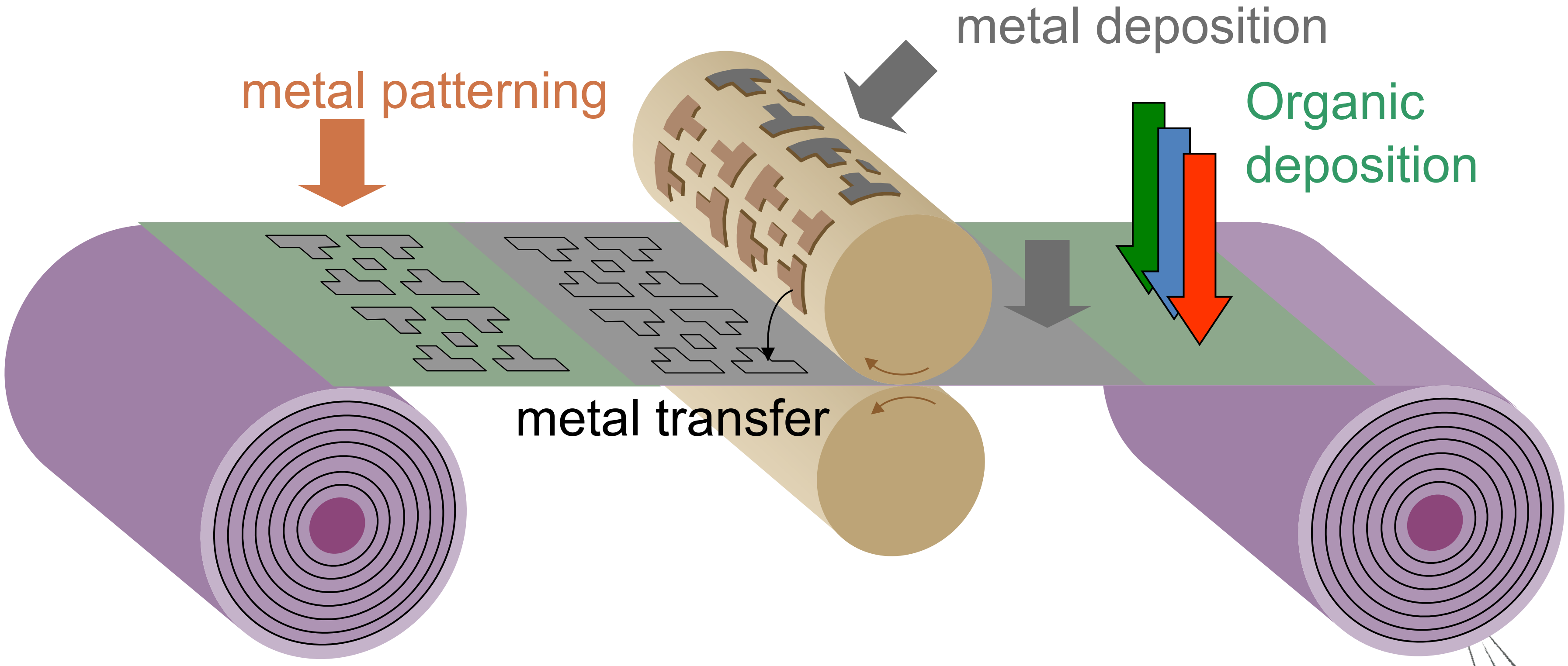


Biological Molecules

Increasing Complexity

The Promise of Organics

Making Large Area Electronics “By the Mile”



metal deposition

metal patterning

Organic deposition

metal transfer

R2R-processing of organic devices

Organic & Inorganic Semiconductors: What makes them different?

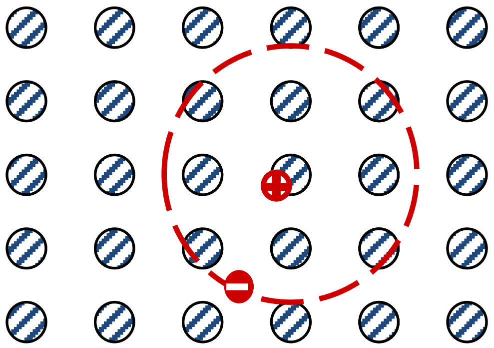
Property	**Organics**	**Inorganics**
Bonding	van der Waals	Covalent/Ionic
Charge Transport	Polaron Hopping	Band Transport
Mobility	~1 $cm^2/V\cdot s$	~1000 $cm^2/V\cdot s$
Absorption	10^5-10^6 cm^{-1}	10^4-10^5 cm^{-1}
Excitons	Frenkel	Wannier-Mott
Binding Energy	~500-800 meV	~10-100 meV
Exciton Radius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

Organic Semiconductors are Excitonic Materials

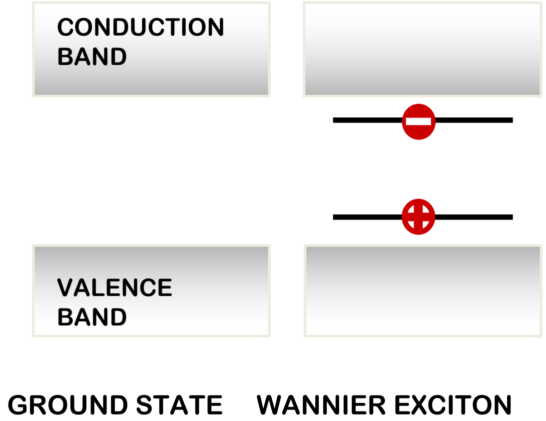
Inorganics **Organics**

Wannier exciton

Inorganic semiconductors



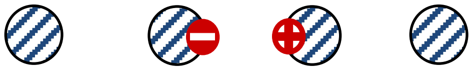
SEMICONDUCTOR PICTURE



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

Charge Transfer (CT) Exciton

(bridge between W and F)

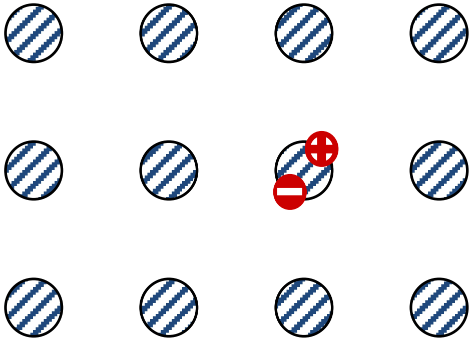


treat excitons as chargeless particles capable of diffusion.

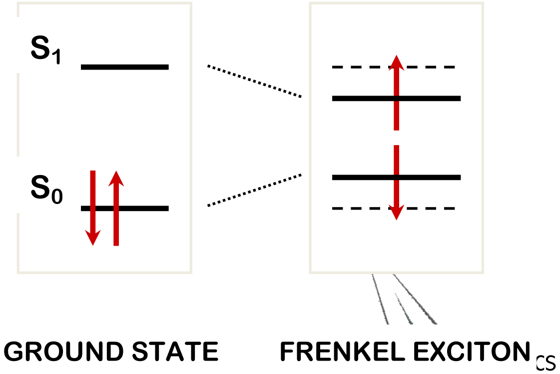
Transport of energy (not charge)

Frenkel exciton

Organic materials



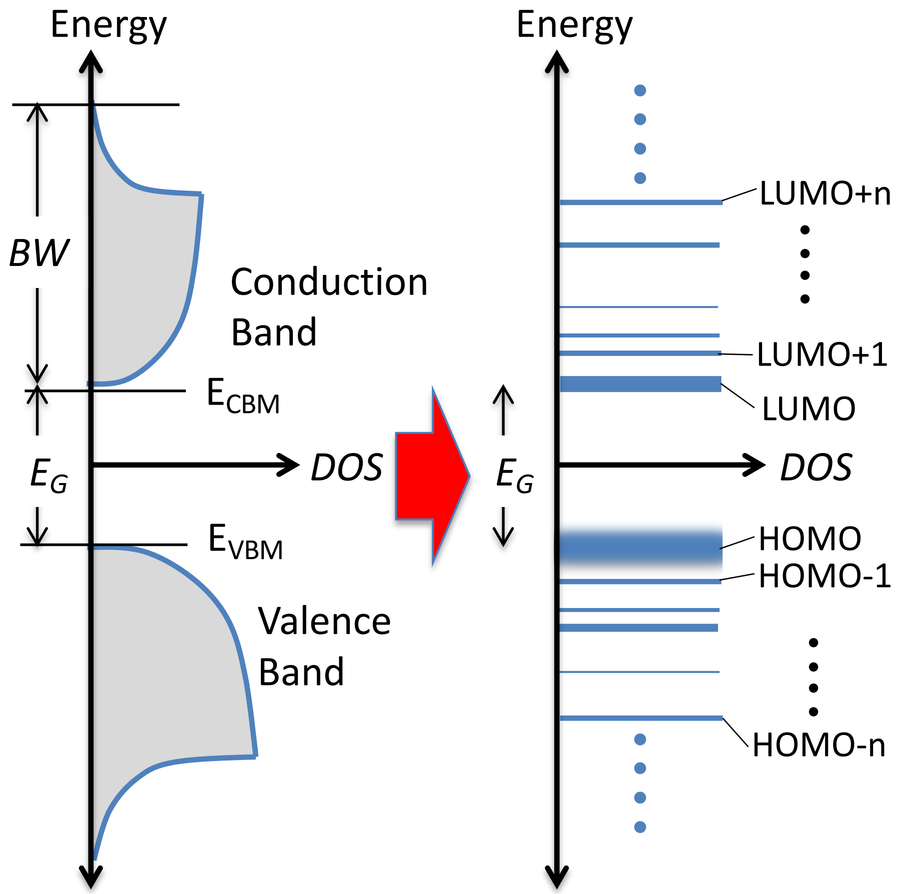
MOLECULAR PICTURE



Stephen R. Forrest

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

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



Conventional Semiconductor

Organic Semiconductor

LUMO: Lowest unoccupied molecular orbital

HOMO: Highest occupied molecular orbital

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…

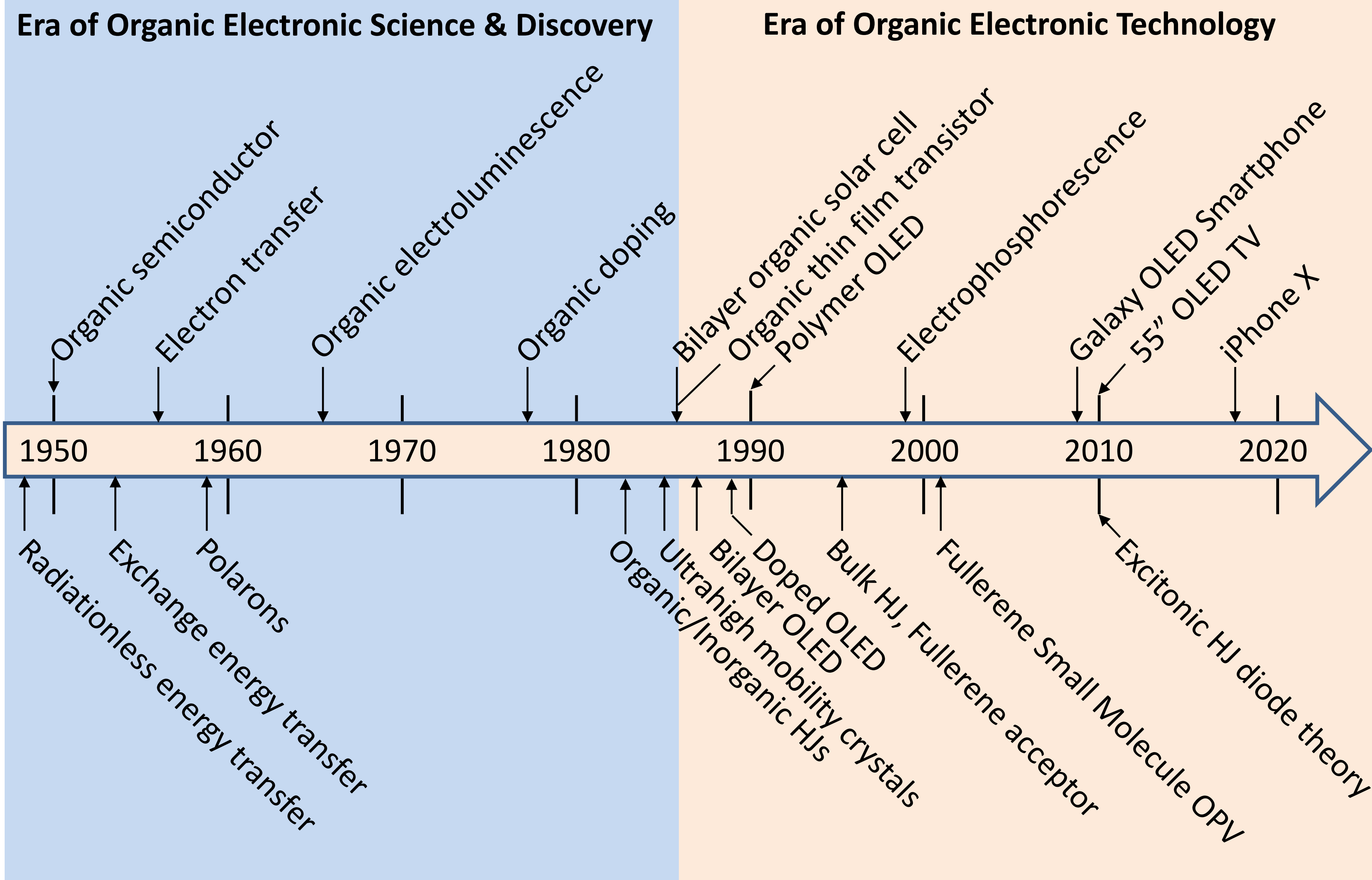
- They are *potentially* inexpensive
- Their properties can be ”easily” modified through chemical synthesis
- They can be deposited on large area, flexible and/or conformable substrates
- They can be very lightweight
- They have excellent optical properties
- They can be manufactured “by the kilometer”

But remember…..

