

CMP-2019 Symposium

# Modeling of electronic properties of organic semiconductors

Andriy Zhugayevych

*Skolkovo Institute of Science and Technology (Skoltech)*

## Acknowledgments

### Team

Nikita Tukachev

### Collaborations

Sergei Tretiak (theory, LANL)

Pavel Troshin (experiment, Skoltech)

Guillermo Bazan (experiment, UCSB)

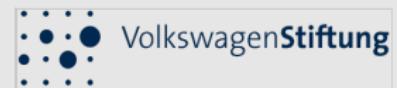
Anna Koehler (U Bayreuth)

Oleg Kharlanov (theory, MSU)

Andrey Sosorev (D.Parashchuk's Lab, MSU)



Skolkovo Institute of Science and Technology



# What is organic semiconductor

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

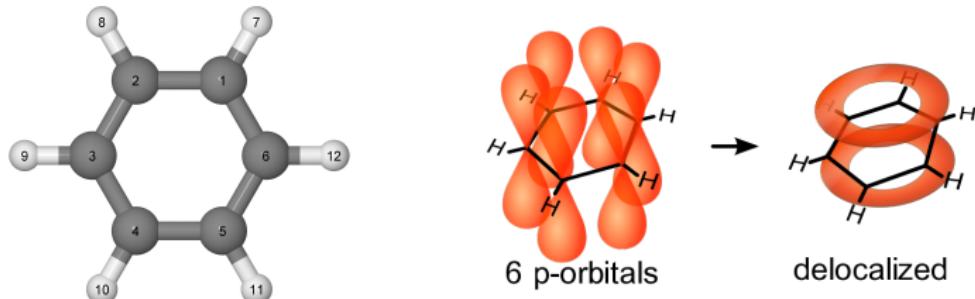
The diagram illustrates the energy levels of electrons. A vertical axis shows energy levels, with a horizontal arrow pointing right labeled "valence" and a downward arrow labeled "shells". A dotted circle surrounds the d-shell elements (Sc, V, Mn, Co, Cu, Ti, Cr, Fe, Ni, Zn) with a label "d-shell" below it. Another dotted circle surrounds the f-shell elements (Y, Nb, Tc, Rh, Ag, Zr, Mo, Ru, Pd, Cd) with a label "f-shell" below it.

(1)	(2)								
H									
Li	Be								
Na	Mg								
K	Ca								
Rb	Sr								
Cs	Ba								
Fr	Ra								
Ac-No									
Sc	V	Mn	Co	Cu	B	C	N	O	F
Ti	Cr	Fe	Ni	Zn	Al	Si	P	S	Cl
Y	Nb	Tc	Rh	Ag	Ga	Ge	As	Se	Br
Zr	Mo	Ru	Pd	Cd	In	Sn	Sb	Te	I
Lu	Ta	Re	Ir	Au	Tl	Pb	Bi	Po	At
Hf	W	Os	Pt	Hg					Rn

*strong sp-hybridization*

*strong relativistic effects*

## What is $\pi$ -conjugated system: example of benzene



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

The diagram illustrates the periodic table with several highlighted regions:

- Valence shells:** A dashed circle labeled "valence" encompasses groups 13-18 (B, C, N, O, F, Ne), group 1 (H), and group 2 (Li, Be).
- d-shell:** A dashed circle labeled "d-shell" encompasses Sc, V, Mn, Co, Cu, Ti, Cr, Fe, Ni, Zn.
- f-shell:** A dashed circle labeled "f-shell" encompasses Y, Nb, Tc, Rh, Ag, Zr, Mo, Ru, Pd, Cd.
- Strong relativistic effects:** A dashed circle labeled "strong relativistic effects" encompasses Lu, Ta, Re, Ir, Au, Hf, W, Os, Pt, Hg, Tl, Pb, Bi, Po, At, Rn.

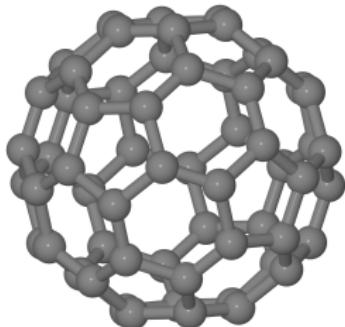
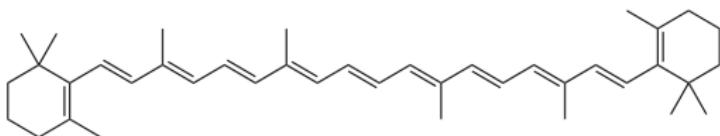
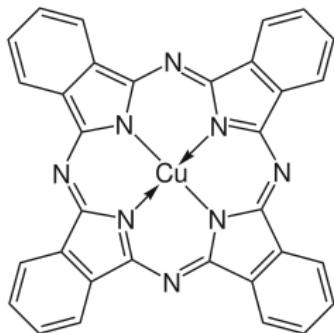
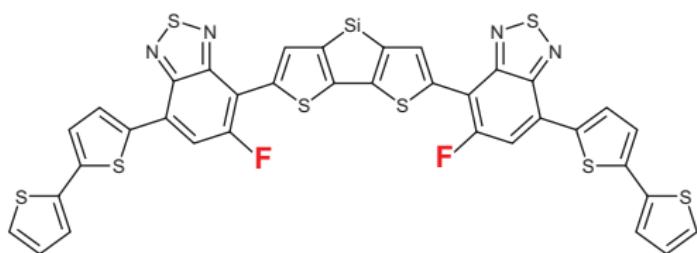
Numbered circles (1-8) are placed above the first two columns (H, Li/Be) and the last two columns (He/F). The first two columns are grouped under "valence shells". The last two columns are grouped under "strong sp-hybridization".

(1)	(2)						
H							He
Li	Be						
Na	Mg						
K	Ca						
Rb	Sr	f-shell	Sc V Mn Co Cu Ti Cr Fe Ni Zn	Al	Si	P	S
Cs	Ba		Y Nb Tc Rh Ag Zr Mo Ru Pd Cd	Ga	Ge	As	Se
Fr	Ra	La-Yb	Lu Ta Re Ir Au Hf W Os Pt Hg	In	Sn	Sb	Te
		Ac-No		Tl	Pb	Bi	Po
							At
							Rn

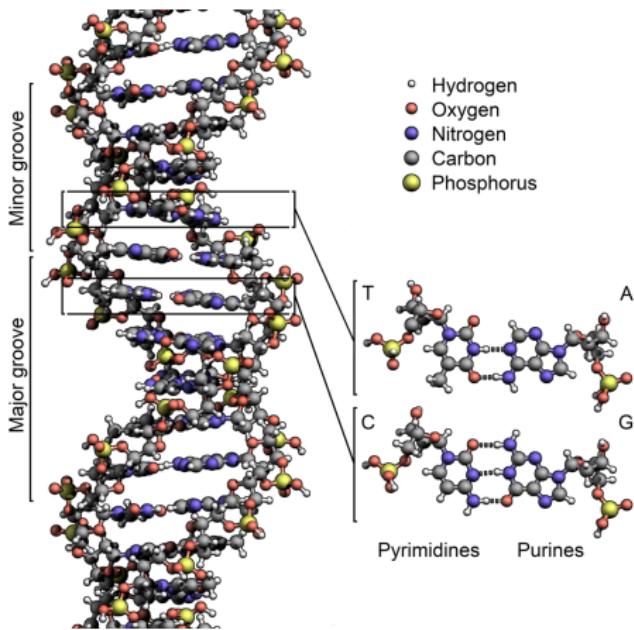
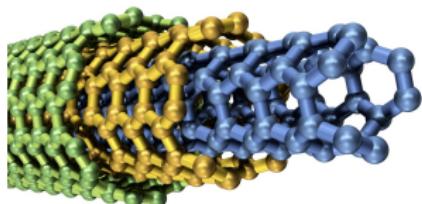
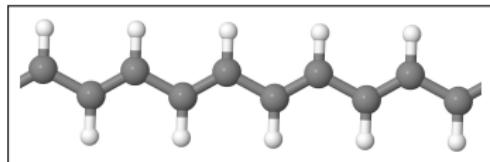
*strong relativistic effects*

- 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

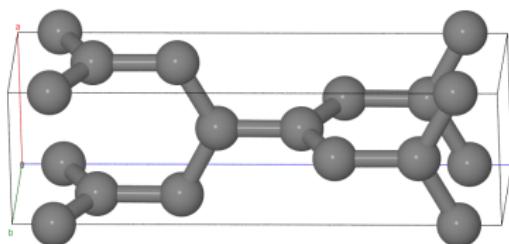
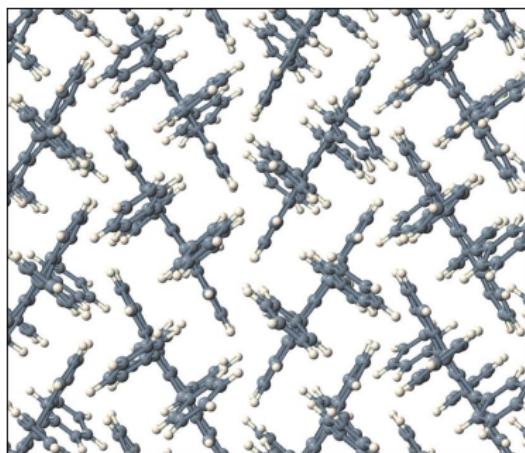
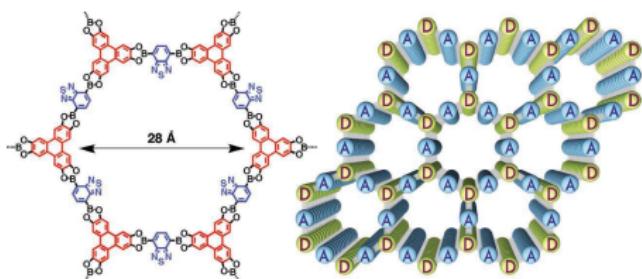
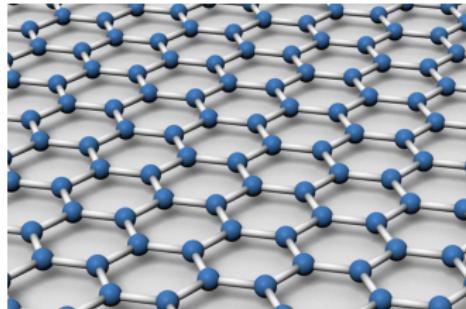
## Examples of $\pi$ -conjugated systems: molecules



## Examples of $\pi$ -conjugated systems: polymers and 1D

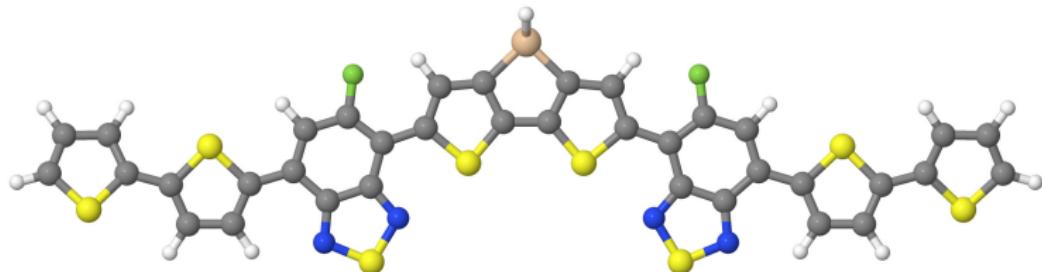


## Examples of $\pi$ -conjugated systems: 2D and 3D



# We will focus on molecular solids and polymers

(quasi-1D  $\pi$ -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

$\Rightarrow$  Success of simple force fields

- The  $\pi$ -conjugated system of each block is closed-shell
- Inter-block couplings  $\sim 1 \text{ eV} \ll$  bandgap of blocks
- Intermolecular couplings  $\sim 0.1 \text{ eV} \ll$  bandgap of molecules

