Computational Chemistry and Materials Modeling

Materials Modeling: Overview

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Outline

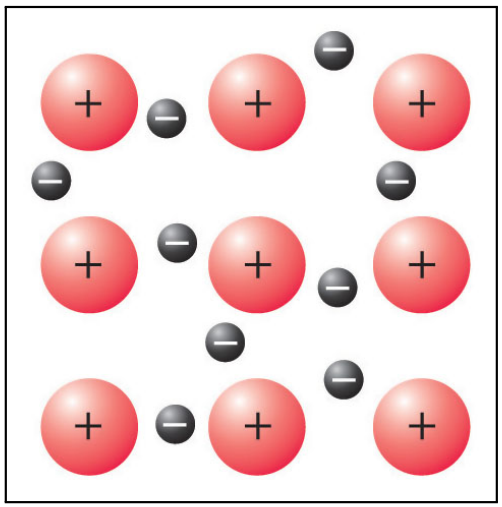
- Content of Part 2 of the course
  - 3 lectures on fundamentals of Materials Modeling
  - 2-4 lectures on software developed by Skoltech CMS faculty (Gonze, Levchenko, Oganov, Shapeev)
- Goals of Part 2 of the course
- Illustrative examples

Reminder: 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)

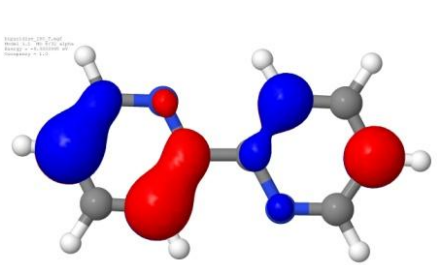


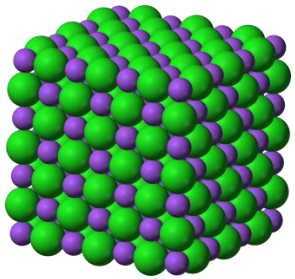
- Computational Chemistry = solving Coulomb problem for $\gtrsim$ 10 particles
- Materials Modeling = relating that solution to real world

Reminder:

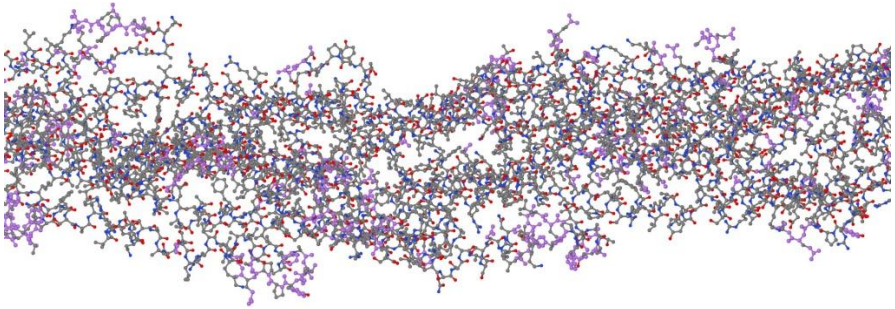
Methods

- $<10^{2\text{-}3}$ atoms (molecule, UC)
  - Density Functional Theory
  - Gaussian, VASP

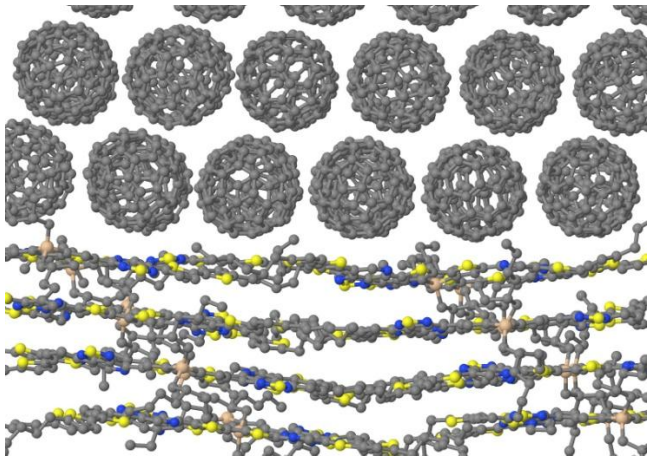




- $<10^{4\text{-}5}$ atoms, <1ns
  - Semiempirical, O(N)-DFT
  - MOPAC

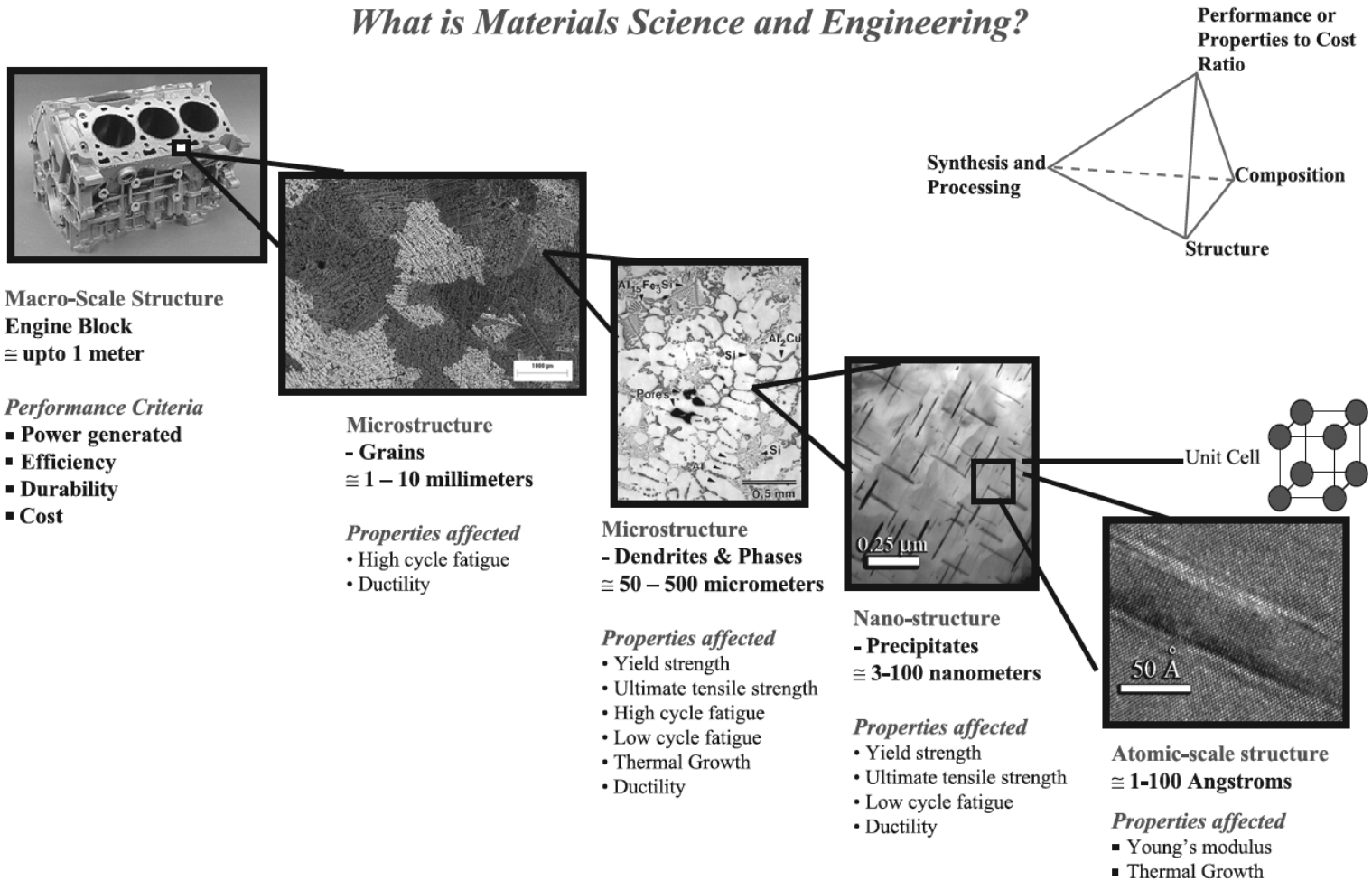


- $< 10^{9}$ atoms
  - Molecular Mechanics, QM/MM
  - LAMMPS, Tinker



- Coarse-grained (not atomistic)
  - Effective Hamiltonian, …

We cannot fully describe functional properties of real-world materials from purely ab initio modeling



A real-world example of important microstructural features at different length-scales, resulting from the sophisticated synthesis and processing used, and the properties they influence. The atomic, nano, micro, and macro-scale structures of cast aluminum alloys (for engine blocks) in relation to the properties affected and performance are shown. The materials science and engineering (MSE) tetrahedron that represents this approach is shown in the upper right corner.

