EPFL

Organic Electronic Materials

EPFL MSE 486 & ETH 327-2142-00L

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École
polytechnique
fédérale
de Lausanne

One Class Across Two Schools

Course Schedule and Resources

- Class is on Tuesdays 14:15–16:00; teaching concepts
- Exercise sessions are on Tuesdays 16:15–17:00, starting on March 11, active learning
- Homework can be done any time; adding depth and detail
- Exam (written, paper & pencil) will take place simultaneously at EPFL and ETHZ during EPFL exam session, as a “graded semester performance” at ETHZ (June; we will do a survey when is the best week for ETHZ students)

- course materials on the EPFL Moodle at https://moodle.epfl.ch/course/view.php?id=15102
  - if you still need to sign up: passcode ETHZ-OEM-2024
  - communication with the teaching assistants
  - slide PDF files, exercises, homework and reading assignments
  - assignment of student presentations later in the semester
  - course live recordings

Course Schedule 2024

	Feb 28	Feb 25	Mar 4	Mar 11	Mar 18	Mar 25	Apr 1	Apr 8	Apr 15		Apr 29	May 6	May 13	May 20	May 27
14–15		1.1	2.1	2.3	3.1	3.2	4.1	5.1	6.1		6.3	6.5	7.2	8.1	8.2
15–16		1.2	2.2	2.3	3.2	3.3	4.2	5.2	6.2		6.4	7.1	7.3	8.2	8.3
16–17		1.2	2.2	(1)	(2)	(3)	(4)	5.3–5.4	(5)		(6)	(7)	(8)	(9)	(10)
17–18															

class (chapter) · exercise (sheet) · homework · presentations

- we have to agree on a week for the exam, because EPFL academic services need to agree

Hoemwork, Exercises, Exam

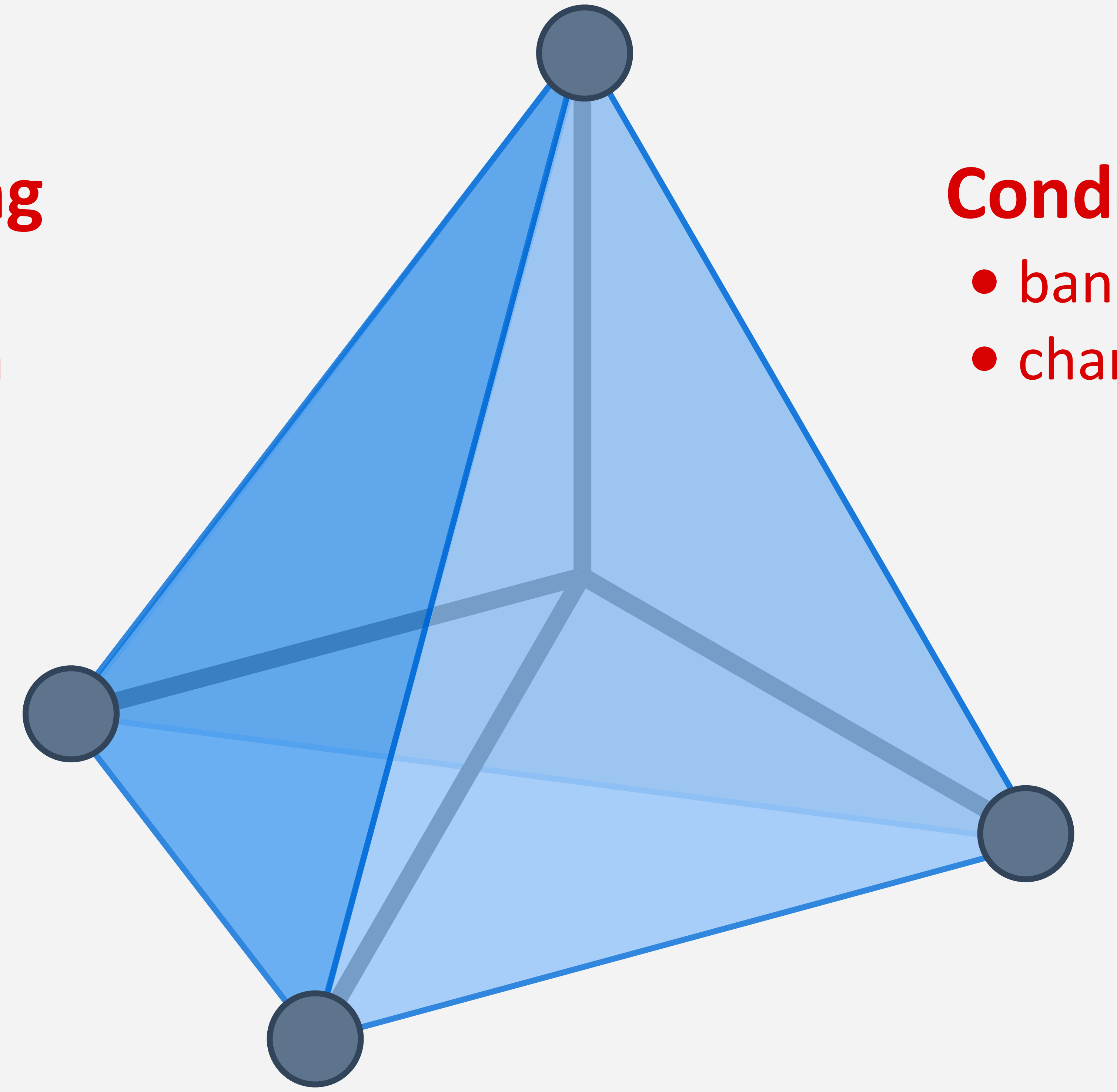
- **homework & reading assignments**
  - each week, there will be an additional reading assignment or similar homework
  - the time for the homework is considered as part of the weekly hours
  - the content of the homework assignment is relevant for the exam
- **exercises**
  - we will distribute exercise sheets every week, starting Feb 27 (overall 10 sheets)
  - you solve them at home or during exercise hours, even with the help of the assistants
  - we do not give actual grades for individual exercise sheets
  - grades for number of reasonable solved sheets (6.0 for 10/10, 5.75 for 9/10 sheets, etc.)

- **total course grade is 75% exam, 25% exercises (only counted if better than exam)**
- **please actively participate and engage in the class and exercises**

Interdisciplinary Research on Organic Electronic Materials

Electrical Engineering
- integrated circuits
- device implementation

Condensed Matter Physics
- band structure
- charge transport



Chemistry
- molecular design
- organic & polymer synthesis

Materials Science
- materials processing
- structure at all levels

Ashby, Shercliff, Cebon, *Materials: Engineering, Science, Processing and Design*, Elsevier, **2018**.

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1 Introduction

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1.1 Brief History of Organic Electronics

Timeline of Discoveries in Electricity and Electronics

600 BC
Greeks discover static electricity

Coulomb
law of electrostatics
1799

1800
Volta
electric battery

Faraday
first dynamo
1831

1878
Swan & Edison
lightbulb

Fleming
vacuum diode
1897

1927
Losev
light-emitting diode

Bardeen & Brattain
point-contact transistor
1947

1958
Jack Kilby
integrated circuit

organic electronics

Akamatu & Inokuchi
organic semiconductors
1950

1948, 1953, 1956, 1959
Förster, Dexter, Marcus, Holstein
energy & electron transfer
polaron concept

Pope, Helfrich & Schneider
organic electroluminescence
1963, 1965

1977
Heeger, MacDiarmid & Shirakawa
conducting polymers

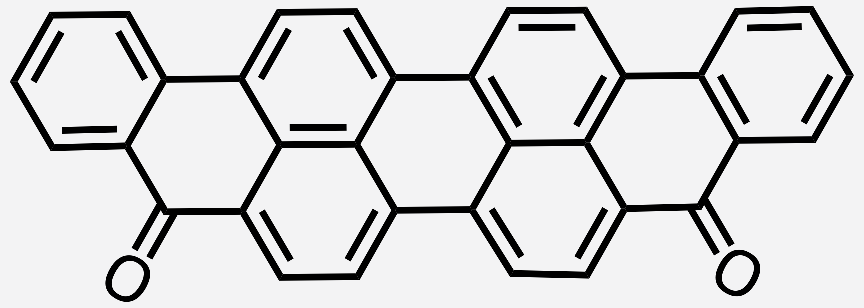
Tang (Kodak)
organic solar cell
1986

1987
Tang (Kodak)
polymer LED

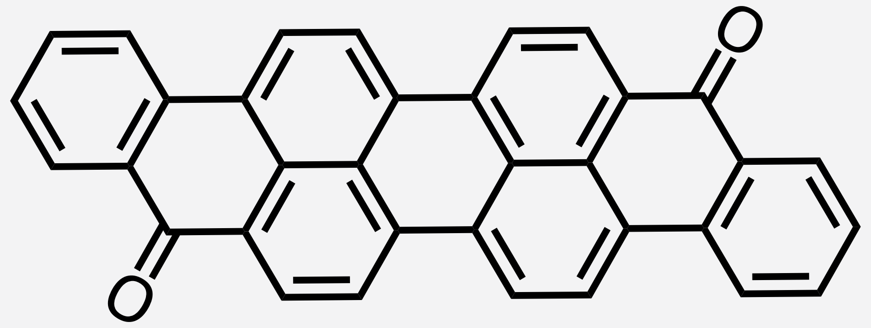
Nobel prizes
organic electronics
1992, 2000

2007, 2009, 2010
Sony, Samsung, LG
OLED TVs & phones

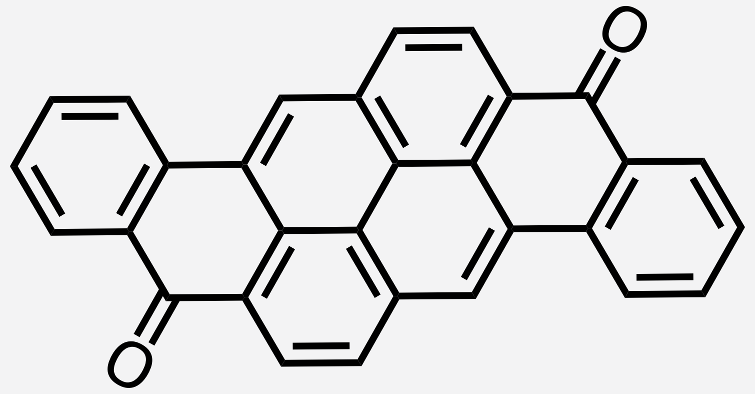
Highlights of Organic Electronics (1950)



violanthrone



isoviolanthrone



pyranthrone

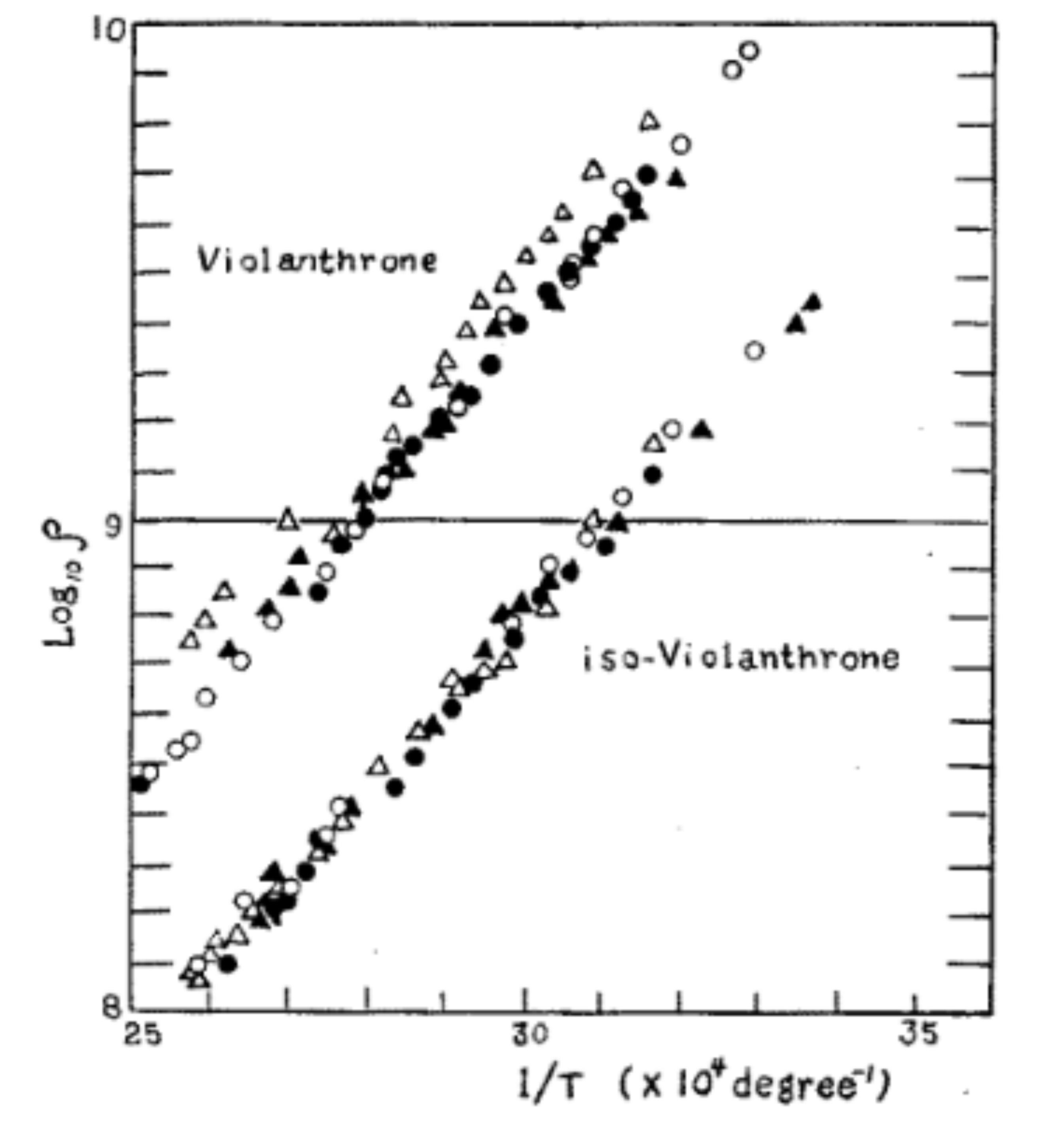


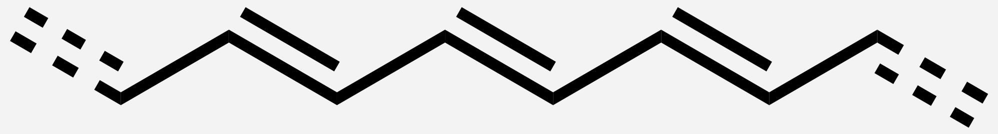
FIG. 3. The relation between resistivity and temperature for violanthrone and iso-violanthrone. △ 82.1 kg/cm², rising temp. ▲ 82.1 kg/cm², falling temp. ○ 119.5 kg/cm², rising temp. ● 119.5 kg/cm², falling temp.

- **first examples of organic semiconductor**
  - large π-conjugated molecules: violanthrone, isoviolanthrone, pyranthrone
  - band gaps between 0.75 eV (isoviolanthrone) and 1.06 eV (pyranthrone)

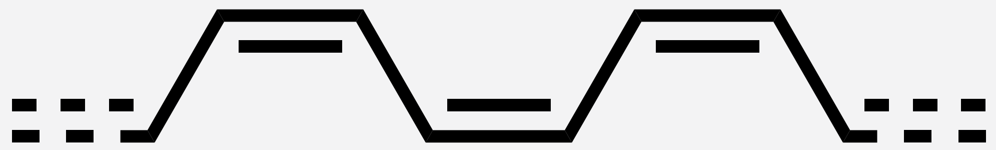
Akamatu, Inokuchi, *J. Chem. Phys.* **1950**, *18*, 810.

Highlights of Organic Electronics (1977)

- discovery of highly conducting doped polymers by Heeger, MacDiarmid, Shirakawa
- Nobel prize awarded in 2000



trans-polyacetylene



cis-polyacetylene

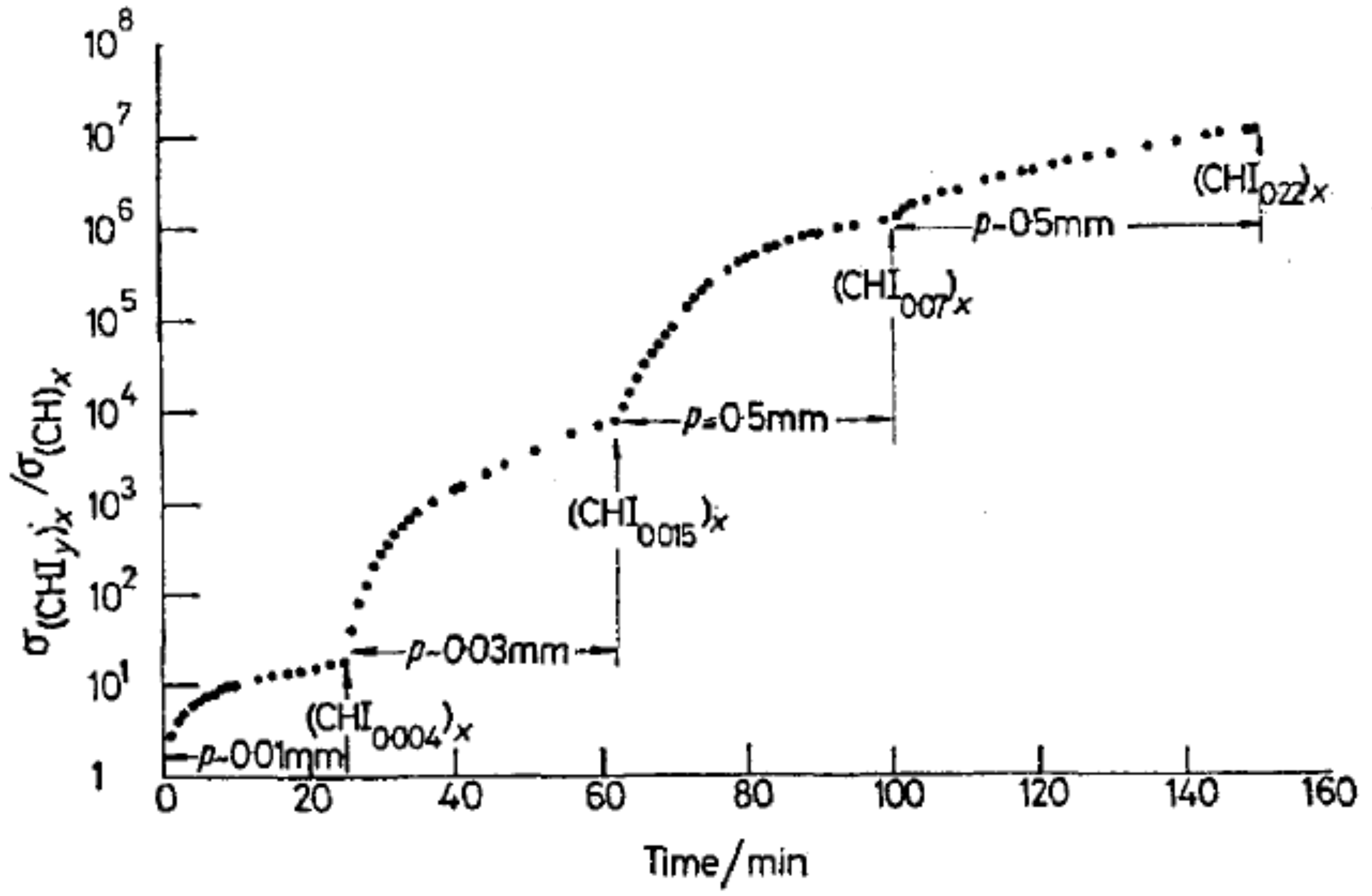


FIGURE. Increase in the room temperature conductivity of *trans*-polyacetylene, $(CH)_x$ as a function of time at fixed iodine vapour pressures. The initial room temperature conductivity is $3{\cdot}2 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$. (In the last experiment some iodine was sublimed onto the glass walls of the conductivity apparatus in order to promote attainment of the equilibrium vapour pressure of the iodine at room temperature in the vicinity of the film).

