Towards rational design of organic solar cells: How to control the structure of a bulk material

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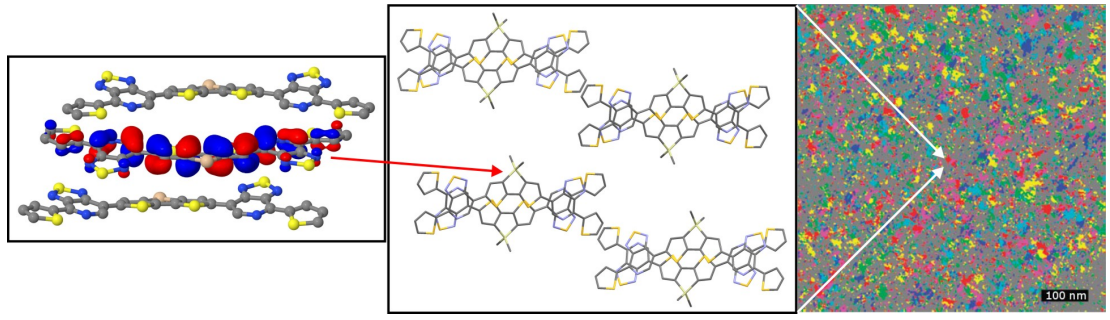
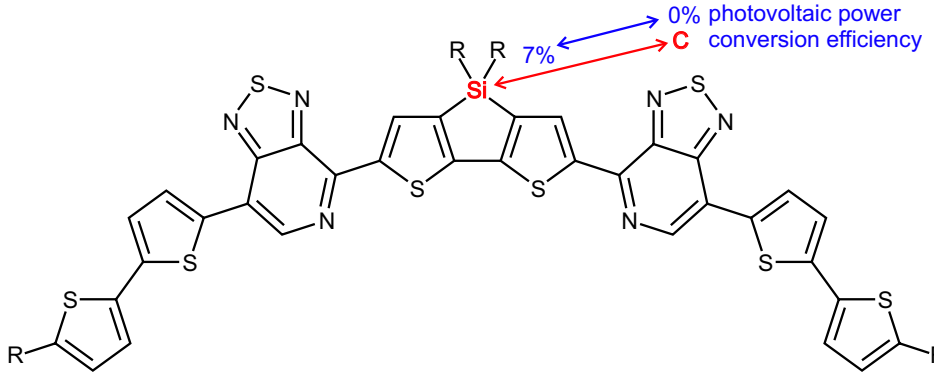
Outline

- **Overview**: Modeling of materials for organic electronics



- **Motivation**: Small changes in chemical composition $\rightarrow$ $\rightarrow$ large changes in macroscopic properties



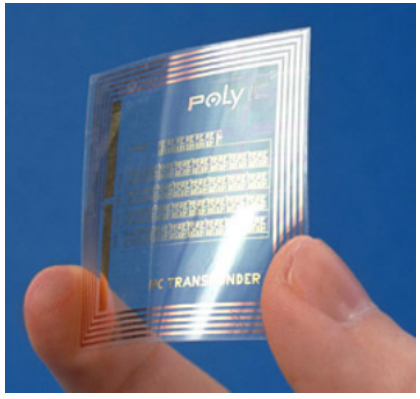
- **Results**: Understanding and controling the above effect

What is organic electronics?

Solar cells

Light emitters

Field effect transistors

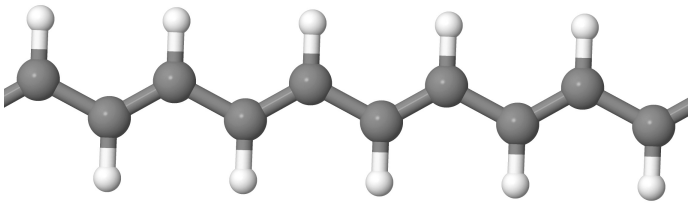


- Cost effective solution
- Unlimited possibilities of nanoscale molecular engineering
- Ease of production and recycling
- Light weight and flexibility

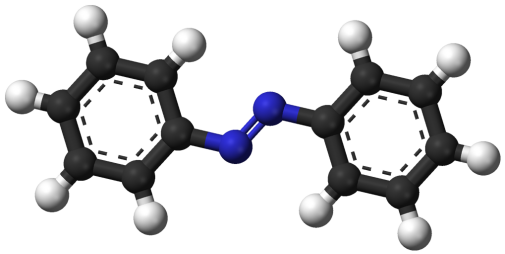
Why π-conjugated molecules are special?

Strong mode-specific electron-phonon coupling

Peierls transition in polyacetylene
(C–C bond streching mode)



Photoizomerization of azobenzene
(librations of non-rigid dihedrals)



also polaron formation ▸ picture, vibronic progression in spectra

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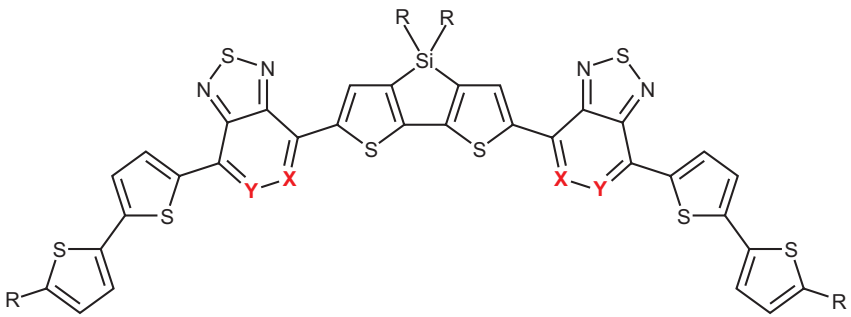
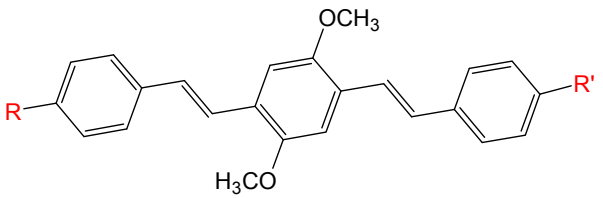
How to utilize it?