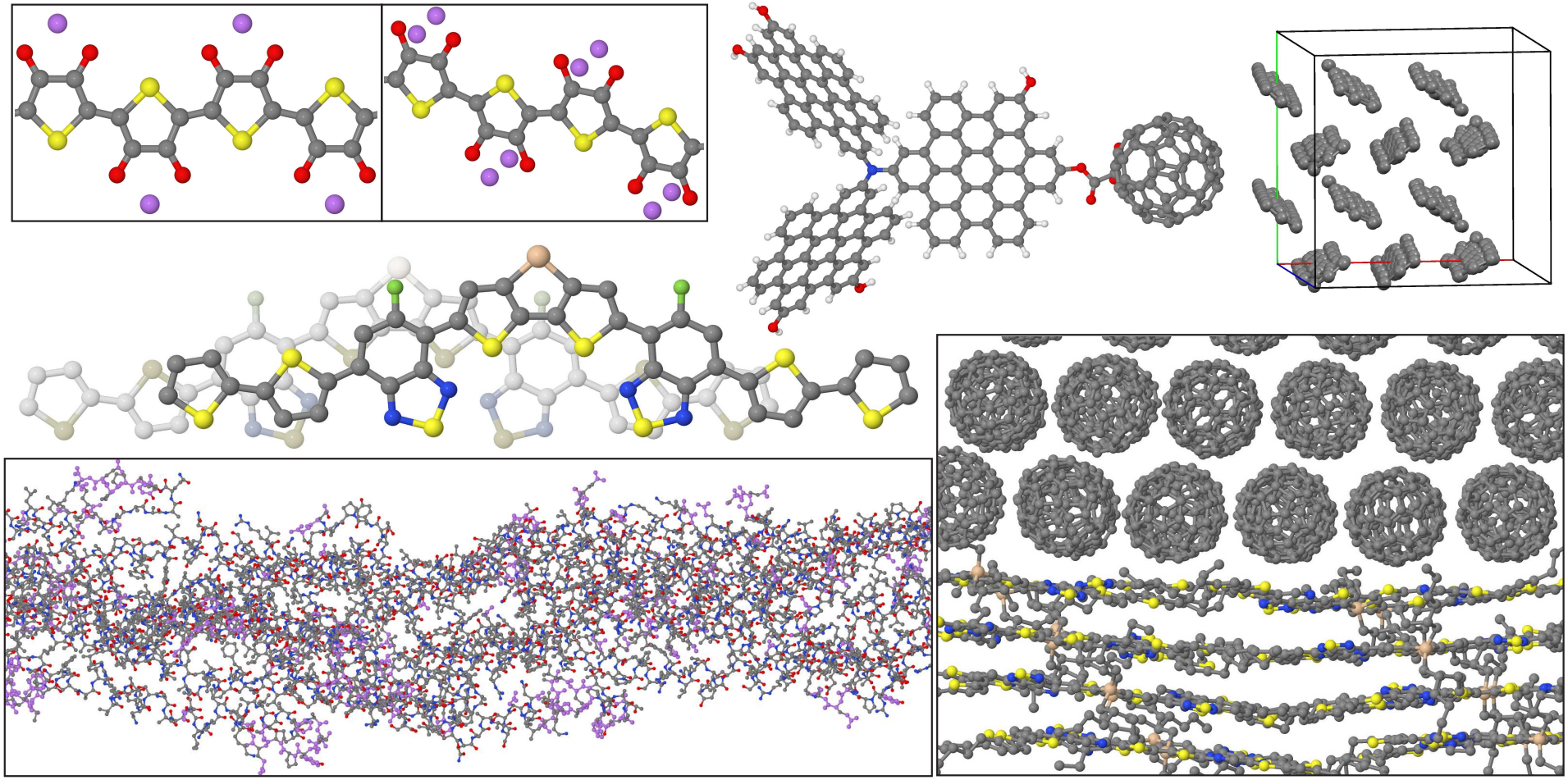
(Illustrations Courtesy of John Allison and William Donlon, Ford Motor Company)

Solution

- Option 1: use empirical models (fitted by experiment)
- Option 2: use first principle approach but with approximations
  - Approximate electronic structure Lecture 7
    (tight binding, empirical Hamiltonian)
  - Avoid explicit consideration of electronic system Lecture 8
    (interatomic potentials, force fields)
  - Coarse grain molecular degrees of freedom
    (united-atom models)
  - Coarse grain dynamics
    (accelerated dynamics, Monte Carlo sampling)
  - Use embedding and fragmentation
  - Use descriptors and machine learning Lecture 9
  - Use multiscale modeling

Methods become nontransferable (material- and problem-dependent)
What we calculate is usually not what we measure

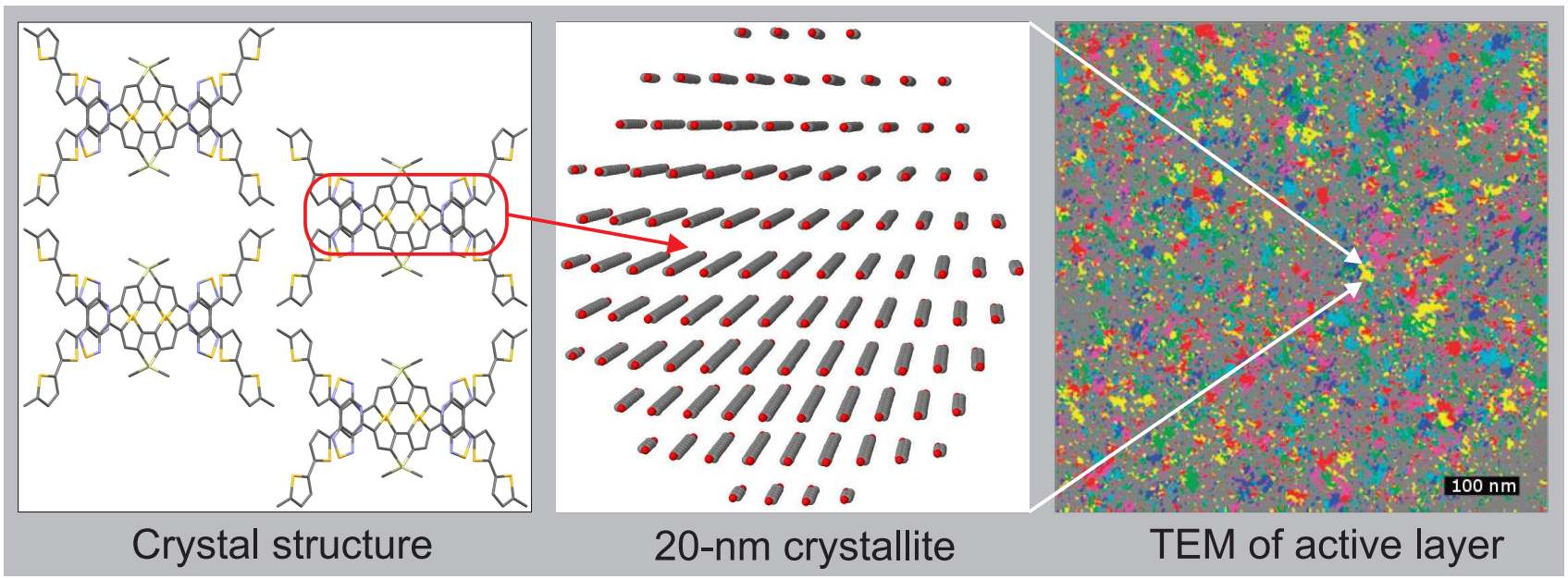
Illustrative example: organic semiconductors