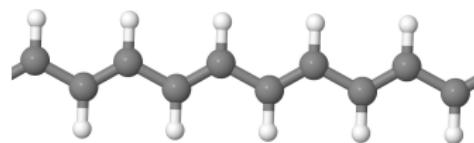
$\Rightarrow$  There must be a set of methods well-tuned for accurate prediction of electronic properties of this class of materials

# But there is one complication:

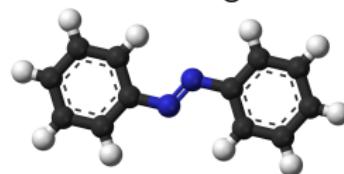
Strong electron-phonon coupling in combination with soft structure

⇒ *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)



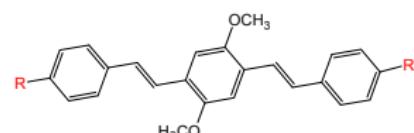
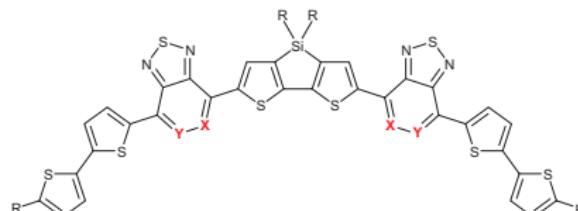
Photoisomerization of azobenzene  
(librations of non-rigid dihedrals)



also polaron formation, vibronic progression in spectra

In fact, it is very useful in applications:

- Change structure ⇒ tune electronic properties
- Affect electronic system ⇒ change structure

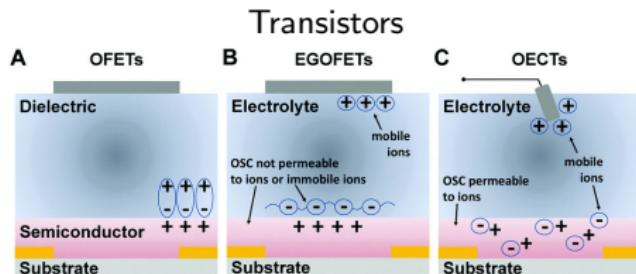


# Outline

- Overview: applications, what to model, challenges
- Benchmarking methods for simple calculations:  
molecular, crystal, electronic structures
- Modeling energy and charge transport

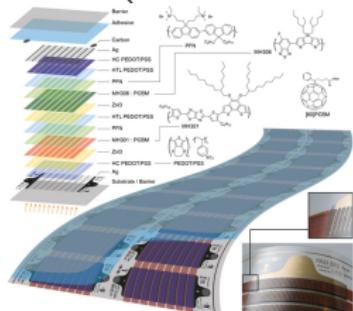
# Some applications of organic semiconductors

Light emitters (most successful)

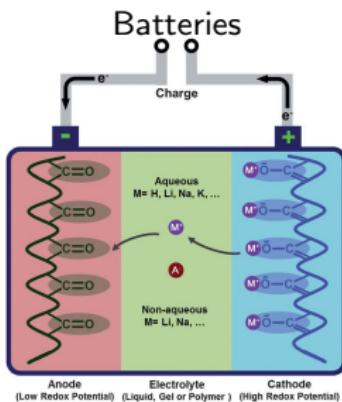


J Mater Chem C 6, 11778 (2018)

Solar cells (best PCE is 16%)

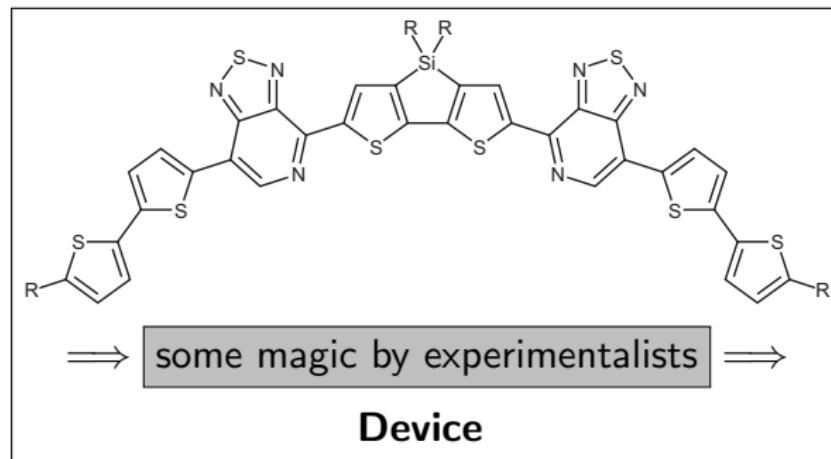


Energy Environ Sci 7, 2925 (2014)



# Examples of what do we need to model/calculate (relevant to energy and charge transport)

- Charge carrier mobility – transistors, other devices
- Exciton diffusion length – solar cells
- Charge separation – solar cells
- Electron-hole recombination – light emitters
- Conductivity – batteries

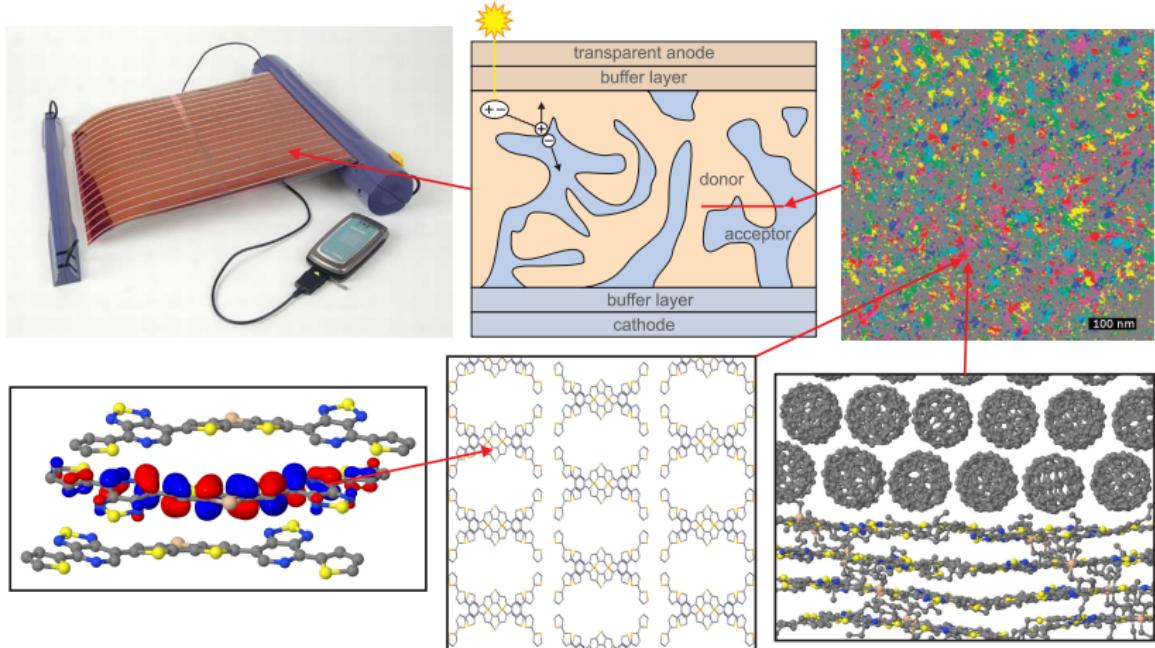


*Computational materials scientists are expected to predict material properties from chemical formula*

# Modeling of organic semiconductors: Main challenges

- Small bandgap ( $\sim 10\%$  of  $\pi$ -bandwidth)
- Soft structure (polymers, molecular solids)
- Strong electron-phonon coupling (compared to e-bandwidth)
- Complex multiscale morphology (up to 10-100 nm)
- Complex device structure

## Challenges: multiple scales – solar cell example



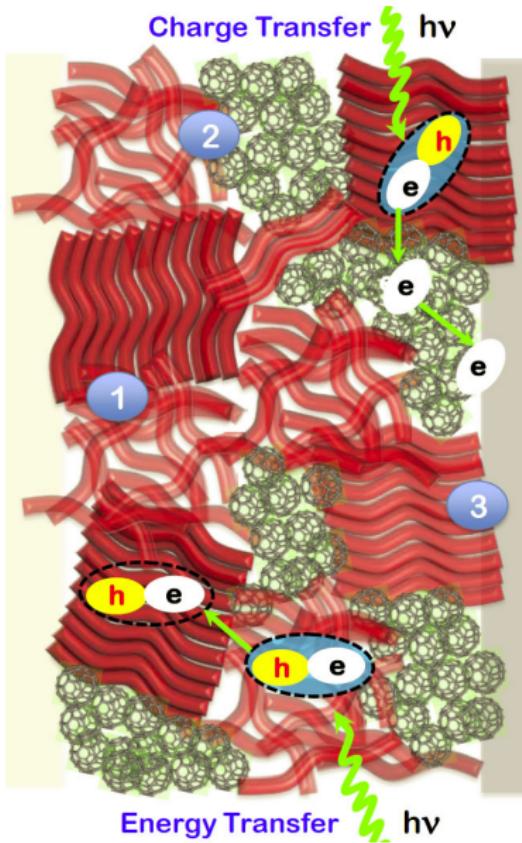
# Multiple scales: broad range of scales – solar cell example

Spatial scales:

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

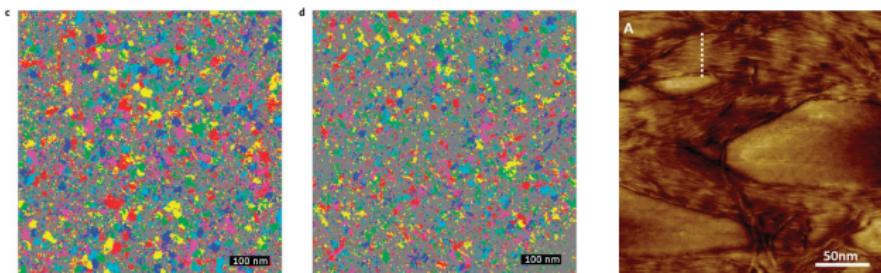
Time scales:

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



# Understanding scales

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

# Outline

- Overview: applications, what to model, challenges
- Benchmarking methods for simple calculations:  
molecular, crystal, electronic structures
- Modeling energy and charge transport

