

Modeling electronic structure of complex organic semiconductors: Electronic coarse-graining

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FOR POLYMER RESEARCH

Outline

- 1) Self-introduction, 2) Motivation, 3) Methodology, 4) Applications

Self-introduction

Education and work experience (before MPIP)



and



- M.S. in Physics from Kyiv State University
- Ph.D. in Solid State Physics, Institute of Physics (Kyiv)
- Institute of Physics, Kyiv State U, U Houston, LANL, Skoltech U

Teaching

- 1000 students, 50 course-years, 10+ courses in Phys/Math/MatSci
- 10+ electronic handbooks and lecture notes
- Available online at zhugayevych.me (lecture notes are in Ukrainian)

Research

- Website cmsos.github.io including FAQ on organic semiconductors
- Open-source code: MolMod (first-principle), LatticeTools (empirical)
- Unique methodology: Electronic coarse-graining – **main subject**
- Next 4 slides relevant for collaborations at MPIP

Free-time activities

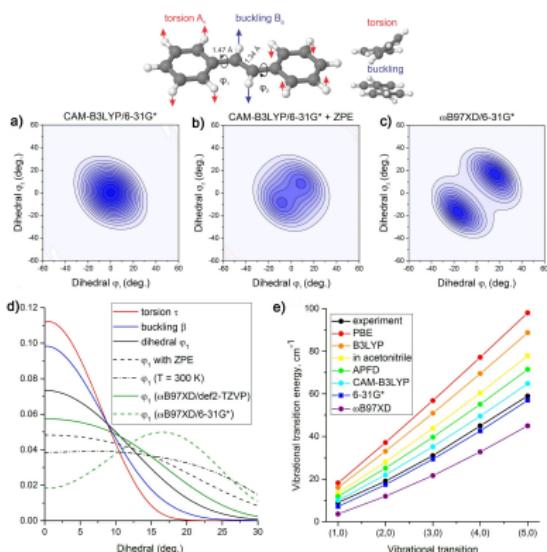
- Puzzle solving [J Phys A 58, 025209 \(2025\)](https://doi.org/10.1088/1751-8121/ac9f3c) – took 20 years

Structural studies: slide 1 of 2

(first-principles at DFT-D accuracy, up to 1000 atoms in simulation cell)

Molecules

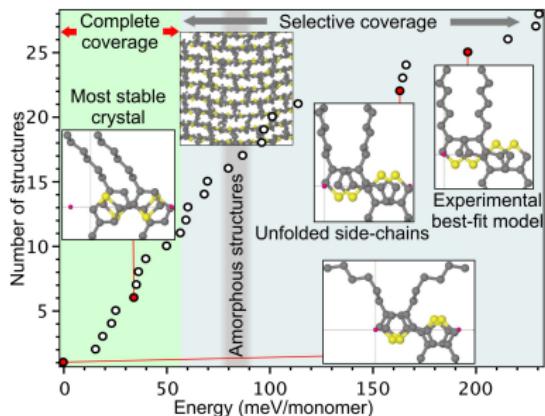
Is stilbene (and PPV) planar or not?



J Phys Chem Lett 10, 3232 (2019)

Structure prediction for polymers

What is the local structure of P3HT?

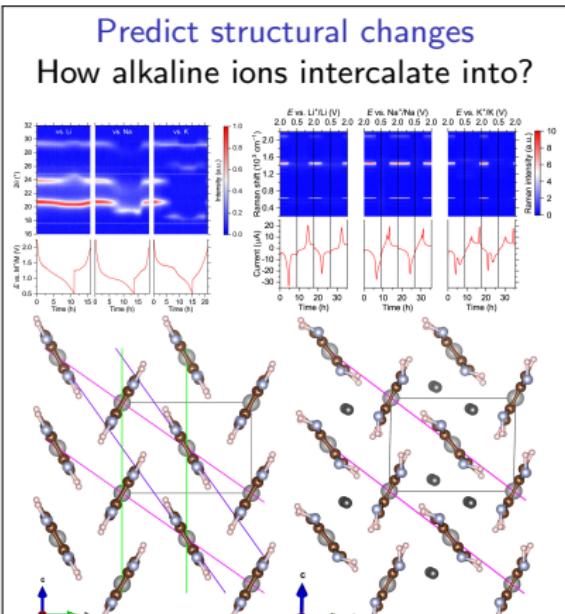


J Phys Chem C 122, 9141 (2018)

Ongoing efforts:
cmsos.github.io/escp

Structural studies: slide 2 of 2

(first-principles at DFT-D accuracy, up to 1000 atoms in simulation cell)

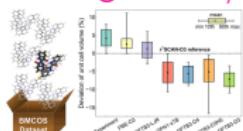


Ongoing efforts: impurities creating electronic traps

Computer-aided design of materials

- Structure refinement
 - ▶ from experiment
 - ▶ from structural models
 - ▶ from force field models