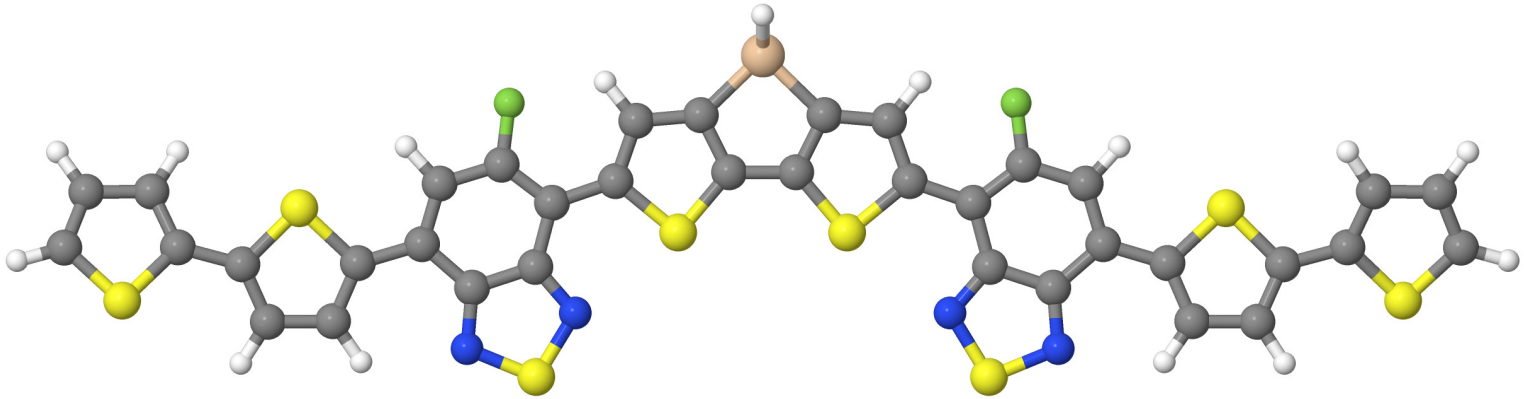
- Optical properties: UV-Vis absorption, Raman spectra
- Transport properties: charge carrier mobility

Scales

- Single crystals: unit cell with 50-1000 atoms
- Homogeneous at scales 20-200 nm ($10^6 - 10^9$ atoms)



Special features: quasi-1D π-conjugated systems



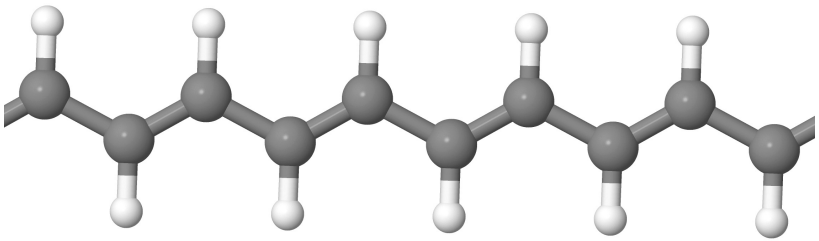
- Have block structure with few interconnections per block
  $\Longrightarrow$ Use monomers as structural building blocks
- Each block is rigid, limited number of local structural patterns
  $\Longrightarrow$ Simple force fields should work well
- The π-conjugated system of each block is closed-shell
- Inter-block couplings ~ 1 eV $\ll$ bandgap of blocks
  $\Longrightarrow$ Use to coarse grain electronic system
- Intermolecular couplings ~ 0.1 eV $\ll$ bandgap of molecules
  $\Longrightarrow$ Defines additional scale for coarse graining of electronic system

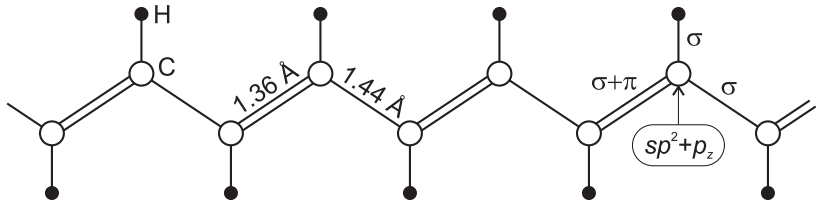
$\Longrightarrow$ *There must be a set of methods well-tuned for accurate calculation of electronic structure of this class of materials*

Universal approaches are not always applicable

What is the smallest real-world material for which majority of mainstream approaches fail?

Trans-polyacetylene – 5 electrons in repeating unit (10 in UC)