## Commonly used high-level methods (up to 1000 atoms)

- CCSD(T) – only fragments, be careful with approximations
- MP2 – no, only for CBS extrapolation of CCSD
- DFT+D – for intermolecular structure, D3 is safe choice
- LDA – no
- PBE – only for crystal structure
  - ▶ PBE-D3 – fastest available
  - ▶ PBE-MBD – most accurate available
  - ▶ vdW-DF2 – analytic gradients
- B3LYP – underestimates bandgap, dihedrals, ep-couplings
- APFD – might be best hybrid (needs more benchmarking)
- Range separated hybrids are the most accurate
  - ▶ CAM-B3LYP – safe choice for organic semiconductors
  - ▶  $\omega$ B97XD – another good functional
  - ▶ HSE06 – best available for plain waves
- Basis set
  - ▶ 6-31G\* – safe choice for organic semiconductors
  - ▶ Def2-TZVP – for high accuracy

## Some low-level methods (thousands of atoms)

- Semiempirical – no accurate parameterizations yet
  - ▶ AM1 – bad geometry
  - ▶ PM7 – best available but still inaccurate
  - ▶ PM7+D – is also inaccurate
- DFTB – very promising but needs to be well parameterized
- TB – yes but always requires parameterization
- QM+MM – naturally the best (for conjugated systems)
  - ▶ MM3 – most transferable for conjugated molecules
- Force fields – no accurate parameterizations
  - ▶ OPLS – good starting point
  - ▶ CHARMM, AMBER – no atom types
  - ▶ ML – let's see

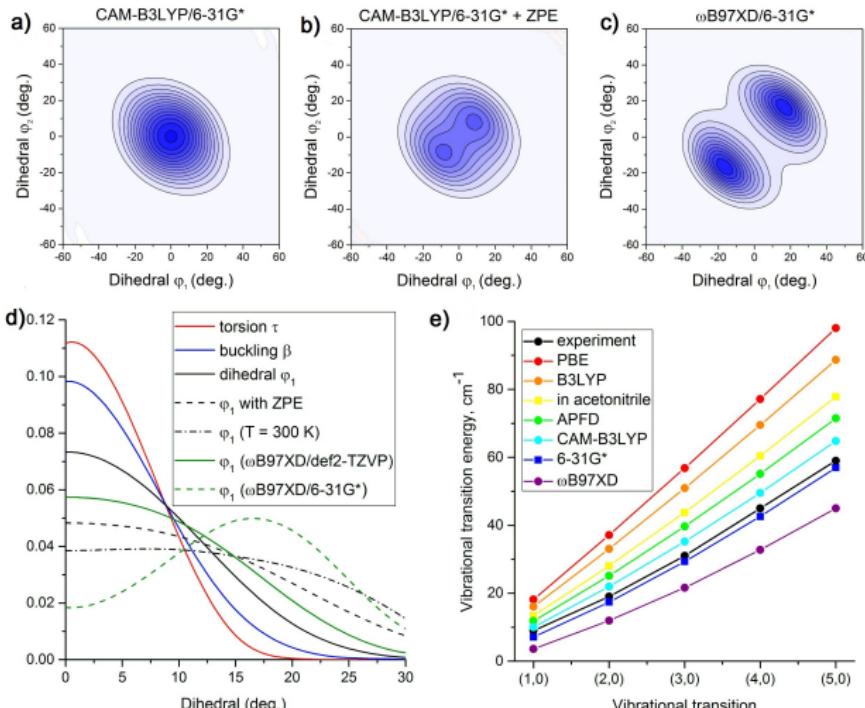
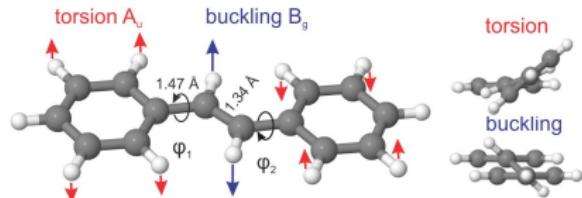
*Parameterization is the main problem*

## Structural properties sensitive to the method

- Bond Length Alternation (BLA) and dihedrals (next slide)
- Conformations
- Intermolecular geometry
- Polymorphism

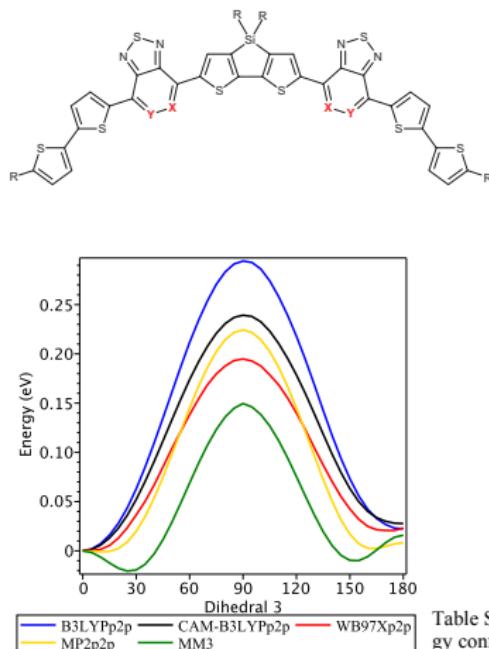
# BLA and dihedrals

J Phys Chem Lett 10, 3232 (2019)



# Conformations: conjugated backbone

J Phys Chem Lett 5, 2700 (2014)



method	solv.	1a	3a
		bb mol.	bb mol.
<b>planarized conjugated base</b>			
B3LYP		2	2
CAM-B3LYP		9	9
ωB97X		17	17
MP2		96	...
MM3		130	251
<b>dihedrals #3,4 are flipped</b>			
ωB97X		119	38
MP2		123	...
CAM-B3LYP		129	128
B3LYP		132	34
MM3		132	21
ωB97X	clf	119	22
CAM-B3LYP	clf	128	33
B3LYP	clf	128	19
<b>dihedrals #1,3,4 are flipped</b>			
ωB97X		147	65
CAM-B3LYP		159	105
B3LYP		165	67
ωB97X	clf	142	242
CAM-B3LYP	clf	155	102
B3LYP	clf	158	64
<b>saddle point for dihedral #3</b>			
ωB97X		377	169
CAM-B3LYP		407	209
B3LYP		468	253

Table S4. Energies (in meV) of different conformations relative to the energy of the lowest energy conformation: dependence on method. The geometry is fully relaxed from crystalline geometry to local extremum. The default basis set is 6-31g\*. Note that conformations with  $C_2$  symmetry is slightly lower in energy than that with  $\sigma_h$  symmetry (typically less than 1 meV difference). Here “bb” means conjugated backbone, “mol.” means the whole molecule. Entries are ordered by the third column (“1a bb”).

# Conformations: aliphatic chains

J Phys Chem C 122, 9141 (2018)

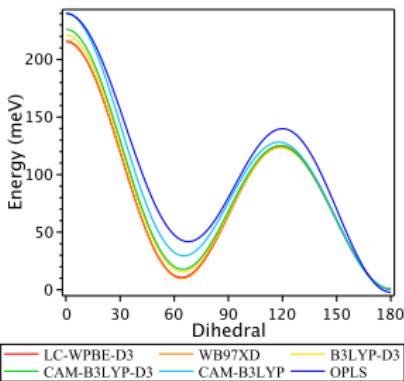
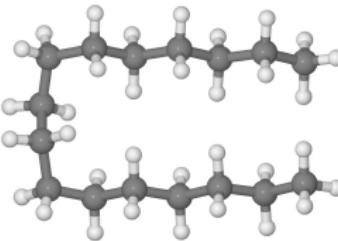


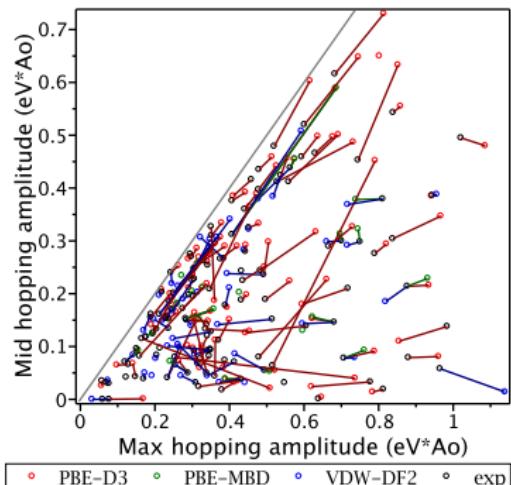
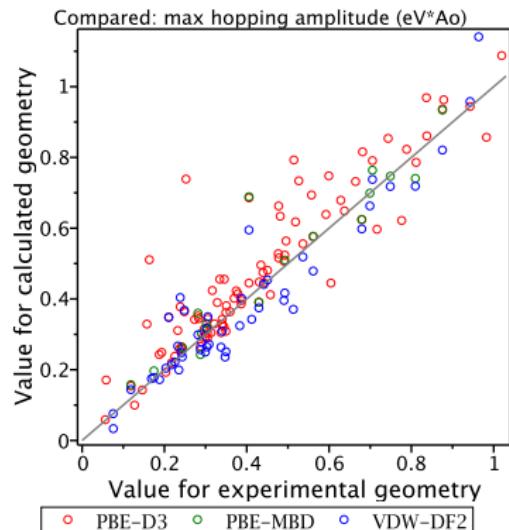
Table S4: Comparison of different methods estimating the relative, hairpin minus trans, energy for a set of polyethylene oligomers (8 to 18 carbons). The geometry is fixed at MP2/cc-pVTZ geometry obtained in Ref.,<sup>2</sup> except for the last block in the table. The entries correspond to energies in meV. Here  $\sigma$  is RMSD with respect to the reference method which is CCSD(T)/cc-pVTZ.<sup>2</sup> “Optimized OPLS” means optimized C-C-C-C dihedral. The supercell size for plane waves is  $40 \times 20 \times 20 \text{ \AA}$ . See also graphical representation in Fig. S5.

	$\sigma$	8	10	12	14	16	18
Reference data							
CCSD-T/cc-pVTZ	0	65	52	37	5	-30	-73
6-311G*							
CAM-B3LYP-D3	5	71	61	42	10	-30	-72
B3LYP-D3	16	60	50	31	-12	-53	-98
vdW-DF2	19	90	83	62	14	-31	-71
PBE-MBD	22	66	55	34	-21	-62	-108
LC-wPBE-D3	50	29	15	-5	-47	-88	-140
wB97XD	90	24	11	-10	-95	-145	-215
CAM-B3LYP	195	138	143	148	227	222	227
6-311+G(3df,2p)							
CAM-B3LYP-D3	10	78	67	49	7	-33	-75
B3LYP-D3	21	65	54	36	-20	-61	-106
LC-wPBE-D3	39	41	29	10	-39	-77	-127
wB97XD	84	33	20	1	-90	-138	-207
CAM-B3LYP-D3							
6-311G*	5	71	61	42	10	-30	-72
6-311G**	8	68	57	38	-2	-43	-86
6-311+G(3df,2p)	10	78	67	49	7	-33	-75
6-311G(2d,p)	10	78	68	49	9	-30	-72
6-311+G(2d,p)	14	82	72	54	16	-23	-65
6-31G(2d,p)	18	73	61	37	-11	-56	-103
6-31G*	19	66	56	33	-12	-58	-104
6-31G**	20	67	57	34	-14	-59	-106
6-31+G(2d,p)	29	94	84	67	34	-4	-45
Geometry relaxed with the same method							
CAM-B3LYP-D3	4	67	57	38	4	-36	-79
optimized OPLS	8	54	41	27	3	-34	-72
B3LYP-D3	18	56	45	25	-14	-55	-100
LC-wPBE-D3	51	28	15	-6	-49	-88	-141
wB97XD	96	21	8	-13	-103	-154	-223
OPLS	118	160	161	149	135	97	58
CAM-B3LYPp3p	128	127	129	128	128	128	128

