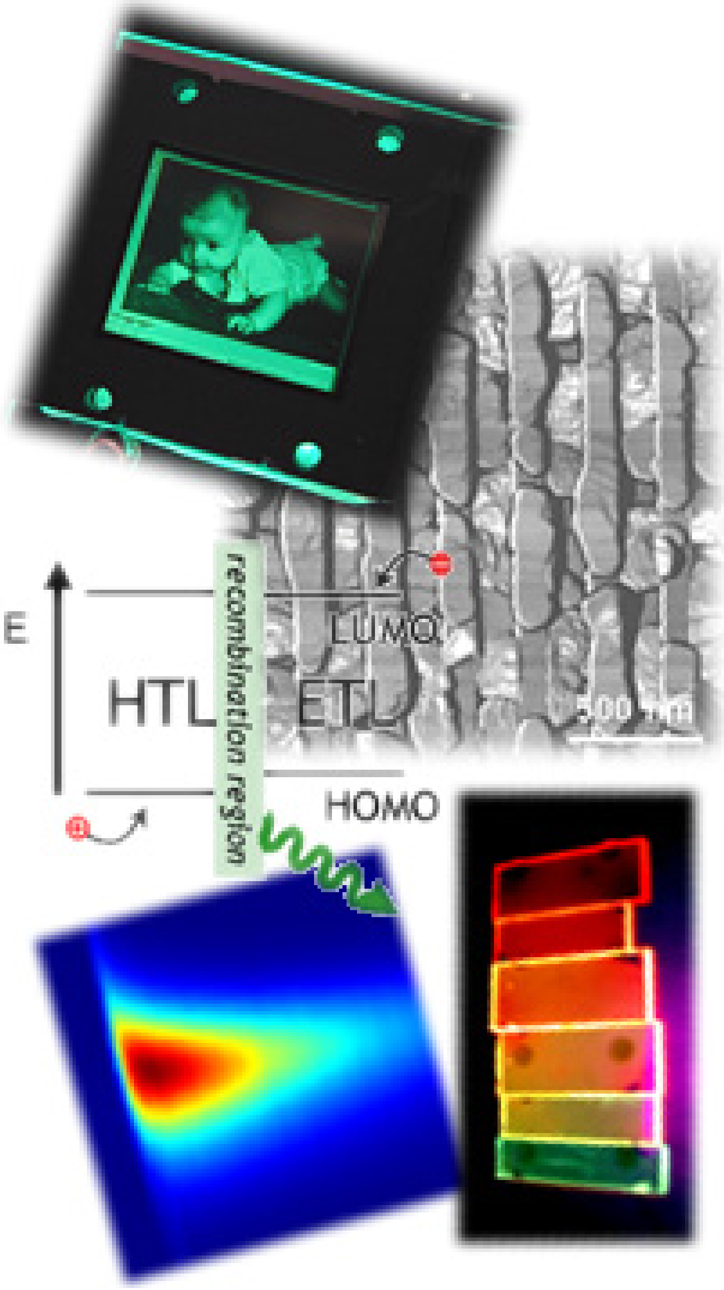
Welcome to 6.973
~ Organic Opto-Electronics ~

Vladimir Bulović

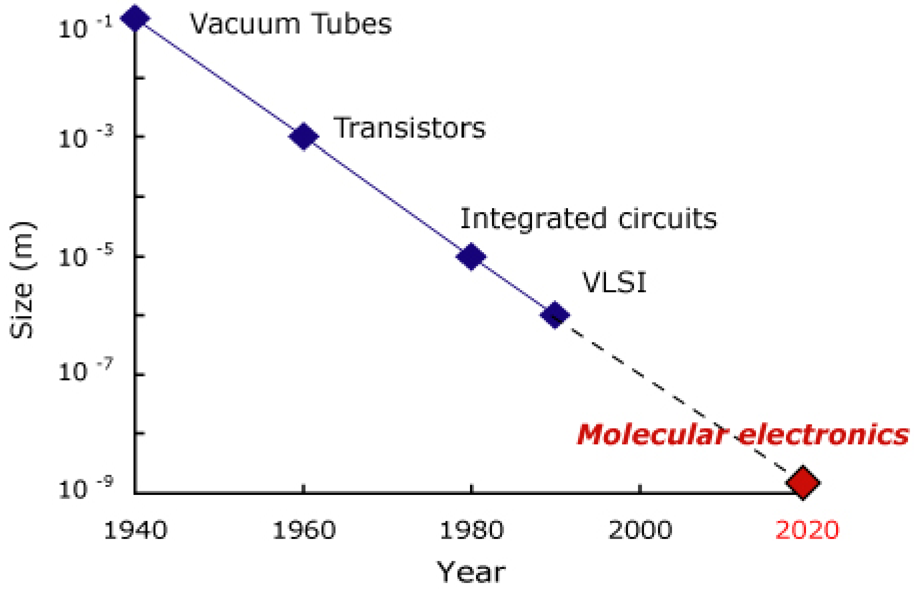


COURSE MISSION

examine optical and electronic processes
in organic molecules and polymers
that govern the behavior of practical
organic optoelectronic devices

looe
@ MIT

March Towards Molecular Electronics

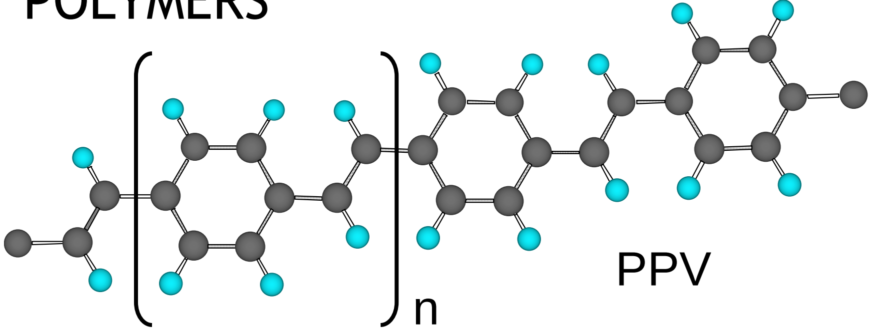


The shrinkage of electronic components. The length scale reached by technology has dropped steadily from the millimeter scale of the early 1950s to the present-day atomic scale. In 1950, the first transistor measured 1mm. Quantum-dot turnstiles of the 1980s measured 10um. Quantum corrals, invented in the 1970s measured 100nm. The latest device is a one-atom point contact.

Adapted from L.L. Sohn, Nature 394, 131 (1998).

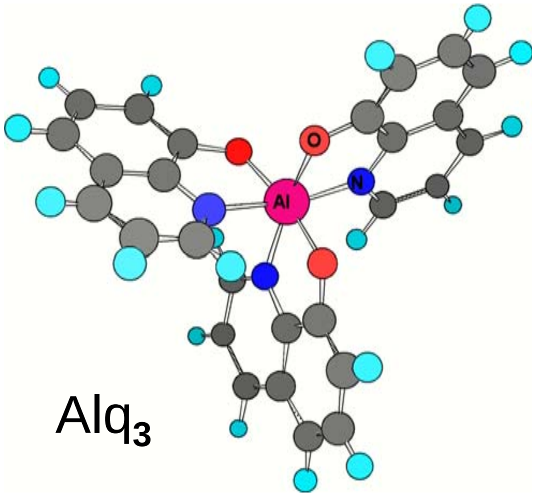
Organic Materials … *TWO GENERAL CLASSES*

POLYMERS



PPV

MOLECULAR MATERIALS



Alq_3

Attractive due to:

- Integrability with inorganic semiconductors
- Low cost **(fabric dyes, biologically derived materials)**
- Large area bulk processing possible
- Tailor molecules for specific electronic or optical properties
- Unusual properties not easily attainable with conventional materials

But problems exist:

- Stability
- Patterning
- Thickness control of polymers
- Low carrier mobility

Scientific Interest in Organic Materials

- 1828 - Wöhler first synthesized urea
  without the assistance of a living organism
- 1950's - steady work on crystalline organics starts
- 1970's - organic photoconductors (xerography)
- 1980's - organic non-linear optical materials
- 1987 - Kodak group published the first
  efficient organic light emitting device (OLED)
- Since then, the field has dramatically expanded
  both commercially and scientifically
  (OLEDs, transistors, solar cells, lasers, modulators, ...)

to date, about two million organic compounds have been made
- this constitutes nearly 90% of all known materials -

Nobel Prize in Chemistry for 2000

The Royal Swedish Academy of Sciences awards the Nobel Prize in Chemistry for 2000 jointly to:

- **Alan J. Heeger,** University of California at Santa Barbara, USA,
- **Alan G. MacDiarmid,** University of Pennsylvania, Philadelphia, USA,
- **Hideki Shirakawa**, University of Tsukuba, Japan

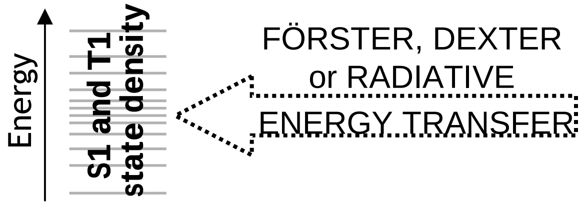
"for the discovery and development of conductive polymers"

Plastic that conducts electricity

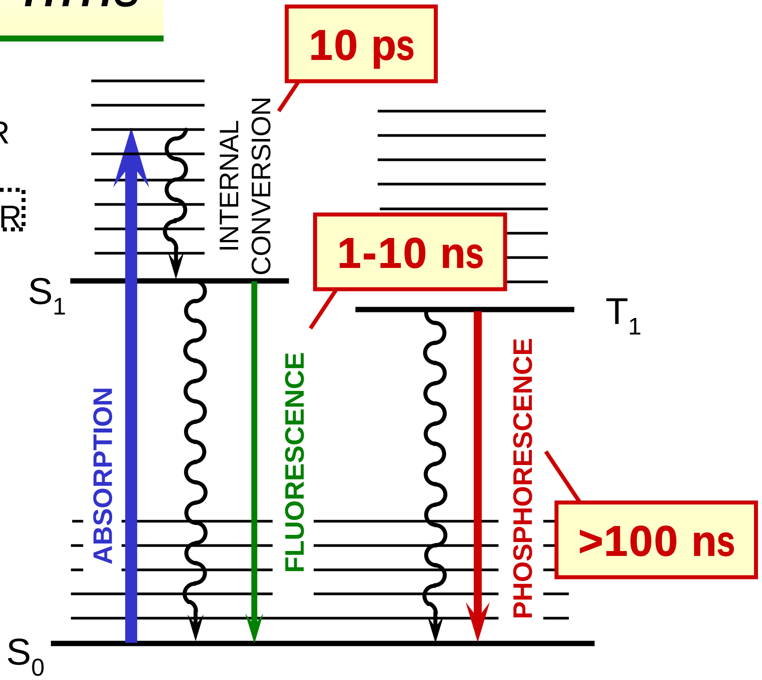
We have been taught that plastics, unlike metals, do not conduct electricity. In fact plastic is used as insulation round the copper wires in ordinary electric cables. Yet this year's Nobel Laureates in Chemistry are being rewarded for their revolutionary discovery that plastic can, after certain modifications, be made electrically conductive. Plastics are polymers, molecules that repeat their structure regularly in long chains. For a polymer to be able to conduct electric current it must consist alternately of single and double bonds between the carbon atoms. It must also be "doped", which means that electrons are removed (through oxidation) or introduced (through reduction). These "holes" or extra electrons can move along the molecule - it becomes electrically conductive. Heeger, MacDiarmid and Shirakawa made their seminal findings at the end of the 1970s and have subsequently developed conductive polymers into a research field of great importance for chemists as well as physicists. The area has also yielded important practical applications. Conductive plastics are used in, or being developed industrially for, e.g. anti-static substances for photographic film, shields for computer screen against electromagnetic radiation and for "smart" windows (that can exclude sunlight). In addition, semi-conductive polymers have recently been developed in light-emitting diodes, solar cells and as displays in mobile telephones and mini-format television screens. Research on conductive polymers is also closely related to the rapid development in molecular electronics. In the future we will be able to produce transistors and other electronic components consisting of individual molecules - which will dramatically increase the speed and reduce the size of our computers. A computer corresponding to what we now carry around in our bags would suddenly fit inside a watch.

http://www.nobel.se/chemistry/laureates/2000/press.html

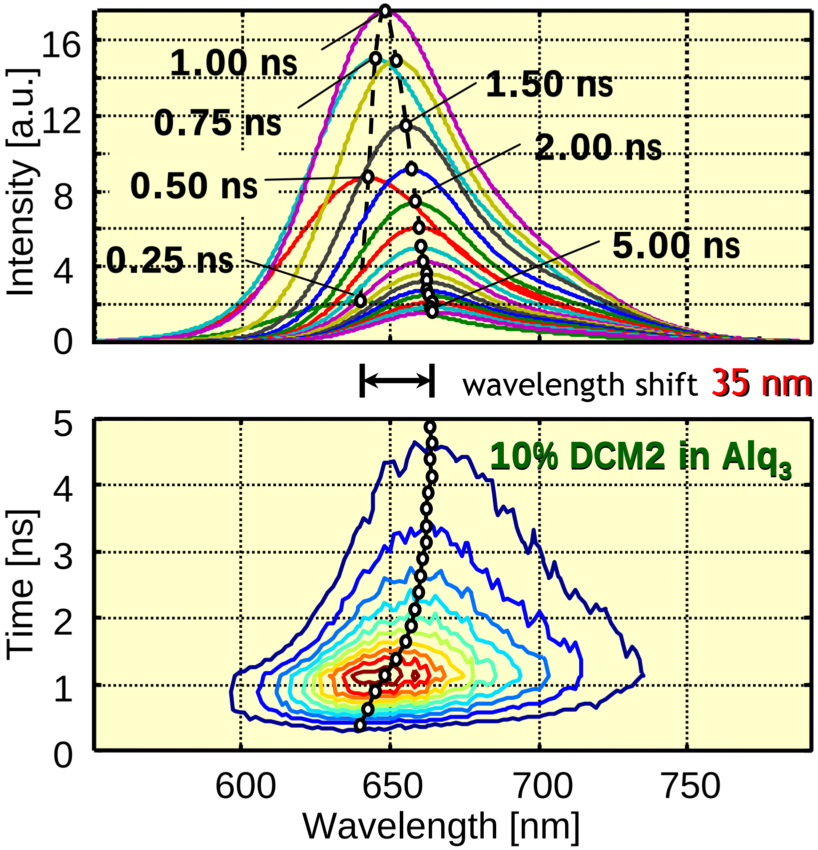
Electronic Processes in Molecules / Aggregates / Thin Films



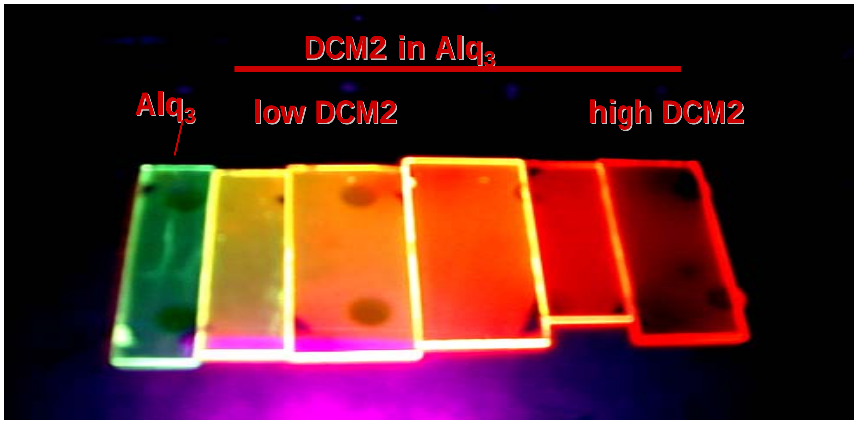
FÖRSTER, DEXTER or RADIATIVE ENERGY TRANSFER



Temporal Response

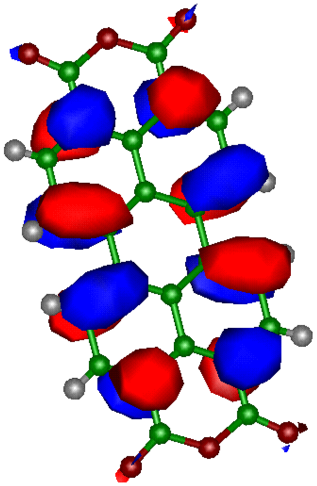


Solid State Solvation



Bulovic´*et al.*, *Chem. Phys. Lett.* 287, 455 (1998); 308, 317 (1999).