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



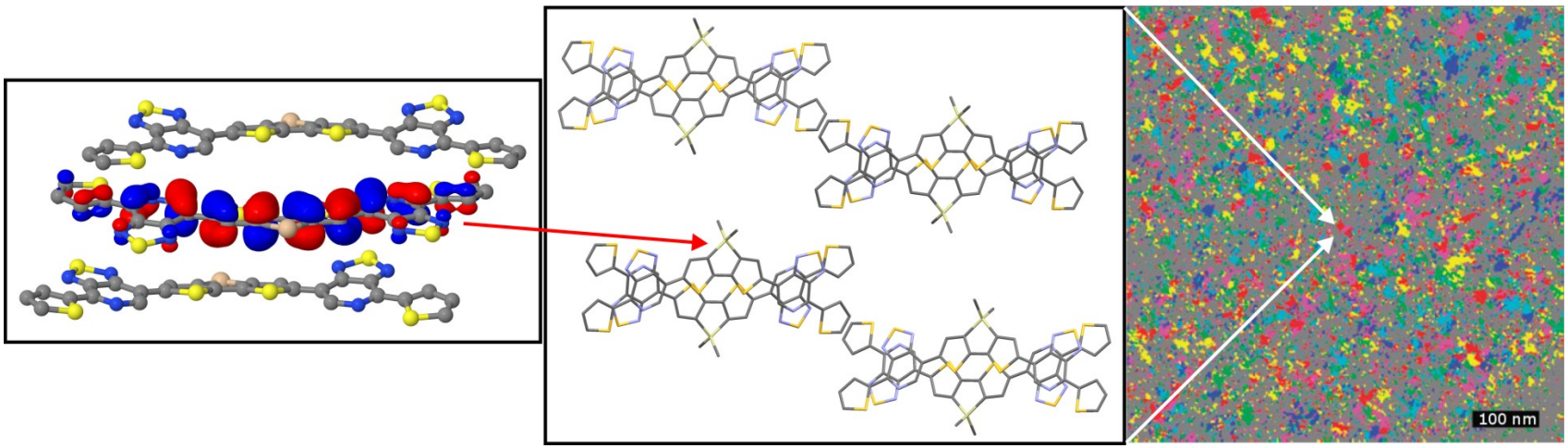


How to describe it?

- Adiabatic calculations and non-adiabatic molecular dynamics
- Holstein–Peierls Hamiltonian and mean-field polaron approach

First-principles multiscale modeling: bird's eye view

- Combine different approaches on different scales
- Control the accuracy (errors accumulate through the scales)



- Density functional theory on few-molecules scale
- Model Hamiltonian on intermolecular scale
- Molecular mechanics + kinetic equation on mesoscale
- Continuum models on larger scales (diffusion + electrostatics)

A.Z., S. Tretiak, Ann. Rev. Phys. Chem. 66, in press (2015)

Calculating single-crystal characteristics

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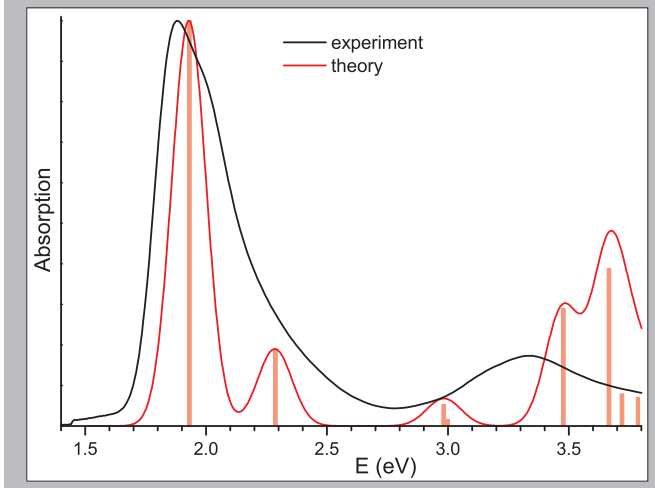
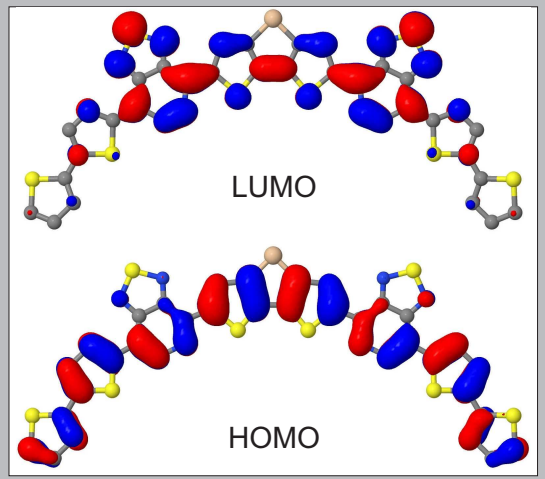
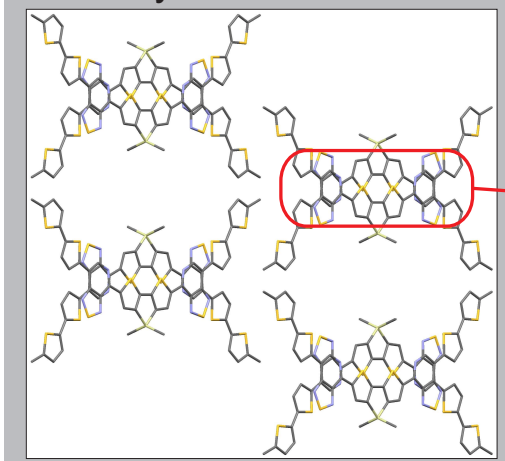


