Survey of Materials

Organic semiconductors

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October 8, 2020

Outline

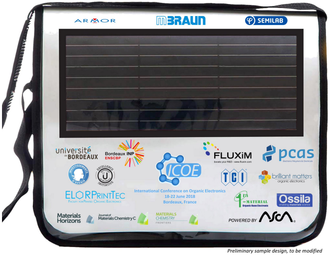
- Introduction: real world examples
- What is π-conjugated system
- Examples and Applications
- Structure, Functional properties, Challenges
- Research at Skoltech
- Resources: references, links, further reading

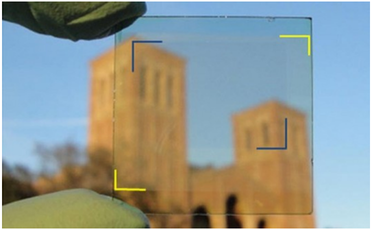
Real world examples: OLEDs

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

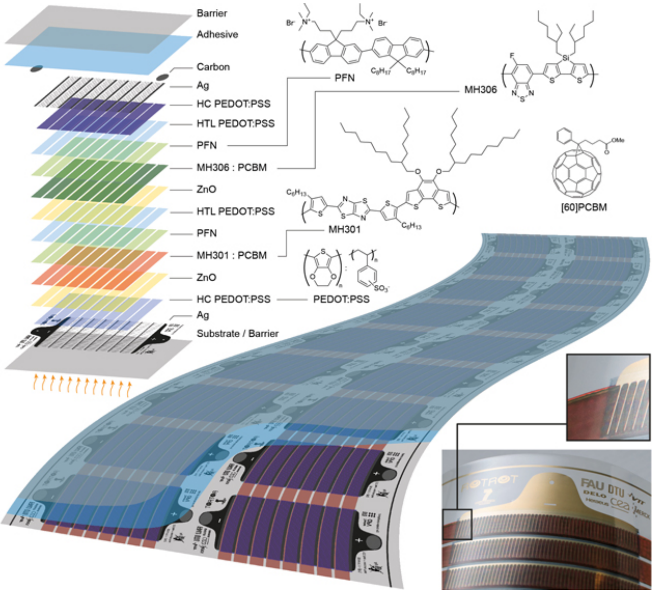
Real world examples: Solar cells

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



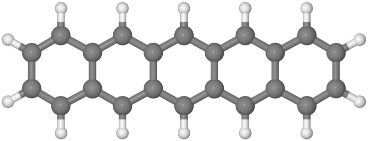


How is it made: Solar cells – R2R roll-to-roll processing

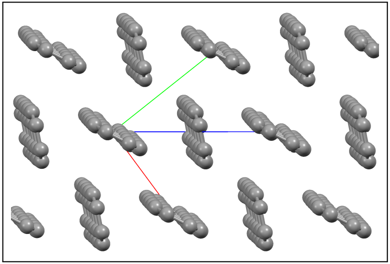


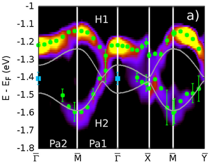
Historical example: A century-long story of pentacene

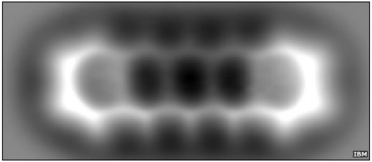
Charge carrier mobility $\sim 10\ \frac{cm^2}{V{\cdot}s}$
($>$ a-Si, 1/100 of c-Si)



