

IFSOE-2016 Tutorial Lecture

# First-principle modeling of energy and charge transport in organic semiconductors

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## Acknowledgments

Team (see poster P31)

Oleg Kharlanov

Artem Naumov

Collaborations

Sergei Tretiak (theory, LANL)

Guillermo Bazan (experiment, UCSB)

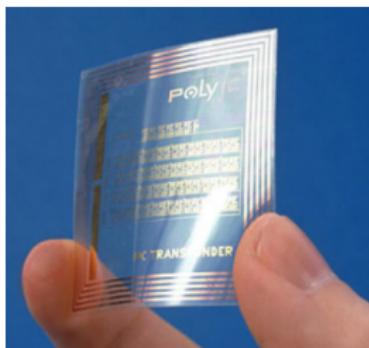


# Outline

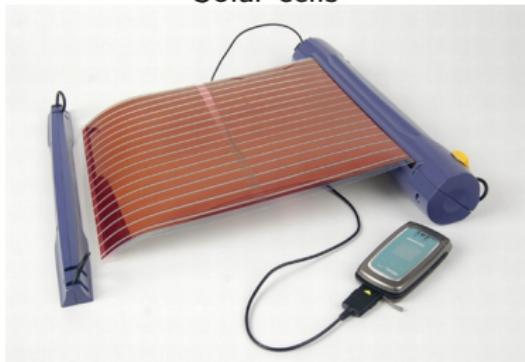
- Overview
- Simplified approach
  - *well established and routinely used, but not in textbooks yet*
- Beyond the simplified approach
  - *recent and current developments*
- Illustrative case studies

# Charge/energy flow is key process in many devices

Field effect transistors



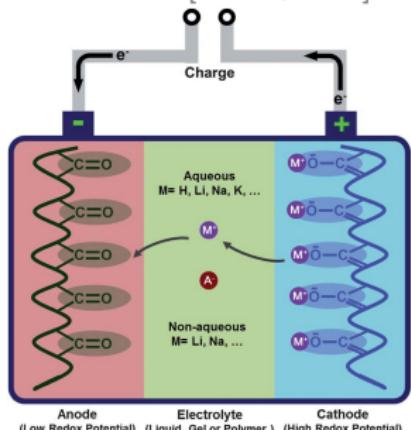
Solar cells



Light emitters



Batteries [EES 6, 2280]



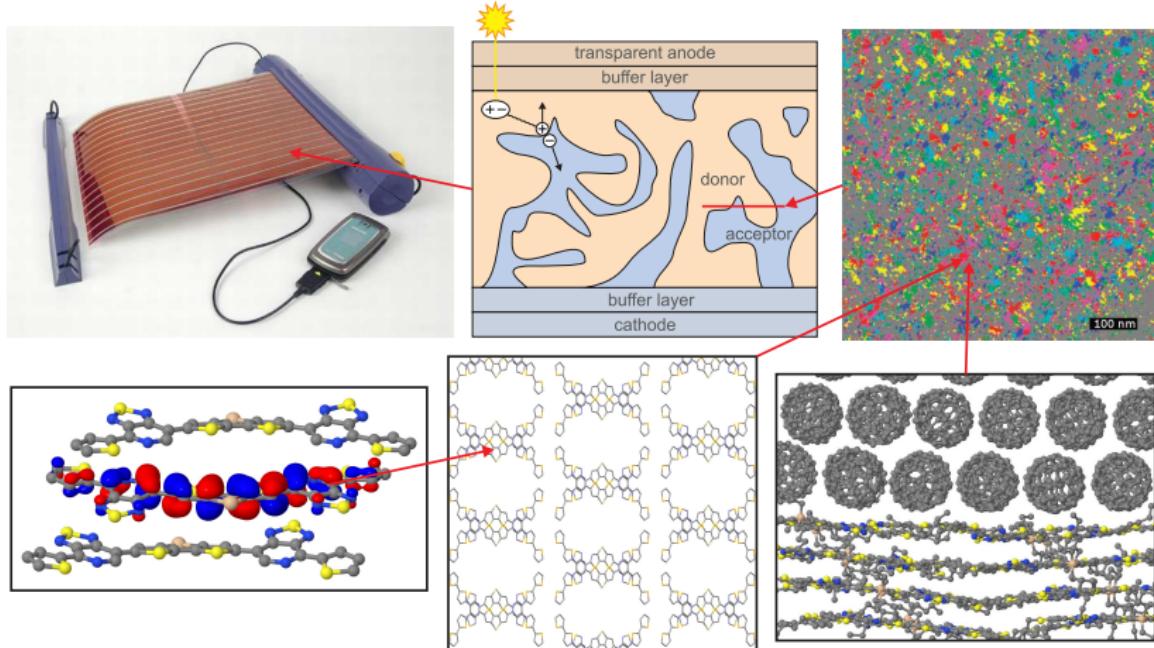
7 lectures at IFSOE-2015

# 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

# Challenges: multiple scales



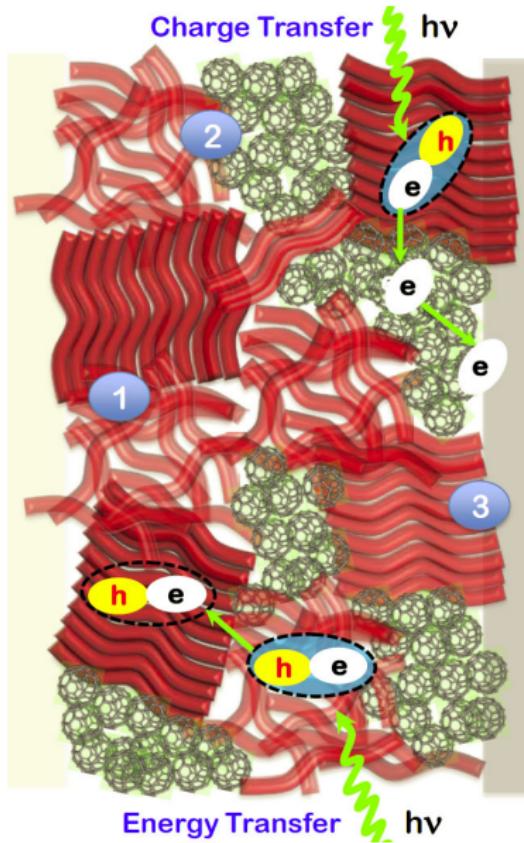
# Multiple scales: broad range of scales

