Welcome to 6.973
~ Organic Opto-Electronics ~

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COURSE MISSION

examine optical and electronic processes in organic molecules and polymers that govern the behavior of practical organic optoelectronic devices
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.
Organic Materials ... TWO GENERAL CLASSES

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 -
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.

Electronic Processes in Molecules / Aggregates / Thin Films

- **Fluorescence**
- **Phosphorescence**
- Energy Transfer
- Förster, Dexter or Radiative Internal Conversion
- Absorption

**Temporal Response**

- $S_1$ and $T_1$ state density
- Energy

**Solid State Solvation**

- Wavelength shift 35 nm
- 10% DCM2 in Alq3

**Intensities**

- 0.25 ns
- 0.50 ns
- 0.75 ns
- 1.00 ns
- 1.50 ns
- 2.00 ns
- 5.00 ns

**Wavelengths**

- 600 nm
- 650 nm
- 700 nm
- 750 nm

**Time**

- 0 ns
- 1 ns
- 2 ns
- 3 ns
- 4 ns
- 5 ns

**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
Tetracene Thin Film Growth is affected by...

Mascaro, et al., unpublished.
**Improved Molecular Ordering**

- Larger grain sizes
- Lower defect densities
- Enhanced mobility

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

Organic Light Emitting Devices

Electrons and holes form excitons (bound e⁻-h⁺ pairs) in the recombination region. Some excitons radiate light. The diagram shows the structure of an OLED device with layers such as ITO, Alq₃, TPD, Mg:Ag, and Ag. The device is ~2 mm thick, and the HOMO and LUMO energy levels are indicated. The Kodak/Sanyo AM-OLED QVGA Display is shown in the image.
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

Sample-Mask Storage

Source Storage

Load Lock

Wet N2 Glove Box

Dry N2 Glove Box

Probe Station
with Cryostat

Ante Chamber and Oven

UV-Ozone Laminar Flow Hood

Physical & Vapor Phase Dep.
- molecular organics
- nano-dots **
- solvated polymers **
- colloids **

Evaporative Deposition
- molecular organics (amorphous and crystalline)
- metals

Sponsored by AFOSR and NSF
Double Glove Box

Moisture Level < 1 ppm

MIT lab of ORGANIC OPTICS & ELECTRONICS

14
Thermal Evaporator

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

- E-Beam Evaporation
  - Single Pocket
- Shadow Mask Storage-Exchange
- Six Thermally Heated Sources
  - Two Independent Banks of Three Sources Each
- Independent Source Monitoring During Co-Deposition
- Source Storage
- Evaporative Deposition
  - Molecular Organics (Amorphous and Crystalline)
  - Metals
- Chemical Vapor Deposition
  - Chemically Selective Materials Deposition
- Sputtering
  - ITO
  - Ceramics
- Chemical Vapor Deposition

Integrated Materials Growth System

- Wet N2 Glove Box
- Load Lock
- Ante Chamber and Oven
- UV-Ozone Lamellar Flow Hood
- Dry N2 Glove Box
- Sample-Mask Storage
- Probe Station with Cryostat

MIT Lab of Organic Optics & Electronics

Physical & Vapor Phase Deposition

- Molecular Organics
- Nano-Dots
- Solvated Polymers
- Colloids

Sputtering
- ITO
- Ceramics

Chemical Vapor Deposition
- Chemically Selective Materials Deposition

Evaporative Deposition
- Molecular Organics (Amorphous and Crystalline)
- Metals

Source Storage

SHADOW MASK STORAGE-EXCHANGE

SIX THERMALLY HEATED SOURCES

TWO INDEPENDENT BANKS of THREE SOURCES EACH

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

λ = 325 nm
θ = 30°
P = 325 nm

SiO_x interlayer
photoresist
anti-reflection coating (ARC)

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**


![Graph showing current vs voltage for a molecular switch.](image)

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Hewlett-Packard
Solar Cells and Photodetectors

Image of Photosynthetic Machinery of Purple Bacteria
Photoinduced Charge-Transfer

Processes occurring at a Donor-Acceptor heterojunction

1. Exciton generation by absorption of light
2. Exciton diffusion over $\sim L_D$
3. Exciton dissociation by rapid and efficient charge transfer
4. Charge extraction by the internal electric field
Organic Solar Cells

I-V Response Under Solar Illumination


Energy Band Diagram

- Broad spectral response
- 300 - 800 nm
- $\eta_p \sim 3\%$
- In concentrator geometry

Voltage [V]

Current [mA/cm$^2$]

- I$_{MAX}$
- V$_{MAX}$
- V$_{OC}$

1300 mW/cm$^2$

= 17 suns (AM1.5)

- CuPc ($E_g=1.7$)
- PTCBI ($E_g=1.7$)
- BCP ($E_g=3.5$)

HOMO

- 0.85 eV

LUMO

- 0.7
- 0.9
Solar Cell Power Efficiency

- Crystalline-Si
- Poly-Si
- Amorphous-Si
- Organic

Legend:
- Laboratory
- Production

Graph showing power efficiency percentages.
Donor-Acceptor Multilayer Organic Photodetectors


100um diameter, -9V, 1.4ps excitation @ 670nm under an average optical power of (250-70)mW/cm
Estimated carrier velocities: \( v = d\tau = (1.1 + 0.1) \times 10 \text{ cm/s} \)

**Normalized Response**

**PTCBI lifetime** = (1.8±0.1) ns

**f_{3dB}** = (430±40) MHz

**FWHM** = (720±50) ps

**Chemical Structures**

- CuPc: Copper phthalocyanine
- BCP: Bathocuproine
- PTCBI: 3,4,9,10-perylenetetracarboxylic bis-benzimidazole
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

120 million Rods - brightness
6 million Cones - color

B 5-10%
G ~30%
R ~60%

From the NASA website
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 unexploded 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

![Diagram of Pentiptycene and Polymer Backbone]
FIDO 4D Field Test

Determining the TNT Concentration Profile of a AP-Landmine

$\approx 10^{-16}$ g Detection Limit
(100,000 Molecules)
Organic Semiconducting Lasers

Lateral Structures

Edge Emission

Vertical Structures

Electrode
Alq₃
Alq₃:DCM
HTL
ITO
DBR
Quartz

δλ = (0.2 ± 0.1) Å

INORGANIC

ORGANIC

Temp. Insensitivity
T₀ = 1000

Wavelength (Å)

Laser Wavelength (nm)

Organic LEDs

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

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

Organic Displays
20 to 30% growth per year

$70 Billion business in 2005
Multi-Function

Video Watch

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

Automotive

Dashboard displays, external indicator lights, and road signs
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

- a-NPD
- Alq3
- Host molecules (charge transport material)
- Dopant molecule (luminescent dye)
- Transparent anode
- Low work function cathode
- Exciton
- Trap states
- Electrons

Energy levels:
- 2.6 eV
- 5.7 eV
- 2.7 eV
- 6.0 eV
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

OLEDs as Backlights in AMLCDs

Bulovic, patent pending.
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)

CdSe Core
$D = 17-120\text{Å}$

TOPO caps
Triocetylphosphine oxide


$\text{Alq}_3$
Tri(8-hydroxyquinoline)
Aluminum (III)

$\text{TAZ}$
3-(4-Biphenyl)-4-phenyl-5-tert-butylphenyl-1,2,4-triazole

$\text{TPD}$
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 QD devices

*Photo by F. Frankel*
Flexible Internet Display Screen

THE ULTIMATE HANDHELD COMMUNICATION DEVICE

UDC, Inc.