

Computational Chemistry and Materials Modeling

Introduction

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Outline

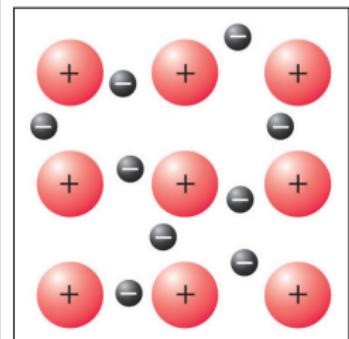
- What is this course about
- General guidelines for Computational Materials Science
- Case studies: from basic applications to student projects
- Course logistics

What is this course about

Computational Chemistry + Materials Modeling

“The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.”

P A M Dirac, Proc Royal Soc London 123, 714 (1929)

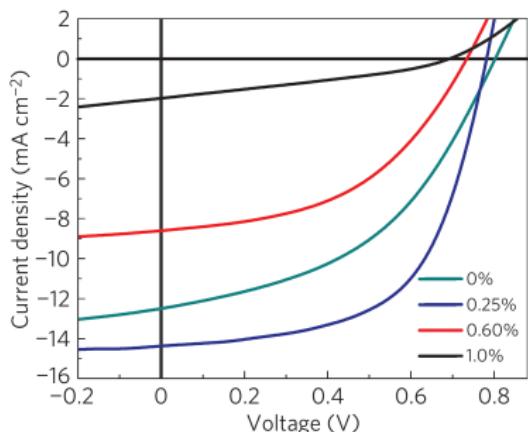


- Computational Chemistry = solving Coulomb problem for $\gtrsim 10$ particles
- Materials Modeling = relating that solution to real world

Whom is this course for

- Theoreticians and experimentalists studying materials with atomic resolution (most of recent high-technology devices)
-

Example



- You would like to understand the overall shape of an I-V curve
⇒ you don't need this course
- You would like to understand the difference in these I-V curves
⇒ you do need this course

Level of coverage

Our approach

- Pragmatic & practical guide to start working in the research lab (theory/experiment) right away

Out of scope

- Other scales than atomistic
- Underlying quantum chemistry, condensed matter theory, and computational mathematics
- Technical implementation
- Limited-use and highly specialized methods

Primary learning outcomes

- Professionally perform most common calculations including understanding of what you are doing
- Understand the results of calculations including quality assessment
- Avoid common mistakes and slips
- Hands-on experience in use of software/hardware including solution of common technical problems
- **Support or start your research project**

Demand for computational materials scientists

(good knowledge of materials science + experience in computational chemistry)

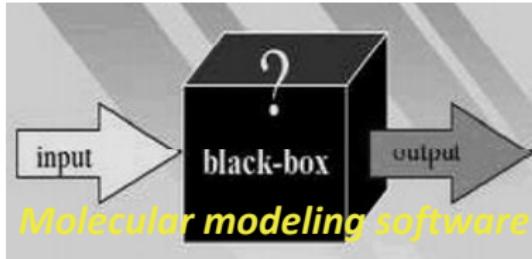
- Any research group in modern materials science performs or needs theoretical modeling
- Research institutions: Skoltech, MSU, MIPT, MIT, LANL, IMEC
- Computational materials science at Skoltech:
Artem Oganov, Vasili Perebeinos, Andriy Zhugayevych
- Los Alamos National Lab (Sergei Tretiak): several postdocs per year and infinite number of summer internship students
- R&D Labs: Samsung, Boeing, IBM
- Software developers: Gaussian, MedeA, Continuum Analytics
- Skolkovo startups: Kintech

General guidelines for Computational Materials Science

- Approaching the computational “black box”
- Calculate or measure?
- Understand scales

Approaching the ‘black box’

*Molecular
structures*



*Materials
properties*

How to deal with it?