Benchmarking methods
cmsos.github.io/bmcos



JCTC 19, 8481 (2023) – 67 crystals

- Exploring novel architectures
 - ▶ frameworks
 - ▶ 2D/3D polymers
 - ▶ wiremesh Chem Mater 33, 966 (2021)
 - ▶ nonplanar π -systems
 - ▶ interdigitated herringbone

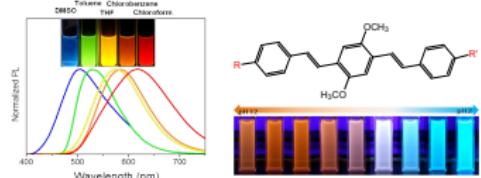
Electronic properties of materials: slide 1 of 2

(scalable approaches \Rightarrow multiscale modeling, DFT-parametrized effective Hamiltonian)

Electronic/vibrational spectroscopy

Commonly used to probe local structural and electronic properties

- Derive structural information
J Phys Chem Lett 10, 3232 (2019) – stilbene
Chem Sci 13, 8161 (2022) – charging
- Screen out inaccurate methods
Chem Sci 13, 8161 (2022) – by bandgap
- Understand spectral changes



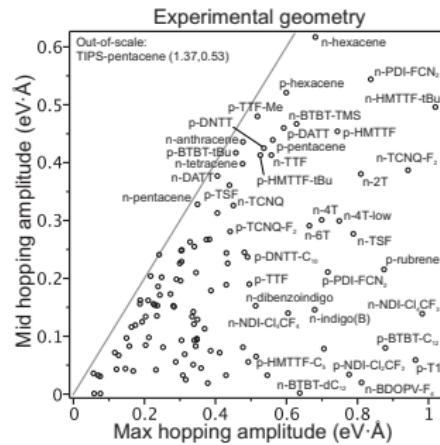
ACS Appl Mater Interfaces 5, 4685 (2013)

Chem Sci 6, 789 (2015)

Chem Phys 481, 133 (2016)

Charge carrier transport

How to quickly estimate mobility?



(ongoing project)

What is the origin of nonmonotonic temperature dependence of luminescence kinetics?

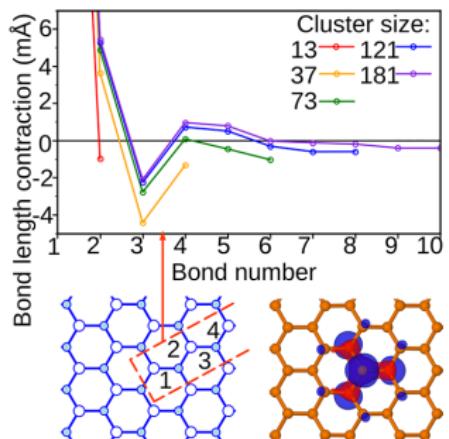
Low Temperature Physics 28, 706 (2002)

Electronic properties of materials: slide 2 of 2

(scalable approaches \Rightarrow multiscale modeling, DFT-parametrized effective Hamiltonian)

Polarons, electron-phonon dynamics

Do small polarons exist in nonpolar inorganic semiconductors?



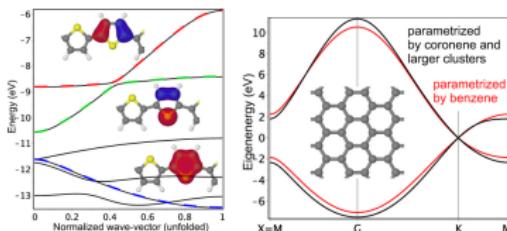
J Phys Chem Lett 12, 4674 (2021)

How to model electron-phonon dynamics faster than NAMD but more accurately than KMC?

Electronic coarse-graining

Method+code to model electronic structure of complex semiconductors

zhugayevych.me/research/ECG



J Chem Phys 159, 024107 (2023)

Ongoing efforts:

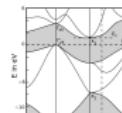
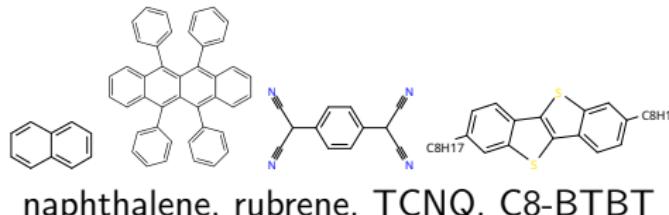
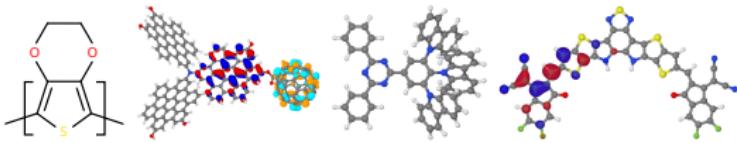
- cmsos.github.io/escp
- cmsos.github.io/tbm
(library of electronic prototypes)
- excited states
- add vibronic couplings

Motivation: Why for semiconductors we need to know/calculate electronic structure?

