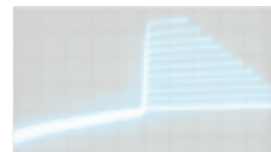
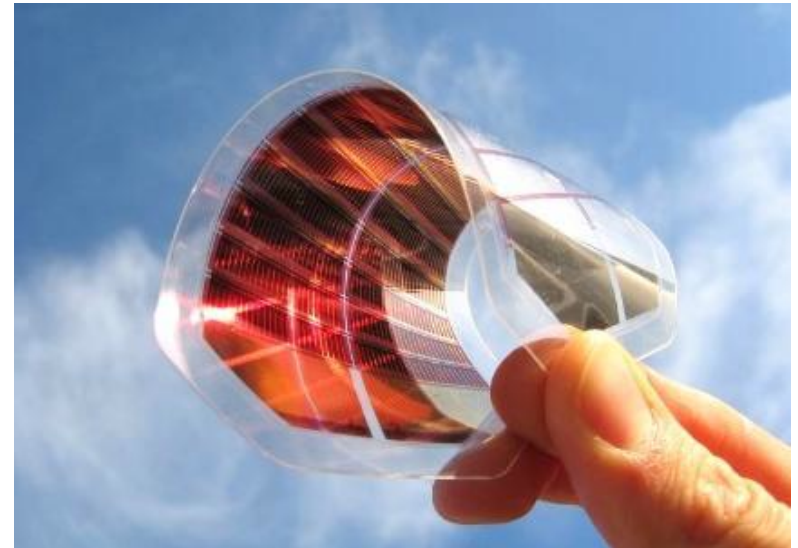
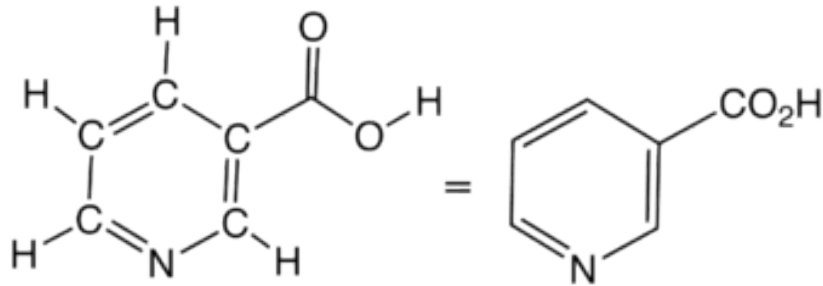


8.X – Organic Light Emitting Diode Displays and Organic Photovoltaics, *and Organic TFTs!*



- ▶ The next few slides are for your benefit (so you are not clueless about the emerging field of organic electronics), if I test you on anything it will be on basic/general information...
- ▶ Inorganic materials: all the molecules/materials that are not organic! So all we need to do is define what organic is...
- ▶ Organic materials: Some text books define an organic compound as one containing one or more C-H bonds.



= $C_5H_4N-3-CO_2H$ = pyridine-3-carboxylic acid

= niacin = vitamin B₃

- ▶ Here are some approx. bond energies:

C-H - 3.5 eV

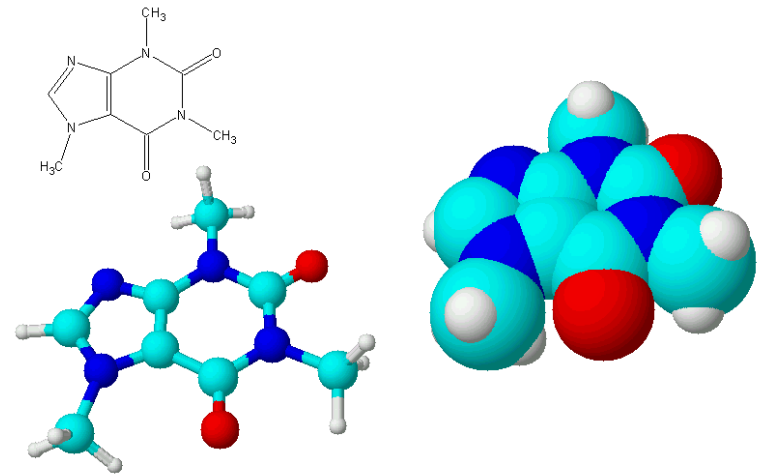
GaN - 8.9 eV

GaAs - 6.5 eV

*what does this tell you
about organic electronics?
Think about blue LEDs too!*



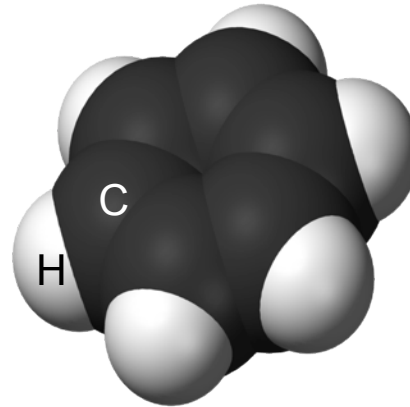
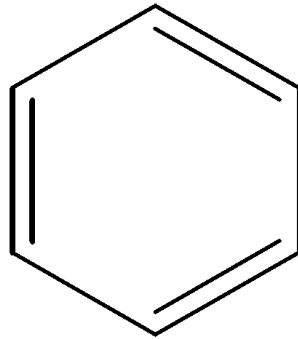
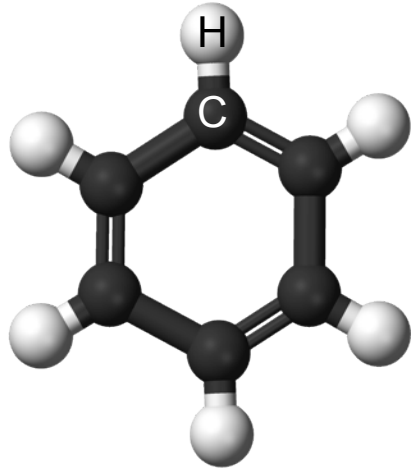
This is the organic molecule that made Starbucks wealthy, what is it?



Note, we are talking about the energy for breaking apart two atoms... Split open 1 atom? Nuclear fission = 200 MeV for U-235!



▶ There is a special conjugated bonding (alternate double/single carbon-carbon bond) associated with most organic semiconductors... results in metallic or semiconducting materials. Before we talk about semiconducting conjugated polymers, look at a real simple conjugated molecule: benzene.



1

▶ How many electrons does Si need to fill its outer shell (the magic 8)? How does Si crystal bond?

▶ Okay, Carbon is in the same column as Si and needs to covalently bond (share) with four other electrons from other atoms... How many 'shared' electrons do you see above for each carbon?

3

4

5

6

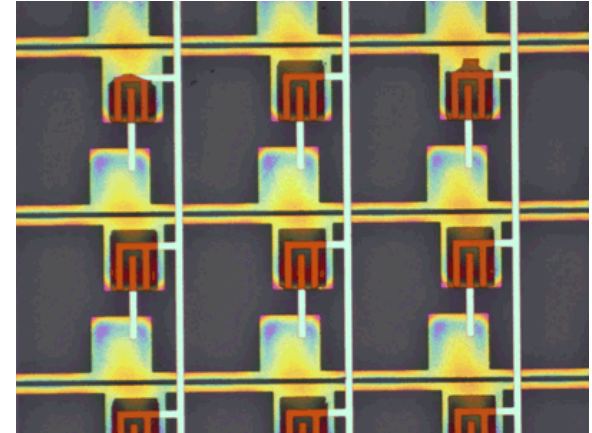
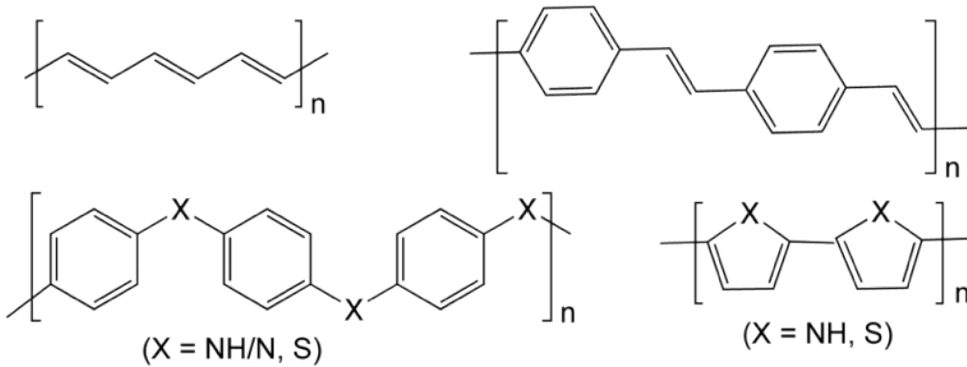
7

8

hydrogen 1 H 1.0079	beryllium 4 Be 9.0122
lithium 3 Li 6.941	magnesium 12 Mg 24.305
sodium 11 Na 22.990	calcium 20 Ca 40.078
potassium 19 K 39.098	

scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	helium 2 He 4.0026
										aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
										gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80

► Here are some semiconducting conjugated polymers: polyacetylene; polyphenylene vinylene; polypyrrole (X = NH) and polythiophene (X = S); and polyaniline (X = NH/N) and polyphenylene sulfide (X = S).

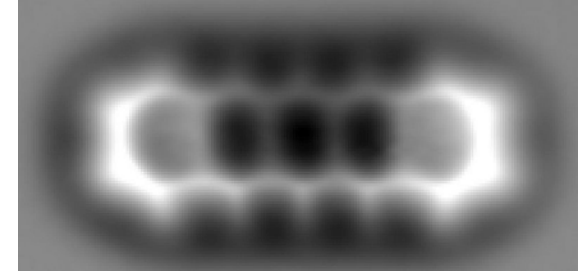
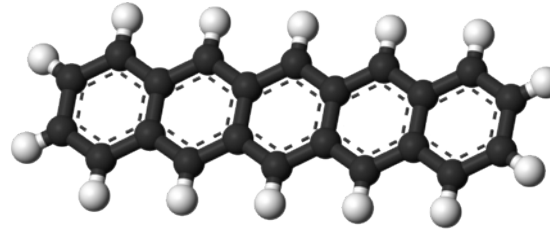
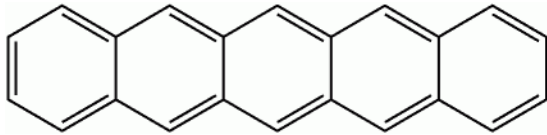


► Most of the semiconducting AND light emitting polymers (fluorescent dyes) are conjugated...

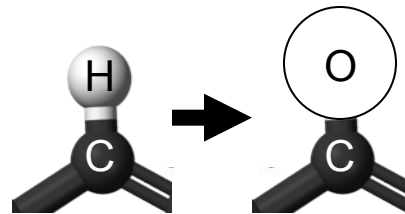
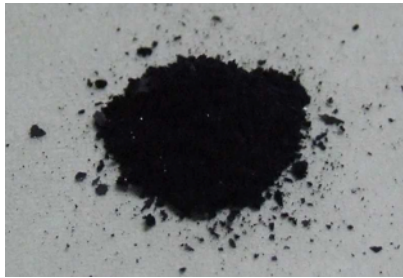
► Lets look at the most famous conjugated polymer on the next slide...