Light absorption

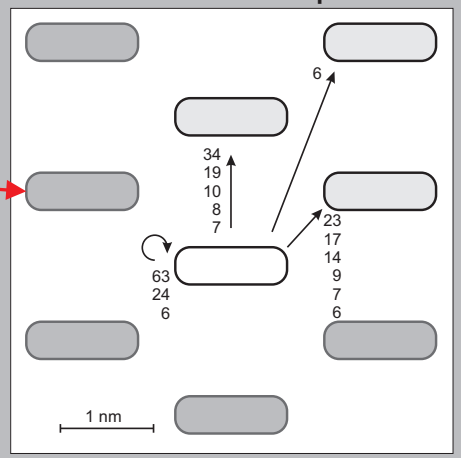


Electronic structure

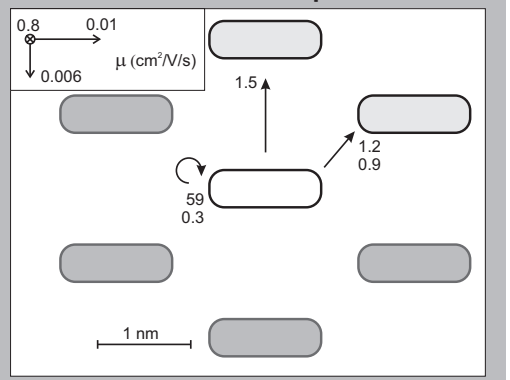
Crystal structure



Exciton transport



Hole transport



Exciton diffusion length $\sim$ 100 nm, hole mobility $\sim$ 1 $cm^2/V{\cdot}s$

Single-crystal properties of the given molecule are perfect for photovoltaics

A.Z., O. Postupna, R. C. Bakus II, G. C. Welch, G. C. Bazan, S. Tretiak, J. Phys. Chem. C 117, 4920 (2013)

Modeling exciton dissociation

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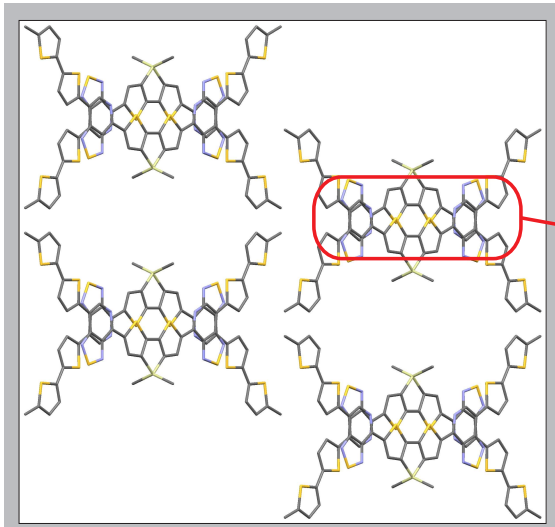
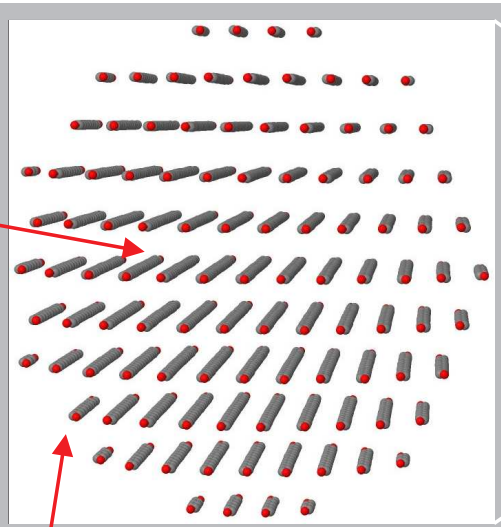
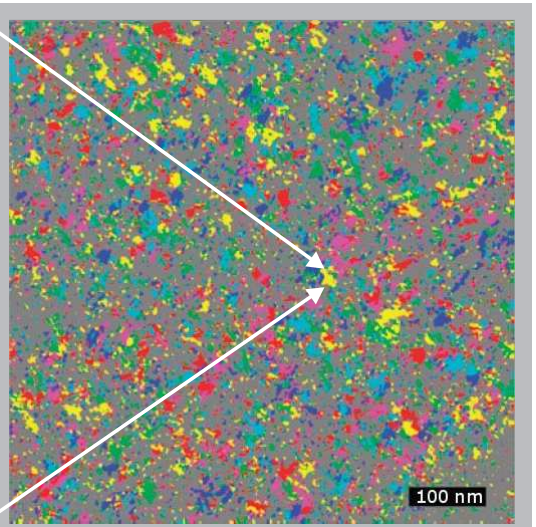