- Because most of their properties are determined by their electronic structure
(for theoreticians: inaccurate ground state electronic structure
⇒ inaccurate other properties)
- Prediction of many nonelectronic properties (e.g. crystal structure) also requires calculation of the electronic structure, at least for the training set

State of the art in electronic structure calculations

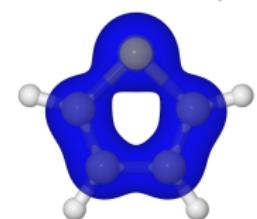
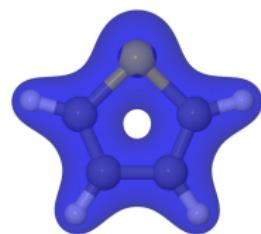
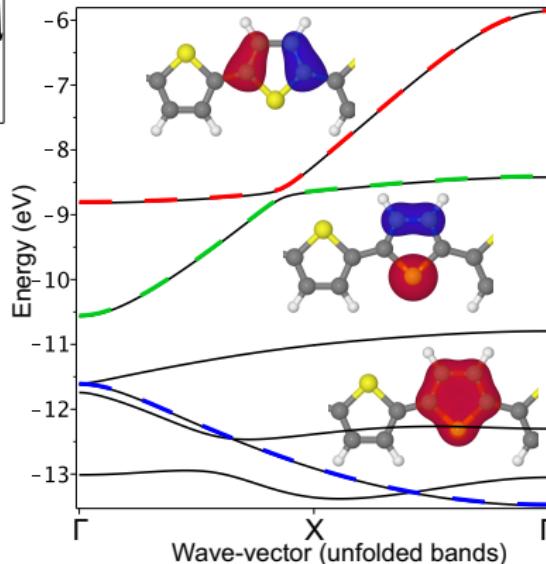
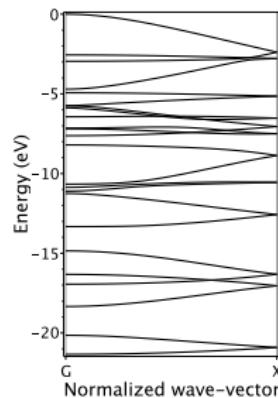
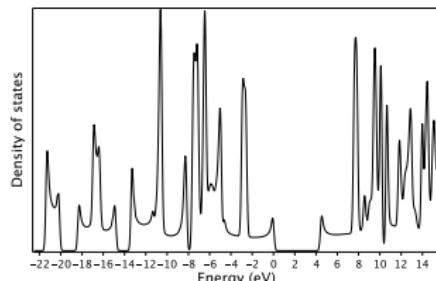
Scalable methods for solid state semiconductors \Rightarrow most accurate is DFT
 \Rightarrow we can play with density functional (no ideas for π -conjugated systems)
and **electronic basis** by reducing its size using **electronic coarse-graining**

class	basis	examples
Broadband semiconductors ("free" e/h)	plane waves	 Si, graphene, black P, GaAs
Small-molecule organic semiconductors (intermolecular hopping)	HOMO /LUMO	 naphthalene, rubrene, TCNQ, C8-BTBT
Other organic semiconductors (intra- and intermolecular dynamics)	fragment HOMO /LUMO	 polymers, large molecules, MOF, OLED, OPV

Goal is to model complex organic semiconductors at level of small-molecule ones:
1) black-box, 2) scalable, 3) compatible technology, 4) controllable accuracy