▶ Most famous and widely used organic semiconductor is pentacene (5 fused benzene rings), with a mobility as high as $10 \text{ cm}^2/\text{V-s}$ when 'doped' by oxidation (but is <0.1 in real switchable devices).



non-contact atomic force microscopy



Most organic semiconductors are more p-type, think about how many electrons wanted by O vs. H. ★

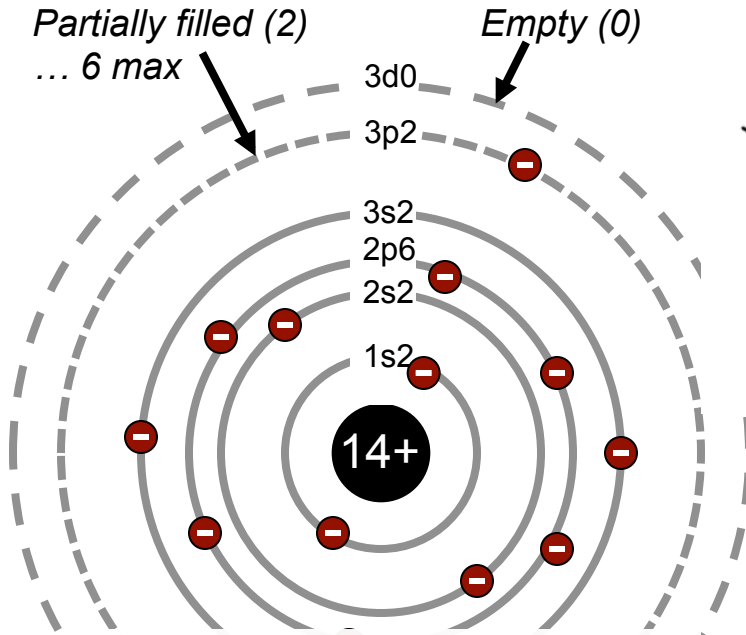
▶ Most organic semiconductors increase their conductivity by oxidation doping... What molecule does the oxygen replace?

scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
potassium 19 K 39.098	calcium 20 Ca 40.078	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80	aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948	helium 2 He 4.0026	

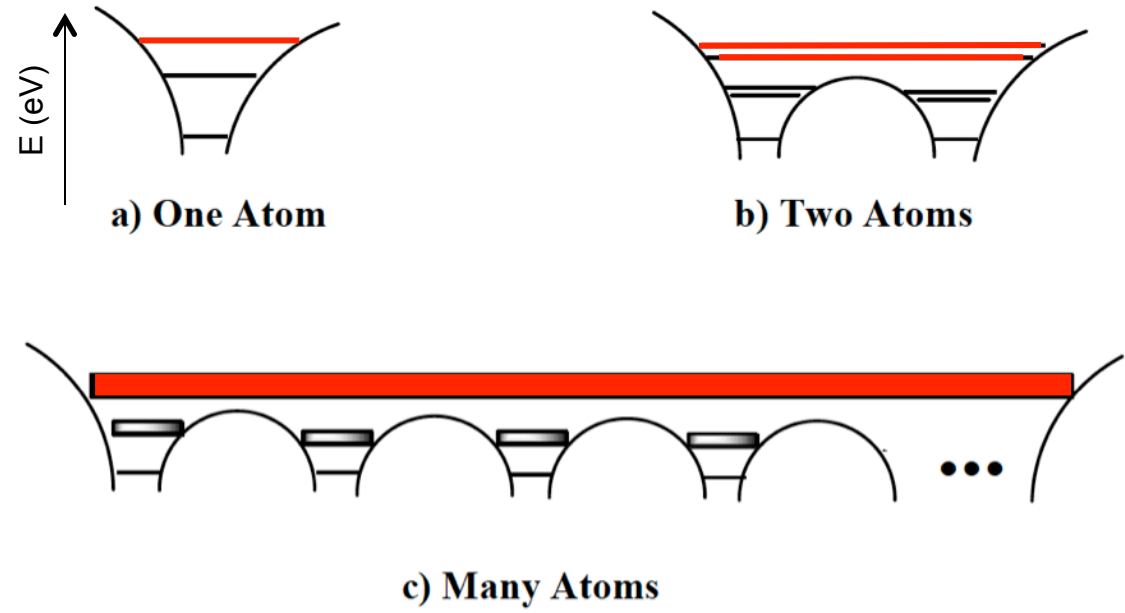
1

▶ What about band diagrams? Lets start with something familiar... (but not organic)

▶ Pauli Exclusion Principle (only one electron per quantum state, n, l, m, s)



Higher energy = further away from the atom/molecule = start to overlap with each other and can therefore exchange electrons!

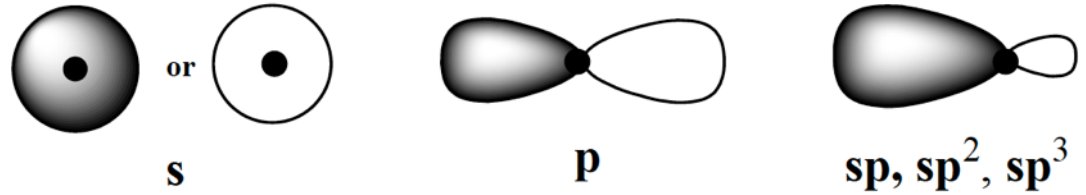
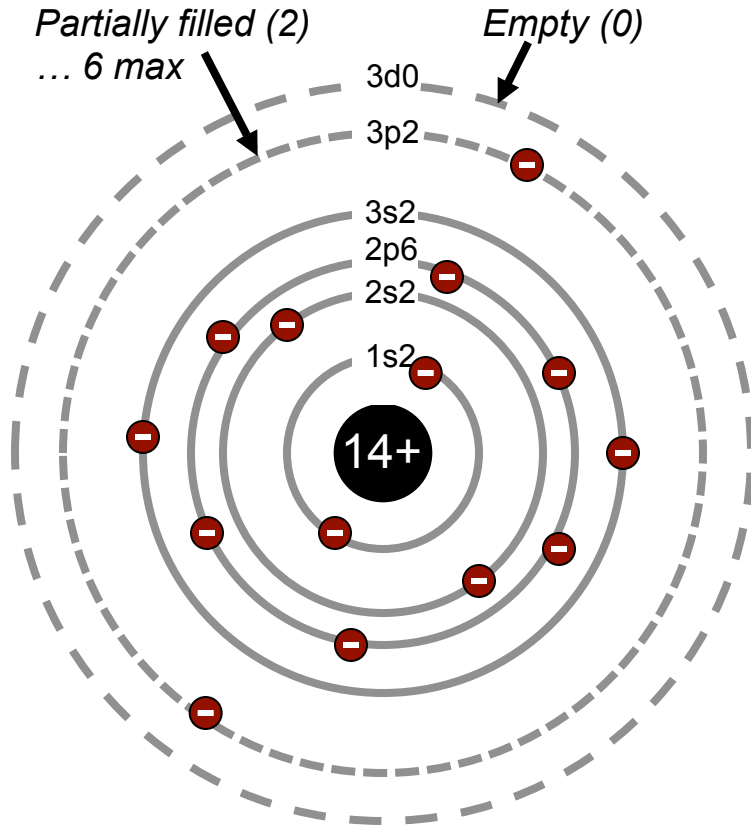


▶ Fig. 3.3 – Atomic electronic potential wells (like a quantum well) and electron orbitals (generic, any atom/molecule).

▶ Notice how 2 atoms causes levels to shift, and many atoms creates a band. Red lines are delocalized electron bands that can conduct!

Why are the red lines the higher energy ones?

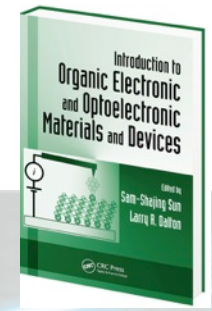


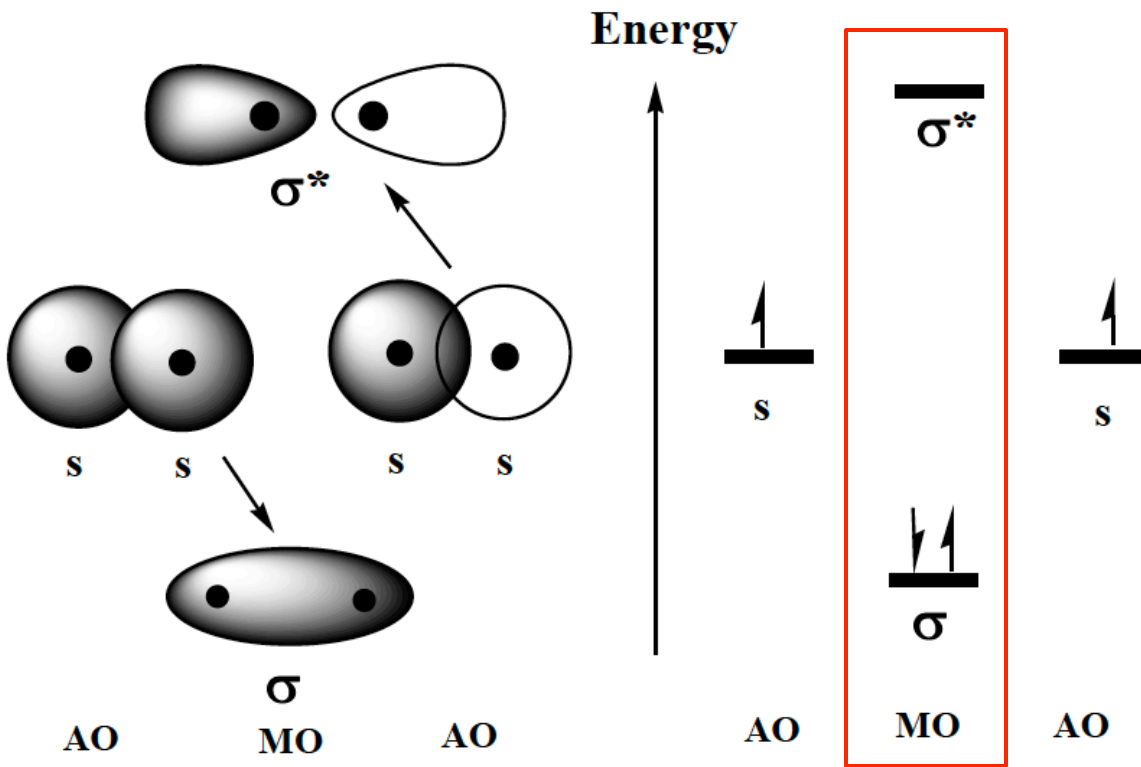


► In an actual atom, the electrons do not orbit in perfect circles...

► Fig. 3.5 – Shapes of atomic electron orbitals (dark dot is nucleus). Two colors represent the positive and negative phases of the electron wavefunctions. Orbital shapes roughly represent the electron probability density.

There are many, many, more variations! (http://en.wikipedia.org/wiki/Atomic_orbital).





► Bring two 's' electron atomic orbitals (AOs) together and Pauli exclusion principle forces them to into molecular orbitals (MOs).

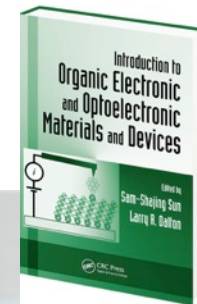
There is a lowest energy possibility (bonding) and higher energy (, anti-bonding state).*

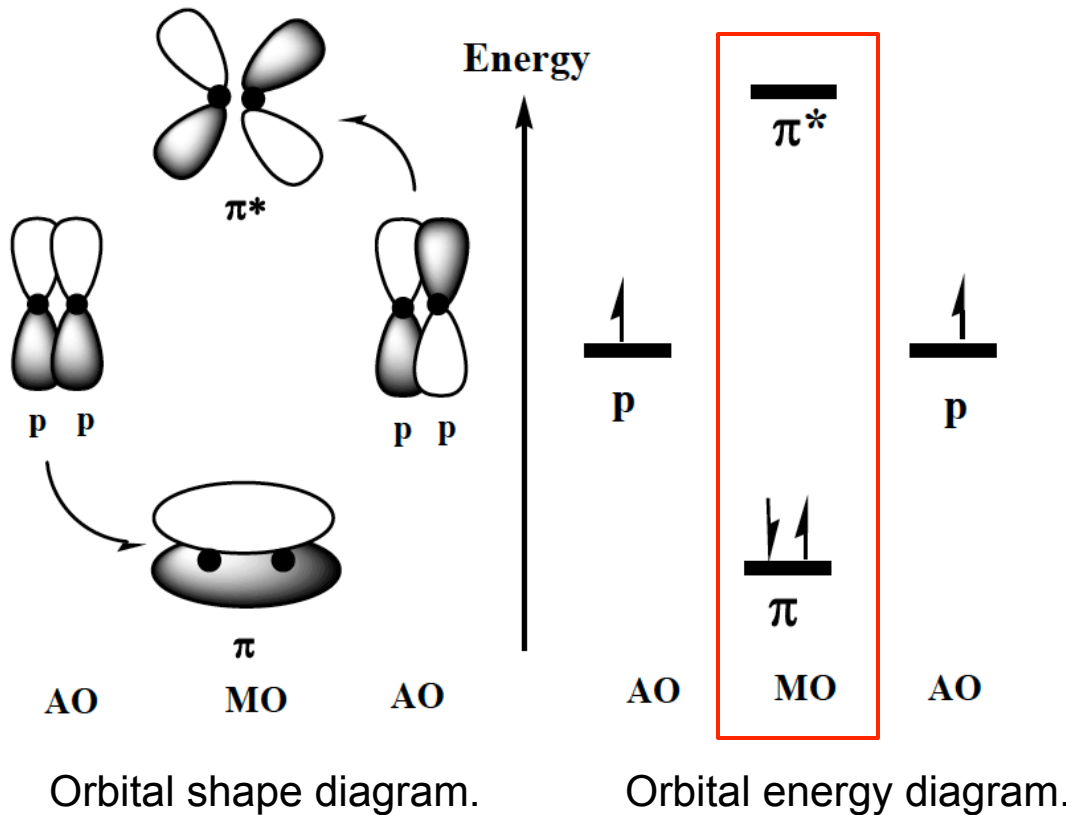
See where we are headed with this...?

FYI, this is how we started when we created band diagrams by bringing a bunch of Si atoms together... see Lecture 1!

Orbital shape diagram.

Orbital energy diagram.