- 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

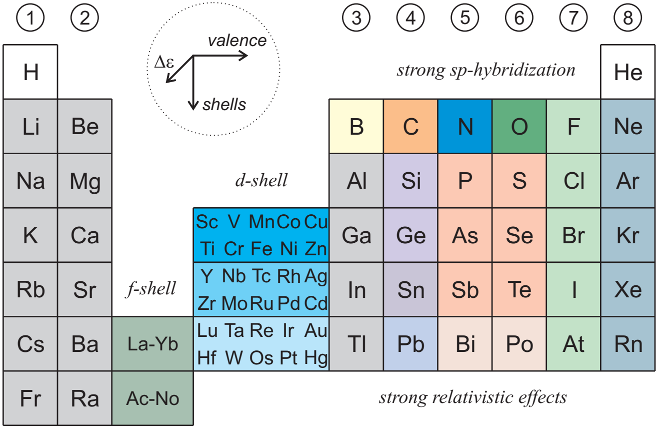






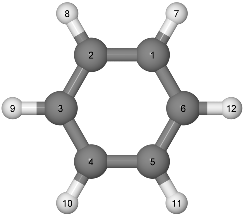
What is organic semiconductor

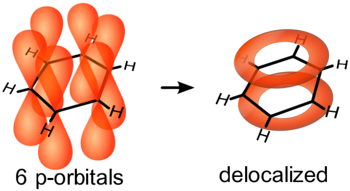
1. **Organic** – built from C with terminal H, possibly with isovalent substitutions (N for CH, O/S for CH_2, F/Cl for H)
2. π-**conjugated** – π-electrons on frontier orbitals (next slide)



Number of organic semiconductors is comparable to number of inorganic ones

What is π-conjugated system: example of benzene



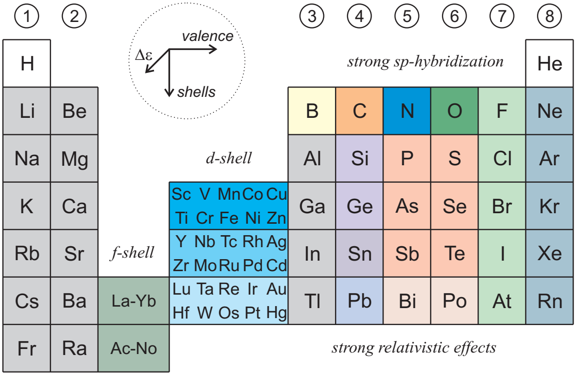


- each carbon has 3 sp^2 AOs connected by σ-bonds and 1 $pp\pi$-connected AO
- energy of bonding MO is $-t$ per electron
- $t_{sp2} = 3.26\frac{\hbar^2}{md^2} \gg t_{pp\pi} = 0.63\frac{\hbar^2}{md^2}$ [Harrison]

$$\Longrightarrow$$

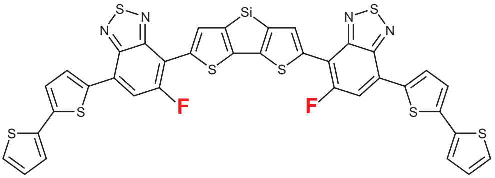
- *π-conjugated electronic system is separated from sp^n-MOs* (by 10 eV in terms of NBO energies)
- primary bonding is sp^n, modulated by $pp\pi$ (secondary bond)

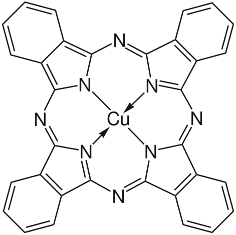
What elements can participate in π-conjugation

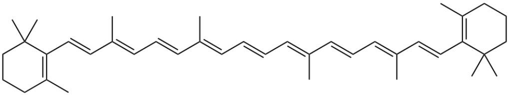


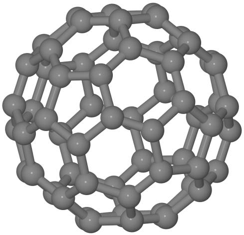
- C, N, B as building blocks
- O, F, S, Cl via LP and terminal contacts
- *d*-elements via $pd\pi$
- any electronic system in resonance

Examples of π-conjugated systems: molecules

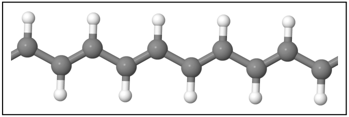


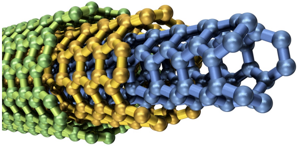


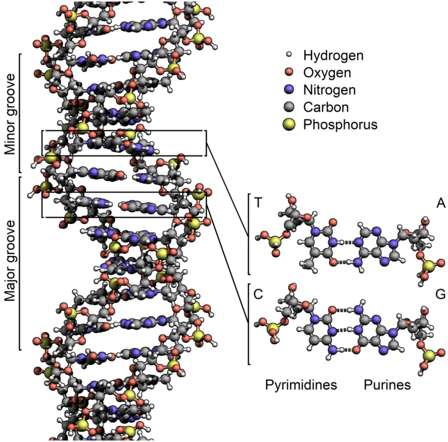




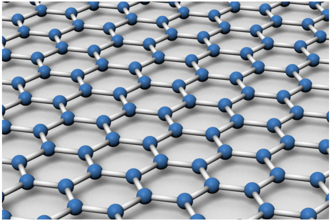
Examples of π-conjugated systems: polymers and 1D

