Organic Materials for Energy and Optoelectronics

Overview of Organic Semiconductors

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Outline

- Introduction: real world examples
- What is π-conjugated system
- Examples and Applications
- Structure, Functional properties, Challenges
- Research at Skoltech
- Resources: references, links, further reading

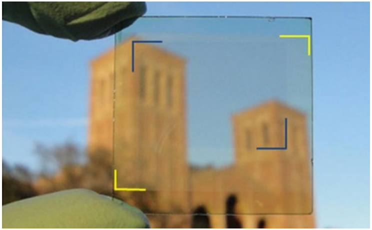
Real world examples: OLEDs

Commercially most successful application of organic semiconductors, $30 billion in 2019

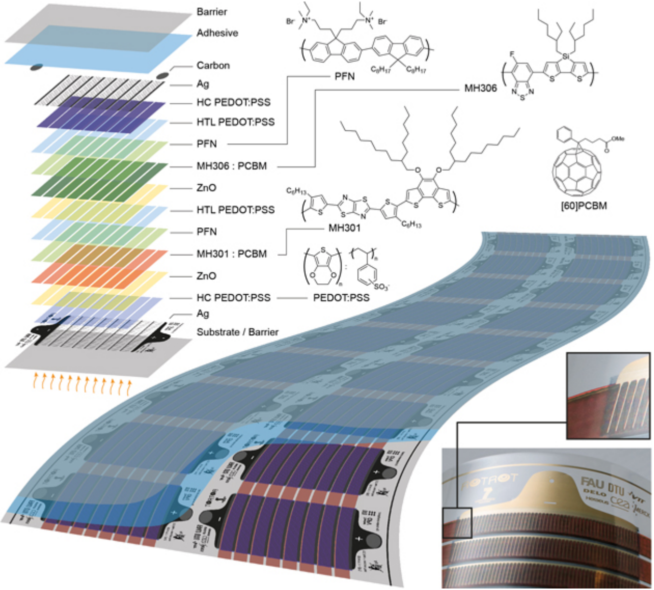
Real world examples: Solar cells

Largest PCE progress: from 4 to 18% compared to 13-26 for Si and 15-25 for perovskites

Preliminary sample design, to be modified

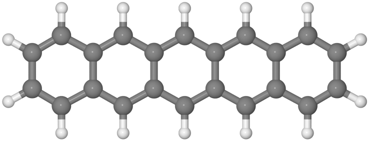


How is it made: Solar cells – R2R roll-to-roll processing

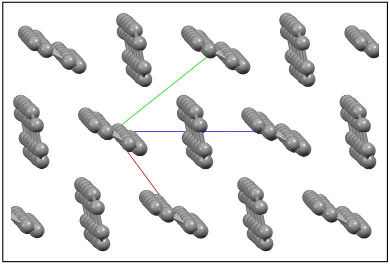


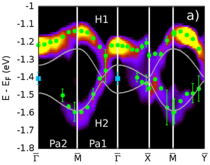
Historical example: A century-long story of pentacene

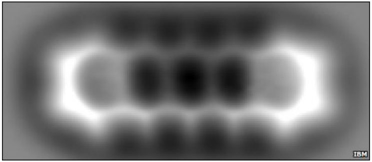
Charge carrier mobility $\sim 10 \, \frac{\text{cm}^2}{\text{V·s}}$
($>$ a-Si, 1/100 of c-Si)



- Synthesized in 1920s
- Crystal resolved in 1960s
- Used in OFET since 1980s
- Good-quality crystals in 2000s
- Bands resolved in ∼2010
- Atoms resolved in 2009
- Solution-processable TIPS-P 2007