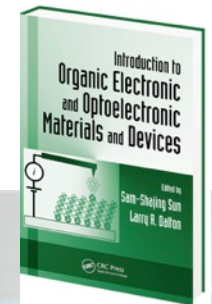


▶ Bring two 'p' electron atomic orbitals (AOs) together and Pauli exclusion principle forces them to into molecular orbitals (MOs).

There is a lowest energy possibility (bonding) and higher energy (, anti-bonding state).*

See where we are headed with this...?

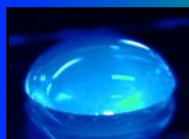
I showed you ss, pp. There are many more examples (sp, dd, etc..) for other orbital types (, but you get the picture...



400nm - - - - - 450 nm - - - - - 500 nm - - - - - 550 nm - - - - - 600 nm - - - - - 650 nm

excited with UV light...

organic light emitters dissolved in liquid...



2.6 eV



2.3 eV



2.0 eV

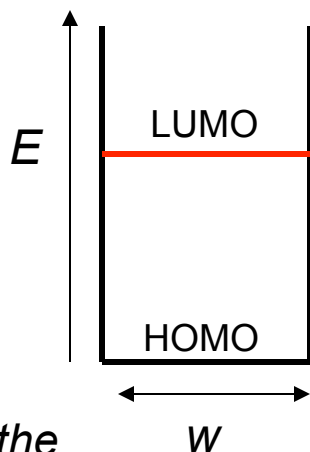
3.1 eV

▶ LUMO: lowest ★ unoccupied molecular orbital... *think conduction band*

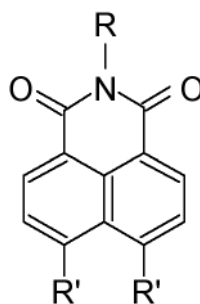
▶ HOMO: highest ★ occupied molecular orbital... *think valence band*

▶ Anything special about the bonding at right?

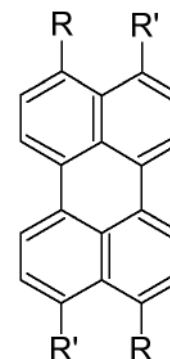
▶ How does E_g change with molecule size and why? ★



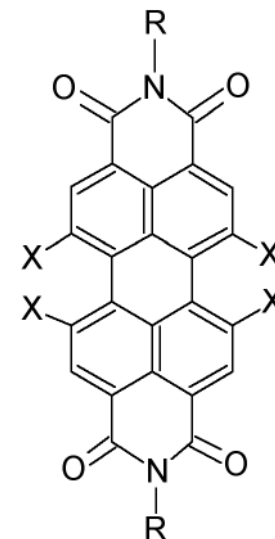
Blue



Green

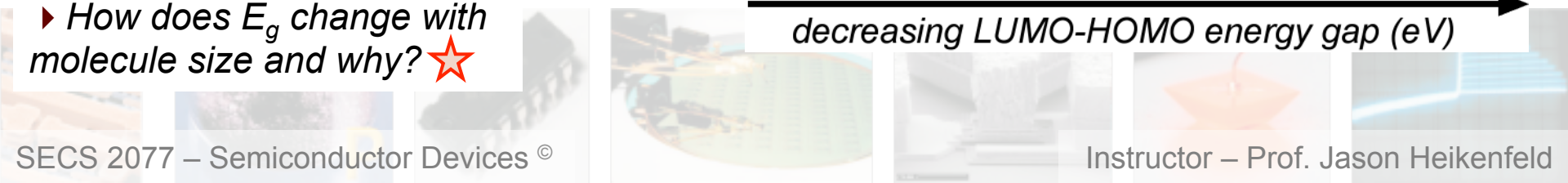


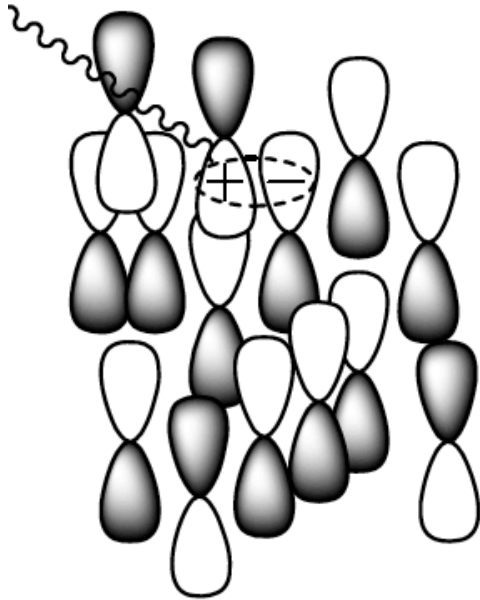
Red




increasing electron delocalization

decreasing LUMO-HOMO energy gap (eV)



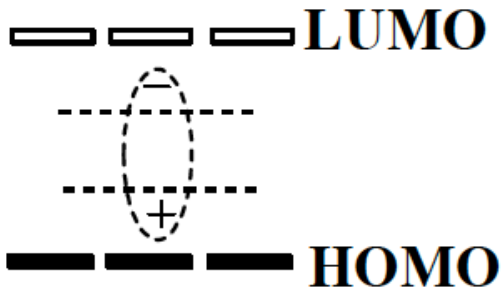


▶ We don't have EHPs as we knew it for Si (but they draw it that way for convenience).

▶ The EHPs are actually 'excitons'.  Energy comes in (photon for example) and the electron is energetically kicked out of its normal orbital, which leaves behind a lack of an electron (+ charge).

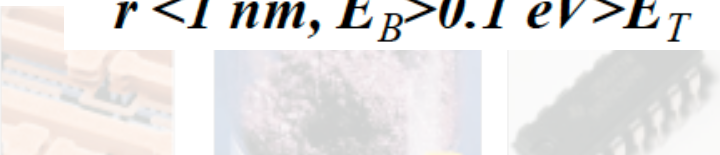
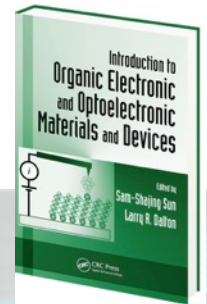
▶ How do they move?

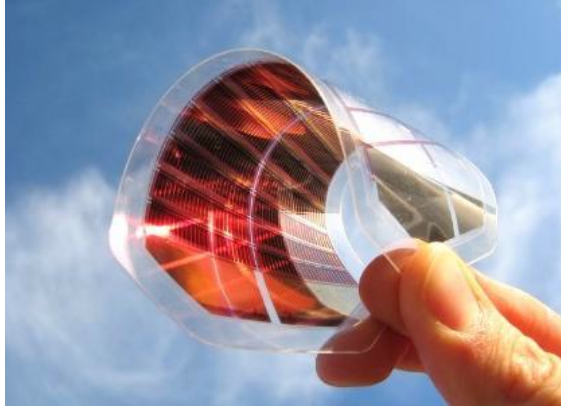
- This exciton (energy) can be transferred around from molecule to molecule!
- However, unlike other types of energy transfer, the carrier is not 'free' like an electron in Si, it has to move charge through a bunch of other 'bumps' of orbitals and charges.
- This is one reason why mobility's in organics are 100's to 1000's of times lower than in semiconductors...



"Frenkel Exciton"

$$r < 1 \text{ nm}, E_B > 0.1 \text{ eV} > E_T$$





► Advantages: ☆

- low cost (potentially)
- low temperature fabrication (on plastic)
- flexible / rollable / impact-resistant (all are advantages for portable displays)

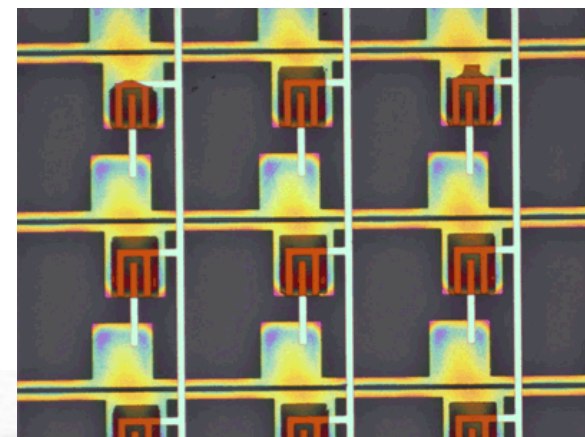
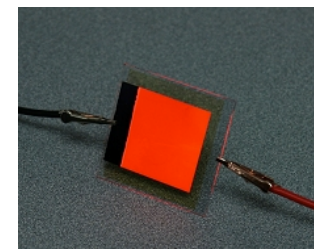
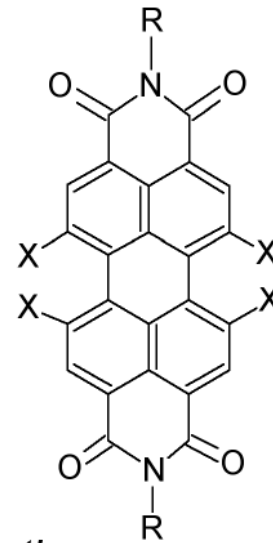
► Disadvantages: ☆

- bond energies are much lower than inorganics – why is this a problem?
- mobility's are not as high... so no high speed or high current applications!

► Lets briefly cover:

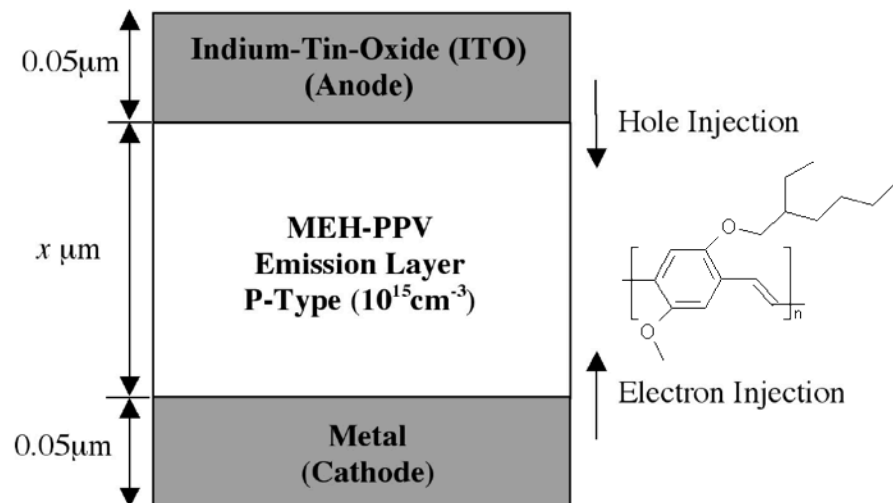
- (1) OLEDs
- (2) OLED displays
- (3) Organic thin-film transistors (TFTs) used for e-Paper
- (4) Organic photovoltaics

- ▶ Organic semiconductors, what type of bonding do they typically have?
- ▶ How are they similar to Si (atoms) when you bring a bunch of molecules together? What happens?
- ▶ We don't have conduction and valence bands, what do we have instead?
- ▶ Why do larger molecules tend to absorb or emit shorter wavelength light?
- ▶ What are some of the main advantages, and limitations for organic semiconductor devices?