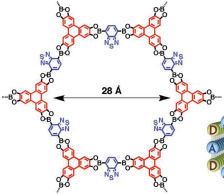


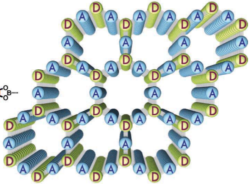


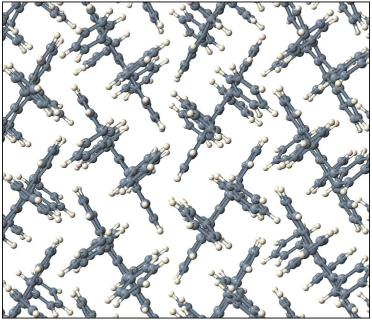


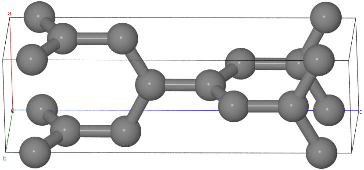
Examples of π-conjugated systems: 2D and 3D











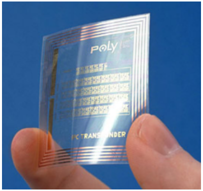
Currently we explore only a small set of possible structural forms

Applications: Organic electronics

Solar cells

Light emitters

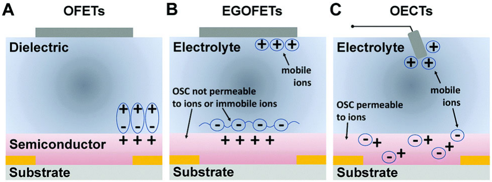
Field effect transistors



- 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

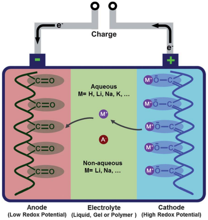
Other applications

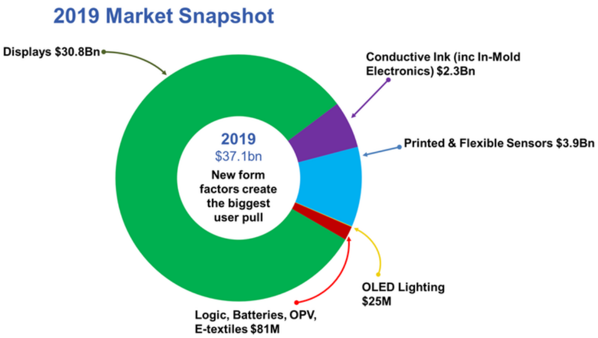
Electrochemical transistors



J Mater Chem C 6, 11778 (2018)

Batteries





More examples and applications

- UV-protection of DNA
- Vision, bioluminescence, sunlight harvesting
- Fluorescent probes for bioimaging
- Charge transport layers
- 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

Let's discuss

Lessons for "startupers"

1. How Konarka bankrupted
2. How solar cell research moved to Asia

"Debunking" myths

3. Are organic semiconductors cheap?
4. Are organic semiconductors environmentally friendly?

Looking for applications

5. Organic batteries: major problems and possible solutions
6. Short operational lifetime: when it is problem and when is not

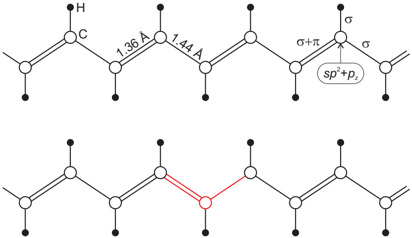
Why π-conjugated molecules are special?

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?

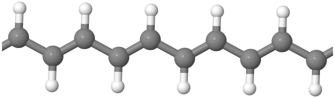
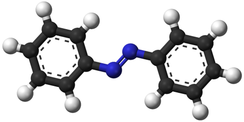


$\Longrightarrow$ Unique quasiparticles – solitons in transpolyacetylene

Why π-conjugated molecules are special?