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 ( $>ns$ )



## Multiple scales: how to approach

Scale	Method	Electronic processes
molecular complex (1000 atoms)	NAMD	intramolecular relaxation internal conversion intermolecular transfer redox reactions
single bulk phase (crystal, amorphous)	MF	intraband relaxation charge carrier scattering
mesoscale (up to continuum)	KMC MD ??	hopping ionic transport electronic + ionic
device	PDE	diffusive transport

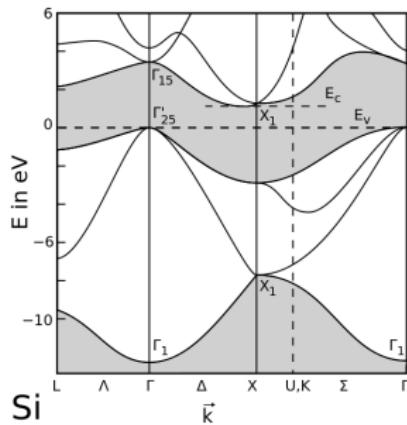
Challenge: no black-box tools, it is complex problem (combine different approaches on different scales, error accumulation through scales)

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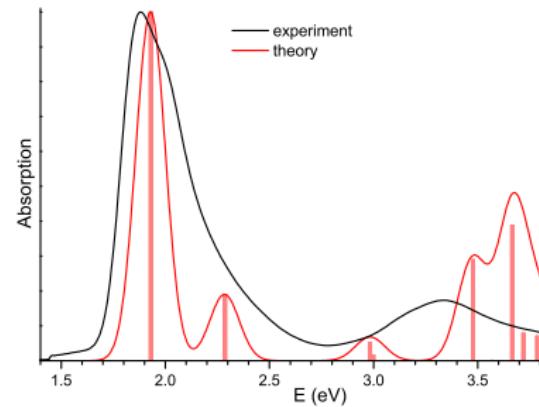
NAMD=nonadiabatic MD, MF=mean field, KMC=kinetic Monte Carlo,  
MD=molecular dynamics, PDE=partial differential equations

# Challenges: strong electron-phonon correlations

## Basic definitions



Electronic bandwidth



Vibronic bandwidth

$$W_{\text{el}}^2 = \langle \Delta \varepsilon^2 \rangle + \langle \Delta \varepsilon^2 \rangle_T$$

$$W_{\text{vib}}^2 = \sum_{\alpha} g_{\alpha}^2 \hbar^2 \omega_{\alpha}^2 \coth \frac{\hbar \omega_{\alpha}}{2T}$$

For bandwidth  $W$ , correlation function decreases as  $e^{-W^2 t^2 / 2\hbar^2}$  at small  $t$

# Strong electron-phonon correlations

Electron-phonon couplings are always large for bonding electrons, with  $W_{\text{vib}}$  of the order of tenths of eV. The difference is in  $W_{\text{el}}$ :

“Inorganic electronics”

$$W_{\text{el}} \gg W_{\text{vib}}$$

(weak el-ph correlations)

⇒ model of free charge carriers scattered by phonons

“Organic electronics”

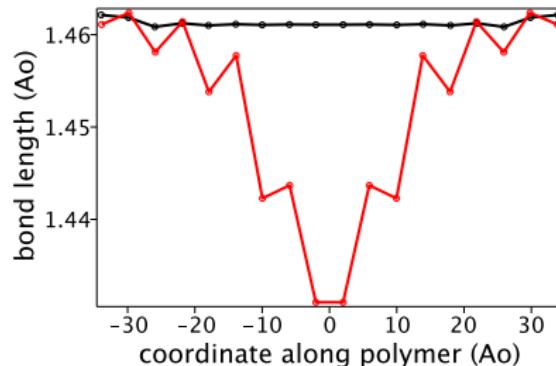
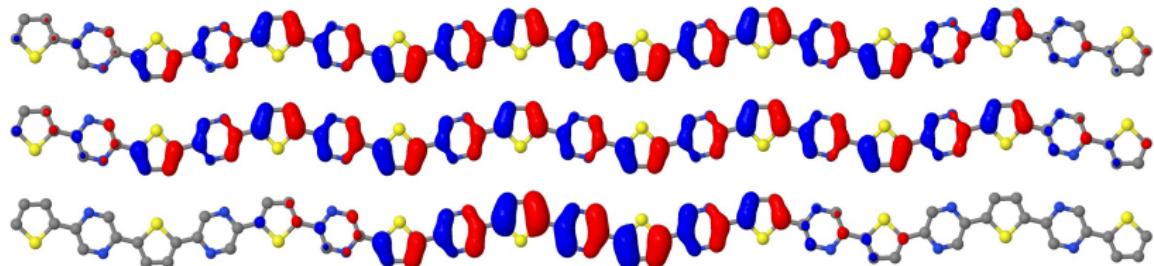
$$W_{\text{el}} \sim W_{\text{vib}}$$

(strong el-ph correlations)

⇒ more complicated models

# Polaron formation

(HOMO, cation NO, polaron NO)