# Intermolecular geometry

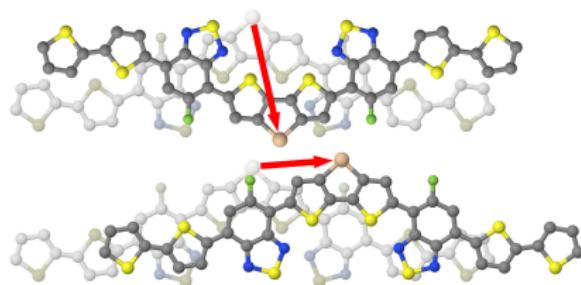
Tested here is product of electronic coupling and hopping distance

Test set: > 50 crystals, including all high- $\mu$  from Chem Soc Rev 47, 422 (2018)



# Polymorphism of molecular crystals

- DFT-D correctly predicts relative energy of polymorphs for small-molecule crystals (TCNQ, indigo, rubrene)
- Force fields can be used for prescreening (MM3 in [J Phys Chem Lett 5, 2700 \(2014\)](#), OPLS in [J Phys Chem C 122, 9141 \(2018\)](#))
- For large molecules with aliphatic chains kinetic and entropic factors might be essential:

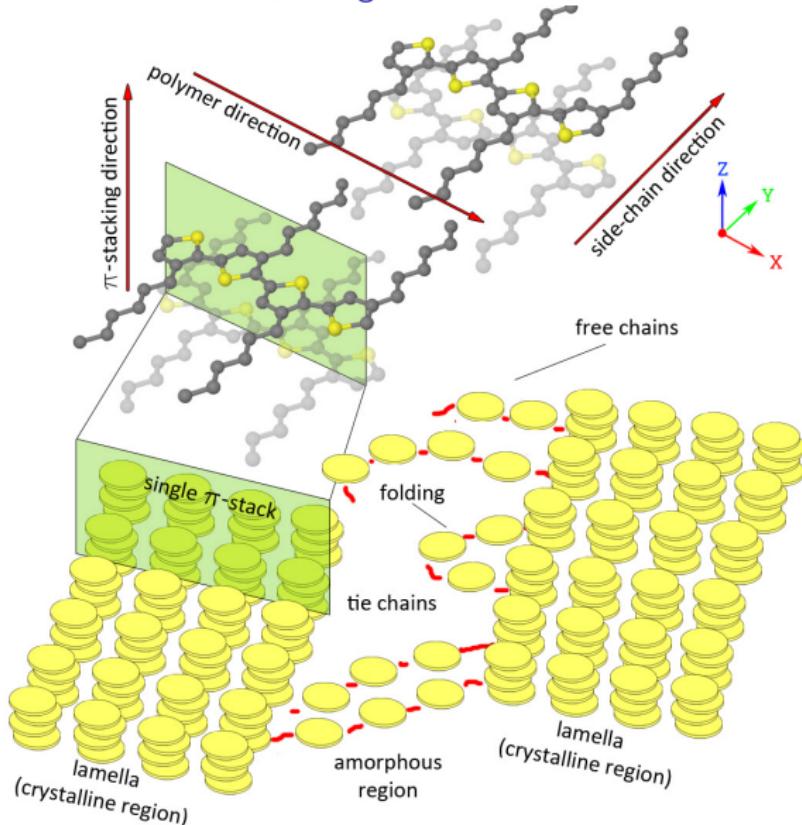


[Adv Funct Mater 28, 1702073 \(2017\)](#)

DFT-D predicts that antiparallel stacking is 0.18 eV/mol lower in energy than observed parallel stacking

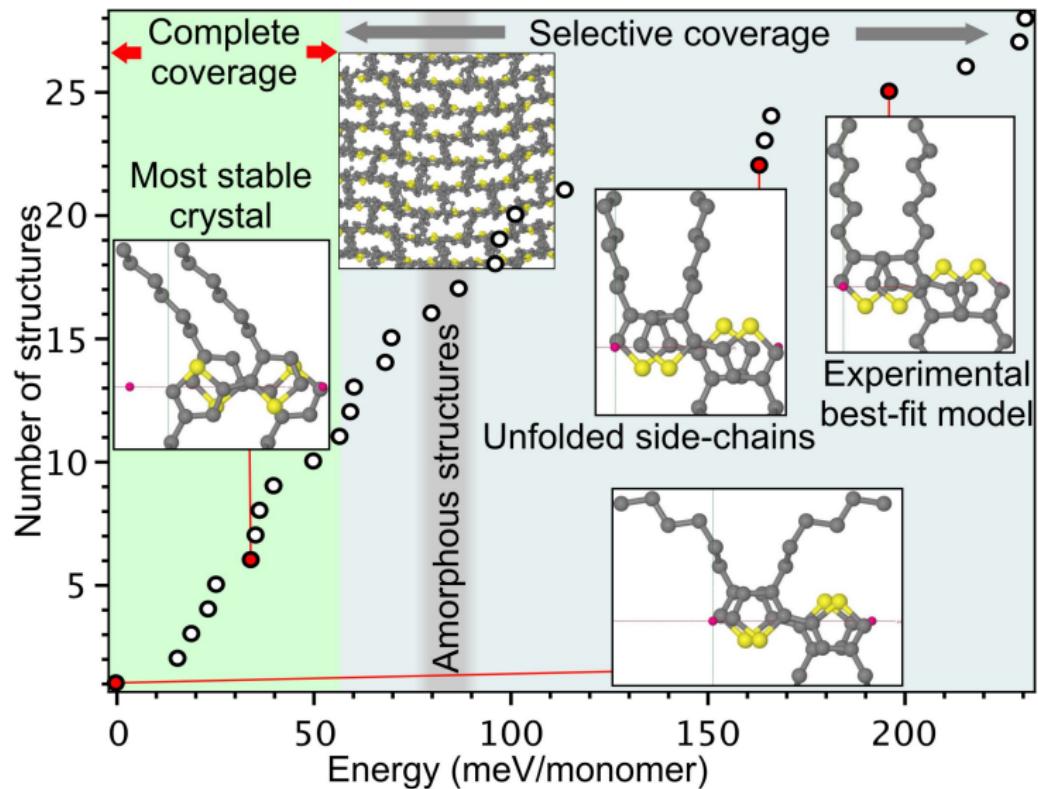
# Polymerization of bulk polymers: example of P3HT

Atomic positions remain unresolved, though structure is well known down to nanometers



# Polymer polymorphism: example of P3HT

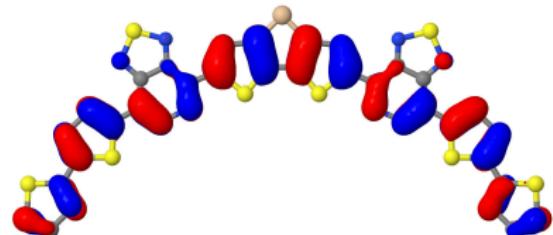
J Phys Chem C 122, 9141 (2018)



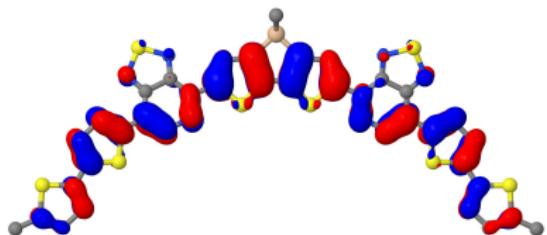
## Electronic properties

- Wave-function
- Effective mass
- Bandgap
- IP/EA, excitations, polaron relaxation energy
- Vibronic couplings, UV-Vis spectra, Raman spectra
- Charge transfer states, singlet-triplet splitting, . . .

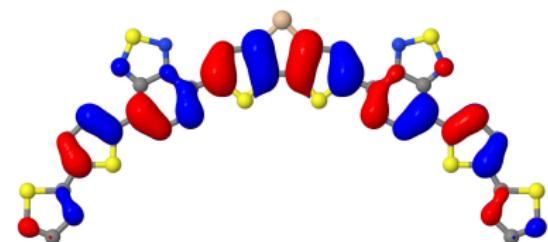
## Electronic properties: wave-function (not sensitive to the method)



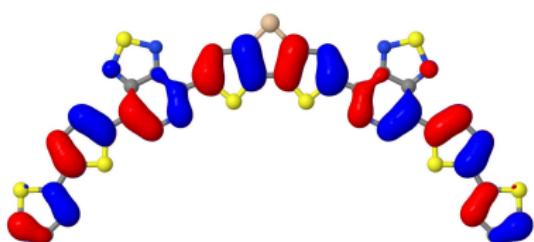
HOMO (CAM-B3LYP)



HOMO (PM6)



hole NO (CAM-B3LYP)



hole NO (B3LYP)

## Electronic properties: effective mass

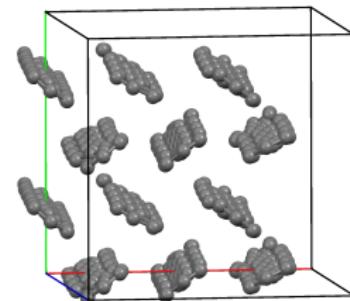
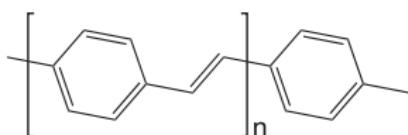
(not very sensitive to the method)

Effective mass for holes in trans-polycetylene:

- 0.074 – PBE
- 0.076 – HSE06
- 0.076 – B3LYP
- 0.090 – CAM-B3LYP
- 0.097 –  $\omega$ B97X

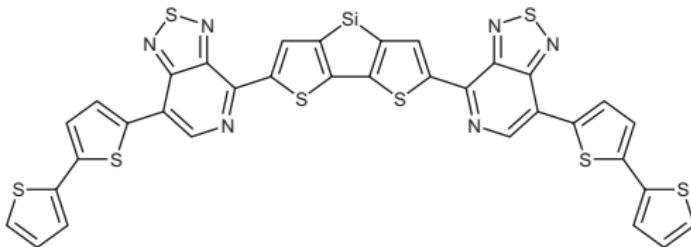
## Electronic properties: HOMO-LUMO gap

	bandgap (eV)	
	crystal	polymer
wB97X	5.9	6.6
CAM-B3LYP	4.4	4.8
experiment	3.5	–
B3LYP	2.2	2.5
HSE06	1.7	2.1
PBE	1.1	1.3



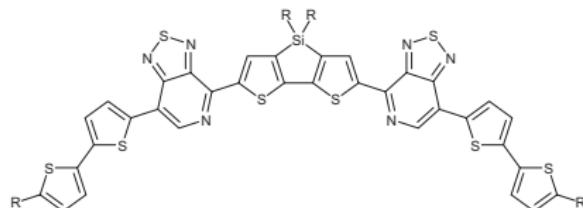
## Electronic properties: total energies (in eV)

	IP	$\lambda$ ,hole	$\lambda$ ,exciton	$E$ ,exciton	main exc.
wB97X	5.57	0.50	0.66	0.47	2.64
wB97XD	5.45	0.43	0.56	0.39	2.36
CAM-B3LYP	5.30	0.43	0.52	0.43	2.21
experiment	5.2				1.9
B3LYP	4.90	0.20	0.29	0.46	1.46