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

Organic Electronics: A Brief History

(with apologies for all that I have omitted)



Era of Organic Electronic Science & Discovery

Era of Organic Electronic Technology

Organic semiconductor

Electron transfer

Organic electroluminescence

Organic doping

Bilayer organic solar cell

Organic thin film transistor

Polymer OLED

Electrophosphorescence

Galaxy OLED Smartphone

55” OLED TV

iPhone X

1950

1960

1970

1980

1990

2000

2010

2020

Radiationless energy transfer

Exchange energy transfer

Polarons

Organic/Inorganic HJs

Ultrahigh mobility crystals

Bilayer OLED

Doped OLED

Bulk HJ, Fullerene acceptor

Fullerene Small Molecule OPV

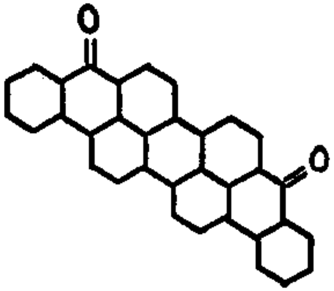
Excitonic HJ diode theory

A Brief History of Organic Electronics

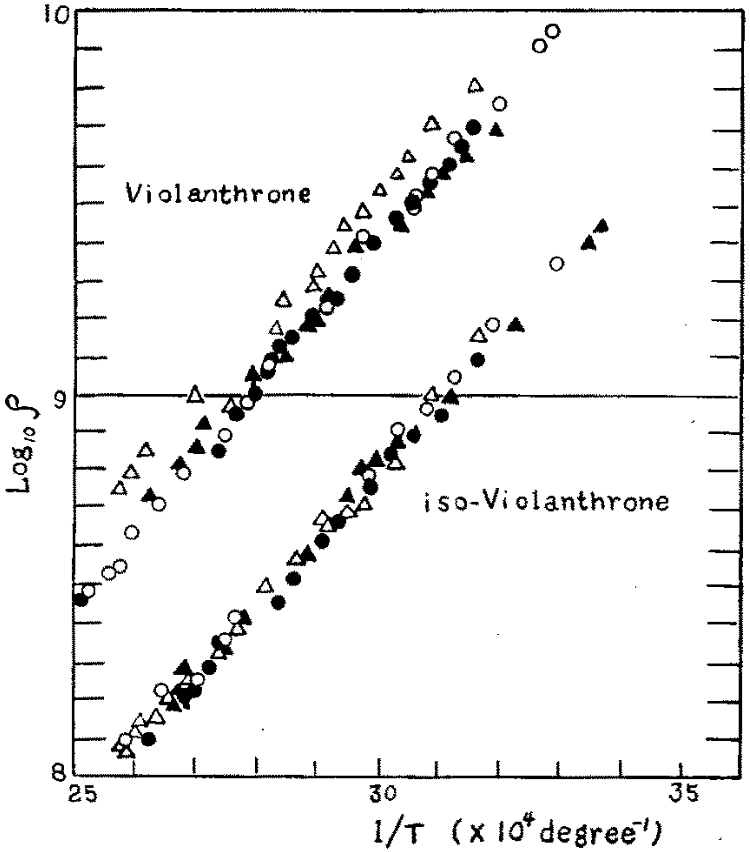
Author	Contribution	Date	Fund./Tech.
Forster	Radiationless energy transfer	1948	F
Inokuchi	Organic semiconductors	1950	F
Dexter	Exchange energy transfer	1953	F
Marcus	Theory of electron transfer	1956	F
Holstein	Polaron theory	1959	F
Helfrich, Schneider	Organic electroluminescence	1965	F
Heeger, MacDiarmid, Shirakawa	High conductivity doped polymers	1977	F
Forrest, Kaplan, Schmidt	Organic/inorganic HJ, PTCDA	1982	F
Warta, Shtele, Karl	Mobility of ultrapurified organics	1985	F
Tang, vanSlyke	Organic solar cell	1986	T
Tang	Bilayer OLED	1987	T
Koezuka, Tsumura, Ando	Polymer TFT	1987	T
Tang, vanSlyke, Chen	Doped OLED	1989	T
Bradley, Holmes, Friend	Polymer OLED	1990	T
Heeger, PCBM	Bulk HJ, PCBM acceptor	1995	T
Baldo, Thompson, Forrest	Electrophosphorescence	1998	T
Peumans, Forrest	C_{60} acceptor	2001	T
Samsung	i7500 Galaxy phone with AMOLED display	2009	T
Giebink, Forrest	Diode theory of organic junctions	2010	F
LG	55” OLED TV	2012	T

Organics Can Be Semiconductors

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



Violanthrone

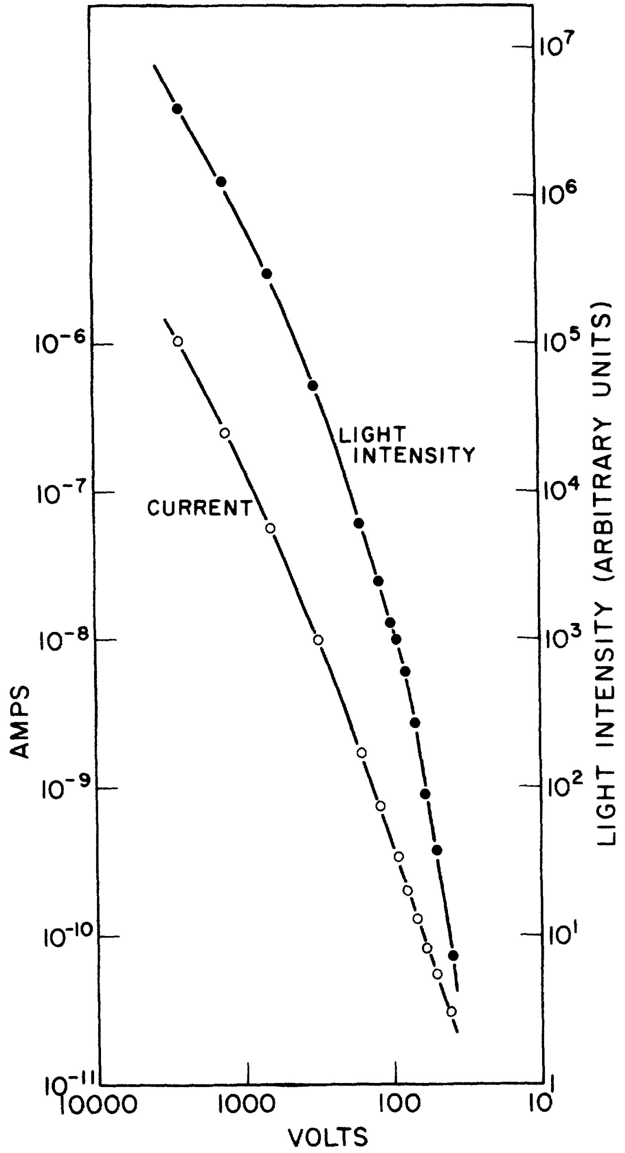


$$\sigma = \sigma_0 \exp(-\Delta\epsilon/2kT),$$

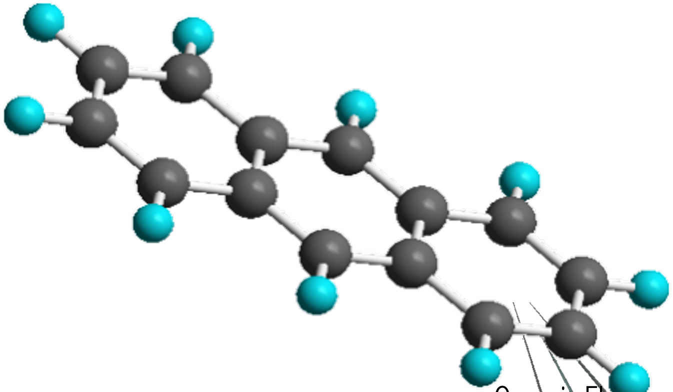
See also B. A. Bolto, R. McNeill and D. E. Weiss: Aust. J. Chem., 16, 1090 (1963) for similar data on polymers (polypyrroles)

Organic Electroluminescence

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

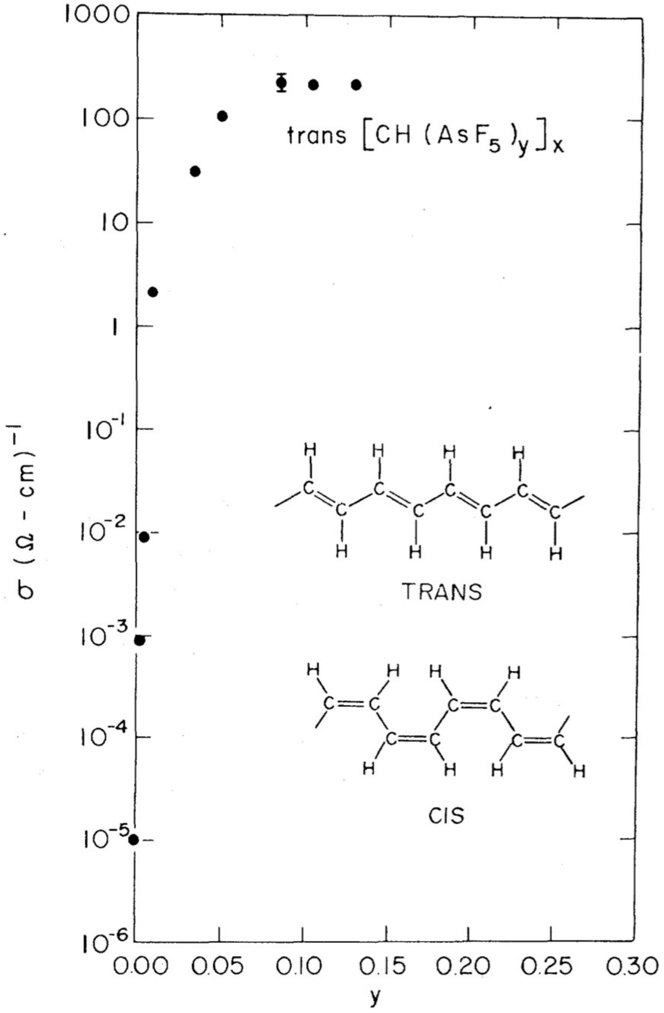


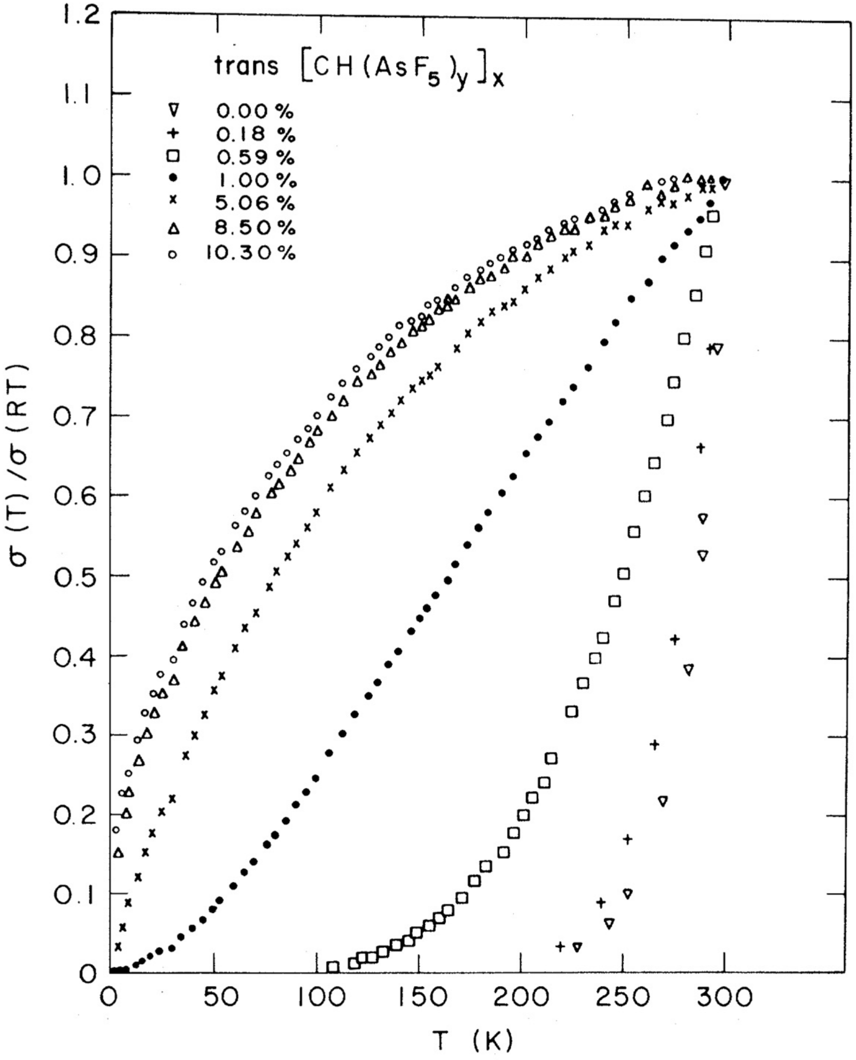
- Anthracene single crystal
- Several mm thick
- Aqueous ionic electrodes
- Blue glow