- Basic understanding of what is going on inside;
- Interpretation of experimental data;
- Understanding of dominating physical phenomena;
- Rational choice of optimal electronic structure methodology;
- Efficient analysis of the numerical results;
- Developing physical intuition: ‘does it make sense?’

What is Computational Materials Science?

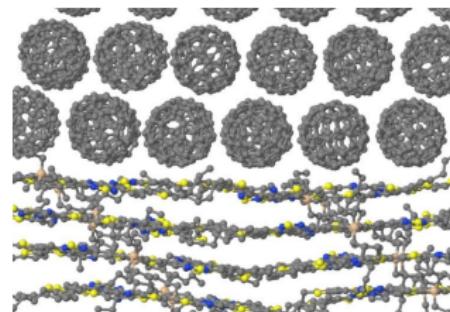
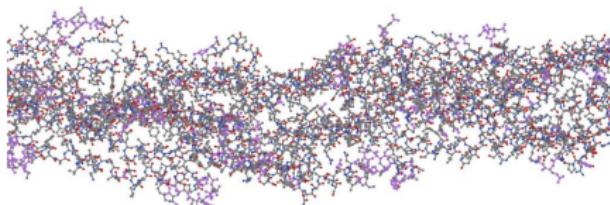
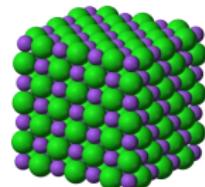
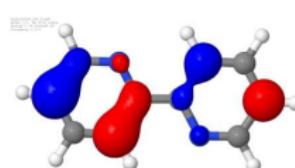


	Measure	Compute
Research costs	✗	✓
Research time	✗	✓
Accuracy	?	?
Reliability	✓	?
Relevance for practical use	✓	✗

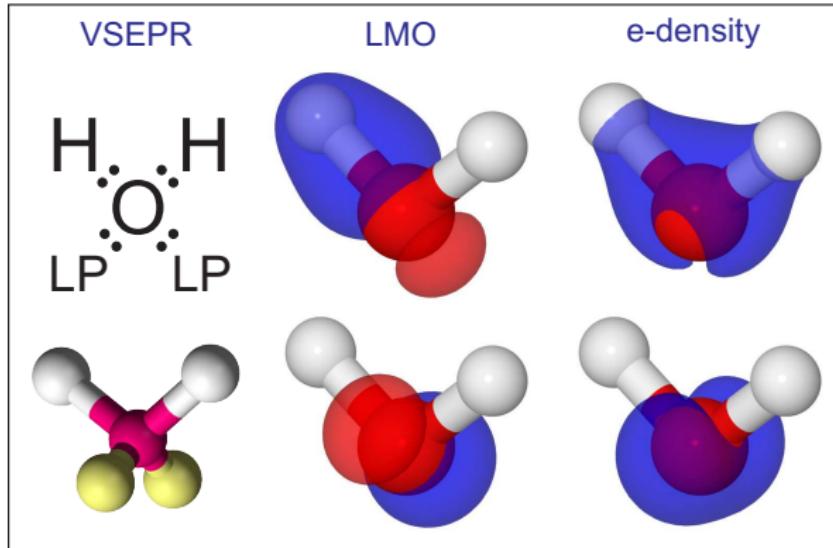
Which approach to choose?

Methods

- < 10^{2-3} atoms (molecule, UC)
 - Density Functional Theory
 - Gaussian, VASP
- < 10^{4-5} atoms, < 1ns
 - Semiempirical, O(N)-DFT
 - MOPAC
- < 10^9 atoms
 - Molecular Mechanics, QM/MM
 - LAMMPS, Tinker
- Coarse-grained (not atomistic)
 - Effective Hamiltonian, ...



Case study: Understanding chemical bonding



- Valence shell electron pair repulsion (VSEPR) theory
 - are lone pairs (LP) real or virtual?
- Hypervalency in SF_6 – $3c4e$ bonding or sp^3d^2 -hybridization?
- Directional noncovalent interactions in π -conjugated molecules and electron-rich covalent solids – secondary bonds?

