New Tools for Simulating Charge and Exciton Transport on the Nanoscale

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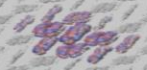
University College London



Seminar

Chair of Materials Science and Nanotechnology, TU Dresden

16. September 2021

European Research Council

IAS TUM Institute for Advanced Study

European Commission

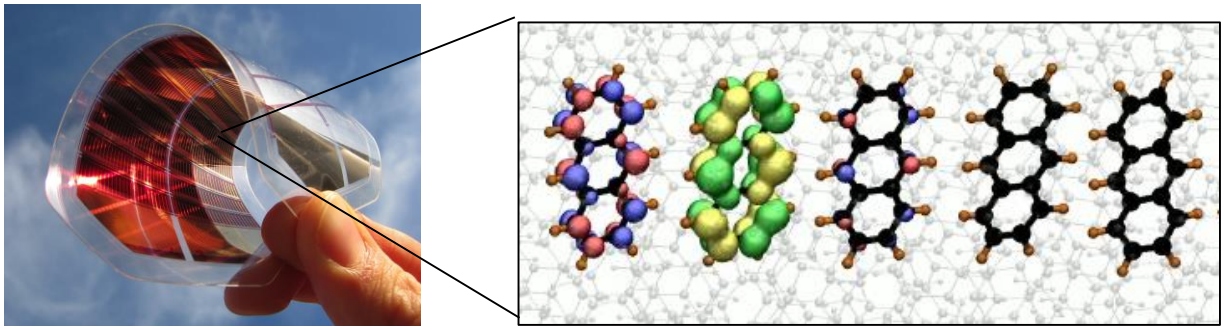
EPSRC Engineering and Physical Sciences Research Council

Pacific Northwest NATIONAL LABORATORY

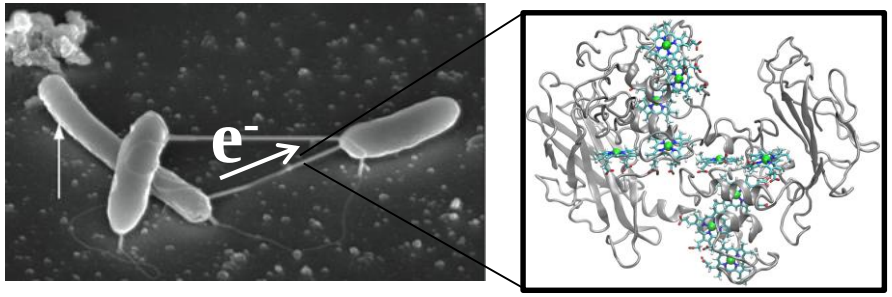
UCL

Current research areas in my group

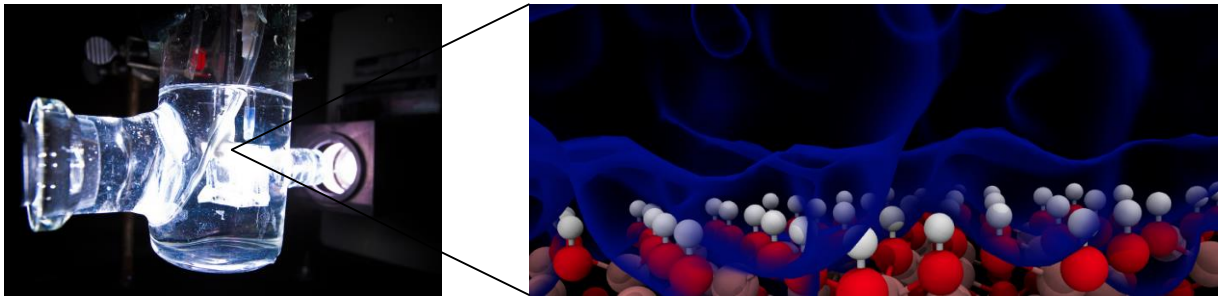
1 Charge and Exciton dynamics in organic materials (solar to electricity)



2 Electron transfer/transport in biology (bioelectronics)



3 Transition metal oxide-liquid water interfaces (solar to fuel)



Methods:

-Mixed quantum/classical non-adiabatic dynamics

-Neural Networks

-DFT

-QM/MM

-Molecular dynamics (MD)