High Conductivity in Doped Polymers

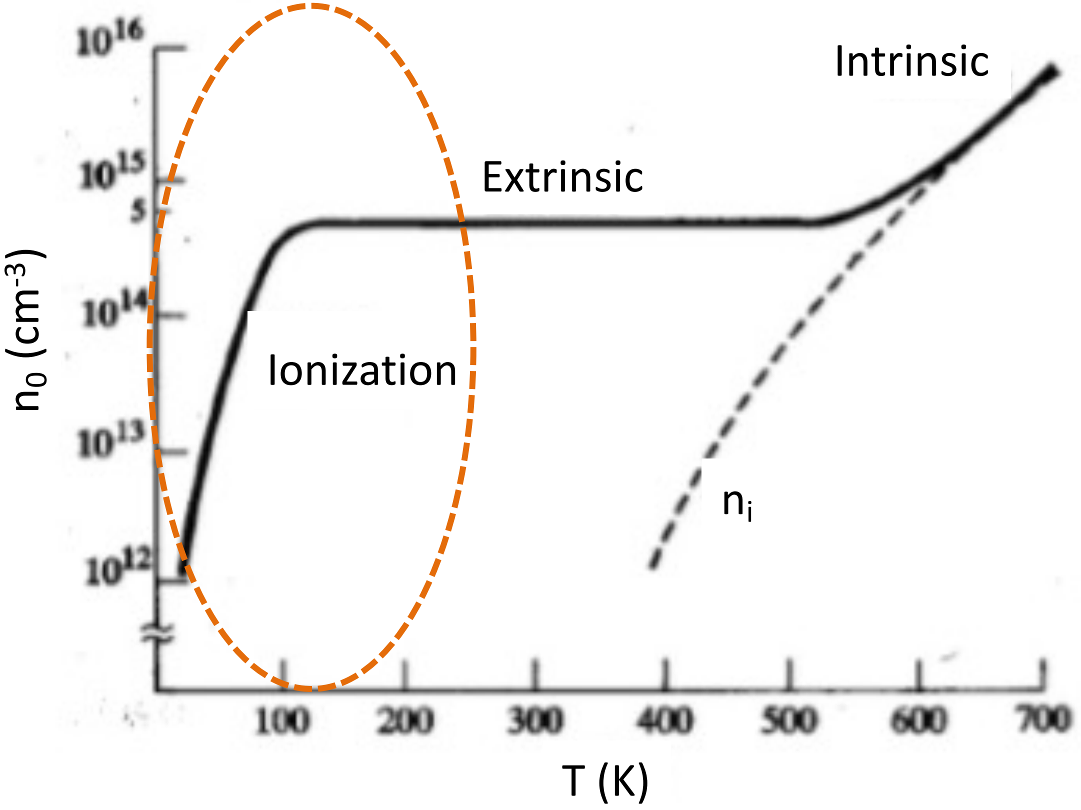
Heeger, Shirakawa, MacDiarmid, et al. Phys. Rev. Lett., **39** 1098 (1977)





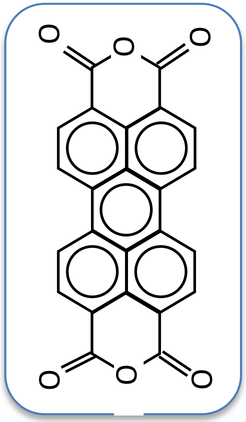
Extrinsic Semiconductor (Extrinsic carrier concentration)

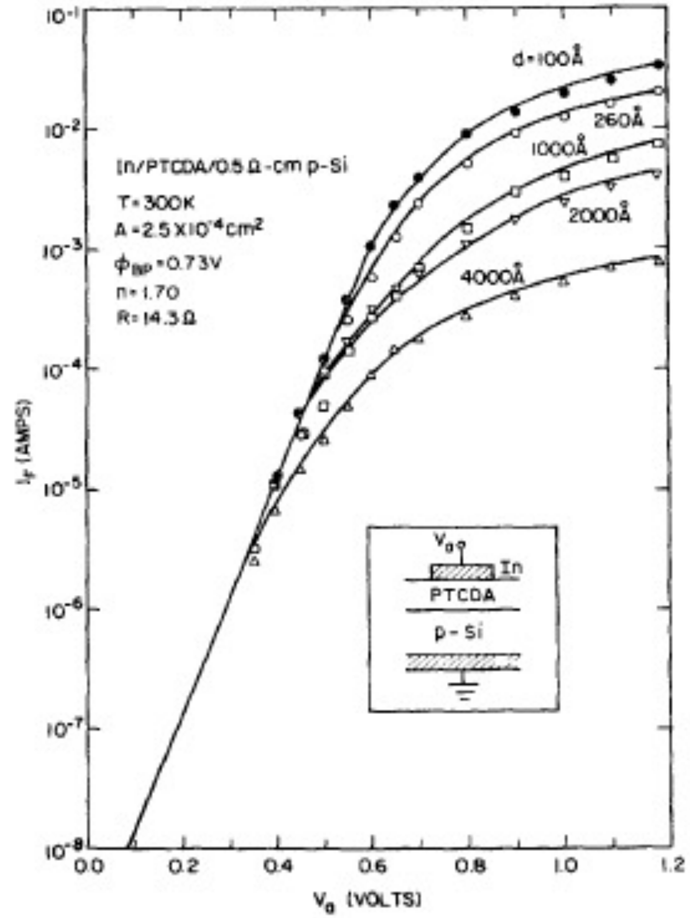
Electron density as a function of temperature

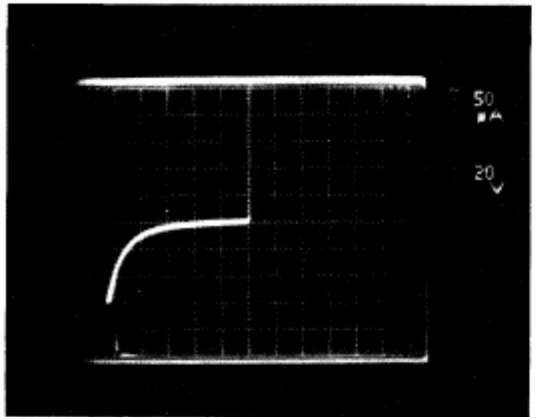


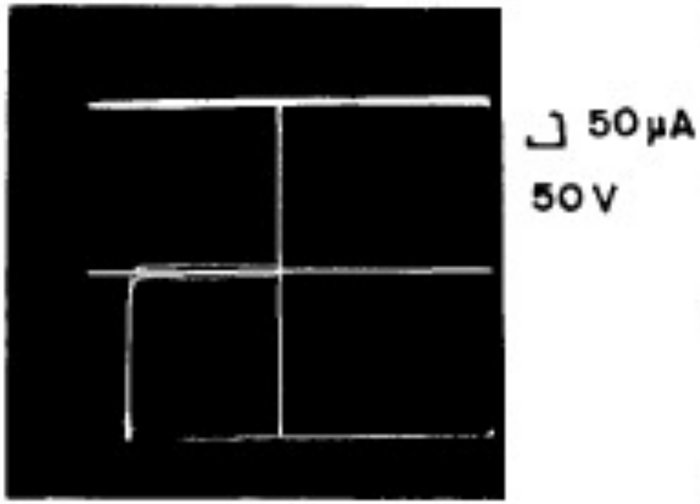
Organic/Inorganic Heterojunctions; PTCDA