Crystal structure

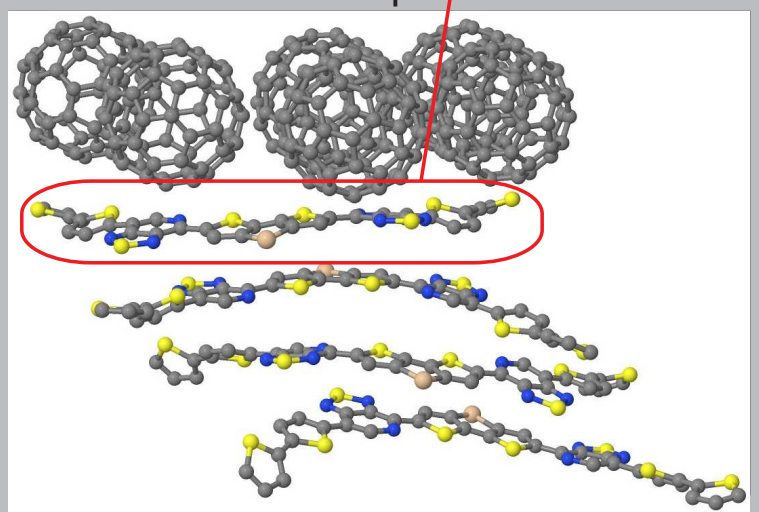


20-nm crystallite

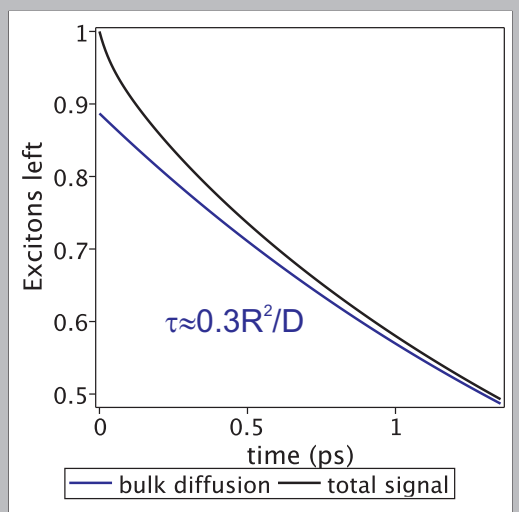


TEM of active layer

Microscopic model



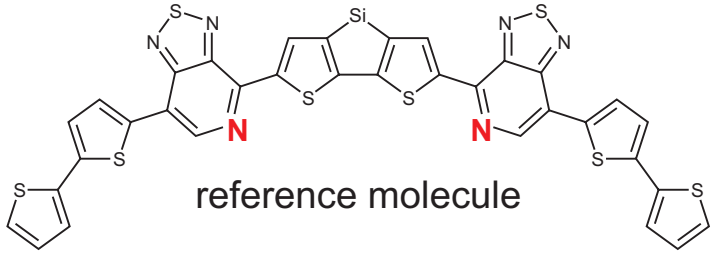
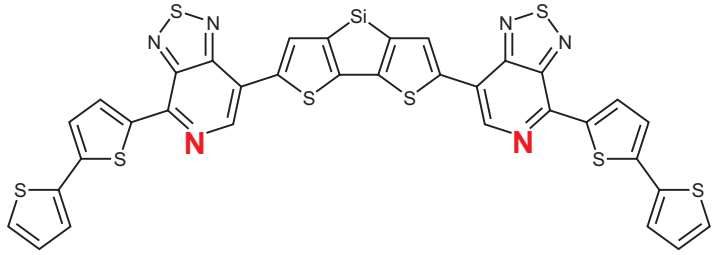
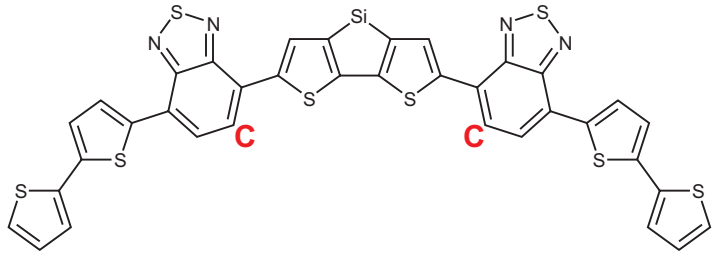
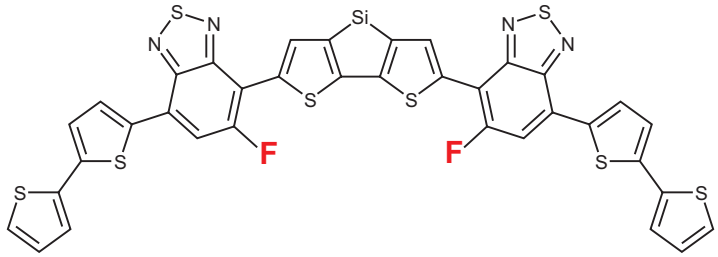
Exciton dissociation kinetics



In absence of traps exciton dissociation proceeds in picoseconds

A.Z., K. Velizhanin, S. Tretiak, in preparation

How small changes influence macro-properties: experiment

molecular structure	PCE*	notes
 reference molecule	7%	
	6%	similar but downgraded properties
	0.2%	low J_{SC} & FF no crystallites
	7%	10-fold increase in hole mobility

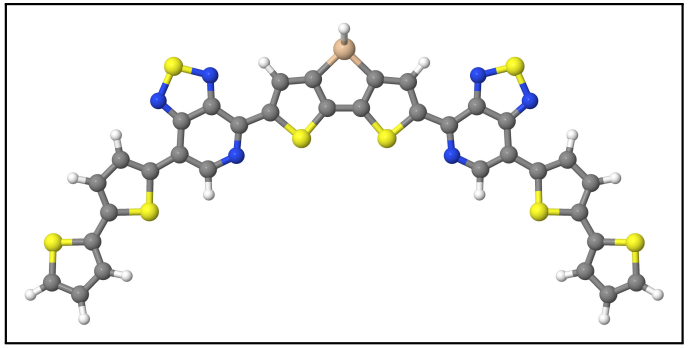
* PCE = photovoltaic Power Conversion Efficiency