- **polyacetylene doped with iodine showed drastic increase in conductivity**
- **7 order increase reaching conductivity of inorganic semiconductors**

Why Organic Electronics?

Alan J. Heeger

Alan G. MacDiarmid

Hideki Shirakawa

… thus when asked to explain the importance of the discovery of conducting polymers, I offer two basic answers:

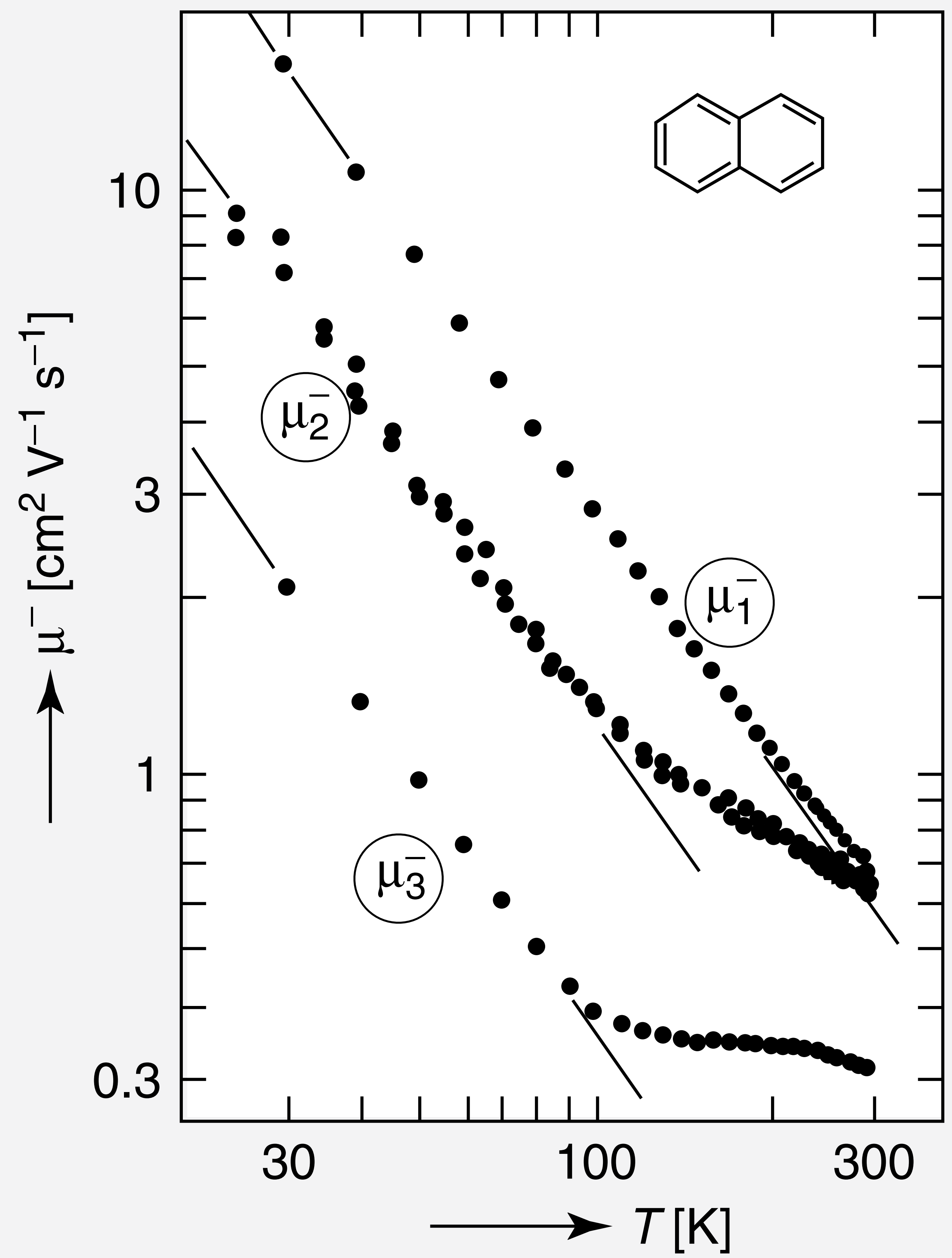
- They did not (could not?) exist.
- They offer a unique combination of properties not available from any other known materials.

The first expresses an intellectual challenge; the second expresses promise for a utility in a wide variety of applications …

Nobel Lectures, *Reviews of Modern Physics* **2001**, *73*, 681; *ibd.* 701; *ibd.* 713.

Example of Band Transport at Low Temperature

- aromatic molecules can exhibit band transport in single crystals at low temperatures



- **band transport occurs at T < 100 K, in all lattice directions, indicated by a temperature dependence** $\mu \propto T^{-n}$
- **different mobilities in different lattice directions reflect the anisotropy of the interaction**
- **breakdown of the band concept at higher temperatures**
- **at room temperature, incoherent transport in two lattice directions becomes equal**

- **very few examples because a crucial element was the extreme care of excluding impurities**

Karl, *Mol. Cryst. Liq. Cryst.* **1989**, *171*, 31.

First Organic Solar Cell

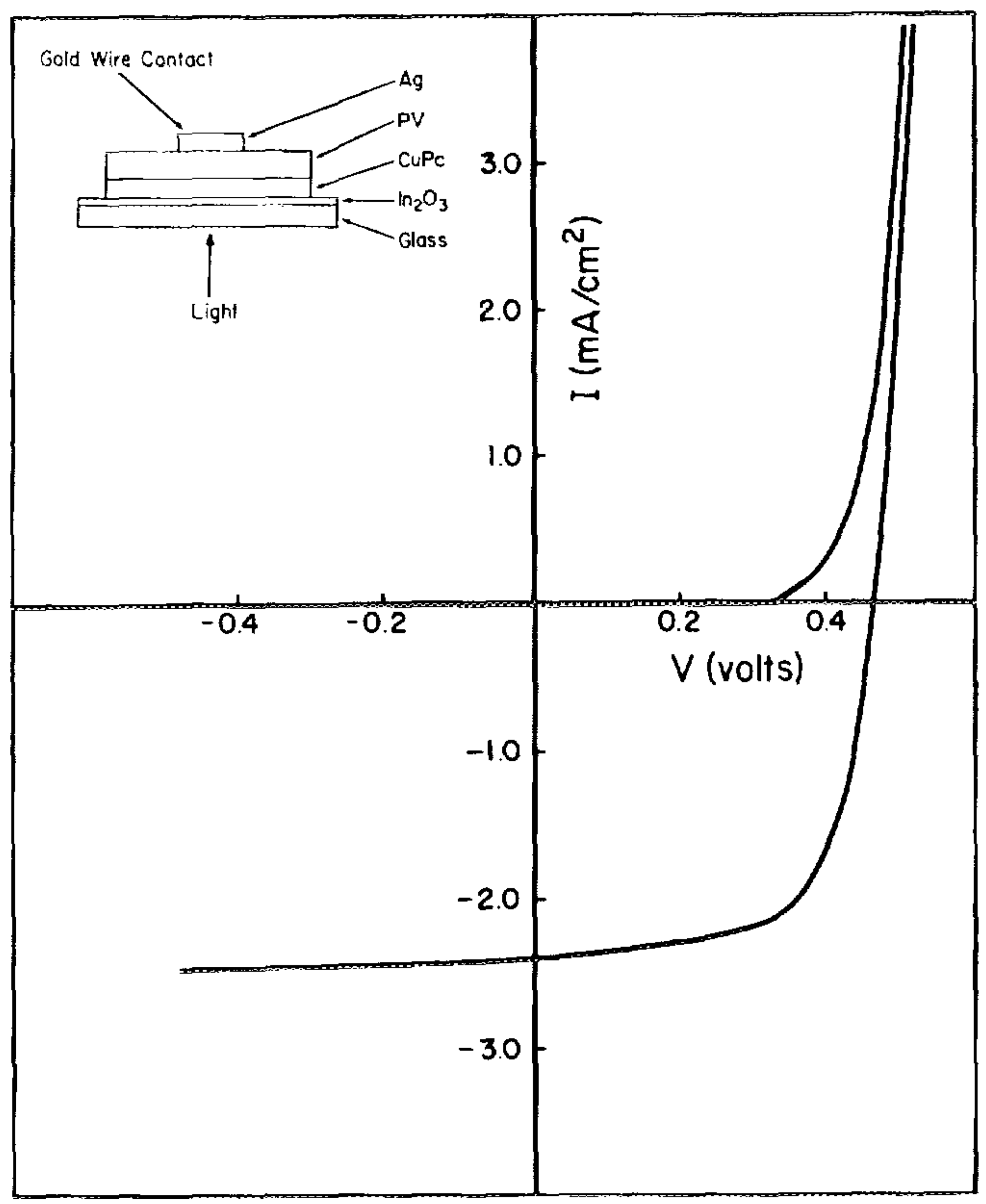
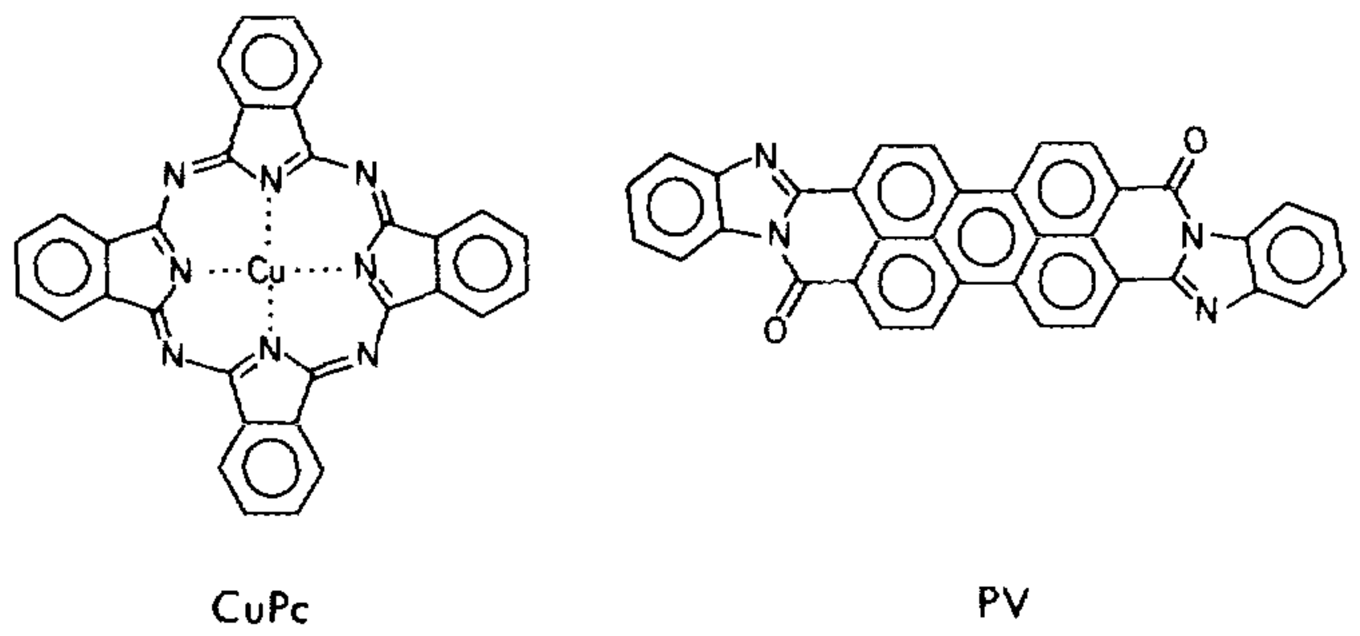


FIG. 1. Configuration and current-voltage characteristics of an ITO/CuPc (250 Å)/PV(450 Å)/Ag cell.



- thin-film, two-layer organic photovoltaic cell
- copper phthalocyanine as donor material
- perylene bisimide derivative as acceptor
- bilayer donor-acceptor junction
- power conversion efficiency of about 1%

Highlights of Organic Electronics: 2001

Published online 26 September 2002 | Nature | doi:10.1038/news020923-9

News

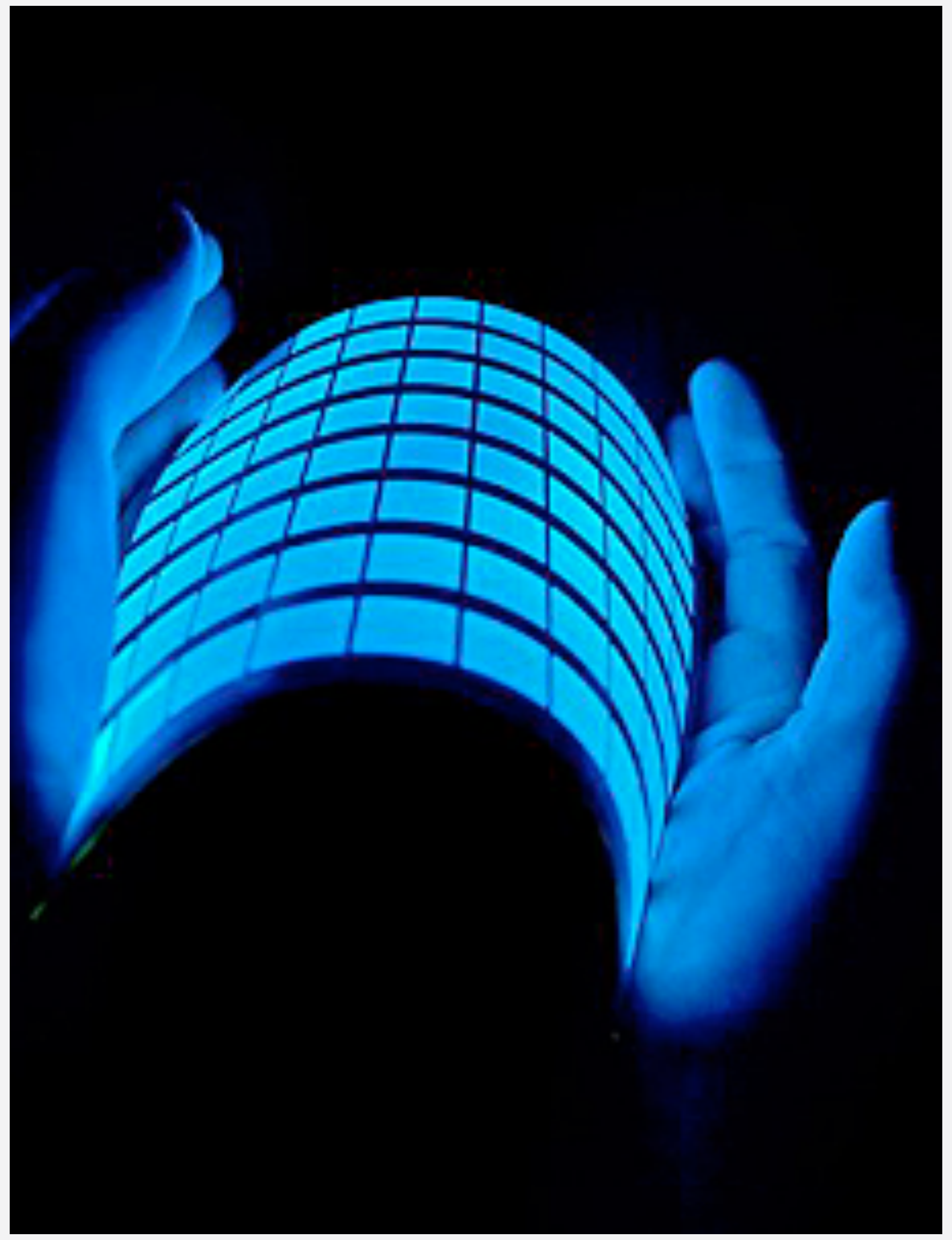
Physicist found guilty of misconduct

Bell Labs dismisses young nanotechnologist for falsifying data.