Case study: Computational discovery of new materials

High-throughput screening of materials

- Skoltech: Artem Oganov, Sergei Tretiak, Andriy Zhugayevych
- The Harvard Clean Energy Project (A. Aspuru-Guzik)
- The Materials Project (founded by G. Ceder and K. Persson)
- EFRC for Inverse Design (theory by A. Freeman, A. Zunger)

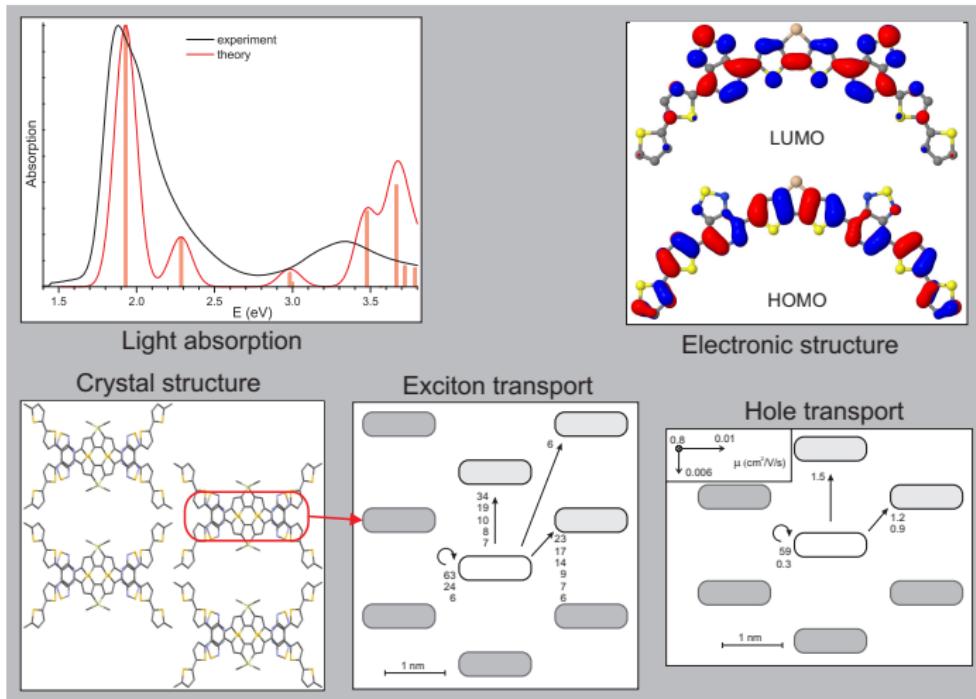
How it works e.g. for organic solar cells:

$$E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}} - E_{\text{exciton}}$$

$$eV_{\text{OC}} \approx E_{\text{LUMO}}^{\text{acceptor}} - E_{\text{HOMO}}^{\text{donor}} - 0.3 \text{ eV}$$

Case study: Calculation of material properties

Solar cells: where is the bottleneck in power conversion efficiency?