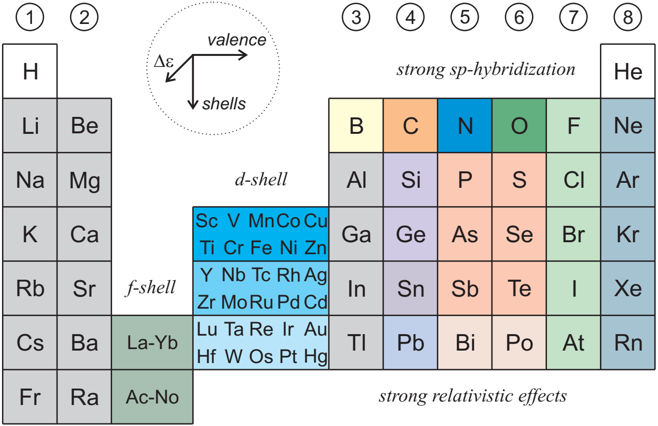






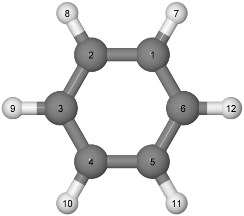
What is organic semiconductor

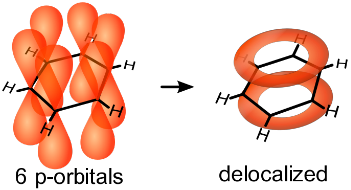
1. **Organic** – built from C with terminal H, possibly with isovalent substitutions (N for CH, O/S for CH_2, F/Cl for H)
2. π-**conjugated** – π-electrons on frontier orbitals (next slide)



Number of organic semiconductors is comparable to number of inorganic ones

What is π-conjugated system: example of benzene



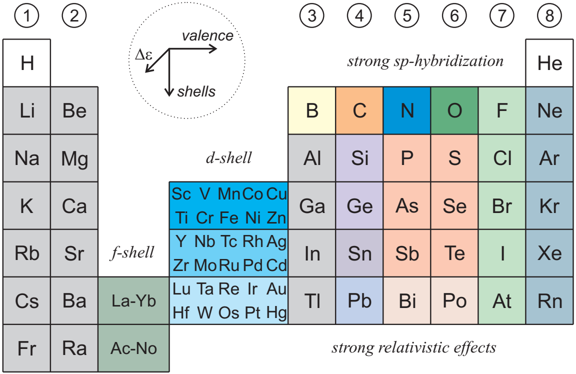


- each carbon has 3 sp^2 AOs connected by σ-bonds and 1 $pp\pi$-connected AO
- energy of bonding MO is $-t$ per electron
- $t_{sp2} = 3.26\frac{\hbar^2}{md^2} \gg t_{pp\pi} = 0.63\frac{\hbar^2}{md^2}$ [Harrison]

$$\Longrightarrow$$

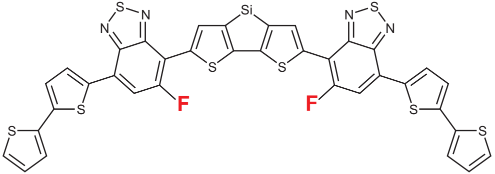
- *π-conjugated electronic system is separated from sp^n-MOs* (by 10 eV in terms of NBO energies)
- primary bonding is sp^n, modulated by $pp\pi$ (secondary bond)

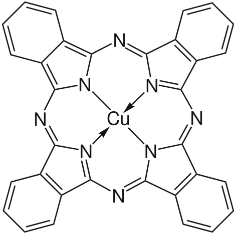
What elements can participate in π-conjugation

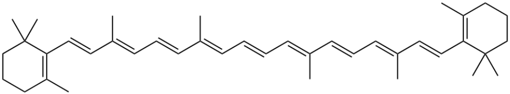


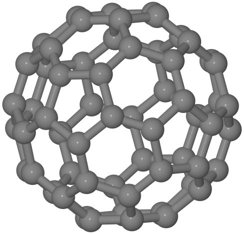
- C, N, B as building blocks
- O, F, S, Cl via LP and terminal contacts
- *d*-elements via $pd\pi$
- any electronic system in resonance

Examples of π-conjugated systems: molecules

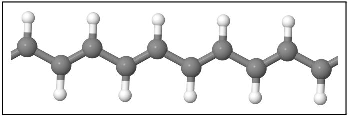


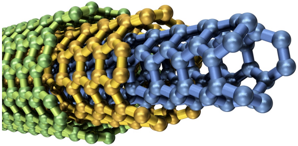


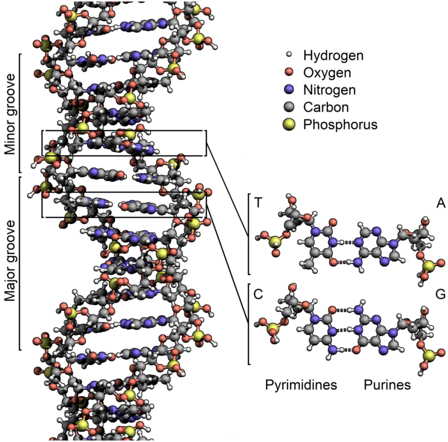




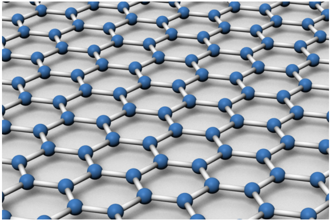
Examples of π-conjugated systems: polymers and 1D