Electronic coarse-graining: example of polythiophene

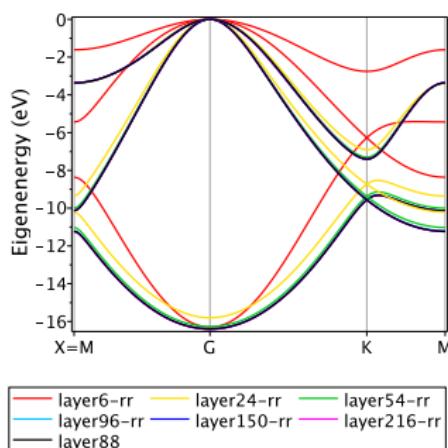
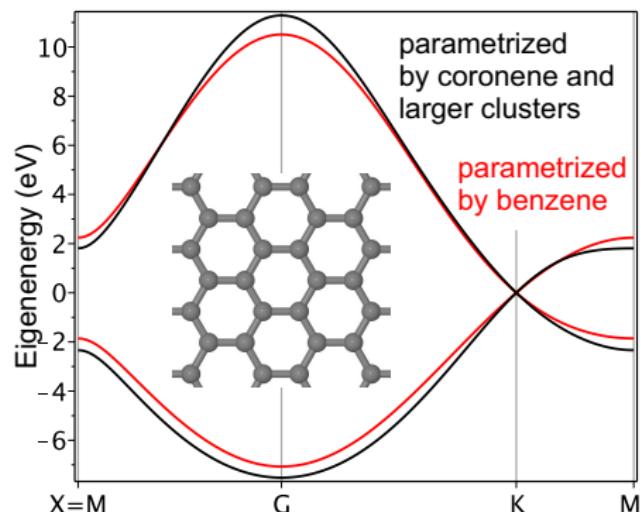
(valence band of single planar polythiophene chain, min basis = 2 LMOs per monomer)



The proposed approach solves electronic structure problem for any π -conjugated system which can be fragmentized into π -closed-shell monomers

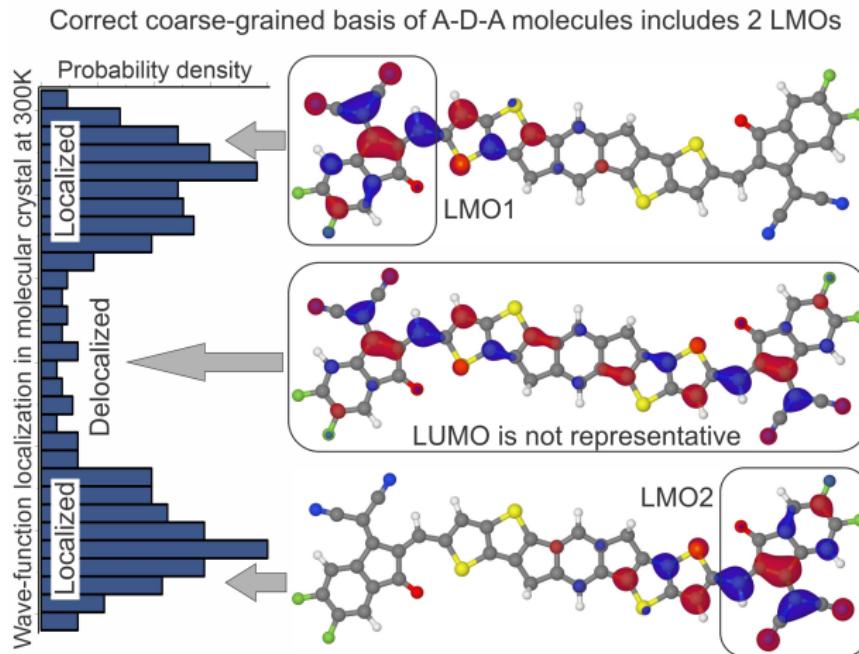
Electronic coarse-graining: example of graphene

The same methodology can be applied to other semiconductors, e.g. to calculate electronic structure of infinite systems with methods available only for finite systems



Why HOMO/LUMO basis is deficient for large molecules?

JCP 159, 024107 (2023)



MO states are statistically insignificant and transient at sub-ps scale

For molecular solids, the geometry is sampled by classical MD.

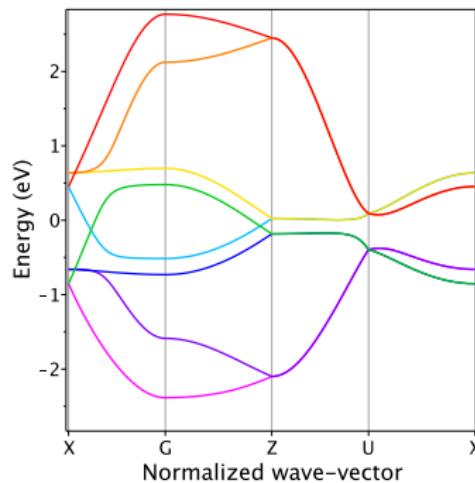
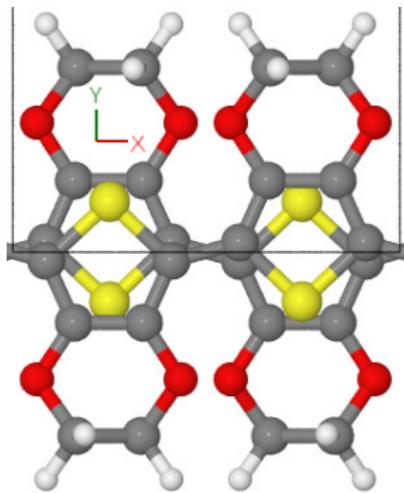
For molecules, quantum effects are considered by sampling thermal vibrations.