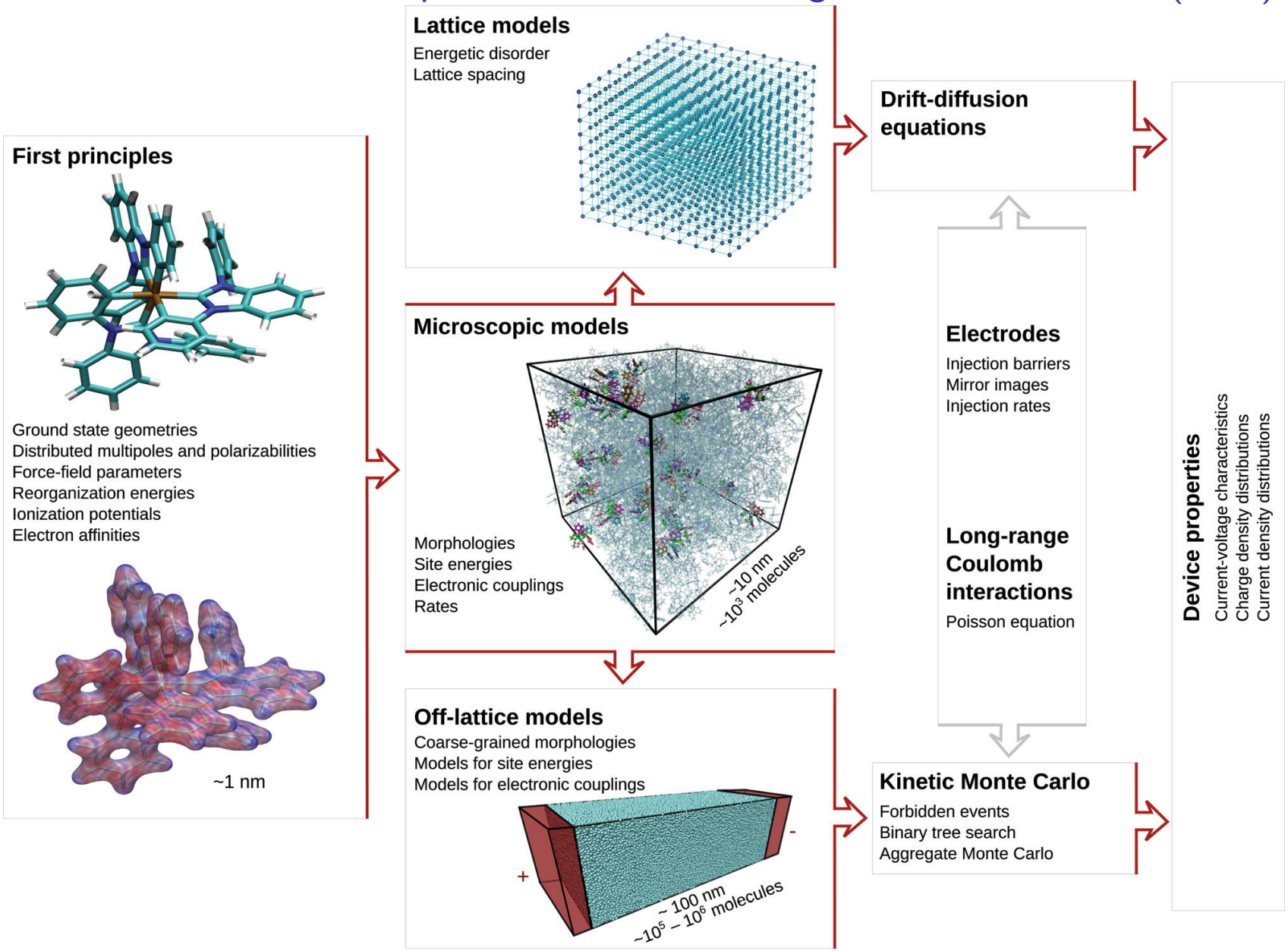


	isolated polymer		crystal		
Method	E_{gap}(eV)	BLA(Å)	BLA(Å)	b(Å)	c(Å)
PBE	0.1	.01	0	7.5	3.8
HSE06	0.8	.05	?		
PBE0	1.5	.06			
experiment	≈2	.08	.09	7.3	4.2
CAM-B3LYP	3.8	.09	.09	7.6	4.3

6-31G* is used for isolated polymer and all CAM-B3LYP calculations
D3 is used for crystals in PAW600 for PBE and HSE06

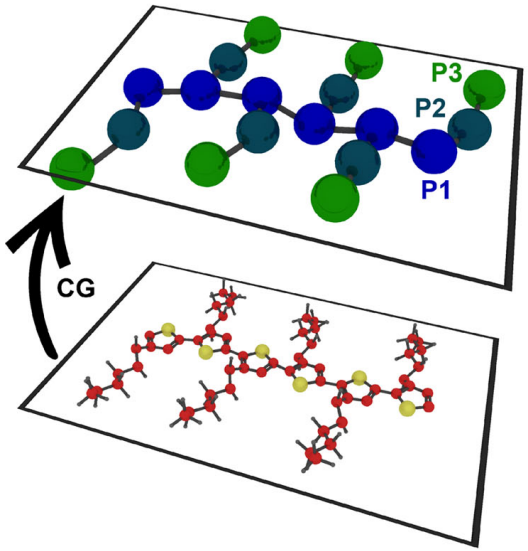
Multiscale modeling is the most appropriate

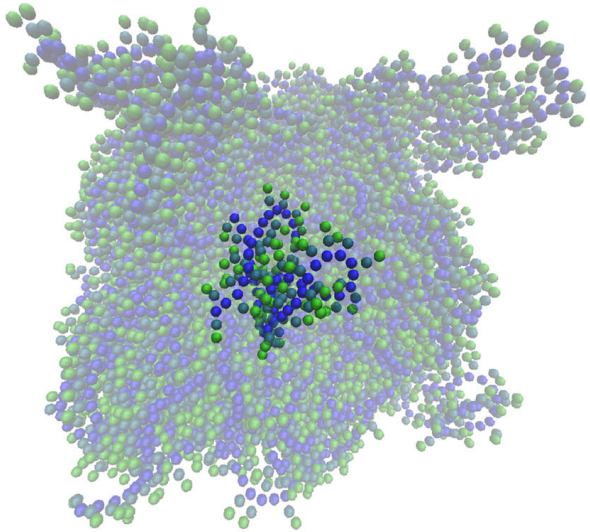
D Andrienko, Multiscale Concepts in Simulations of Organic Semiconductors (2018)

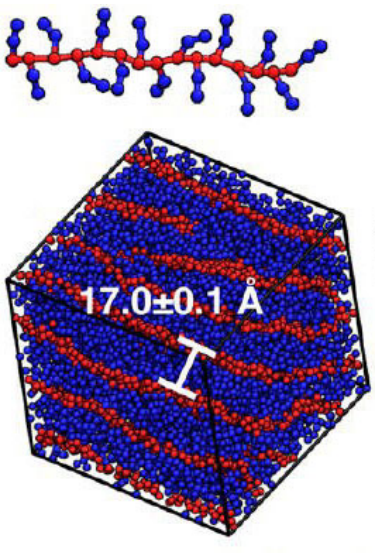


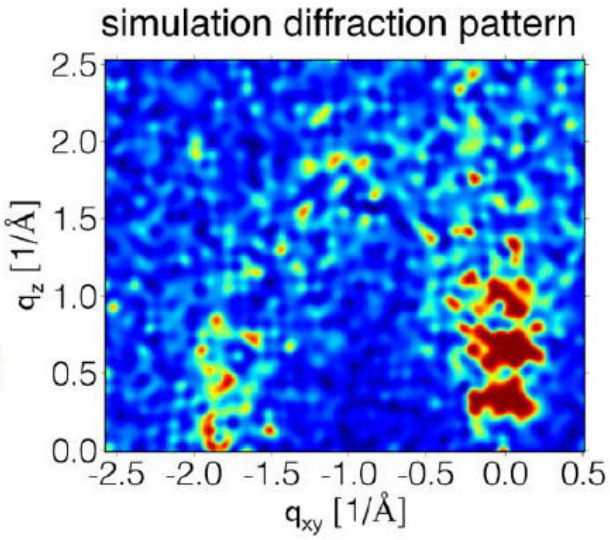
Large scale structure: use coarse graining

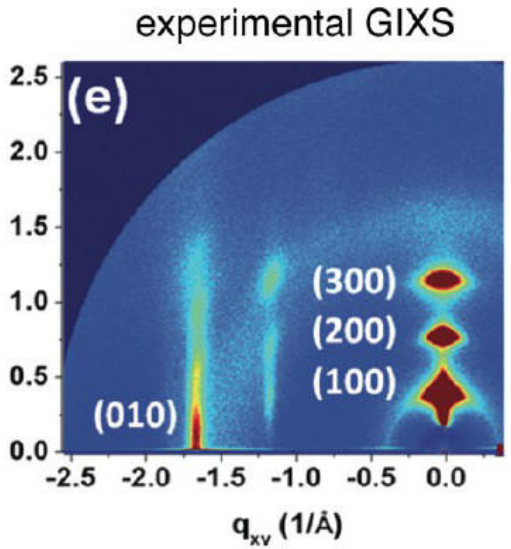
M L Jones, E Jankowski, Molec Simul 43, 756 (2017)





