Organic Functional Materials
Liquid Crystals, Organic Electronics, Nanoelectronics

Prof. Dr. Peer Kirsch
Merck KGaA
Definition

What are „Functional“ Materials?

Functional Materials

• Compounds which are reacting in a defined way to an external stimulus, by
  – movement, conformation change or reorientation
  – transition between electronic states
  – change of redox state

Structural Materials

• Compounds which in a bulk state have a purely structural function
Organic Functional Materials

- **Liquid Crystals**
  - Materials for Display Applications

- **Organic Electronics**
  - Organic Conductors, Semiconductors and Superconductors
  - Organic Field Effect Transistors (OFET)
  - Organic Light-Emitting Diodes (OLED)
  - Organic Photovoltaics (OPV)
  - Dye-Sensitized Solar Cells (DSSC)

- **Nanoelectronics**
  - Basics of Molecular Electronics
  - Molecular Memory
  - Complex Unimolecular Circuits

<table>
<thead>
<tr>
<th>Functional Response</th>
<th>Relevant State of Matter</th>
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<td>Bulk movement, induced anisotropy</td>
<td>bulk</td>
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<tr>
<td>Redox reaction, electronic excitation</td>
<td>bulk</td>
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<tr>
<td>Redox reaction, electronic excitation, conformation change, quantum interference</td>
<td>molecular</td>
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Order Arising from Anisotropy of Shape

Salvador Dali: “Disintegration of the persistence of memory”

calamitic phase

smectic “banana” phase

discotic phase
The Liquid Crystalline State of Matter

The Liquid Crystalline State of Matter

$S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle$

clearing point
Classification of Monomeric Liquid Crystals

- Monomeric LCs
  - Lyotropic
    - Achiral Nematic
    - Chiral Nematic
  - Thermotropic
    - Calamitic
    - Discotic
  - Nematic
    - Achiral Nematic
    - Chiral Nematic
  - Smectic
    - Achiral Smectic
    - Chiral Smectic

TN  IPS  STN  FLC
VA
The Twisted Nematic (TN) Cell
How Does it Work?

“Super-fluorinated materials” (SFM), 1985+

R. Eidenschink et al., 1976
D. Demus et al., 1975
G. W. Gray et al., 1972
F. Reinitzer, 1888
Plastic Electronics

Nobel Prize in Chemistry 2000

- Awarded “for the discovery and development of conductive polymers”

Alan Heeger

Alan G. MacDiarmid

Hideki Shirakawa
Plastic Electronics

Applications

• Inexpensive, lightweight, flexible, printable electronics, for use in OLED, RFID, active matrix backplane for displays and e-paper, photovoltaics and many other types of devices
Solid State Electronics

From Molecular Orbitals to Band Structure

- **Pauli Exclusion Principle**: Identical quantum states within the same system are forbidden
- On close contact all molecular orbitals split into slightly different energy states
- In continuous solid state discrete orbitals fuse to energy bands

![Diagram](image)
Charge Transport Mechanism

Hopping Mechanism: Molecular Perspective

**n-type semiconductor**: electron injection (reduction), followed by electron hopping

**p-type semiconductor**: "hole" injection (oxidation), followed by reverse electron hopping or "hole migration"
Conduction Mechanism

Charge Carrier Traps

- In organic semiconductor, the direction of charge carrier migration is determined by the applied electric field gradient. The hopping itself is thermally activated.
- If energy states lie more than $\sim kT (~ 0.1 \text{ eV})$ below the conduction band average, charge carriers cannot be thermally activated, become "trapped" and might locally accumulate. Accumulated charges build up electrical potential, impeding further charge transport.