Applications: Electronic structure of crystalline polymers

Challenges

- Combination of strong intrachain and weak interchain couplings
- Unit cell and supercell are too large for brute force methods
- No experimental crystal structure [JPCC 122, 9141 \(2018\)](#); [JCTC 19, 8481 \(2023\)](#)

⇒ Little is known about electronic structure of crystalline polymers



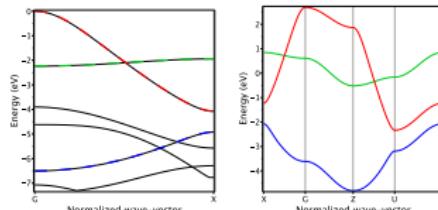
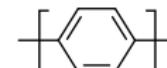
Electronic coarse-graining allows for calculation of electronic structure of polymers at the level of accurate density functionals

Fundamental questions that can be addressed

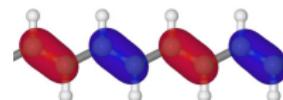
(Electronic structure of PPP and thiophene-based polymers: poly-T, P3HT, PEDOT)

- How large are electronic couplings?
250 meV in perfectly aligned π -stacks.

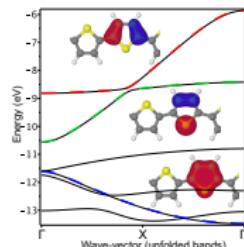
Max-symmetry π -stack at 3.8 Å



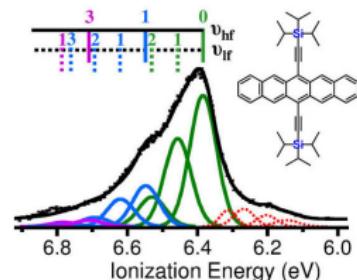
- What prevents perfect alignment?
Flat PES wrt to tilts and shifts.
0 to max coupling upon shift by 1 bondlength



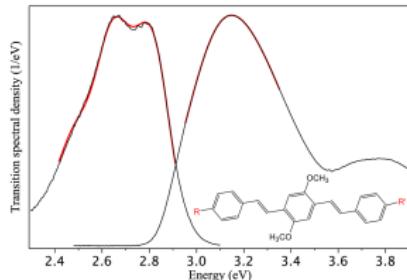
- What is the “best” thiophene-based polymer?
2D PEDOT – (1) is well-aligned and (2) has small fluctuations.
- What other guidelines we can give for thiophenes?
Localize HOMO on sulfur to increase couplings.
TT,TBT fusing is good, TTT,TTTT is not



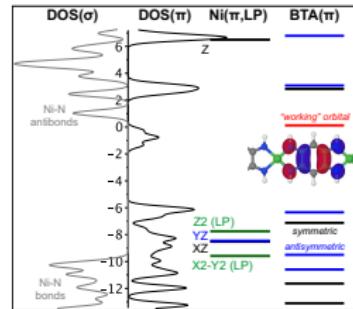
Density of electronic states in organic semiconductors (eDOS or simply DOS)



JACS 134, 14185 (2012)



Chem Phys 481, 133 (2016)



Chem Sci 13, 8161 (2022)

- Fundamental property of a molecule/material
- Measurable by spectroscopy (UPS, UV-Vis)
- Often, only edge peak position is used to get IE/EA/optical gap
- Much more informative if analyzed thoroughly (composition)
- Can be misinterpreted if composition (electronic model) is undetermined

Using electronic coarse-graining we can analyze eDOS in terms of appropriate electronic model of a molecule or material

DOS in simple electronic model

(small rigid molecules with a single well-separated electronic state)

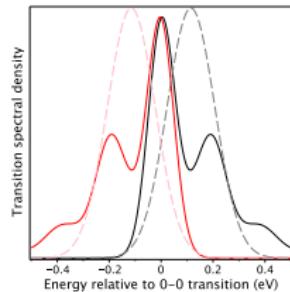
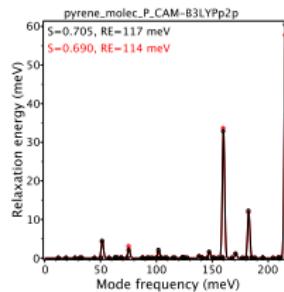
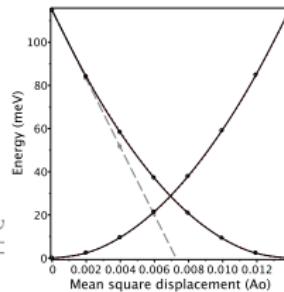
Holes in pyrene at room temperature (hopping regime)