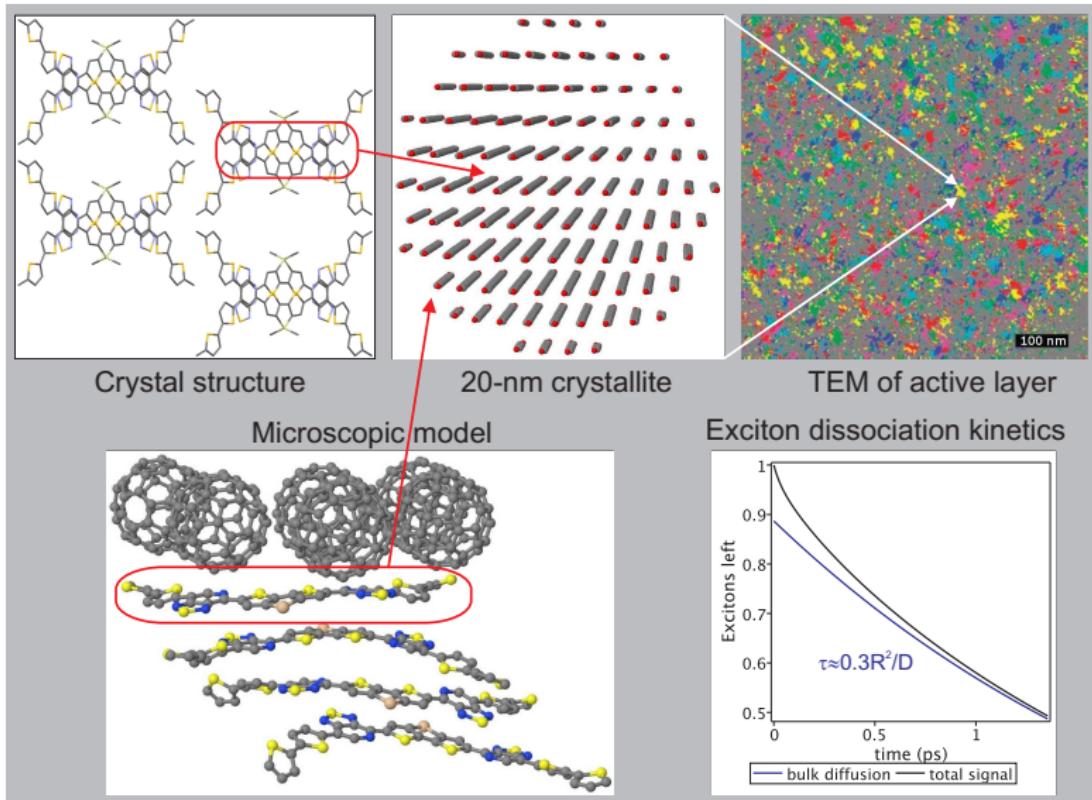


Exciton diffusion length ~ 100 nm, hole mobility $\sim 1 \text{ cm}^2/\text{V}\cdot\text{s}$

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

Case study: Simulation of processes

Explain pump-probe experiment: JACS 134, 19828 (2012); Nat Mater 11, 44 (2012)

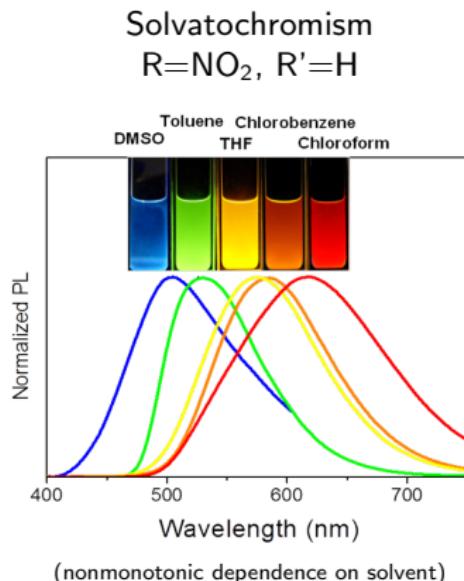


In absence of traps exciton dissociation proceeds in picoseconds

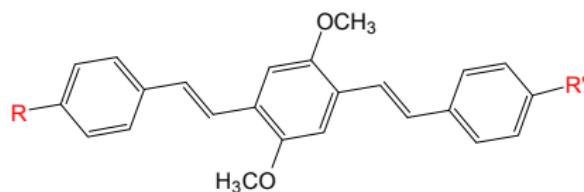
Case study: Materials design for OLEDs

Olena Postupna, 2012, 2013 internships at LANL, advisor A.Z. and Sergei Tretiak

Practical goal:
solution-processable OLED
with tunable color
Theory: explain and predict