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







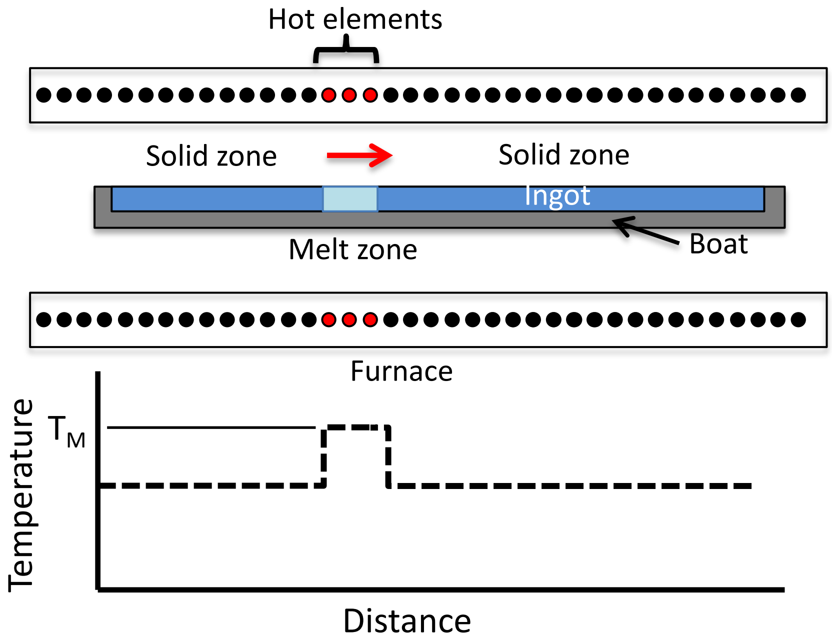


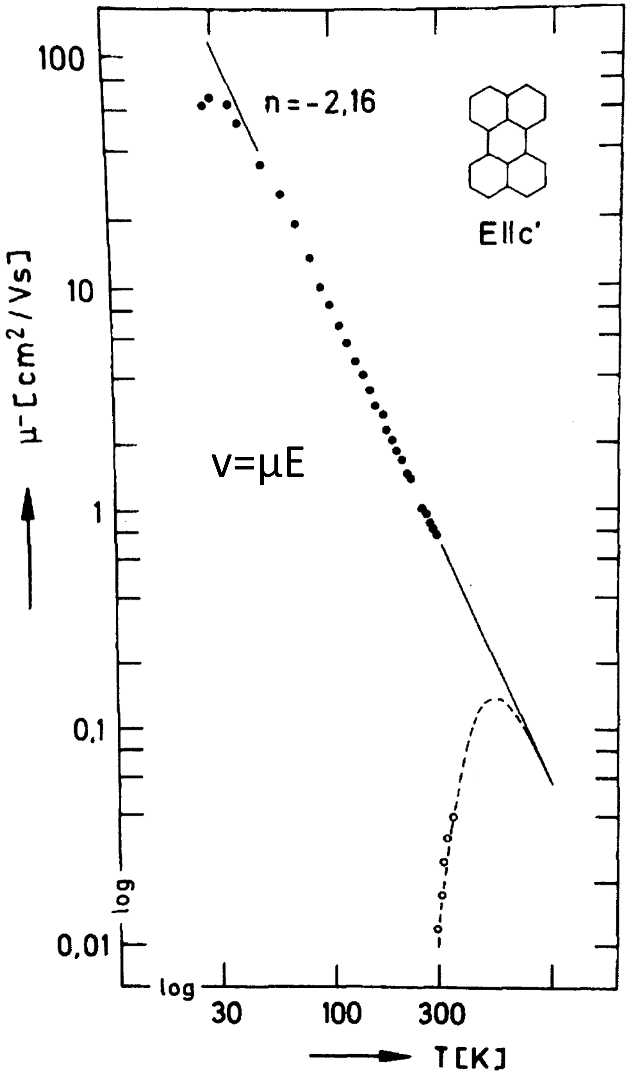
(a) In/PTCDA/10Ω-cm p-Si

PTCDA: An organic electronic archetype

High Mobility in Ultrapure Organics

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

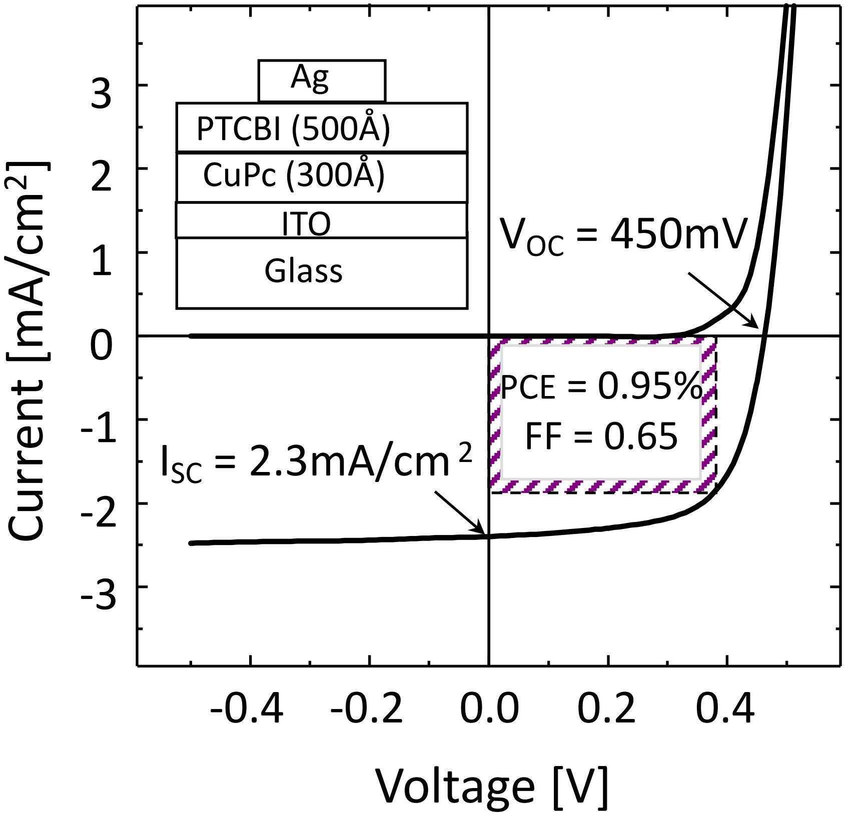




Thin Film Organic Solar Cells

Single Heterojunction Solar Cell

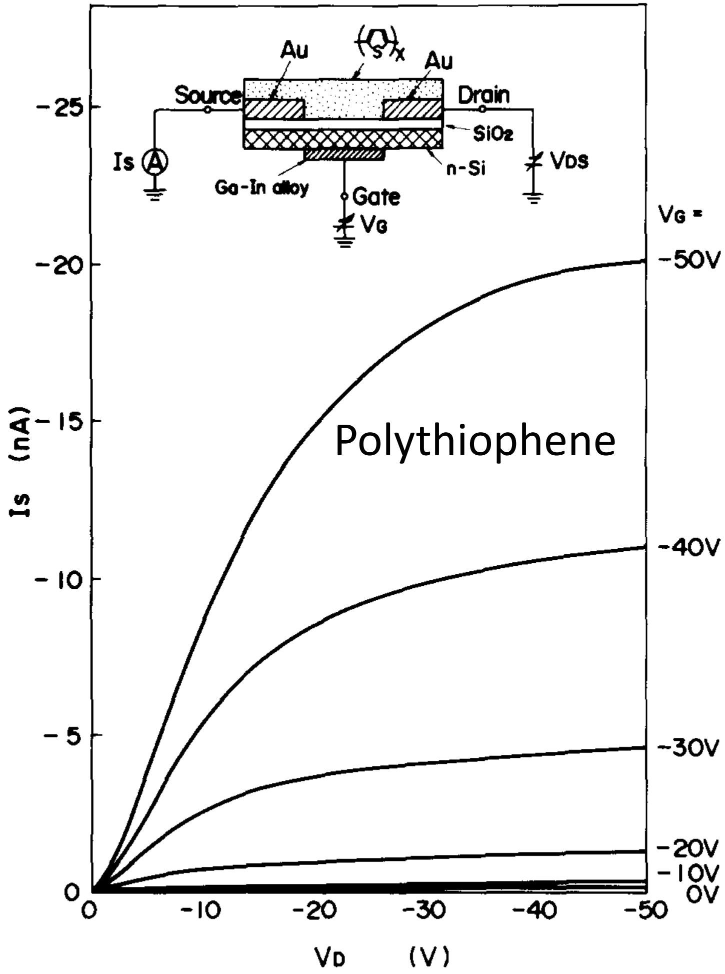
C.W. Tang, Appl. Phys. Lett., **48**, 183 (1986).



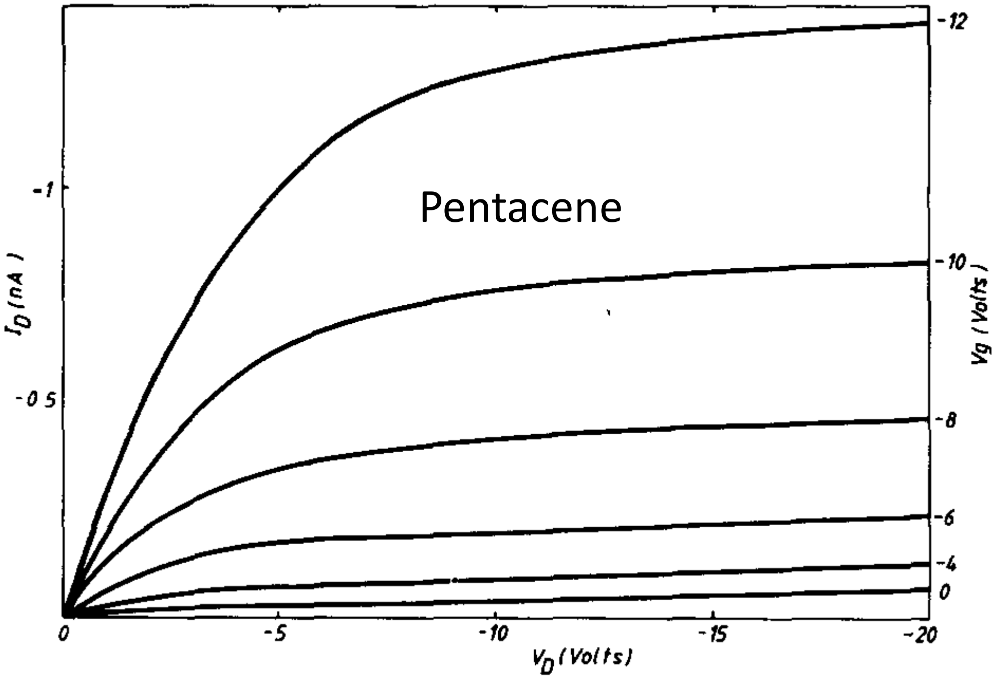
- first **heterojunction** for efficient charge generation
- ~**0.95%** conversion efficiency
- nearly ideal IVs (FF~0.65)
- **full solar illumination** (1 sun)

Organic Thin Film Transistors

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



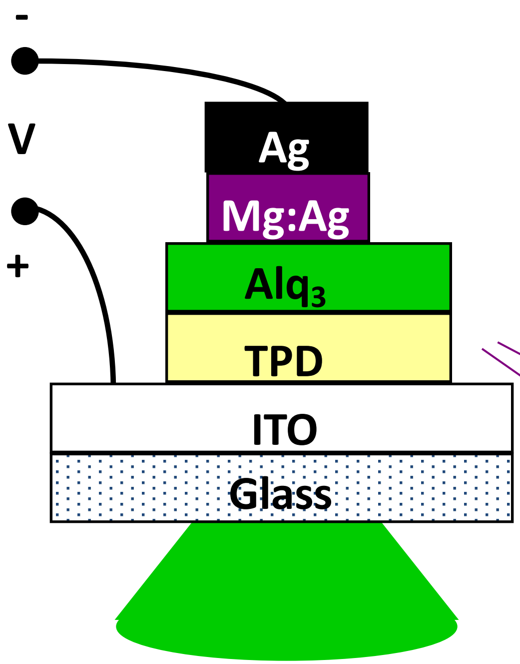
Polythiophene

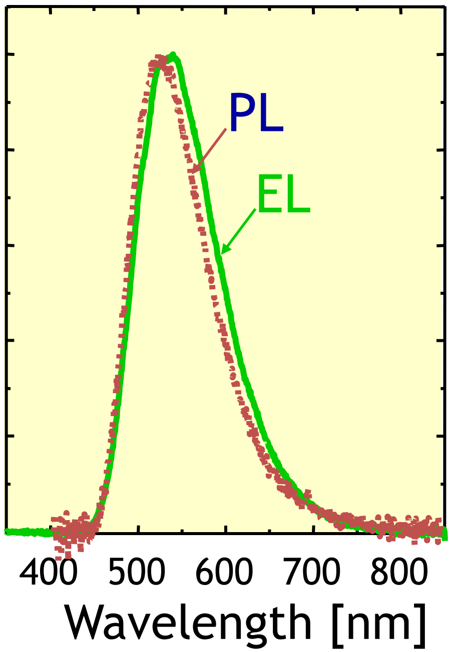


Pentacene

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

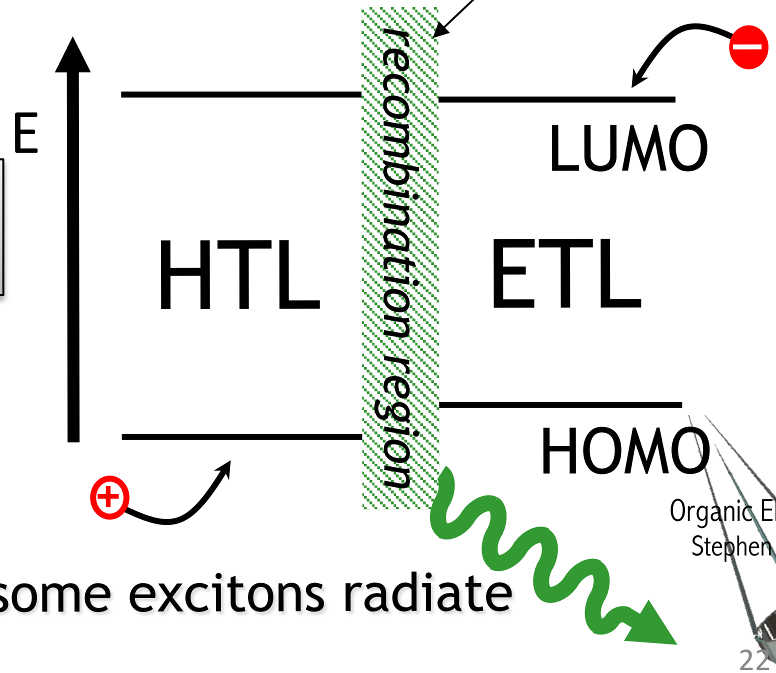
Organic Light Emitting Diode (OLED)



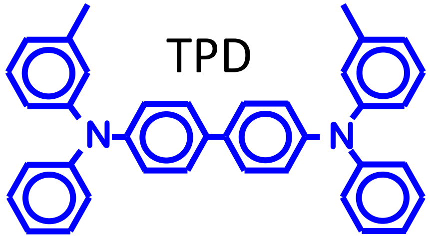


electrons and holes form ***excitons*** (bound e^--h^+ pairs)