# Violation of Koopman's theorem

J Phys Chem C 117, 4920 (2013)

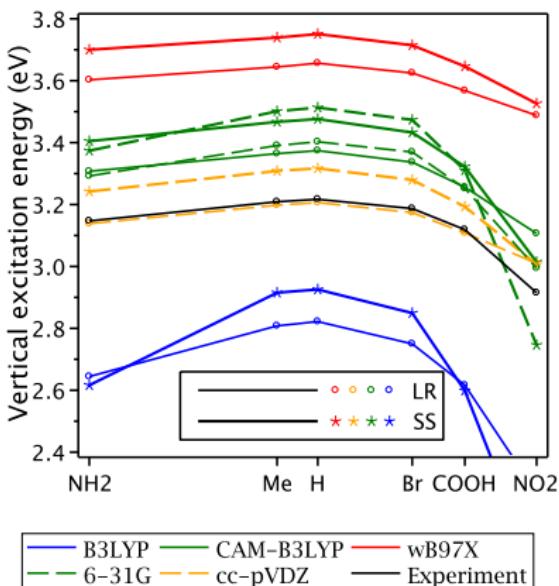
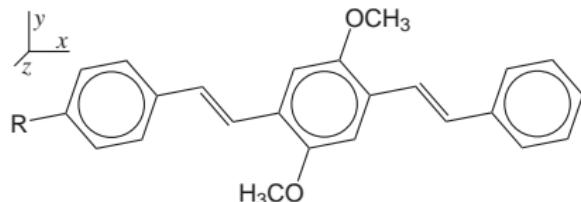


functional	IP+ $E_{\text{HOMO}}$ (eV)	EA+ $E_{\text{LUMO}}$ (eV)
PBE	+1.1	-1.1
B3LYP	+0.8	-0.9
M06-2X	+0.3	-0.4
CAM-B3LYP	+0.1	-0.2
$\omega$ B97X	-0.6	+0.4
LC- $\omega$ PBE	-0.7	+0.4

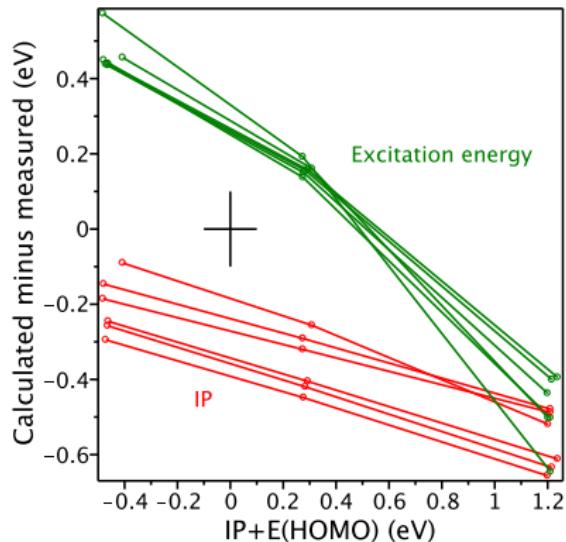
Inconsistency with experimental data strongly correlates with violation of Koopman's theorem

# Violation of Koopman's theorem

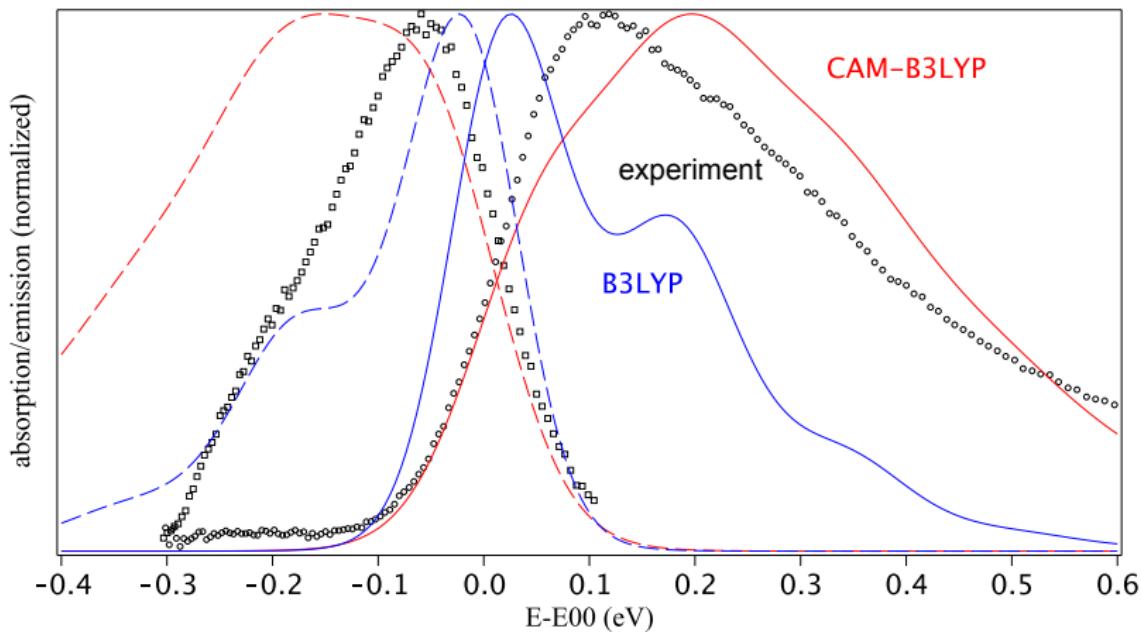
Chem Phys 481, 133 (2016)



functional	$\text{IP} + E_{\text{HOMO}}(\text{eV})$
B3LYP	+1.2
CAM-B3LYP	+0.3
$\omega\text{B97X}$	-0.4



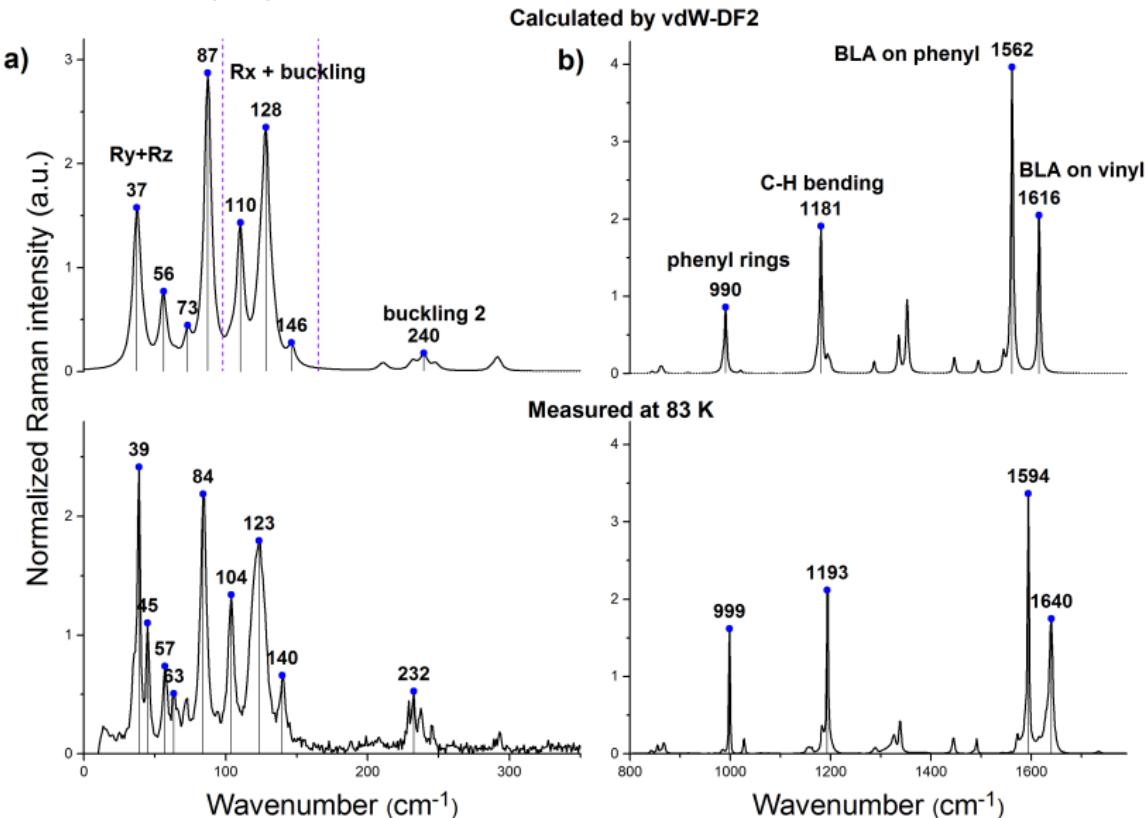
## Vibrationally resolved UV-Vis spectra



B3LYP underestimates vibronic couplings for low- $\omega$  modes  
CAM-B3LYP overestimates vib. couplings for high- $\omega$  modes

# Raman spectra of stilbene crystal

J Phys Chem Lett 10, 3232 (2019)



## Short summary to this part (simple calculations)

- CAM-B3LYP-D3/6-31G\* is a safe choice for organic semiconductors
- PBE-D3 can be used for crystal structure relaxation

## Energy and charge transport

- Simplified (commonly used) approach
- Beyond the simplified approach

# Charge carrier mobility

Basic equations in homogeneous medium

$$\text{Current density} \quad j = \mu \cdot n \cdot e \mathcal{E}$$

Free charge carriers	Localized charge carriers
Drude formula	Hopping
$\mu = \frac{e \tau_{\text{scattering}}}{m_{\text{effective}}}$	$\mu = \frac{2\pi e}{\hbar} f \cdot (aV)^2 \frac{J}{T}$

\* Purely electronic and electron-phonon interaction terms are factorized

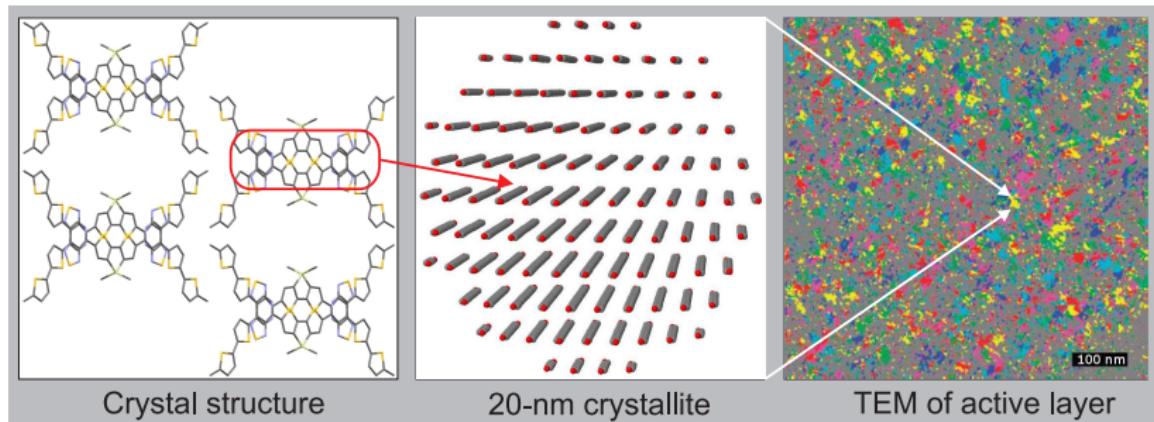
Scattering (or localization) mechanisms:

- dynamic lattice defects (phonons, intramolecular vibrations)
- extrinsic disorder: from lattice defects to mesoscopic inhomogeneity (grain boundaries, interfaces, composites)
- carrier-carrier interaction

---

$f$  = lattice form-factor,  $a$  = lattice spacing,  $V$  = electronic inter-site coupling,  $J$  = spectral overlap, mobility definition  $v = \mu \mathcal{E}$ , zero-field mobility =  $eD/T$ , exciton diffusion length =  $\sqrt{D \cdot \text{lifetime}}$

# Simplified approach for a molecular solid



- Coarse grain electrons to one site per molecule
- Simplify molecular motions to harmonic vibrations
- Linearize coupling between electrons and molecular motions

$$\Rightarrow \sum_{ij} H_{ij}^{1p} c_i^\dagger c_j + \sum_\alpha \hbar \omega_\alpha \left( b_\alpha^\dagger b_\alpha + \frac{1}{2} \right) + \sum_{ij\alpha} \hbar \omega_\alpha g_{ij\alpha} (b_\alpha^\dagger + b_\alpha) c_i^\dagger c_j$$

Then solve this Hamiltonian (e.g. in small polaron hopping approximation)

# Holstein–Peierls Hamiltonian

$$\sum_{ij} H_{ij}^{1p} c_i^\dagger c_j + \sum_\alpha \hbar\omega_\alpha \left( b_\alpha^\dagger b_\alpha + \frac{1}{2} \right) + \sum_{ij\alpha} \hbar\omega_\alpha g_{ij\alpha} (b_\alpha^\dagger + b_\alpha) c_i^\dagger c_j$$

here  $c_i$  – quasiparticles (excitons, holes etc.) described by coarse-grained Hamiltonian,  $b_\alpha$  – normal modes or phonons,

$$H_{ij}^{1p} = \delta_{ij} \varepsilon_i + (1 - \delta_{ij}) V_{ij},$$

$\varepsilon_i$  – onsite energy,  $V_{ij}$  – transfer integral,  $g_{ij\alpha}$  – electron-phonon coupling (local for  $i = j$ , nonlocal otherwise)

---

## Approximations:

- mean field approximation for electrons (one may add interaction terms)
- harmonic approximation for atomic motion (essential for quantum modes)
- linear electron-phonon coupling

# Calculating coarse-grained electronic Hamiltonian

See also [Chem Rev 117, 10319 (2017)]

**Definition:** For all possible atomic configurations, the lowest eigenvalue of  $H^{1p}$  should match the exact electronic energy

---

Dimer approximation:

- Frenkel excitons: from excitations energies and transition dipoles [J Phys Chem C 117, 4920]
- Electrons/holes: from DFT Fock matrices [JPCC 117, 4920] (HOMO/LUMO=hole/electron, HOMO×LUMO=exciton)
- Semiempirical approaches [Int J Q Chem 108, 51; JACS 127, 4744]

Hole=HOMO, electron=LUMO, exciton=HOMO×LUMO

	HOMO	LUMO
ground state $n_h = 2$ $n_e = 0$		
cation/anion $n_{h/e} = 1$ $\Delta n_2 = .07/.06$		
singlet exciton $n_h = 1 + .12$ $n_e = 1 - .12$		
triplet exciton $n_h = 1 + .17$ $n_e = 1 - .18$		

## Excitation=exciton

	hole NTO/NO	electron NTO/NO
singlet exciton $n_h = 1 + .12$ $n_e = 1 - .12$		
singlet transition $n_{h/e} = 1 \pm .17$		
triplet exciton $n_h = 1 + .17$ $n_e = 1 - .18$		
triplet transition $n_{h/e} = 1 \pm .25$		

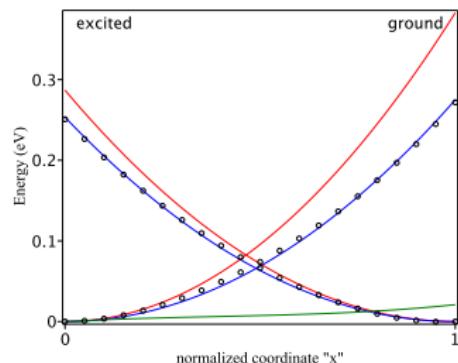
# Calculating vibronic couplings

## 1. Local couplings (Holstein model):

$$\sum_{ij} H_{ij}^{1p} c_i^\dagger c_j + \sum_{\alpha} \hbar \omega_{\alpha} \left( b_{\alpha}^\dagger b_{\alpha} + \frac{1}{2} \right) + \sum_{i\alpha} \hbar \omega_{\alpha} g_{i\alpha} \left( b_{\alpha}^\dagger + b_{\alpha} \right) n_i$$

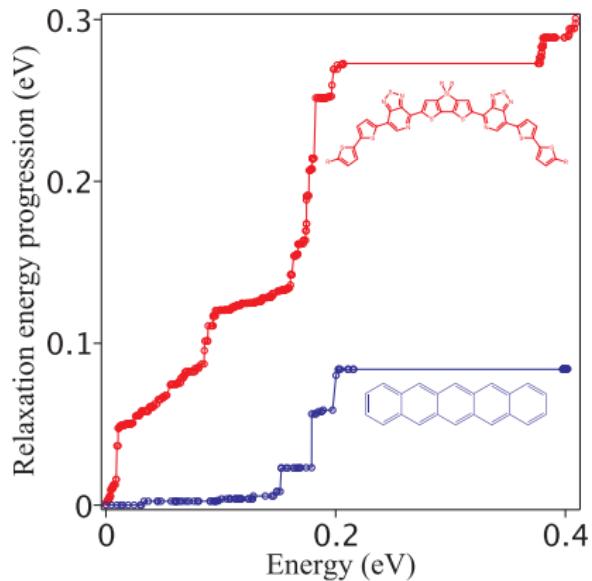
and  $g_{i\alpha} g_{j\alpha} = 0$  for  $i \neq j$

- Get two relaxed geometries: for zero and one quasiparticle at site
- Project atomic displacement onto normal modes  $\xi_{\alpha}$ , then  $g_{\alpha} = -\frac{\xi_{\alpha}^{(0)}}{\sqrt{2}}$
- Rescale  $g$  and  $\omega$  for weak anharmonic effects



## 2. Nonlocal (intermolecular) couplings see [Phys Stat Sol B 248, 511], but is challenging computationally

## Vibronic couplings: example

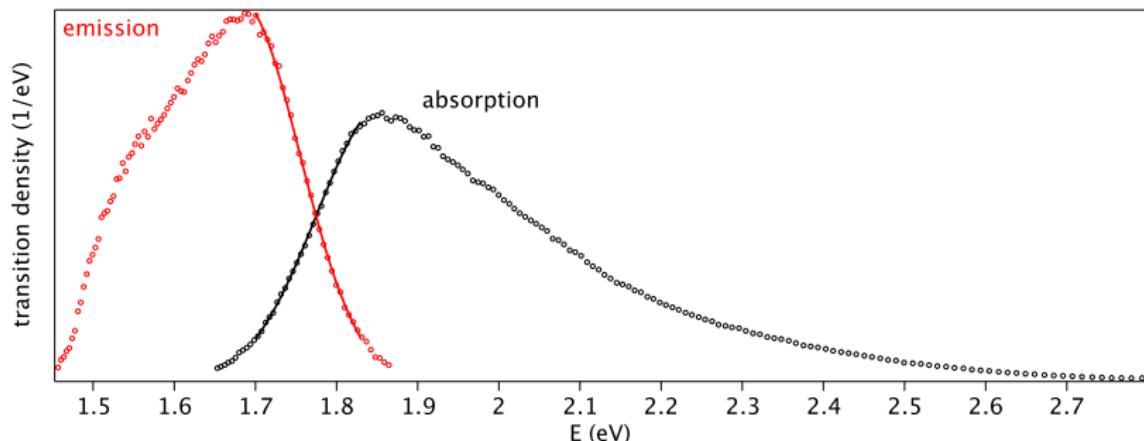


$$\lambda(E) = \sum_{\hbar\omega_\alpha < E} g_\alpha^2 \hbar\omega_\alpha$$

# Solving Holstein–Peierls Hamiltonian: hopping regime

Calculate hopping rates using Fermi's golden rule:

$$w_{(i \rightarrow j)} = \frac{2\pi}{\hbar} |V_{ij}|^2 J_{ij}, \quad J_{ij} = \int \rho_i^{\text{emi}}(E) \rho_j^{\text{abs}}(E) dE \text{ is spectral overlap}$$



# Spectral overlap via phonon correlator

$$J_{ij} = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \left\langle e^{itH_i^{\text{vib}}/\hbar} e^{-itH_j^{\text{vib}}/\hbar} \right\rangle dt$$

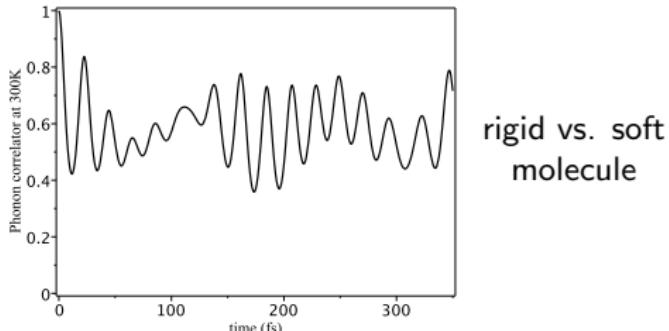
Independent boson model (displaced harmonic oscillator):

$$J_{ij} = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \hat{\delta}(t) e^{-i\omega_{00}t} \prod_{\alpha} C_{\alpha}(t) dt,$$

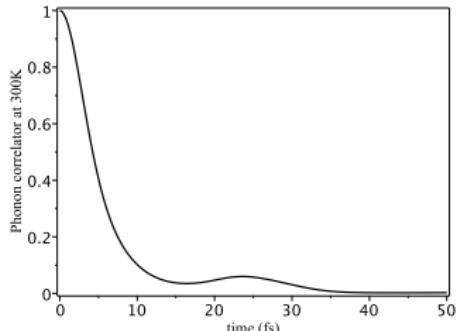
where  $C_{\alpha}(t) = \exp \left[ g_{\alpha}^2 \left( \coth \frac{\hbar\omega_{\alpha}}{2T} (\cos \omega_{\alpha} t - 1) - i \sin \omega_{\alpha} t \right) \right]$ ,

$\hbar\omega_{00}$  is 0-0 transition energy,

$\hat{\delta}$  is lineshape function (inhomogeneous broadening) e.g.  $e^{-\sigma^2 t^2 / 2\hbar^2}$



rigid vs. soft  
molecule

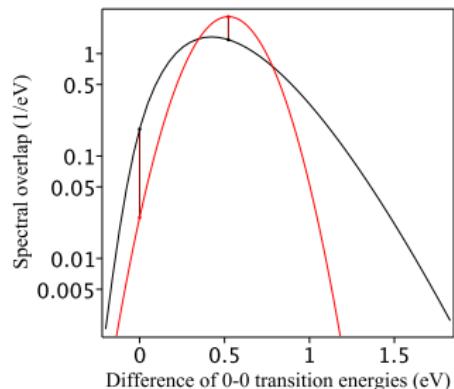
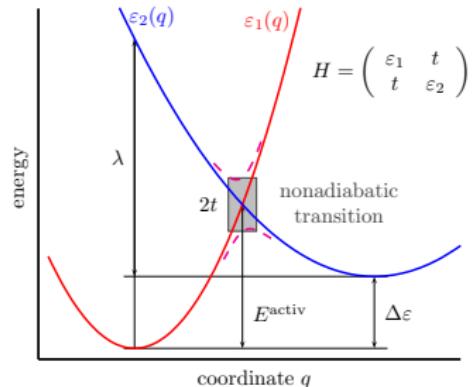