# Charge carrier mobility

Basic equations in homogeneous medium

Current density	$j = \mu n e \mathcal{E}$
Mobility	$\nu = \mu \mathcal{E}$
Zero-field mobility	$\mu = \frac{e}{T} D$

Free charge carriers	Localized charge carriers
Drude formula	Hopping
$\mu = \frac{e \tau_{\text{scattering}}}{m_{\text{effective}}}$	$\mu = \frac{e}{T} f a^2 w, \quad w = \frac{2\pi}{\hbar} V^2 J$

Scattering (or localization) mechanisms:

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

$f$  is lattice form-factor,  $a$  is lattice spacing,  $w$  is hopping rate,

$V$  is electronic inter-site coupling,  $J$  is spectral overlap

Exciton diffusion length =  $\sqrt{D * \text{lifetime}}$

# Outline

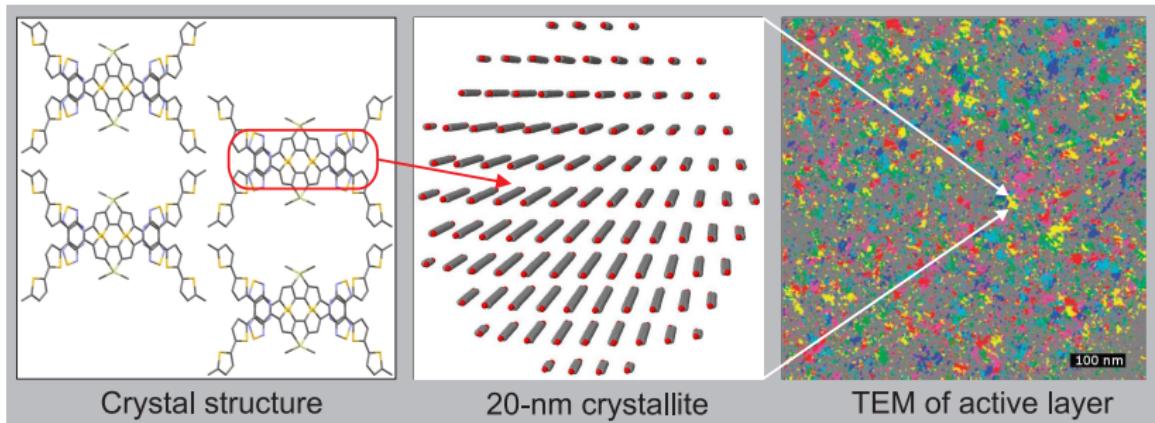
Overview

- Simplified approach

Beyond the simplified approach

Illustrative case studies

# 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)

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Approximations:

- mean field approximation for electrons
- harmonic approximation for atomic motion
- linear electron-phonon coupling

# Calculating coarse-grained electronic Hamiltonian

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

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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 $n_{h/e} = 1 \pm .25$		

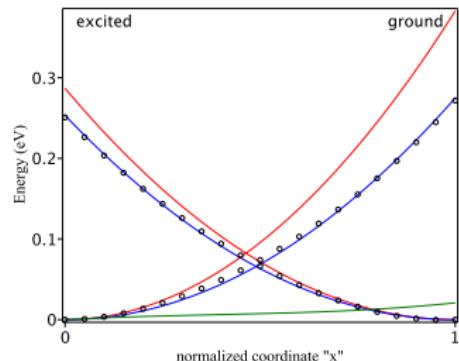
# Calculating vibronic couplings

## 1. Local couplings (Holstein model):

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

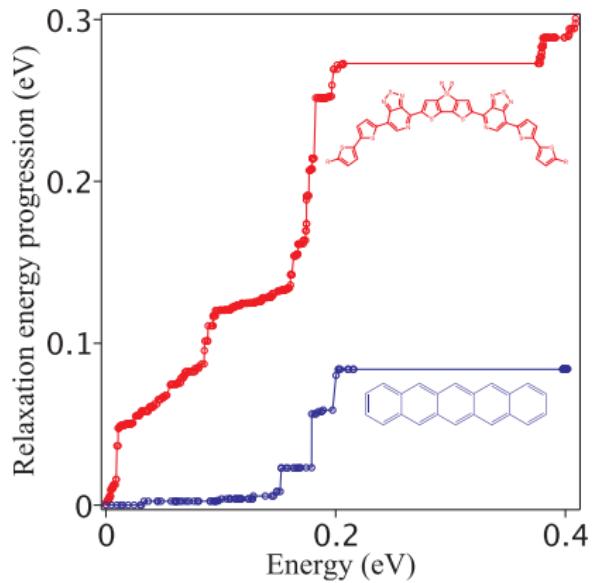
and  $g_{i\alpha} g_{j\alpha} = 0$  for  $i \neq j$