Low voltage
EQE=1%

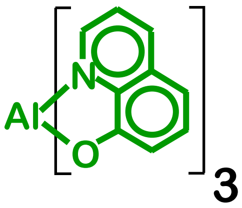


some excitons radiate



TPD

Alq_3

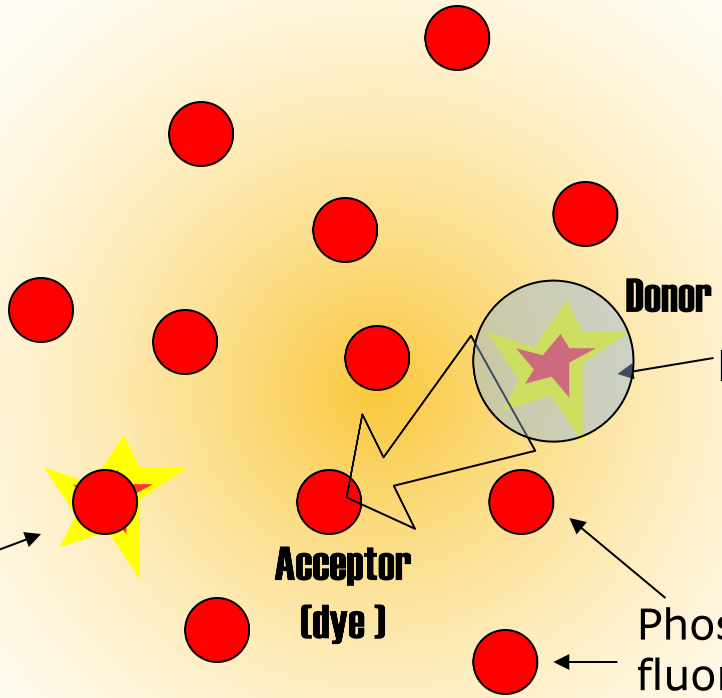


Tang & van Slyke, Appl. Phys. Lett., **51**, 913 (1987)

Luminescence of dye improves if dispersed in host material

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

But excitons must be captured by dispersed dye



Donor

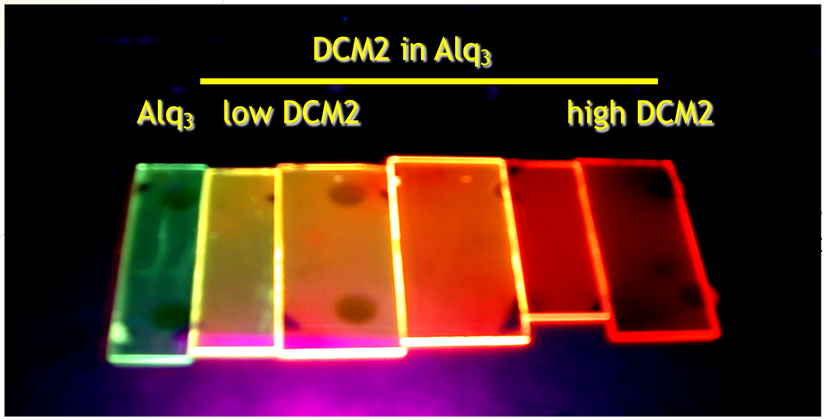
Energy transfer up to ~ 100Å

Charge trapping

Acceptor (dye)

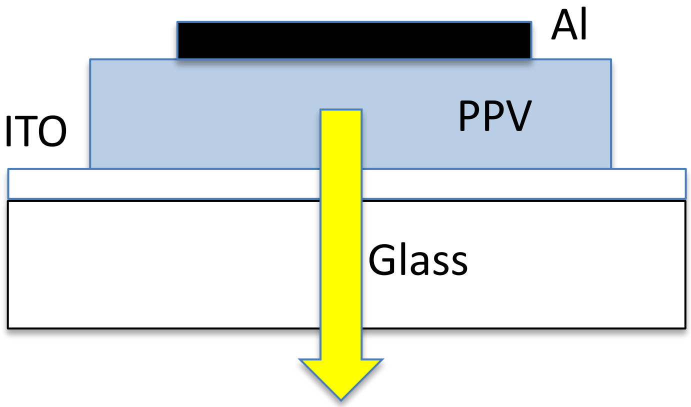
Phosphorescent or fluorescent molecules

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

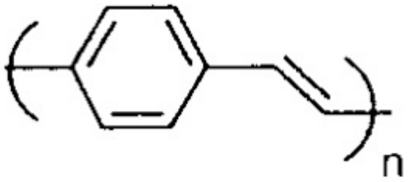


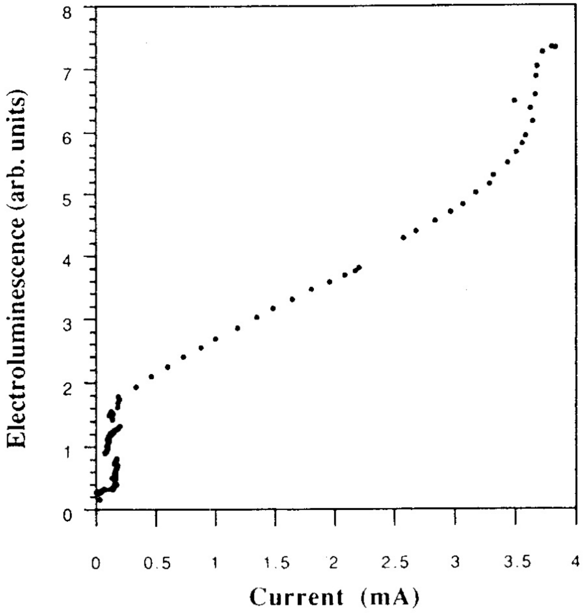
Polymer OLED

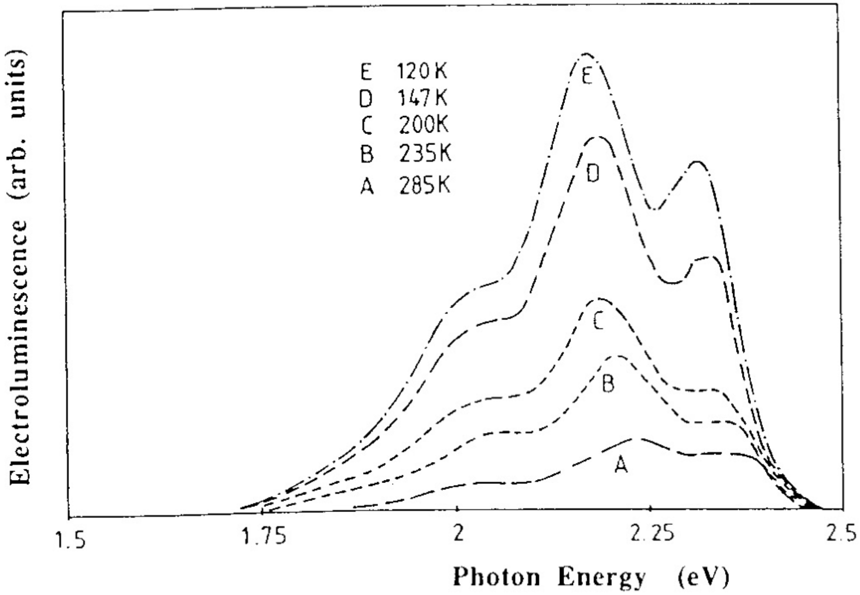
Burroughs, Bradley, Friend et al., *Nature* (1990) **347** 539



EQE ~ 0.05%

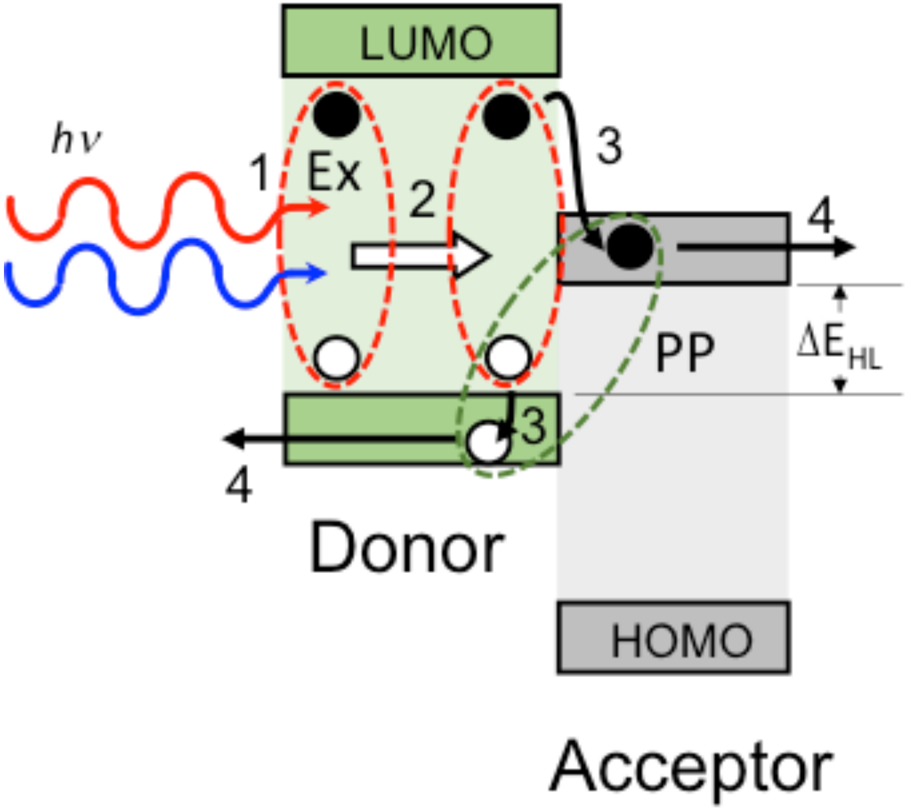






Photogeneration in organics

Processes occurring at a Donor-Acceptor Heterojunction



① Exciton generation by absorption of light

② Exciton diffusion over ~L_D

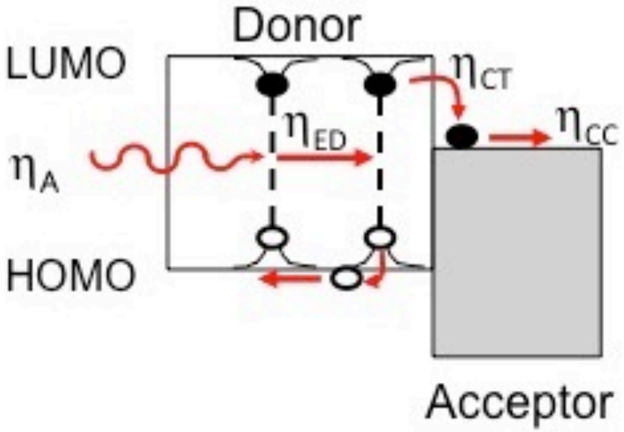
③ Exciton dissociation by rapid and efficient charge transfer

④ Charge extraction by the internal electric field

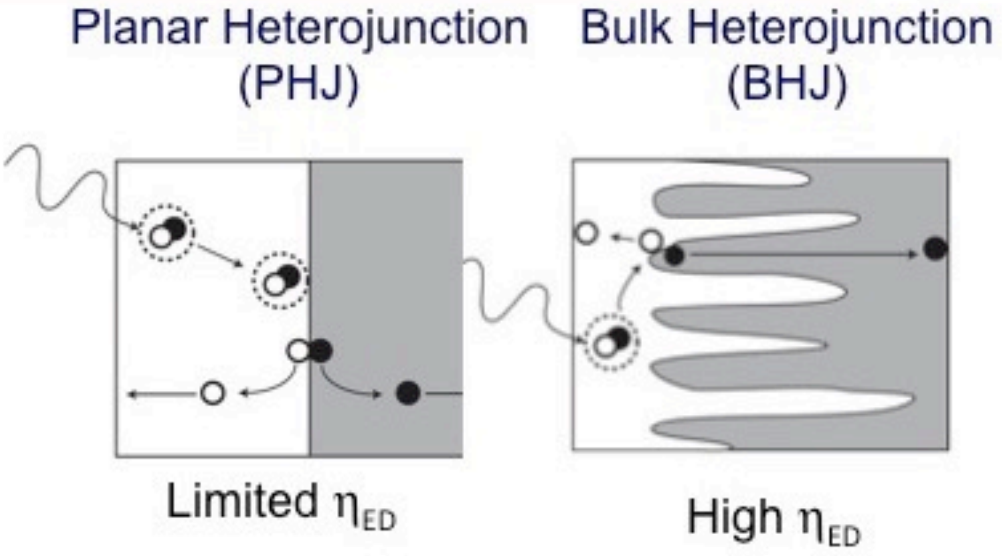
Typically: $L_D << 1/\alpha$

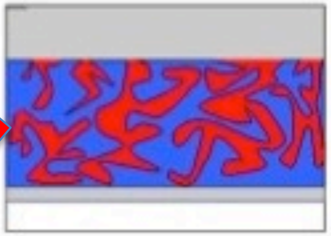
Bulk Heterojunctions Increase OPV Efficiency