Imperfect crystal or amorphous solid: statistical distribution (Boltzmann) of energy levels

Trap State: charge carrier is caught in lower energy state cannot be thermally re-elevated into "conduction band"
Organic Semiconductors

Charge Carrier Mobilities and Solid State Structure

**n-Type Organic Semiconductors**

**Perfluoropolyacenes**

- Acenes and perfluoroacenes: systems with inverse electron demand and electrostatic potential

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*Figure 6.* B3LYP/6-1G** electrostatic surface potentials mapped onto a surface of total electron density for TET (left) and PFT (right). Regions of higher electron density are shown in red and of lower electron density in blue (values in atomic units).

Charge Transport Mechanism

Implications for Charge Carrier Mobility

- Transfer integral depends strongly on intermolecular HOMO-SOMO-LUMO overlap, via interplanar distance or relative orientation

Crystal and Morphology Design
Making Use of Arene-Perfluoroarene Interactions

ORGANIC LIGHT EMITTING DIODES (OLED)
ORGANIC SENSORS
Organic Electronics

ORGANIC PHOTOVOLTAICS (OPV)
DYE-SENSITIZED SOLAR CELLS (DSC)
Dye-Sensitized Solar Cells (DSSC)

Working Principle

Dye-Sensitized Solar Cells (DSSC) are a type of solar cell that uses dye molecules to capture light and generate electrical current. The working principle of DSSC involves a series of reactions that take place in the presence of light.

![Diagram of DSSC working principle](image)

- **Substrate (glass or plastic)**
- **FTO**
- **Dye-coated TiO₂ nanoparticles**
- **I⁻ → I₃⁻ → e⁻ → e⁻**
- **Platinum or graphite**
- **FTO (fluoride-doped SnO₂)**
- **Ionic liquid-based electrolyte**

### Advantages of IL electrolyte

- Not volatile
- Low thermal expansion during day-night temperature cycles
- High chemical stability

### Challenges

- Lower ion conductivity compared to solvent-based electrolyte
- Design of printable formulations for roll-to-roll process

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Design of DSSC Dyes

- In order to avoid reverse electron transfer from TiO$_2$ to oxidized dye, positive charge has to be far away
- LUMO should have large amplitude close to TiO$_2$ surface in order to achieve efficient electron transfer

Nanoelectronics

MOLECULAR DEVICES
“There’s Plenty of Room at the Bottom“

“I don’t know how to do this on a small scale in a practical way, but I do know that computing machines are very large; they fill rooms. Why can’t we make them very small, make them of little wires, little elements – and by little, I mean little. For instance, the wires should be 10 or 100 atoms in diameter, and the circuits should be a few thousand angstroms across... there is plenty of room to make them smaller. There is nothing that I can see in the physical laws that says the computer elements cannot be made enormously smaller than they are now. In fact, there may be certain advantages.”

R. Feynman, „There’s Plenty of Room at the Bottom“, Annual Meeting of the American Physical Society, California Institute of Technology, Dec 29, 1959
Nanoelectronics

**BASICS OF MOLECULAR ELECTRONICS**
That often limit yields in chemical reactions; it is not even necessary to do any fundamental research or to replace present processes. Only the engineering effort is needed.

In the early days of integrated circuitry, when yields were extremely low, there was such an incentive. Today ordinary integrated circuits are made with yields comparable to those obtained for individual semiconductor devices. The same pattern will make larger arrays economical, if other considerations make such arrays desirable.

Heat problem
Will it be possible to remove the heat generated by tens of thousands of components in a single silicon chip?

If we could shrink the volume of a standard high-speed digital computer to that required for the components themselves, we would expect it to glow brightly with present power dissipation. But it won’t happen with integrated circuits. Since integrated electronic structures are two-dimensional, they have a surface available for cooling close to each center of heat generation. In addition, power is needed primarily to drive the various lines and capacitances associated with the system. As long as a function is confined to a small area on a wafer, the amount of capacitance which must be driven is distinctly limited. In fact, shrinking dimensions on an integrated structure makes it possible to operate the structure at higher speed for the same power per unit area.