Organic Thin Films … *may be AMORPHOUS or CRYSTALLINE*

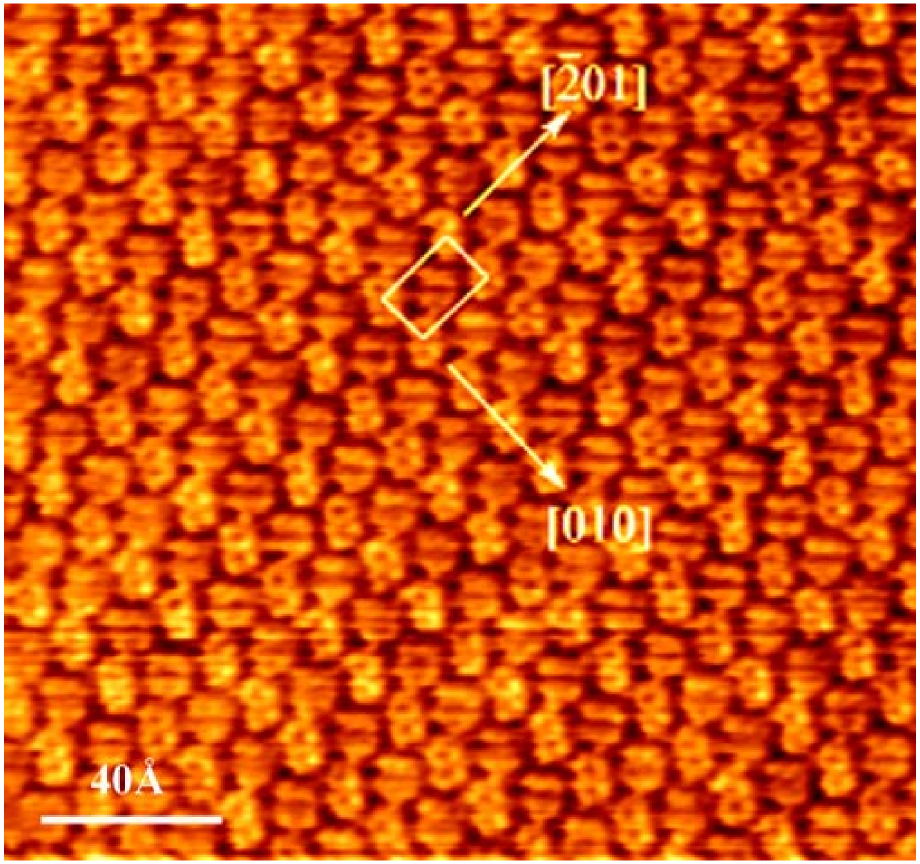


molecular orbital calculation of the electron density in the highest occupied molecular orbital of a PTCDA molecule

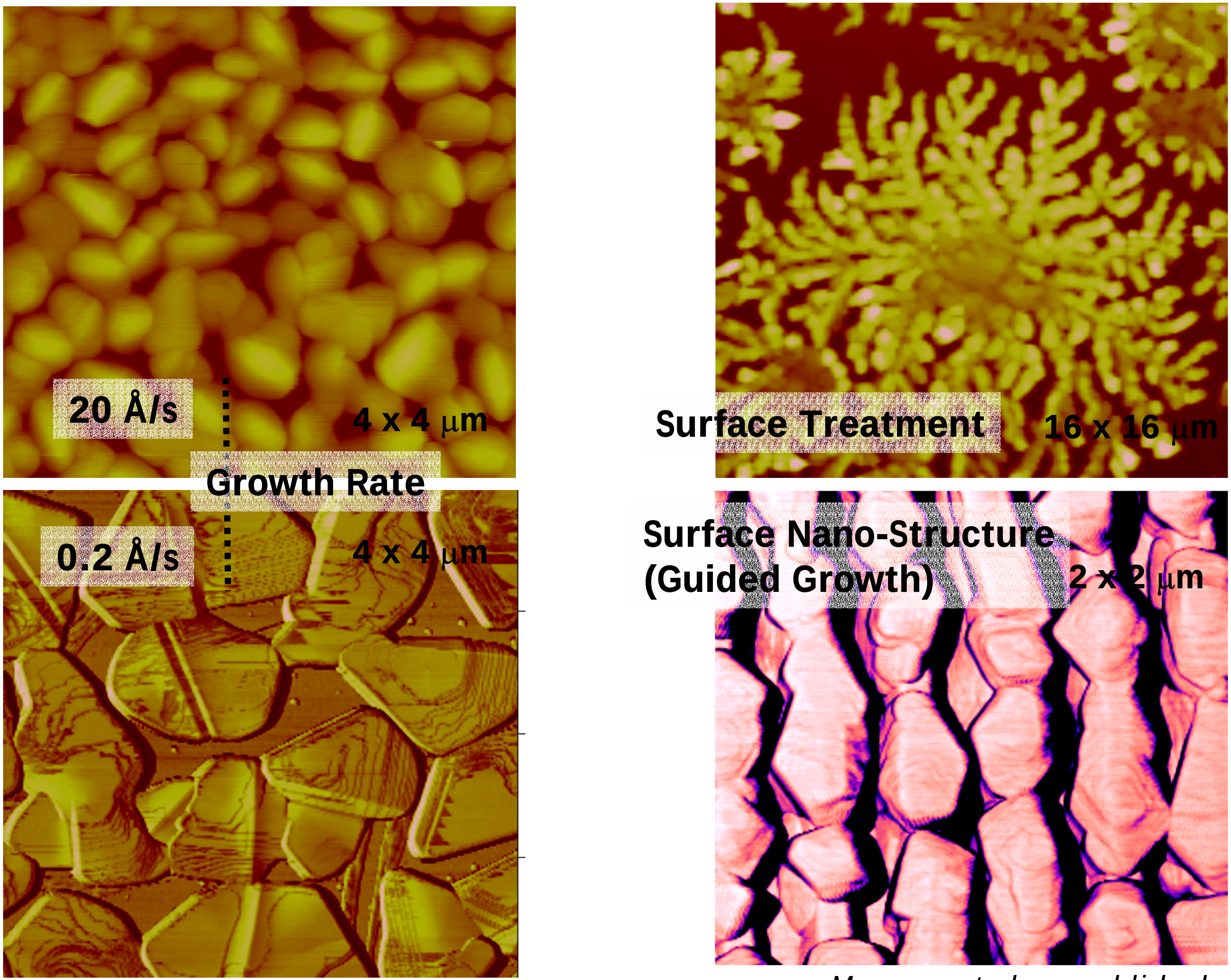
Agreement between the calculation and the experiment exemplifies maturity of detailed understanding of electronic arrangement on molecules.

However, …
DYNAMIC ELECTRONIC PROCESSES in
MOLECULES and MOLECULAR ASSEMBLIES
are NOT WELL UNDERSTOOD
and present a topic of our research

STM scan of
ordered PTCDA monolayer on HOPG



Tetracene Thin Film Growth is affected by ...



Growth Rate

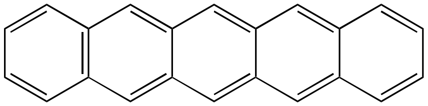
Surface Treatment

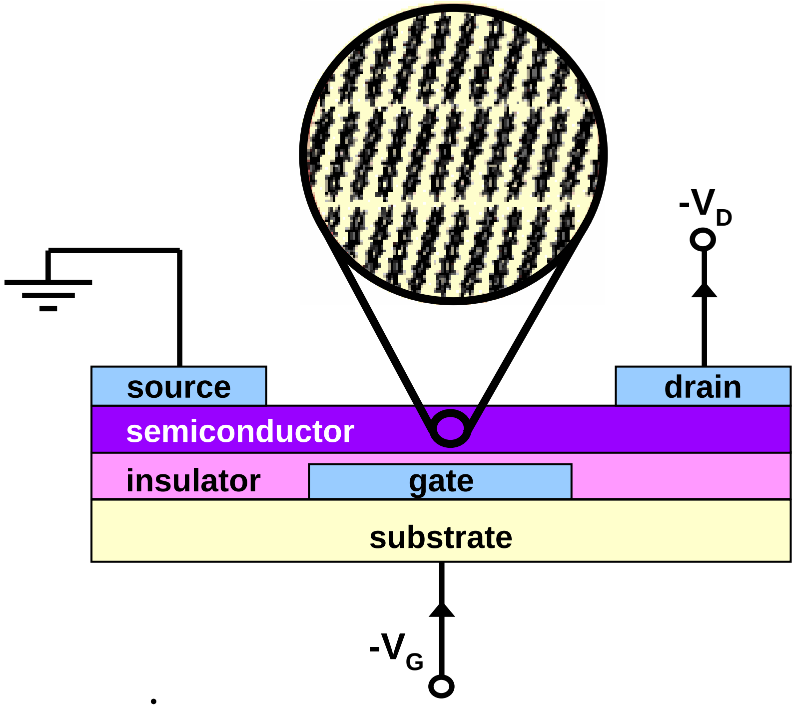
Surface Nano-Structure (Guided Growth)

Mascaro, et al., unpublished.

Organic Field Effect Transistors

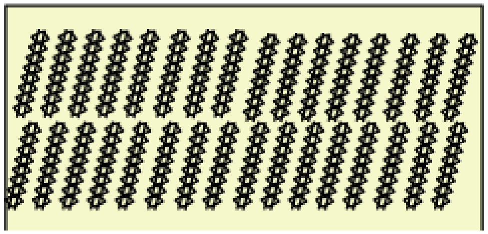
pentacene





IBM

Plastic Logic



$T_{deposition}$=27 °C
DR=1.0 Å/sec ⇨ μ~0.6 $cm^2\ V^{-1}\ s^{-1}$

Charge carrier mobility is dependent on molecular order within the semiconducting thin film

IMPROVED MOLECULAR ORDERING

⇩

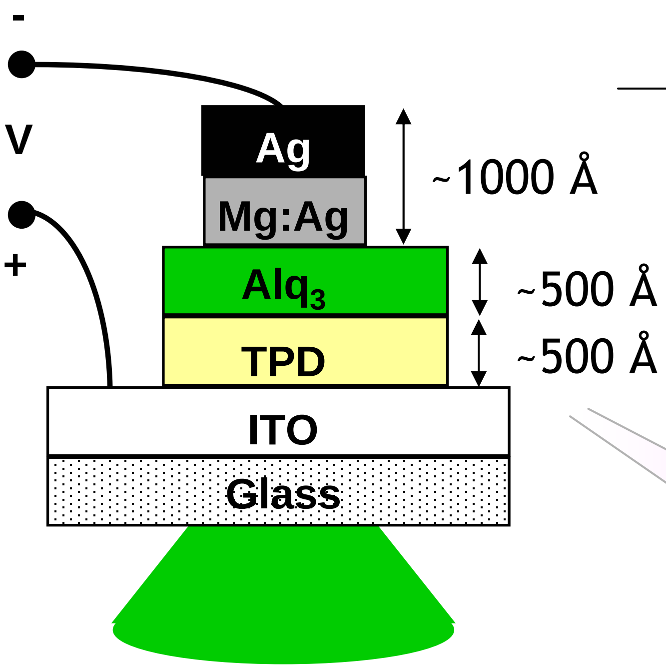
Larger grain sizes
Lower defect densities

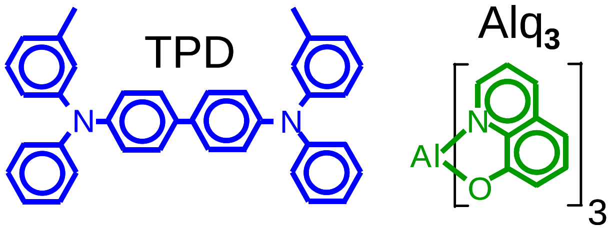
⇩

Enhanced mobility

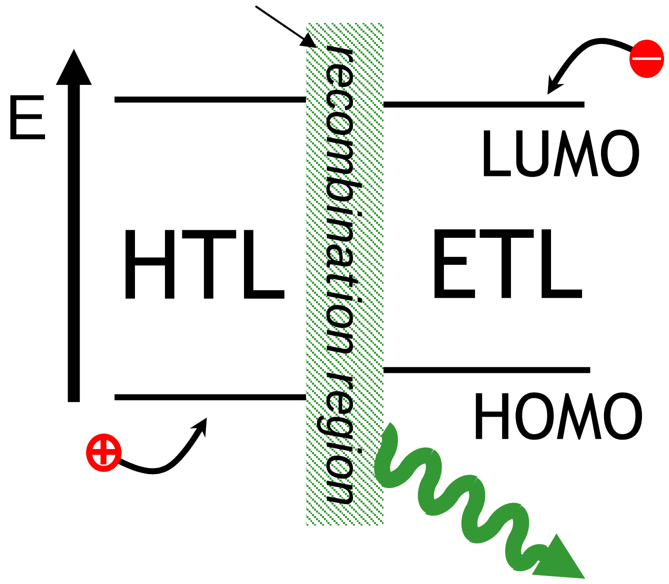
Adapted from Dimitrakopoulos, et. al., IBM J. Res. and Devel. 45, 11 (2001).

Organic Light Emitting Devices





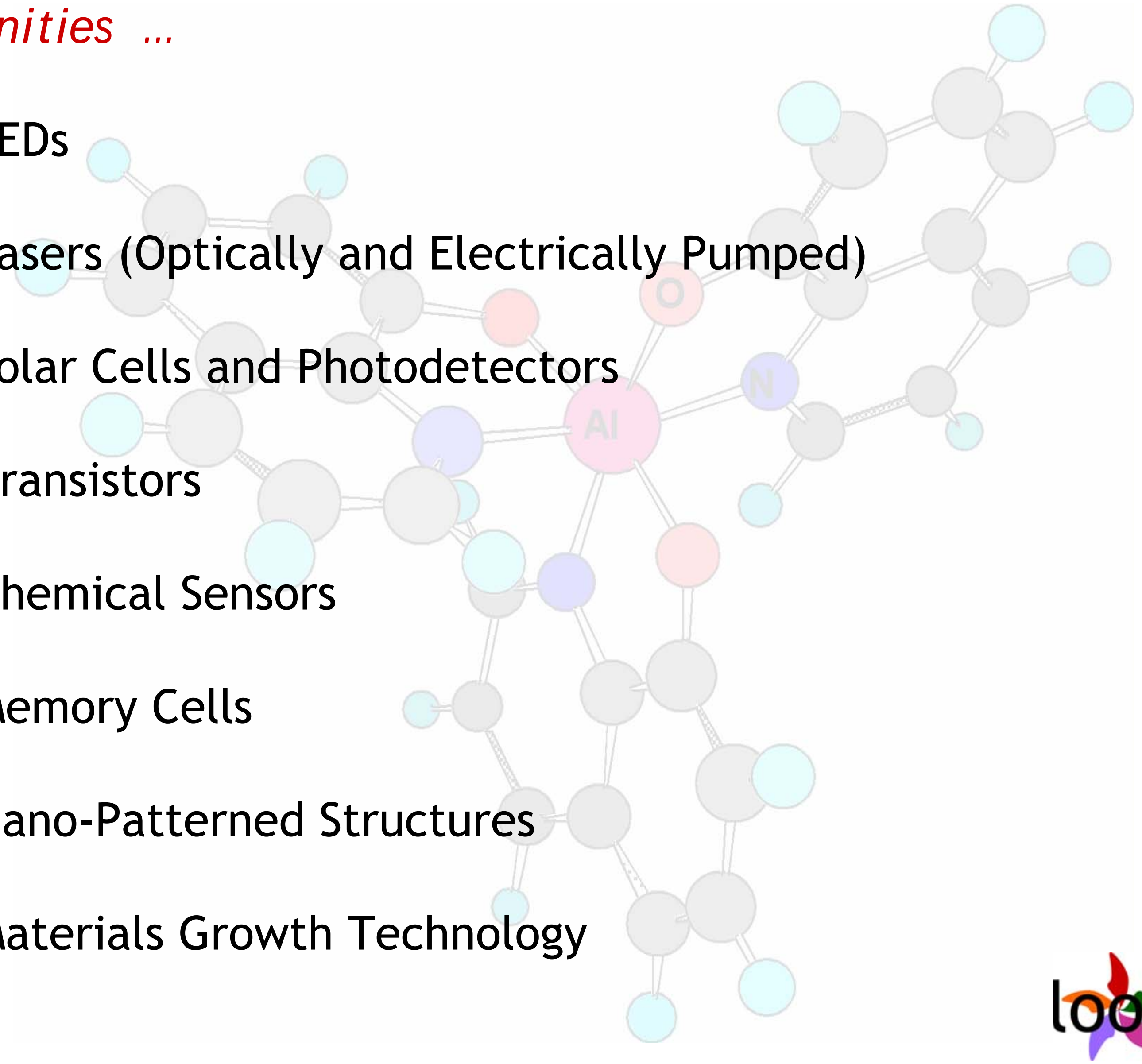
electrons and holes
form ***excitons***
(bound e^--h^+ pairs)



some excitons radiate

Kodak/Sanyo AM-OLED QVGA Display

Opportunities …

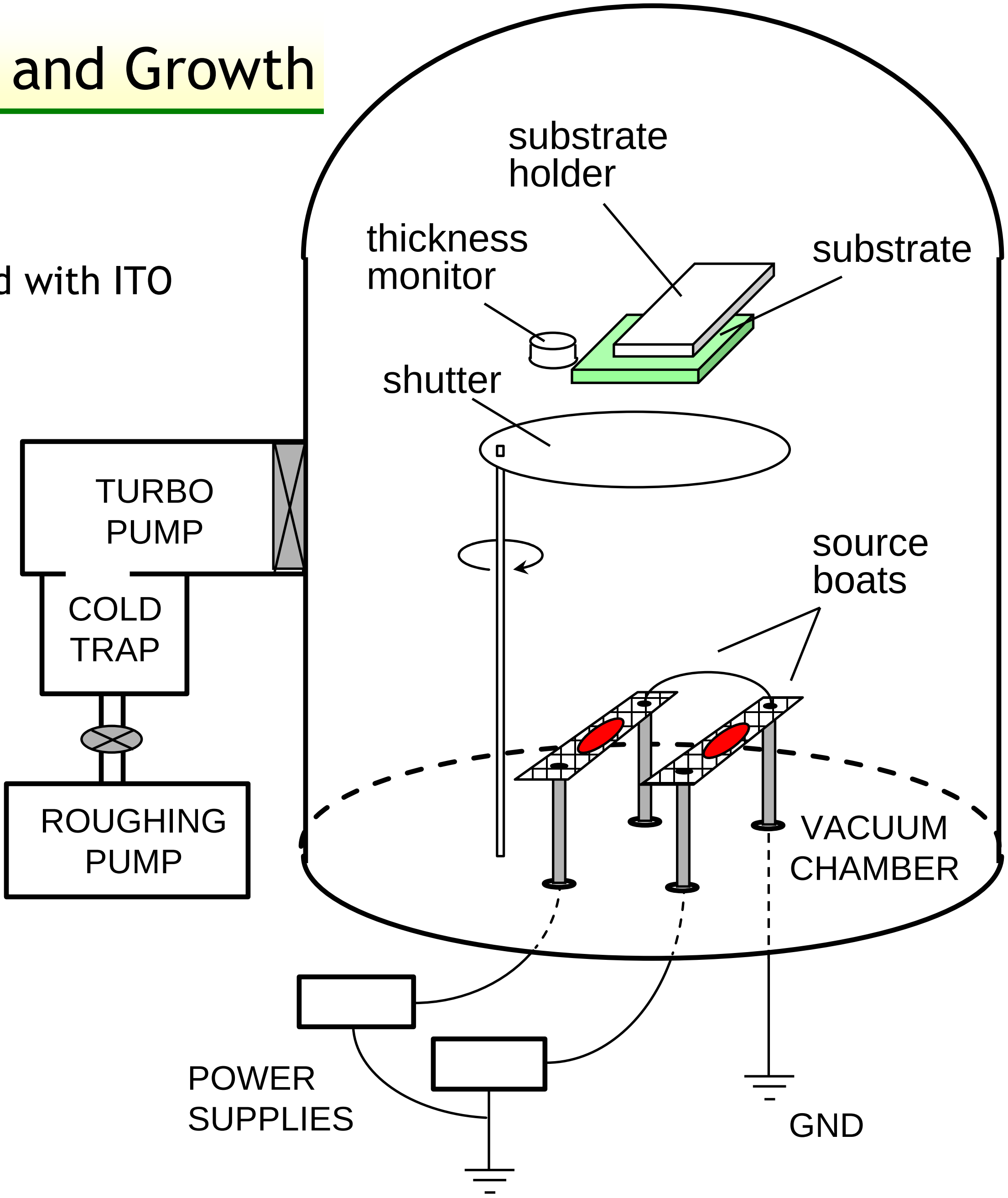


- LEDs
- Lasers (Optically and Electrically Pumped)
- Solar Cells and Photodetectors
- Transistors
- Chemical Sensors
- Memory Cells
- Nano-Patterned Structures
- Materials Growth Technology

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

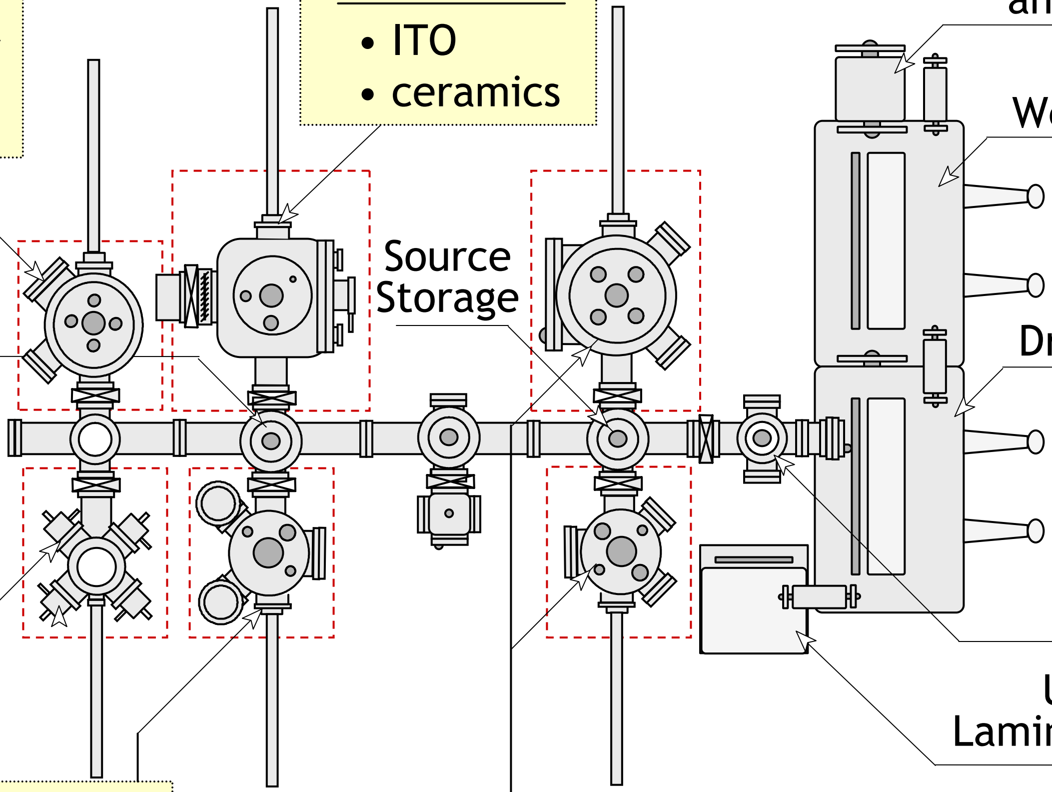
  - 20 to 2000 Å
    layer thickness



Integrated Materials Growth System

Sponsored by AFOSR and NSF

capable of in-situ growth and testing of multilayer structures and devices



Chemical Vapor Dep.

chemically selective materials deposition

Sputtering

- ITO
- ceramics

Ante Chamber and Oven

Wet N2 Glove Box

Sample-Mask Storage

Source Storage

Dry N2 Glove Box

Probe Station with Cryostat

Load Lock

UV-Ozone Laminar Flow Hood

Physical & Vapor Phase Dep.