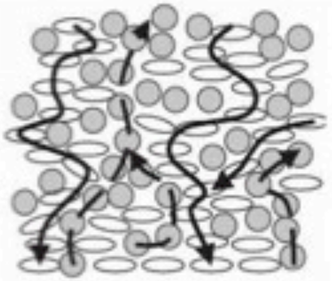
Function follows (nano)structure

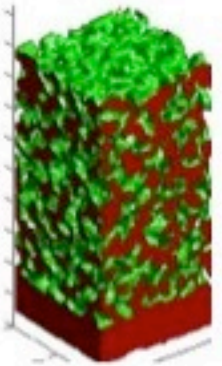


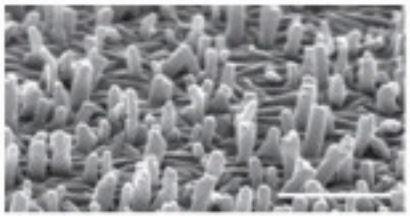
$$\eta_{ext} = \eta_A \eta_{int} = \eta_A \eta_{ED} \eta_{CT} \eta_{CC}$$

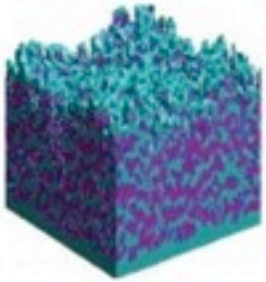










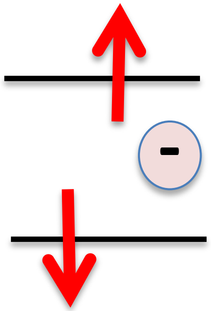


G. Yu, et al., 1995. *Science,* 270, 1789.
Halls, J. J. M. et al., (1995) Nature, 376, 498.

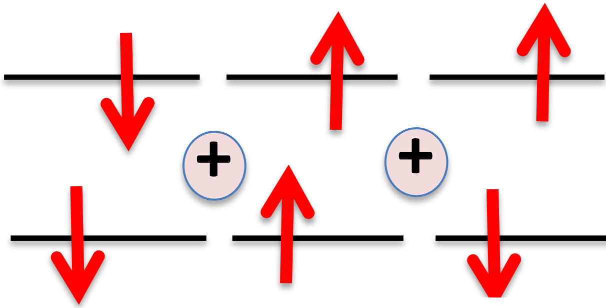
100% Internal Efficiency via Spin-Orbit Coupling

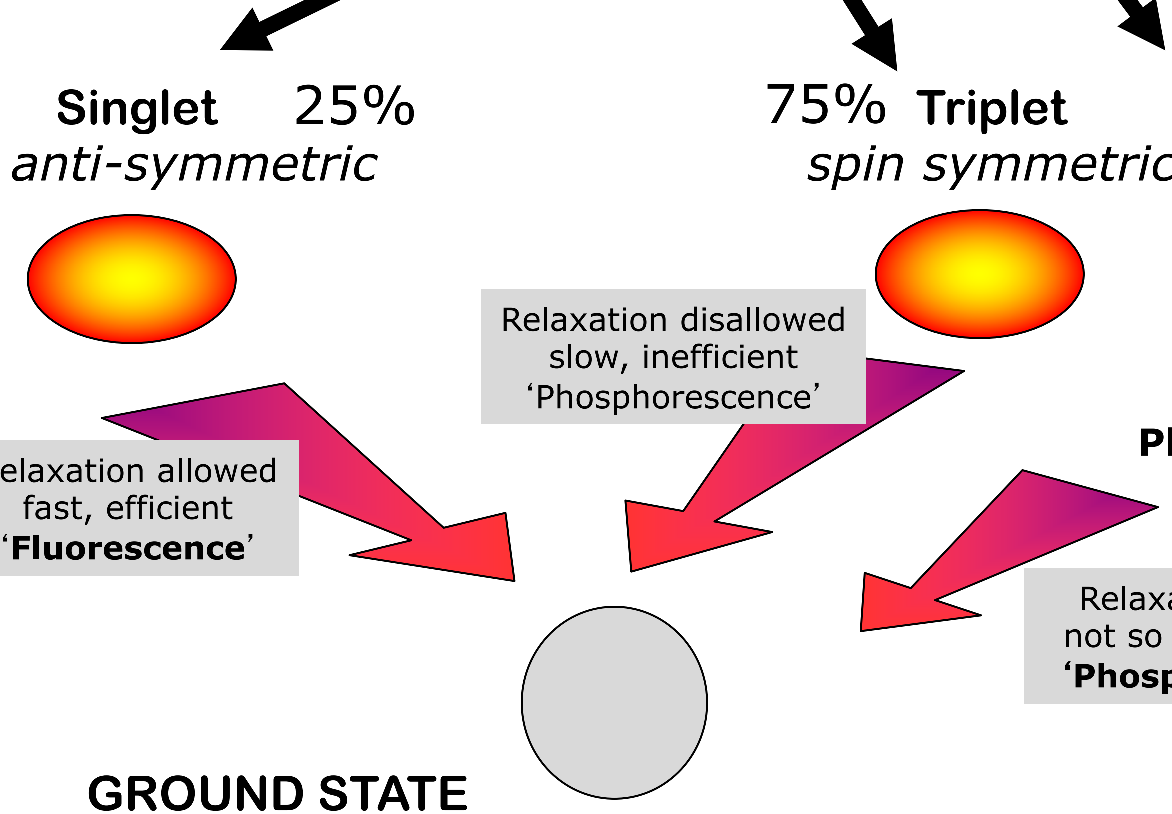
Heavy metal induced electrophosphorescence ~100% QE

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



MOLECULAR EXCITED STATES
AFTER ELECTRICAL EXCITATION

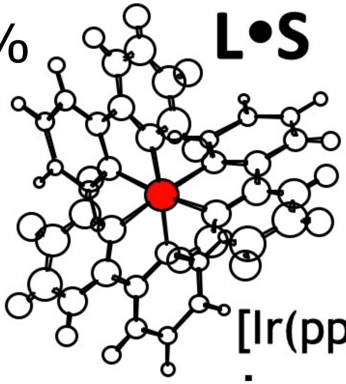




Singlet 25%
spin anti-symmetric

75% **Triplet**
spin symmetric

100%



[Ir(ppy)$_3$]

Relaxation disallowed
slow, inefficient
'Phosphorescence'

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

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

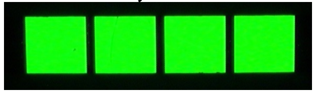
Relaxation allowed
not so slow, efficient
'**Phosphorescence**'

GROUND STATE
spin anti-symmetric

Organic Electronics
Stephen R. Forrest

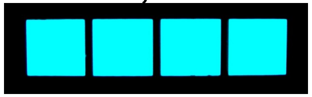
PHOLEDs Cover the CIE and Super CIE Gamuts