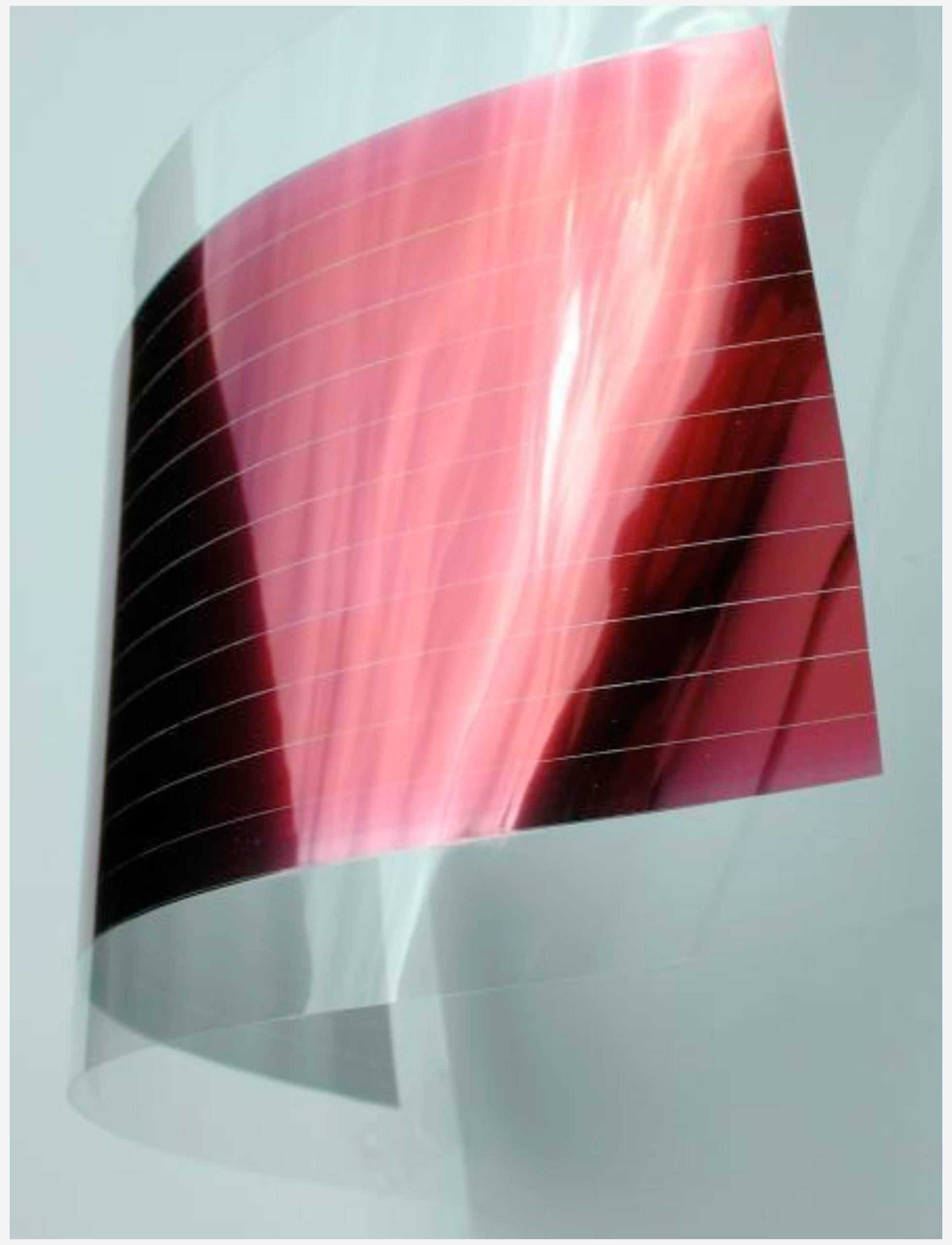
- **Jan Hendrik Schoen**
  - PhD from ETH Zurich (Prof. Bertram Batlogg)
  - Postdoc at Bell Labs
- **publication scandal in molecular electronics**
  - “confirmed” organic compounds to be superconductors and lasers
  - was found to have first manipulated, later completely fabricated data
  - samples inexistent or destroyed and no proper lab record was held
  - 28 withdrawals from journals, including *Science* and *Nature*
  - ETHZ doctoral degree revoked due to dishonorable conduct
  - debate of scientific ethics, scientific coauthorship, performance-driven science

E. S. Reich, *How the Biggest Fraud in Physics Shook the Scientific World*, **2009**.

Organic Electronic Materials



light-emitting diodes

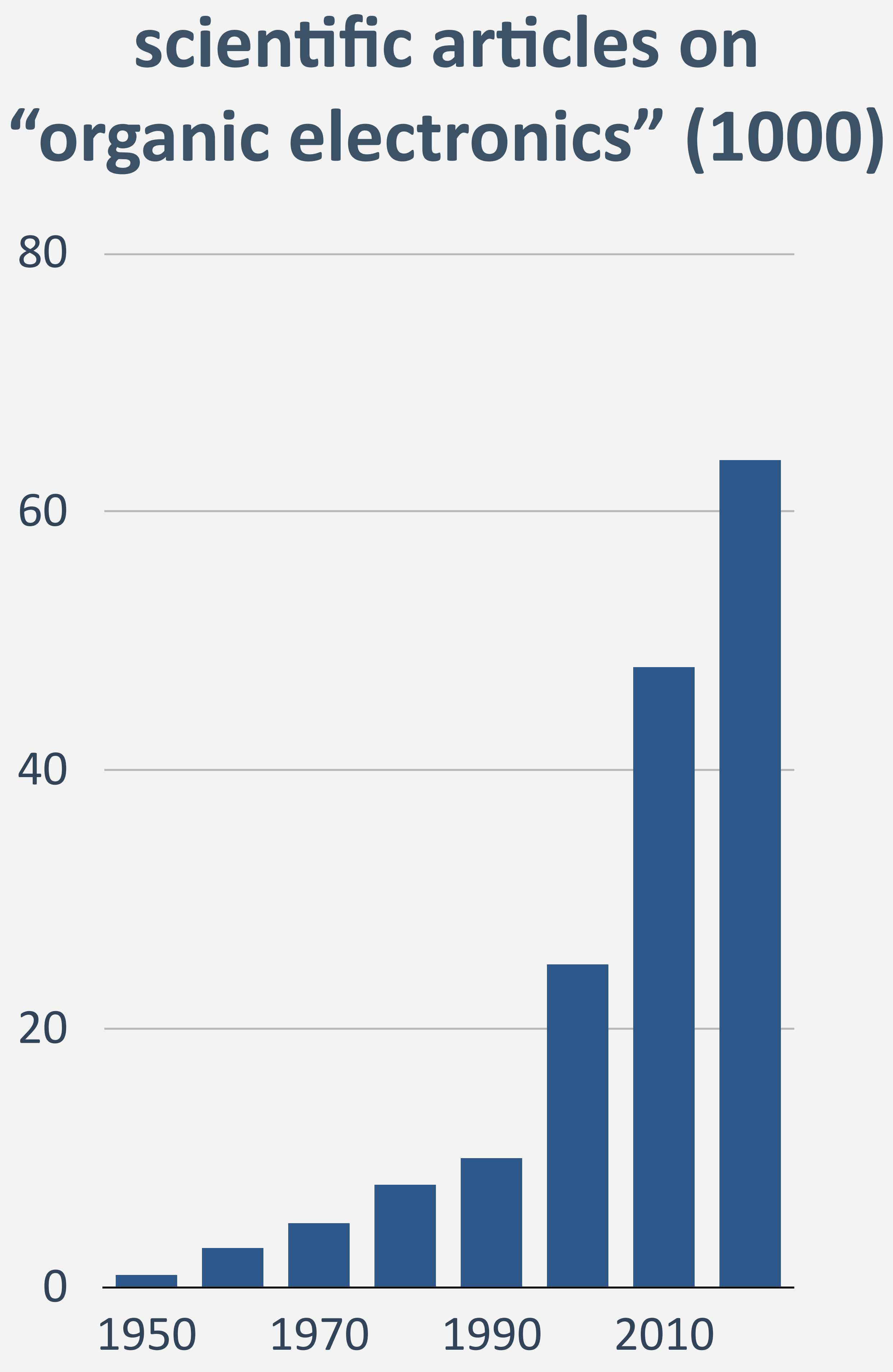


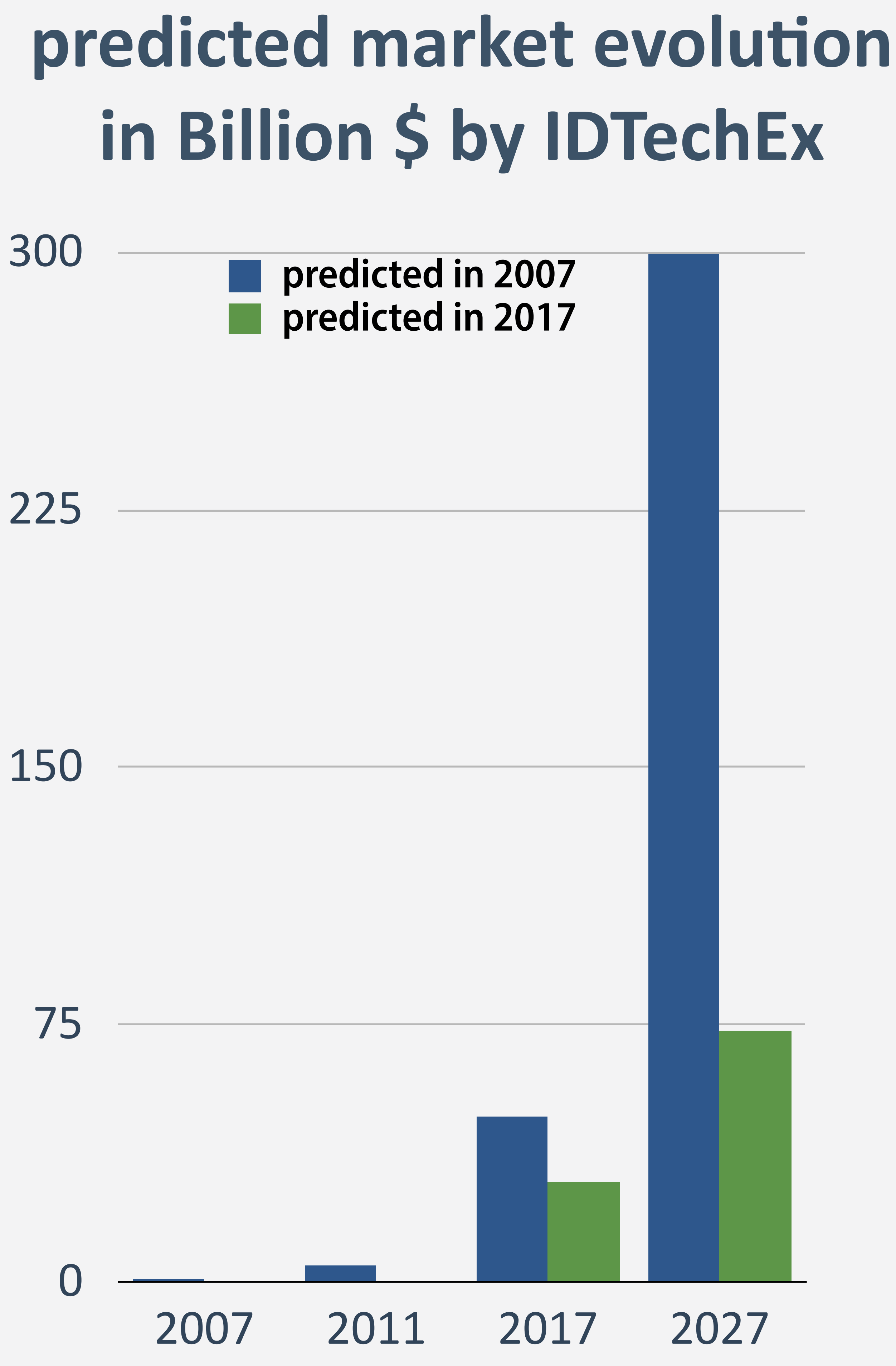
solar cells

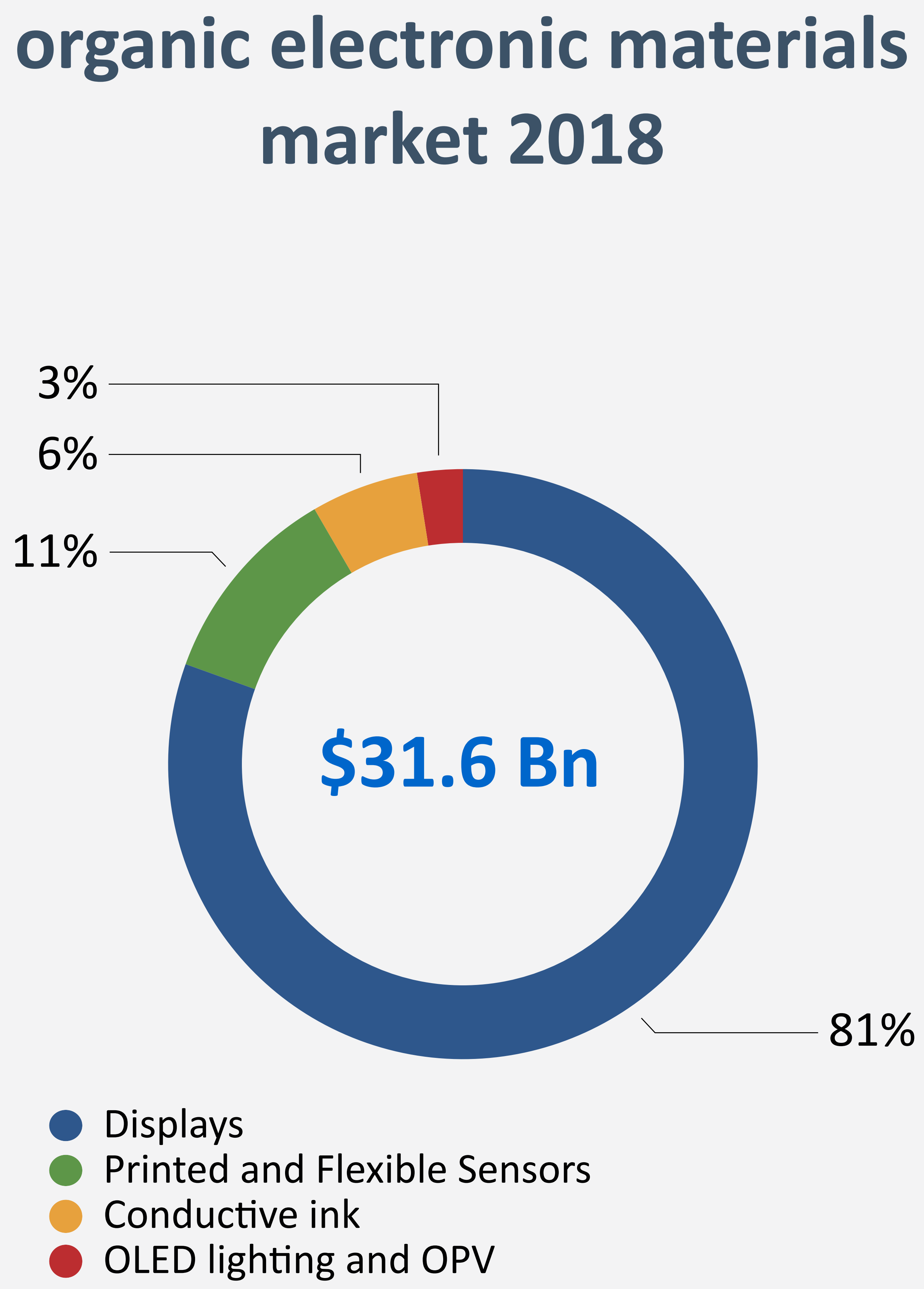
field-effect transistors

- **organic electronic materials have found their way into technological applications**
  - low-cost production using scalable large-area fabrication (spraying, printing)
  - lower weight and mechanical flexibility (if polymer semiconductors are used)