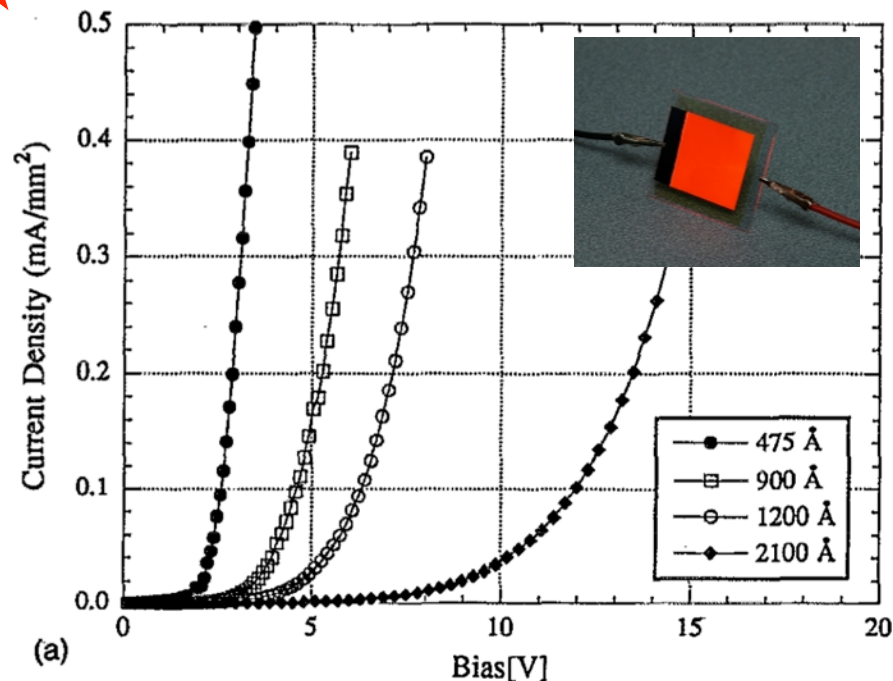
► Here is a most basic OLED structure... (metal/polymer/metal) The electrodes act like PN junctions for injection... *more on next slide.*

► Look at the bandgap and mobility, especially the mobility. Also look at the IV plot which is for really thin films of MEH-PPV (much thinner than the 1 μm base of a high current BJT). What does this tell you? ★



J. Appl. Phys. **75**, 1656 (1994); doi:10.1063/1.356350

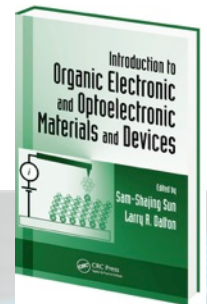
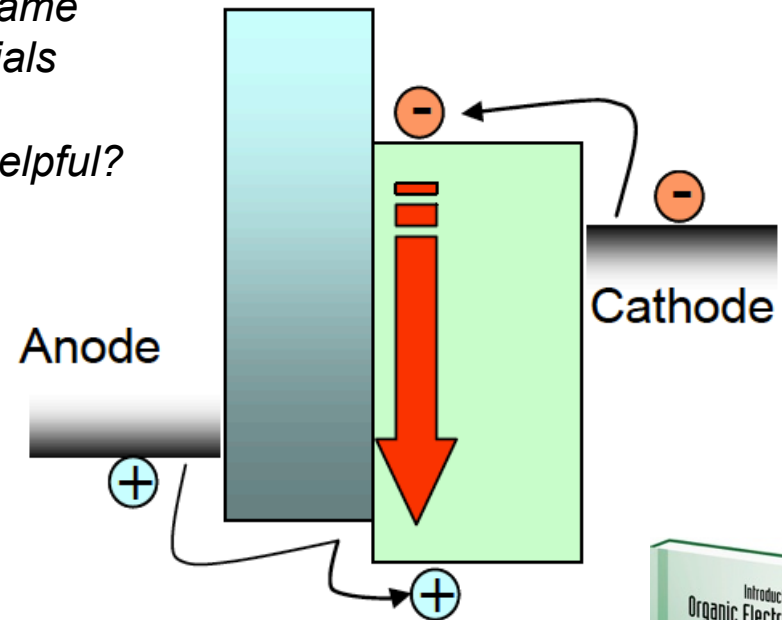
Parameter	Magnitude	Units
Bandgap energy, E_g	2.1	eV
Temperature, T	300	K
Affinity	2.8	eV
ITO Workfunction	4.7	eV
Density of State, N_0	2.5×10^{19}	cm^{-3}
Hole mobility, μ_p	0.5×10^{-4}	$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$
Electron mobility, μ_n	0.5×10^{-5}	$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$
Exciton lifetime, τ	1×10^{-9}	s
Exciton diffusion length, L_D	1×10^{-6}	cm



▶ Here is a bit more advanced OLED structure (metal/polymer/polymer/metal) optimized for carrier injection... how does the extra layer at left help? ☆

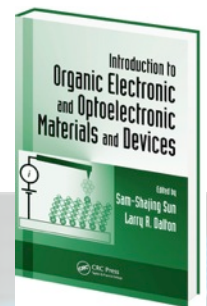
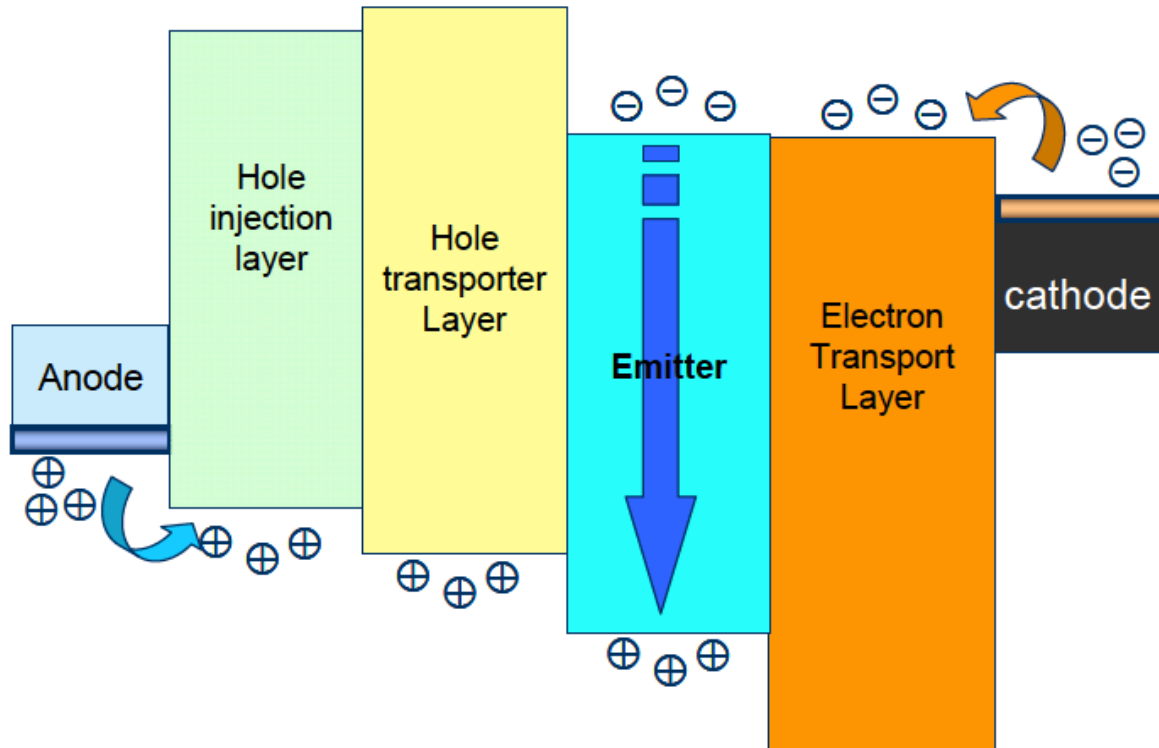
- *help inject the holes... otherwise one big barrier*
- *like regular LEDs/solar cells where we don't want e-EHPs near the edge of the semiconductor, same applies for excitons (EHPs) in organic materials*
- *lastly, it helps block electrons... why is this helpful?*

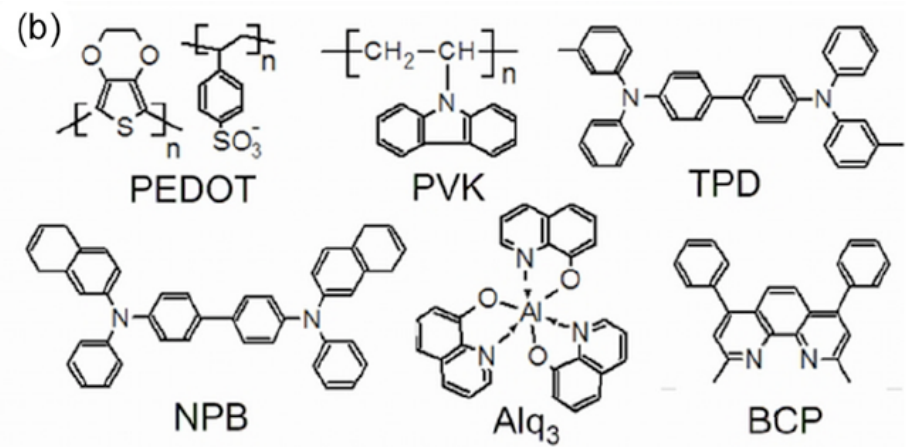
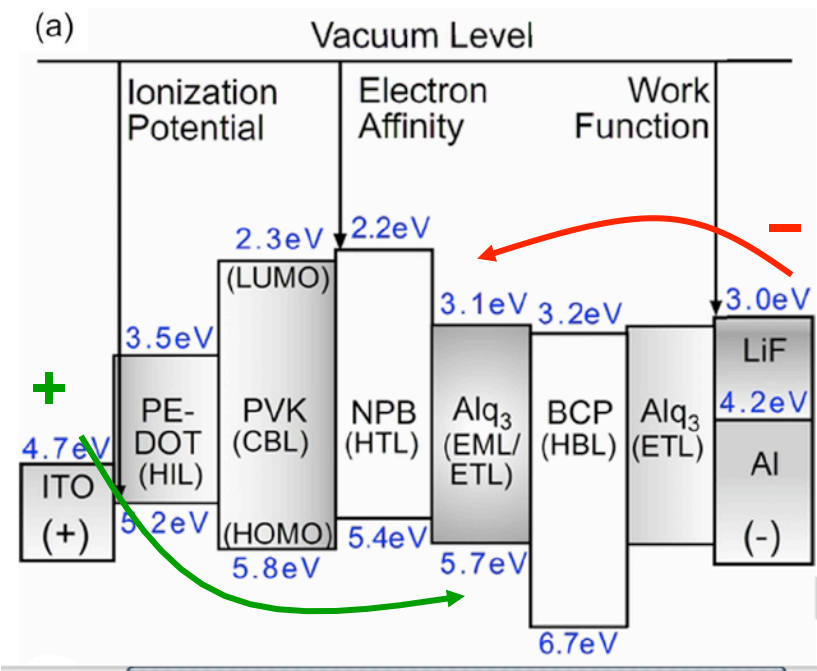
▶ The anode is typically transparent, typically made of low-cost In_2O_3 doped 10% SnO_2 , called 'ITO'. What type of semiconductor is this?



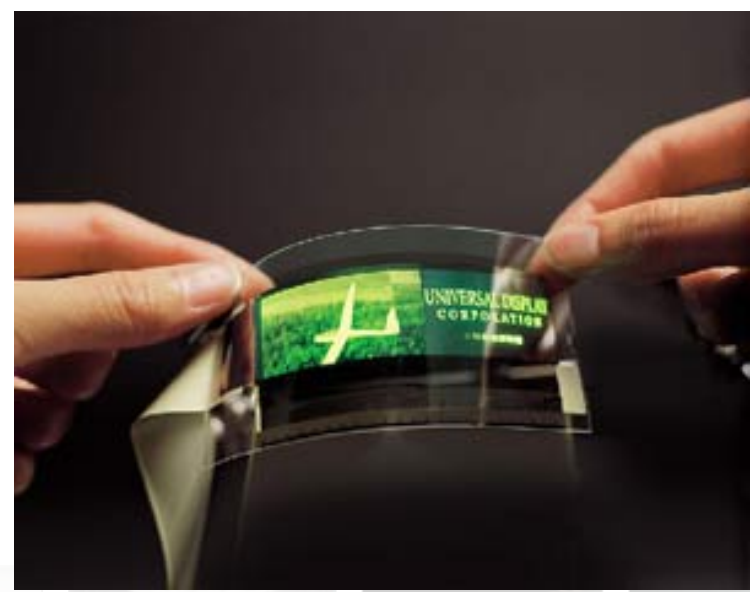
► Here is a more advanced OLED device... ☆

- why do we have a hole injection layer?
- why did we add a hole transport layer? (what does it do)
- why did we add an electron transport layer? (what does it do)
- why don't we need an 'electron injection layer'?



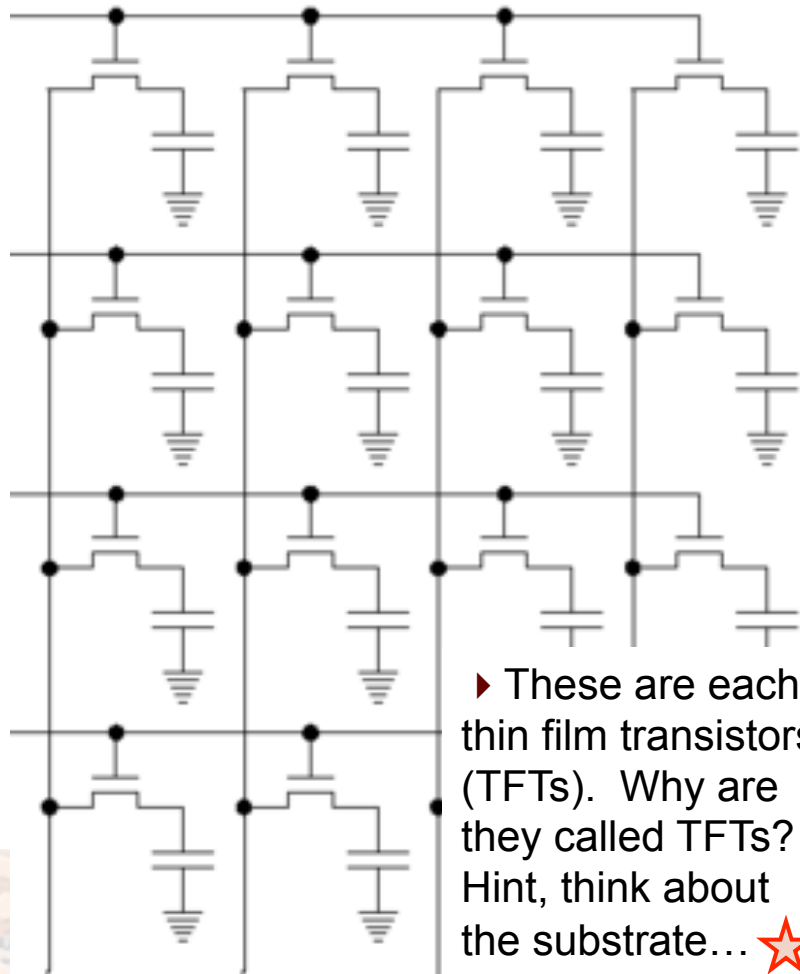


- ▶ Best devices are more complex...
- ▶ Alq₃ is the workhorse material for the industry (green), but how do they create full color displays?