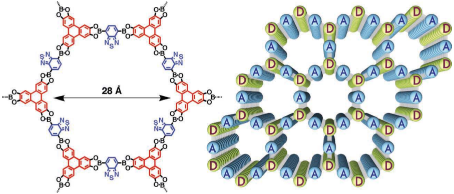


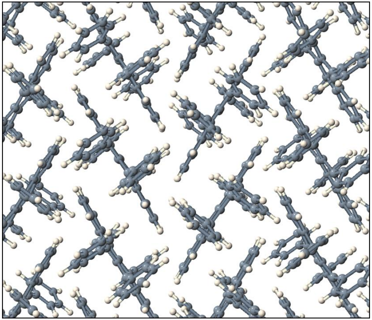


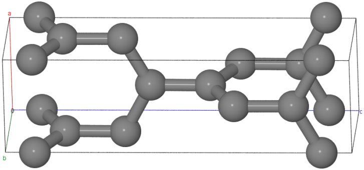


Examples of π-conjugated systems: 2D and 3D









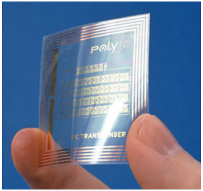
Currently we explore only a small set of possible structural forms

Applications: Organic electronics

Solar cells

Light emitters

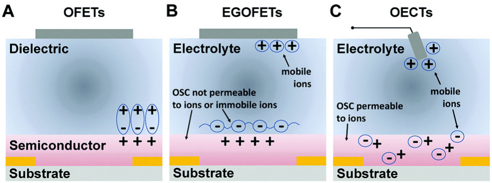
Field effect transistors



- Unlimited possibilities of nanoscale molecular engineering
- Cost effective solution – perfect for consumer markets
- Ease of production – dominates printed electronics market
- Ease of recycling – green technology
- Light weight and flexibility – more versatile in use

Other applications

Electrochemical transistors



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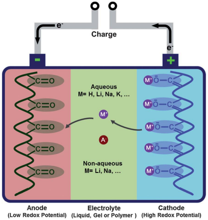
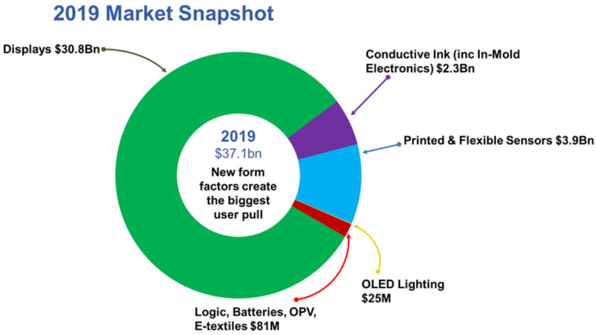
Batteries





More examples and applications

- UV-protection of DNA
- Vision, bioluminescence, sunlight harvesting
- Fluorescent probes for bioimaging
- Charge transport layers
- Capacitors (PEDOT/PSS) and supercapacitors
- Chemical sensors
- Catalysts (transition metal complexes, e.g. water splitting)
- Membranes for water desalination
- THz generators, electrochromic devices, photodiodes, polyelectrolytes, explosives, piezo-, pyro-, ferroelectrics, ...

Any electronic device can be made all-organic

Discussion

"Debunking" myths

1. Are organic semiconductors cheap?
2. Are organic semiconductors environmentally friendly?
3. Are organic semiconductors poor-performers?

Looking for applications

4. What organic materials have industry-scale applications
5. Organic batteries: major problems and possible solutions
6. Short operational lifetime: when it is problem and when is not

Lessons for "startupers"

7. How Konarka bankrupted
8. How solar cell research moved to Asia

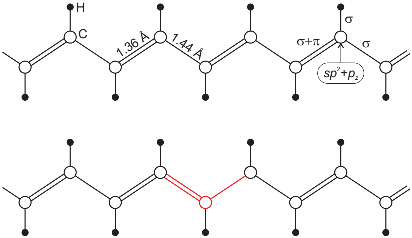
Why π-conjugated molecules are special?