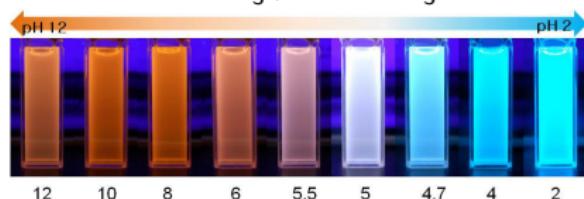


Donor-acceptor π -conjugated molecule



Halochromism

$R=NH_3^+$, $R'=NMe_3^+$



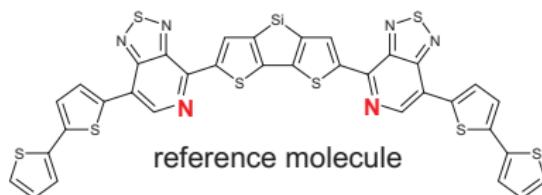
High sensitivity to chemical modifications and environment

- solvatochromism – ACS Appl Mater Int 5, 4685 (2013)
- halochromism – Chem Sci 6, 789 (2015)
- functionalization – Chem Phys (2016)

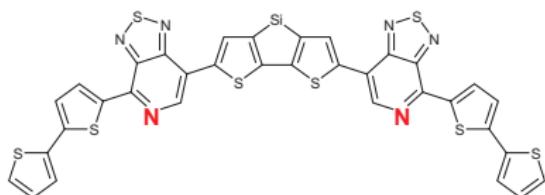
Case study: Tuning performance by isovalent substitutions

Thomas van der Poll, 2013 internship at LANL, advisor A.Z. and Sergei Tretiak

Good molecule for solar cells
(good single-crystal properties)



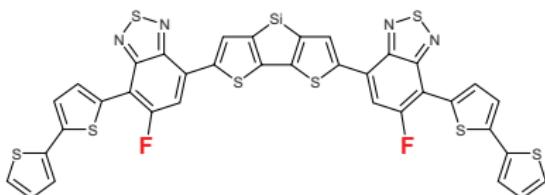
Bad performance
(nonplanar – no crystallites)



Improved hole mobility
(better intramolecular packing)



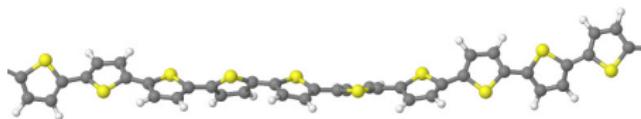
No improvements
(too floppy – high disorder)



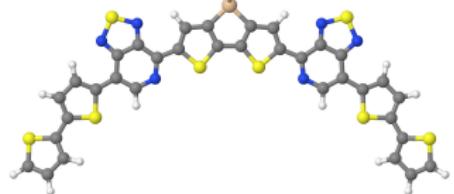
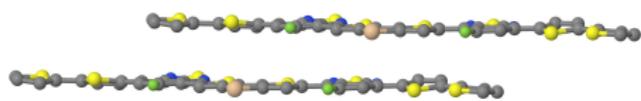
T S van der Poll, A.Z., E Chertkov, R C Bakus II, J E Coughlin, G C Bazan, S Tretiak, J Phys Chem Lett 5, 2700 (2014)

Case study: Rational design of molecular shapes

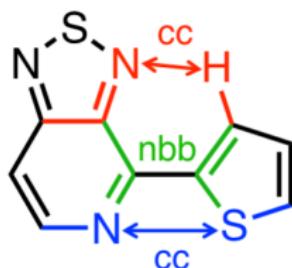
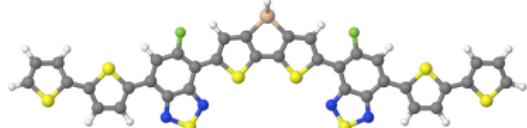
Jessica Coughlin, 2013 internship at LANL, advisor A.Z. and Sergei Tretiak