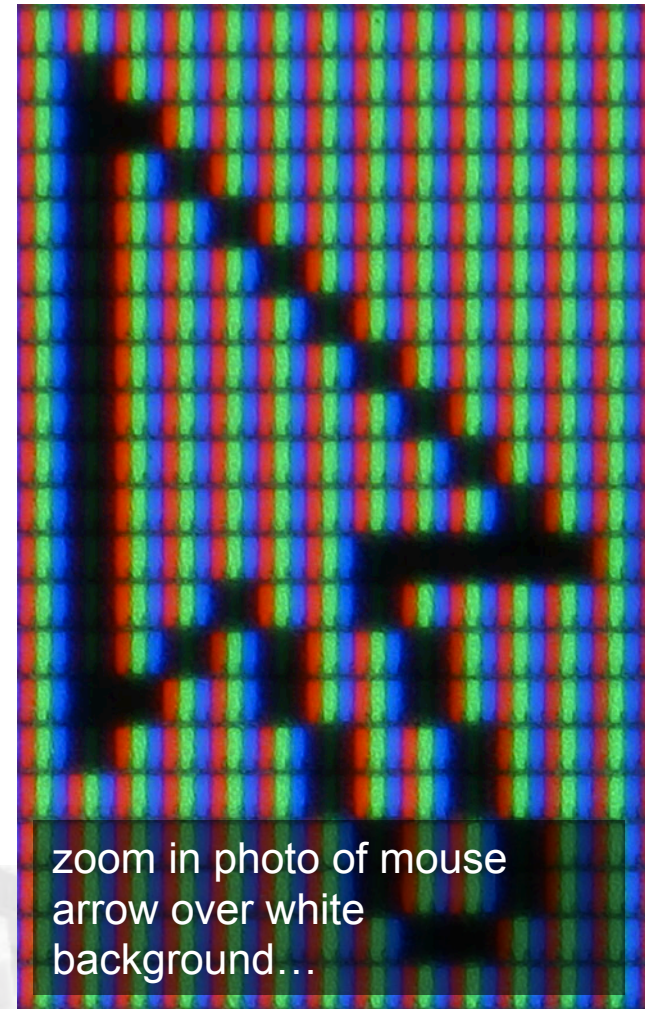


▶ Get to OLED displays in a second...

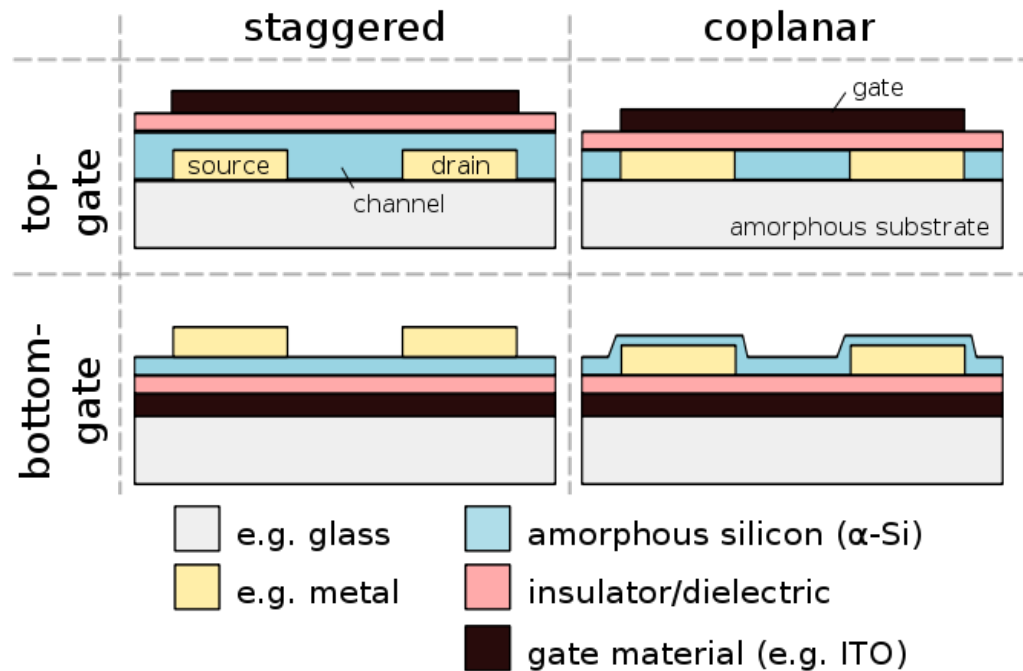
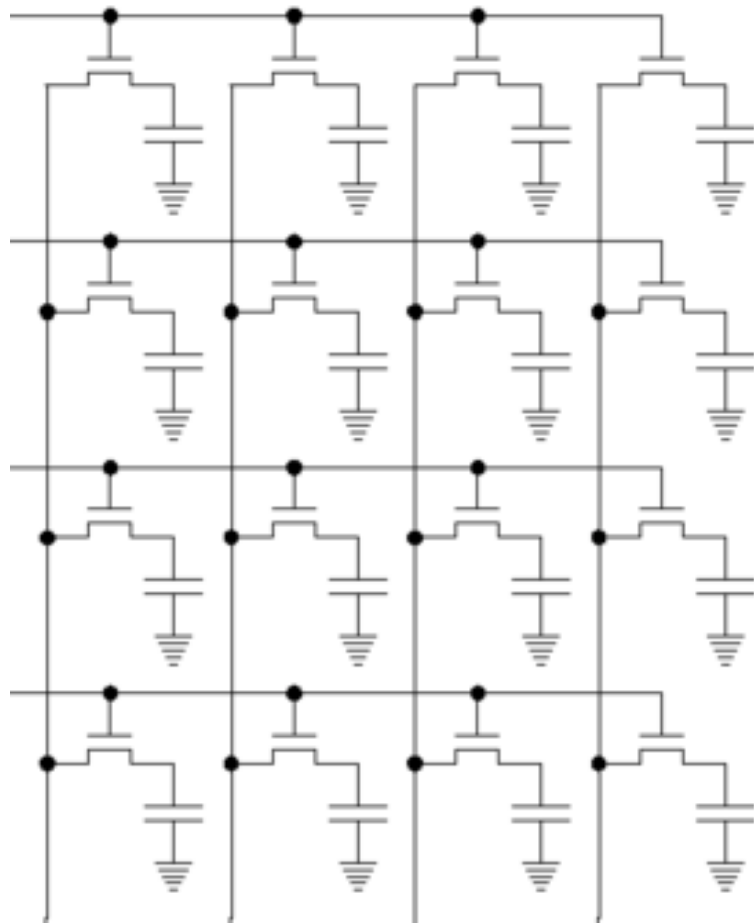
▶ This is the 'active matrix' pixel circuit for a liquid crystal display. Electrically the liquid crystal is like a capacitor, and is just a light valve for a white backlight (3 sub-pixels each with an R, G, or B color filter).



▶ These are each thin film transistors (TFTs). Why are they called TFTs? Hint, think about the substrate... ☆

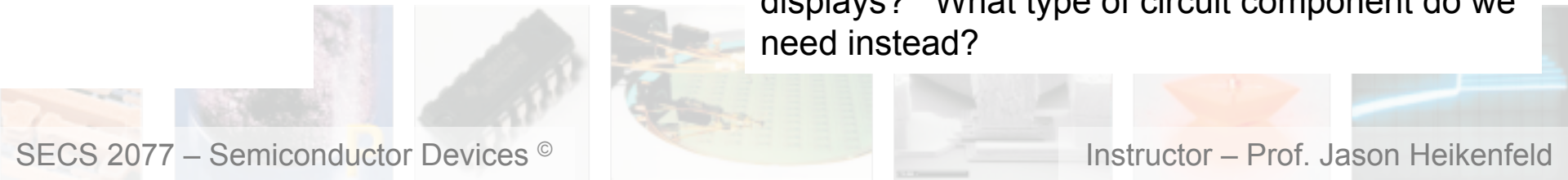


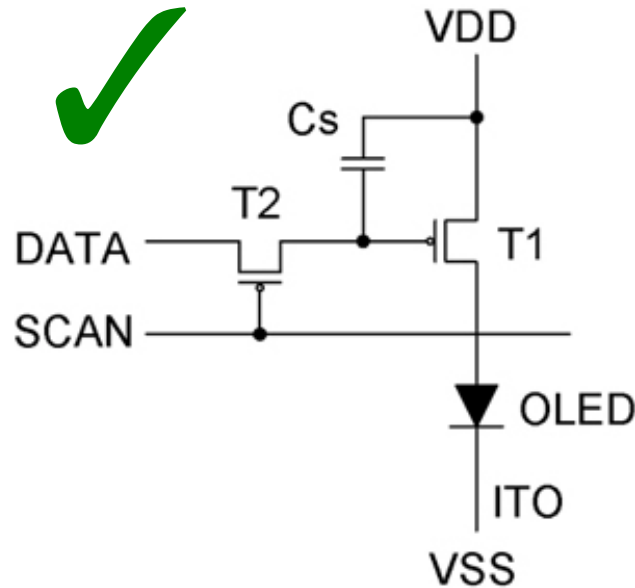
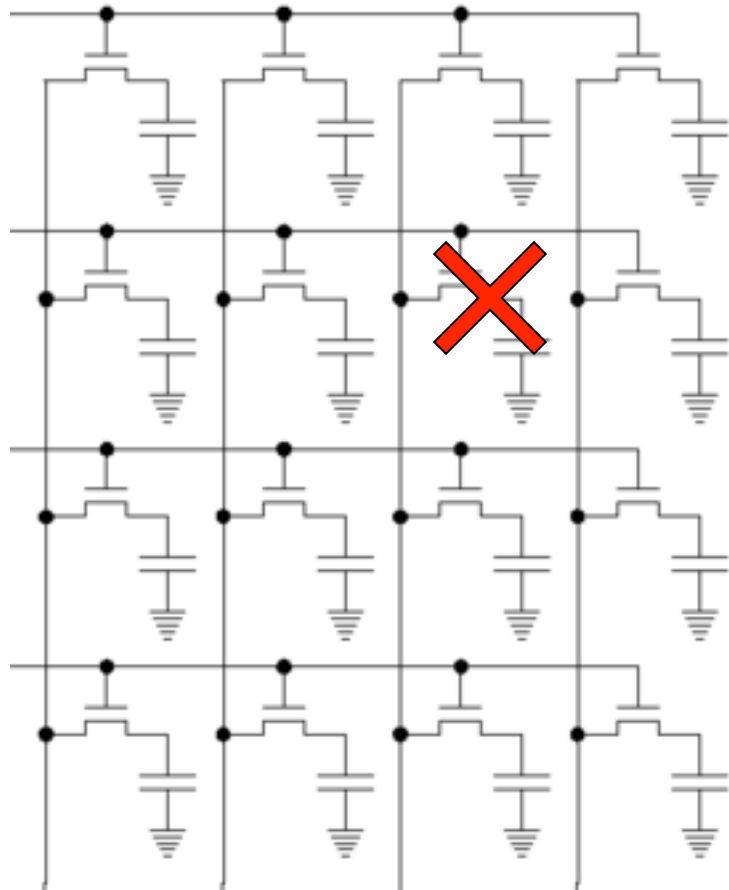
Two types of TFTs...



Why is this 'amorphous' Si? Why not crystalline? ☆

So this 'active matrix' works for LCD pixels (capacitors), why will it not work for OLED displays? What type of circuit component do we need instead?





▶ Remember, in active matrix drive, you cannot keep providing voltage to any given pixel, for OLED you need to maintain current even as the row line is turned off!

▶ a-Si does not have the mobility needed for high current pixels like OLEDs, so the new trend is oxide TFTs or laser-annealed poly-Si.