Strong mode-specific electron-phonon coupling

What is electron-phonon coupling?

- piezoelectric coupling: mechanical stress $\leftrightarrow$ electric field
- e-phonon coupling: molecular deformations $\leftrightarrow$ electronic levels

Why electron-phonon coupling in π-conjugated systems is special?

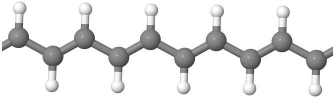
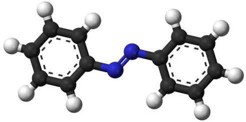


$\Longrightarrow$ Unique quasiparticles – solitons in transpolyacetylene

Why π-conjugated molecules are special?

Strong electron-phonon coupling in combination with soft structure

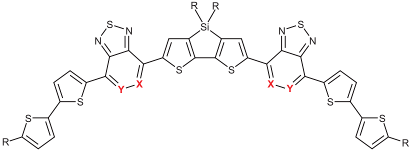
$\Longrightarrow$ *Electronic properties strongly depend on material morphology, and electronic dynamics is strongly bound to molecular dynamics*

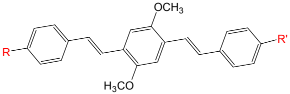
Peierls transition in polyacetylene (C–C bond stretching mode)	Photoizomerization of azobenzene (librations of non-rigid dihedrals)
	

also polaron formation, vibronic progression in spectra

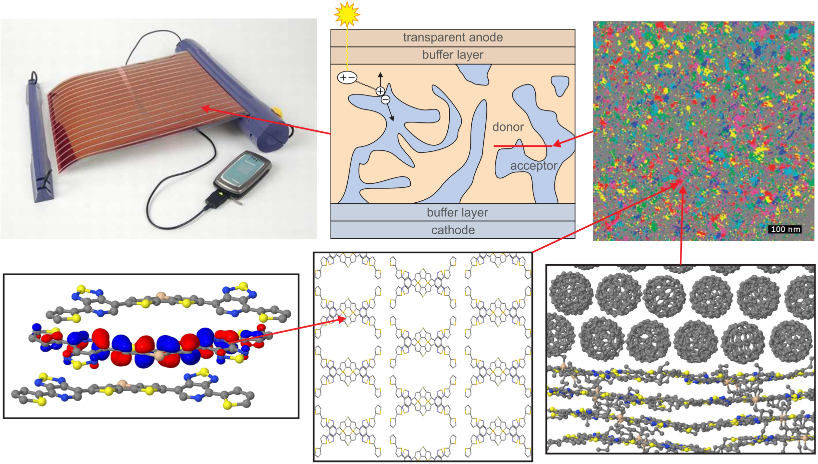
In fact, it is very useful in applications:

- Change structure $\Longrightarrow$ tune electronic properties
- Affect electronic system $\Longrightarrow$ change structure





Scale problem in organics: solar cell example



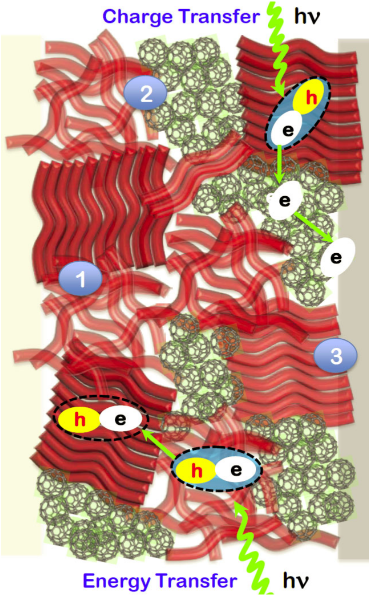
Understanding scales: solar cell example

Spatial scales:

- molecule ($\lesssim$ 1 nm)
- single phase ($\sim$ 10 nm)
- interfaces (intra and inter)
- functional layer ($\gtrsim$ 100 nm)

Time scales:

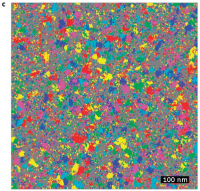
- ultrafast intramolecular (fs)
- intermolecular transfer (ps)
- electronic transport (ns)
- transients, degradation (>ns)

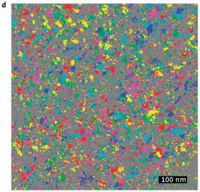


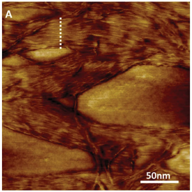
Understanding scales: computational perspective