Market Evolution and Prediction of Organic Electronics



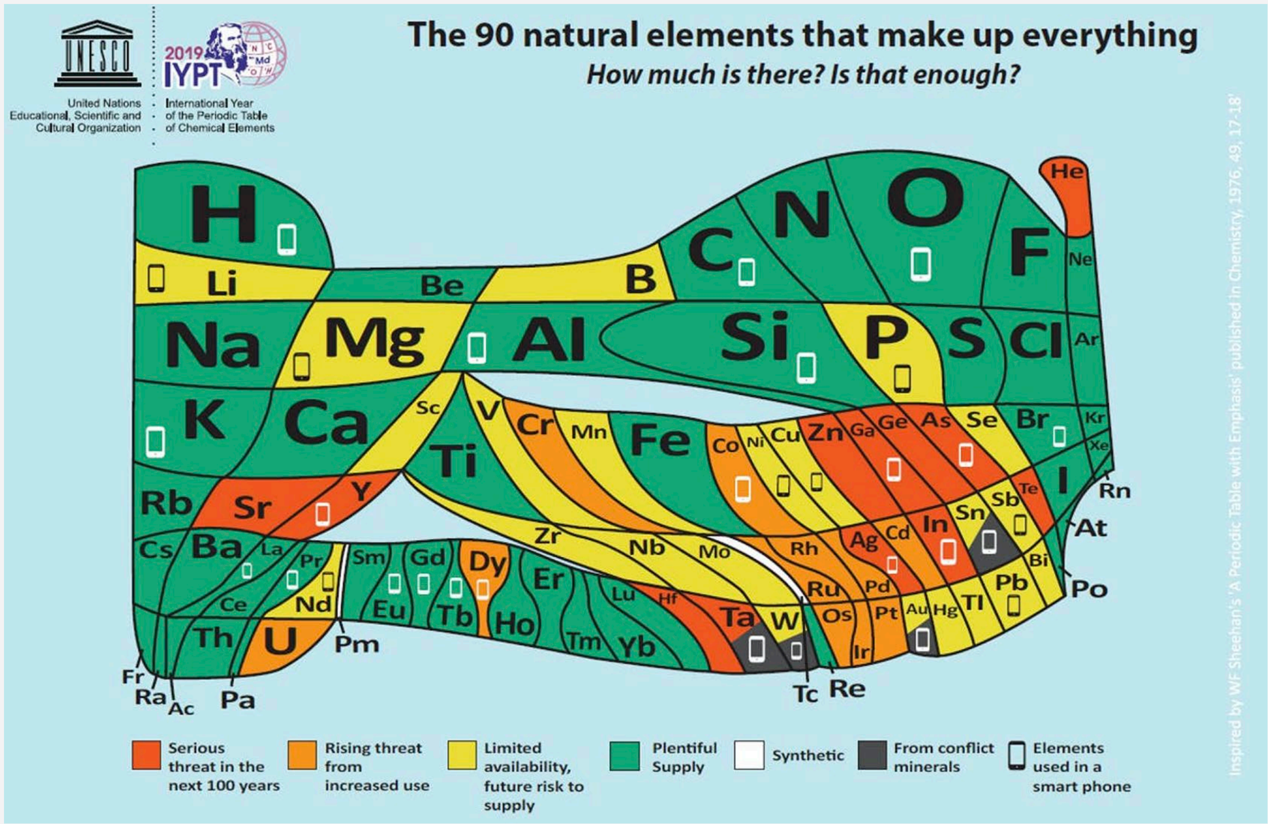


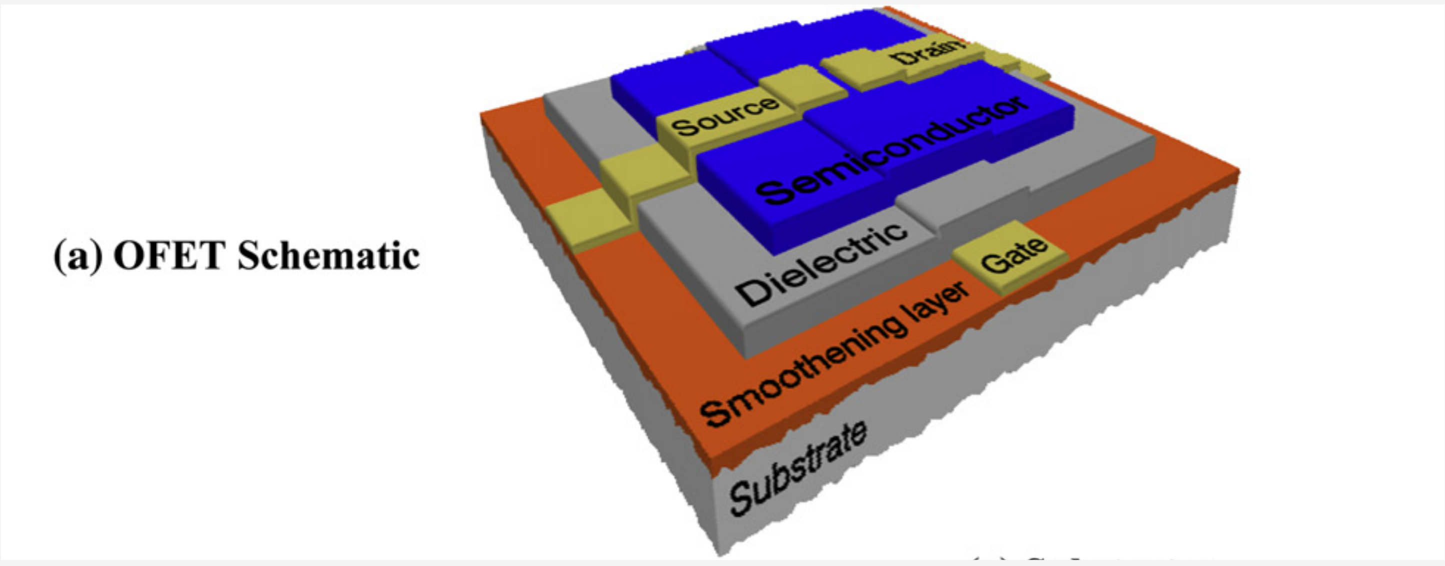


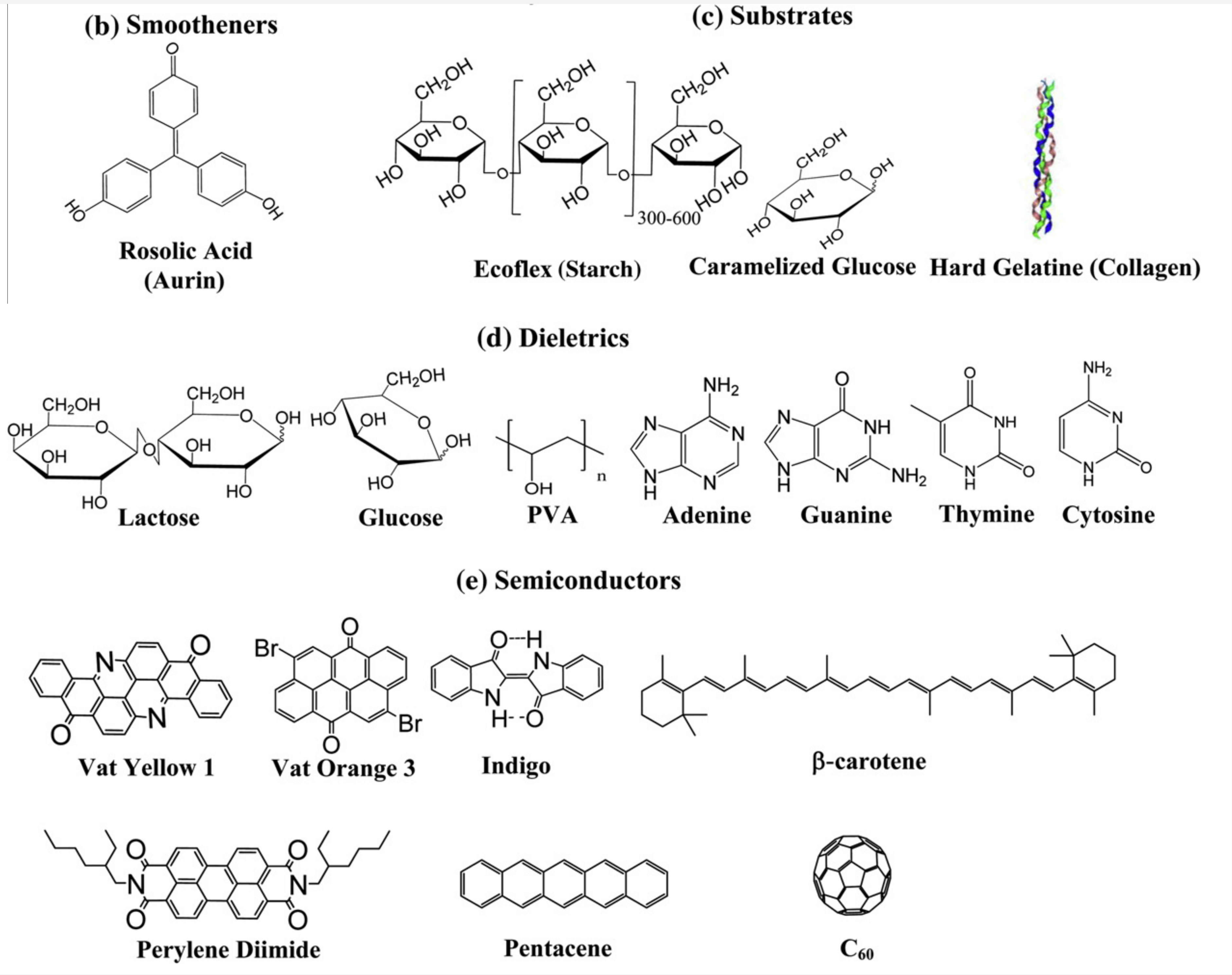
Global Organic Electronics Market Size by Material, by Application, by Geographic Scope and Forecast, IDTechEX

Organic Electronics for Sustainable Engineering

- abundant sensing, tracking, data processing required for a data-driven circular economy
- but what about the sustainability of the data generation technology layer itself?





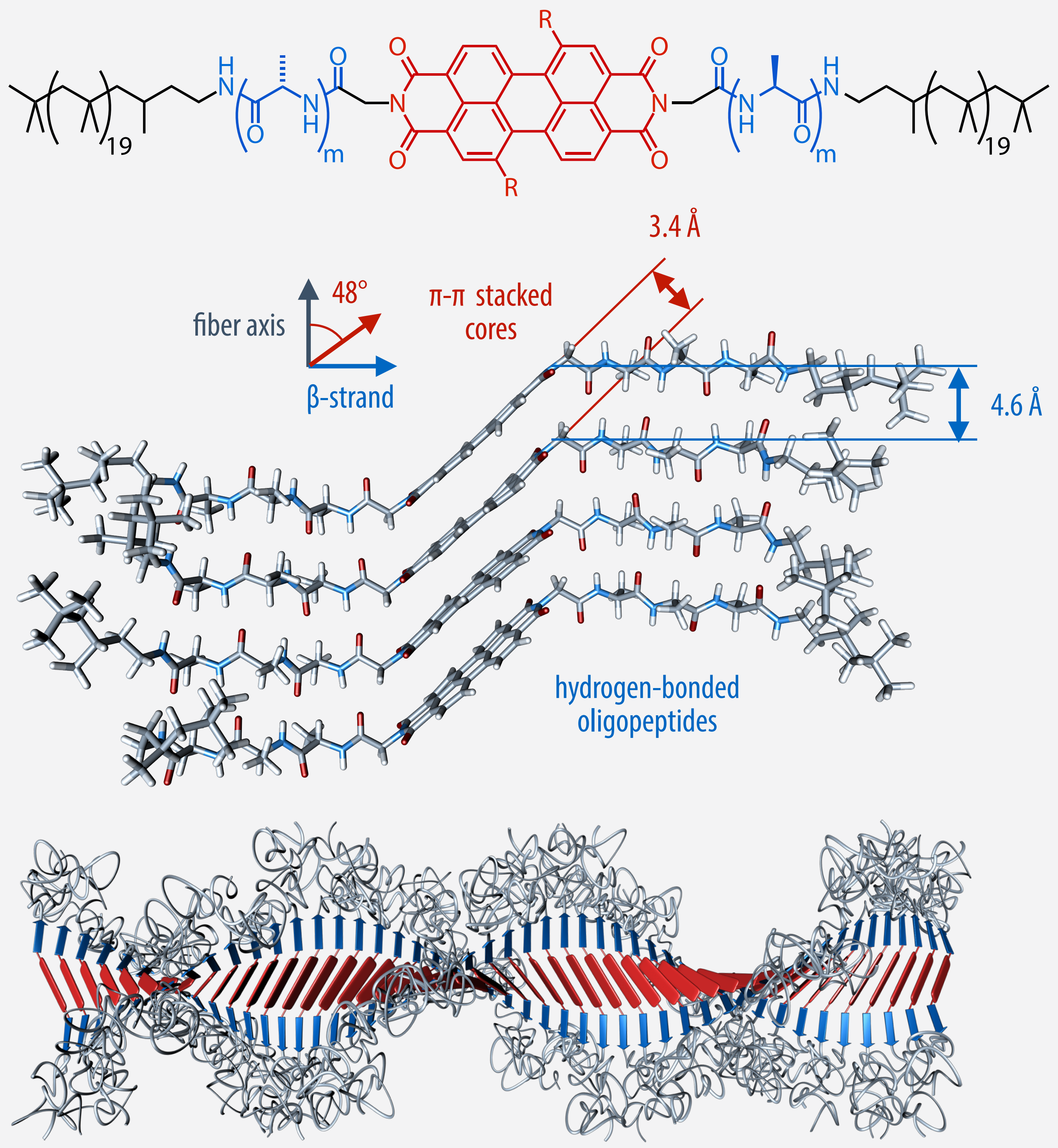


- **organic electronics hold the promise for sustainable abundant data generation technology**

Research Vision and Technology Platforms at the LMOM

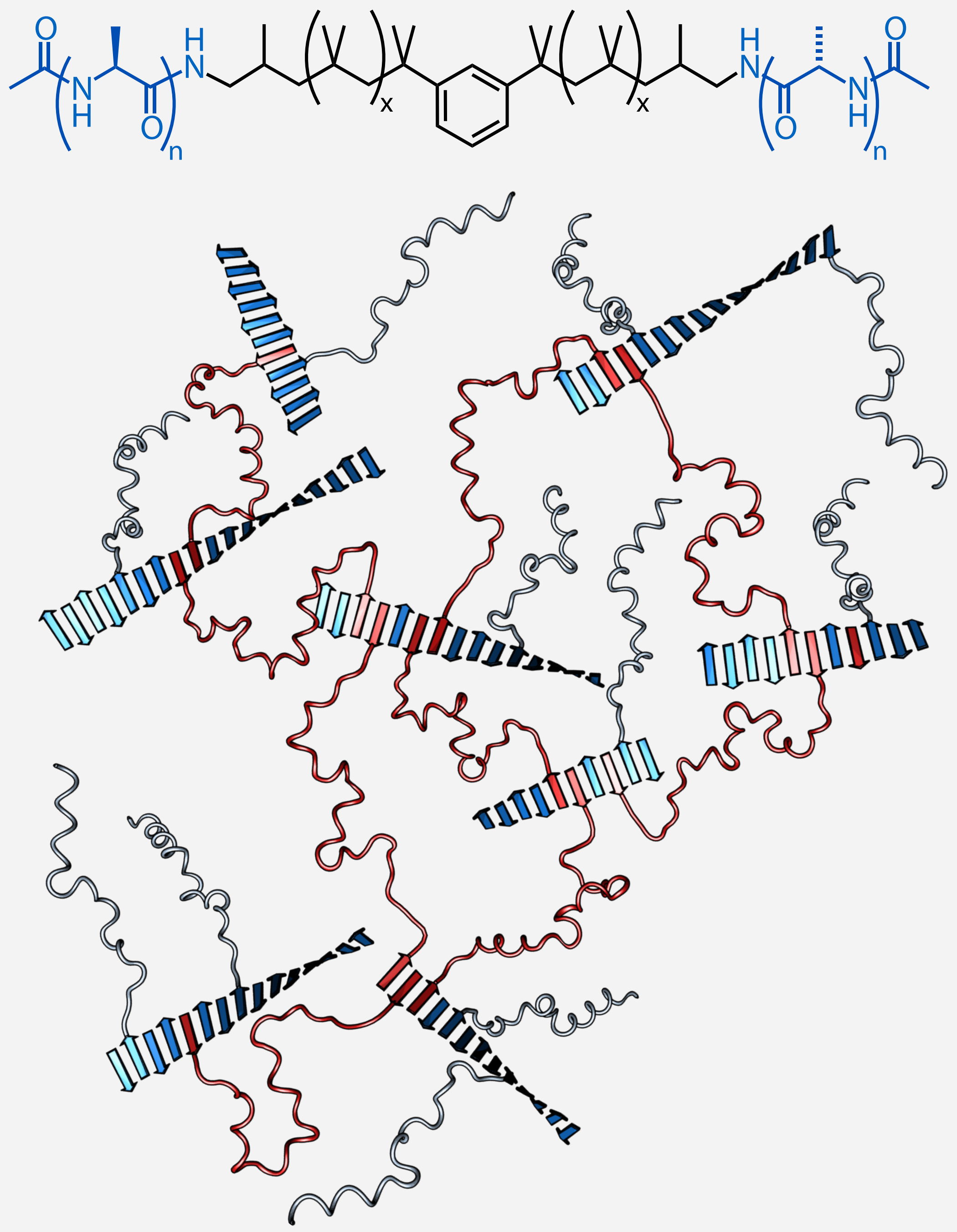
- **universal supramolecular approach** to control diverse functions in different materials classes

electronic properties



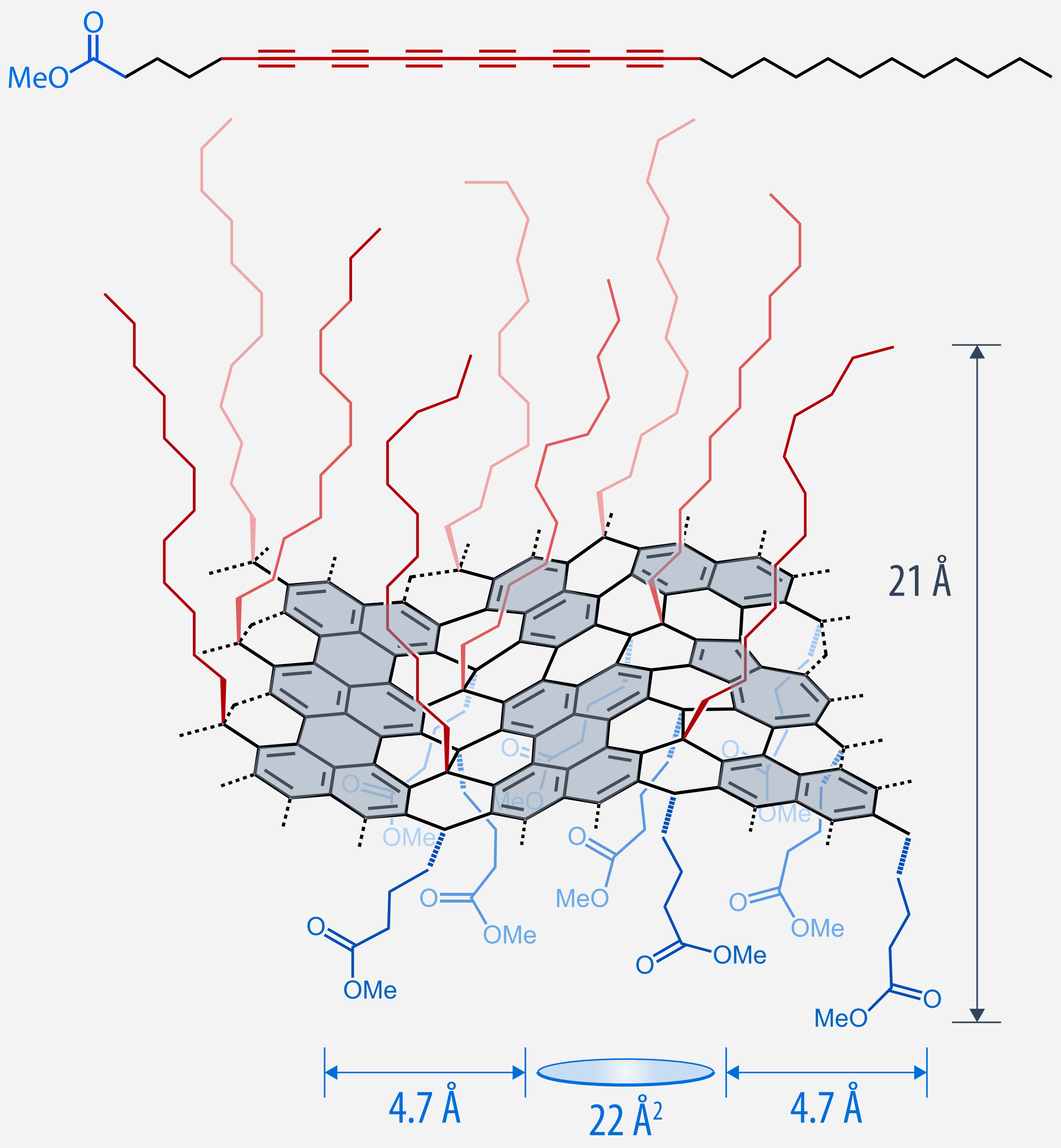
organic semiconductor nanostructures

mechanical properties



hierarchically structured supramolecular materials

chemical reactivity



carbon nanomaterials at room temperature

- **control of the balance of order and disorder across length scales to tailor structure and function**

From Molecular Design to Materials and Devices

molecular design & synthesis

synthetic chemistry,
NMR, MS, MALDI

physicochemical characterization

UV/vis/NIR, CD, fluorescence,
IR, Raman, ESR, DLS, CV

materials processing

extrusion, drawing, blowing,
injection molding, microfluidics

materials characterization

AFM, TEM, SEM, SAXS, WAXD
rheology, DMA, mechanical testing

device fabrication

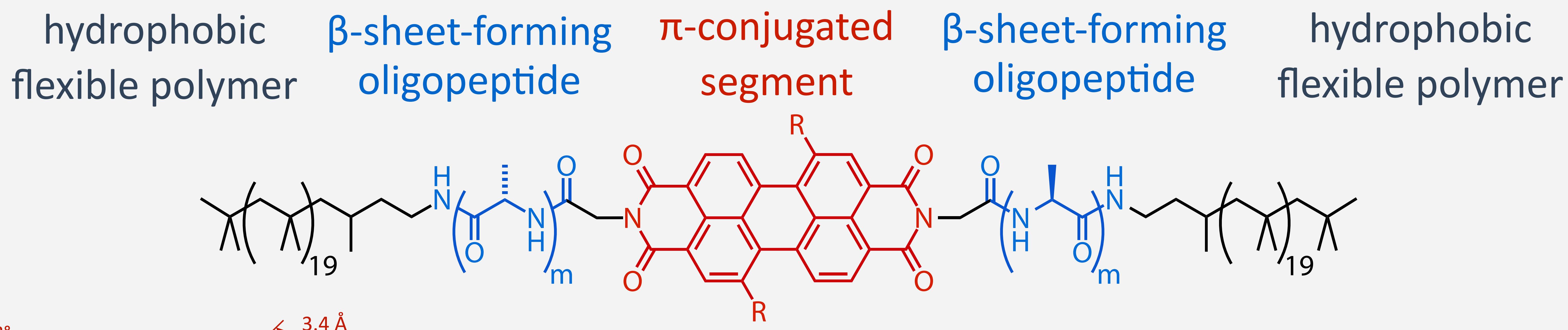
damping structures, railpads,
food containers, OFETs