From: "Sharp Announces Oxide-TFT LCD Production, and the Display Ground Shifts" IZO = Indium-Zinc-Oxide

	IZO	a-Si	poly-Si	Organics
μ (cm ² /V-s)	10-50	0.5-1	30-300	0.1
Process Temp	200°C	350°C	450°C	<150°C

AMOLED TV Sets are Coming. Really. by Ken Werner, March 17th, 2011

We all know that large-screen AMOLED-TV sets will not be produced in volume for a long time because a Gen 8 fab is required to make them, and nobody is ready to make a Gen 8 AMOLED plant yet. Over 95% of the world's AMOLED displays are currently being made in Samsung Mobile Display's (SMD's) Gen 4 fab.

But wait. LG Display is planning to jump directly from Gen 4.5 to Gen 8. It is ordering manufacturing equipment now for installation in Paju...

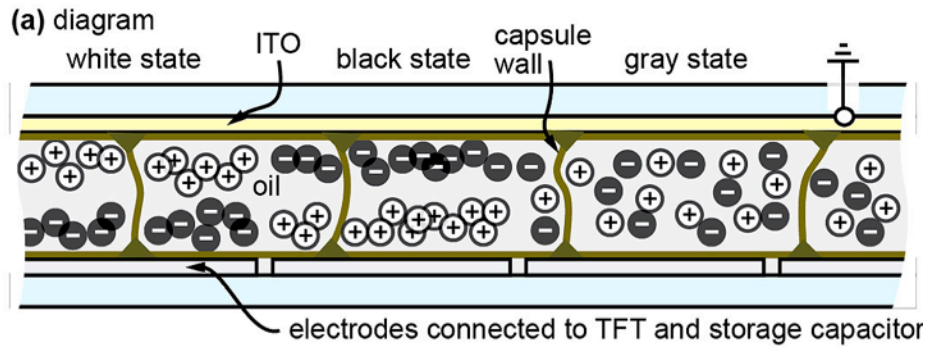
Is Gen 4.5 to Gen 8 a big leap? It certainly is, but the leap may seem a little more manageable if you know that LGD will be using color-by-white; that is, all of the subpixels will be white, and they will shine through an RGBW matrix color filter. That may seem familiar. It was the approach Kodak came to favor for large AMOLED displays, and LGD bought Kodak's OLED business last year. The Gen 8 substrates will be 2200×2500mm.

Sources said that LGD intends to produce AMOLED panels up to 55-inches at the Paju line.



Why are OLED panels thinner than LCDs?

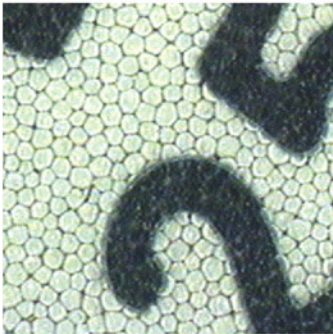
- ▶ So OLEDs are obviously organic, but the TFTs that drive them are NOT organic (mobility is too low to drive constant current).
- ▶ However, organic TFTs might be fine for displays that are capacitive based and okay if slow in switching speed... A disadvantage in performance, however, can be made rollable!



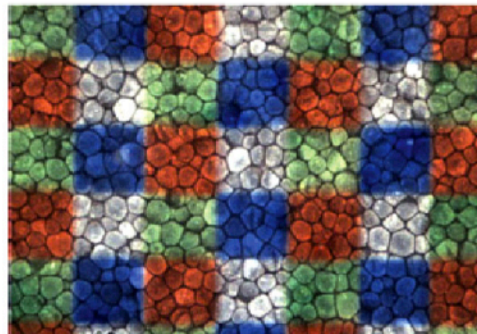
- ▶ The only thorough review on e-Paper technology can be found here:

http://secs.ceas.uc.edu/devices/NDL_Publications.html

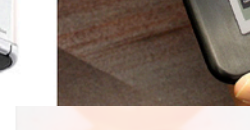
(b) photo of E Ink capsules on segmented electrodes



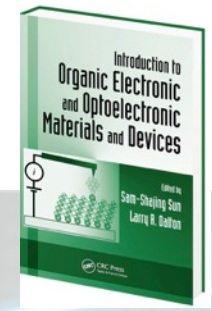
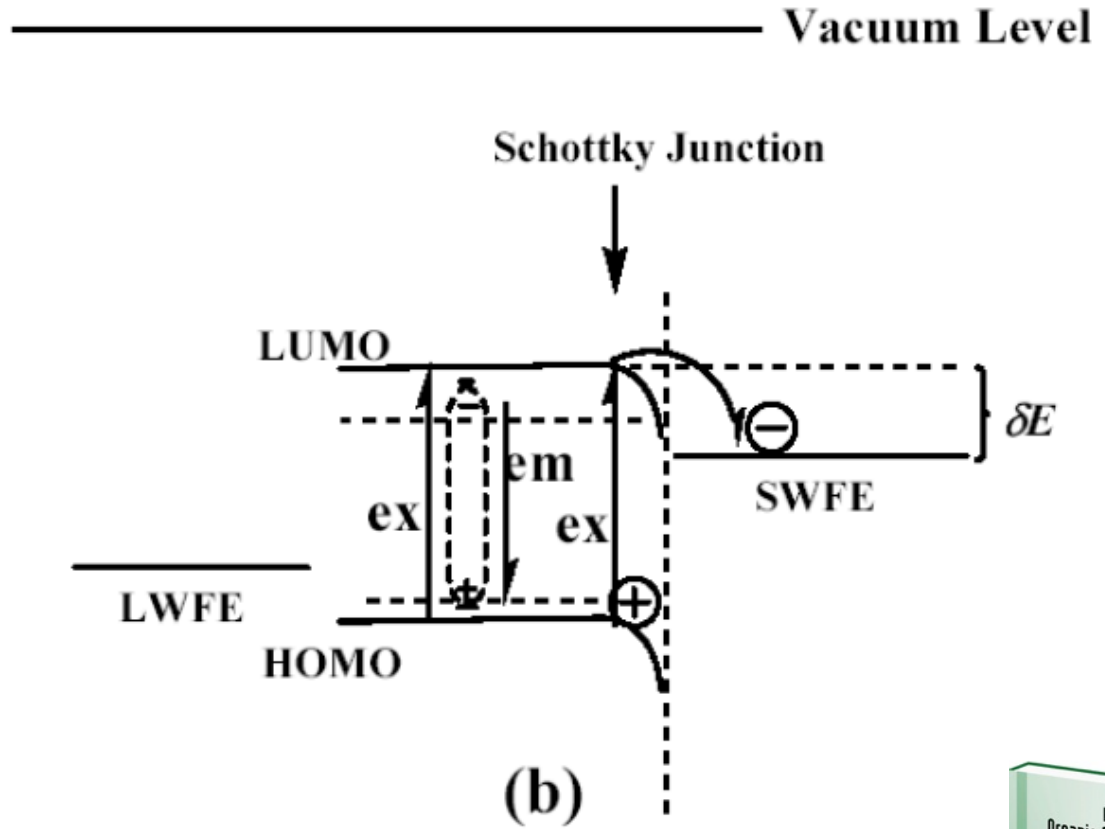
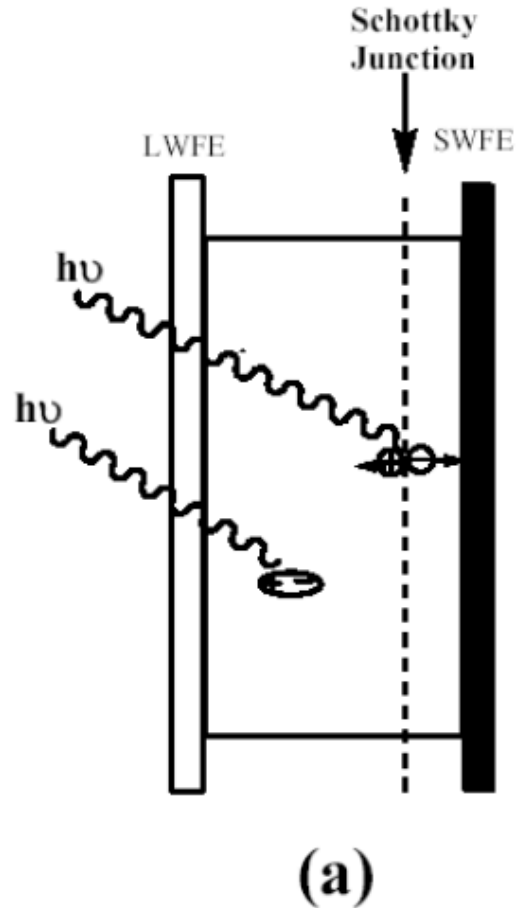
(c) E Ink film + RGBW color filter array



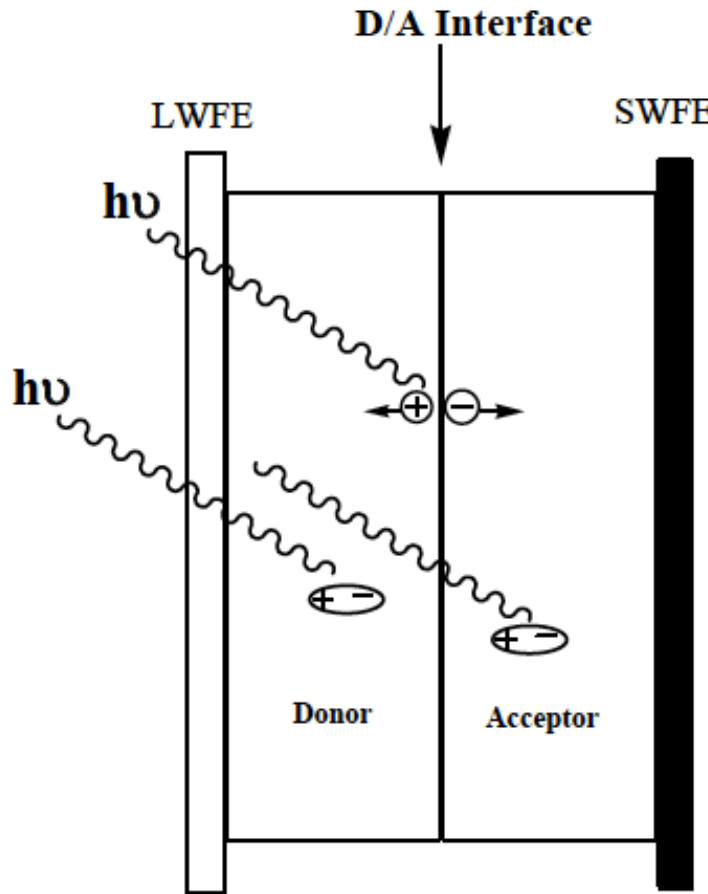
(d) E Ink Vizplex film applied to rollable (Polymer Vision) demonstrators and photograph of the new E Ink color demonstrator



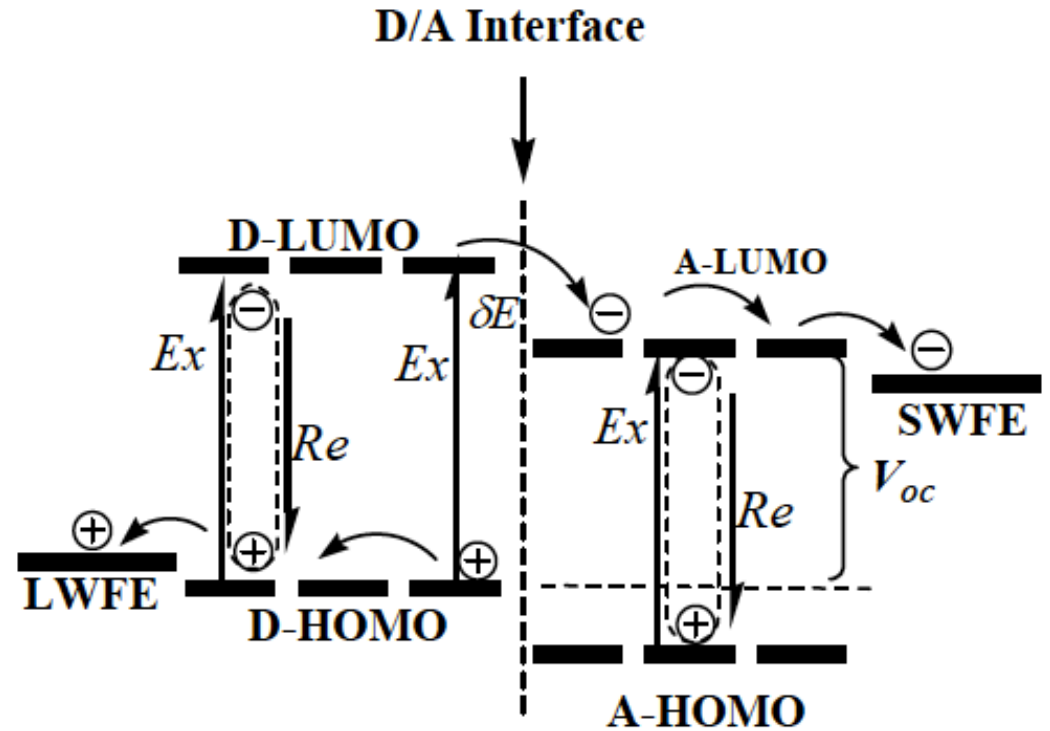
► Simple '1st generation' OPV based on Schottky diode... (not highly efficient, only 1/2 the depletion width...)