- molecular organics
- nano-dots **
- solvated polymers **
- colloids **

Evaporative Deposition

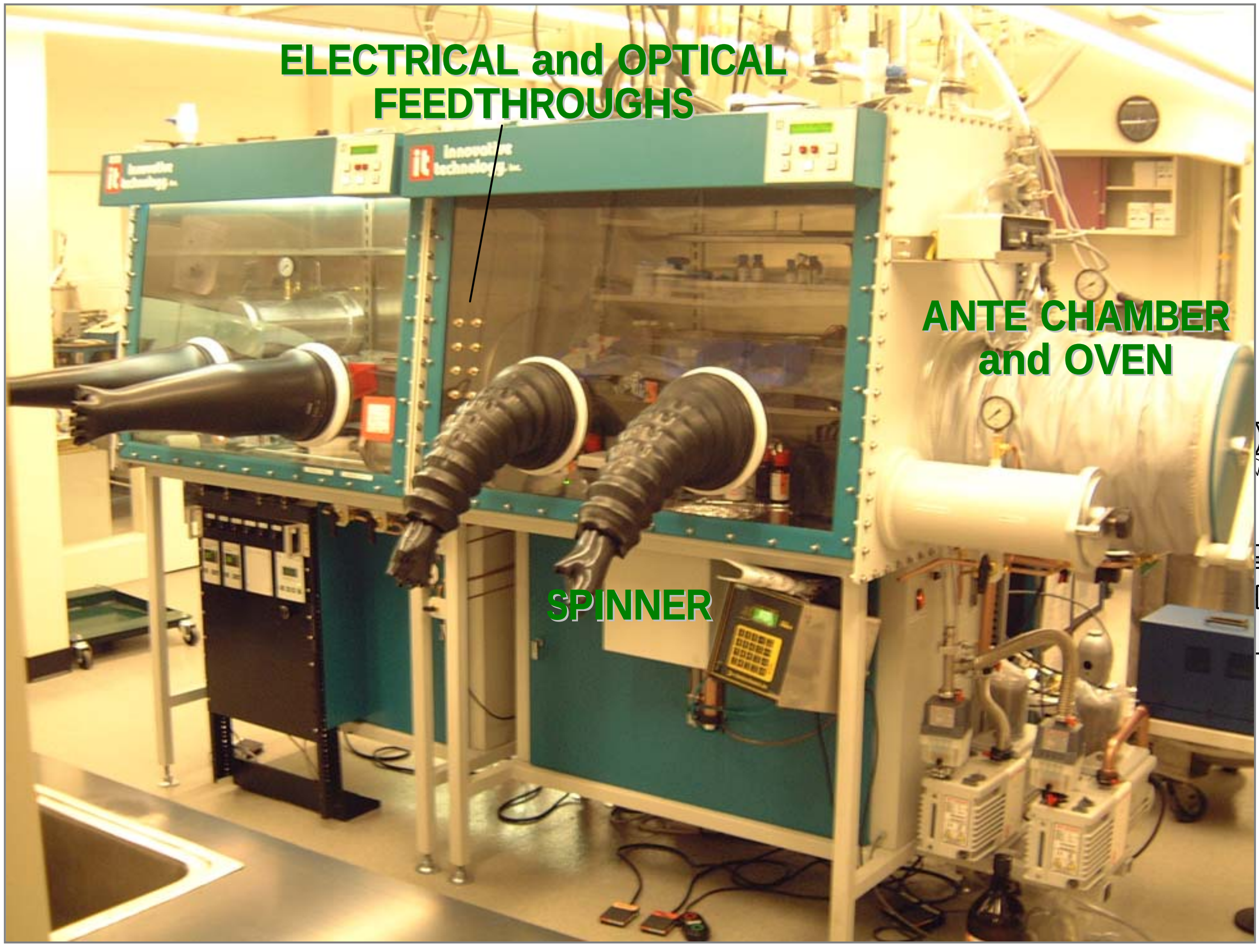
- molecular organics
  (amorphous and crystalline)
- metals

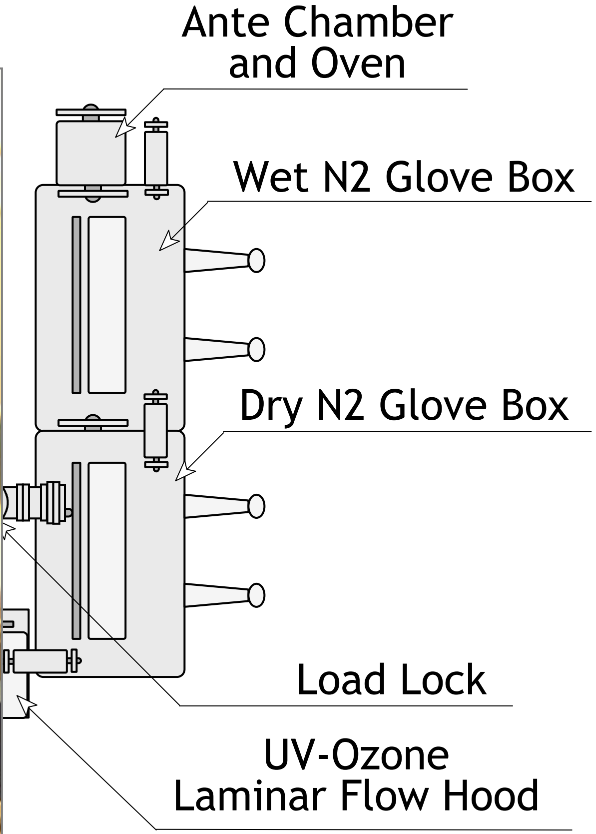
MIT lab of ORGANIC OPTICS & ELECTRONICS

looe @ MIT

Double Glove Box

Moisture Level < 1 ppm




Ante Chamber and Oven

Wet N2 Glove Box

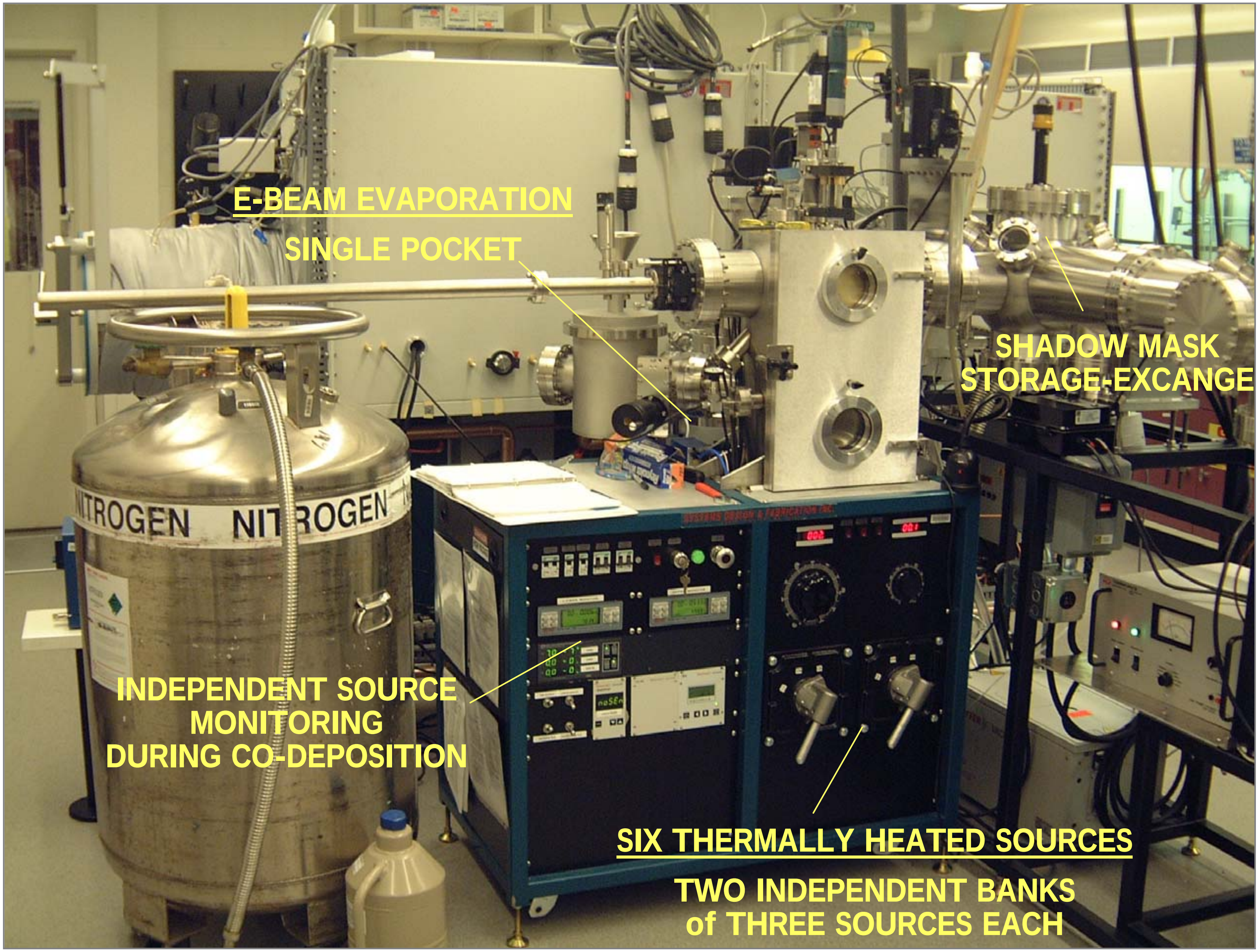
Dry N2 Glove Box

Load Lock

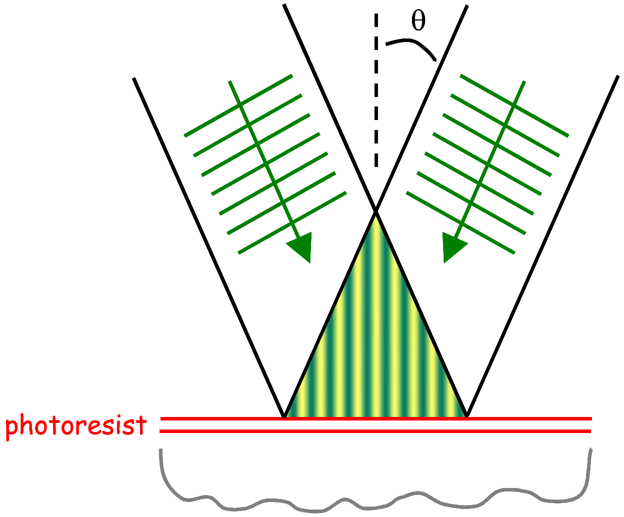
UV-Ozone Laminar Flow Hood

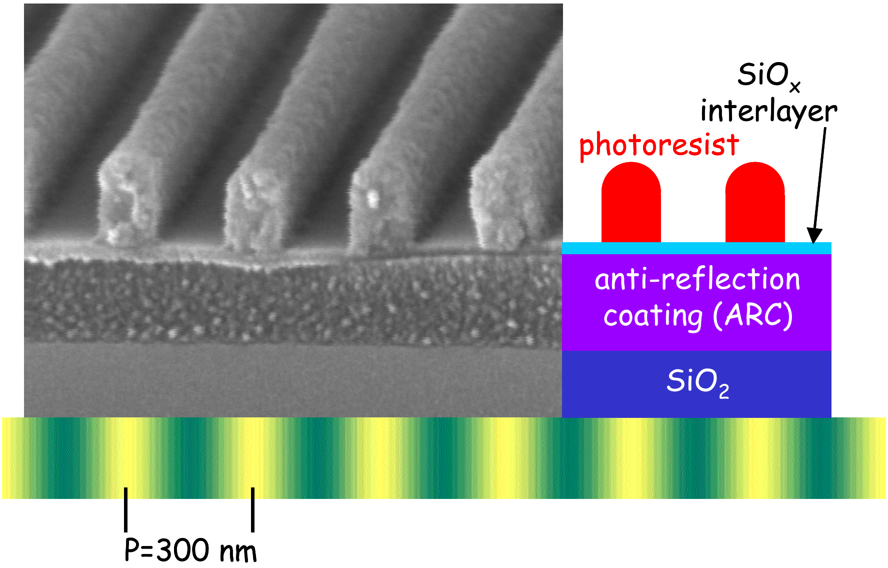
Thermal Evaporator

BASE PRESSURE ~ 7 X 10^{-8} torr



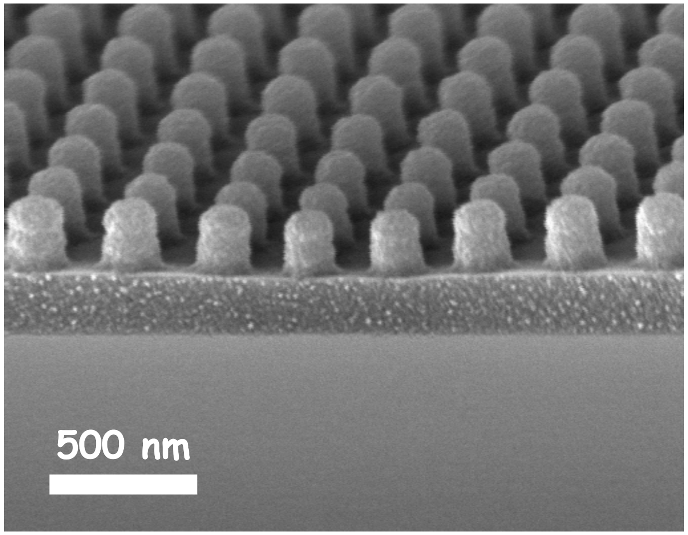
Interference Lithography

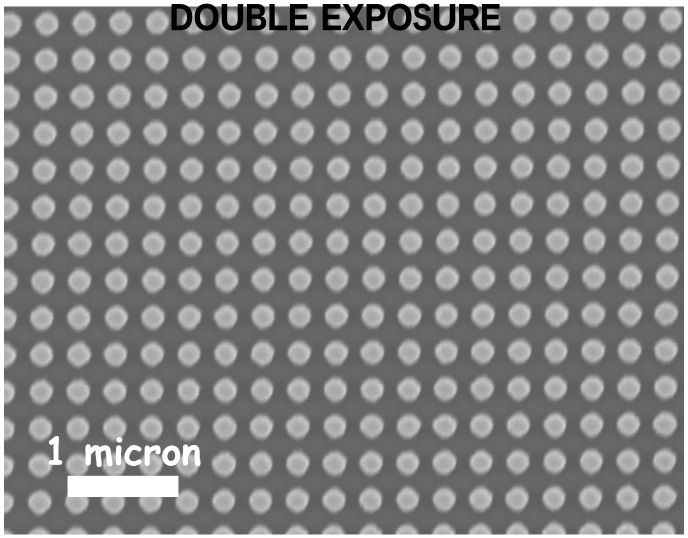




λ =325 nm

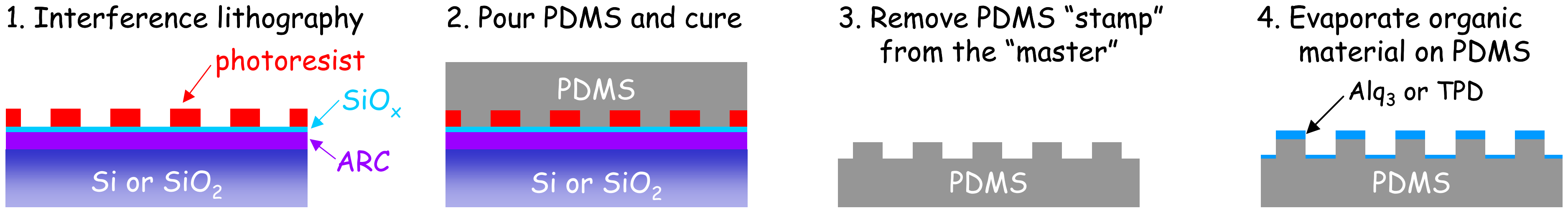
θ=30° → P=325 nm



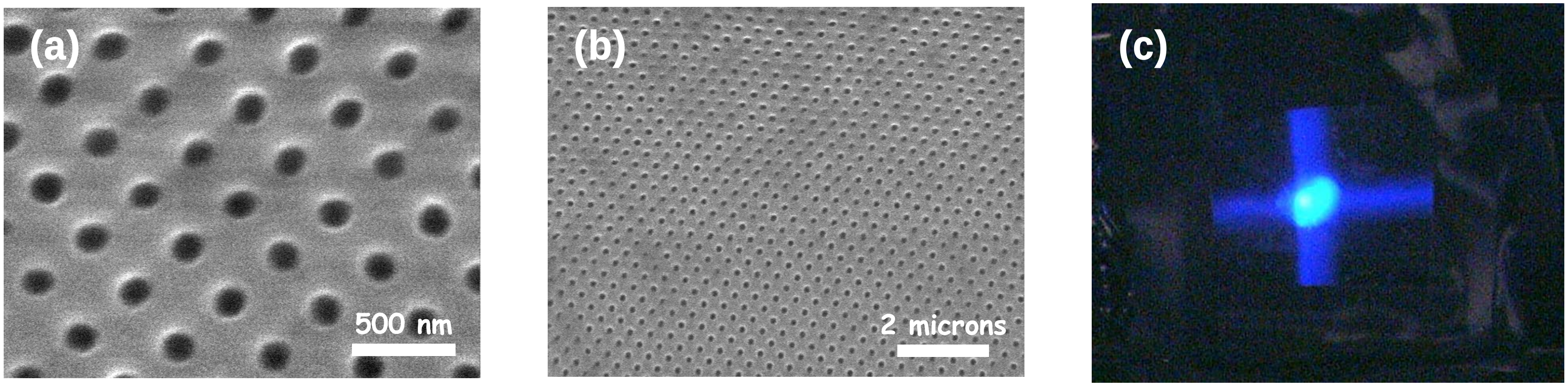


Mascaro, et al, unpublished

Sequence of steps for generating a PDMS PBG structure with an organic luminescent layer on top