# Spectral overlap in high temperature limit: Marcus formula

If  $T \gg \hbar\omega$  then

$$J_{ij} = \frac{1}{\sqrt{4\pi\lambda T}} \exp \left[ -\frac{(\lambda + \varepsilon_j - \varepsilon_i)^2}{4\lambda T} \right],$$

where  $\lambda = E_i^{\text{polaron}} + E_j^{\text{polaron}}$  is the reorganization energy



— independent bozon model — Marcus formula

## Final step: solving master equation for hopping

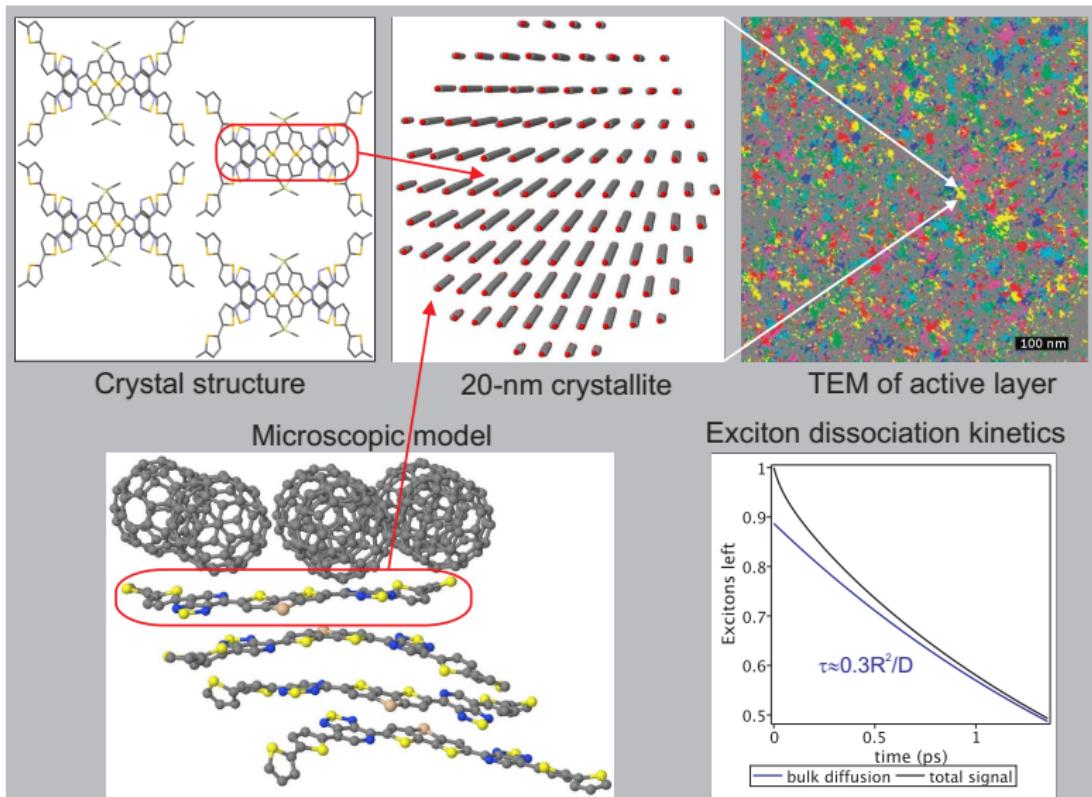
Master equation for average site occupation  $n_i(t)$ :

$$\frac{dn_i}{dt} = \sum_j (n_j w_{ji} - n_i w_{ij})$$

Kinetic Monte Carlo (KMC) or direct solution?

- Use direct formulas whenever is possible, see [JPCC 117, 4920]
- If system size is too large for matrix methods or if the problem is nonlinear use KMC

## Example: Modeling exciton dissociation



*In absence of traps exciton dissociation proceeds in picoseconds*

## Beyond hopping: Mean-field polaron approximation

$$\sum_{ij} H_{ij}^{1p} c_i^\dagger c_j + \sum_\alpha \hbar\omega_\alpha \left( b_\alpha^\dagger b_\alpha + \frac{1}{2} \right) + \sum_{i\alpha} \hbar\omega_\alpha g_{i\alpha} \left( b_\alpha^\dagger + b_\alpha \right) n_i$$

1. Do polaron transformation:

$$H \rightarrow e^S He^{-S}, \text{ where } S = \sum_{i\alpha} g_{i\alpha} \left( b_\alpha - b_\alpha^\dagger \right) n_i$$
$$\implies H^{\text{electron}} + H^{\text{phonon}} + H^{\text{int}} \rightarrow H^{\text{polaron}} + H^{\text{phonon}}$$

but  $H^{\text{polaron}}$  includes phonon operators.

2. Take “late” thermal average over phonons in  $H^{\text{polaron}}$   
 $\implies$  renormalized onsite energies and transfer integrals:

$$\varepsilon_i^{\text{polaron}} = \varepsilon_i - \lambda_i, \quad V_{ij}^{\text{polaron}} = r_{ij} V_{ij}$$

here

$\lambda_i = \sum_\alpha g_{i\alpha}^2 \hbar\omega_\alpha$  is polaron relaxation energy,

$r_{ij} = \exp \left( -\frac{1}{2} \sum_\alpha g_{i\alpha}^2 \coth \frac{\hbar\omega_\alpha}{2kT} - \frac{1}{2} \sum_\beta g_{j\beta}^2 \coth \frac{\hbar\omega_\beta}{2kT} \right)$  is band narrowing factor.

## Challenges (small-molecule solid)

- Structure prediction (polymorphism, accurate force field)
- Multiple sites per molecule (benzene, C<sub>60</sub>, large molecules)
- Nonlocal couplings (accuracy vs. feasibility)
- Efficient implementation of mean field polaron approach
- ... combine with deformation potential theory
- Slow and anharmonic molecular motions ✓

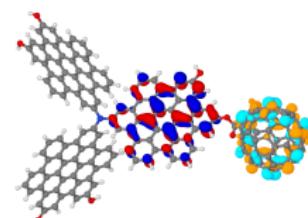
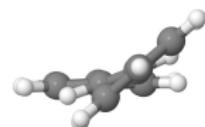
# Beyond the simplified approach

(not intended to cover all research groups and all recent publications)

- More accurate model (*up to all-quantum dynamics*)
  - ▶ J.Blumberger [Nat Comm 10, 3843 (2019)]
  - ▶ S.Tretiak [Acc Chem Res 47, 1155 (2014)]
  - ▶ O.Prezhdo, [J Chem Theory Comp 12, 1436 (2016)]
  - ▶ P.Rosky [J Chem Phys 142, 244112 (2015)]
- Larger scales (*up to empirical models*)
  - ▶ D.Andrienko [J Chem Theory Comp 10, 2508 (2014)]
  - ▶ *empirical*: H.Bassler, many others
- Electron-phonon correlations (*up to solvable models*)
  - ▶ F.Spano [Chem Rev 118, 7069 (2018)]
  - ▶ K.Hannewald, F.Ortmann [Phys Stat Sol B 248, 511 (2011)]
  - ▶ I.Burghardt [Z Phys Chem 225, 541 (2011)]
  - ▶ S.Fratini, S.Ciuchi, [Adv Funct Mater 26, 2292 (2016)]
  - ▶ A.Bakulin [Nat Comm 6, 7880 (2015)]

# Why do we need more accurate model

- Realistic potential energy surface  
(intramolecular librations, intermolecular motions)
  - ▶ Nonadiabatic molecular dynamic (NAMD)
    - classical molecular dynamics with nonadiabatic electronic transitions
- [Acc Chem Res 47, 1155]
- Realistic electron-electron interaction  
(ultrafast photodynamics, charge separation)
  - ▶ NAMD
  - ▶ Hubbard-Peierls models
- Coarse-grained electronic sites are ill-defined  
(large molecules, polymers)
  - ▶ NAMD
  - ▶ Next slide

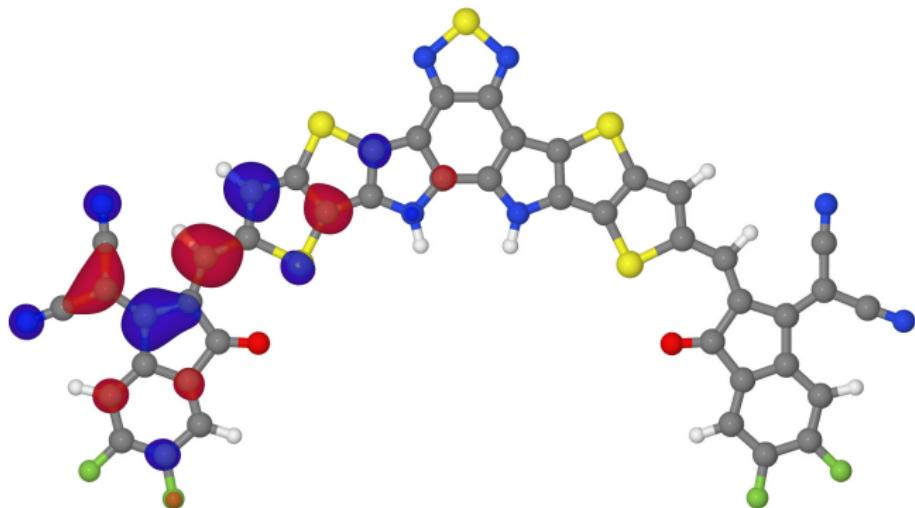


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Current NAMD implementations: 1) not scalable; 2) systematic error due to classical dynamics of atoms (nuclei)

### Nontrivial coarse graining: Large molecules

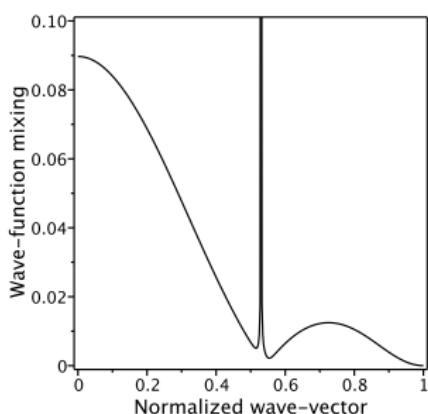
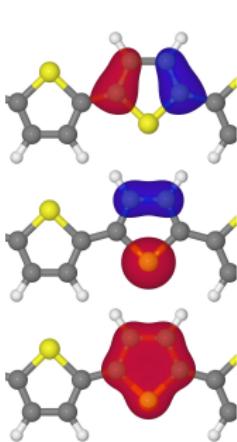
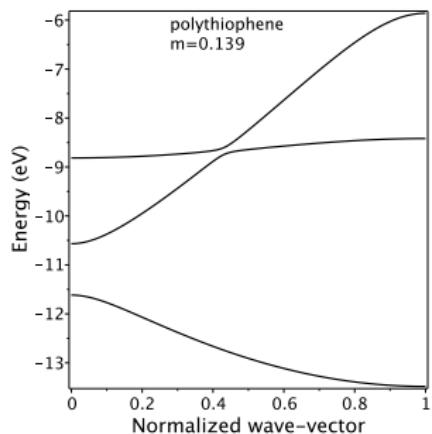
(in particular novel non-fullerene acceptors for high-efficiency solar cells)