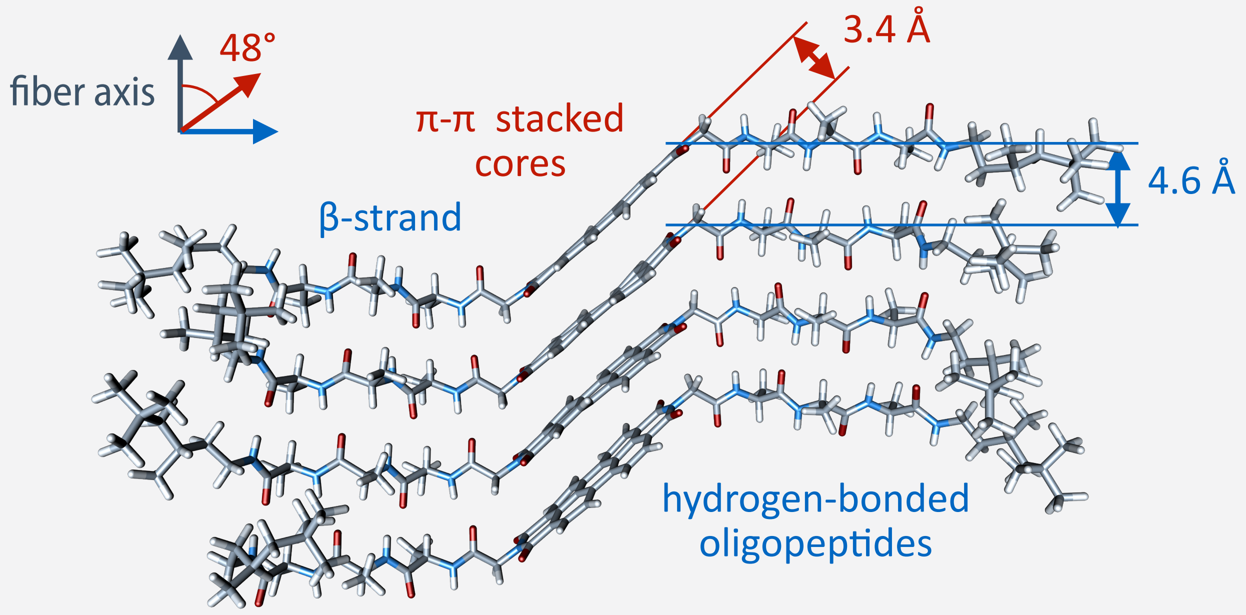
device testing & applications

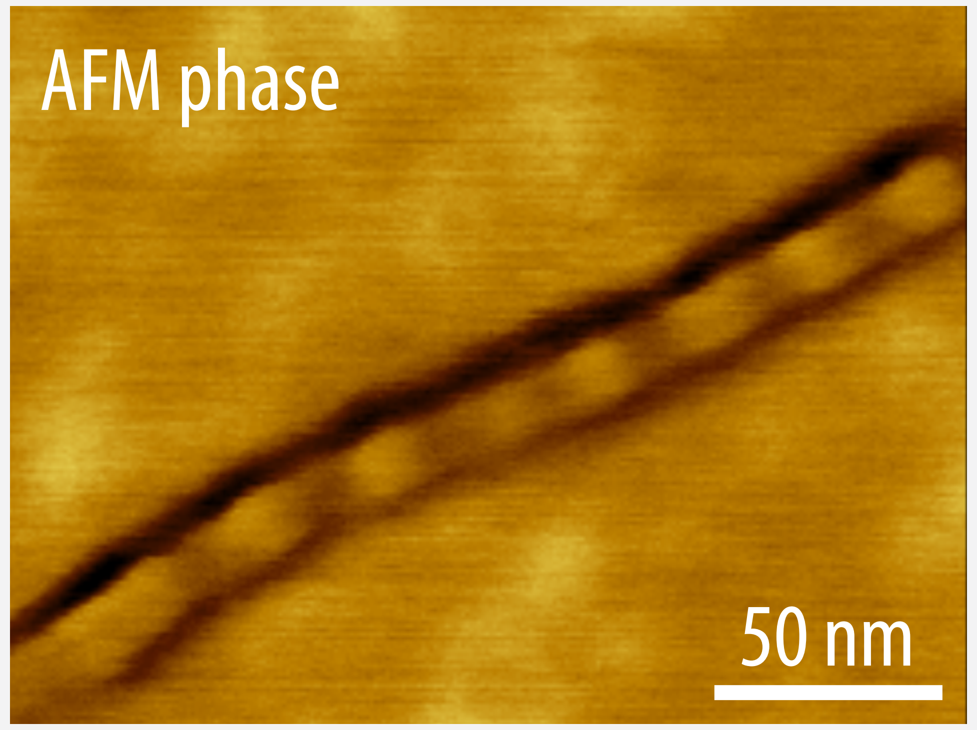
damping, acoustics, barriers,
packaging, recycling, degradation

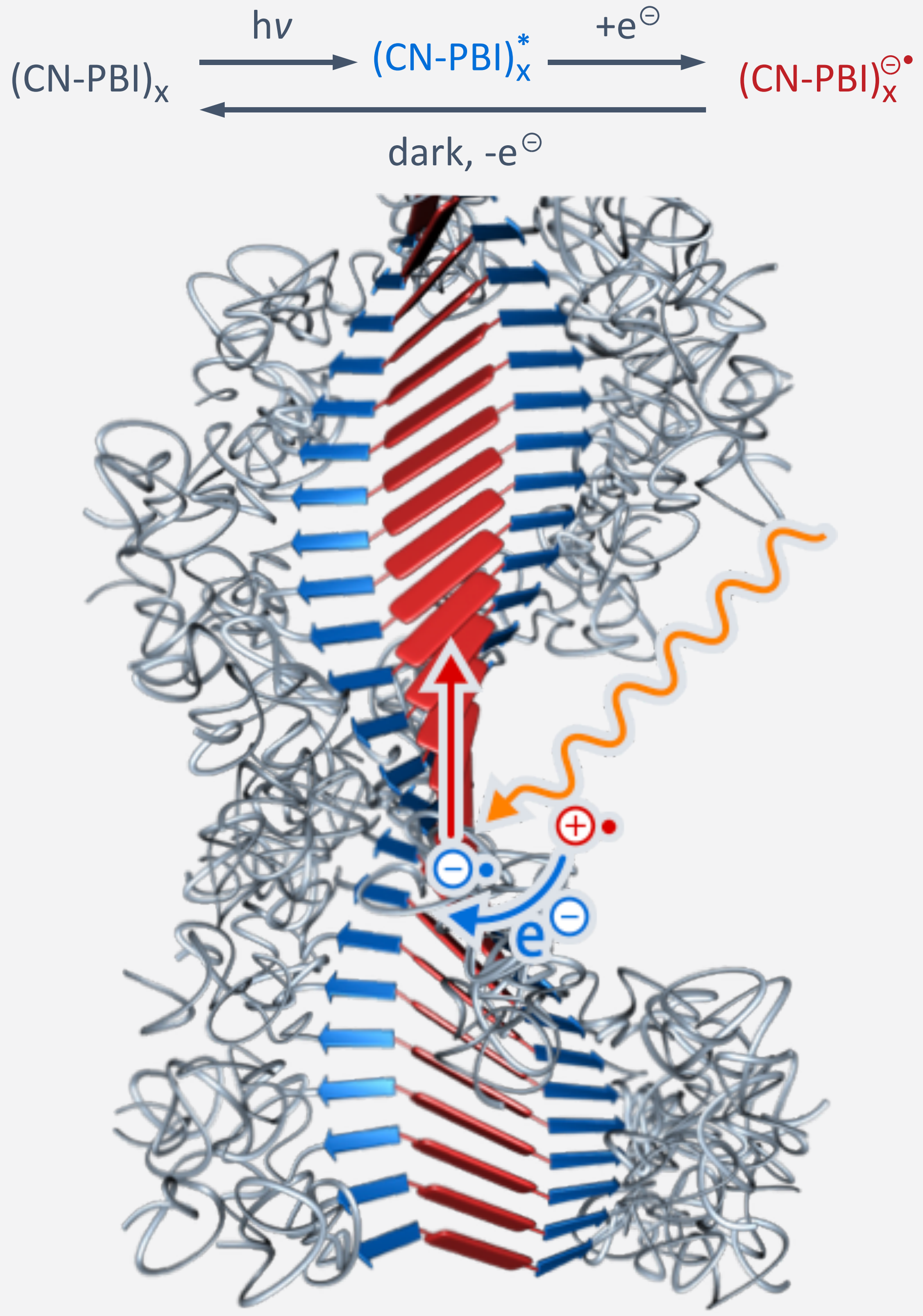
- **control of order/disorder balance across multiple length scales to tailor structure and function**

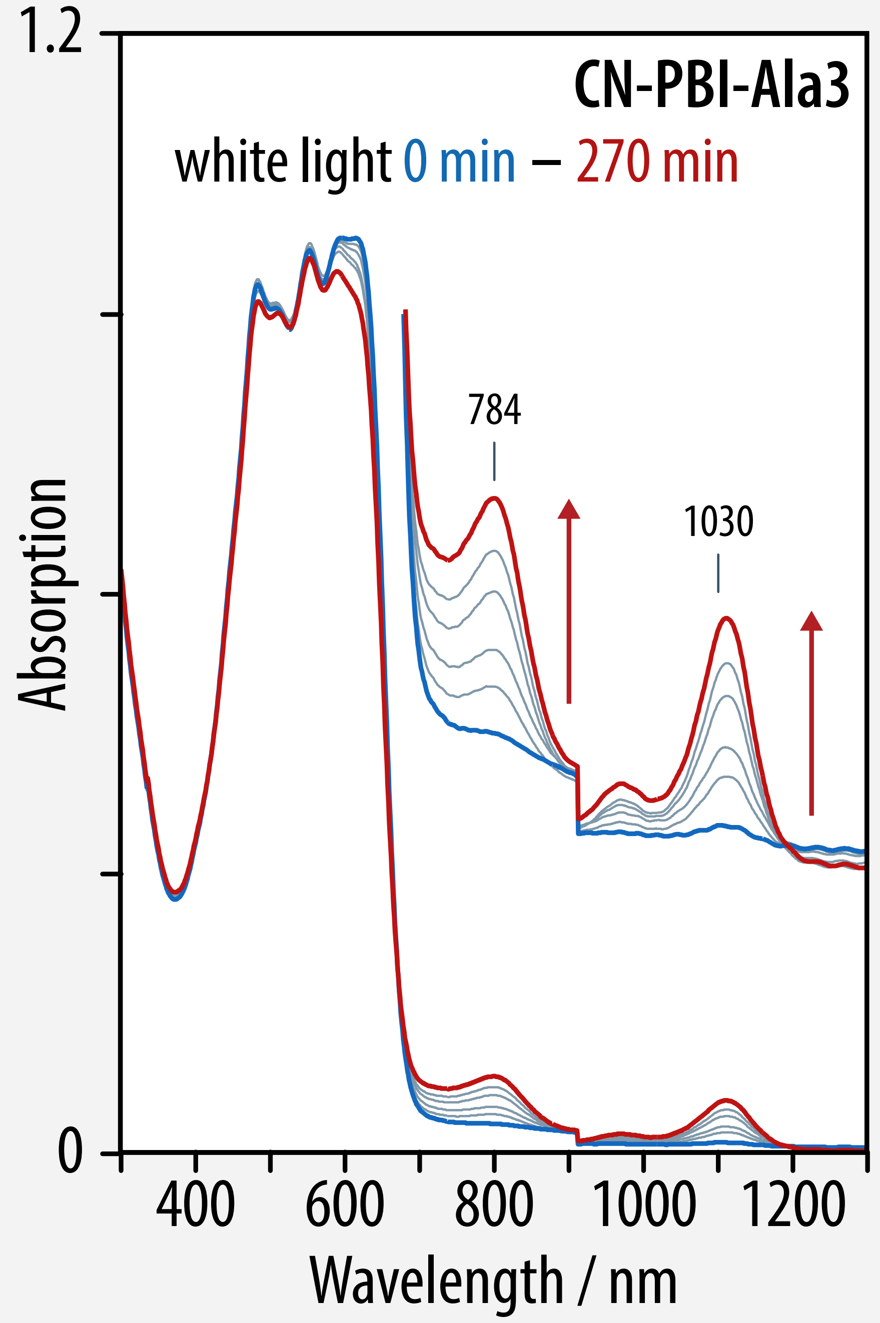
Organic Semiconductor Nanostructures





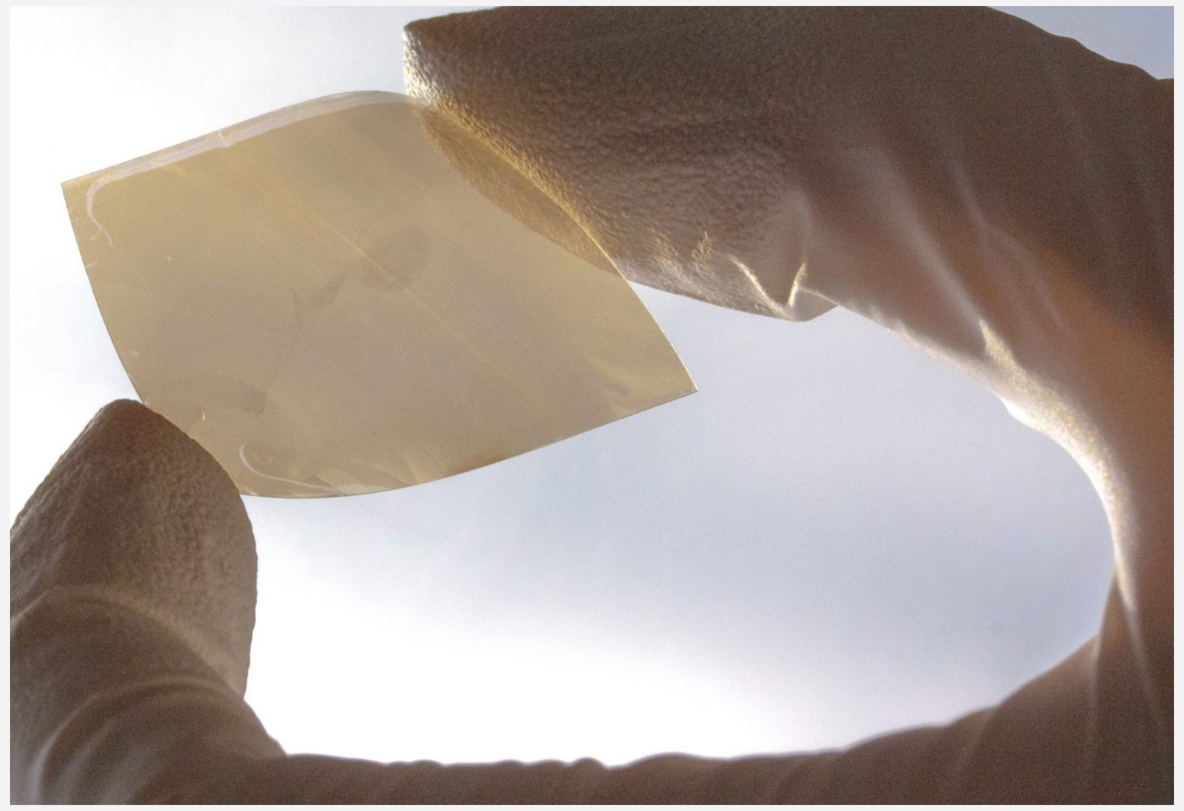




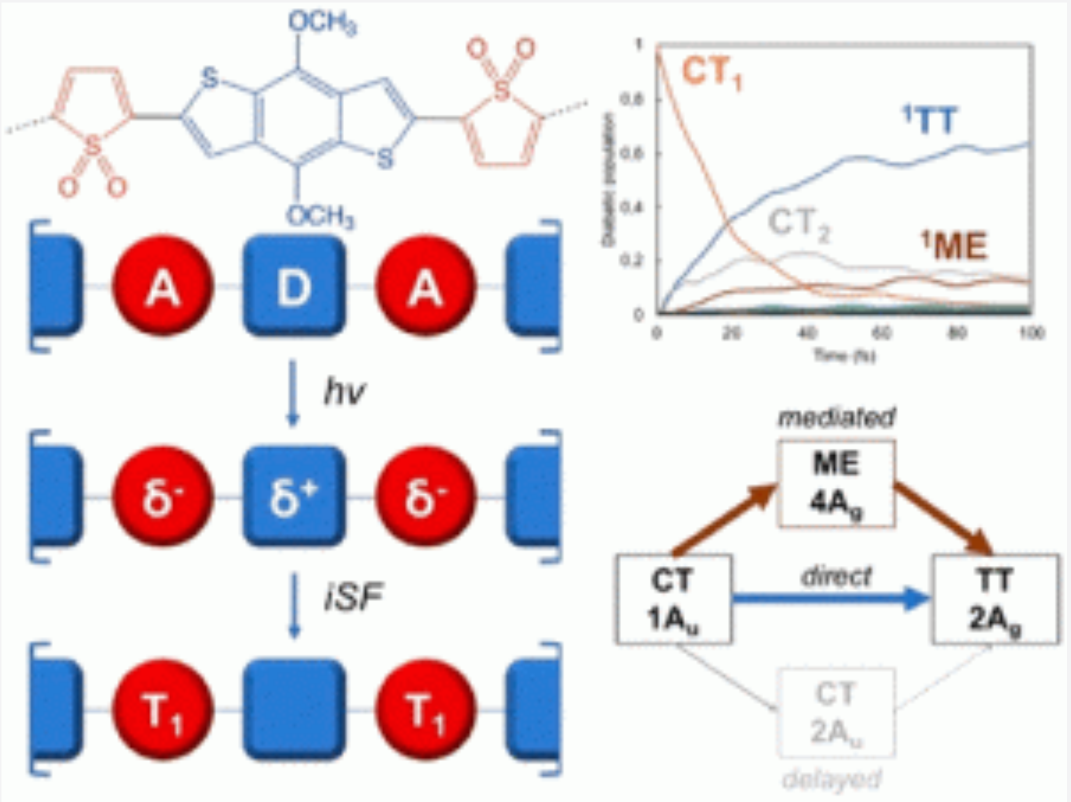


- **Efficient supramolecular approach to prepare single stack of π-conjugated molecules**
- **Photo-generation in aggregates of long-lived and air-stable radical ions in high densities**

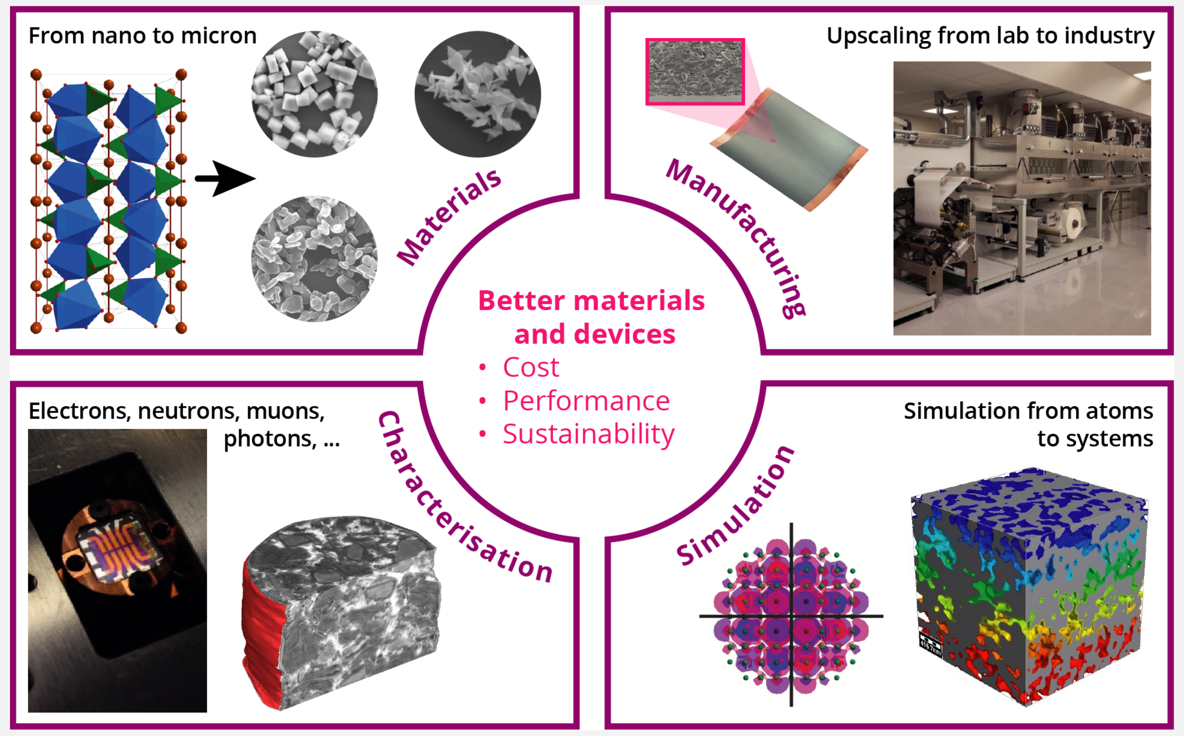
EPFL Laboratories with Research on Organic Electronics