1. Interference lithography
2. Pour PDMS and cure
3. Remove PDMS “stamp” from the “master”
4. Evaporate organic material on PDMS

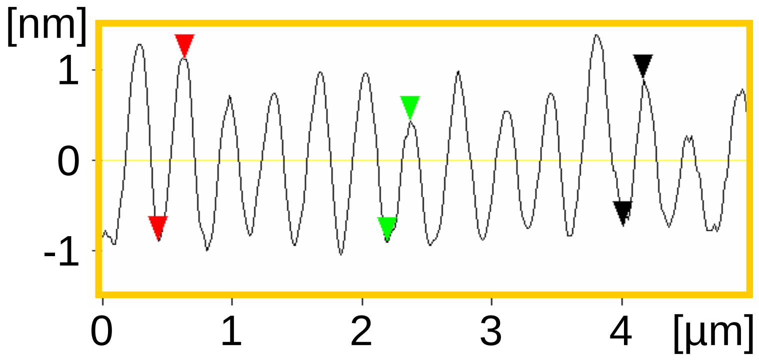


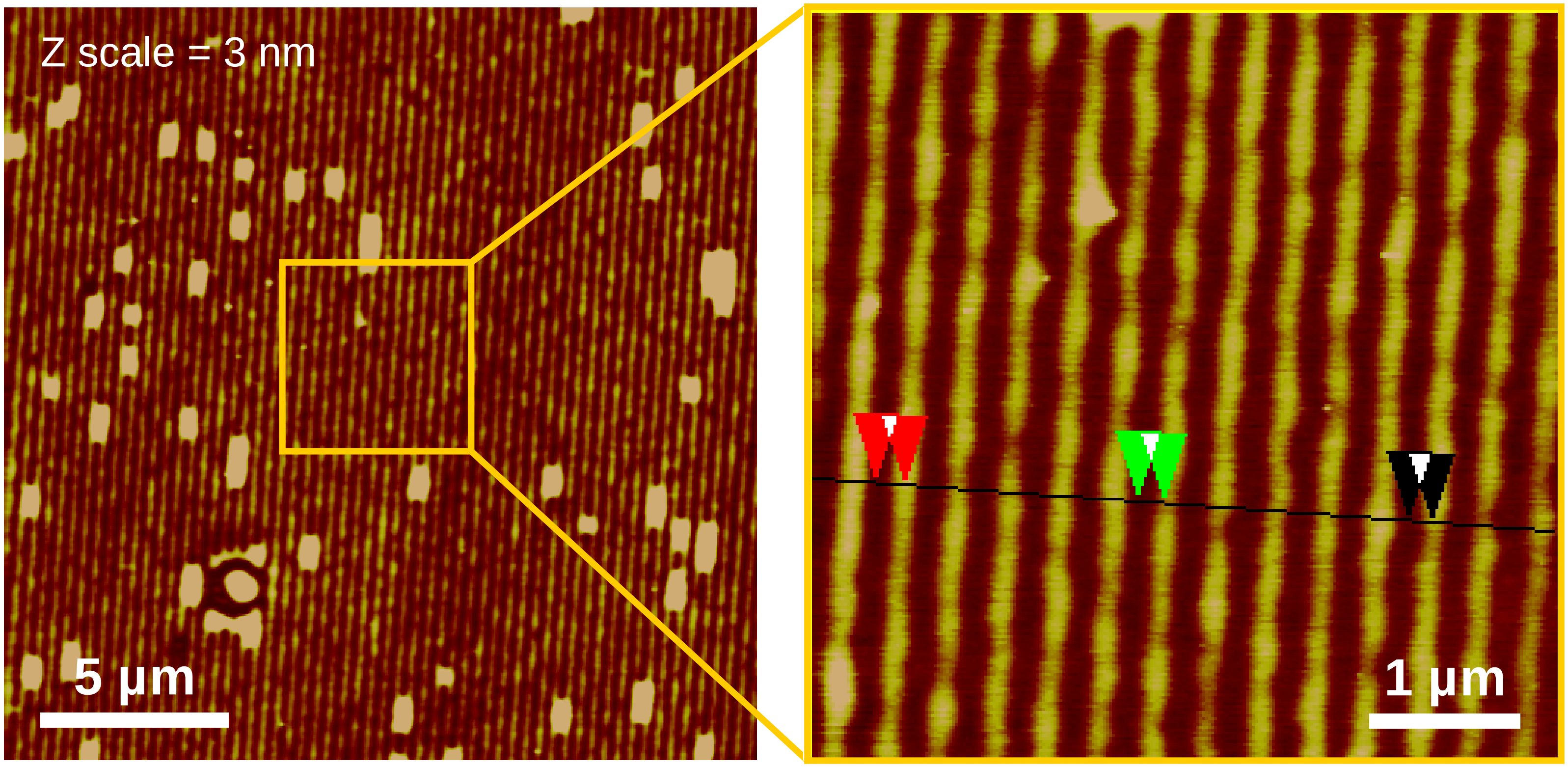
Lowell, Mascaro, et al

Reduce the size of active structures

… by stamping nano-features
of monolayer thickness

Mascaro, et al., unpublished.

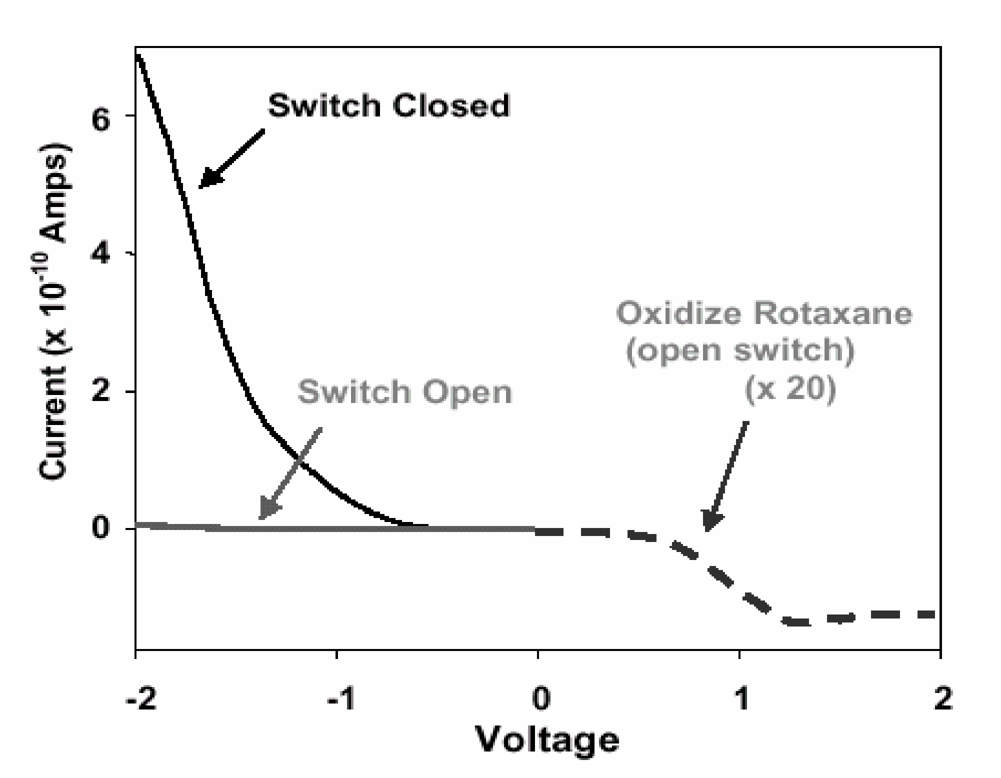




Memory Cells and FETs

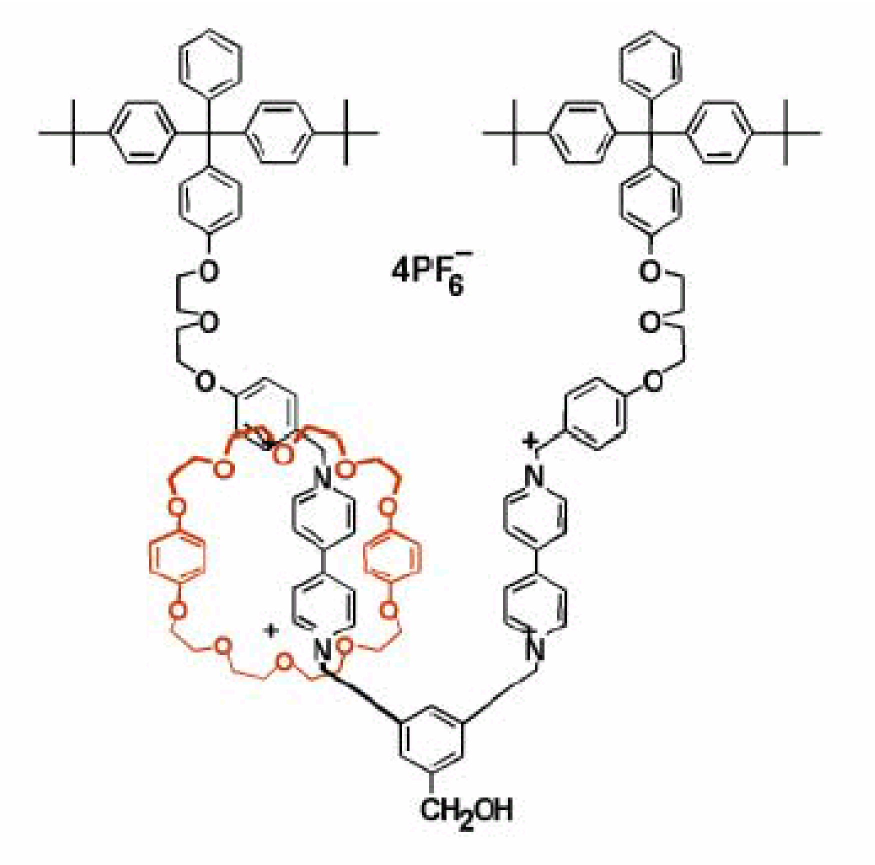
Molecules Get Wired

Good connections. Molecules can now be crafted into working circuits. Constructing real molecular chips will be a big challenge.



Molecular Switch

C. Collier, et al. Science 285, 391 (1999)



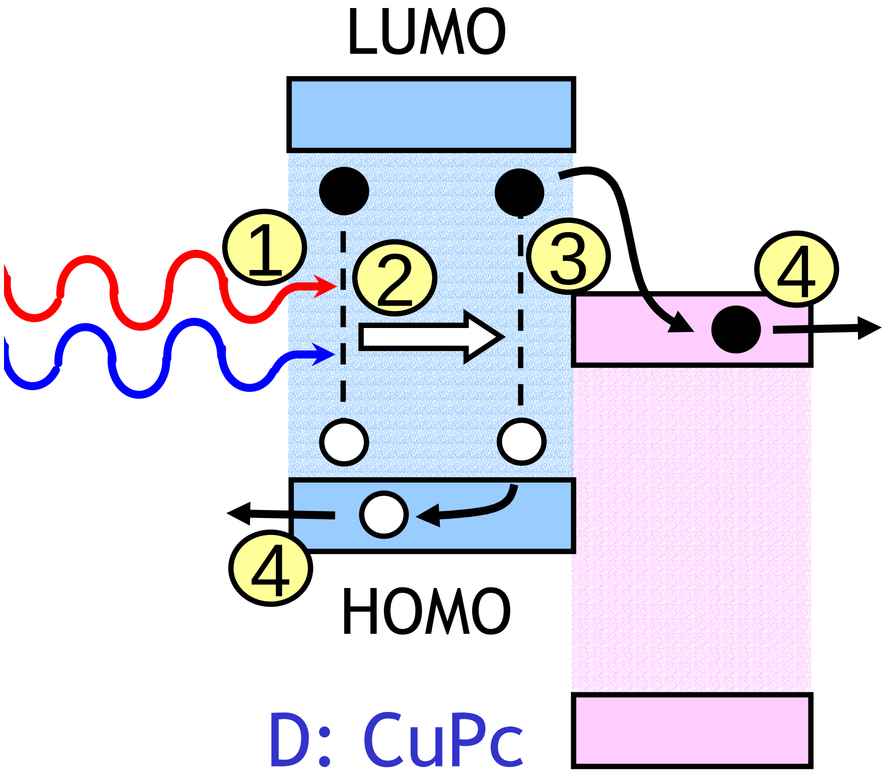
Hewlett-Packard

Solar Cells and Photodetectors

Image of Photosynthetic Machinery of Purple Bacteria

Photoinduced Charge-Transfer

Processes occuring at a Donor-Acceptor heterojunction



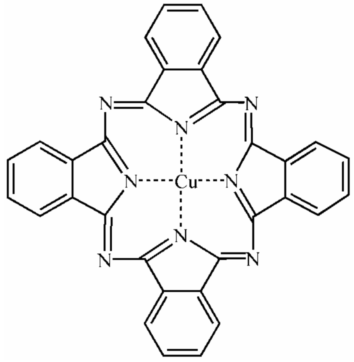
① Exciton generation by absorption of light

② Exciton diffusion over ~L_D

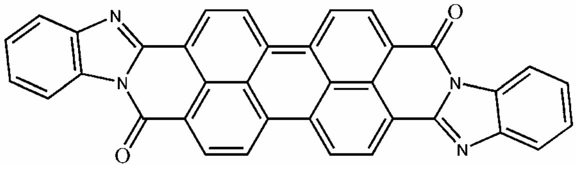
③ Exciton dissociation by rapid and efficient charge transfer

④ Charge extraction by the internal electric field

D: CuPc



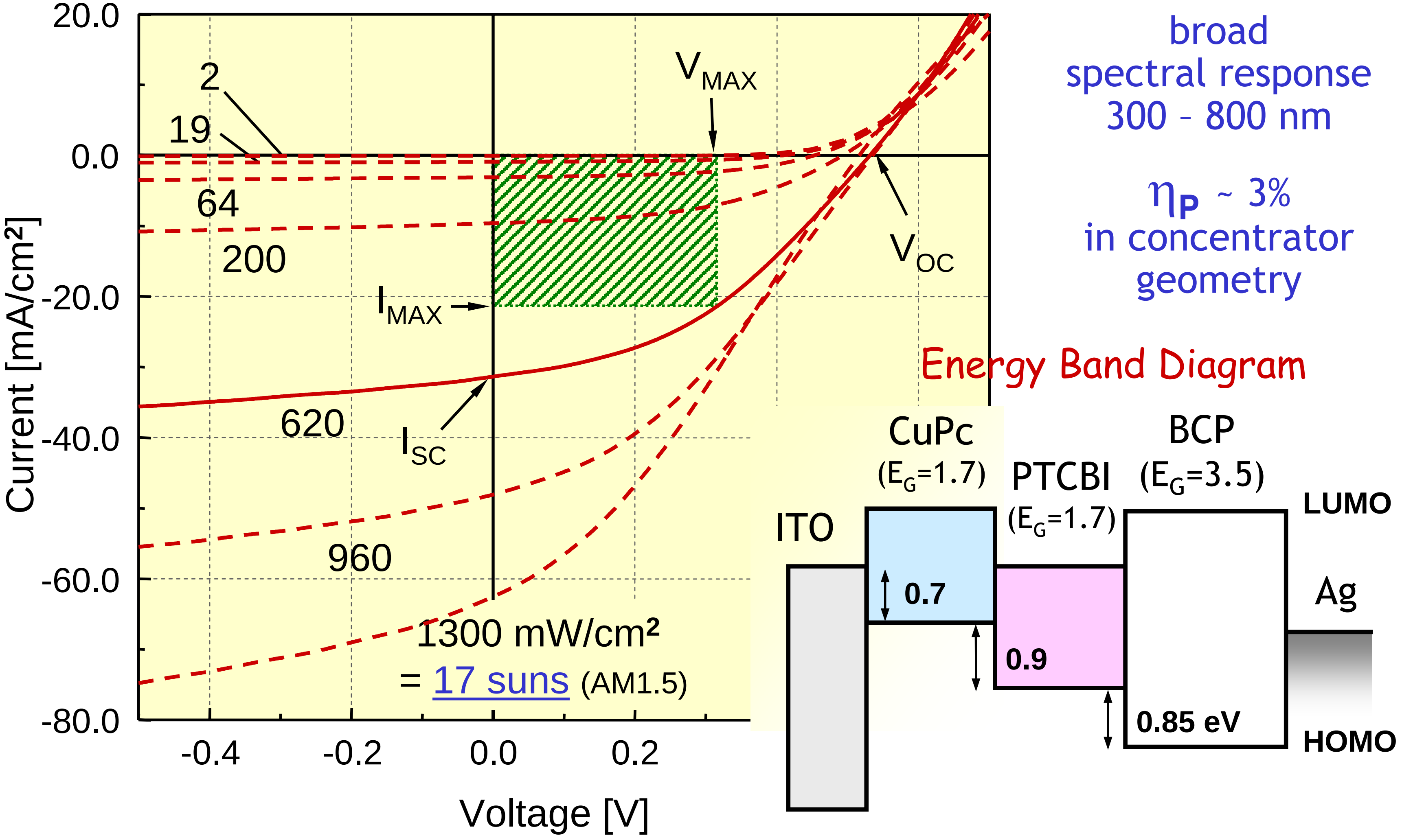
A: PTCBI



Organic Solar Cells

I-V Response Under Solar Illumination

Peumans, Bulovic, Forrest, Appl. Phys. Lett. (2000) Vol 76. p2650.