(1 eV to next MO, perfect displaced harmonic oscillator, weak intermol. couplings)



$$\Delta E = \sum_{\omega} \lambda_{\omega}$$

$$\sigma^2 = 2T \sum_{\omega} \lambda_{\omega} \cdot \frac{\hbar\omega}{2T} \coth \frac{\hbar\omega}{2T}$$

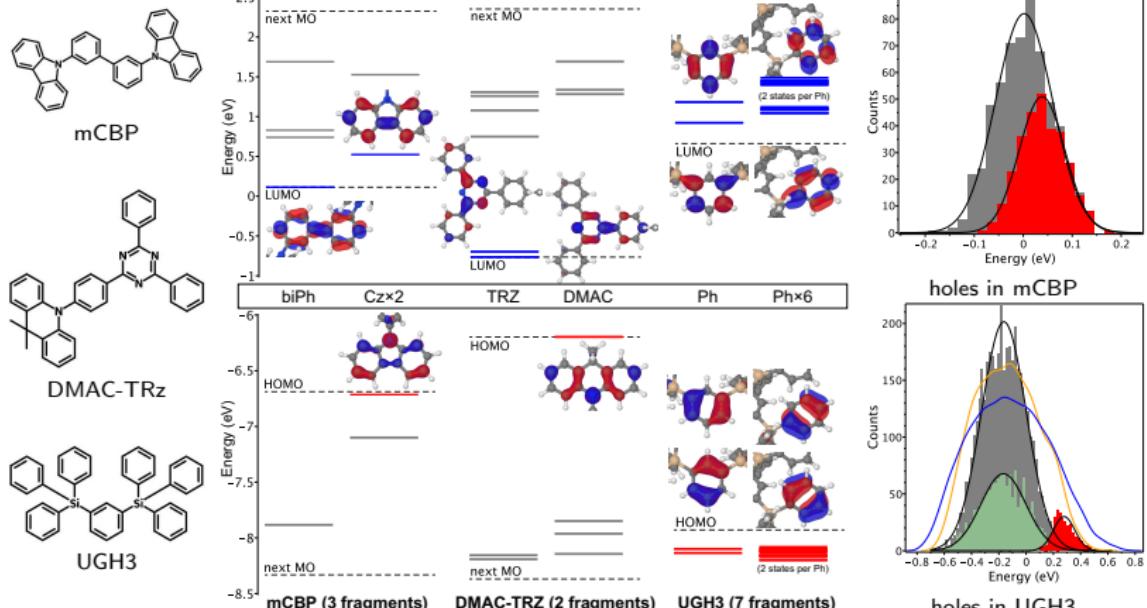


We have clear physical picture of holes (electrons) in such materials:

- HOMO of each molecule is stable at room temperature, and hole wave-function is a superposition of single-molecule HOMOs.
- DOS of each molecule is shaped by vibronic couplings, and solid state DOS is a superposition of molecular DOS shifted by solvation and static disorder.
- A hole is localized predominantly on a single HOMO and moves by hopping with transfer rate proportional to squared couplings and DOS/spectral overlap.
- In classical MD this simplifies to Gaussian disorder model with Marcus rates.

Large molecules can be fragmentized into such “small rigid molecules”

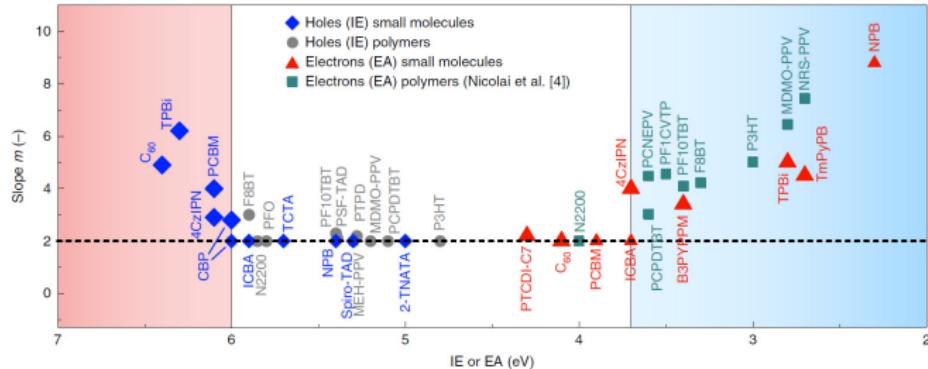
Examples of electronic DOS of host-guest systems