** Single-molecule electronic properties are nearly the same for all 4 molecules

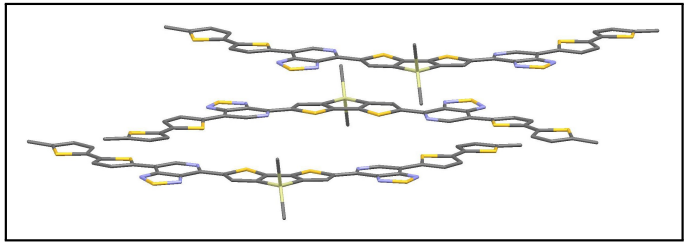
Structure: multiple scales from nm to μm

Small-molecule bulk-heterojunction organic solar cells

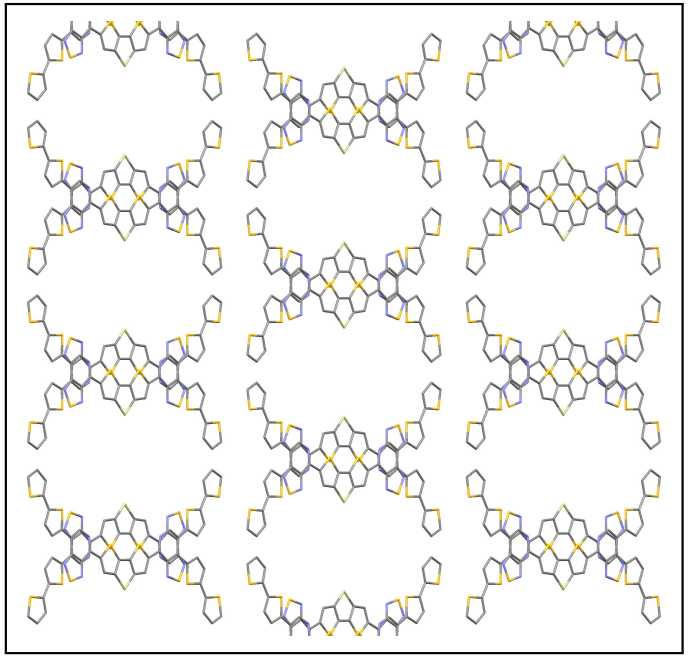
Conformers
30 meV/dihedral

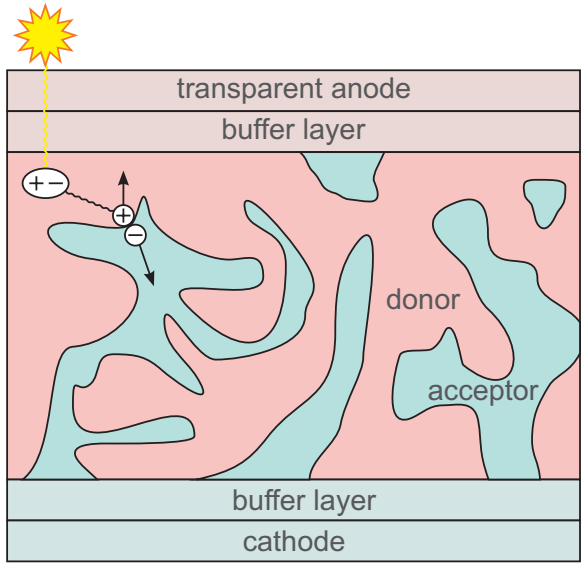


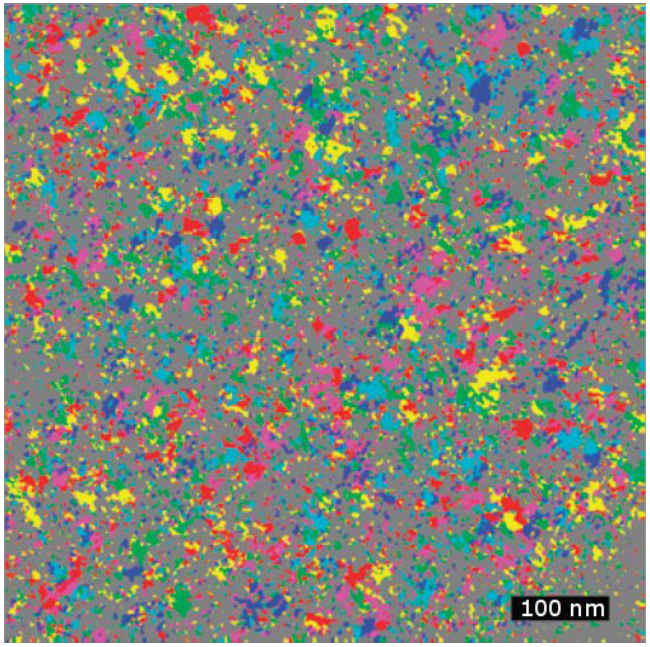
Intra-stack
binding
2 eV/molecule



Inter-stack
binding
0.4 eV/molecule

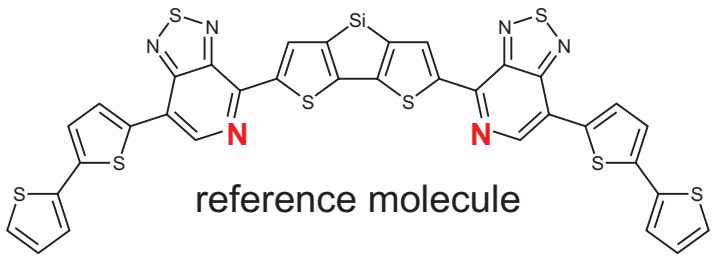
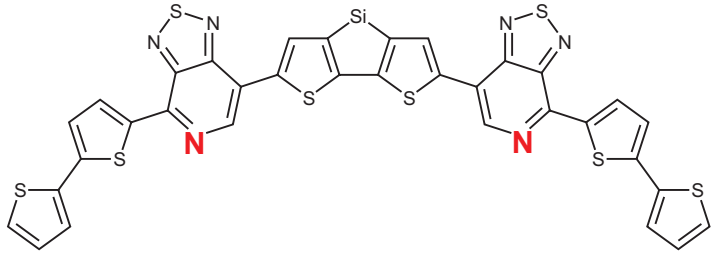
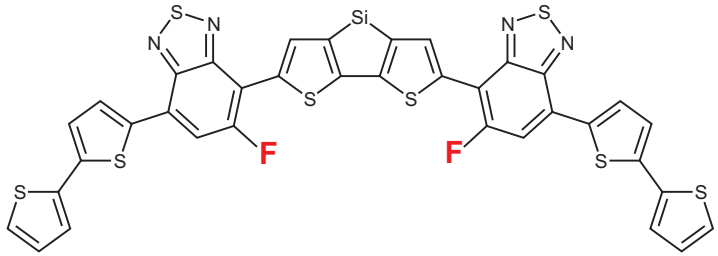
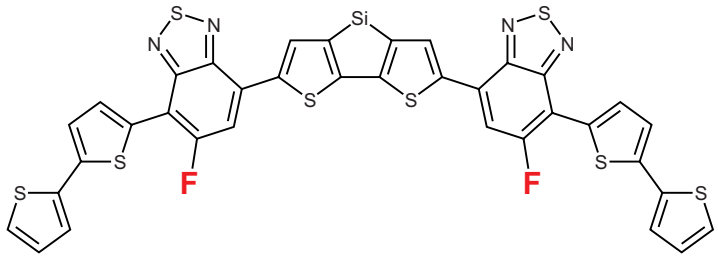






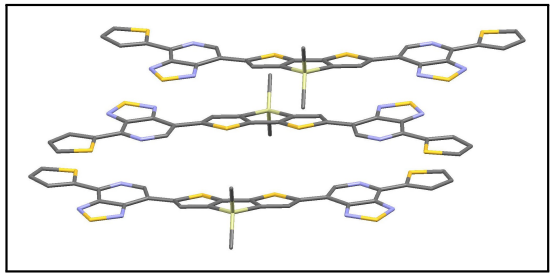