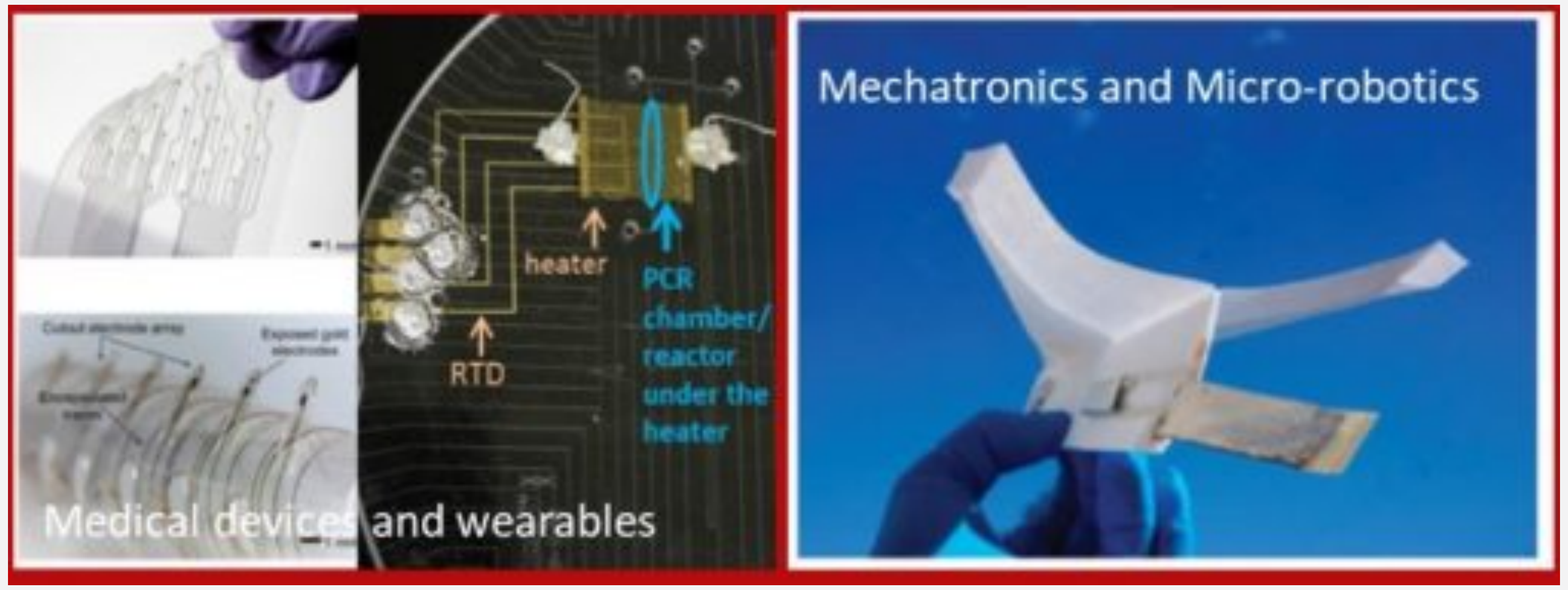
Kevin Sivula (EPFL/LIMNO)
organic photovoltaics



Clémence Corminboeuf (EPFL/LCMD)
computational organic electronics



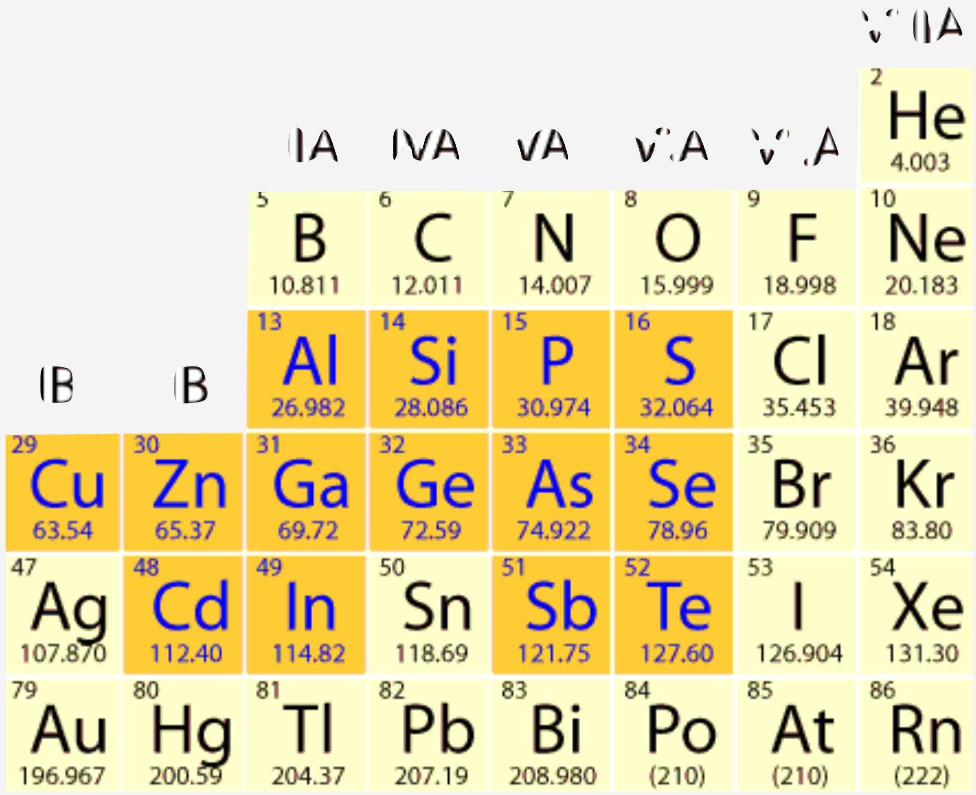
Vanessa Wood (ETHZ/MADE)
materials & device engineering

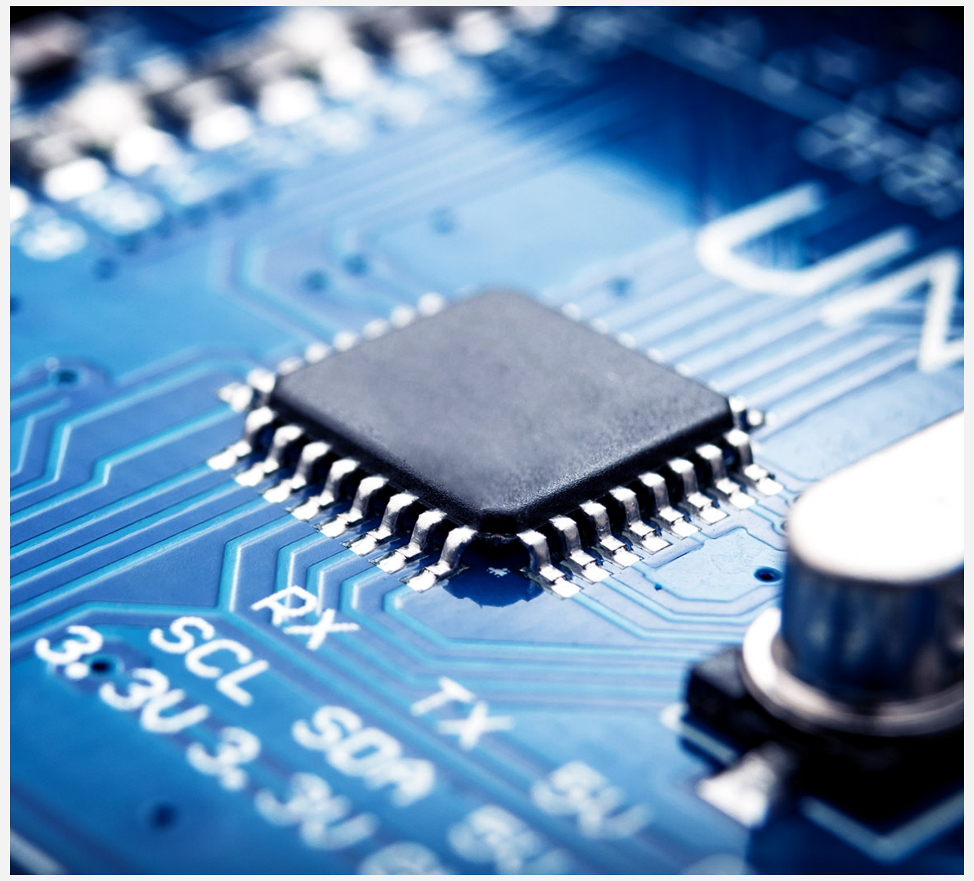


Vivek Subramanian (EPFL/LAFT)
wearables & medical devices

1.2 Challenges in Organic Electronics

Typical Inorganic Semiconductors

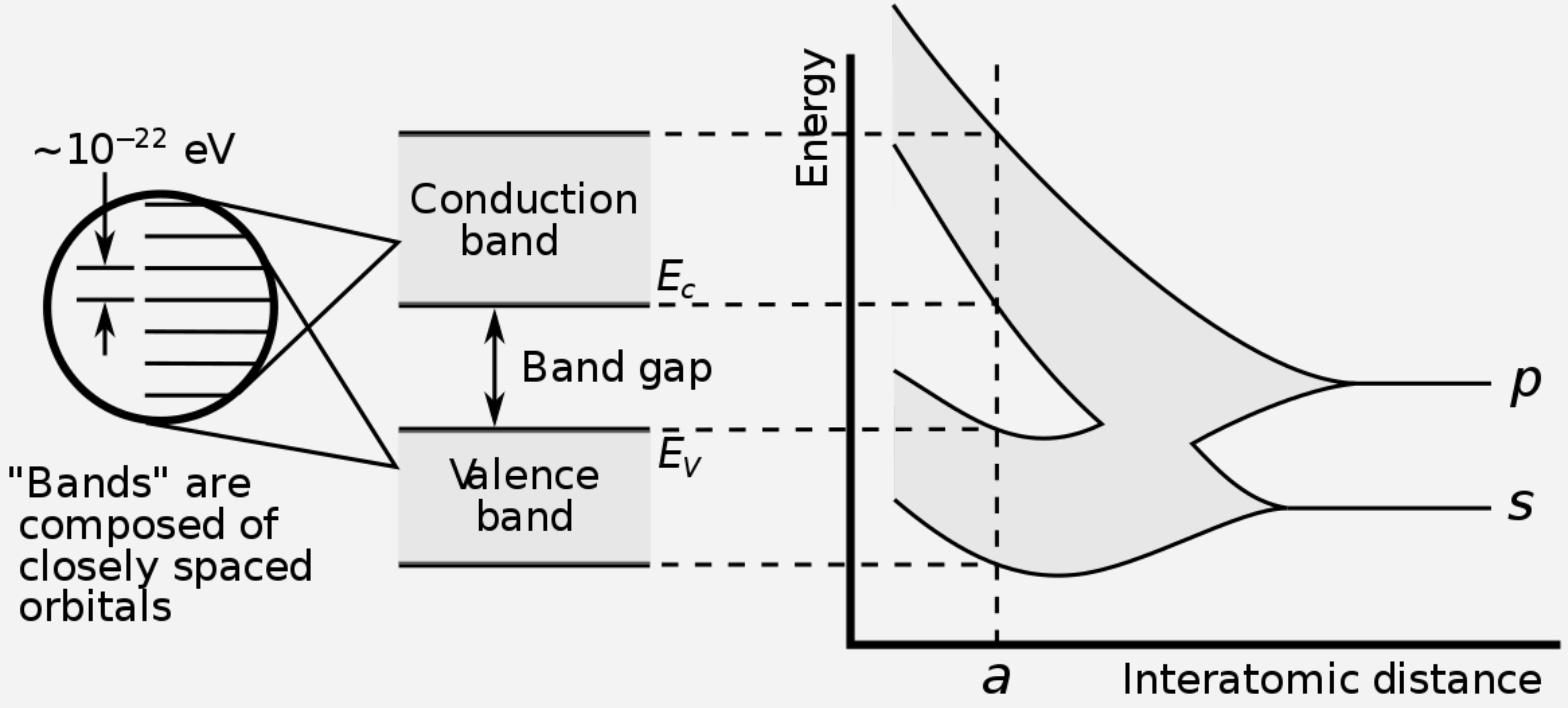




- elements or elemental compounds
- important examples are silicon (crystalline or amorphous), germanium, gallium arsenide.
- inorganic semiconductors are typically crystalline solids, sometimes glasses (amorphous)
- semiconductors have an electrical conductivity between a conductor and an insulator
- possibility to form junctions by having two differently doped regions.
- behavior of charge carriers (electrons, holes, ions) at junctions defines the functioning of diodes, transistors, and all other components of modern electronic devices

Band Formation in Inorganic Semiconductors

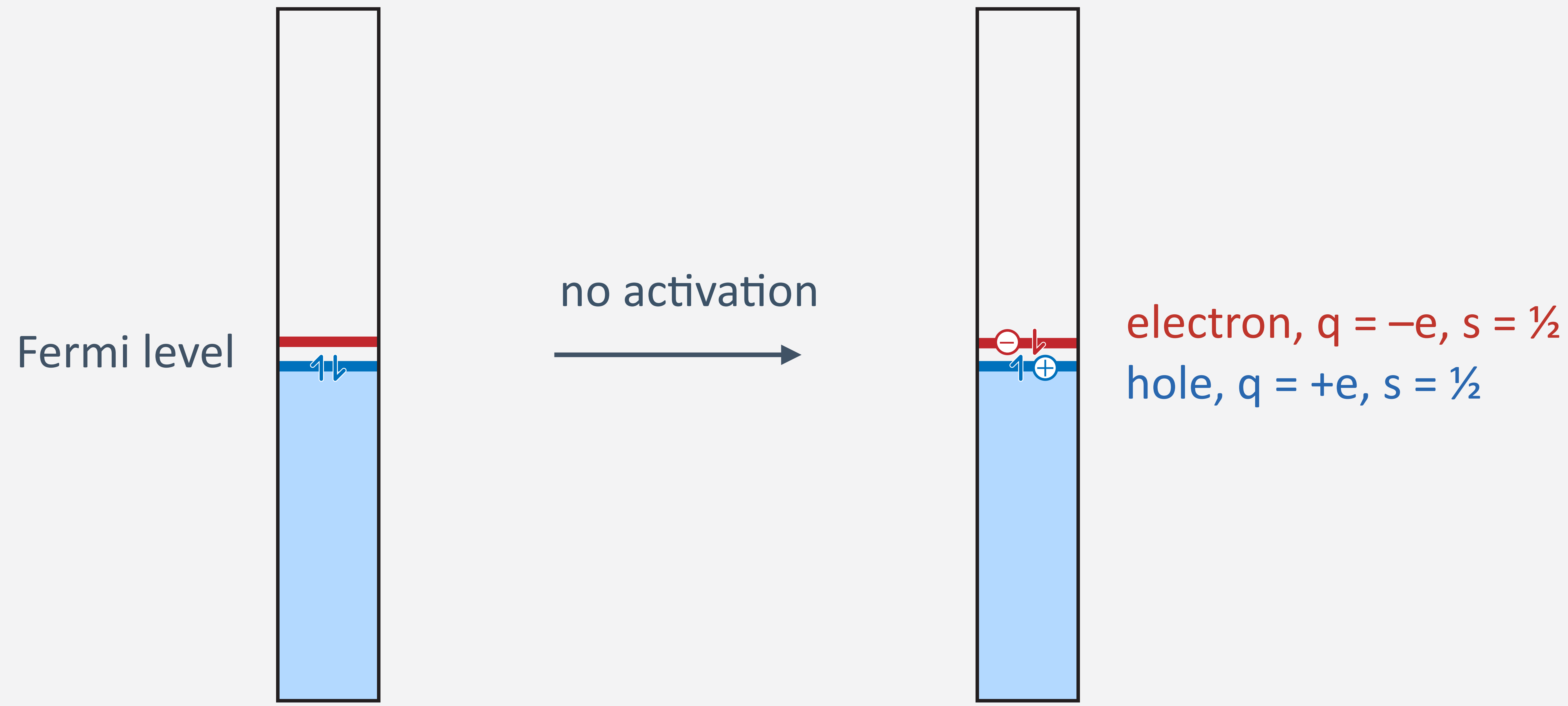
- bands form when atomic or molecular orbitals interact
- the more orbitals interact the more energy levels are created
- the resulting states are macroscopic in dimension and the difference between energy levels becomes so small that they are a continuous band and not discreet levels anymore



- **bands are described by solving the Bloch equation, that is, a variation of the Schrödinger equation for the boundary condition of a periodic lattice of atoms**

Charge Generation and Transport in Inorganic Metallic Conductors

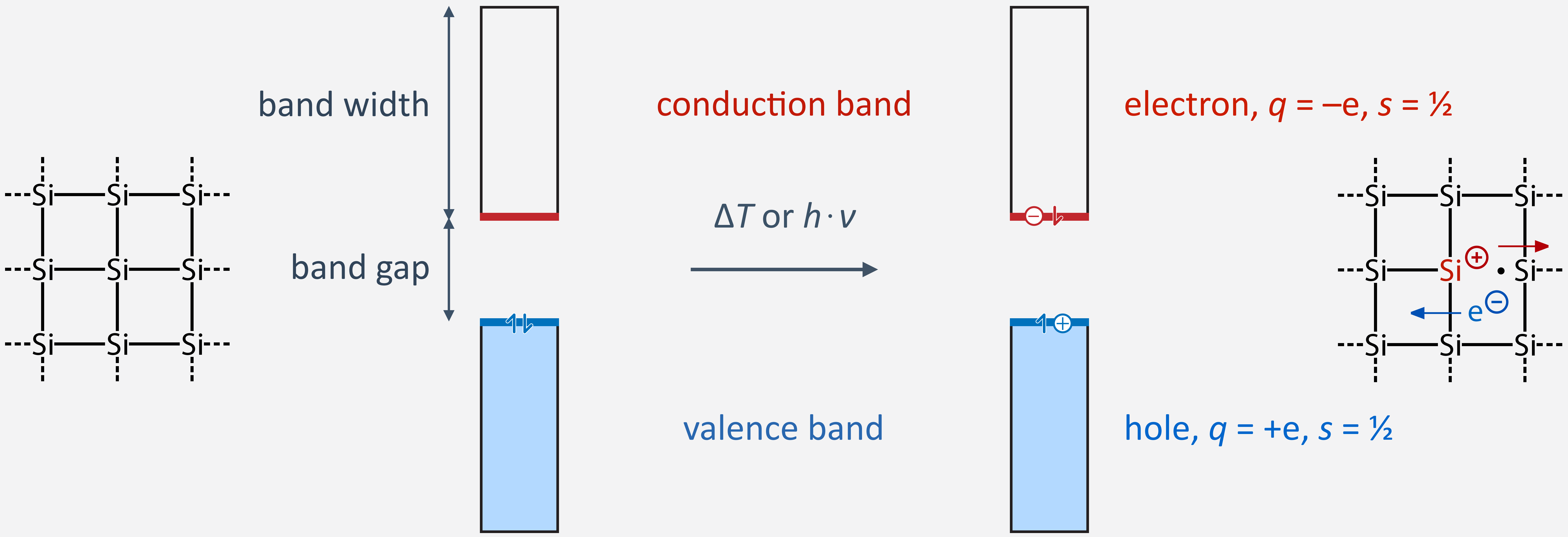
- band conductivity: charge transport in electric field at finite temperature without activation