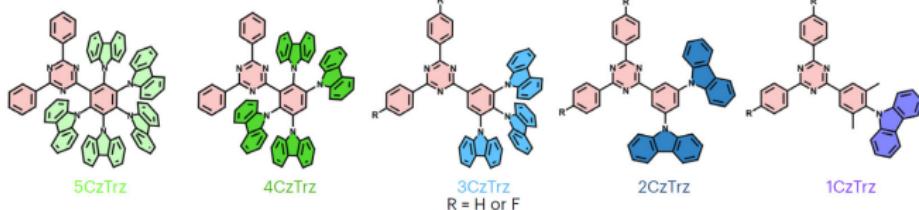
- In comparisons, it is important to use complete electronic DOS (e.g. small broadening of simulated^[2018] HOMO/LUMO of UGH2 is not due to small disorder but is an artifact of using incomplete DOS)
- Intramolecular dynamics is important (often overlooked)
- Marcus transition rates are for isolated levels (holes in DMAC-Trz), Miller–Abrahams transition rates are more appropriate for complex systems

Electronic traps in organic semiconductors

(preliminary results of theoretical investigations)



Trap-free charge transport window – Nat Mater 18, 1182 (2019)

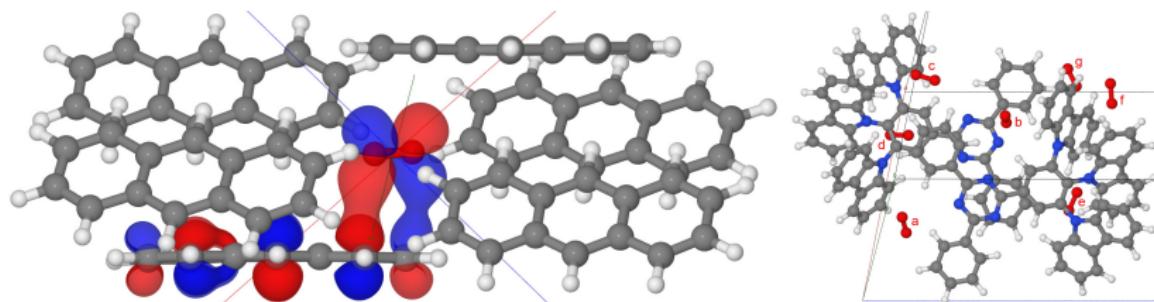


Puzzling dependence on chemical composition – Nat Mater 22, 1114 (2023)

*Understand the origin of trapping beyond the trap-free window
(electron affinity EA~3.0-3.5 eV, ionization energy IE~6 eV)*

Extrinsic traps in organic semiconductors: Oxygen impurity

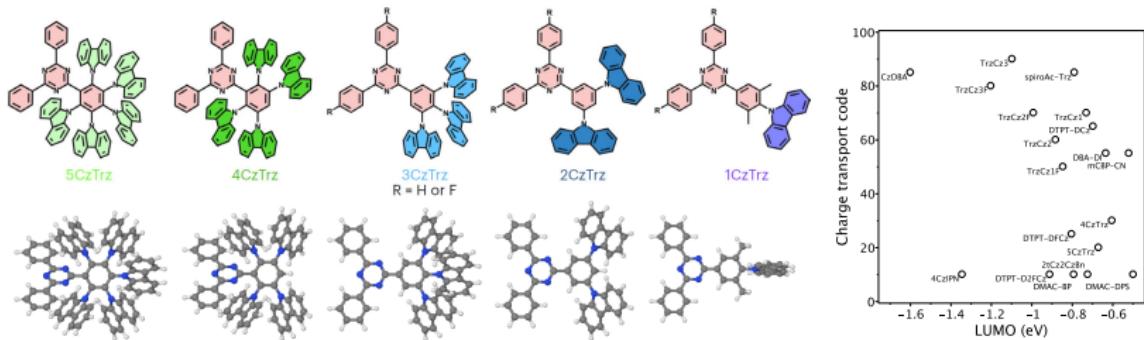
(Molecular oxygen has the highest electron affinity (EA) among unavoidable impurities)



- O₂ does not intercalate into organic semiconductors
- Solvation energy of electron on O₂ is large resulting in EA of up to 3.5 eV coinciding with the edge of trap-free window
- For materials with EA~3.0-3.5 eV trapping by O₂ is possible only in “squeezed” positions (energetically unfavorable)
- Scalable DFT-level computational protocol has been developed

Charge transport and trapping by O₂ in CzTrz series

(crystal structures by R Graf, M Bauer, U Kolb, and from [Nat Mater 22, 1114 (2023)])



- (4,5)CzTrz fall out of the series because of different acceptor
- 2CzTrz falls out of the series because it is not “orthogonal”
- The rest show the same packing motif:
 - 1) segregation of Cz and Trz, 2) dimerized π -stacking of Trz
- Electronic connectivity is moderate for all crystals
- Nonspecific trapping by O₂ is the most consistent hypothesis