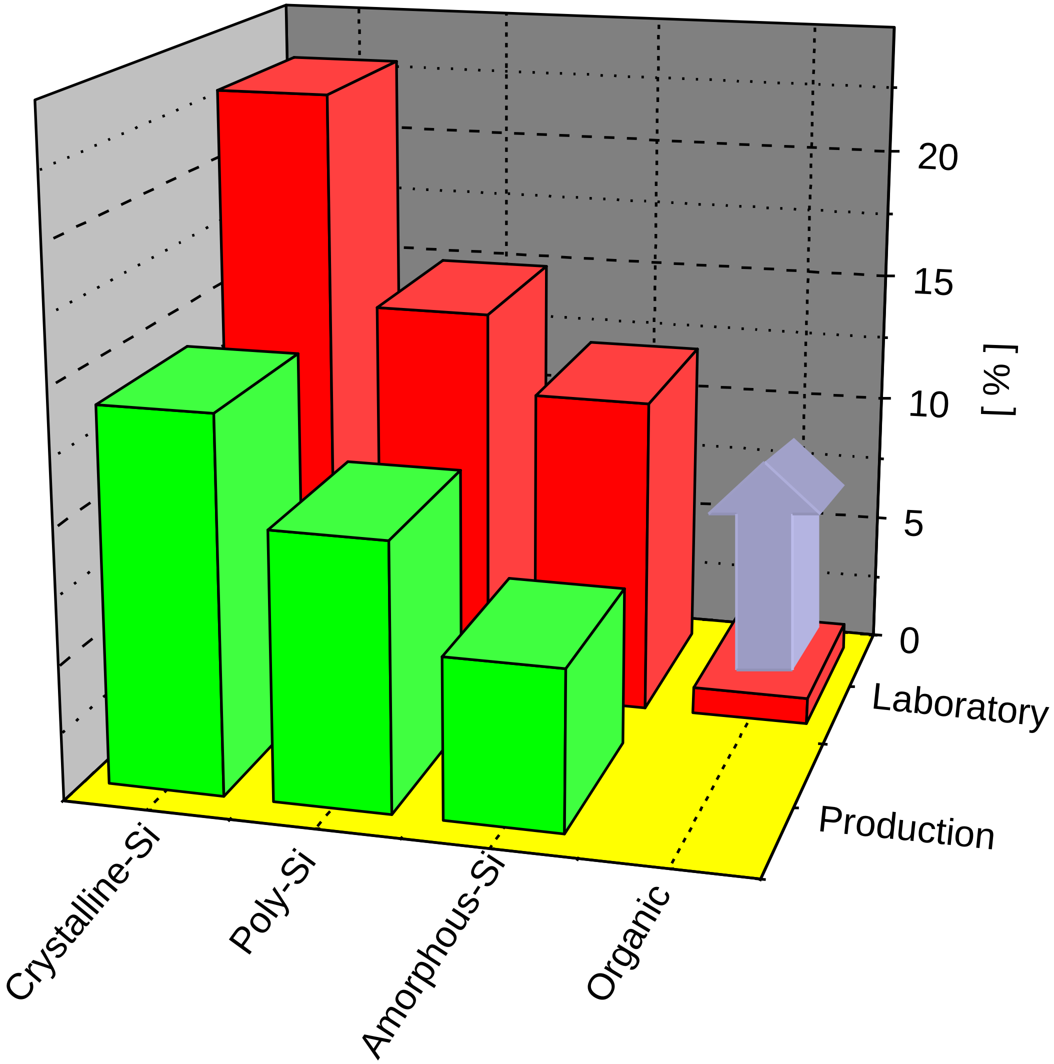


broad
spectral response
300 – 800 nm

η_P ~ 3%
in concentrator
geometry

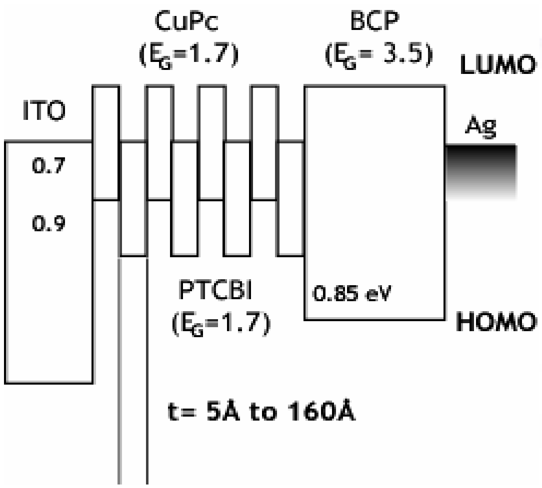
Energy Band Diagram

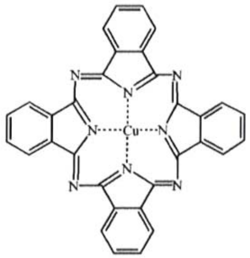
Solar Cell Power Efficiency



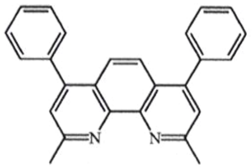
Donor-Acceptor Multilayer Organic Photodetectors

Adapted from Peumans, Bulovic, Forrest,
Applied Physics Letters (2000), Vol 76, p3855

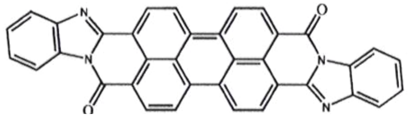




CuPc
copper phthalocyanine

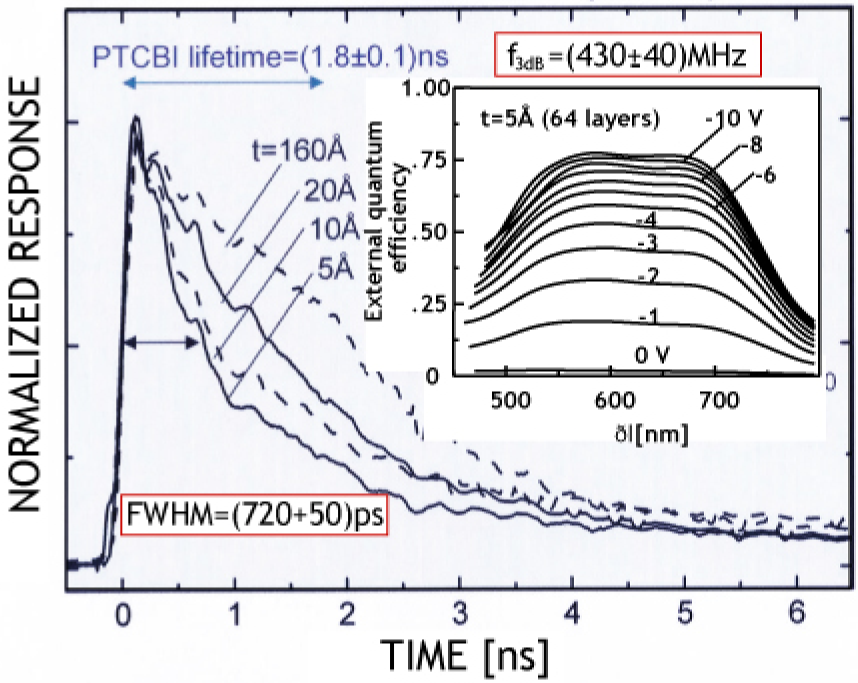


BCP
bathocuproine



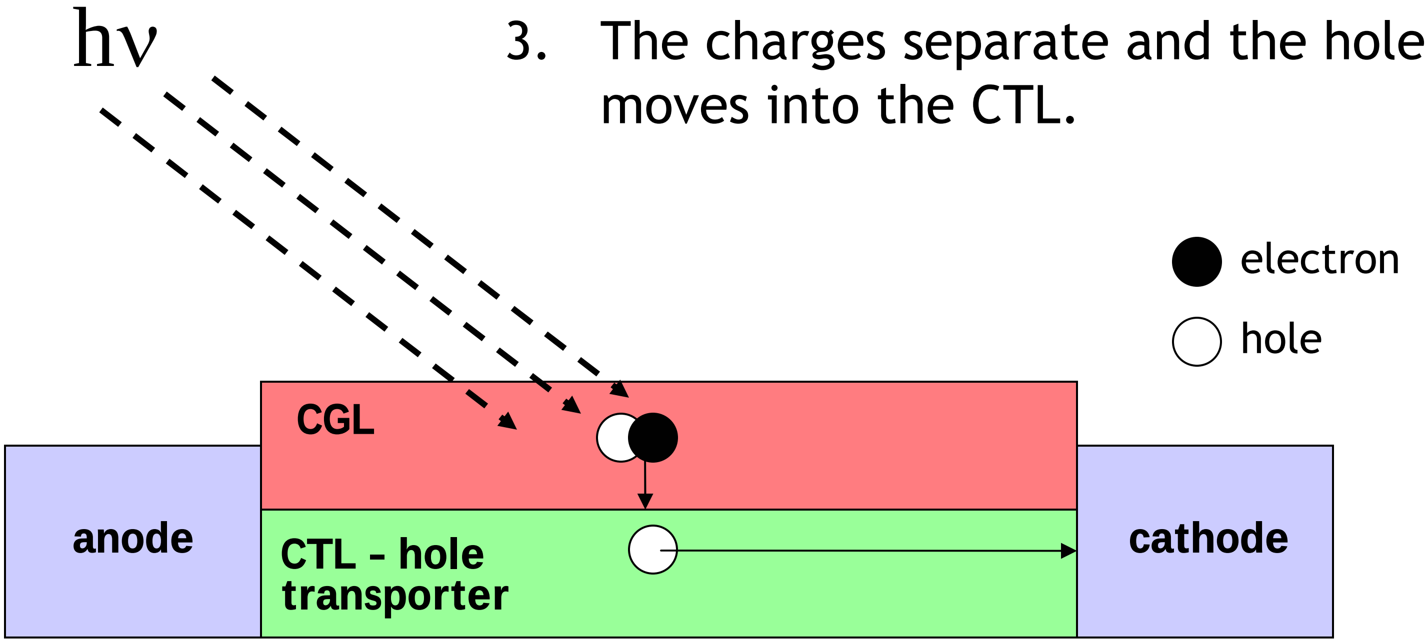
PTCBI
3,4,9,10-perylenetetracarboxylic
bis-benzimidazole

100um diameter, -9V, 1.4ps excitation @ 670nm
under an average optical power of (250+70)mW/cm^2
Estimated carrier velocities: v=d/t =(1.1+0.1)x10^4 cm/s)



Xerography

1. A photon is absorbed into the CGL where it generates an exciton.
2. The exciton migrates to the interface between the two layers.
3. The charges separate and the hole moves into the CTL.



What is Color?

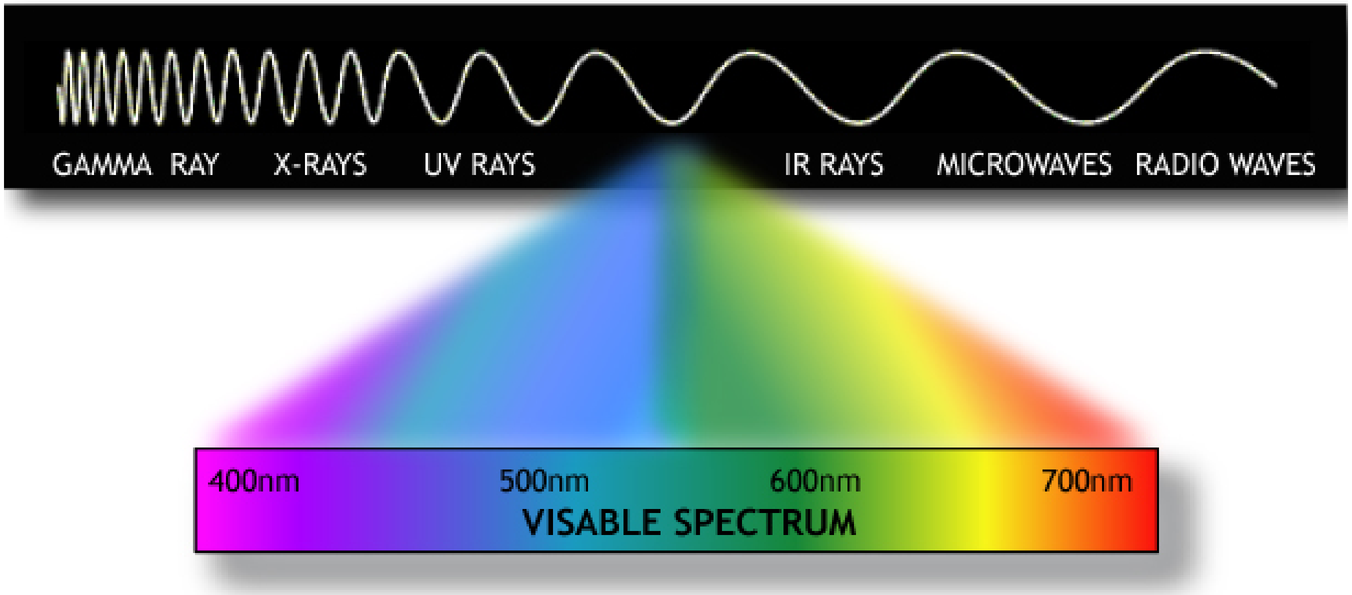
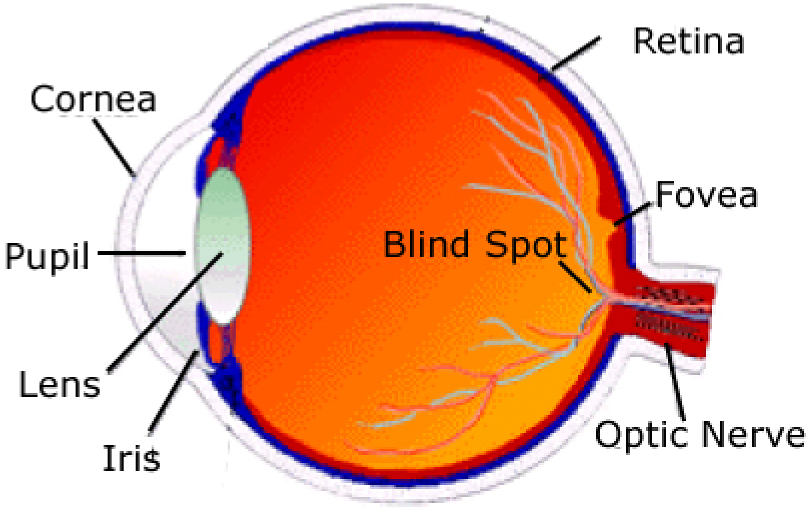
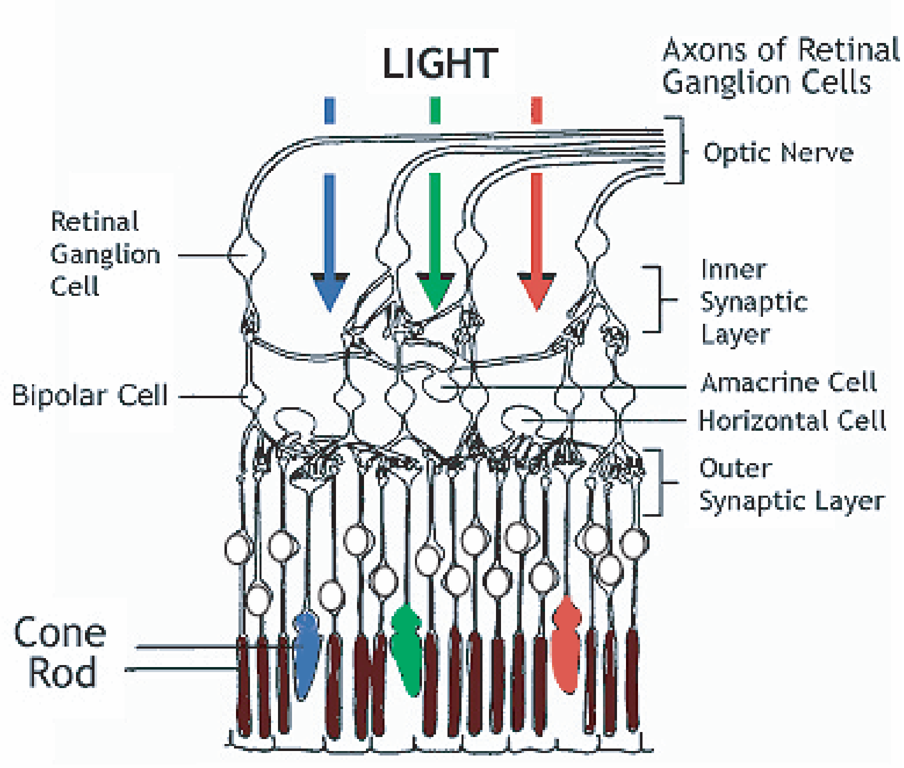


Diagram of the Human Eye



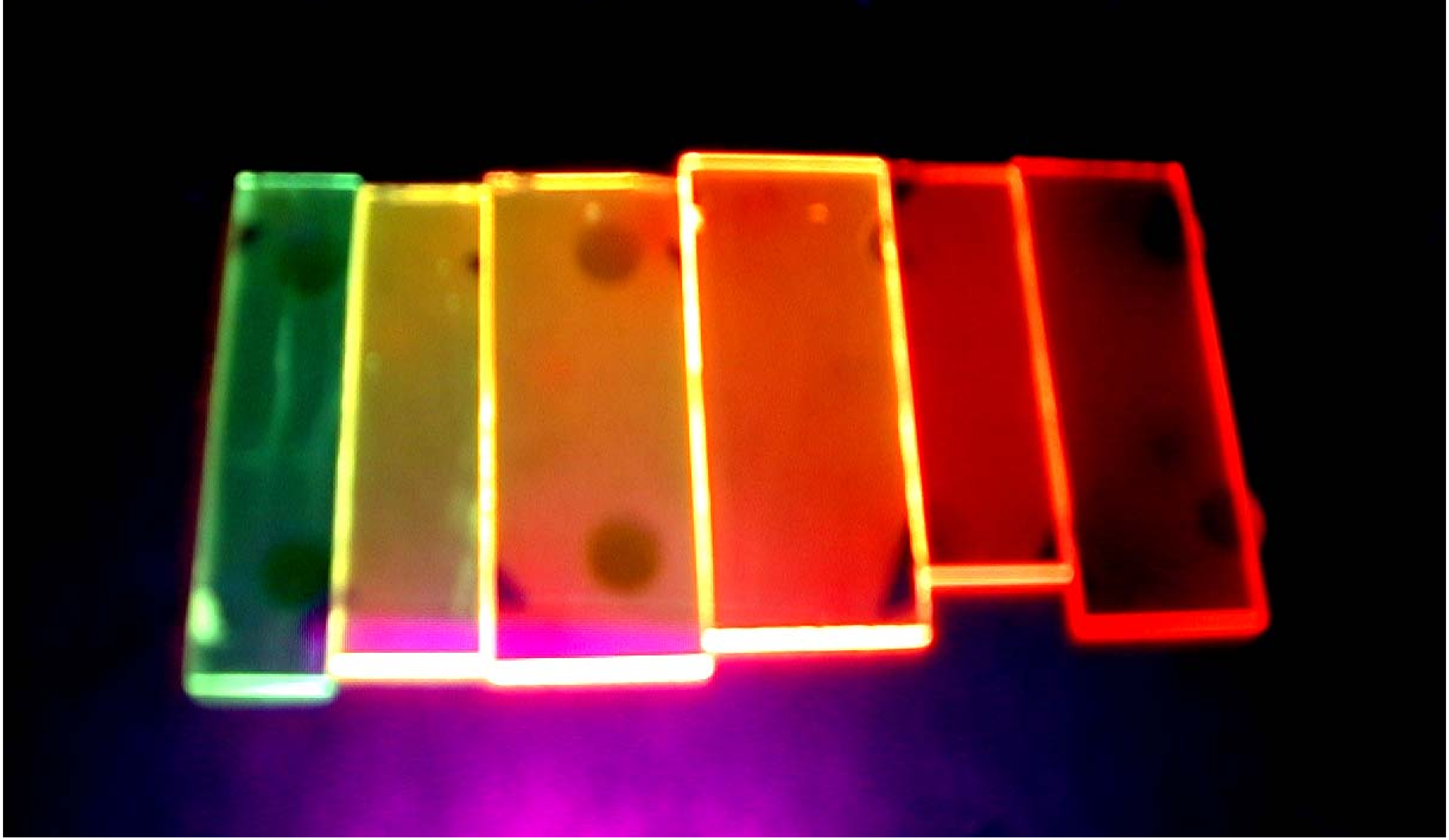
From the NASA website

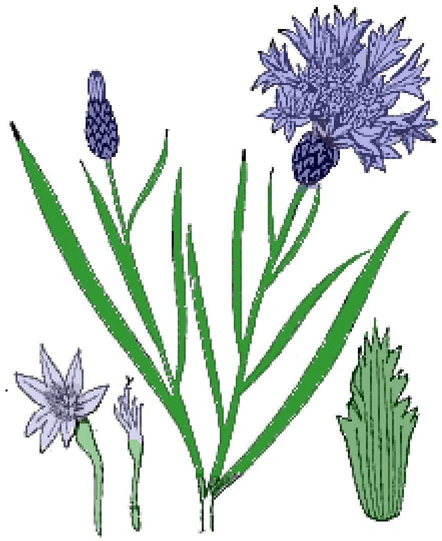
120 million Rods – brightness
6 million Cones – color
B 5-10%
G ~30%
R ~60%