Understanding structural preferences

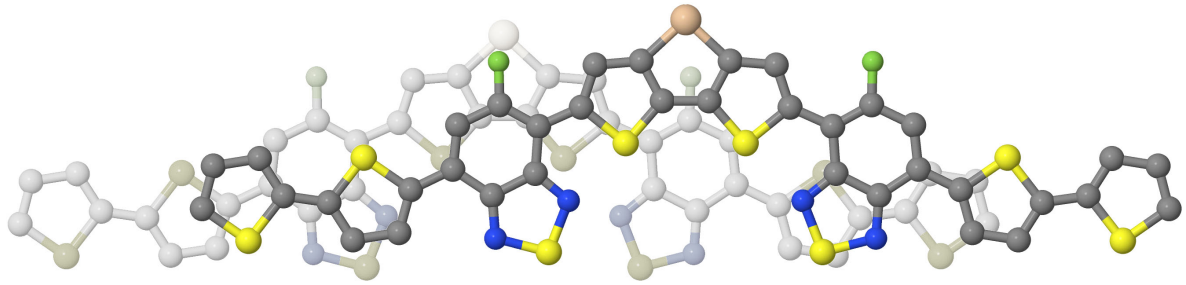
Four molecules – four different intermolecular packings

molecular structure	bulk material	theoretical analysis
	perfect crystal	all interactions cooperate
	no crystal	frustration between intra- and inter-stack interactions
	crystal with some disorder	not the lowest energy conformer
	two polymorphs	flat energy distribution for conformers

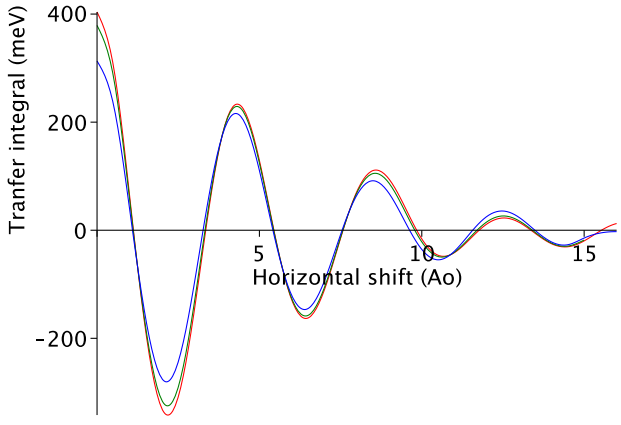
T. van der Poll, A.Z. *et al.* J. Phys. Chem. Lett. 5, 2700 (2014)

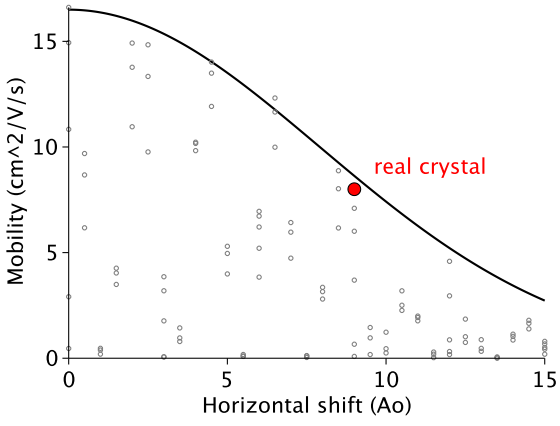
Dependence of transfer integral on intermolecular geometry