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



- Increase mobility



The interplay of the three interaction components

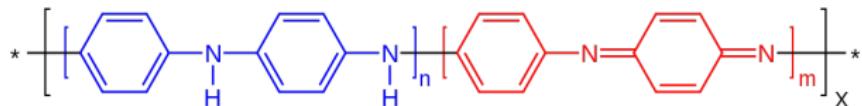
- Near-bridge bond interaction (nbb)
- Steric repulsion between contact atoms (cc)
- Electrostatics (controllable by environment)

can “lock” the dihedral or enforce nonplanar geometry
⇒ this gives us set of rules for shaping molecules

Case study: Charge transport mechanism in biopolymers

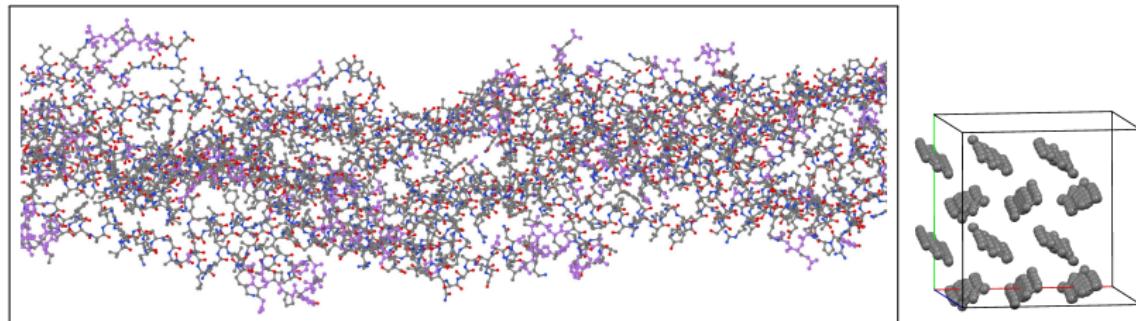
Chern Chuang, 2014 internship at LANL, advisor A.Z. and Sergei Tretiak

- Metallic conductivity in conjugated polymers ✓ heavily doped



[Nature 441, 65 (2006)]

- Metallic conductivity in biopolymers? ✗ no bandwidth

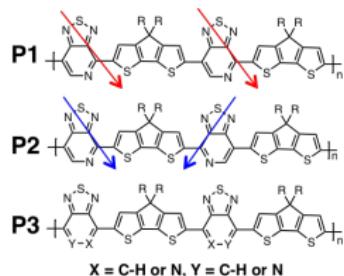


Ionized sites in resonance with π -conjugated system – mixed electronic-ionic transport

Case study: How regiochemistry influences conductivity

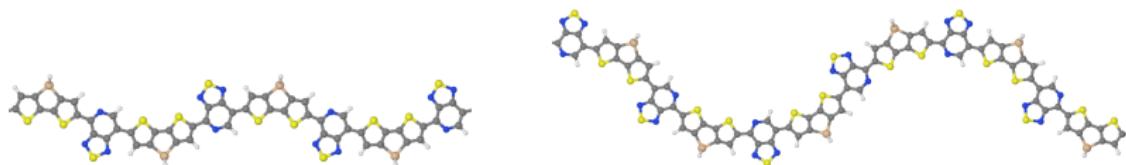
Jessica Coughlin, 2014 internship at LANL, advisor A.Z. and Sergei Tretiak

Experiment: L Ying JACS 133, 18538 (2011)



polymer	P1	P2	P3
$E_{\text{HOMO}}/E_{\text{LUMO}}^a$ [eV]	-5.07/-3.70	-5.16/-3.70	-5.23/-3.69
E_g^{cvb} [eV]	1.37	1.46	1.54
$\lambda_{\text{max}}^{\text{sol}}/\lambda_{\text{max}}^{\text{film}}$ [nm]	930/920	885/885	880/870
E_g^{optd} [eV]	1.09	1.12	1.15
μ_{sat}^c [$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$]	0.4 (0.3)	0.6 (0.5)	0.005 (0.005)
$I_{\text{on}}/I_{\text{off}}$	2×10^3	2×10^4	1×10^4