The Neural Structure of the Retina

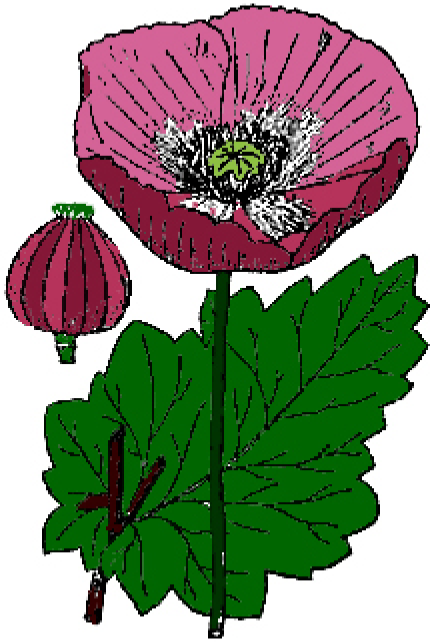
Luminescence and Lasing

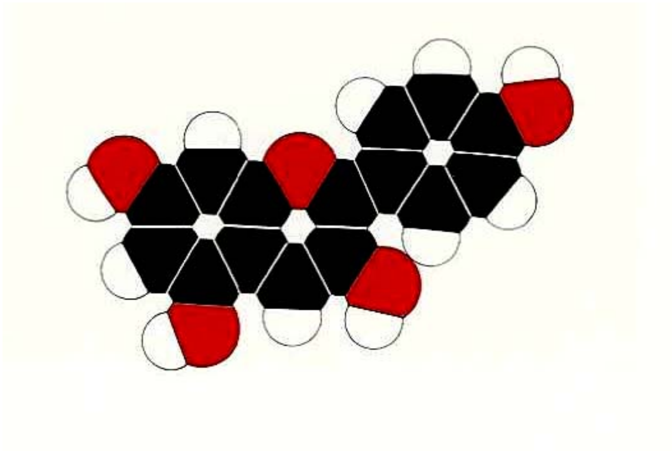




Cornflower
(alkaline sap)

Poppy
(acidic sap)





pelargonodin
(anthocyanidins group)

Organic Luminescence for Sniffing Out Landmines

Prof. Tim Swager

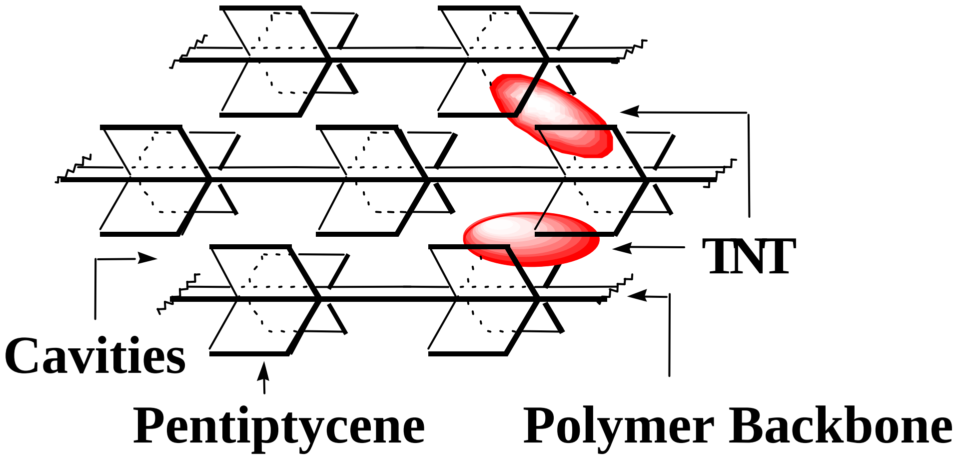
the problem

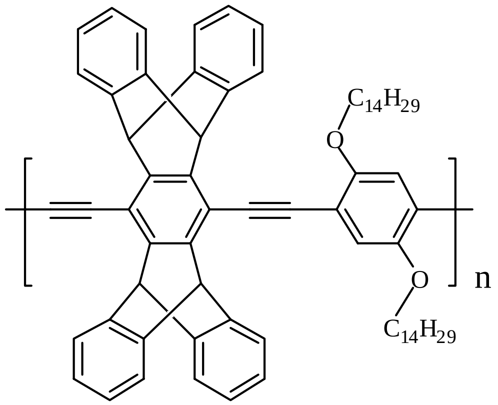
(source C&EN, March 10, 1997):

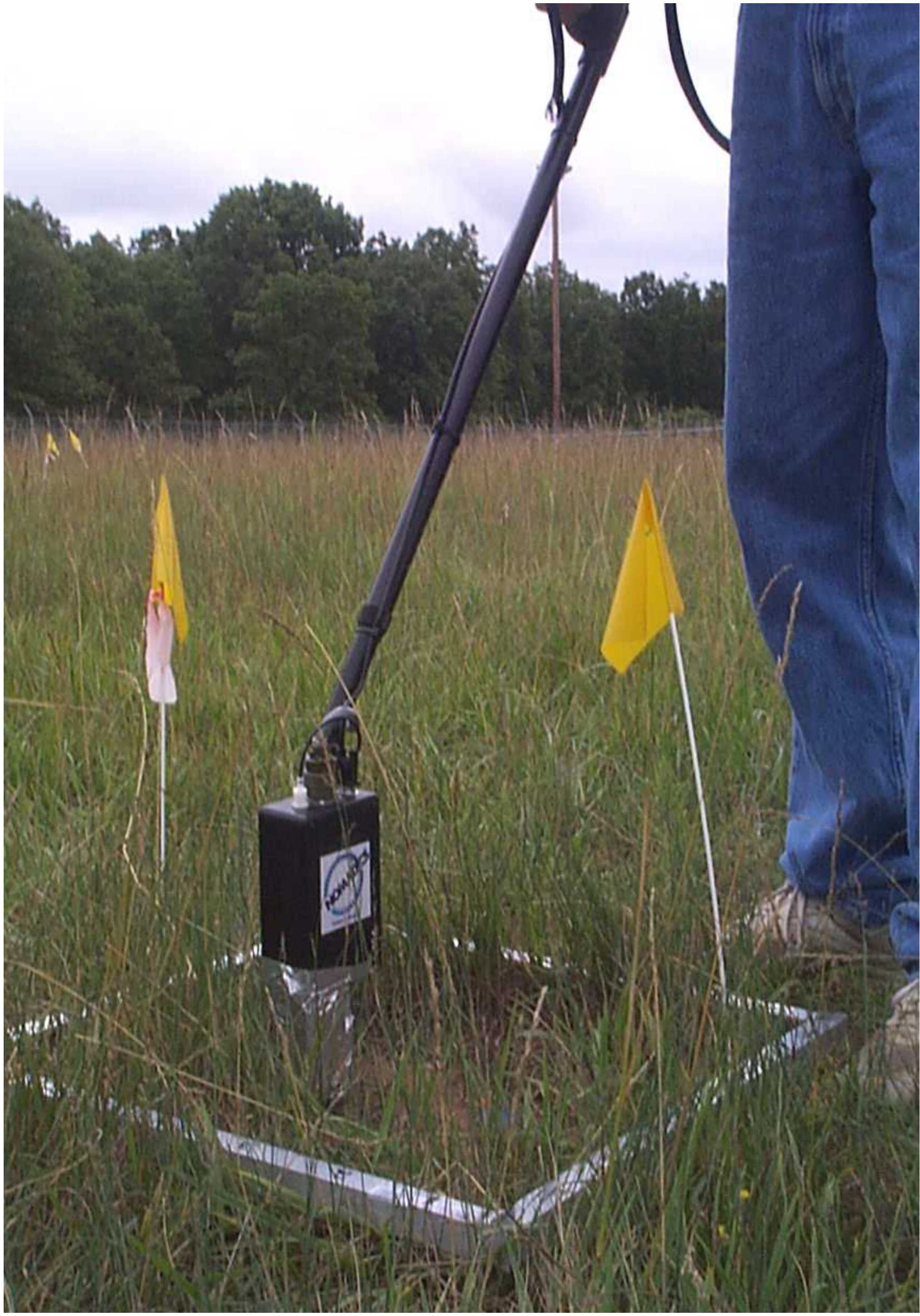
120 million unexpolded Land Mines World Wide
UN Estimates $33 Billion and 1,100 Years to Remove all Land Mines with Current Technology
Presently the Best Technology is the Dog

solution

*** Rigid, Porous 3D-Structure Behaves as a Sponge for TNT**
*** Extended Electronic Structure: Rapid Exciton Transport**







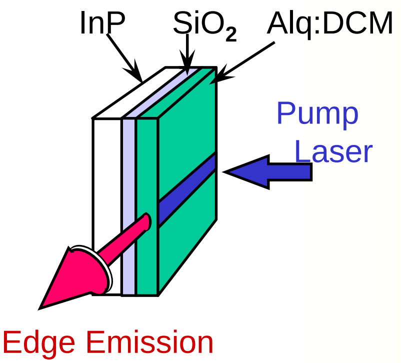
FIDO 4D Field Test

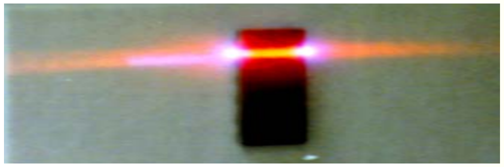
Determining the TNT Concentration Profile of a AP-Landmine

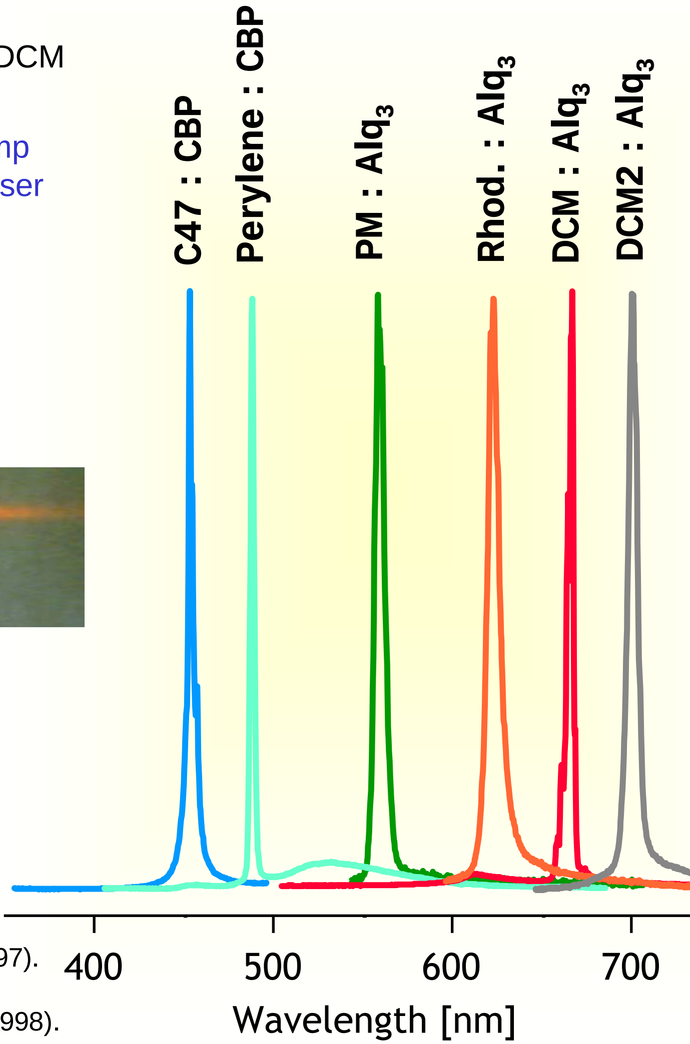
≈10^{-16} g Detection Limit
(100,000 Molecules)

Organic Semiconducting Lasers

Lateral Structures



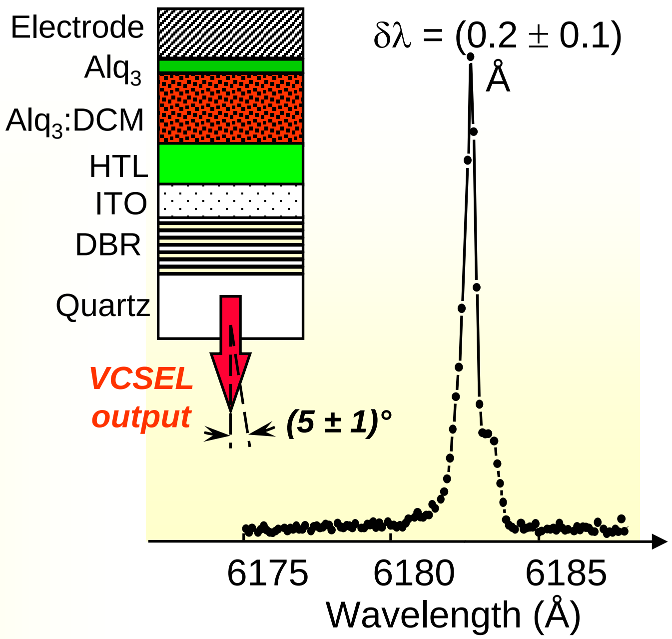


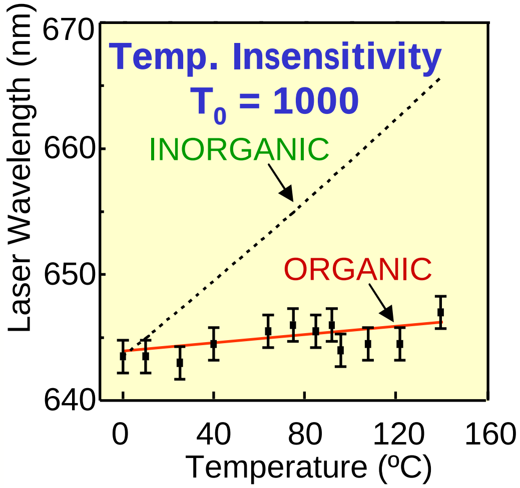


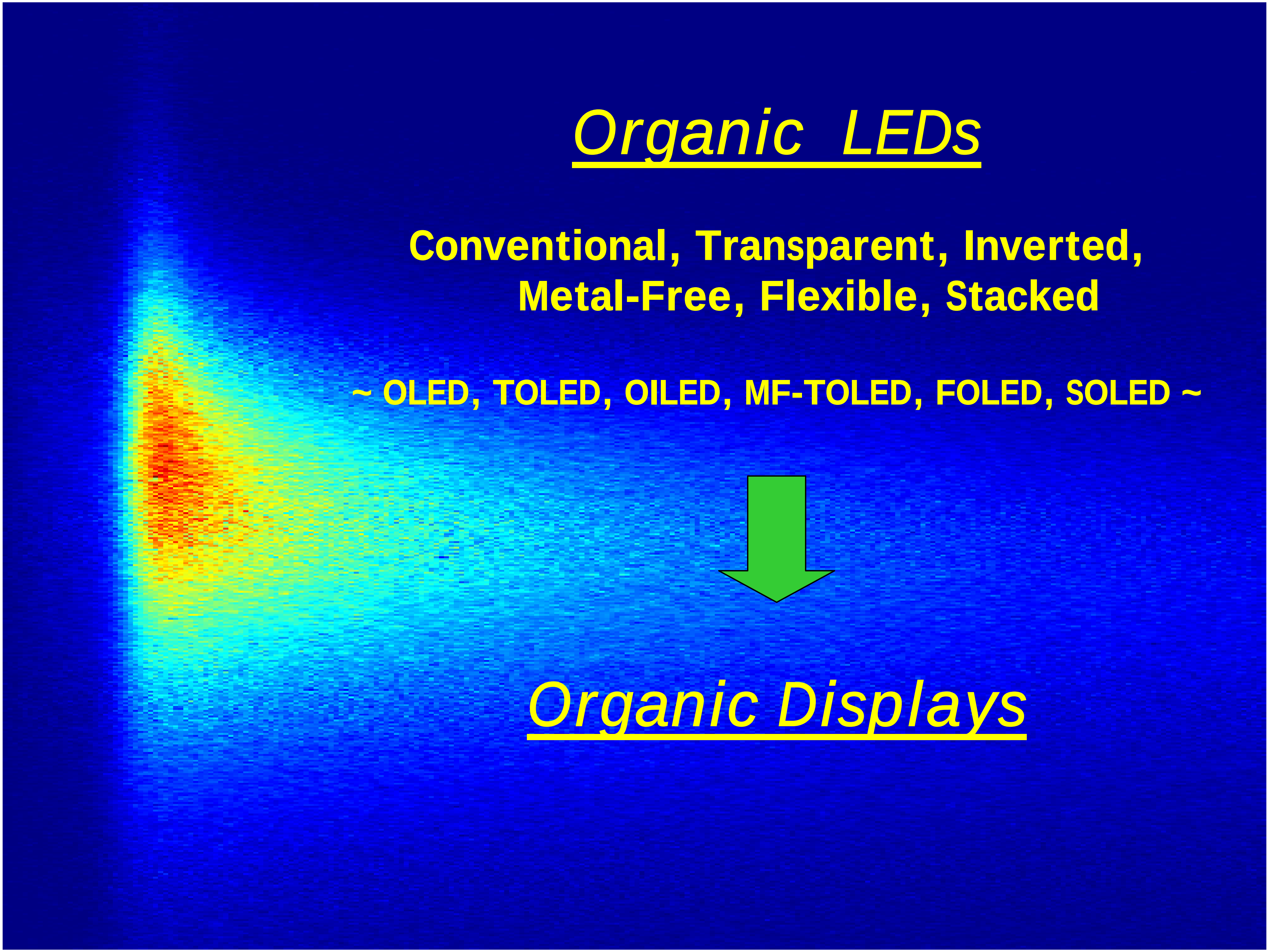
Kozlov, *et al., Nature* **389**, 362 (1997).

Bulović, *et al., Science* **279**, 553 (1998).