Functional properties of organic semiconductors are often determined by structure on scales up to tens of nm

$\implies$ atomistic description is needed for up to 10^6 atoms







Challenges

- realistic mesoscale structure (coarse-grained MD)
- accurate intermolecular geometry (best DFT-D)
- accurate electronic structure (best range-separated hybrids)
- accurate charge dynamics (best NAMD)

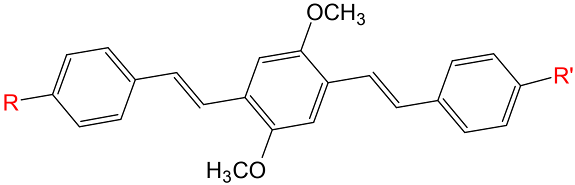
No direct simulation – only multiscale modeling and "machine learning"

Discussion

1. Are there other classes of materials with “split” electronic structure (σ-bonds and π-system)?
2. Are there other classes of materials with similar electron-phonon interaction effects?

Structural motifs

- Locally 2D due to nature of π-conjugation
- Bond length alternation (BLA) pattern
- Rigid fused rings + floppy dihedrals + vdW contacts
- Usually functionalized (tuning, soluble side-chains, transition metals, bridges)

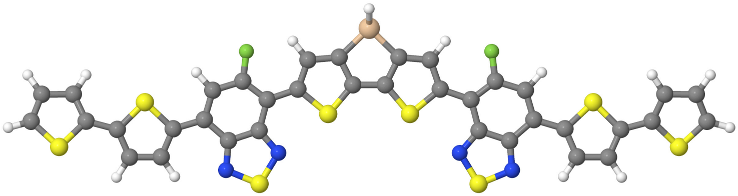


Structural classes

- Graphene, carbon nanotubes
- Conjugated polymers
- Oligomers
- Small-molecule crystals
- All-organic frameworks
- Metal organic frameworks
- Biopolymers with aromatic fragments and macromolecules
- Blends
- Strongly correlated systems

Rational design: Quasi-1D π-conjugated systems

(majority of materials used in organic electronics)



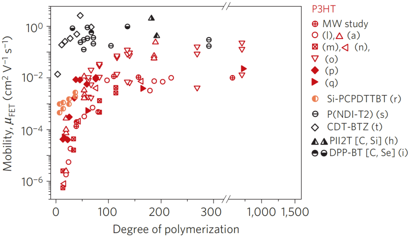
- Have block structure with few interconnections per block
- Each block is rigid, limited number of local structural patterns

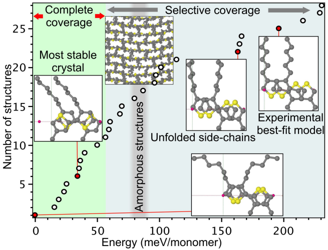
$\Longrightarrow$ *Success of simple force fields*

- The π-conjugated system of each block is closed-shell
- Inter-block couplings ~ 1 eV $\ll$ bandgap of blocks
- Intermolecular couplings ~ 0.1 eV $\ll$ bandgap of molecules

$\Longrightarrow$ *Can be rationally designed by block assembly approach*

Rational design: Improving morphology





- Isovalent substitutions and “side chain engineering”
- Processing conditions, e.g. additives

Challenges

- Fast degradation and aging – mechanisms to be studied
- Large batch-to-batch variations – technology
- Mediocre performance (5% of elements) – hybrids
- Limited charge carrier mobility – improving
- Doping is nontrivial – solvable
- Too complex to characterize/describe – consider it as excellent research opportunity for you

Research at Skoltech and in Russia

Theoreticians:

- Sergei Tretiak, Andriy Zhugayevych – see also this page

Experiment:

- Keith Stevenson (CEST CREI)
- Albert Nasibulin (CPQM CREI) – carbon nanotubes
- Pavel Troshin (IPCP)
- Sergey Ponomarenko (ISPM)
- Dmitry Paraschuk (MSU)

Events:

- IFSOE (International Fall School on Organic Electronics)

Resources

- Wikipedia
- List of references
- A Koehler, H Bassler, Electronic Processes in Organic Semiconductors: An Introduction (Wiley, 2015) *in library*
  More specifically Sections 1.1-1.4
- S R Forrest, Organic Electronics: Foundations to Applications (OUP, 2020)
  More specifically Chapter 1