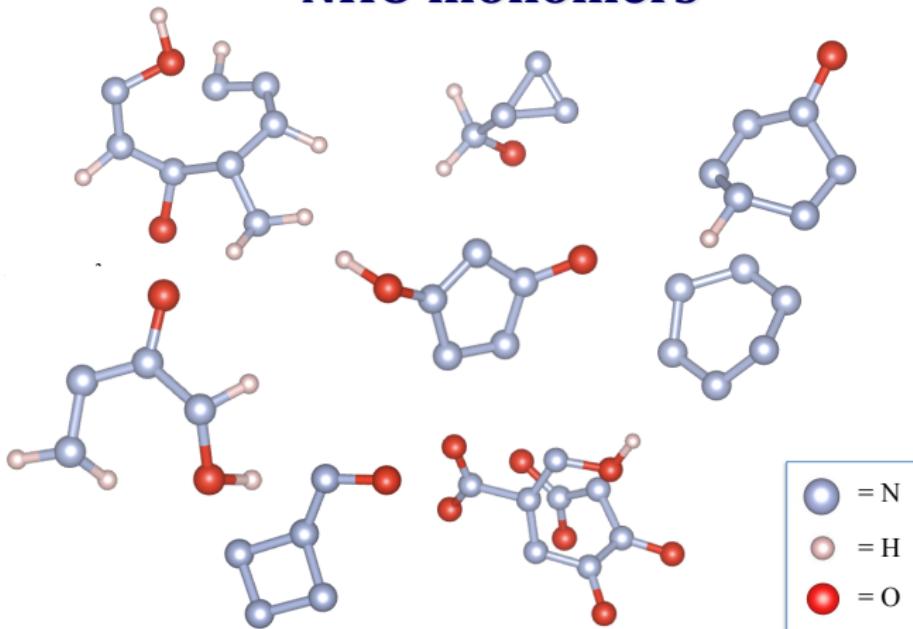
Theory: Electronic structure of ideal polymer is insensitive to regiochemistry
⇒ The difference is in intramolecular conformations influencing packing



Student project: Is there a life on Jupiter?

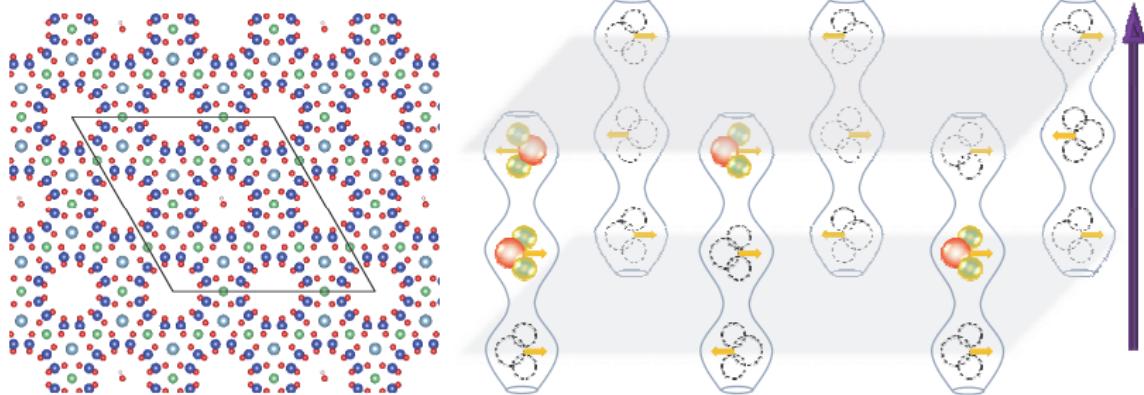
Anastasia Naumova, 2015, advisor Artem Oganov