- 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



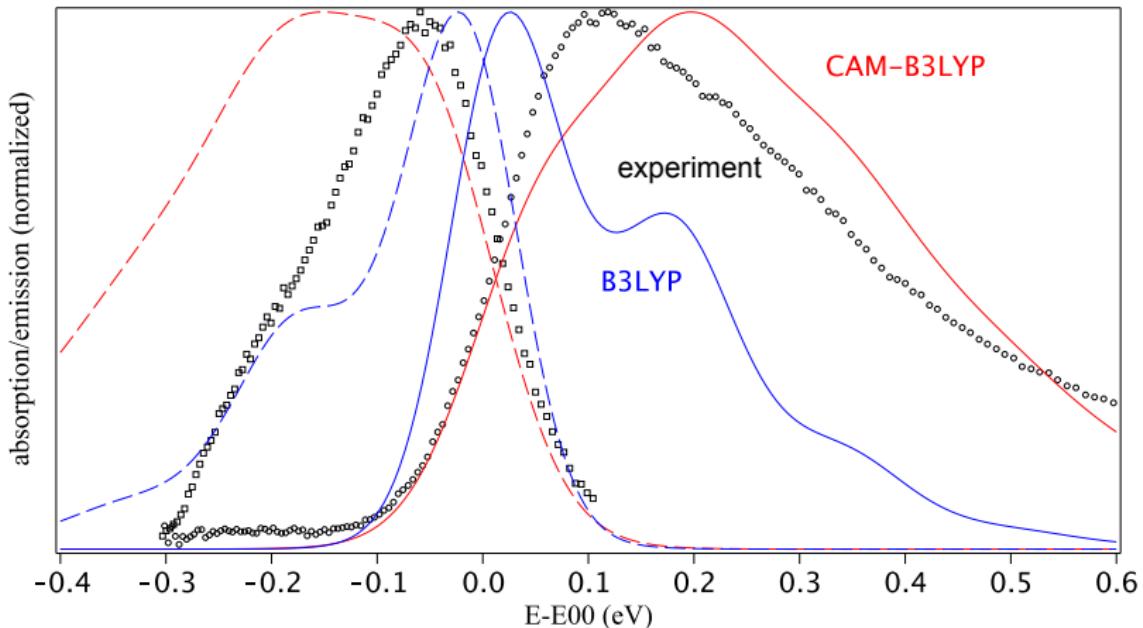
## 2. Nonlocal intermolecular couplings see [Phys Stat Sol B 248, 511]

## Vibronic couplings: example



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

# Vibronic couplings: choice of density functional is critical

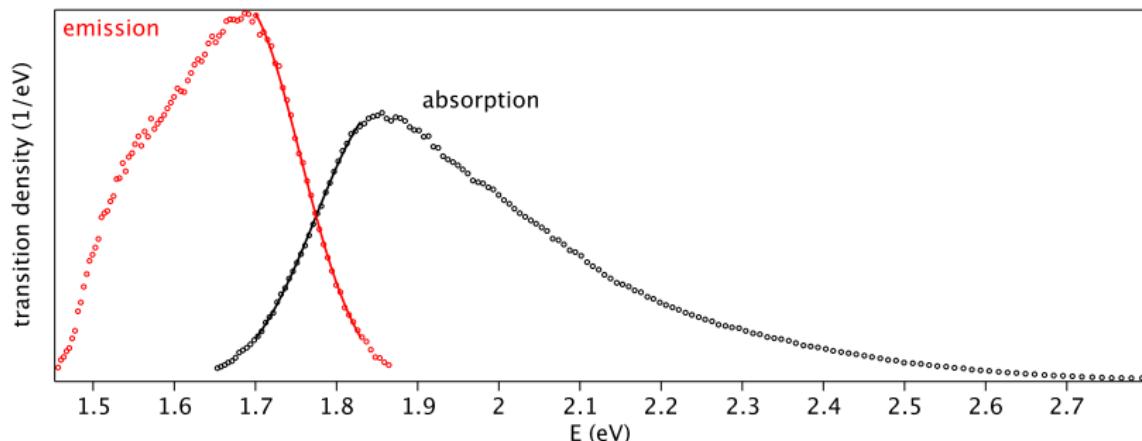


B3LYP underestimates vibronic couplings for low- $\omega$  modes  
CAM-B3LYP overestimates vib. couplings for high- $\omega$  modes

# 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

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

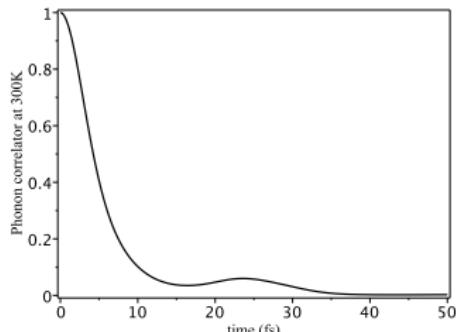
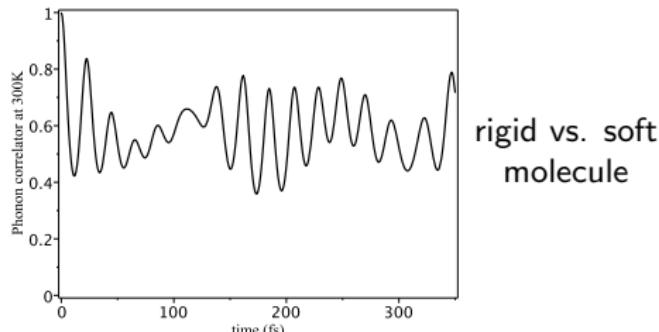
Independent boson model (displaced harmonic oscillator):

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

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.  $e^{-\sigma^2 t^2 / 2\hbar^2}$

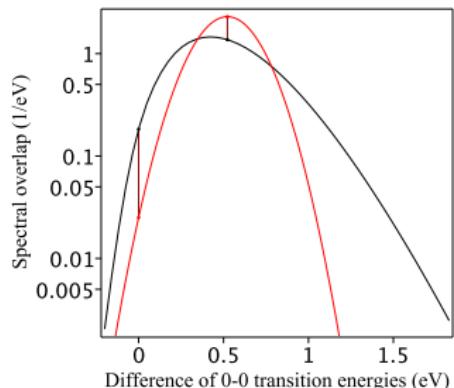
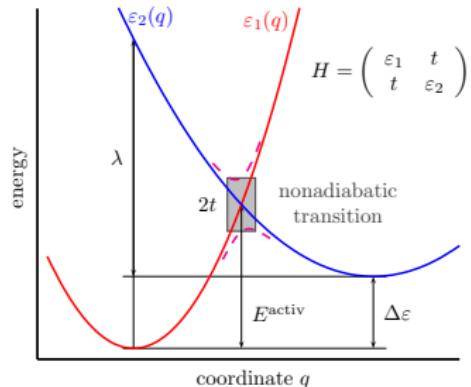