Strong electron-phonon coupling in combination with soft structure

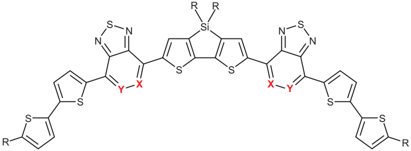
$\Longrightarrow$ *Electronic properties strongly depend on material morphology, and electronic dynamics is strongly bound to molecular dynamics*

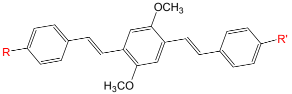
Peierls transition in polyacetylene (C–C bond stretching mode)	Photoizomerization of azobenzene (librations of non-rigid dihedrals)
	

also polaron formation, vibronic progression in spectra

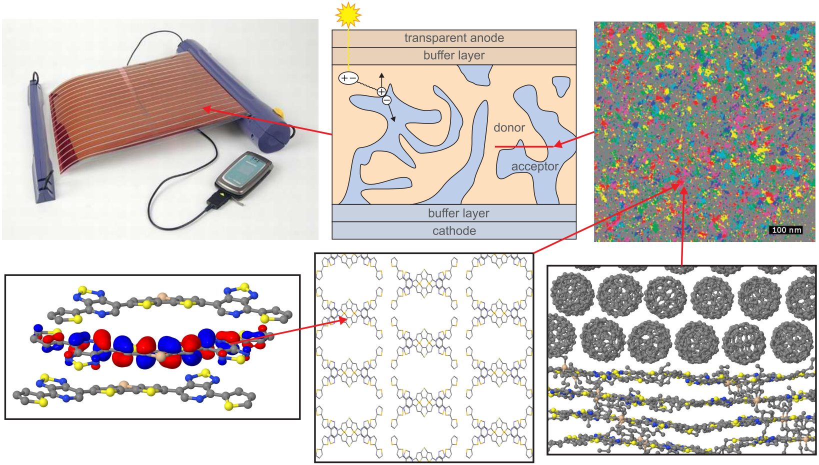
In fact, it is very useful in applications:

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





Scale problem in organics: solar cell example



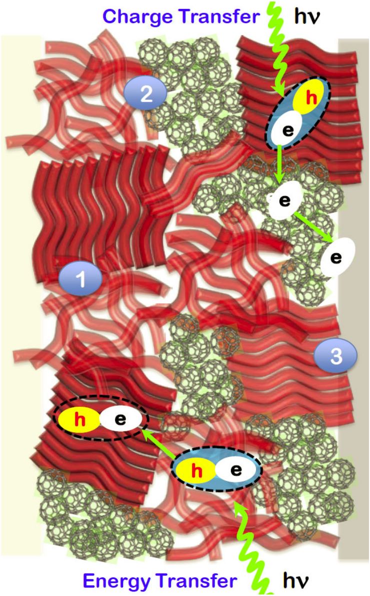
Understanding scales: solar cell example

Spatial scales:

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

Time scales:

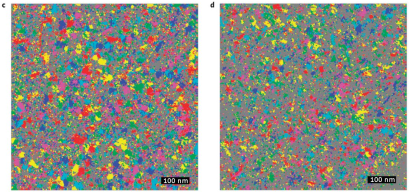
- ultrafast intramolecular (fs)
- intermolecular transfer (ps)
- electronic transport (ns)
- transients, degradation ($>$ns)

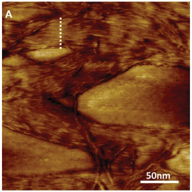


Understanding scales: computational perspective

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

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





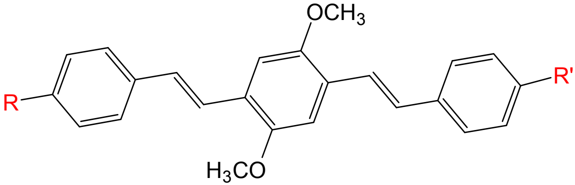
Challenges

- 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"

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)

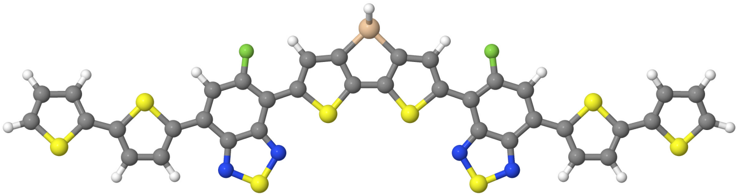


Structural classes

- 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)