0.33, 0.63

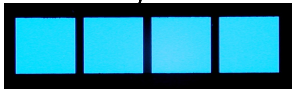


0.17, 0.38

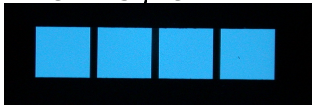
0.16, 0.37



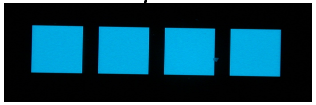
0.16, 0.29



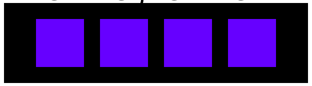
0.15, 0.22

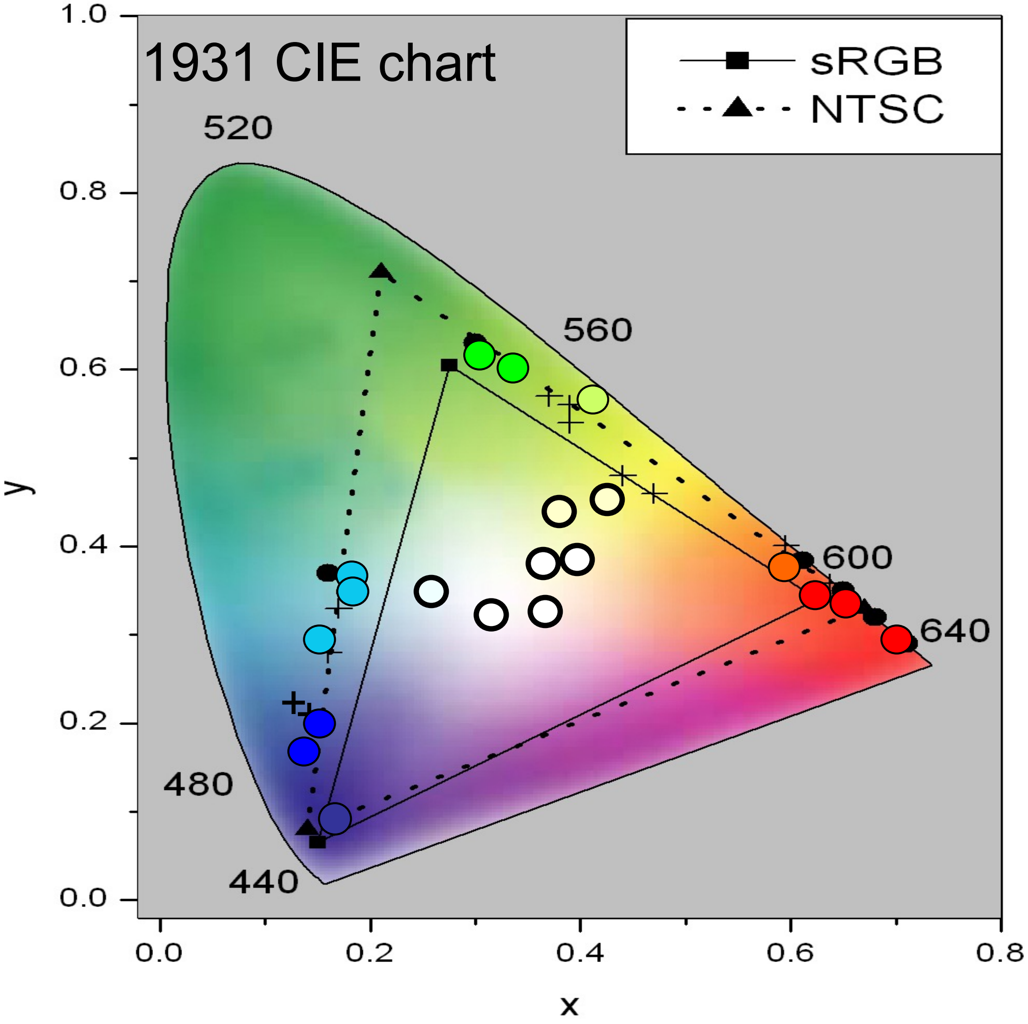


0.14, 0.13

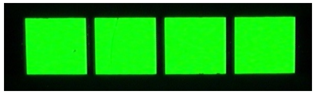


0.16, 0.10

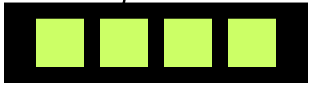




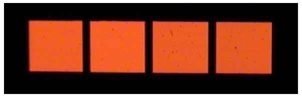
0.35, 0.61



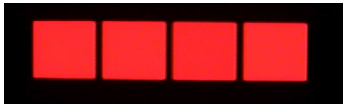
0.42, 0.57



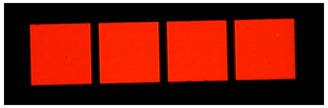
0.62, 0.38



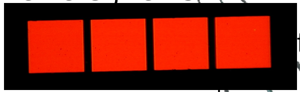
0.65, 0.35



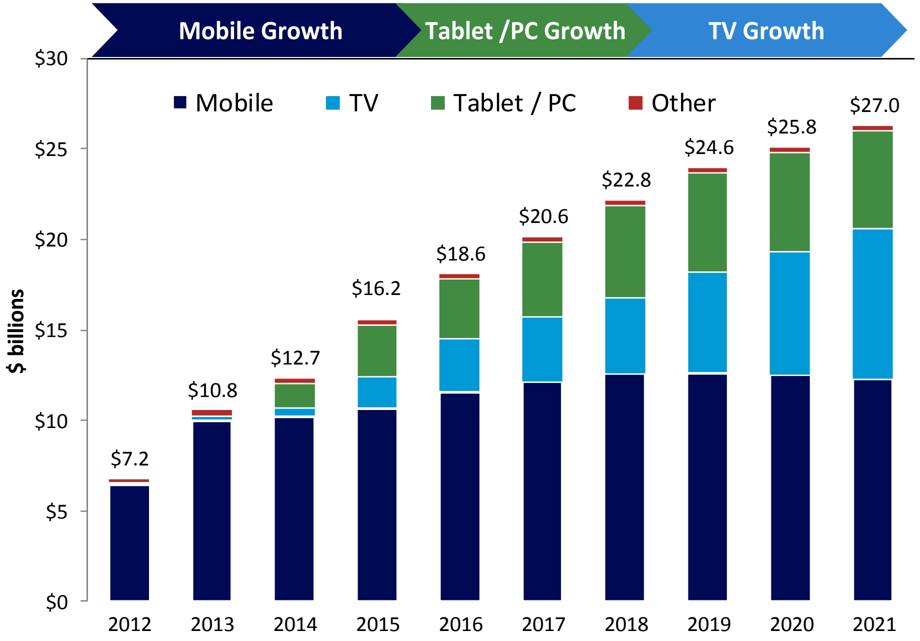
0.67, 0.33



0.68, 0.32



AMOLED Displays: Driving the Technology



Source: DisplaySearch, Q2'14

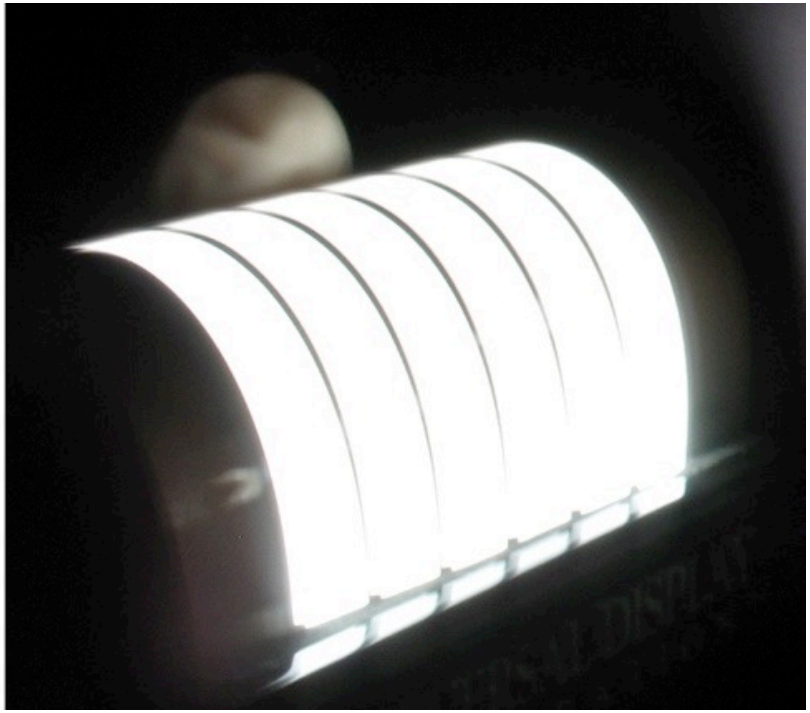
2010: Galaxy Phones
Phosphorescent R,G
>2 Billion sold ?!

2012: LG 55" & Samsung
Phosphorescent TV, $1500
2017: iPhone X

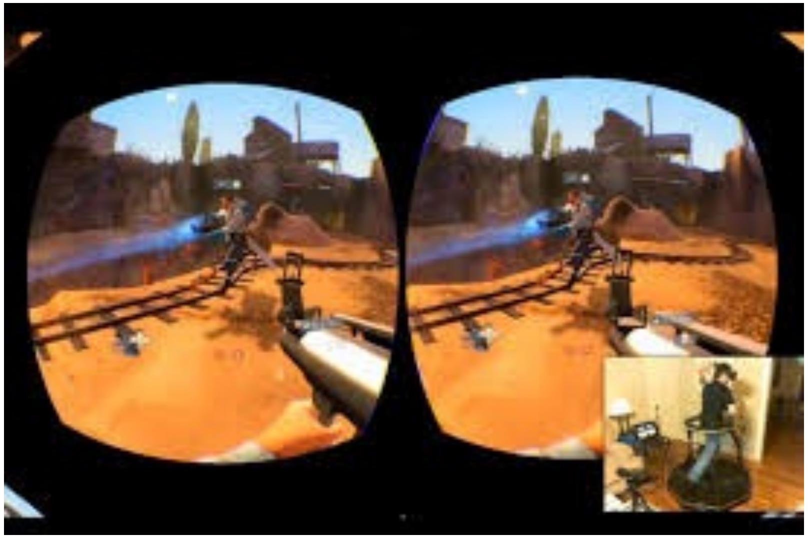
2014-15: 65" and 77" OLED TVs
2016: 4K OLED TV

Panasonic, Sony, Toshiba….(2017)

The Future is Flexible



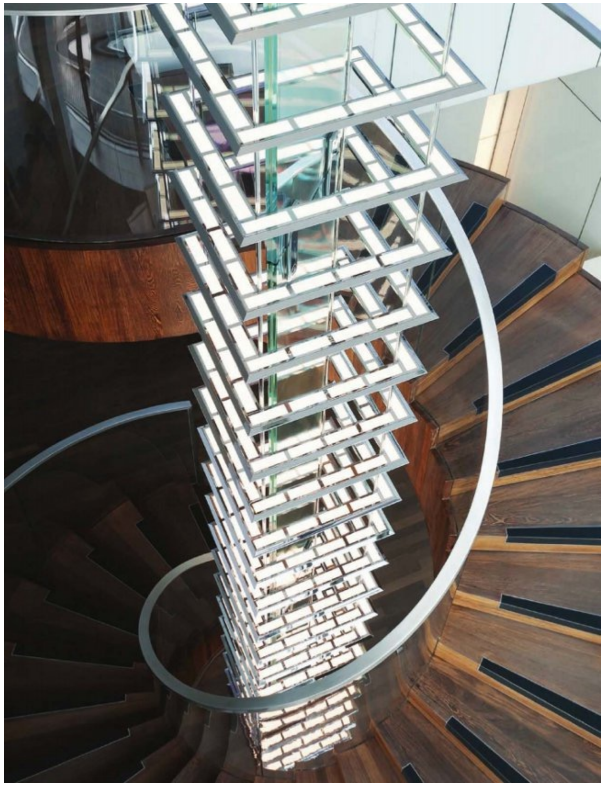
Virtual and Augmented Reality Enabled by OLEDs

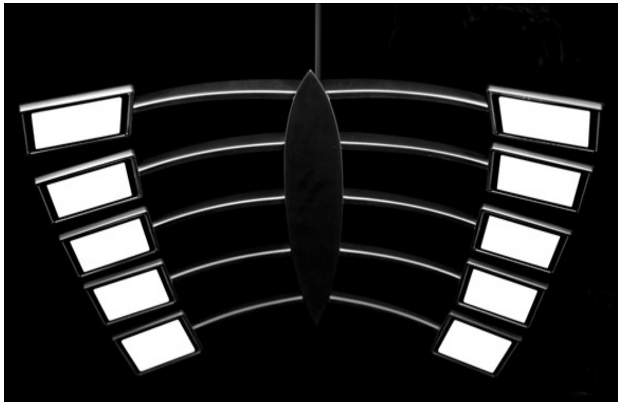


Requirements

Fast
Bright
Ultrahigh resolution

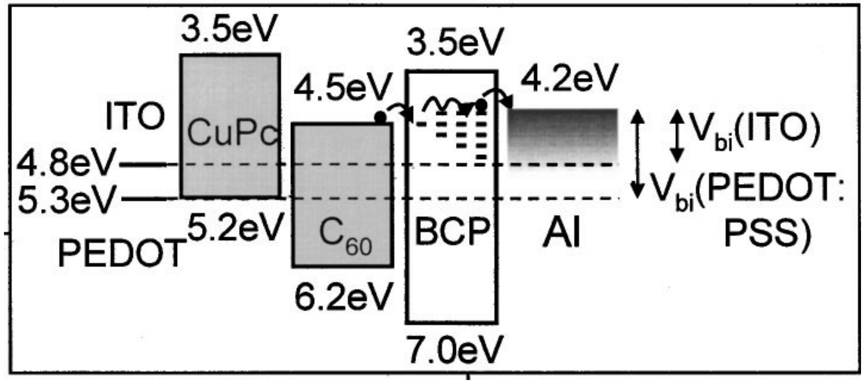
White Lighting is Rapidly Becoming a Reality