Day of reckoning
Clearly, we will be able to build such component-cramped equipment. Next, we ask under what circumstances we should do it. The total cost of making a particular system function must be minimized. To do so, we could amortize the engineering over several identical items, or evolve flexible techniques for the engineering of large functions so that no disproportionate expense need be borne by a particular array. Perhaps newly devised design automation procedures could translate from logic diagram to technological realization without any special engineering.

It may prove to be more economical to build large systems out of smaller functions, which are

Gordon Moore

- founder of Fairchild Semiconductors (1957) and Intel (1968)
- formulates in 1965 “Moore’s Law“:

„The number of transistors on a given area doubles every 18 months“
Moore's Law

Integration Density vs. Basic Structure of Matter

Current Physics' Limit:
- Planck Length

Current Pace of Miniaturization:
- one order of magnitude per decade

Mechanical unit
Vacuum tube
Stand-alone transistor
Feature size in current CPU
Molecule
Atom
Nucleon

Matter's End

Size [m]

10^0 10^-5 10^-10 10^-15 10^-20 10^-25 10^-30 10^-35
Molecular Electronics

Single Molecule Building Blocks

• Requirements for efficient charge injection:
  – Connection to a metallic conductor via a suitable interface, e.g., gold-sulfur (Au-S) bond
  – Good match between electrode Fermi level ($E_F$) and molecular frontier orbitals, i.e. $E_F$ should be between $E_{HOMO}$ and $E_{LUMO}$

• Requirements for good conductance:
  – Conjugated $\pi$ system
  – Small HOMO-LUMO gap
  – Correct orbital phases and amplitudes at the connecting points (quantum interference effect)
Unimolecular Electronics

How Do Single Molecules Conduct?

(a) For the injection of electrons contact barrier has to be overcome. Alignment of electrode Fermi levels with molecular frontier orbitals is necessary.

(b) A small bias voltage shifts the electrode Fermi levels towards the HOMO-LUMO energies, but no sufficient energetic alignment yet: no tunnel current flows.

(c) When bias voltage matches the energy of the HOMO-LUMO gap, resonant tunneling occurs: current flows.

(d) In single molecule transistor operation, an additional, electrical gate field can shift the molecular frontier orbitals in or out of resonance: resonant tunneling can be switched on and off.
Unimolecular Electronics

Characterization Techniques

• **Scanning Tunnel Microscopy (STM)** of self-assembled monolayers (SAM)

![Scanning Tunnel Microscopy (STM) of self-assembled monolayers (SAM)](image)

• **Mechanically Controlled Break-Junction (MCBJ) Technique**

![Mechanically Controlled Break-Junction (MCBJ) Technique](image)
Charge Transport Mechanism

**Tunneling Barriers**

- Contact from conductor to molecule (= „injection barrier“)
- Intramolecular non-conjugated segments (e.g., aliphatic substructures or biaryl 90° twist)
- Intramolecular barriers can be overcome by (resonant) tunneling or hopping
Nanoelectronics

MOLECULAR MEMORY
Unimolecular Electronics

Voltage-triggered Conductance Switching

- Two different resistive states can be selected by voltage pulse
- States are stable over several minutes at 100 K
- Mechanism of switching unclear: „Polaron Switching“? Artefact? Inorganic oxide?

Figure 3. Several repeated switching cycles of the BPDN-DT: If the voltage applied to the metal–BPDN-DT–metal junction exceeds a certain positive threshold value ($V_{\text{Switch, pos}}$), the system switches from the initial “off” state to the “on” state. This state is maintained when operating only at voltages above $V_{\text{Switch, pos}}$. A negative voltage sweep or a pulse below the negative threshold value ($V_{\text{Switch, neg}}$) resets the molecule again to the initial “off” state.

COMPLEX UNIMOLECULAR CIRCUITRY
Molecular Circuits

Chemical Wiring and Soldering

Complex Single Molecule Devices

Hypothetical Integrated Devices: Wiring via CNT