# Spectral overlap in high temperature limit: Marcus formula

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

## 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.

## Calculating diffusion coefficient and mobility

Formally band-like motion is described by the same formula as hopping with rescaled transfer rates\*

$$w_{(i \rightarrow j)} = \frac{2\pi}{\hbar} |V_{ij}|^2 \int_{-\infty}^{\infty} C^{\text{phonon}}(t) C^{\text{polaron}}(t) e^{-\sigma^2 t^2 / 2\hbar^2} dt$$

where  $\sigma$  is inhomogeneous broadening (e.g. scattering by impurities),

$$C_{(i \rightarrow j)}^{\text{phonon}}(t) = \left\langle e^{itH_i^{\text{vib}}/\hbar} e^{-itH_j^{\text{vib}}/\hbar} \right\rangle$$

$$C^{\text{polaron}}(t) = \frac{1}{N_{\text{cells}}} \sum_{k,k'} \rho(k) \exp \left[ i \frac{\varepsilon(k) - \varepsilon(k')}{\hbar} t \right]$$

here  $\varepsilon(k)$  is polaron dispersion,  $\rho(k)$  – thermal population,  
 $H_i^{\text{vib}}$  is phonon Hamiltonian with the oscillators at site  $i$  displaced.

*Hopping approximation can be used far beyond its applicability if the transfer rates are rescaled by a free-polaron correlation function*

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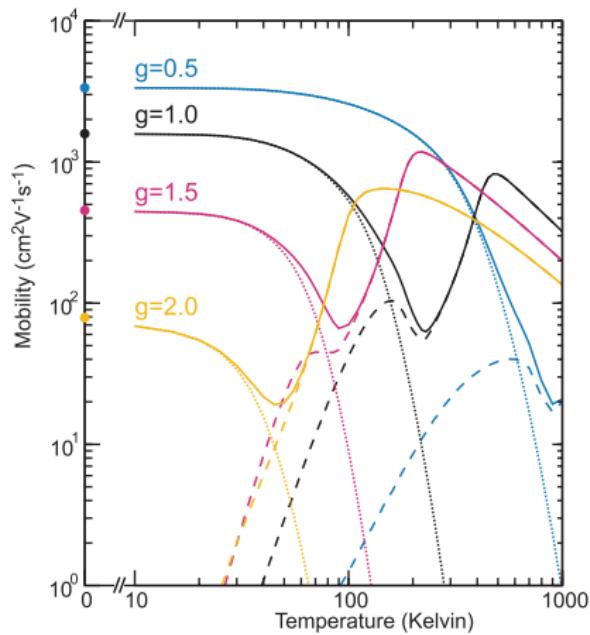
\* Derived from F Ortmann Phys Rev B 79, 235206 (2009)

For nonlocal coupling see K Hannewald Phys Rev B 69, 075211 (2004)

# Mean-field polaron: zero-field mobility in crystal

Two limiting cases:

- band transport for  
 $W_{\text{polaron}} \gg W_{\text{phonon}}$   
( $C^{\text{phonon}}(t) \approx 1$ )
- hopping for  
 $W_{\text{polaron}} \ll W_{\text{phonon}}$   
( $C^{\text{polaron}}(t) \approx 1$ )



$$\hbar\omega = 10 \text{ meV}, V = 50 \text{ meV}$$

[Phys Rev B 79, 235206]

# Outline

Overview

Simplified approach

- Beyond the simplified approach

Illustrative case studies

# Beyond the simplified approach

(not intended to cover all research groups)

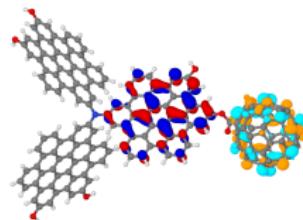
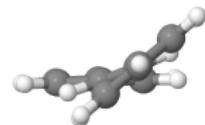
- More accurate model (*up to all-quantum dynamics*)
  - ▶ S.Tretiak [Acc Chem Res 47, 1155]
  - ▶ P.Rossky [J Chem Phys 142, 244112]
- Larger scales (*up to empirical models*)
  - ▶ D.Andrienko [J Chem Theory Comput 10, 2508]
  - ▶ V.Ivanov [IFSOE-2015]
  - ▶ M.Vener [IFSOE-2015]
  - ▶ D.de Leeuw [IFSOE-2015]
  - ▶ *empirical*: S.Novikov [IFSOE-2015], M.Kemerink [IFSOE-2015]
- Electron-phonon correlations (*up to solvable models*)
  - ▶ A.Bakulin [IFSOE-2015]
  - ▶ J.Gierschner [IFSOE-2015]
  - ▶ F.Spano [Ann Rev Phys Chem 65, 477]
  - ▶ K.Hannewald [Phys Stat Sol B 248, 511]
  - ▶ I.Burghardt [Z Phys Chem 225, 541]

See also: D.Beljonne, J.Cornil, Multiscale Modelling... (Springer, 2014)