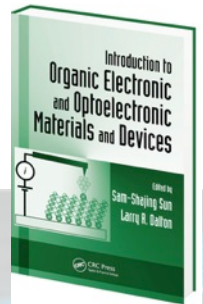
► 2nd generation' OPV based on Schottky diode... more efficient.



(a)



(b)



heliatek



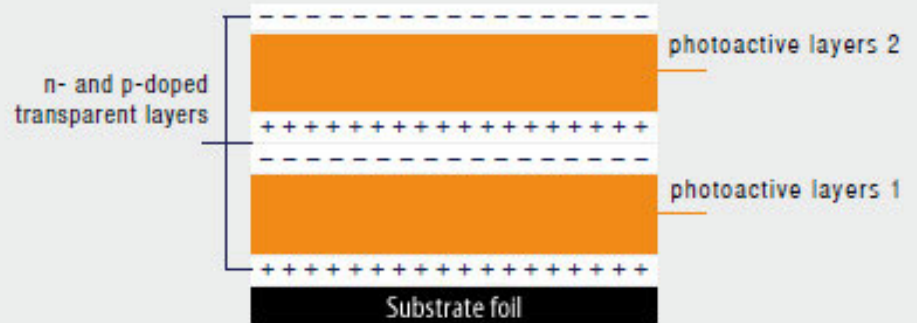
Organic based Photovoltaics

Part of the solution to both the worlds energy and environmental issues

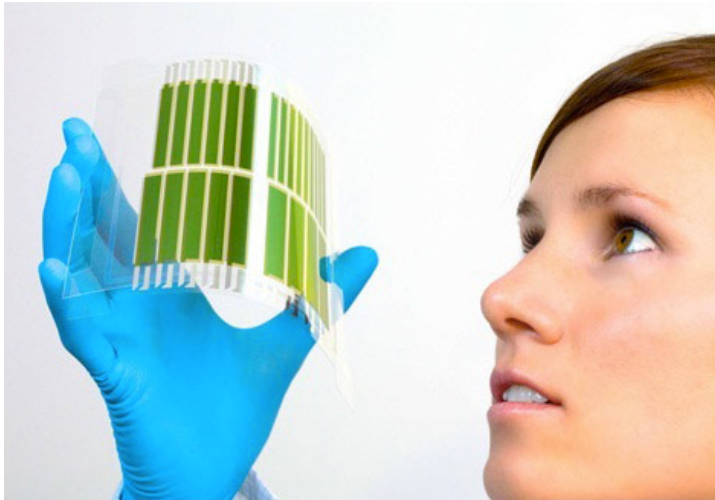
Affordable energy for emerging nations

Light-weight, flexible energy on the move

Build of a tandem cell



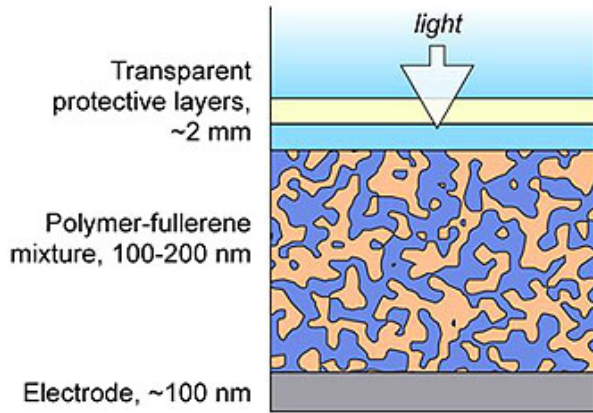
- patented tandem cell technology
- complementary absorber systems
 > optimum harvesting of the complete sun spectrum
- increased open circuit voltage
- loss-free recombination contact between individual cells within tandem cell
- n- and p-doped transparent layers allow for the loss-free charge transport to the electrodes.



► So what is a tandem cell? *Hint, it says 'complimentary absorber systems'?* ★



► Konarka's approach...



Channels formed by polymers (tan) and fullerenes (dark blue) allow electric current to flow into the electrode at bottom (NIST). Konarka's approach is similar.

Advantages: low cost, just deposit one semiconductor layer....(forms all the junctions).

NREL Certifies Konarka OPV Solar Cells at 8.3% Efficiency

29 NOVEMBER 2010

SHARE [social media icons]



Konarka Technologies, Inc., the developer of Konarka Power Plastic, a material that converts light to energy, today announced that the National Renewable Energy Laboratory (NREL) has certified Konarka's organic photovoltaic (OPV) solar cells at 8.3% efficiency, the highest performance

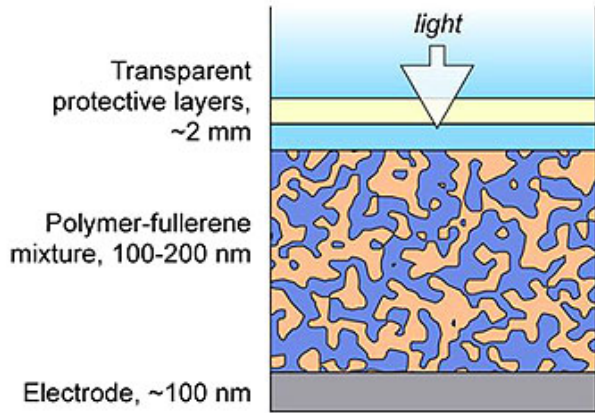
recorded by NREL for an OPV solar cell.

Konarka Power Plastic is a patent-protected thin-film solar material that converts light to energy. The material is lightweight, flexible, scalable and adaptable for use in a variety of commercial, industrial, government and consumer applications. It is suitable for a wide range of applications where traditional PV is not effective.

The latest certification results are for Konarka's large-area single-junction solar cell with a surface area of 1 square centimeter (cm²). This efficiency rating exceeds previous single-junction organic photovoltaic cell measurement on that surface area.



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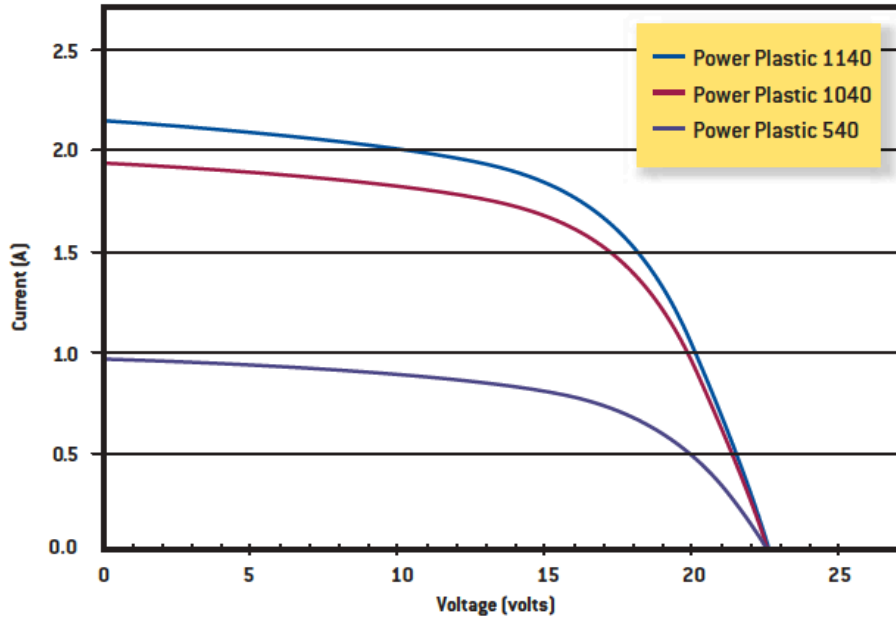
Portable battery charger OPV solar panel by Konarka.



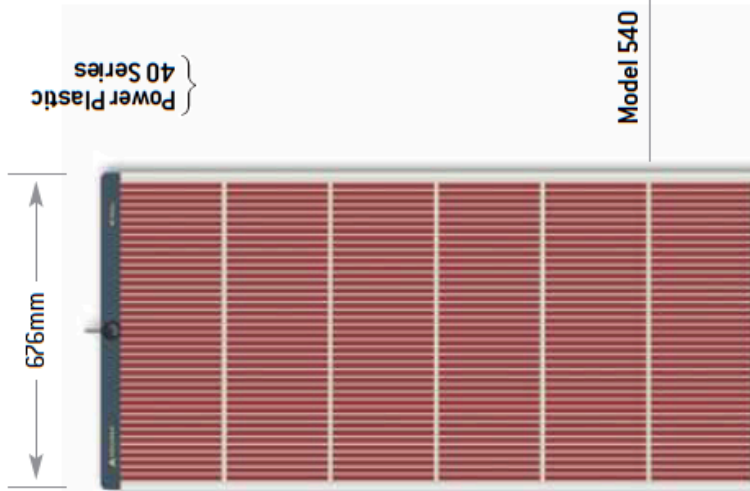
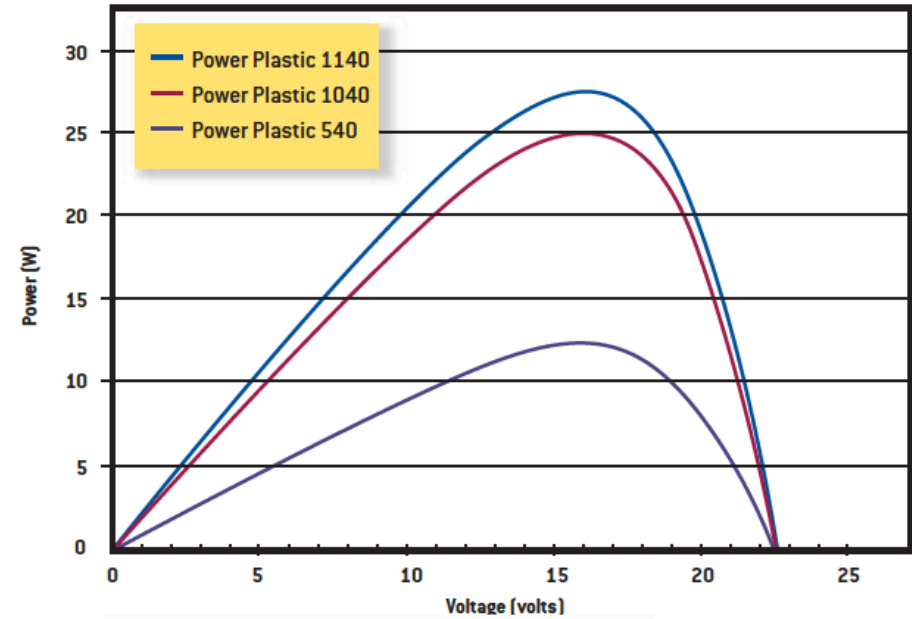
Examples from Konarka (above). Advantages:

- ▶ Portable (potentially rollable)
- ▶ Flexible (impact resistant)
- ▶ Potentially low cost
- ▶ Semitransparent

Power Plastic 40 Series: IV Curves



Power Plastic 40 Series: Power Curves



Outdoor Performance

Electrical Data		Units	1 Sun			1/2 Sun		
All 40 Series	V _{mpp}	V	15.8			15.2		
	★ V _{oc}	V	22.6			21.8		
I _{mpp} / I _{sc}		A	I _{mpp}	I _{sc}	Watts	I _{mpp}	I _{sc}	Watts
Power Plastic 540			0.8	1.0	12.4	0.4	0.5	6.0
Power Plastic 1040			1.6	1.9	24.7	0.8	1.0	12.0
Power Plastic 1140			1.7	2.1	27.2	0.9	1.1	13.2



Lots of excitement about OLEDs and OPV, but they keep struggling to commercialize...

One strong success is OLED displays in smart-phones (small size screen easier to manufacture).

Investors burned as Konarka enters liquidation

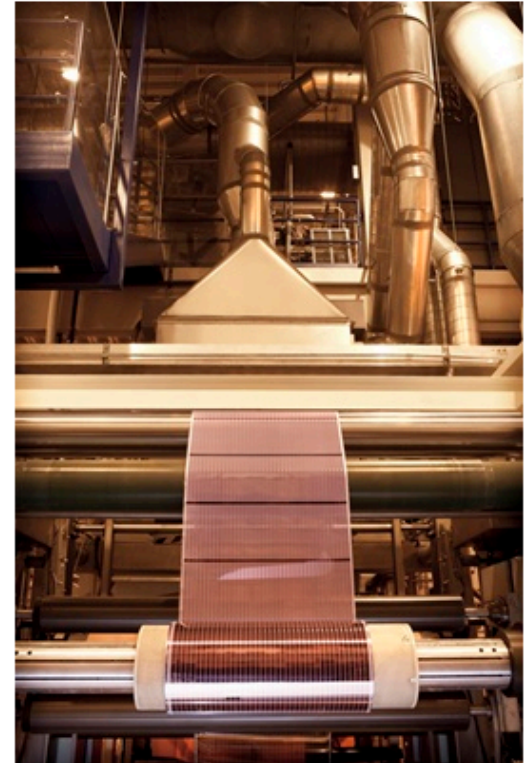
07 Jun 2012

Organic PV company demonstrates that \$200 million and a Nobel prize are no guarantee of commercial success.