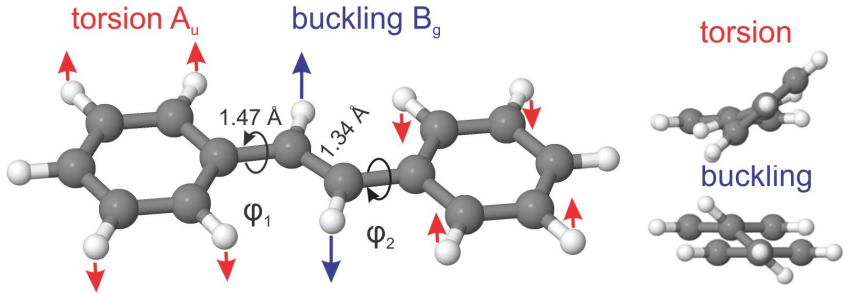


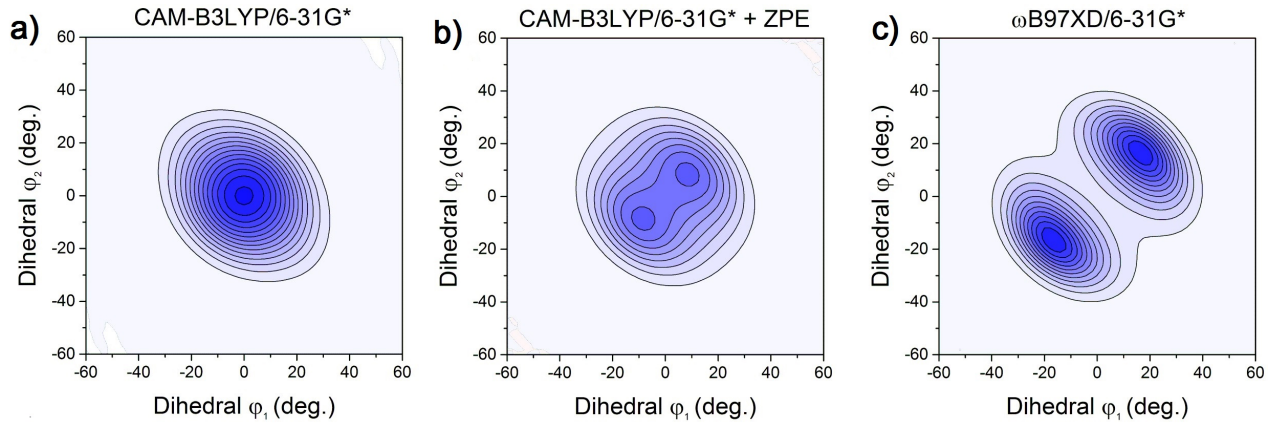


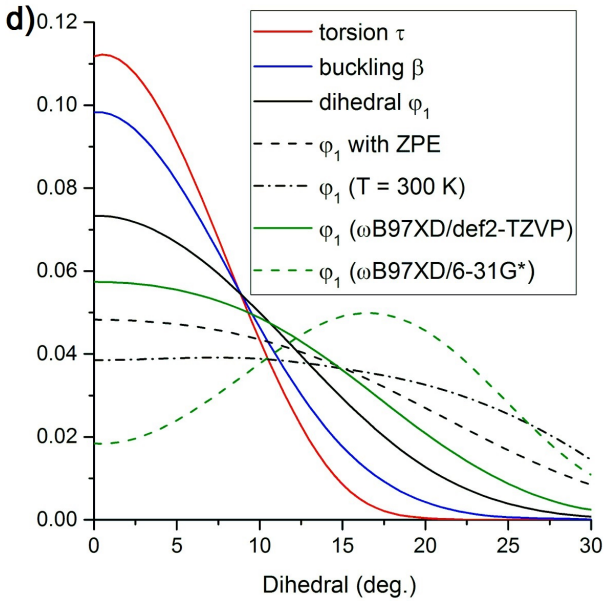


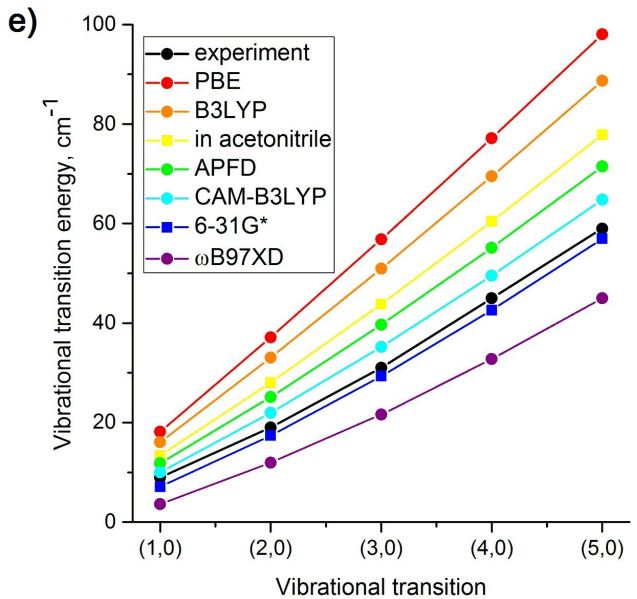
High-resolution structure: use accurate approaches

J Phys Chem Lett 10, 3232 (2019)