Vertical Structures







Organic LEDs

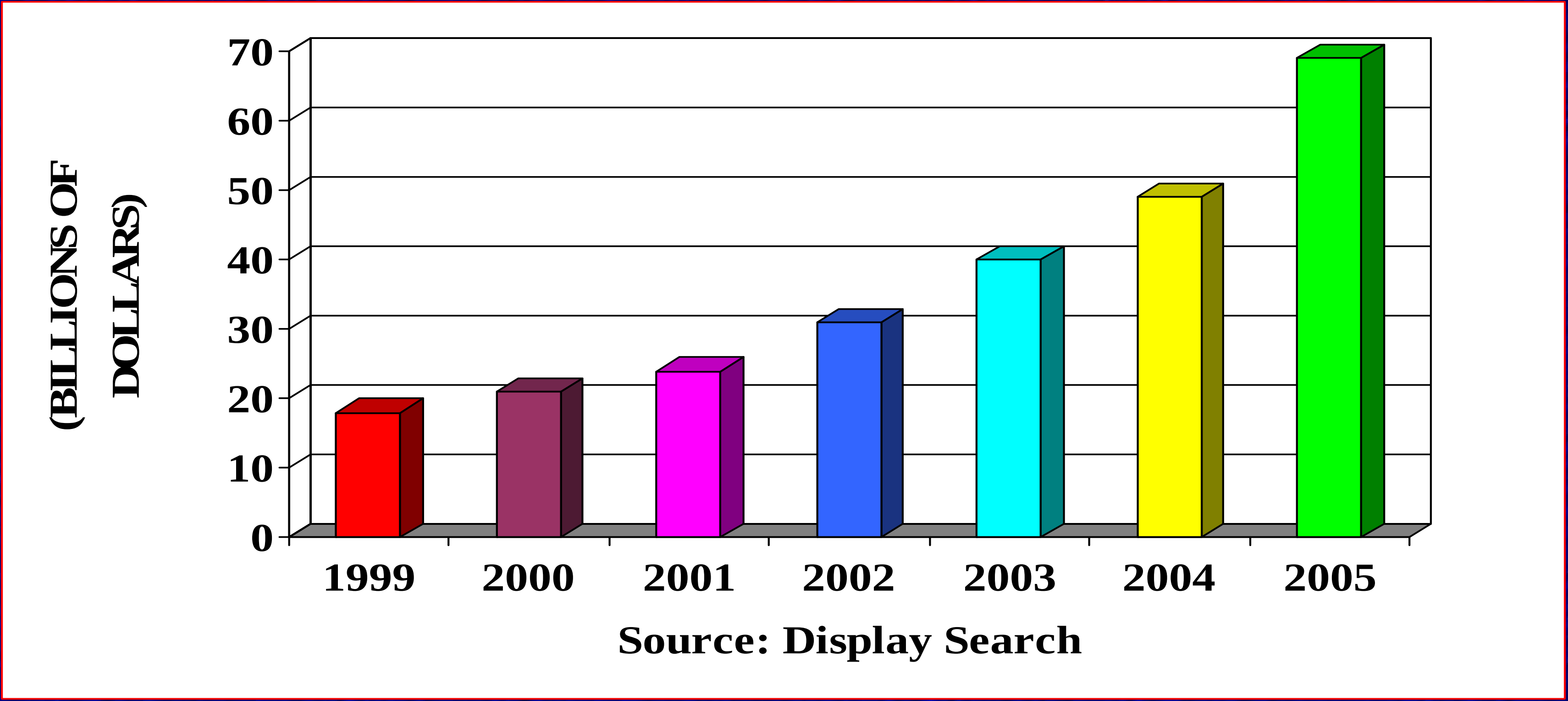
Conventional, Transparent, Inverted,
Metal-Free, Flexible, Stacked

~ OLED, TOLED, OILED, MF-TOLED, FOLED, SOLED ~

↓

Organic Displays

Flat Panel Display Market



Source: Display Search

20 to 30% growth per year

$70 Billion business in 2005

Automotive

Dashboard displays, external indicator lights, and road signs

---

Multi-Function Video Watch

Rugged, high resolution, full-color, video-rate displays enable a multitude of applications

Active Wallpaper

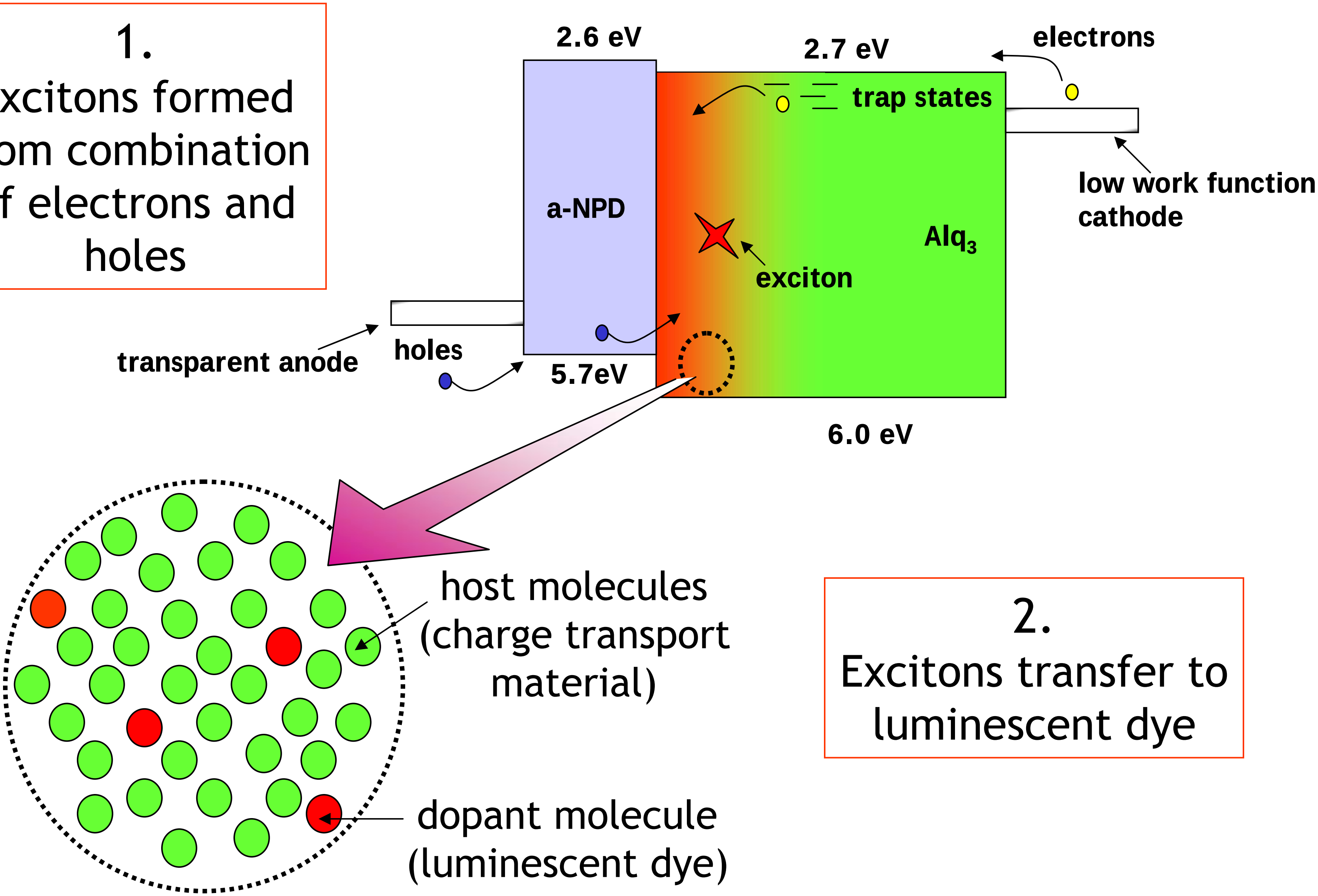
Large area displays

Active Clothing

Light, rugged, low voltage, flexible displays

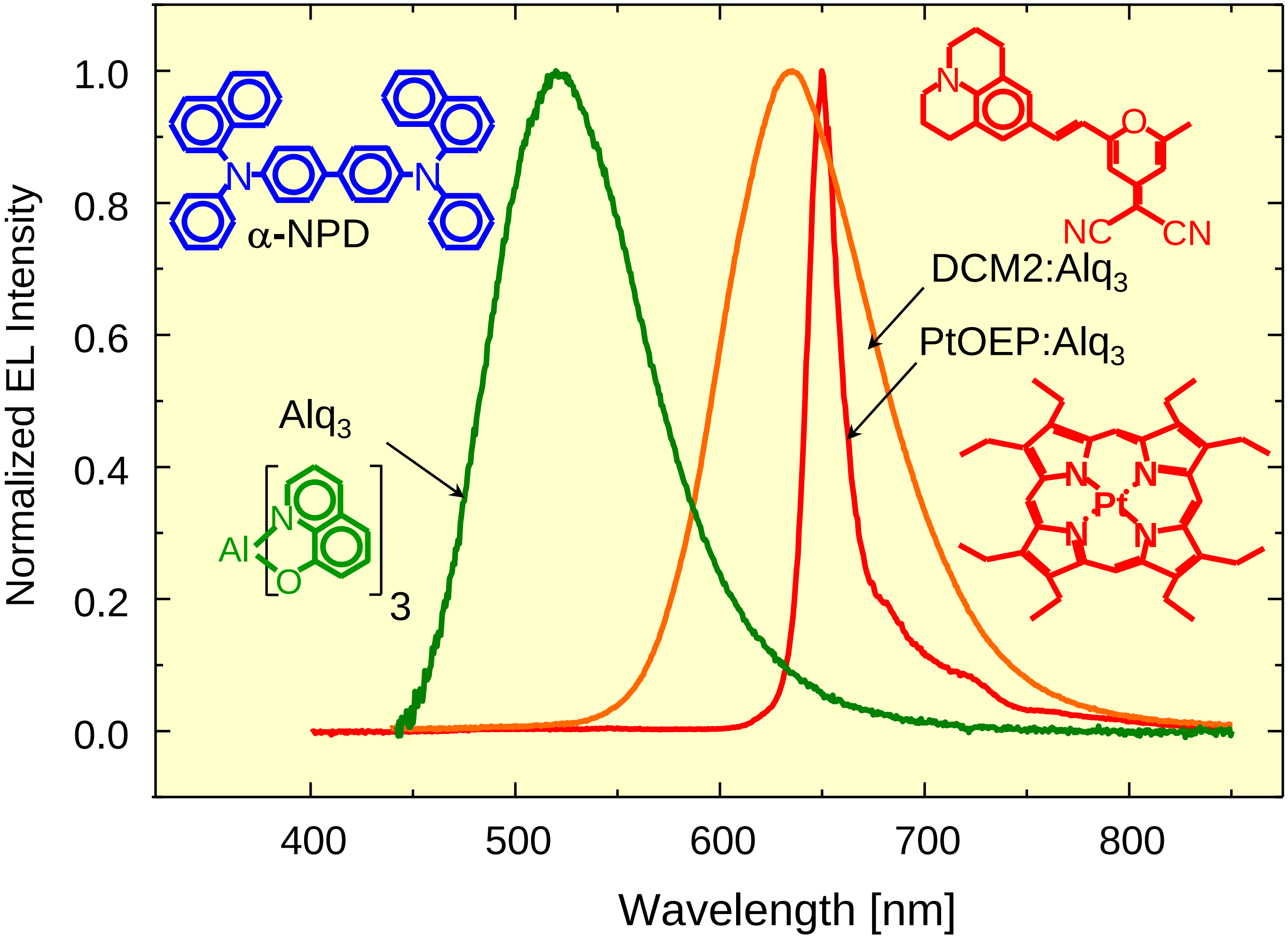
Electroluminescence in Doped Organic Films

1\.
Excitons formed from combination of electrons and holes



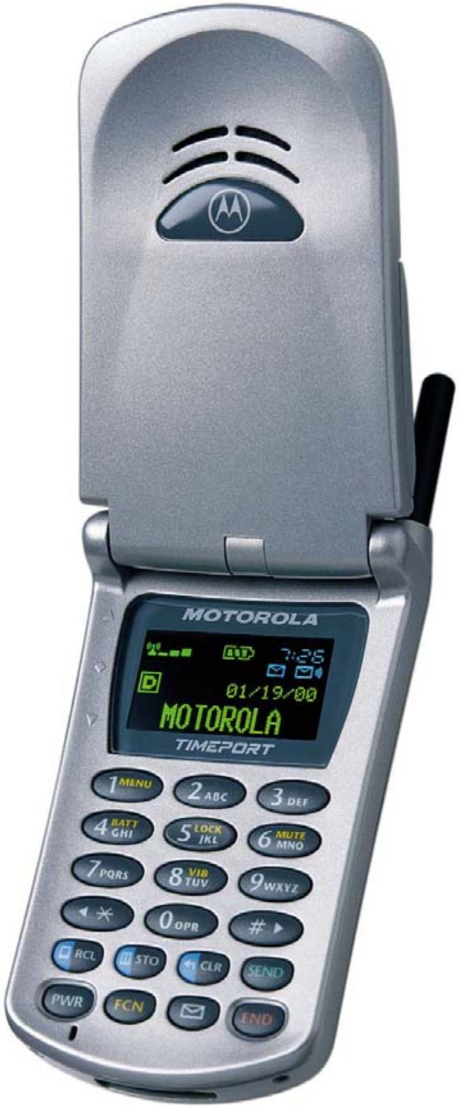
2\.
Excitons transfer to luminescent dye

Effect of Dopants on the OLED EL Spectrum



Cell Phone Display (Motorola/Pioneer)

LCD



OLED

Kodak/Sanyo 5.5” AM-OLED Display, 2000

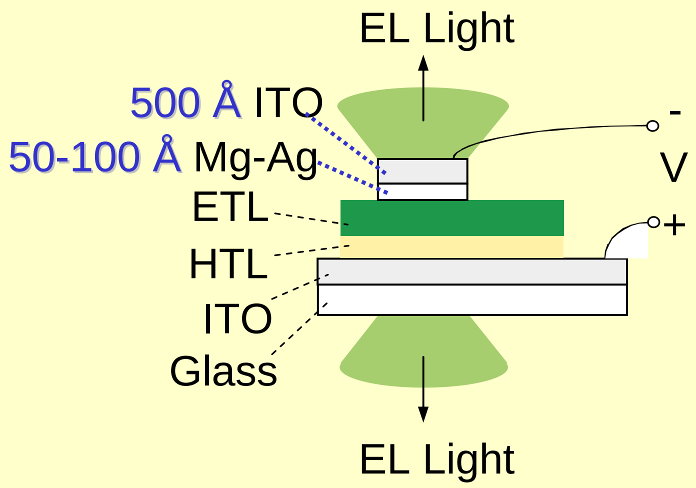
QVGA 5.5”

QVGA 2.4”

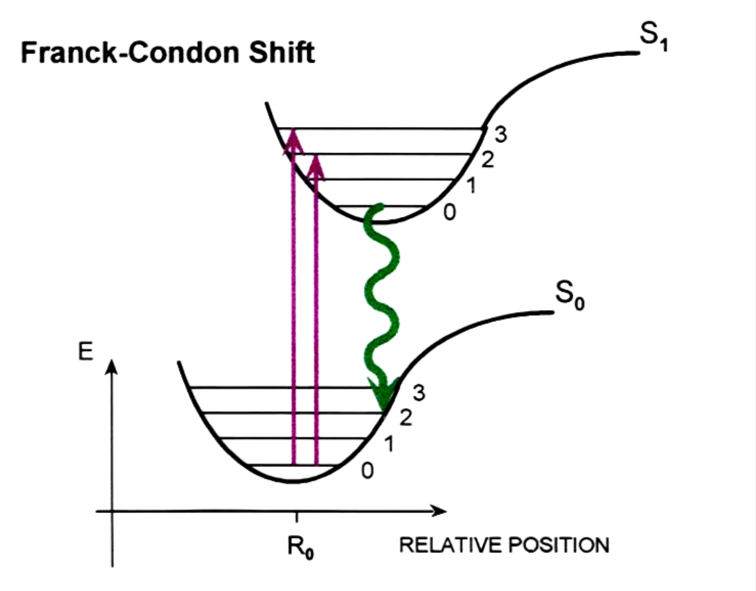
Transparent OLEDs

- Future vision-area applications
- Top emission for active matrix displays

> 70% transparent

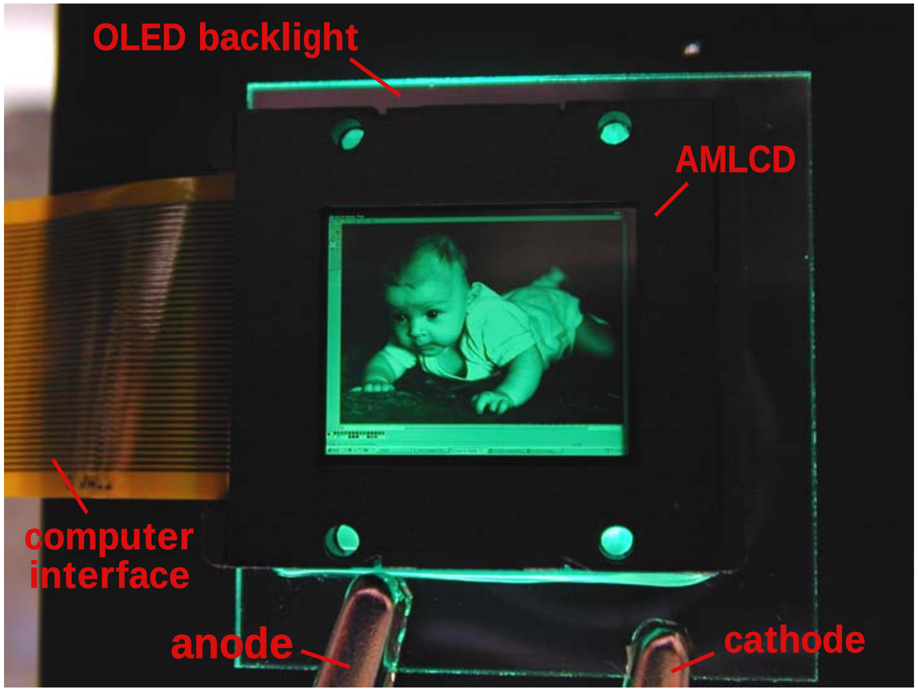


Bulovic´*et al.*, *Nature* 380, 29 (1996).
Parthasarathy *et al.*, *Appl. Phys. Lett.* 72, 2138 (1998).