Konarka Technologies, the heavily financed company at the forefront of organic photovoltaics (OPV) development that was co-founded by a Nobel laureate, has filed for chapter 7 bankruptcy in its home state of Massachusetts.

The demise of the firm represents a significant failure for its investors, which included the energy companies Chevron and Total alongside several venture capitalists. Together, they have invested close to \$170 million in Konarka over the past decade.

Among those with their fingers burned are Vanguard Ventures, New Enterprise Associates, 3i, Good Energies and the Massachusetts Green Energy Fund, who have taken part in one or more of at least



Roll-to-roll production

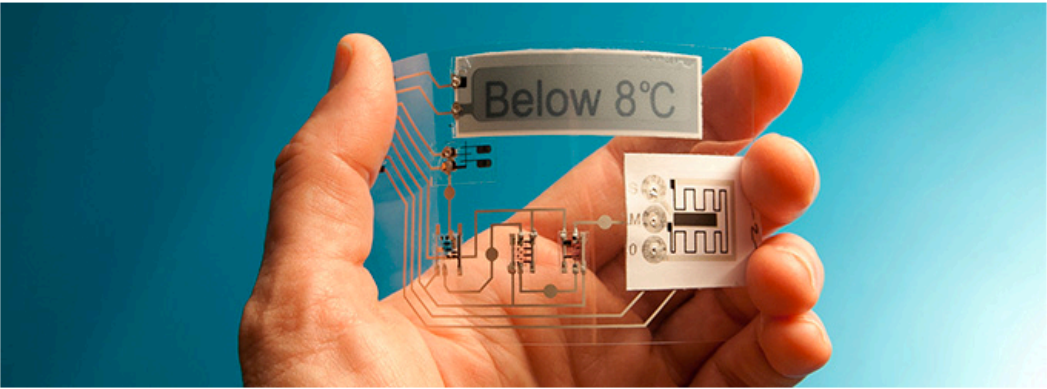




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Home » Our Products

► **SENSOR LABELS**



Memory and sensors together in a disposable electronic label. ★

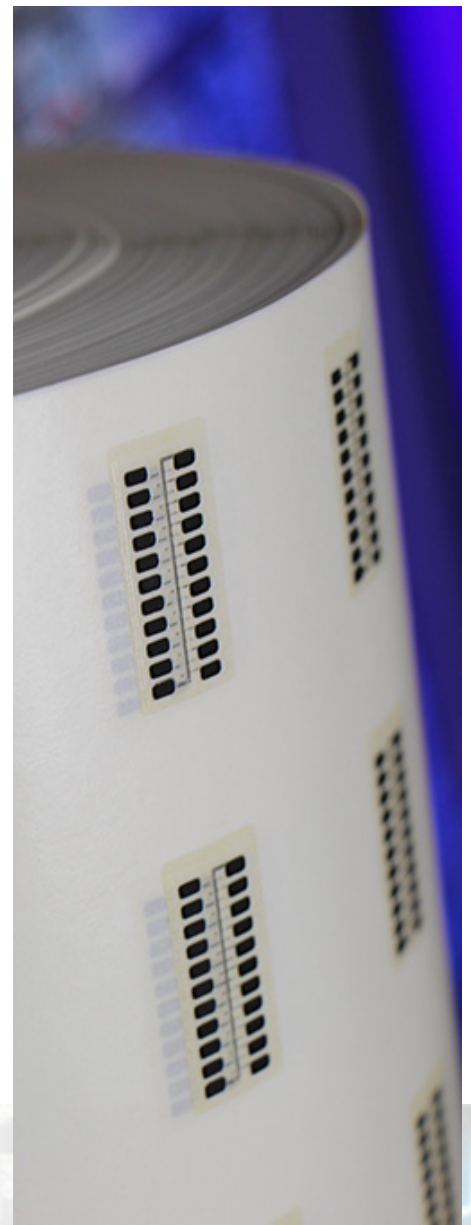
Thinfilm is developing a line of intelligent labels that will sense information and store data for 1/10th to 1/100th the cost of conventional electronics. This is part of Thinfilm's vision to bring the Internet of Things to even the lowest cost items.

PRINTED TEMPERATURE SENSOR

The Thinfilm Time-Temperature Sensor will provide digital temperature and exposure information for perishable products, at a price point that competes with old-style chemical labels. The first proof-of-concept was demonstrated in December 2012, showing that when preset temperature thresholds were detected, data was stored to memory and subsequently read out to a display.



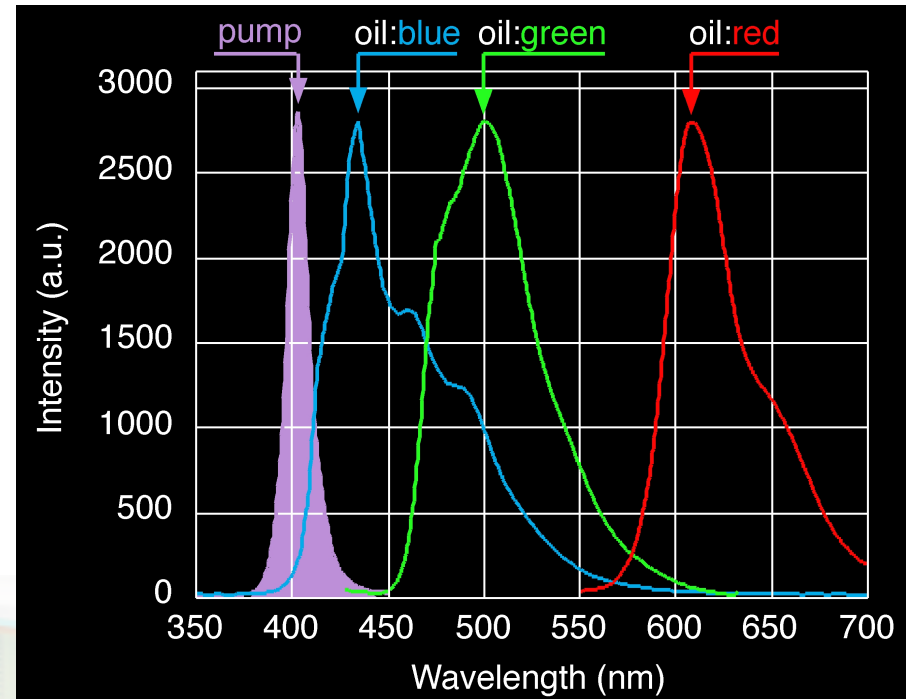
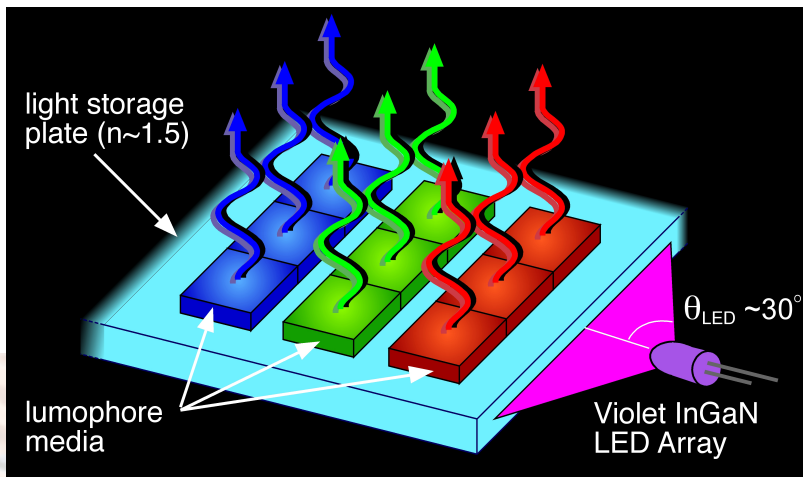
Temperature monitoring is a \$3.5 Billion market today, and over 200 million chemical sensor tags are sold every year at a price point of 30-cents. These devices are used for monitoring temperature sensitive goods such as pharmaceuticals and perishable food products. Thinfilm's electronic tags will be able to not only monitor temperature incursions during shipments, but also provide that data electronically for later use and analysis.





See video at very bottom of page...

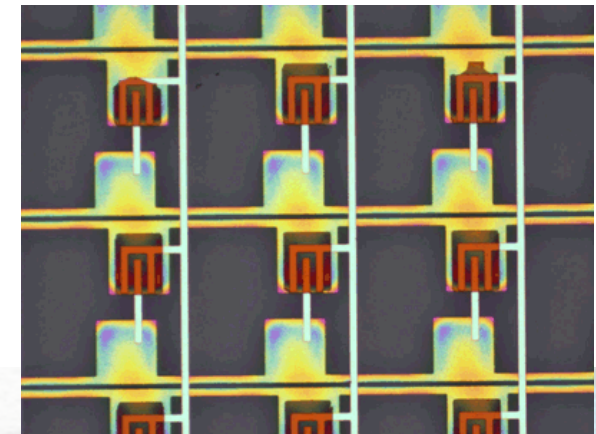
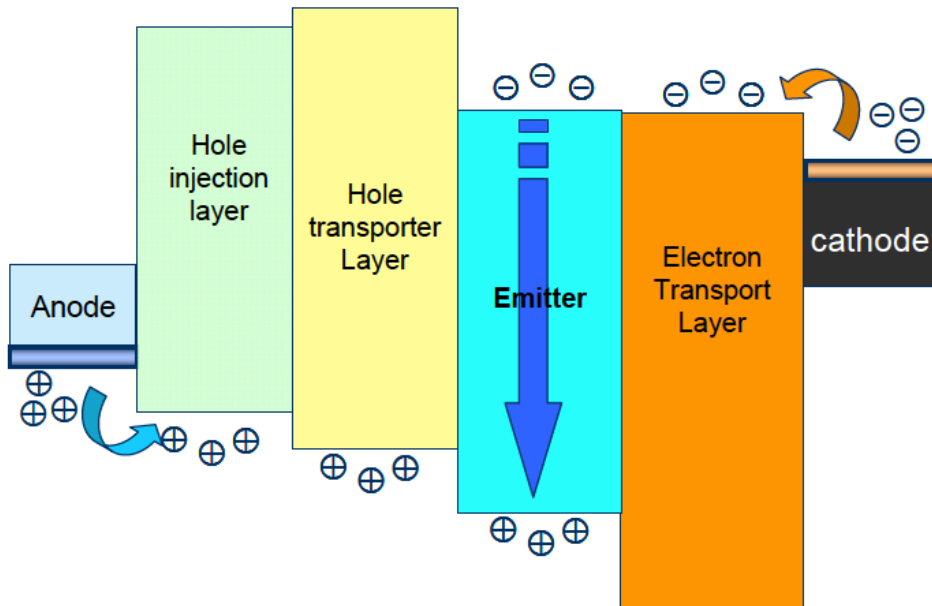
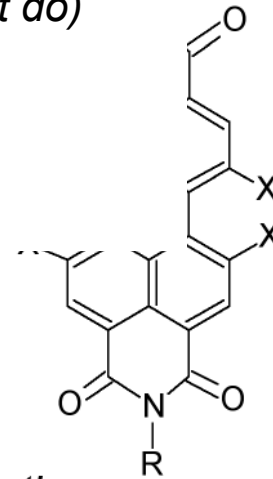
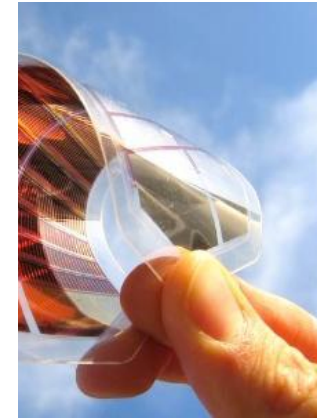
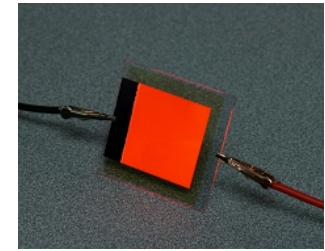
http://secs.ceas.uc.edu/devices/NDL_Video.html



► For the more advanced OLED device shown at bottom...

- why do we have a hole injection layer?
- why did we add a hole transport layer? (what does it do)
- why did we add an electron transport layer? (what does it do)
- why don't we need an 'electron injection layer'?

► How do you electrically drive an OLED display?





Best Research-Cell Efficiencies