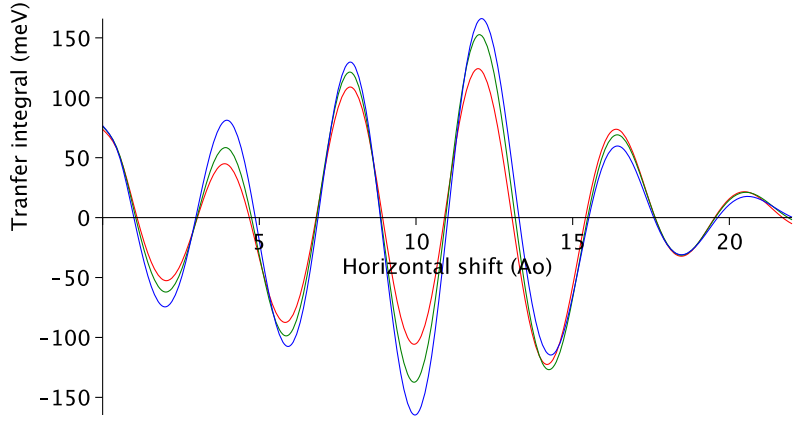


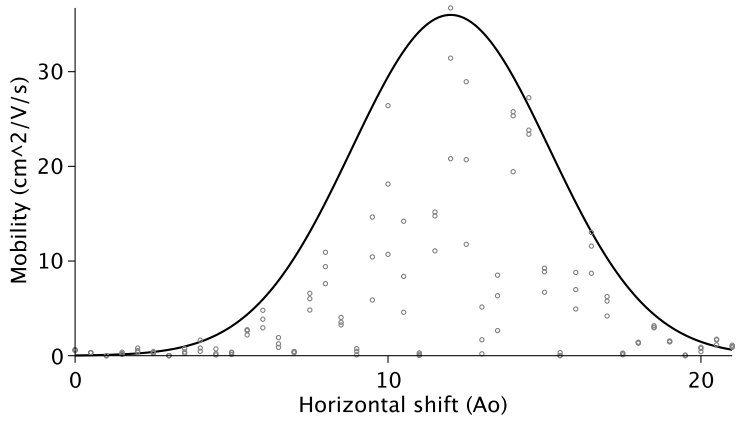
parallel orientation





antiparallel orientation





How to control the structure of bulk material?

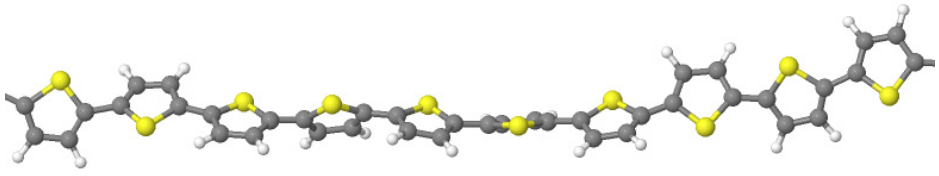
Not changing single-molecule electronic properties

- Isovalent substitutions
- Aliphatic side chains
- Processing: solvent, additives etc.

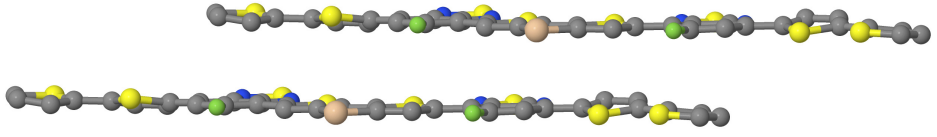
		OPV	mc-Si
Energy balance limit, max 50% for $E_g = 1.1$eV		45%	50%
Recombination, heterojunction losses, eV_{oc}/E_g	$\times$	0.5	0.6
Quantum efficiency, $J_{sc}/J_{sc}^{max}(E_g)$	$\times$	0.5	0.9
Fill Factor, max $JV/J_{sc}V_{oc}$	$\times$	0.6	0.9
Power conversion efficiency	$=$	7%	25%

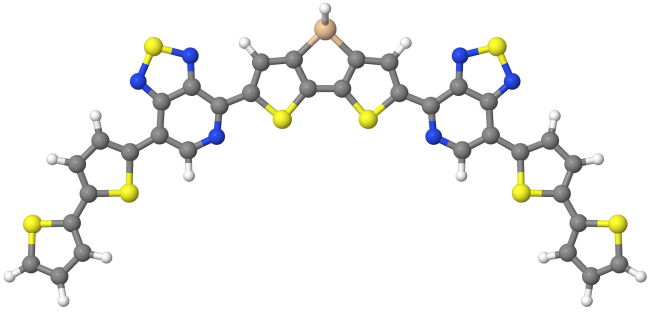
How to shape a molecule

Step 1: Why do we need it

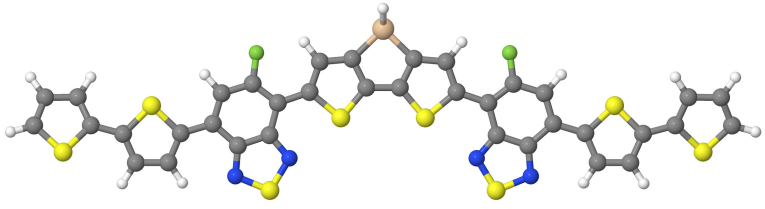


- Stronger π-conjugation
- Tighter intermolecular packing
- Less structural defects