- **partially filled (or overlapping) bands with infinitesimal difference between energy levels**
- **all energy levels macroscopically delocalized**
- **$k_B T$ = 0.025 eV (293 K); promotion of a large number of charge carriers at room temperature**

Intrinsic (Undoped) Inorganic Semiconductors

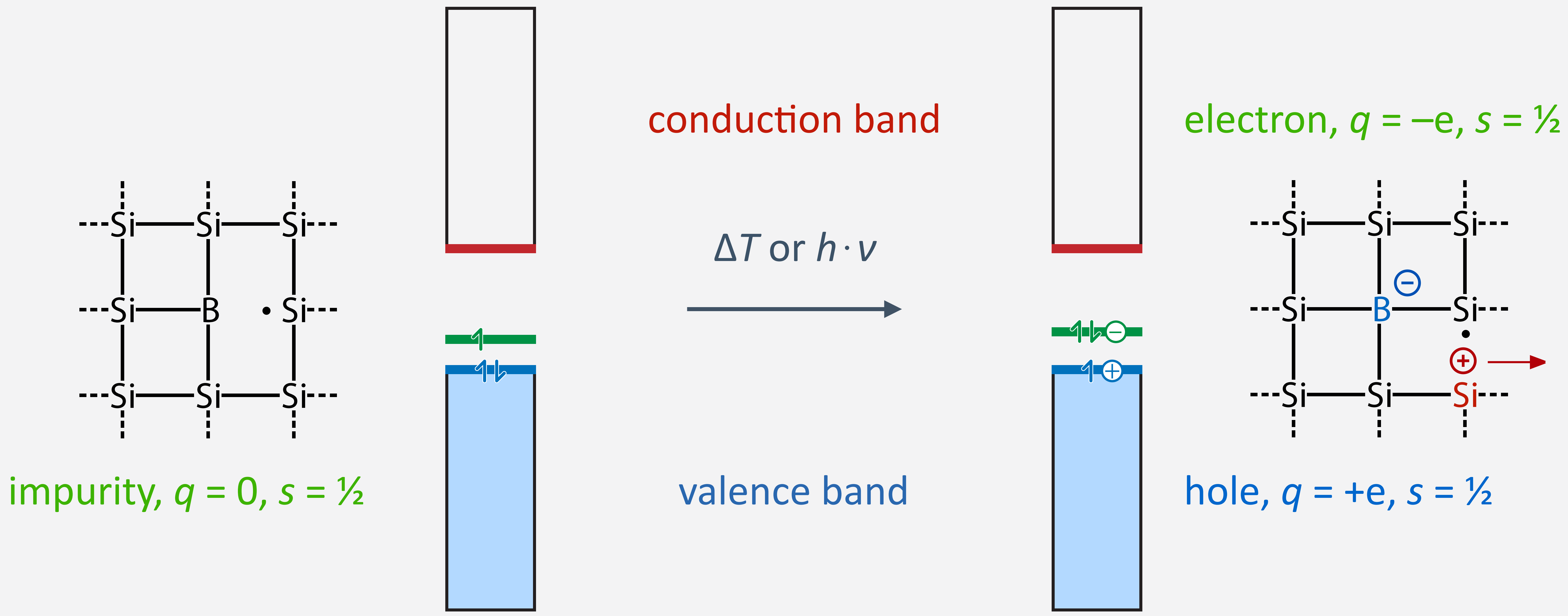
- band gap between valence and conduction band; no "spontaneous" charge separation
- charge separation by promotion (excitation) of electrons into conduction band



- **energy bands delocalized, hole & electron transport in electric field via band conductivity**
- **k_BT = 0.025 eV (293 K); no thermal promotion of charge carriers at room temperature**
- **energy of visible light 3.1 eV (400 nm), 1.6 eV (800 nm); photocurrent generation even in NIR**

Inorganic Semiconductors Doped with p-Type Impurities

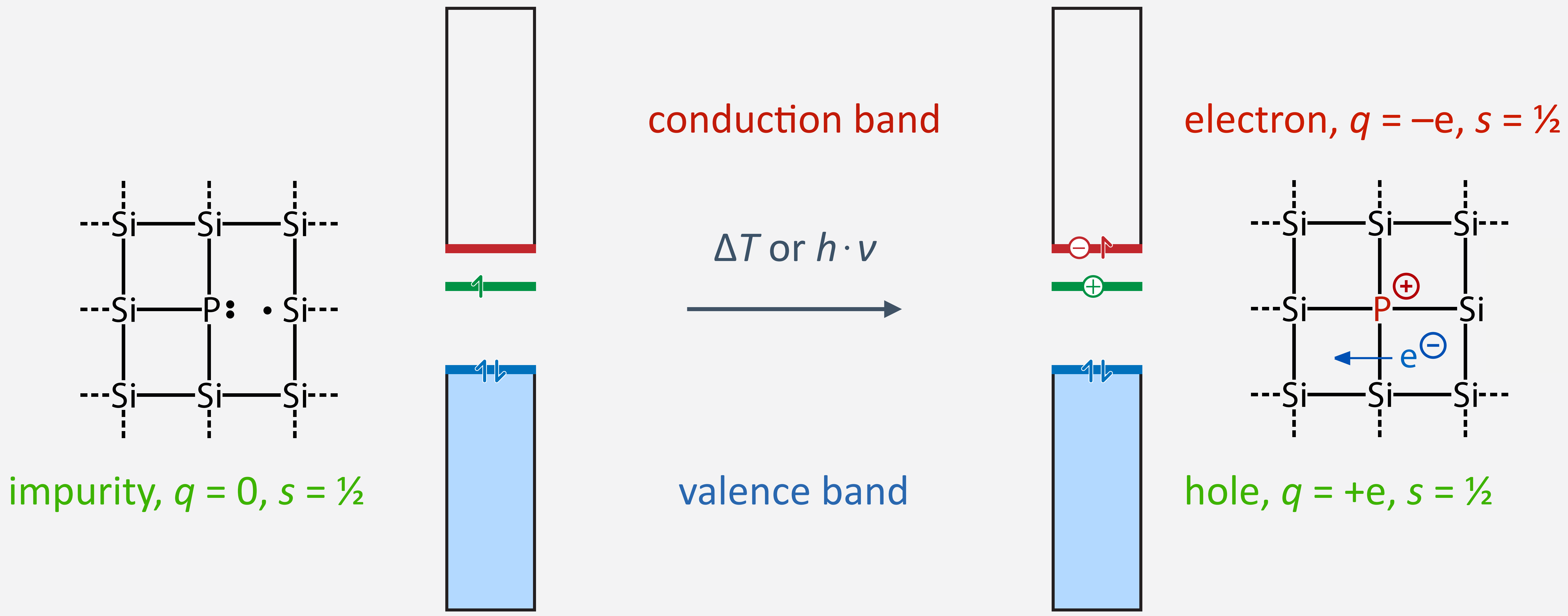
- doping with electron acceptor impurities (e.g., boron) creates extra hole energy levels
- p-type doped silicon is electrically neutral (missing electron compensated by nucleic charge)



- **p-type doped silicon shows mainly hole conductivity (positive charge transport)**
- **band width is related to for charge carrier mobility, hence high hole transport mobility**
- **single energy level of anionic counter charge is located, not mobile**

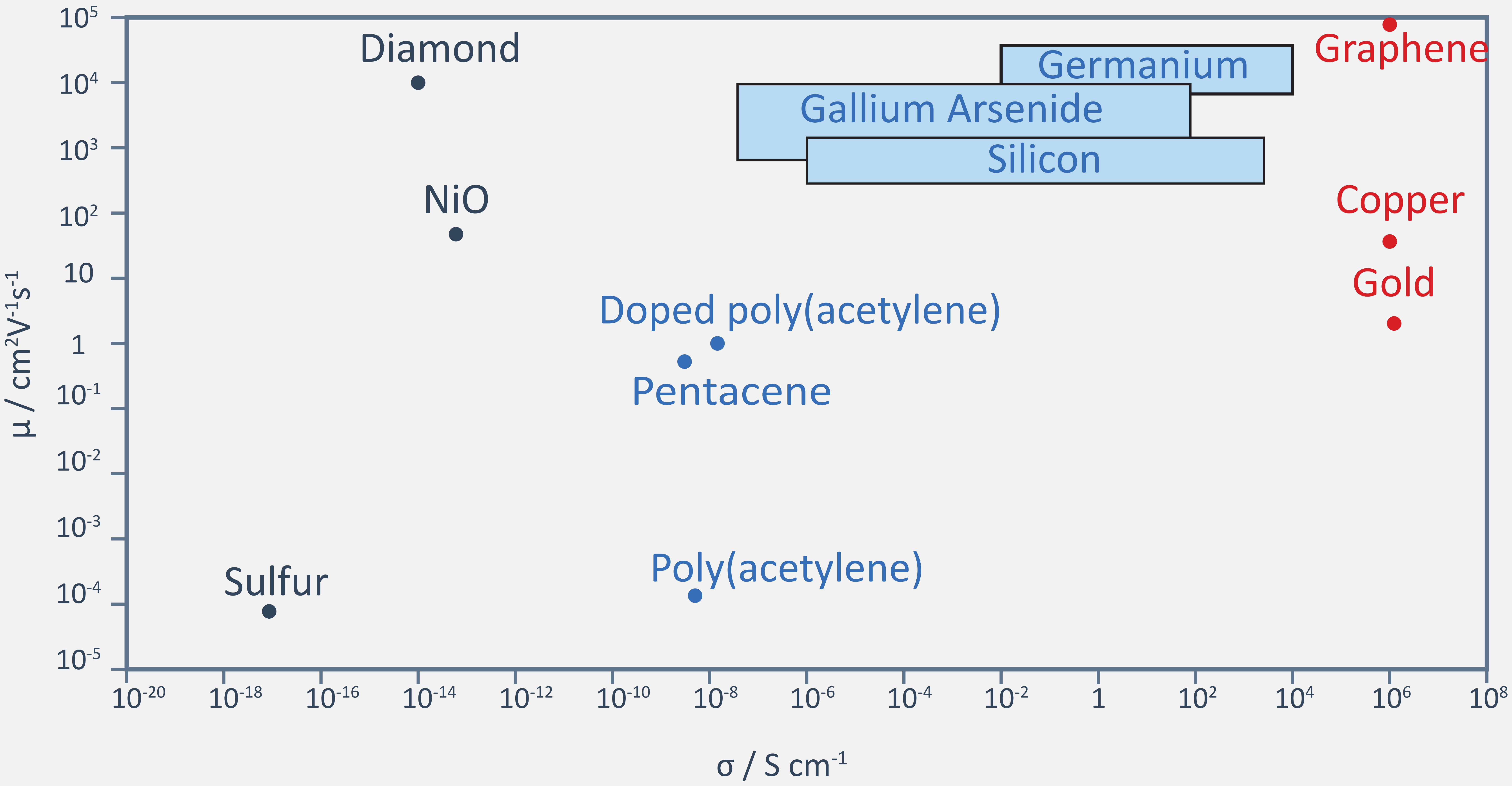
Inorganic Semiconductors Doped with n-Type Impurities

- doping with electron donor impurities (e.g., phosphorus) creates extra electron energy levels
- n-type doped silicon is electrically neutral (excess electron compensated by nucleic charge)



- **n-type doped silicon shows mainly electron conductivity (negative charge transport)**
- **band width is related to charge carrier mobility, hence high electron transport mobility**
- **single energy level of cationic counter charge is located, not mobile**

Electron Mobility versus Electric Conductivity



- **mobility μ does not have a systematic relation to materials classes**
- **conductivity $\sigma = \mu \cdot n \cdot e$ of insulators < semiconductors < metals, due to charge density *n***

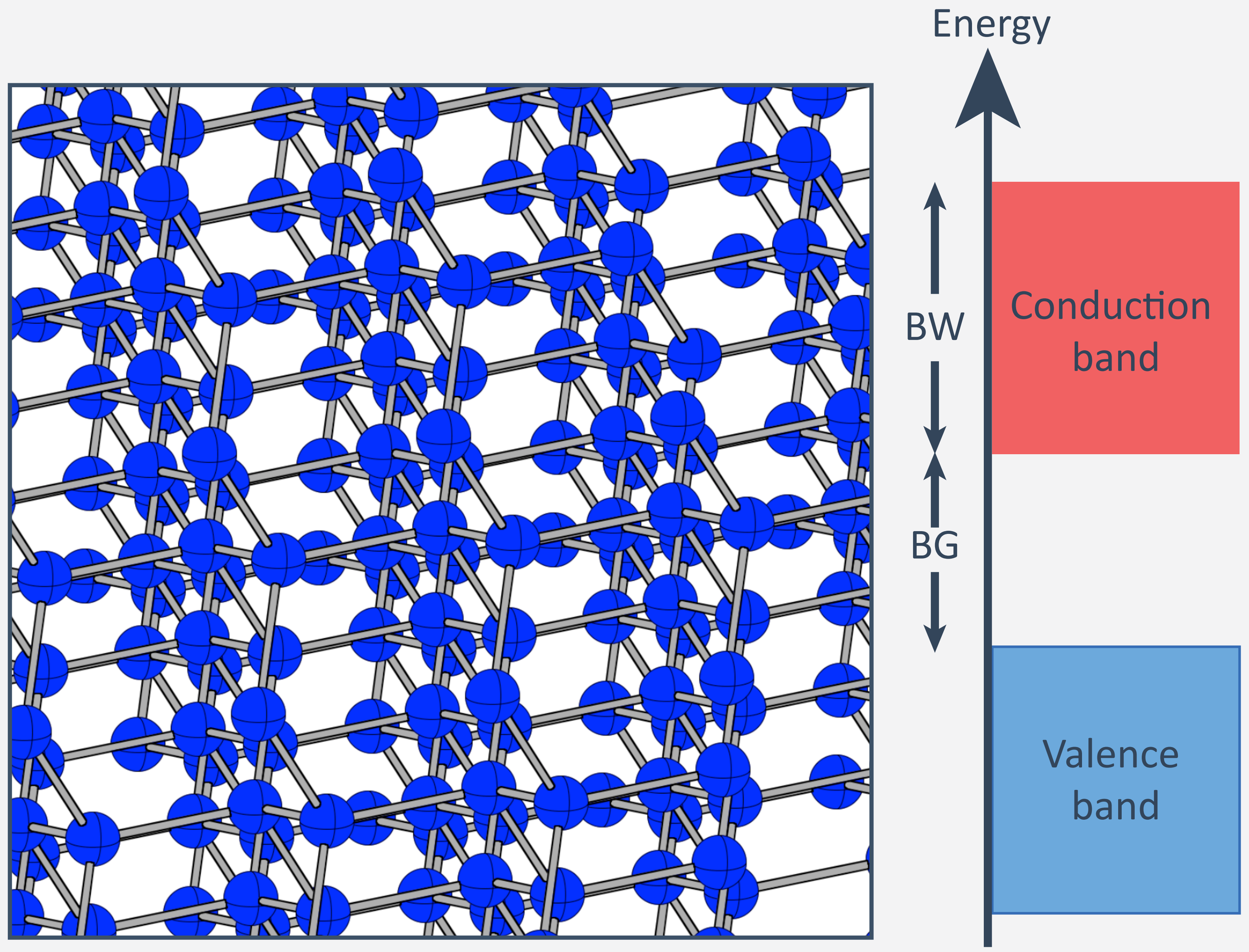
Typical Organic Materials

- **organic compounds are based on covalently bound molecules comprising C and H**
- **they form amorphous (glassy) or crystalline soft materials in the solid state**
- **molecules are “bonded” by weak (Van der Waals and dipolar) intermolecular interactions**

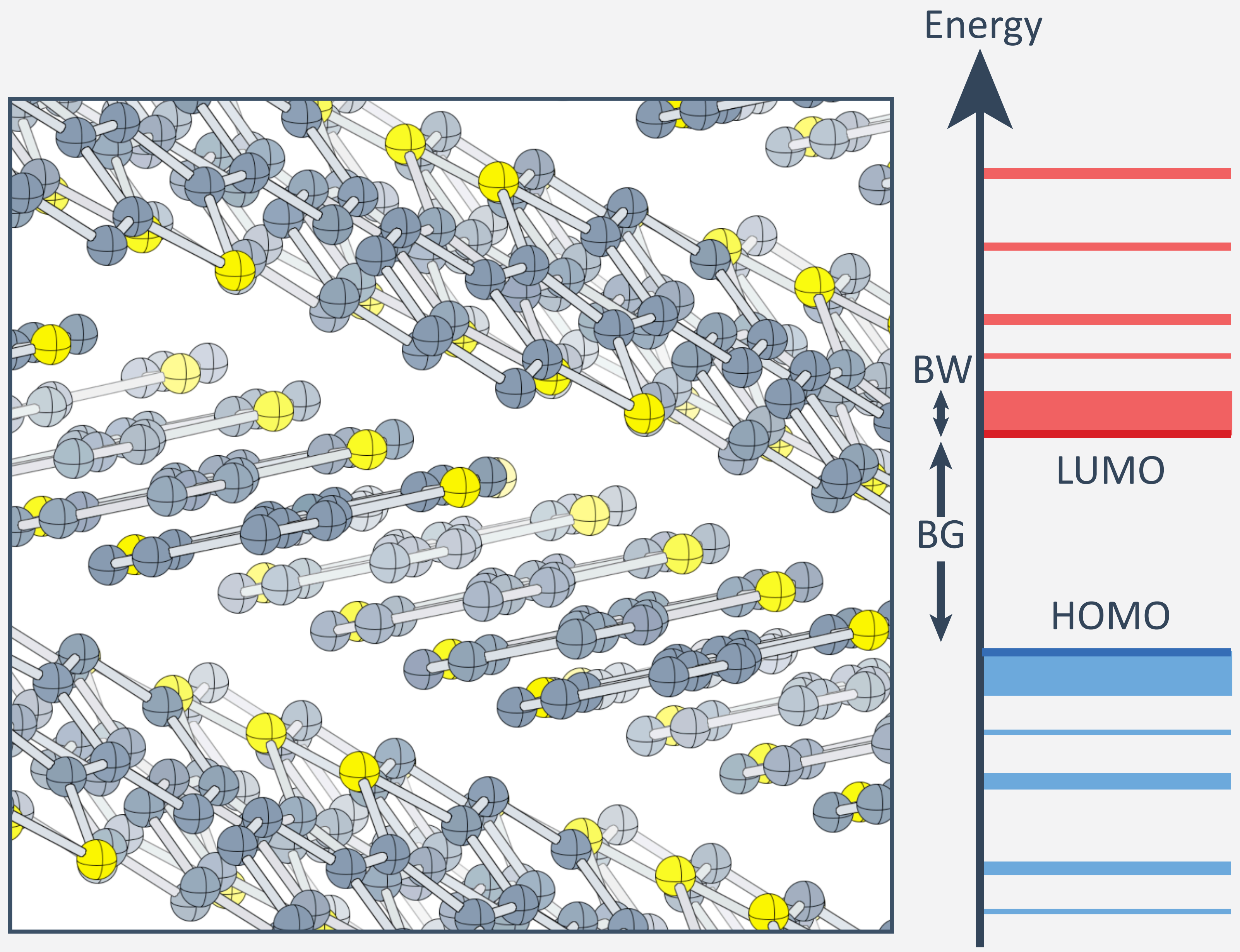
- **one must distinguish (at least) two structure levels:**
  - strong bonding and electronic coupling of atoms within molecules
  - weak intermolecular bonding and electronic coupling
  - low molecular symmetry (compared to atoms) imparts low symmetry crystal unit cells
  - bulk properties hence strongly impacted by packing details as well as static / dynamic disorder