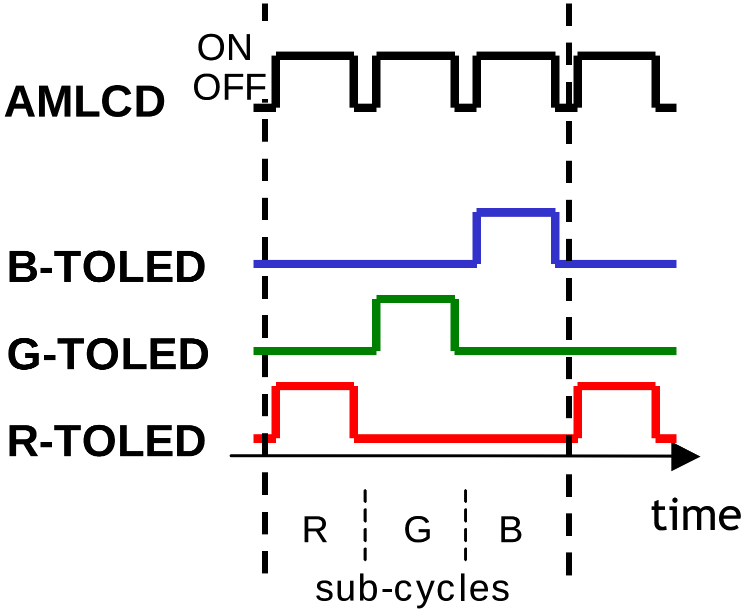


OLEDs as Backlights in AMLCDs

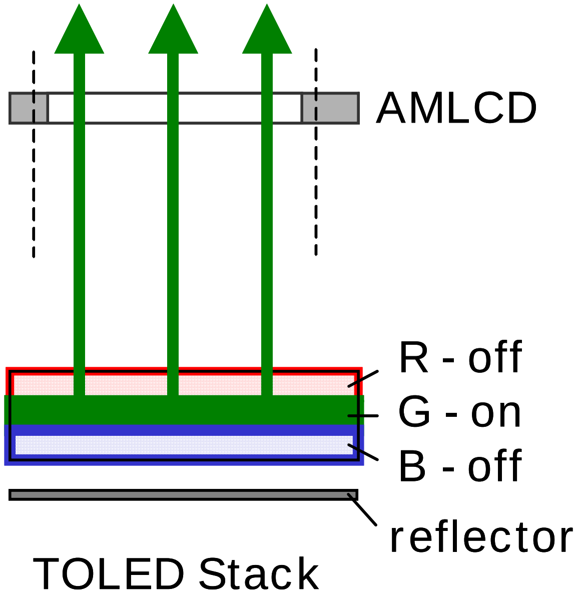
Bulovic, patent pending.



Timing Diagram



G sub-cycle

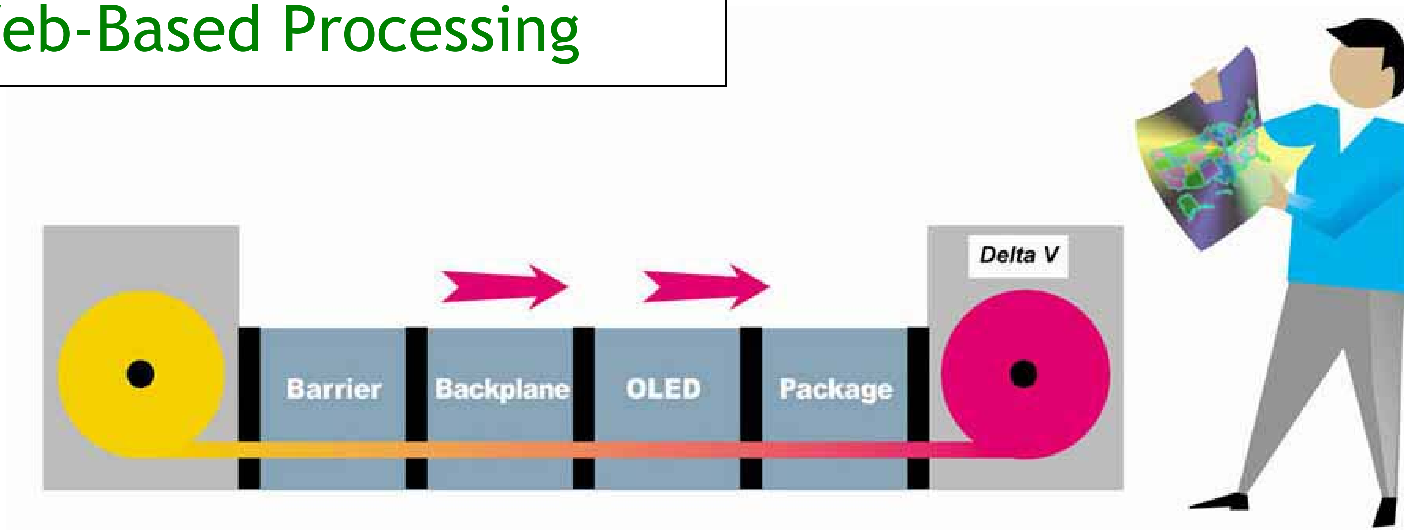


Flexible OLED (FOLED)

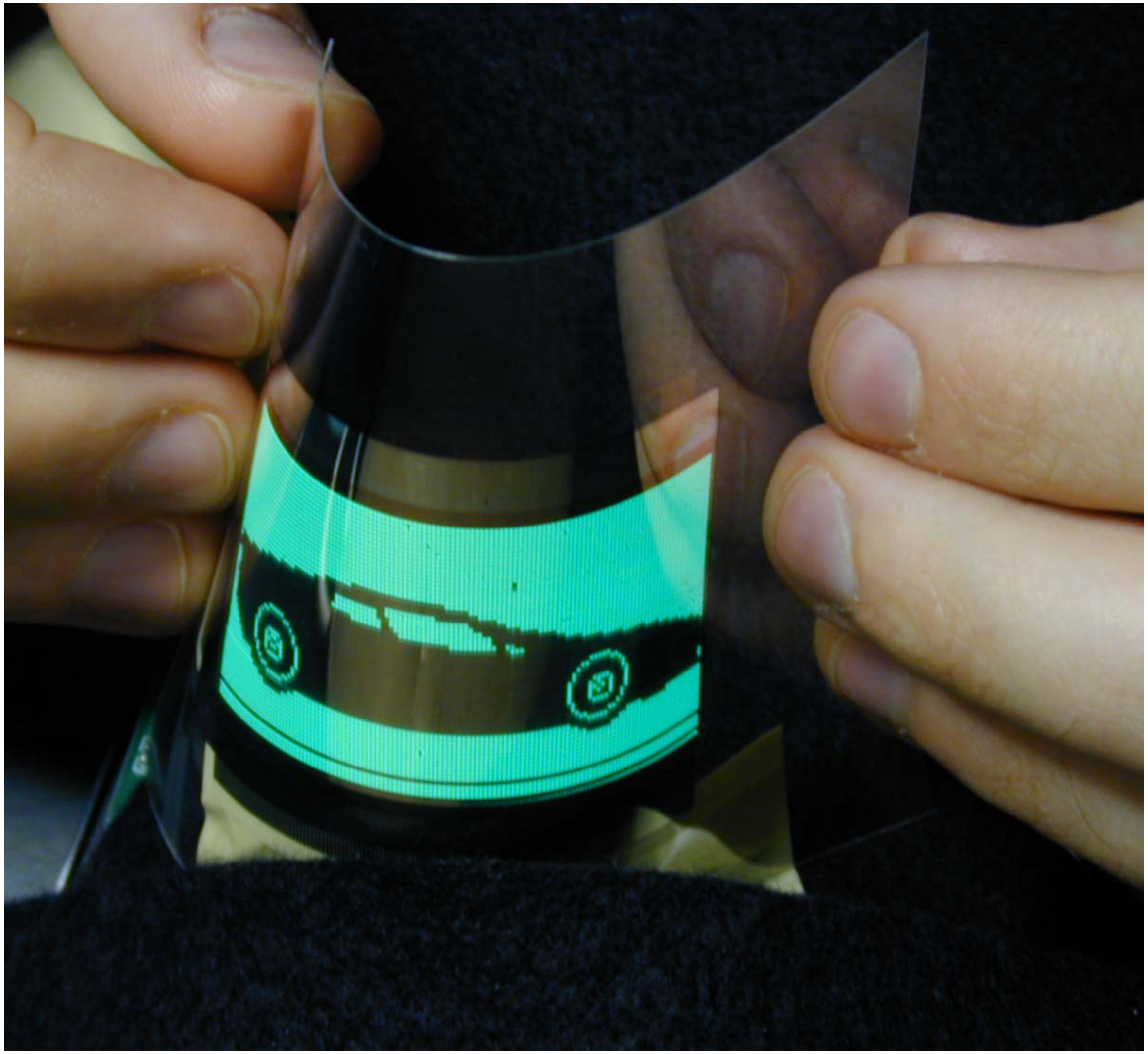
- Ultra lightweight
- Thin form factor
- Rugged
- Impact resistant
- Conformable

Manufacturing Paradigm Shift

Web-Based Processing



FOLED-based Pixelated, Monochrome Display

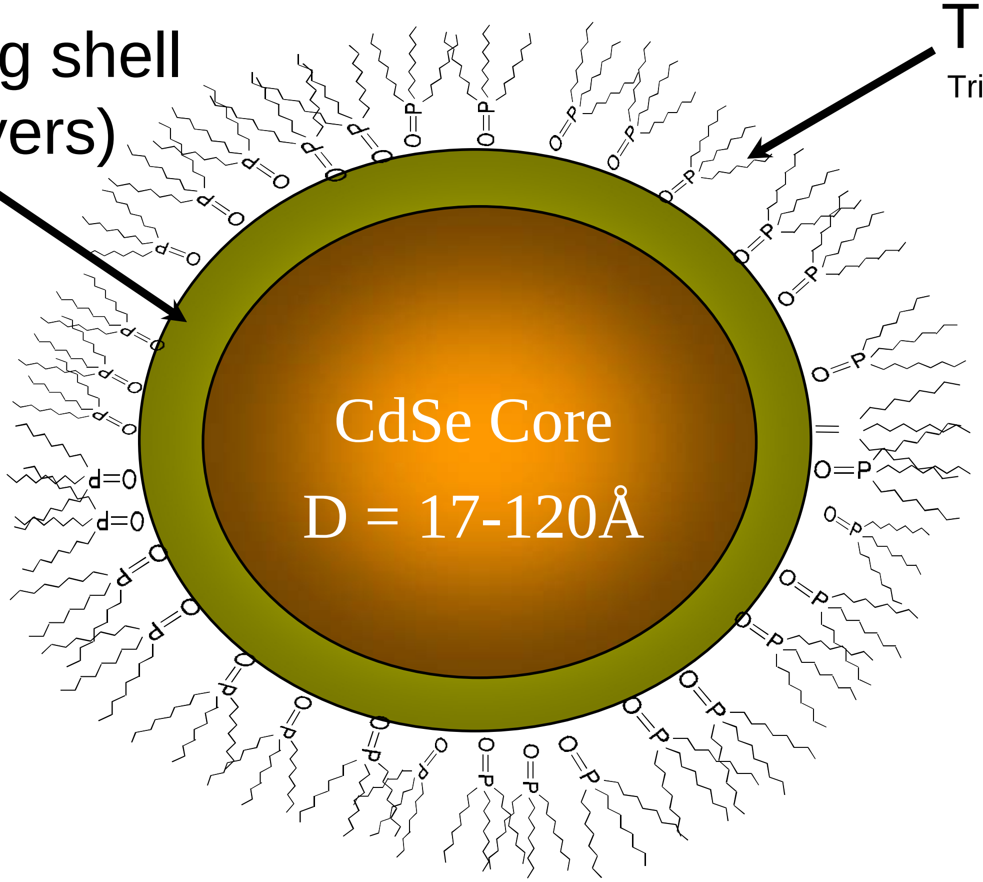


Source: UDC, Inc.

What is a Quantum Dot?

ZnS overcoating shell
(1 to 8 monolayers)

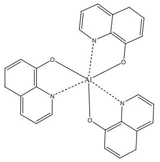
TOPO caps
Trioctylphosphine oxide



Synthetic route of Murray et al, J. Am. Chem. Soc. **115**, 8706 (1993).

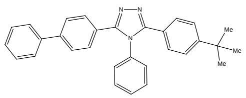
10Å

Alq$_3$



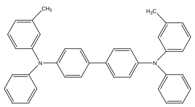
Tri(8-hydroxyquinoline) Aluminum (III)

TAZ



3-(4-Biphenylyl)-4-phenyl-5-tert-butylphenyl-1,2,4-triazole

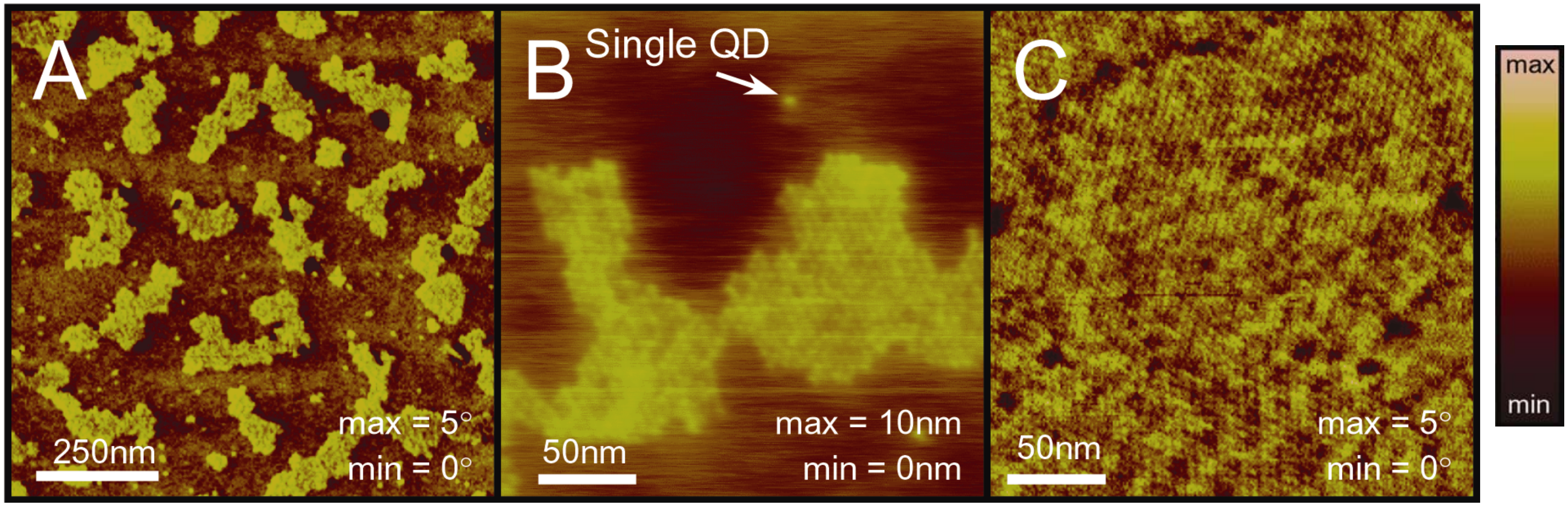
TPD



N, N'-diphenyl-N, N'-bis (3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine

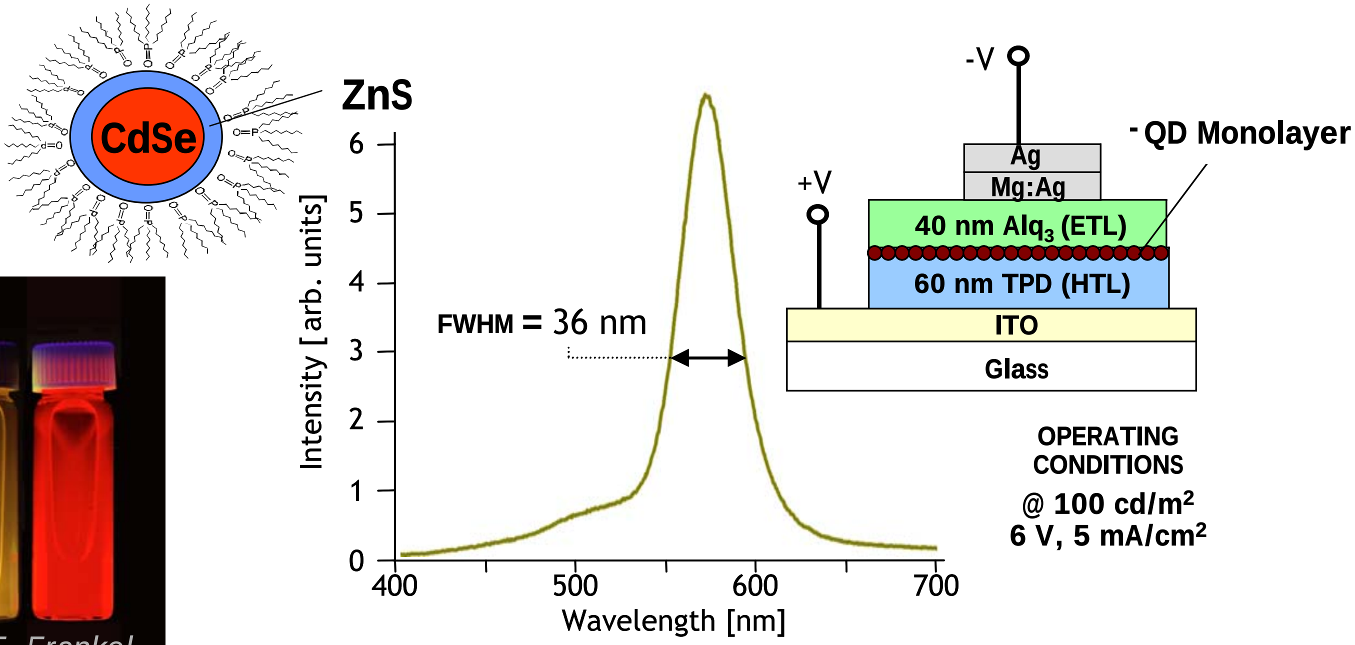
Quantum Dot-based LEDs

Adapted from S. Coe, W. Woo, M. Bawendi and V. Bulovic



active device region contains a single QD monolayer **~5nm thick**

active QD devices



OPERATING CONDITIONS
@ 100 cd/m^2
6 V, 5 mA/cm^2

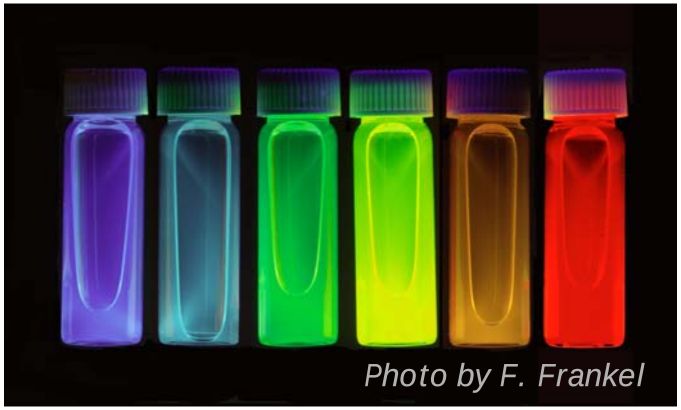


Photo by F. Frankel

Flexible Internet Display Screen

We have only begun to imagine what our OLED technology can create in the way of products for our world and our future. The technology will not only improve existing products, but will also create exciting, new product possibilities.

In the futuristic application depicted here, the wall of a home actually serves as a direct connection to the outside world. This couple can interact and follow all the latest breaking news, sports and weather in the comfort of their home with flat display technology that is not only information rich and easily accessible, but also extremely versatile and space-friendly.

The clarity of the image made possible with our OLED technology may make interaction with distant locations possible with a realism so distinct that physical presence may no longer be necessary.

More Applications

- Multi/Full color cellular phone displays
- Full color high-resolution personal digital assistants (PDAs)
- Heads-up instrumentation for cars
- Bright, lightweight, rugged laptop computers
- Roll-up, electronic, daily-refreshable newspaper
- Automobile light systems without bulbs
- Ultra-lightweight, wall-size high definition television (HDTV)
- Office windows, walls and partitions that double as computer screens
- Home and office lighting that actually "coats" walls or ceilings

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THE ULTIMATE HANDHELD COMMUNICATION DEVICE

UDC, Inc.