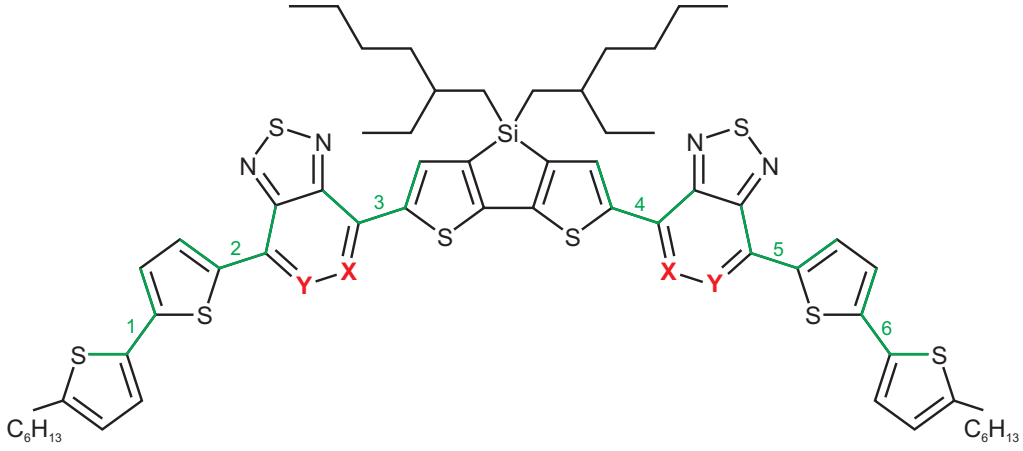


- Increase mobility

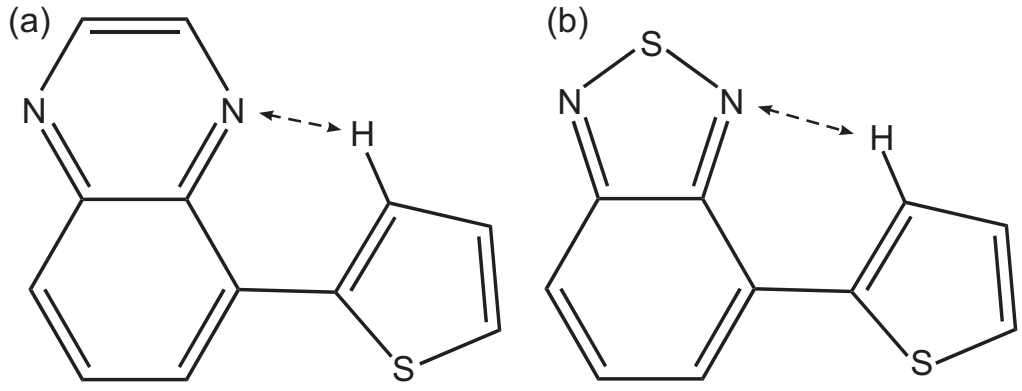


How to shape a molecule

Step 2: Understanding intramolecular interactions

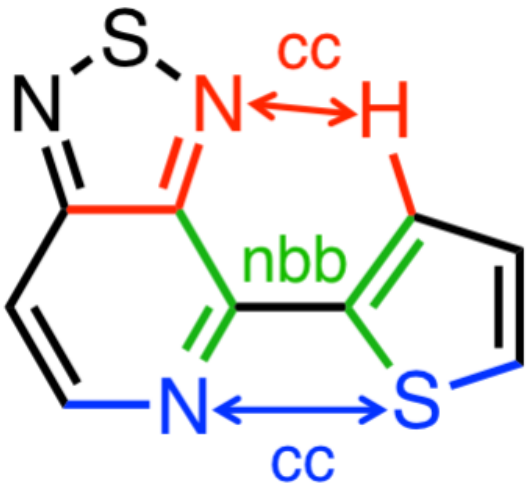


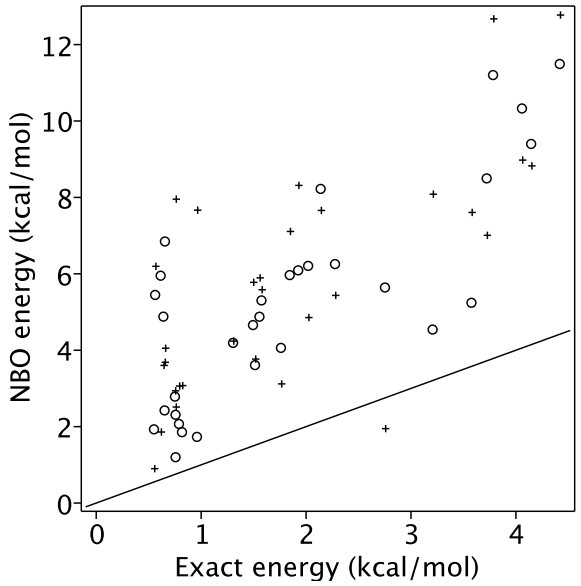
There is a lot of controversial statements about atomic-wise interactions



How to shape a molecule

Step 3: Developing a simplified description of intramolecular interactions





The interplay of the three interaction components

- Near-bridge bond interaction (nbb)
- Steric repulsion between contact atoms (cc)
- Electrostatics (controllable by environment)

can "lock" the dihedral or enforce nonplanar geometry.

J. Coughlin, A.Z. *et al.* J. Phys. Chem. C 118, 15610 (2014)

Conclusions

- Among the most important challenges in rational design of organic semiconductors is ability to control the structure of bulk material as well as predict it theoretically
- To control intermolecular packing without influencing single-molecule properties we can apply isovalent substitutions, modify aliphatic side chains, and change processing conditions (solvent, additives etc.)
- To control molecular shape we are developing a simplified description of intramolecular interactions to use a building-blocks approach

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Open positions: postdoc and PhD students are welcome, see details at http://faculty.skoltech.ru/positions