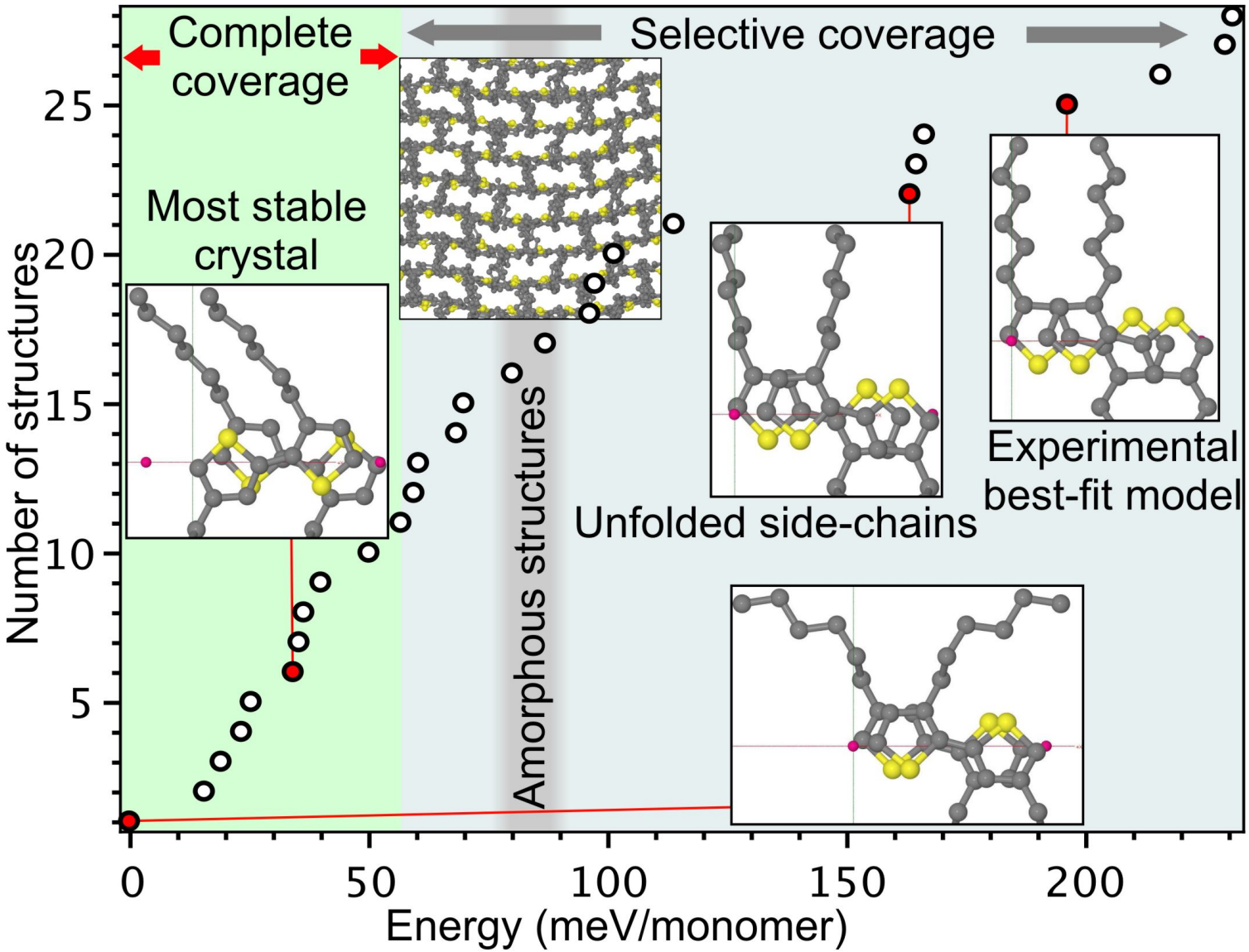






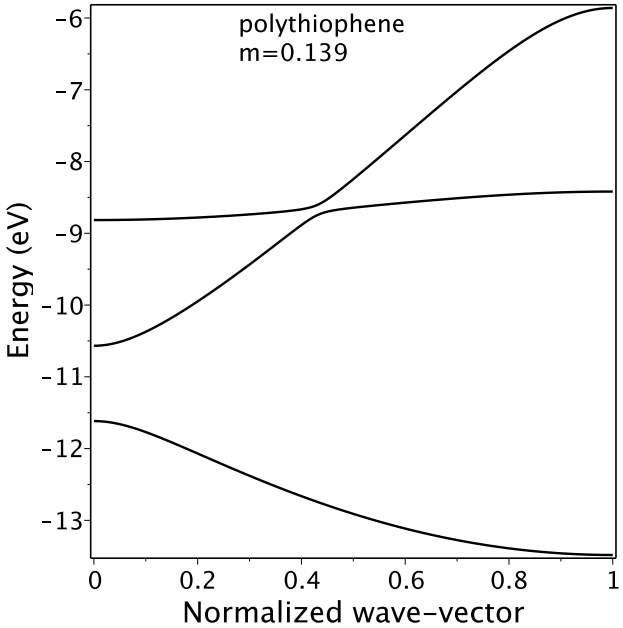
Polymorphism: use ad hoc approaches

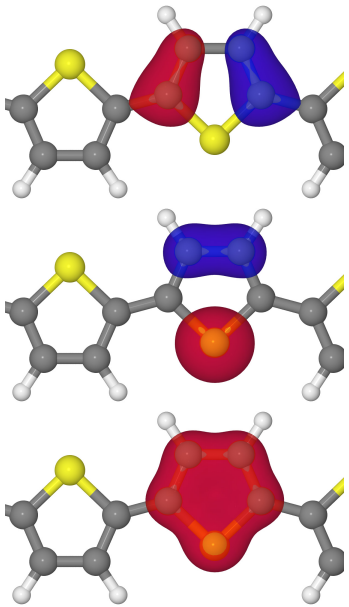
J Phys Chem C 122, 9141 (2018)

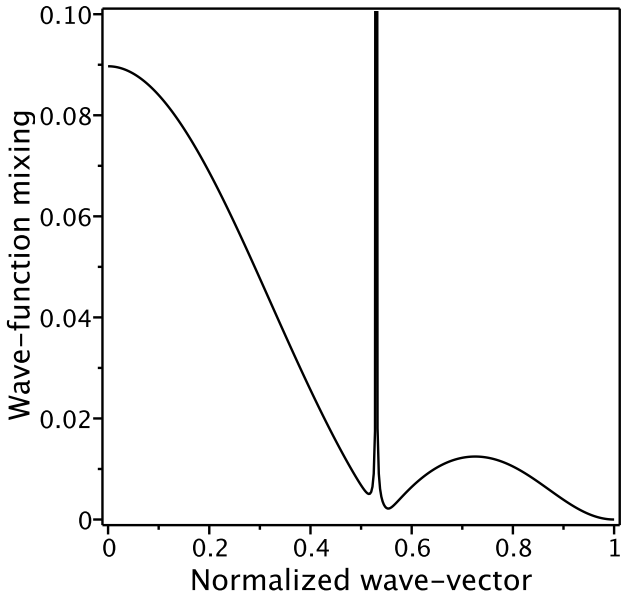


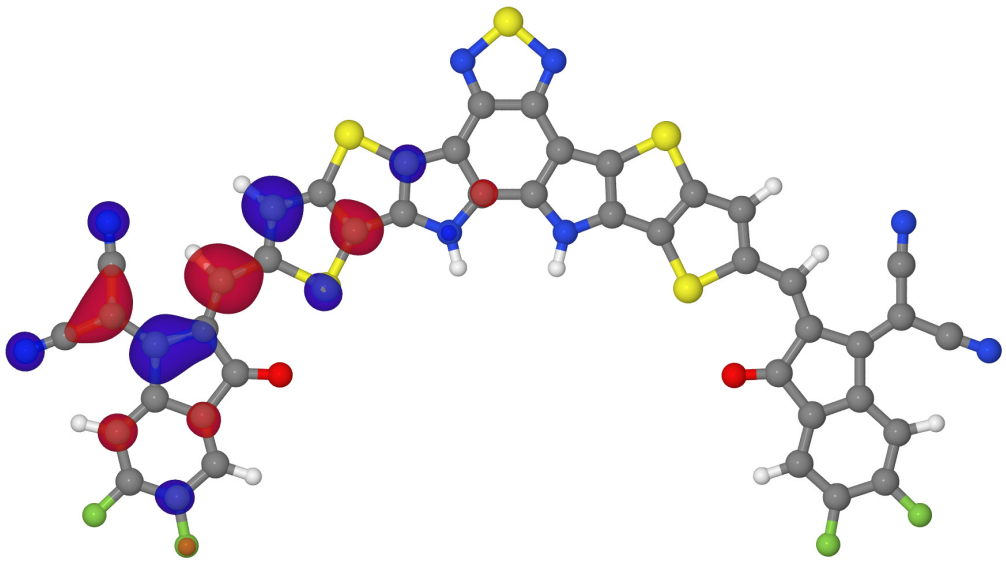
Electronic structure: coarse grain to monomers/molecules

Chem Mater 33, 966 (2021); Chem Sci 8, 1146 (2017); Annu Rev Phys Chem 66, 305 (2015)