Summary

- Electronic Coarse-Graining is a powerful tool (sometimes the only one) for calculation and analysis of electronic structure of complex systems:
 - ▶ Anything that can be monomerized (polymers, COFs, MOFs)
 - ▶ Solids and clusters of large molecules
 - ▶ Defects in solids
 - ▶ Infinite systems from finite-size calculations
- The practical limitation is that any electronic structure calculations require atomically resolved structure on input, which is available only from experiment for crystals and from classical molecular dynamics for amorphous morphologies

Project web-page:

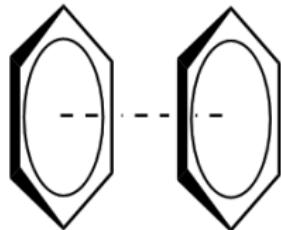
- Electronic Coarse-Graining
<https://zhugayevych.me/research/ECG.html>
- Computational Materials Science of Organic Semiconductors
<https://cmsos.github.io>

Possible applications for design of novel materials

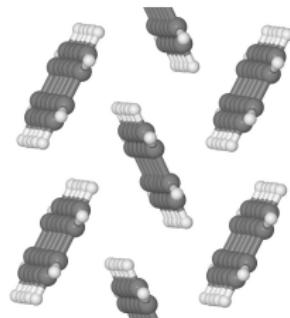
Once we have robust methods for molecular and electronic structure prediction

- Create library of electronic structure prototypes of organic semiconductors (+ charge transport descriptors)
- Search for novel electronic structure architectures
- What is maximum possible charge carrier mobility for organic semiconductors?

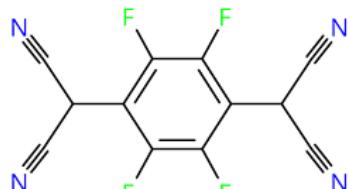
Explored types of electronic connectivity



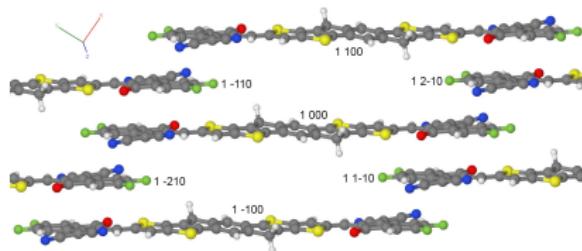
pi-stack



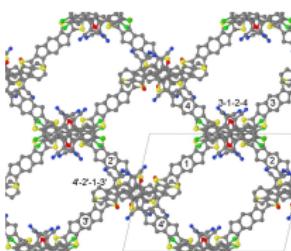
herringbone



H-poor



brickwork



wiremesh



C60

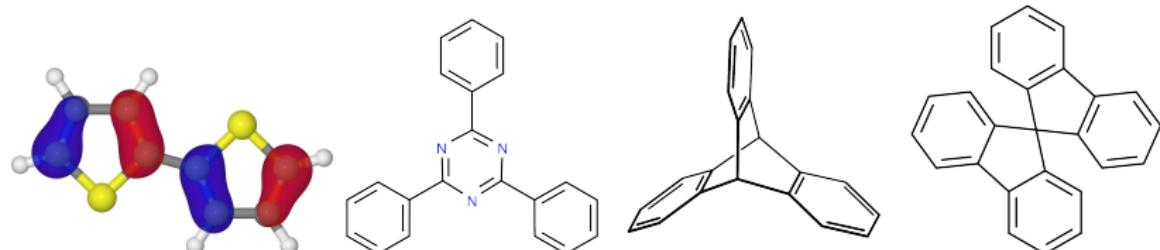
Look at Cambridge Structural Database – there should many more

Electronic structure types of organic semiconductors (molecular crystals)

	D	CN	e-coup.	hop.dist.	examples	gen
π -stack	1	2	largest	smallest	triazine	1
herringbone	2	6	small	small	pentacene	1
H-poor	3	large	small	small	TCNQ	1
mixed	2				rubrene, F2-TCNQ	1
brickwork	2	4	medium	medium	TIPS-pentacene	2
A-D-A brickwork	2	1+2	large	large	(ITIC-4F)	3
A-D-A wiremesh	3	1+2	large	large	Y6, o-IDTBR	3
multi-contact wiremesh	3	n+2	large	large	[Meng16]	4a
nonplanar via sp^3 atoms	3	n+m	large	large	[Kissel14,Xia15]	4b
nonplanar via deformation	3	large			C60 only	
herringbone interdigitated	3	1+6			?	

Electronic couplings for various interconnections

- 4 eV – $pp\pi$ -couplings in Huckel model of benzene
- 1 eV – inter-block couplings in bithiophene (4 eV/4 atoms)
- 300 meV – inter-block couplings in triptycene
- 150 meV – inter-block couplings in spirobifluorene
- 100 meV – π -stack couplings in A-D-A NFAs
- 50 meV – intermolecular couplings in herringbone
- 10 meV – negligible for coherent electronic transport



Complex electronic interconnections are largely unexplored