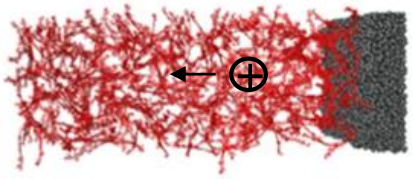
-Master equations

-Kinetic Monte Carlo

-Markov models

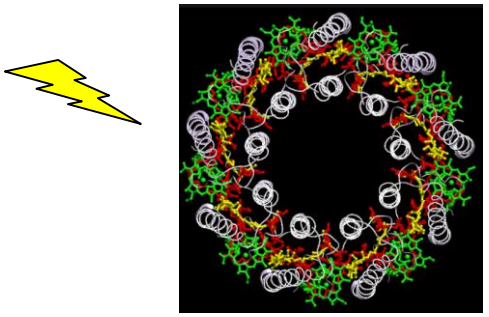
Charge and exciton transport in nanoscale molecular materials

Organic Transistors



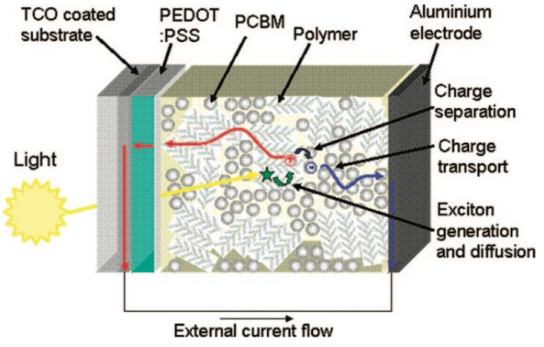
Charge transport

Light harvesters

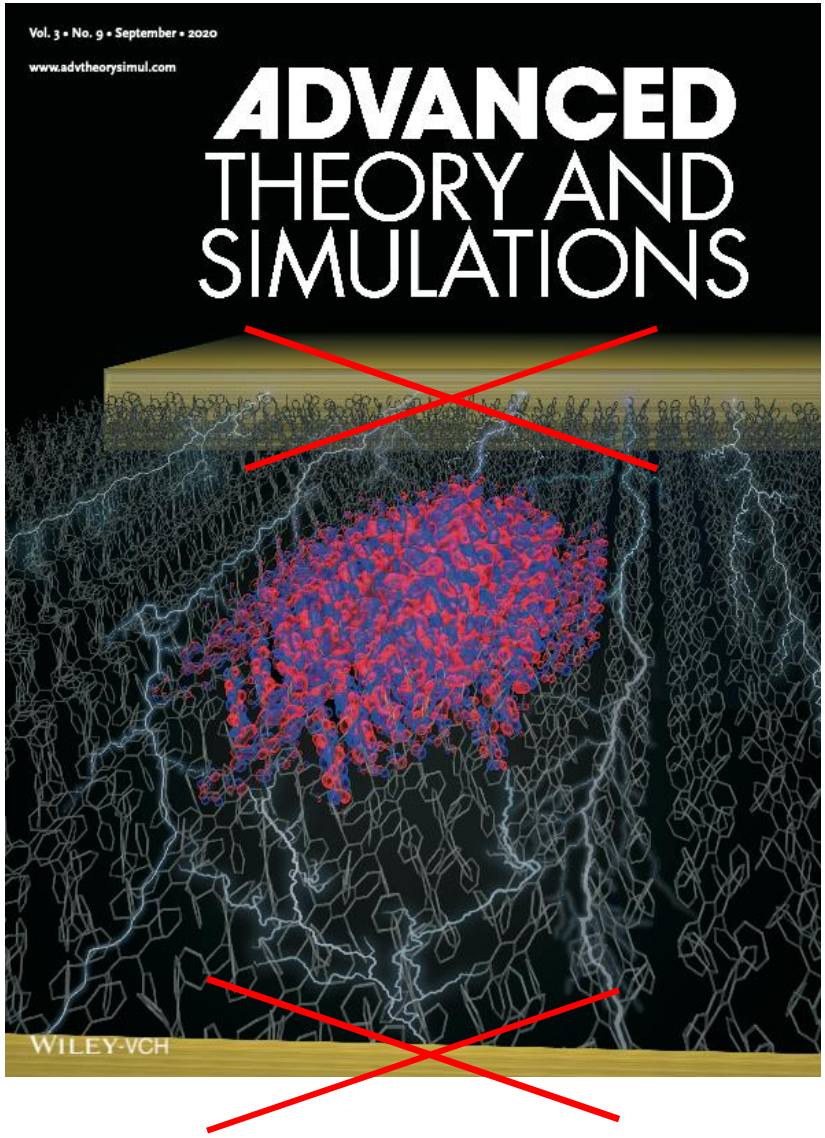


Excitation Energy transfer

Excitonic Solar Cells



Exciton dissociation to charges, recombination



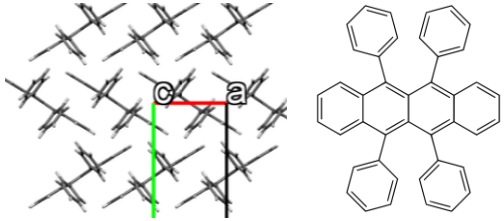
This talk:
No electrodes
No molecule-electrode couplings
No external fields