# Nontrivial coarse graining: Conjugated polymers

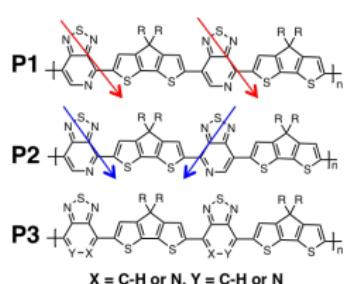
**Problem:** There are no static well-separated coarse graining sites

**Solution, electronic part:** Use of localized molecular orbitals  $\rightarrow$  get coarse grained tight-binding Hamiltonian



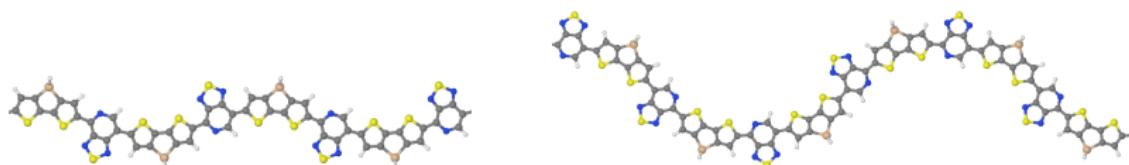
## Example: Influence of regiochemistry

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
$E_g^{\text{cvb}}$ [eV]	1.37	1.46	1.54
$\lambda_{\text{max}}^{\text{sol}}/\lambda_{\text{max}}^{\text{film sc}}$ [nm]	930/920	885/885	880/870
$E_g^{\text{optd}}$ [eV]	1.09	1.12	1.15
$\mu_{\text{sat}}^e$ [ $\text{cm}^2 \text{V}^{-1} \text{ s}^{-1}$ ]	0.4 (0.3)	0.6 (0.5)	0.005 (0.005)
$I_{\text{on}}/I_{\text{off}}$	$2 \times 10^3$	$2 \times 10^4$	$1 \times 10^4$

Theory: Electronic structure of ideal polymer is insensitive to regiochemistry  $\implies$  The difference is in intramolecular conformations influencing also intermolecular packing



## Larger scales

### Challenges:

- absence of well parameterized force fields
- accurate intra/inter-molecular geometry & realistic mesoscale

### Approaches:

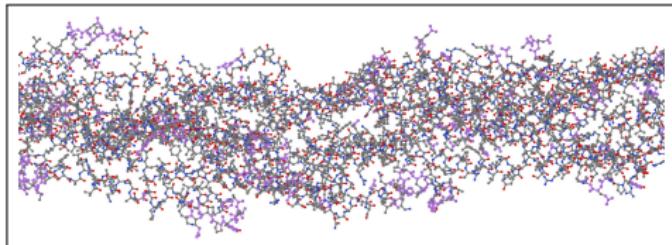
- Efficient/accurate DFT-based parameterization of force fields
- First-principle parameterization of empirical models  
[J Chem Theory Comput 10, 2508]
- Upscaling NAMD and effective Hamiltonian methods

# Electron-phonon correlation effects

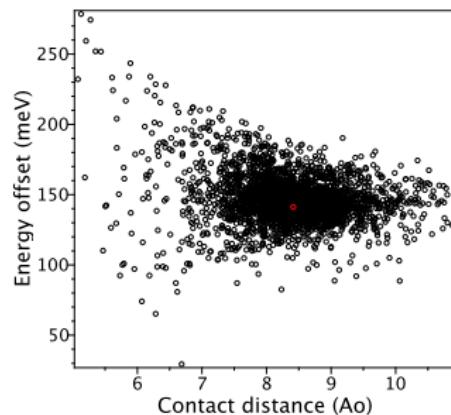
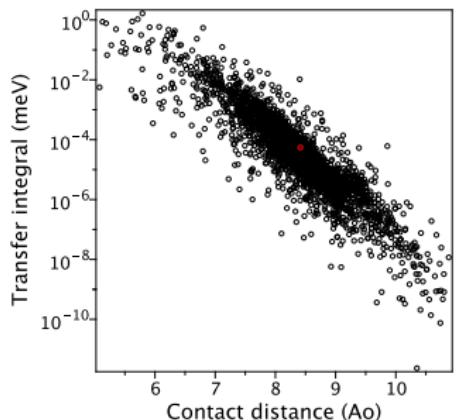
(e.g. effective hopping rate  $\neq$  average rate)

- Statistical correlations
  - ▶ Phonon population fluctuations – usually small effect
  - ▶ Nonequilibrium phonon population:
    - ▶ pumping Nat Comm 6, 7880 (2015)
    - ▶ photoexcitation Phys Rev Lett 116, 057402 (2016)
- Dynamic correlations
  - ▶ Strong deviations from rate theory, coherences in ultrafast energy transfer JACS 137, 11637 (2015)
  - ▶ Large rate fluctuations Adv Mater 27, 1908 (2015)
  - ▶ Localization in a perfect crystal Adv Funct Mater 26, 2292 (2016)

# Dynamic correlations: Intermolecular fluctuations



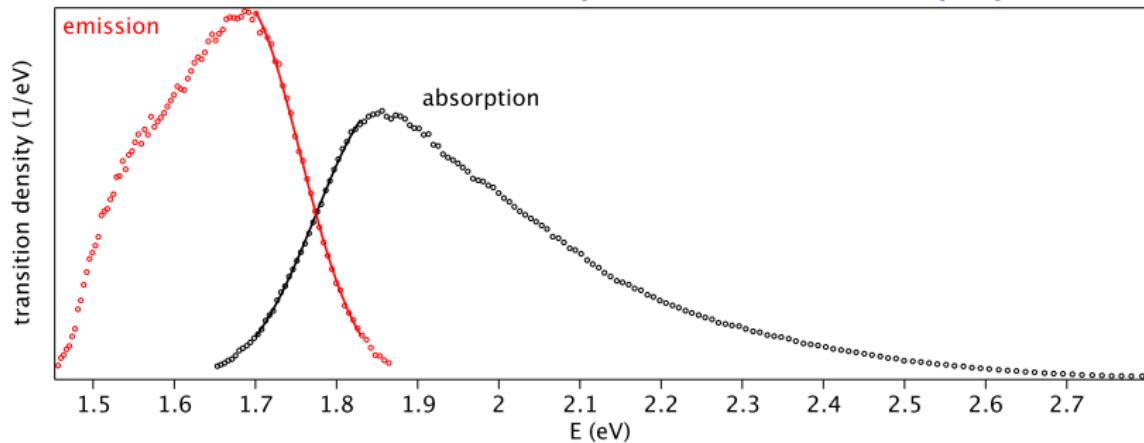
$B(\text{\AA}^2)$	$\lg\langle V^2 \rangle$	$-\lg\langle V^{-2} \rangle$
2.5	-4.1	-5.0
12	-3.4	-6.2
23	-2.8	-7.0
34	-1.4	-8.5



H Yan, C Chuang, A.Z., S Tretiak, F W Dahlquist, G C Bazan, Adv Mater 27, 1908 (2015)

$B$  is Debye–Waller factor (experimentally 20–50  $\text{\AA}^2$ ),  $V$  – electronic coupling

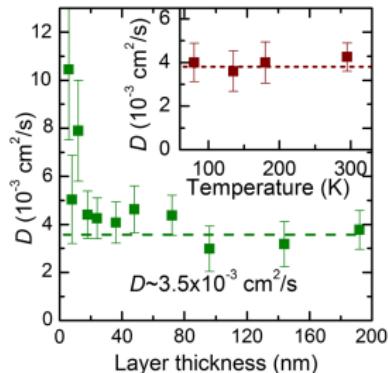
# Statistical correlations: Nonequilibrium initial population



$$\exp\left(-\frac{\lambda}{4T}\right) \rightarrow \exp\left(-\frac{\lambda}{16T}\right)$$

Rate increase factor 1.6 for the shown transition density

Phys Rev Lett 116, 057402 (2016) →



$\lambda$  – Stokes shift (Frenkel exciton reorganization energy),  $T$  – temperature

# Exciton/charge carrier localization in molecular crystals

Holes in pentacene

OFET applications  
rigid



$$V \sim 100 \text{ meV}, W^{\text{bare}} \sim 600 \text{ meV}$$

Intramolecular modes:

$$\lambda = 50\text{-}80 \text{ meV}, W^{\text{polaron}} \sim 350 \text{ meV}$$

Intermolecular modes [1]:

$$\hbar\omega = 5\text{-}20 \text{ meV}, g_{\text{total}}^2 \sim 0.2$$

Experiment at 75 K [2]:  $W = 250 \text{ meV}$

$W$ =bandwidth

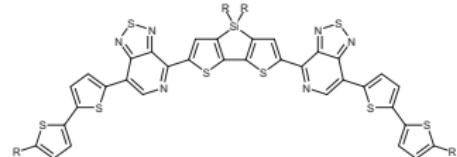
[1] Phys Rev B 69, 075211 (2004)

[2] Phys Rev Lett 108, 256401 (2012)

Two localization mechanisms: band narrowing and quasistatic disorder

Excitons in DTS(PTTh<sub>2</sub>)<sub>2</sub>

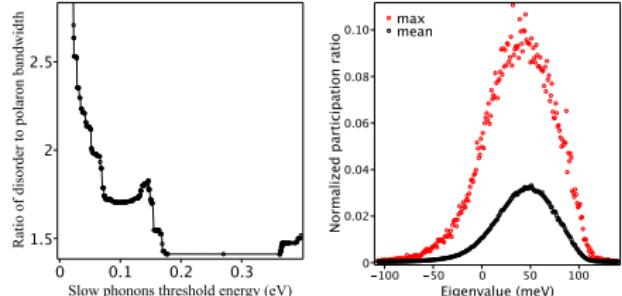
OPV applications  
flexible



$$V = 60 \text{ meV}, W^{\text{bare}} = 260 \text{ meV}$$

Intramolecular modes:

$$\lambda = 110\text{-}260 \text{ meV}, W^{\text{polaron}} = 0$$



## Challenges (beyond the simplified approach)

- Structure prediction and charge transport in polymers
- Charge transport in polycrystals
- Electron-phonon correlations
- Upscaling NAMD

## Summary and outlook (energy/charge transport)

- Intrinsic charge carrier mobility and exciton diffusion length in molecular crystals can be predicted within an order of magnitude accuracy
- Computational prescreening of organic semiconductors for energy/charge transport is possible and limited mainly by structure prediction capabilities
- A concerted experimental and theoretical investigation is required in order to unveil microscopic mechanisms of energy or charge transfer/transport in a particular material

### Anticipated near-future theoretical milestones:

- Upscaling existing methods (NAMD and simpler ones)
- Predictable modeling in establishing chemical structure – macroscopic properties relationships
- Modeling complex systems such as polymers, large supramolecular complexes, hybrid structures