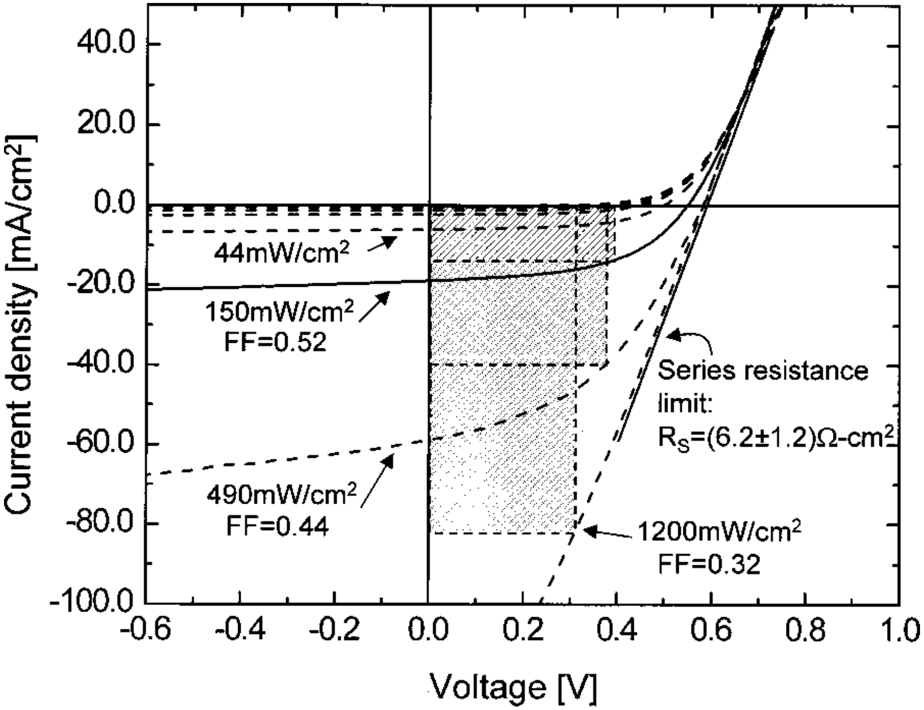


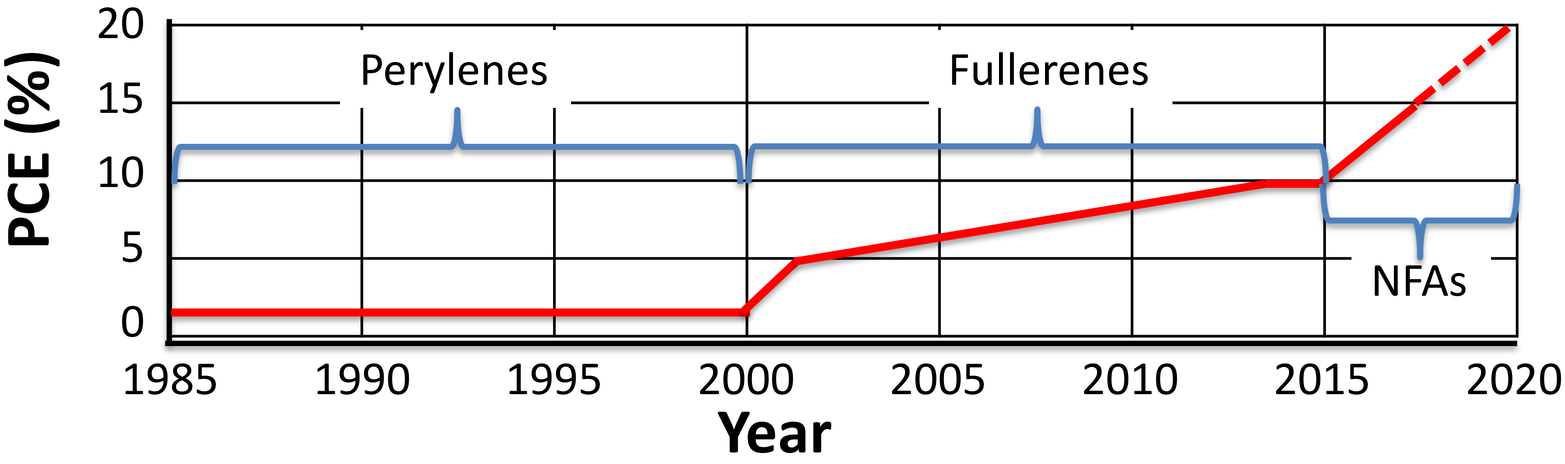
Efficiency Paced by New Materials

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

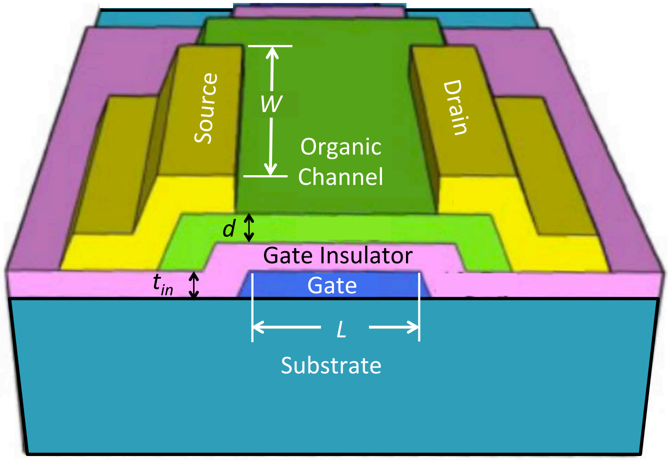


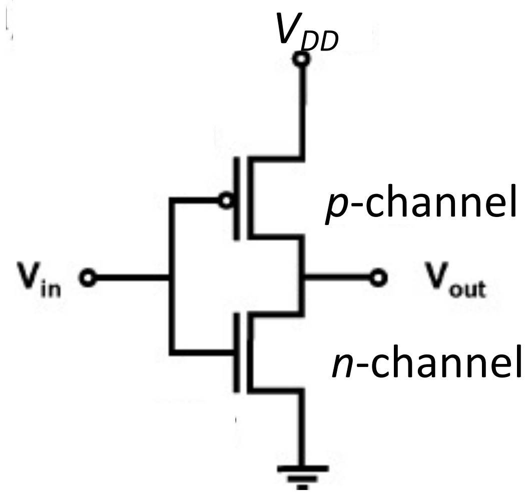
Double Heterojunction confines excitons

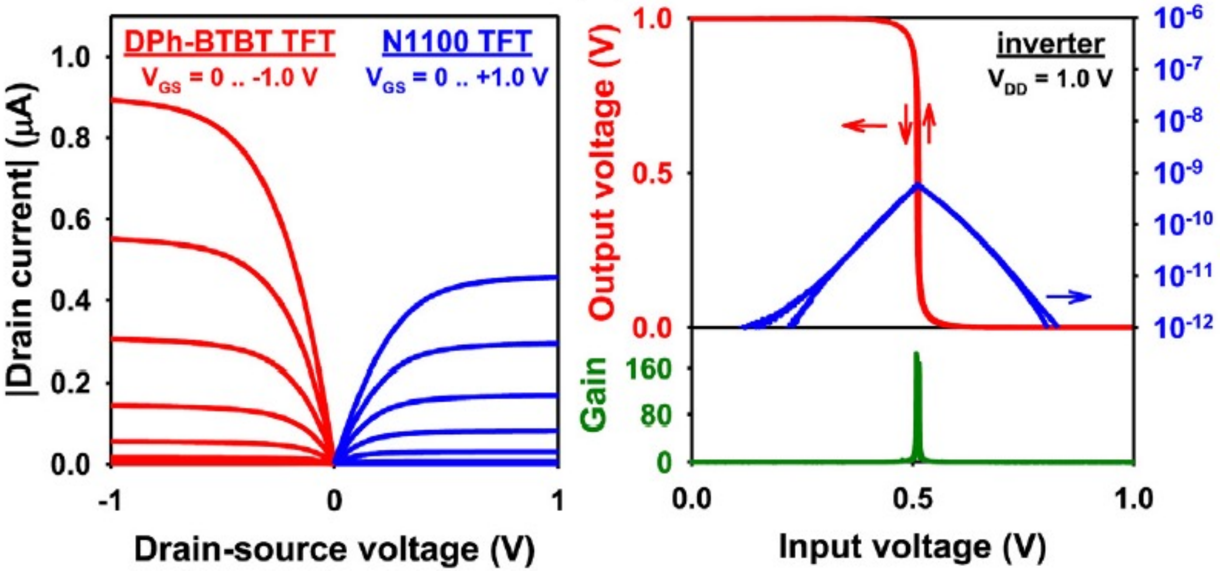




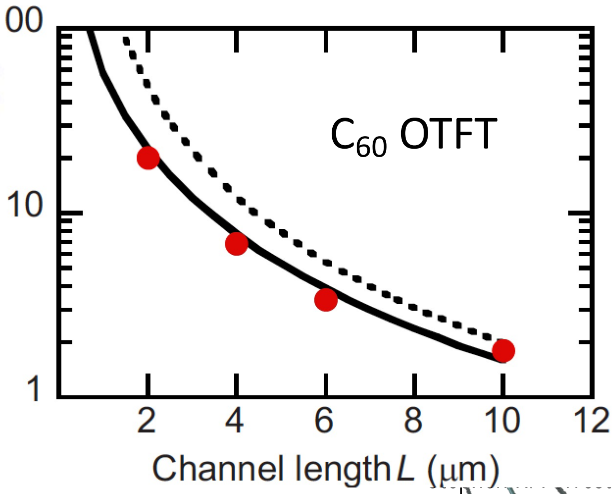
Transistors have come a long way





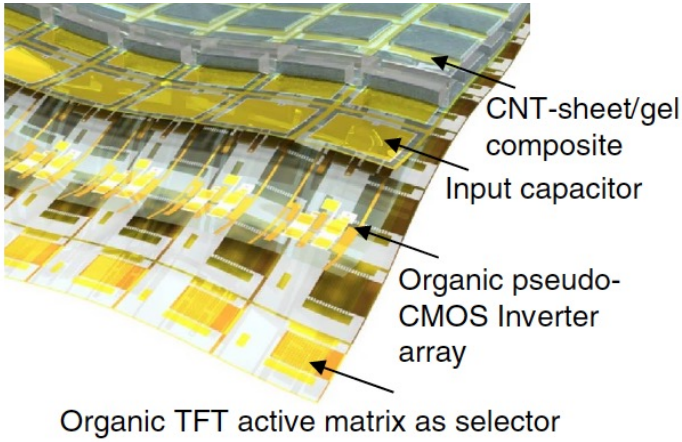


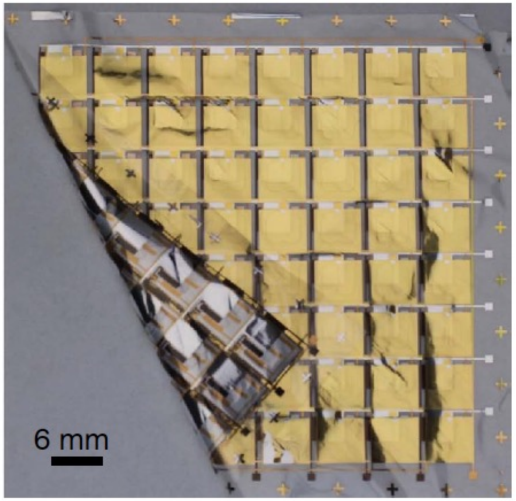
Zschieschang, 2017. *Organic Electronics,* 49**,** 179.

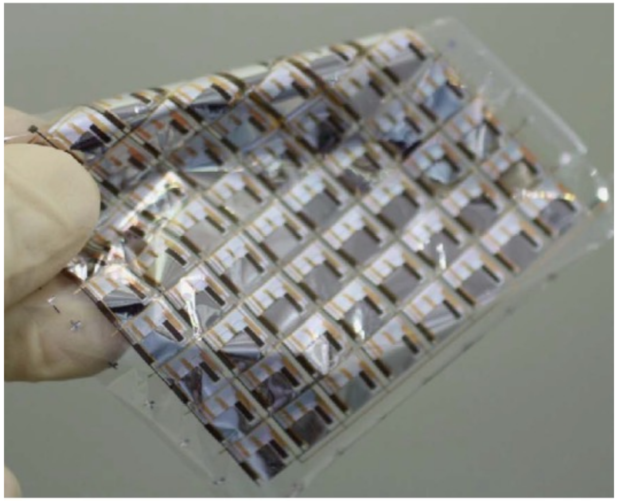


Kitamura, 2009. *Appl. Phys. Lett.,* 95**,** 023503.

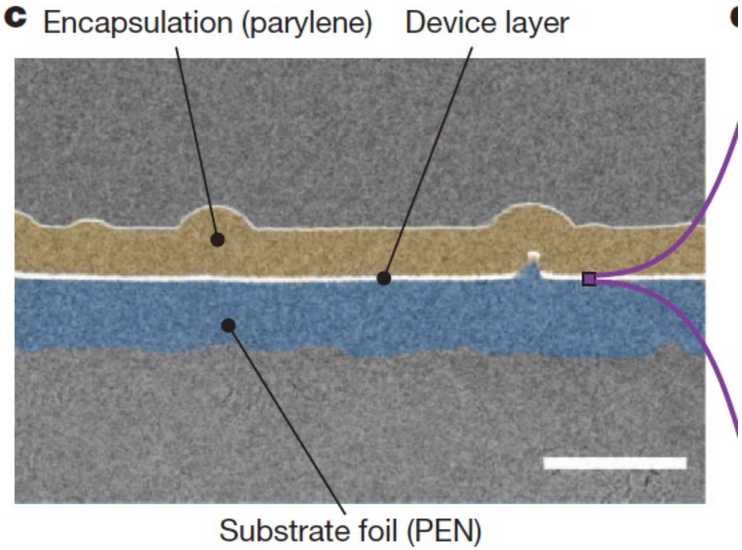
“Imperceptible” Electronics

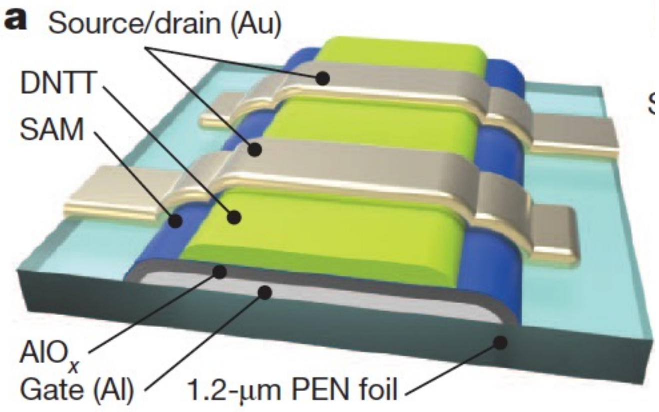






Substrates are 1 µm thick!





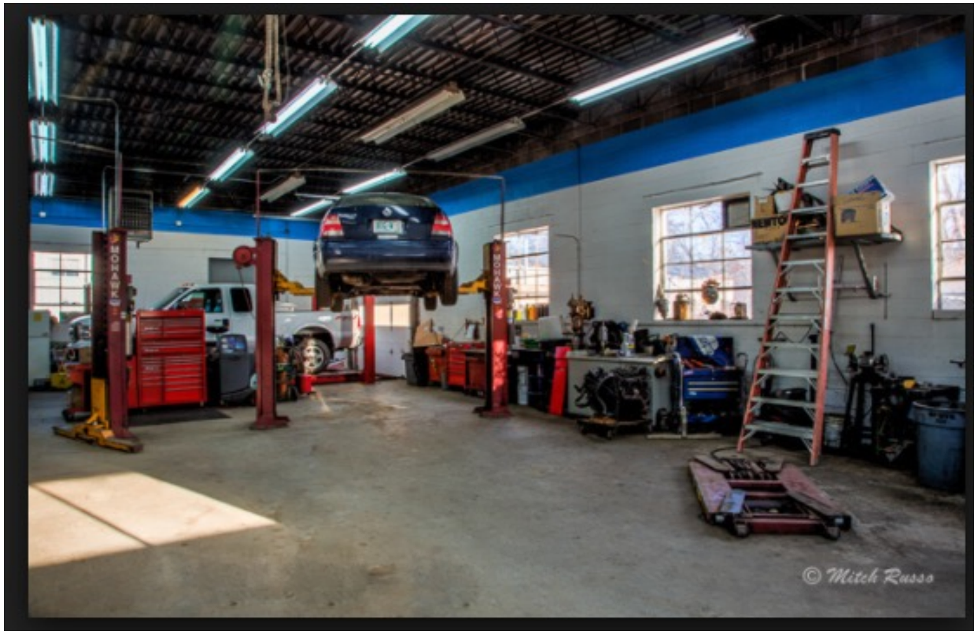
Kaltenbrunner, et al., *Nature*, **499**, 458 (2013).

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
  - o Natural plastics have been around, well, forever
    - ✓ Rubber
    - ✓ Cellulose (plants)
    - ✓ Collagen (cartilage, ligaments…)
  - o First man-made plastics based on cellulose
    - ✓ Parkesine (Alexander Parkes, Birmingham UK, 1856, cellulosic)
    - ✓ John Wesley Hyatt, 1869 (1st synthetic plastic, substitute for ivory)
  - o First fully synthetic plastic: Bakelite (Leo Baekeland, 1907)
  - o 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
  - o 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