Focus:
Intrinsic charge/exciton transport property of material

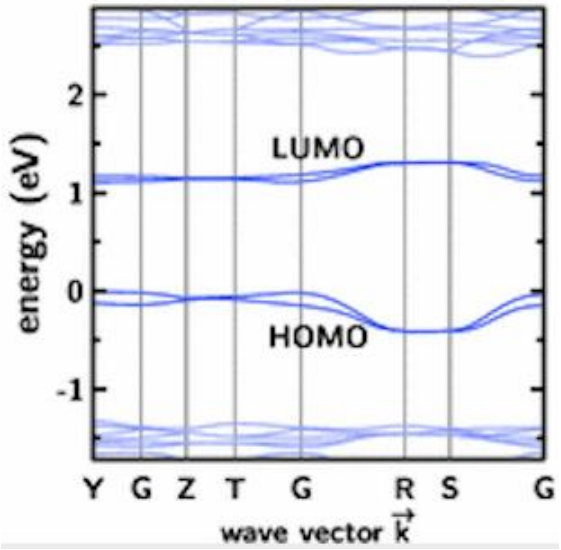
In other words:
Diffusion constants rather than currents

Charge transport in molecular materials

DFT band structure



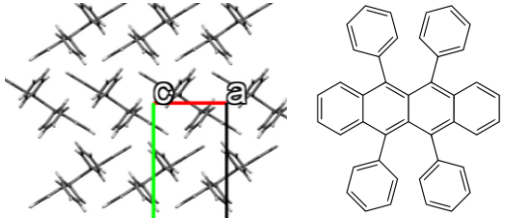
rubrene



→ narrow bands

Charge transport in molecular materials

DFT band structure



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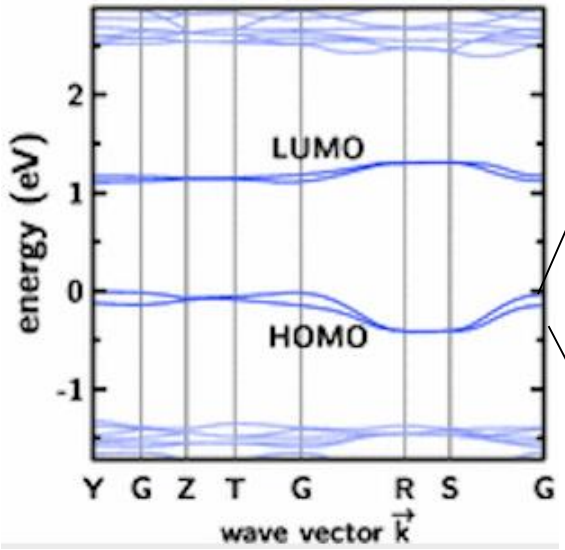
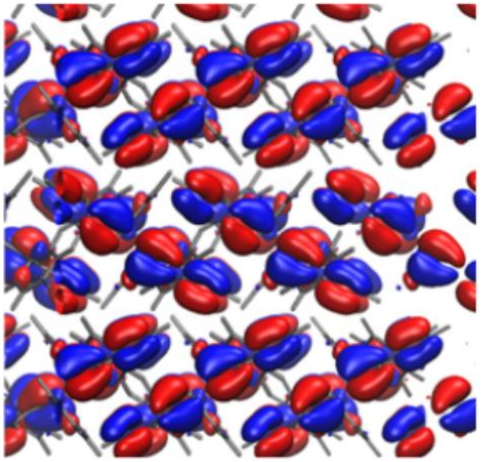
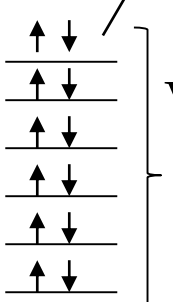


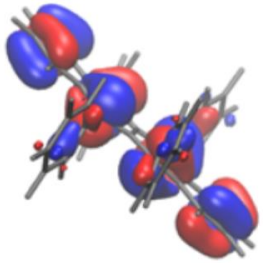
→ narrow bands

Valence Band (VB)