A.Z., S.Tretiak, Annu Rev Phys Chem 66, 305 (2015) and references therein

# 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 and poster **31**



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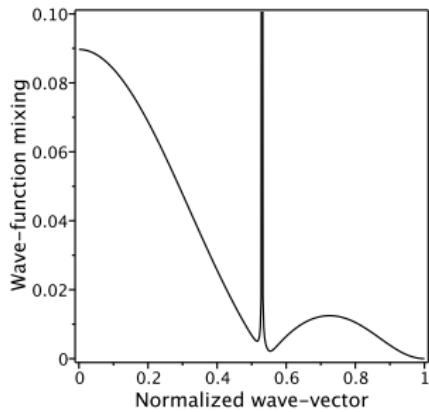
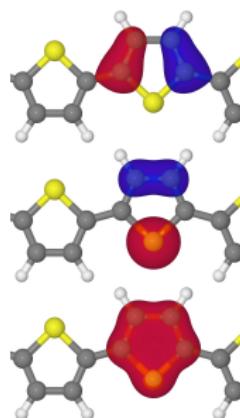
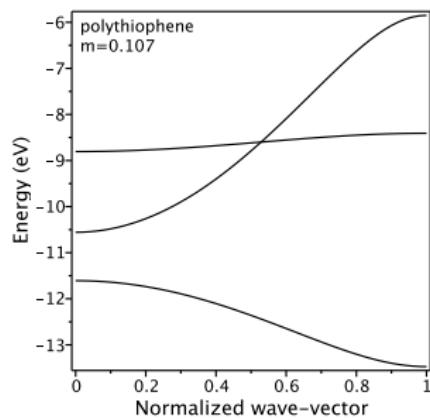
Current NAMD implementations: 1) not scalable; 2) systematic error due to classical dynamics of atoms (nuclei)

# Nontrivial coarse graining: Conjugated polymers

See poster 31

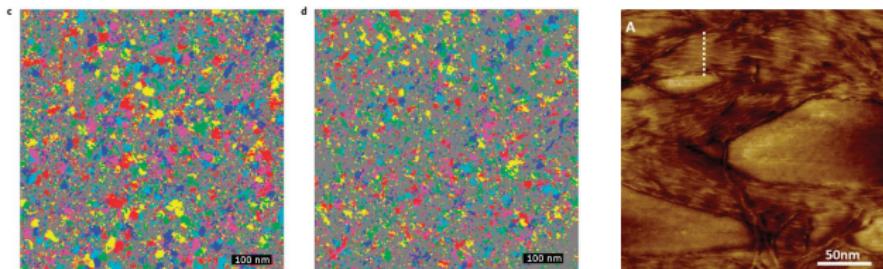
**Problem:** There are no static well-separated coarse graining sites

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



## Larger scales

Functional properties of organic semiconductors are often determined by structure on scales up to tens of nm ( $10^6$  atoms)



### Challenges:

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

### Approaches:

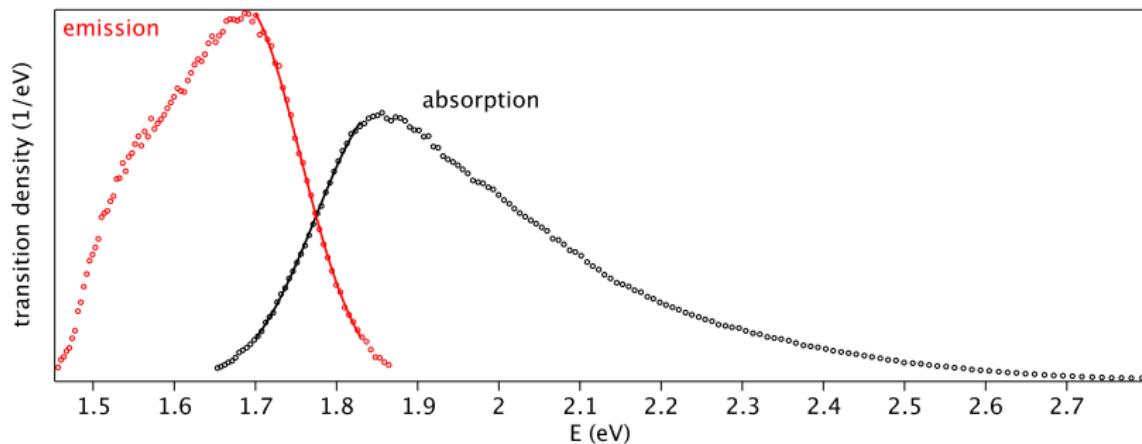
- First-principle parametrization of empirical models  
[J Chem Theory Comput 10, 2508]
- Upscaling NAMD and effective Hamiltonian methods

# Electron-phonon correlation effects

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

- Fine structure of UV-Vis absorption by molecular crystals
  - ▶ F.Spano [Ann Rev Phys Chem 65, 477 and references therein]
- Statistical correlations
  - ▶ Phonon population fluctuations – usually small effect
  - ▶ Nonequilibrium phonon population:  
pumping – A.Bakulin [IFSOE-2015], photoexcitation – next slide
- Dynamic correlations
  - ▶ Strong deviations from rate theory, coherences in ultrafast energy transfer, see e.g. S.Tretiak [JACS 137, 11637]
  - ▶ Large rate fluctuations – next slides
  - ▶ Localization in a perfect crystal – next slides

## Statistical correlations: Nonequilibrium initial population



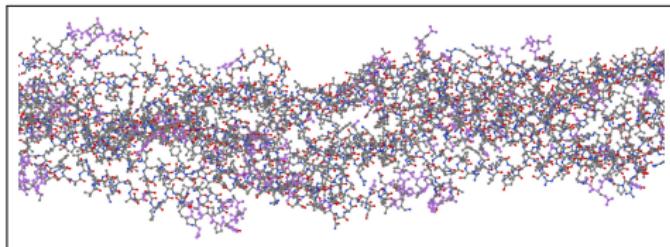
$$\exp\left(-\frac{\lambda}{4T}\right) \rightarrow \exp\left(-\frac{\lambda}{16T}\right)$$