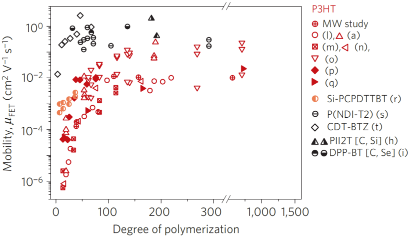
- Have block structure with few interconnections per block
- Each block is rigid, limited number of local structural patterns

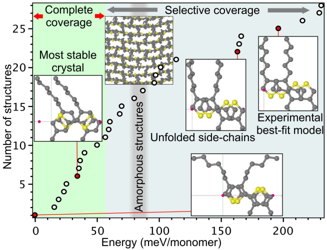
$\Longrightarrow$ *Success of simple force fields*

- 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 – a part of my work

Research at Skoltech

Theoreticians:

- Sergei Tretiak
- Andriy Zhugayevych – see also this page

Experiment:

- Pavel Troshin – solution-processable semiconductors
- Albert Nasibulin – carbon nanotubes

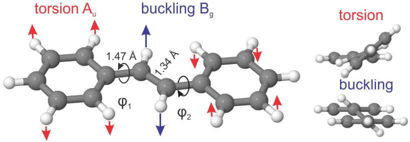
My research

(in collaboration with Sergei Tretiak, Pavel Troshin, MSU, others)

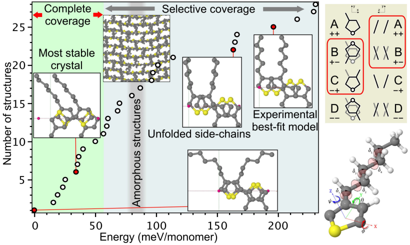
- Developing new methods for modeling of semiconductors
- Solving fundamental problems in this research field
- Design of new materials for various applications

Solving fundamental problems: recent examples

- What is the structure of stilbene molecule? JPCL 10, 3232 (2019) pdf



- What is the structure of P3HT crystal? JPCC 122, 9141 (2018) pdf



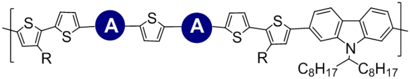
- Why novel NFAs are so efficient in solar cells (+5% PCE)? submitted
- What is the charge transport mechanism in high-performance organic semiconductors? Are charge carriers localized in molecular crystals? What is the maximum achievable charge carrier mobility?

Computer-aided design of new materials: recent examples

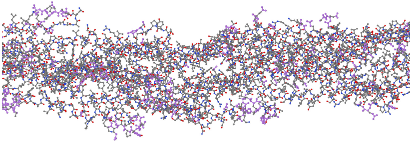
CMS scientists are expected to predict material properties from chemical formula

- Materials for solar cells (polymers/oligomers, donors/acceptors)

  Synthetic Metals 259, 116231 (2020) pdf



- Materials with high charge carrier mobility AFM 28, 1702073 (2018) pdf
- Materials for rechargeable batteries (Pavel Troshin)
- Materials for charge transport layer in pervoskite solar cells
- Biocompatible materials (natural or synthetic) for biodegradable/digestible/wearable/IoT electronics

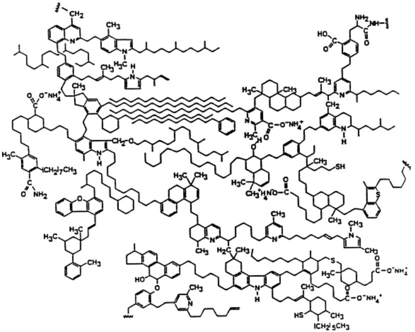


Purely computer design of new materials

- Novel polymers
- Functionalized molecules (and polymers)
- All-organic frameworks
- Novel architectures of molecular crystals

Interdisciplinary projects: Molecular model of kerogen
(CHR CREI – exploring shale oil and gas)

- Molecular model of kerogen



Resources

- Wikipedia
- List of references
- A Zhugayevych, S Tretiak, Theoretical Description of Structural and Electronic Properties of Organic Photovoltaic Materials, Annu Rev Phys Chem 66, 305 (2015) pdf
- Textbooks
- A Koehler, H Bassler, Electronic Processes in Organic Semiconductors: An Introduction (Wiley, 2015) *in library*
- Pavel Troshin's lecture and/or course
- Sergei Tretiak's lecture