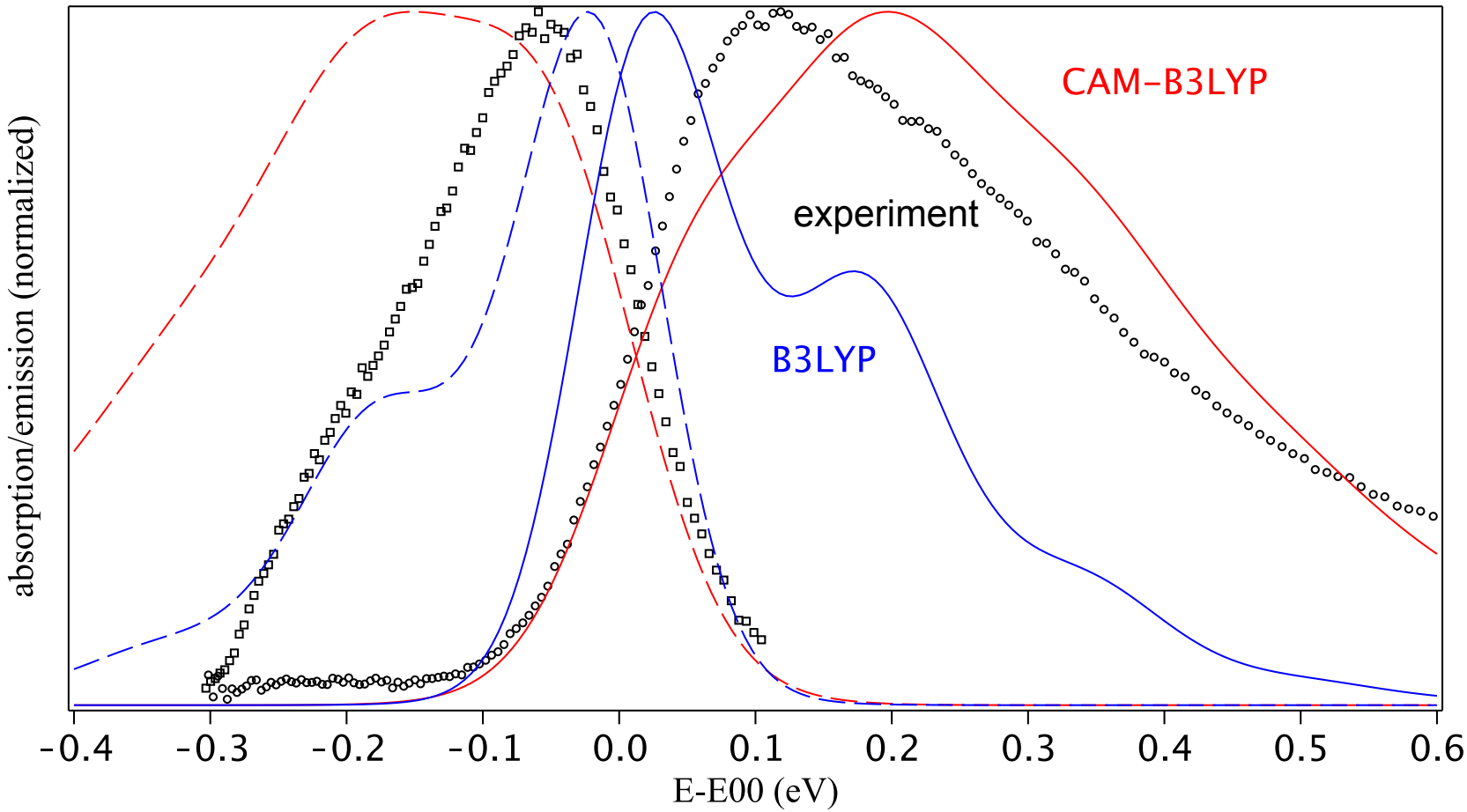






UV-Vis spectra in solution: well developed methodology

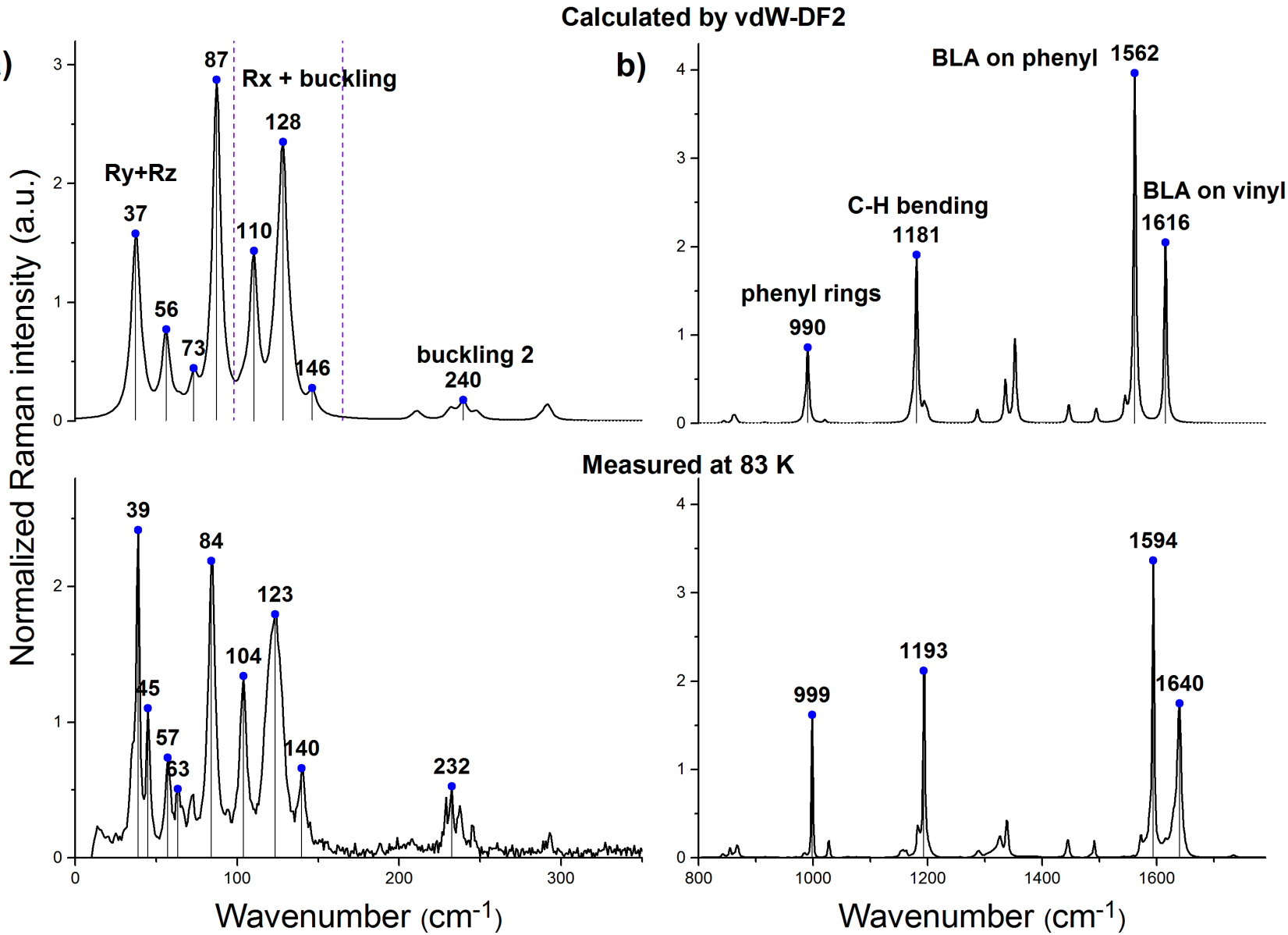
Annu Rev Phys Chem 66, 305 (2015); J Phys Chem Lett 10, 4632 (2019); Chem Phys 481, 133 (2016)