NHO monomers



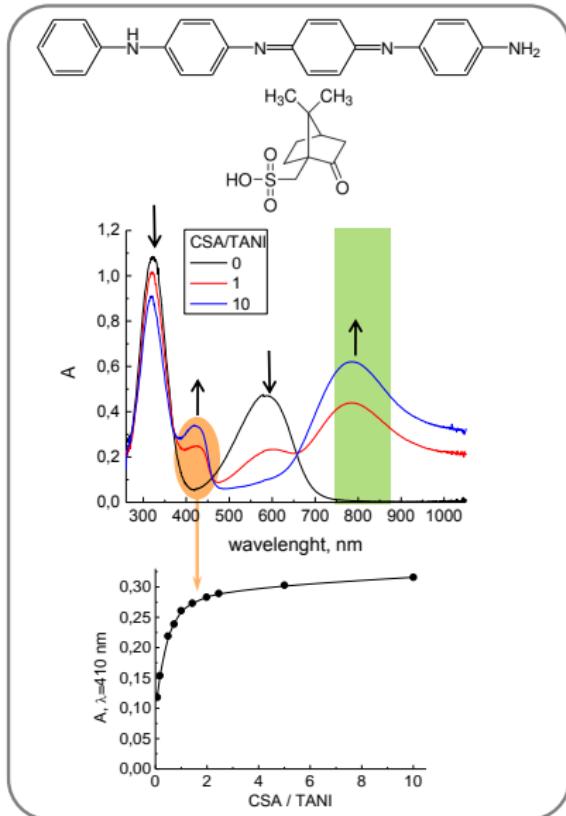
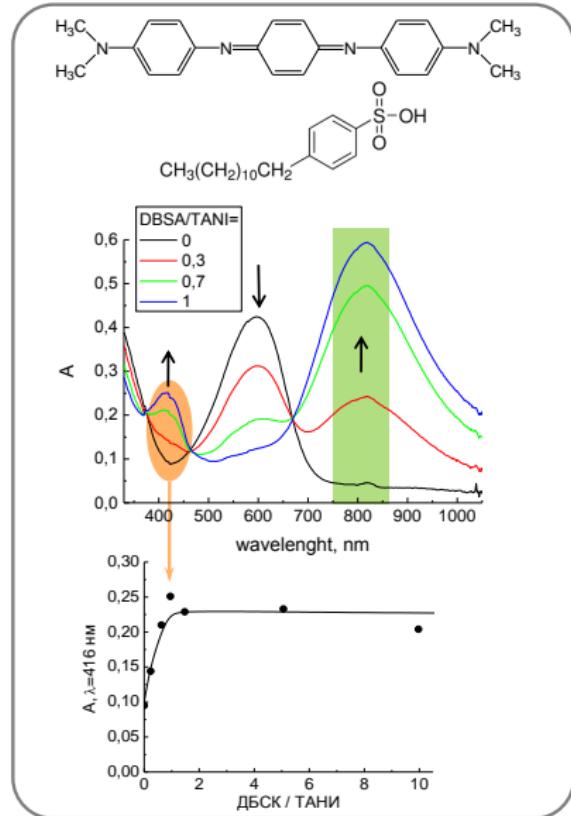
Student project: Ferroelectric water

Mikhail Belyanchikov, 2015, advisor Sergei Tretiak and Boris Gorshunov (MIPT)



Student project: Solvent-structure-spectrum relationship

Pavel Kos, 2015, advisor Alexander Chertovich (MSU)



Summary: when theoretical modeling is essential

- Tool to obtain detailed information on specific properties (intrinsic properties of a material)
- Generally much “cheaper” than experiment
- Interpretation of experimental data (conductivity mechanism)
- Suggesting specific structural modifications for synthesis (tune emission color)
- Establishing structure-property relationships (polar substrate – low electron mobility in graphene)
- Discovery of new materials/properties (graphene)

Course logistics

- Course web-page
- Syllabus
- Schedule and timeline
- Required software
- Literature