Organic versus Inorganic Semiconductors

Inorganic Semiconductors



Organic Semiconductors



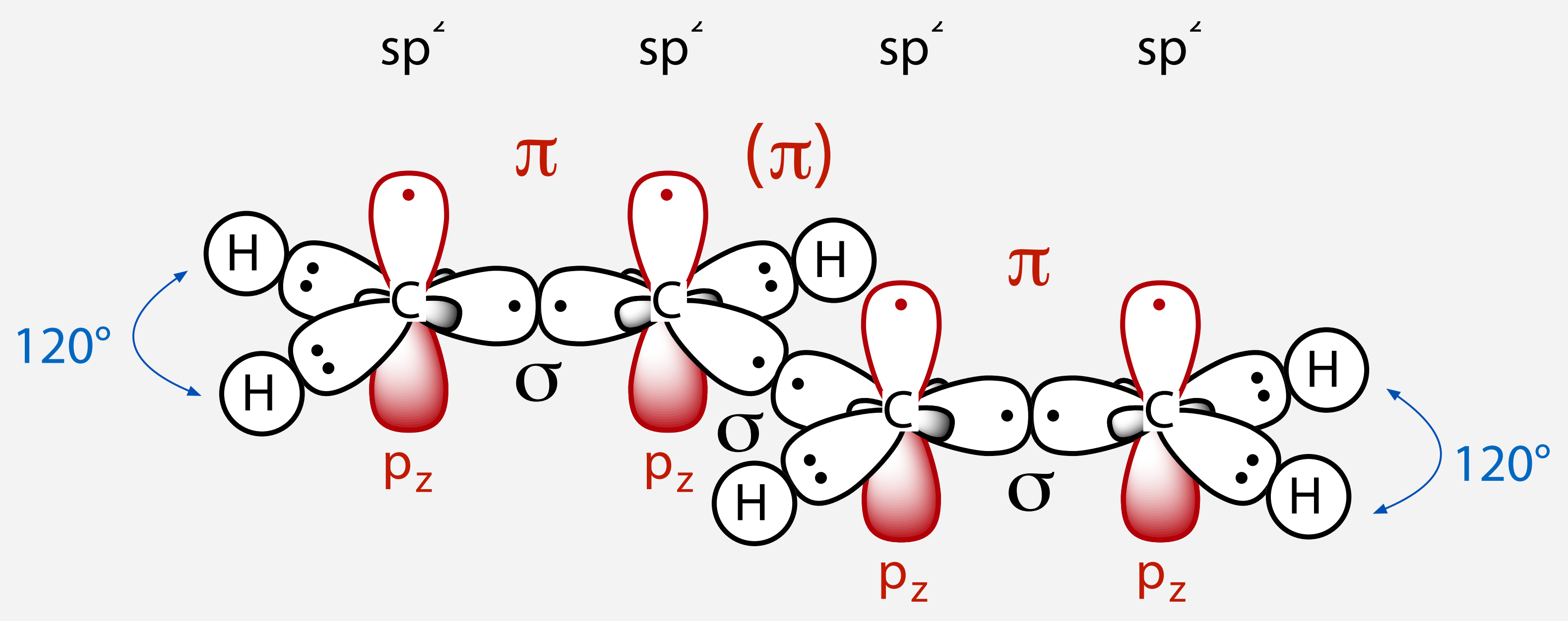
property	inorganic semiconductors	organic semiconductors
bond type	covalent/ionic	van der Waals
intermolecular bond energy	1–5 eV	0.1 eV
energy band width	1–4 eV	0.01–0.5 eV
charge transport	band transport	mostly incoherent transport
charge mobility	10^2–10^4 cm^2/V s	mostly <1 cm^2/V s
dielectric constant	10–15	2–3
exciton (radius) & binding energy	Wannier (100 Å), 5–10 meV	Frenkel (10 Å), 500–1000 meV

How to Design Organic Conductors and Semiconductors

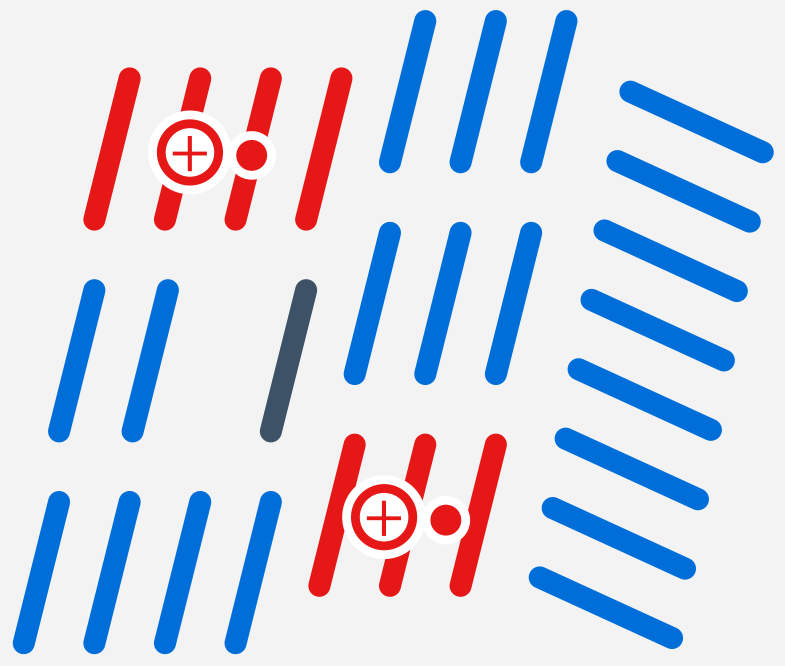
- **requirements for conducting and semiconducting materials**
  - (semi)conductors require macroscopically delocalized electron states
  - (semi)conductors require no or small bandgap
  - (semi)conductors require generation of stable charge carriers

- **challenge: organic solids are amorphous or crystalline molecular materials**
  - molecules formed from localized covalent bonds between atoms
  - molecular materials from discrete molecules by weak Van der Waals forces
  - weak intermolecular electronic coupling
  - most organic molecules have large HOMO-LUMO gaps
  - generation of charged molecules difficult and typically results in reactive species
  - charged species confined on single molecules, cannot be easily transported
  - charge transport impacted by polymorphism defects

Course Overview

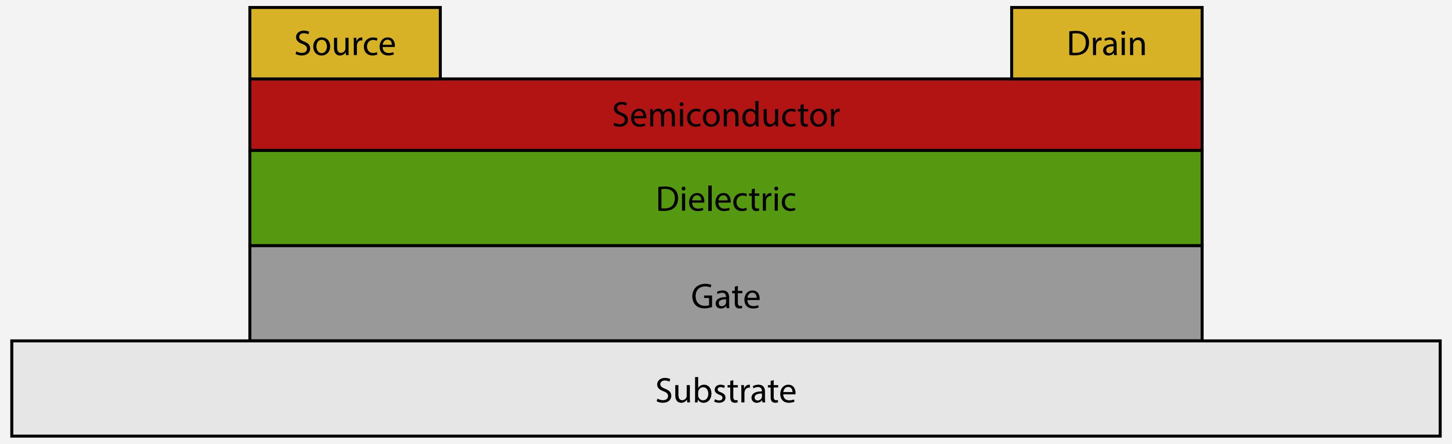


electron delocalization in organic molecules and materials



charge carriers in organic molecules and transport in organic materials

synthesis of molecular precursors and materials processing



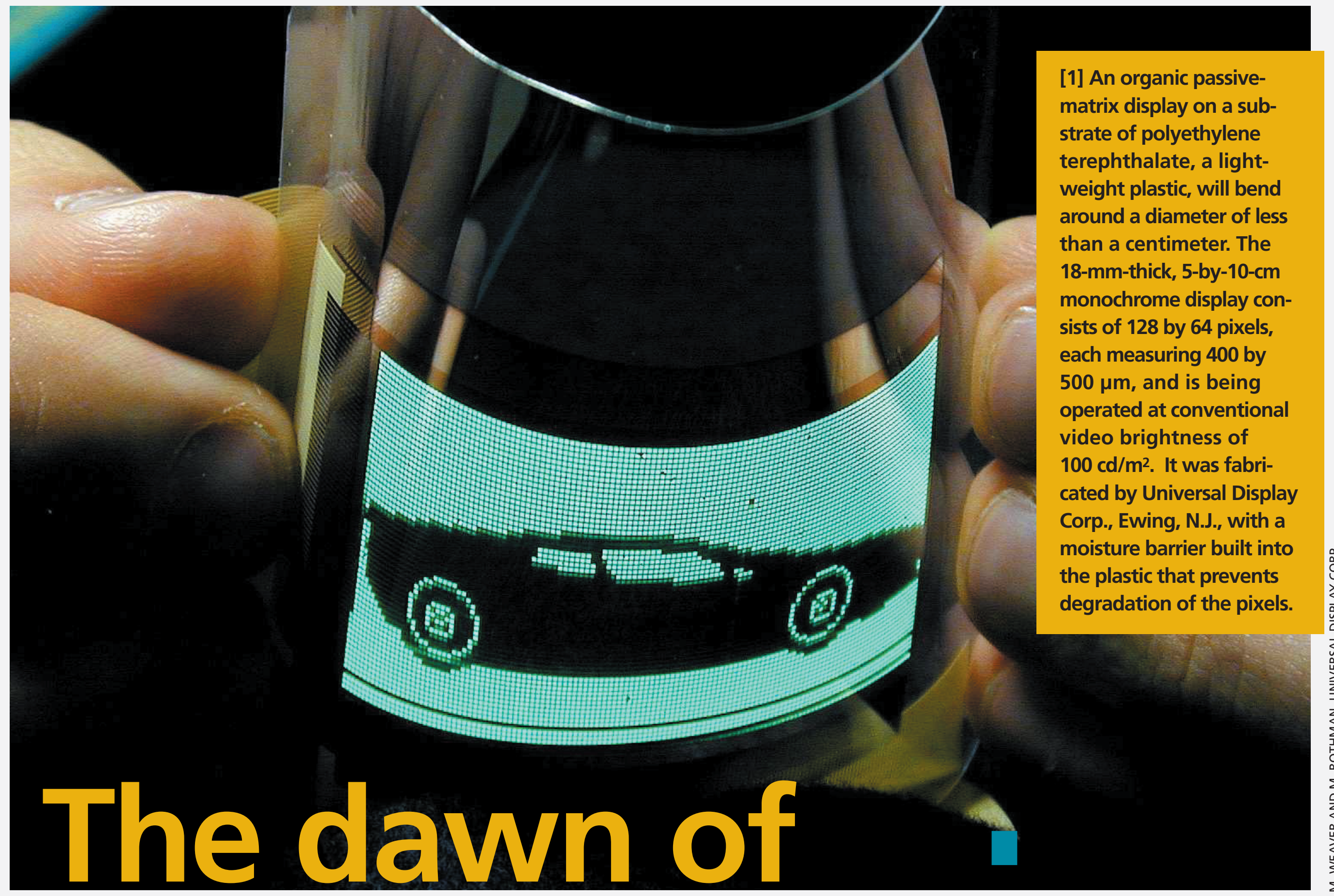
structure and function of organic electronic devices

Learning Objectives of this Class

- **π-conjugated systems give rise to intramolecular electron delocalization**
  - extended π-conjugated systems have comparably small bandgap
  - π-conjugated systems are highly polarizable
- **supramolecular organization of π-conjugated systems in the solid state**
  - π-interactions result in (limited) intermolecular delocalization
  - band-like states in single-crystalline systems
- **charge generation and transport in organic solids**
  - extended π-conjugated systems can sustain charge carriers
  - typical charge carriers are self-localized radical ions (polarons)
  - vibronic coupling due to molecular nature of the materials
  - charge transport mostly involves hopping of discrete charge carriers
- **synthesis of precursors, processing into materials, fabrication of devices**

Homework & Reading Assignments

solid state



[1] An organic passive-matrix display on a substrate of polyethylene terephthalate, a lightweight plastic, will bend around a diameter of less than a centimeter. The 18-mm-thick, 5-by-10-cm monochrome display consists of 128 by 64 pixels, each measuring 400 by 500 μm, and is being operated at conventional video brightness of 100 cd/m². It was fabricated by Universal Display Corp., Ewing, N.J., with a moisture barrier built into the plastic that prevents degradation of the pixels.

M. WEAVER AND M. ROTHMAN, UNIVERSAL DISPLAY CORP.

The dawn of organic electronics

ORGANIC SEMICONDUCTORS ARE STRONG CANDIDATES FOR CREATING FLEXIBLE, FULL-COLOR DISPLAYS AND CIRCUITS ON PLASTIC

STEPHEN FORREST
Princeton University

PAUL BURROWS
Pacific Northwest National Laboratories
&
MARK THOMPSON
University of Southern California

ORGANIC MATERIALS ARE POISED AS NEVER BEFORE TO TRANSFORM the world of circuit and display technology. Major electronics firms such as Philips and Pioneer, and smaller companies such as Cambridge Display Technology, Universal Display, and Uniax, are betting that the future holds tremendous opportunity for the low cost and sometimes surprisingly high performance offered by organic electronic and optoelectronic devices. Using organic light-emitting devices (OLEDs), organic full-color displays may eventually replace liquid-crystal displays (LCDs) for use with laptop and even desktop computers. Such displays can be deposited on flexible plastic foils [Fig. 1], eliminating the fragile and heavy glass substrates used in LCDs, and can emit bright light without the pronounced directionality inherent in LCD viewing, all with efficiencies higher than can be obtained with incandescent light bulbs.

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Progress and Challenges in Commercialization of Organic Electronics

Yueh-Lin Loo and Iain McCulloch, Guest Editors

Abstract

The field of organic electronics is entering its commercial phase. The recent market introduction of the first prototypes based on organic transistors fabricated from solution is set to augment the existing market presence of organic light-emitting diode applications. Organic photovoltaic products are not far behind. In this article, we provide a brief overview of these devices, with our main focus being organic transistor applications. In particular, we examine some of the key performance requirements for working devices. We also review some of the important advances in semiconductor design and device fabrication techniques and discuss some of the technical challenges that remain in the optimization of next-generation products.

Introduction

The basis of organic electronics is predicated on the ability of a class of functional organic molecules known as organic semiconductors to actively transport charge, emit light, or absorb light under appropriate conditions. Devices comprising these organic semiconducting materials include transistors, light-emitting diodes, and photovoltaic cells, all of which are reviewed in detail in this issue. From the fabrication perspective, materials can be broadly classified as processable either by evaporation or by solution. Whereas polymeric semiconductors are clearly in the solution-processable category, discrete small-molecule organic semiconductors can be functionalized to fall into either group. Historically, evaporative processing has led the development of most devices and is therefore more advanced. However, the potential to print at high throughput and high resolution from formulated inks offers the greatest commercial opportunity, driving solution-processable material development. Interest is especially intense in the transistor and solar cell fields, where low cost is a strong market driver.

A prerequisite for the molecular composition of both categories of semiconductor is that they contain a conjugated π-electron system, where the delocalized molecular orbitals are energetically accessible and typically less than 3.5 eV apart. Organic transistors require that the organic semiconductor have a highly organized microstructure, with the molecular orbital systems closely packed together. Currently, most organic transistor's exhibit *p*-characteristics, that is, they transport holes rather than electrons. Work remains to develop robust trap free interfaces in organic transistors so the transport of electrons is also possible.

The active layer in a solar cell comprises a light-absorbing semiconductor, which typically is also the hole-transport material. This component is typically blended with organic semiconductors that exhibit *n*-characteristics. Challenges remain in optimizing transport within the layer, absorbing more photons, and separating charge at the semiconductor interfaces.

Organic light-emitting diode (OLED) devices, particularly small-molecule evaporated devices, are becoming increasingly complex, requiring a range of injection, transport, blocking, and emissive materials. Both fluorescent and phosphorescent electroluminescent semiconductors can be used. Although phosphorescent dopants exhibit excellent efficiencies in both red and green, due in part to their ability to harvest both singlet and triplet excitons, deep blue emission remains a problem. Current displays typically still use fluorescent blue emitters as a result. New doped systems are reducing interfacial energy barriers, leading to lower voltage operation, and there are continual enhancements in device lifetime and efficiency of polymer emitters, as well as improvements in solution printing methods.

Commercial Status of Organic Electronics

Organic light-emitting diode technology is perhaps the most advanced organic device platform. Sony currently markets an 11-in. television based on OLED technology that boasts a 3-mm-thick panel and 178° viewing angle. In the display arena, OLED technology promises to compete with liquid-crystal and plasma technologies and offers unique attributes, such as ultrabrilliant colors and low power consumption in addition to the features mentioned previously. Individual OLED devices, in their simplest form, consist of organic active layers, an emissive layer and transport layers, sandwiched between two electrodes, a cathode and an anode. When a voltage is applied across the electrodes, the cathode injects electrons into the emissive layer, whereas the anode withdraws electrons, generating holes in the whole transport layer. These electrons and holes drift to the interface between the emissive and transport layers under the applied cell potential; it is the recombination of electron–hole pairs that generates radiative emission. In organic semiconductors, holes are more mobile than electrons. Recombination thus frequently happens within the emissive layer.

Although OLED technology has clearly shifted from the research and development phase to the scale-up phase, where primary concerns now deal with processing yields, fundamental science concerning the stability of the active layer when exposed to high current densities over extended periods still remains to be resolved. OLED devices can be fabricated from either polymer or small-molecule materials. Recent scientific