Rate increase factor 1.6 for the shown transition density

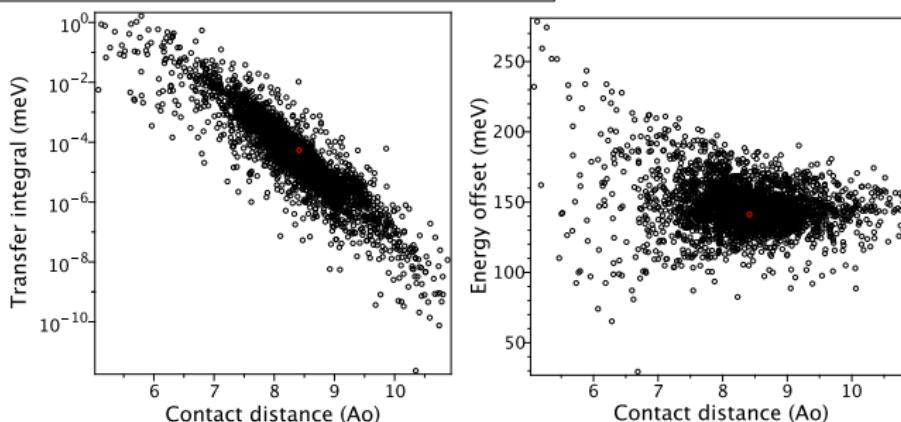
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$\lambda$  – Stokes shift (Frenkel exciton reorganization energy),  $T$  – temperature

# 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



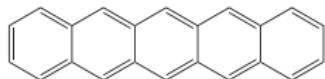
H Yan, C Chuang, A.Z., S Tretiak, F W Dahlquist, G C Bazan, Adv Mater 27, 1908 (2015)

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

# 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]:  $W = 250 \text{ meV}$

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W=bandwidth

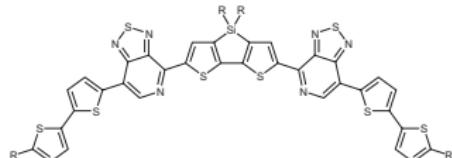
[1] Phys Rev B 69, 075211 (2004)

[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>

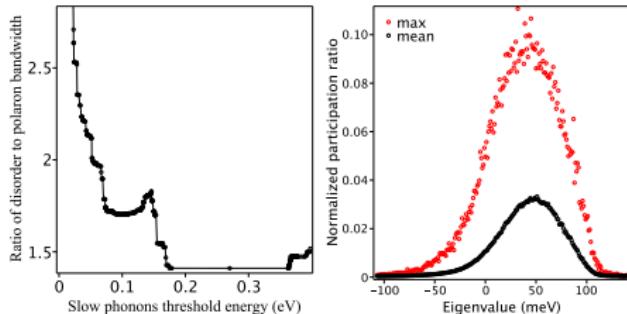
OPV applications  
flexible



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

Intramolecular modes:

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



# Outline

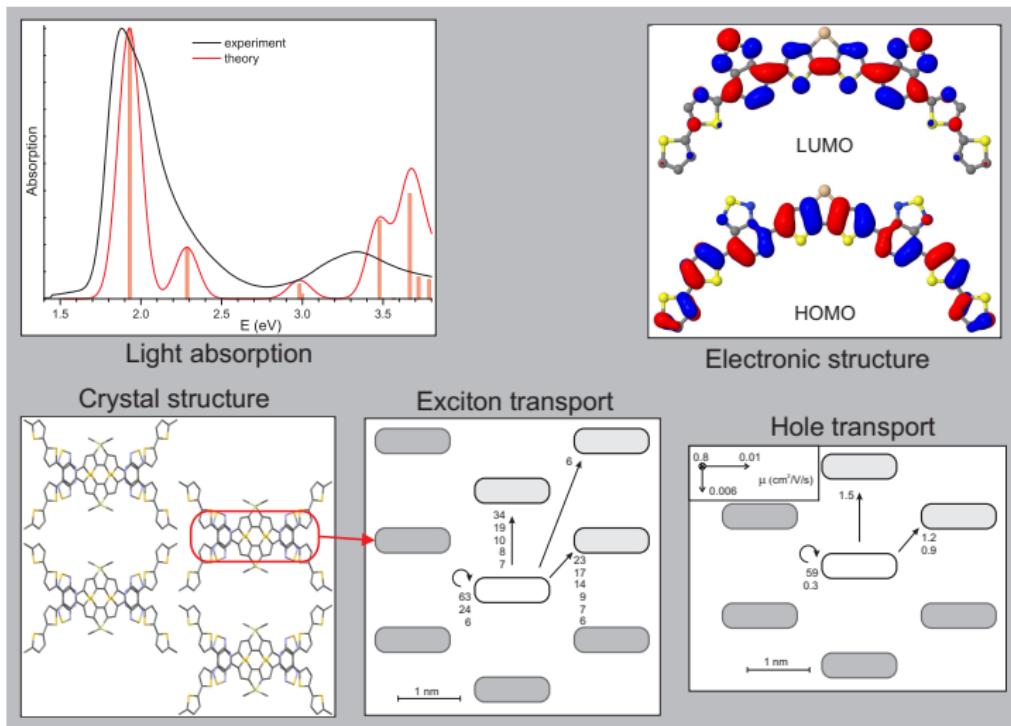
Overview

Simplified approach

Beyond the simplified approach

- Illustrative case studies

# Example: Calculating single-crystal characteristics

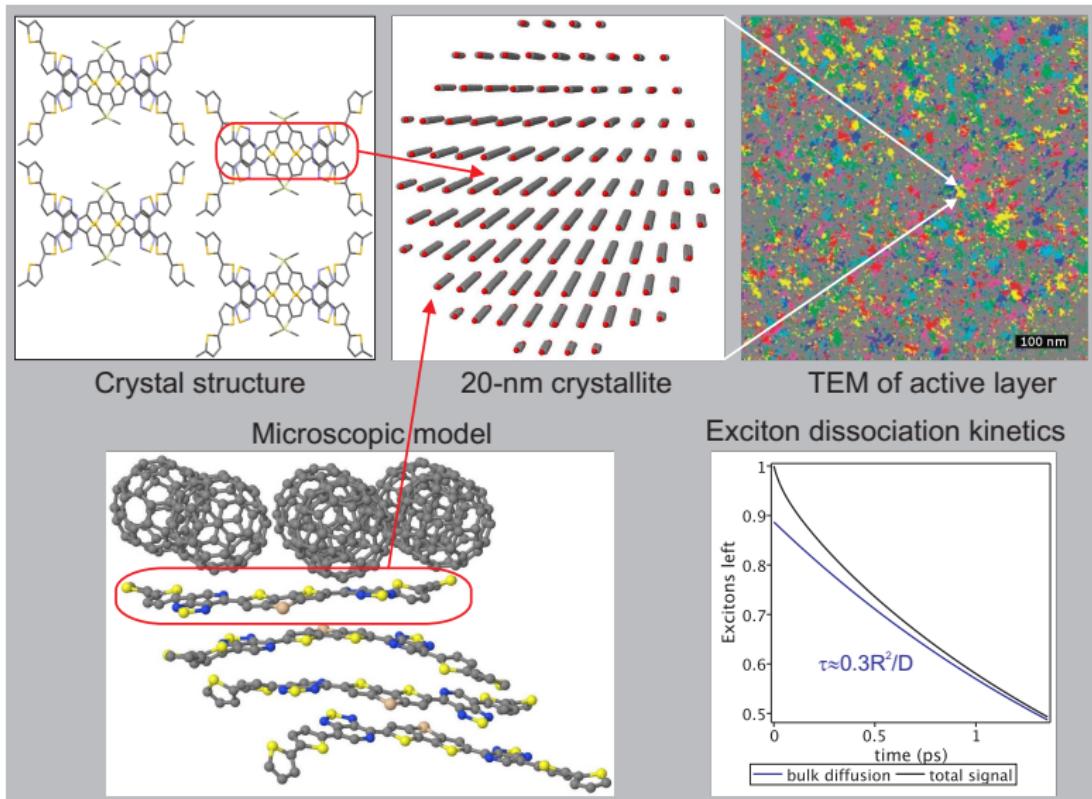


Exciton diffusion length  $\sim 100$  nm, hole mobility  $\sim 1 \text{ cm}^2/\text{V}\cdot\text{s}$

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

A.Z., O Postupna, R C Bakus II, G C Welch, G C Bazan, S Tretiak, J Phys Chem C 117, 4920 (2013)  
T S van der Poll, A.Z., E Chertkov, R C Bakus II, J Coughlin, G C Bazan, S Tretiak, JPCL 5, 2700 (2014)

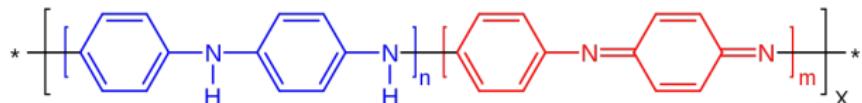
## Example: Modeling exciton dissociation



*In absence of traps exciton dissociation proceeds in picoseconds*

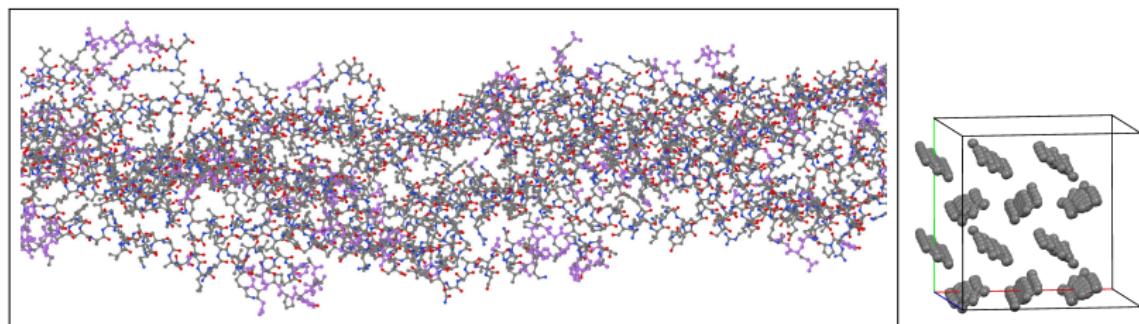
## Example: Charge transport mechanism in biopolymers

- Metallic conductivity in conjugated polymers ✓ heavily doped



[Nature 441, 65 (2006)]

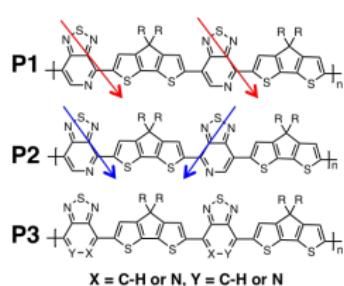
- Metallic conductivity in biopolymers? ✗ no bandwidth



Ionized sites in resonance with  $\pi$ -conjugated system – mixed electronic-ionic transport

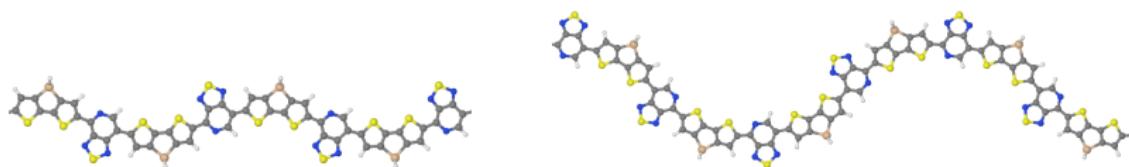
## Example: Influence of regiochemistry

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



## Summary and outlook

- 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