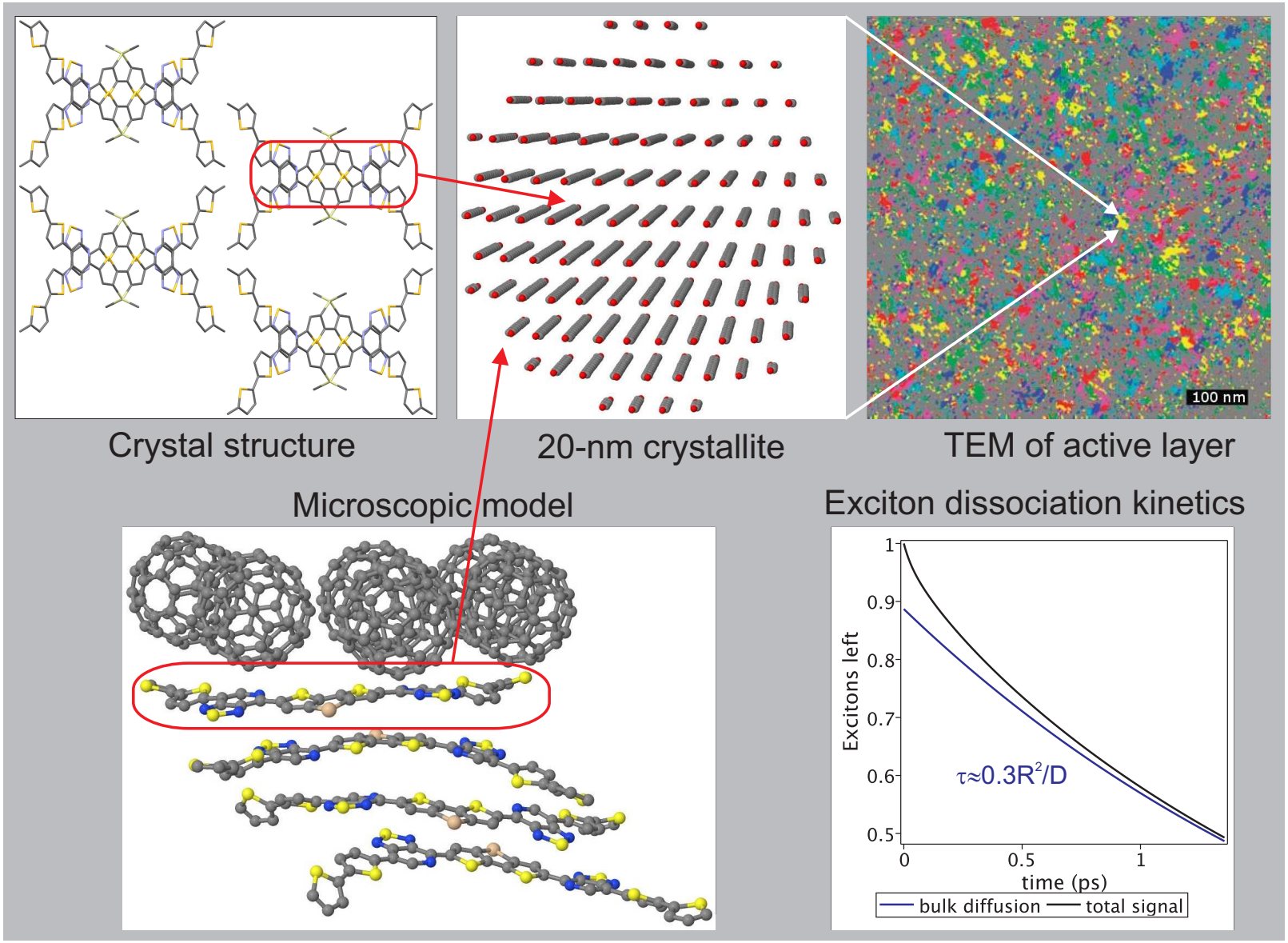
Don't forget to compare at least 2-3 methods

Raman spectra: not trivial for resonance Raman

J Phys Chem Lett 10, 3232 (2019)



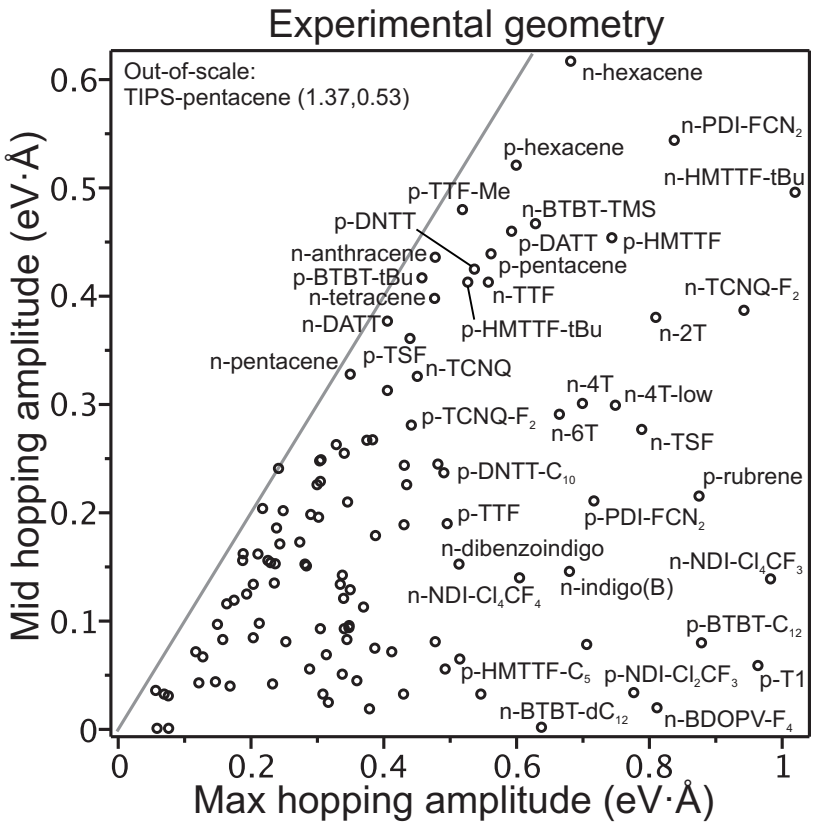
Transport modeling: well developed in hopping regime

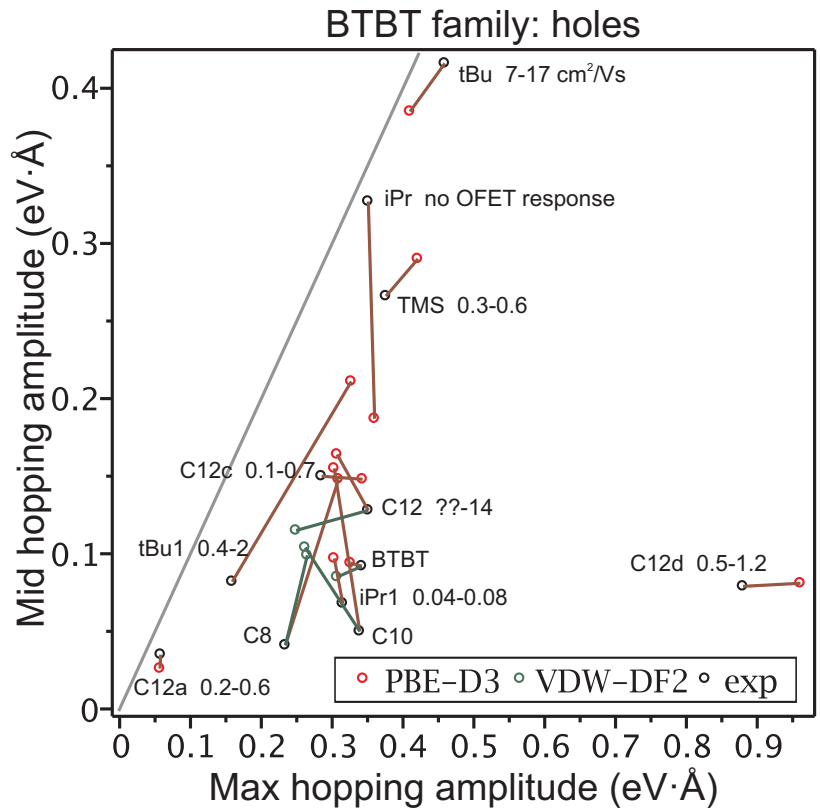


In absence of traps exciton dissociation proceeds in picoseconds

Screening for charge carrier mobility: use descriptors

Hopping amplitudes* for 50 crystals including all high-μ [Chem Soc Rev 47, 422 (2018)]





$\mu = 0.95 \frac{D(t^2)}{W(T)^2} \frac{\mathrm{cm}^2}{\mathrm{V \cdot s}}$, square root of eigenvalues of $D(t^2)$ are hopping amplitudes