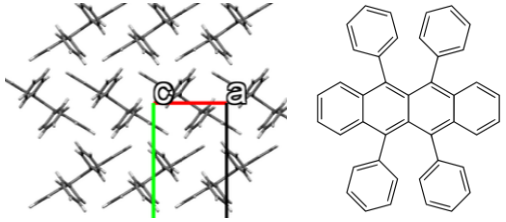


VB ≃ linear combinations of HOMOs



Charge transport in molecular materials

DFT band structure



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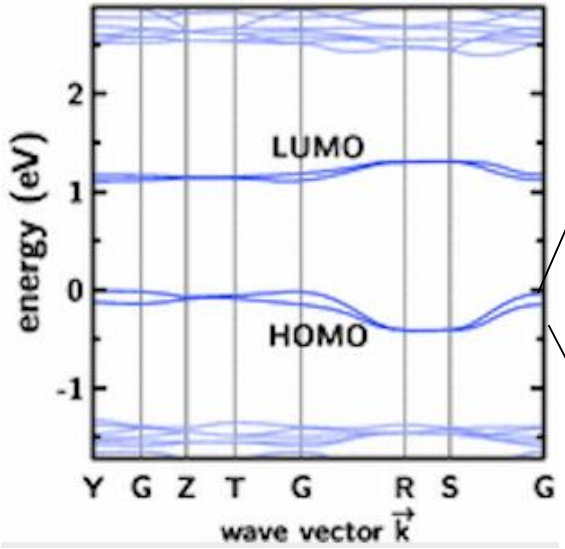

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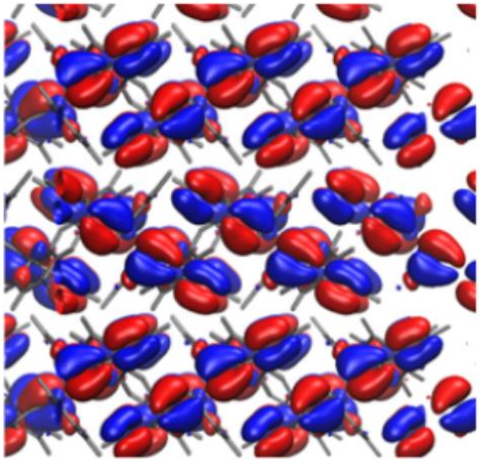

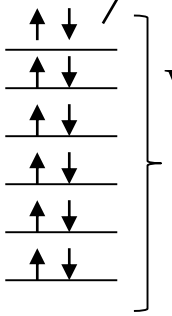

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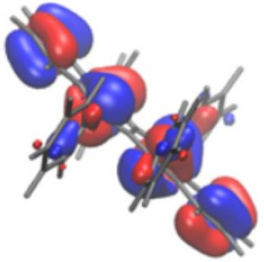
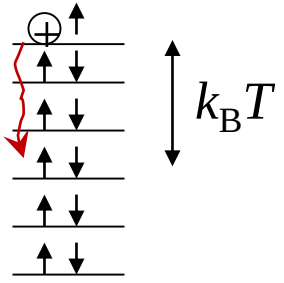


Hole Transport in VB



Charge transport in molecular materials

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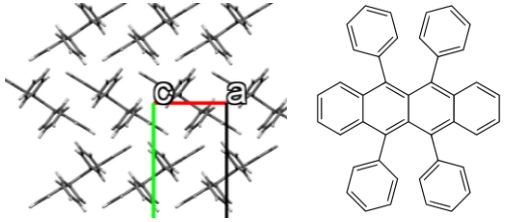

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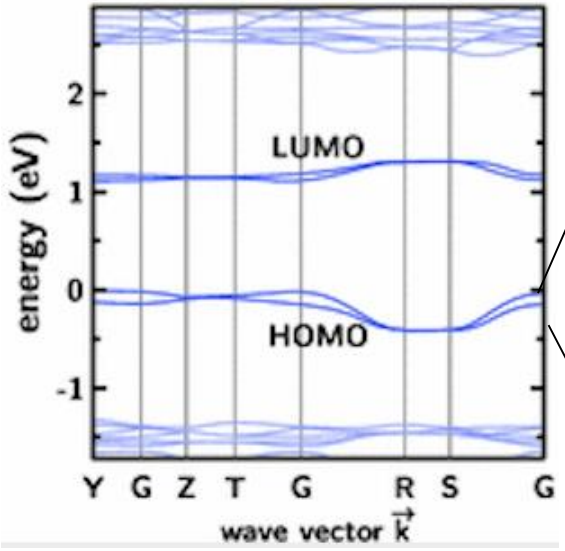

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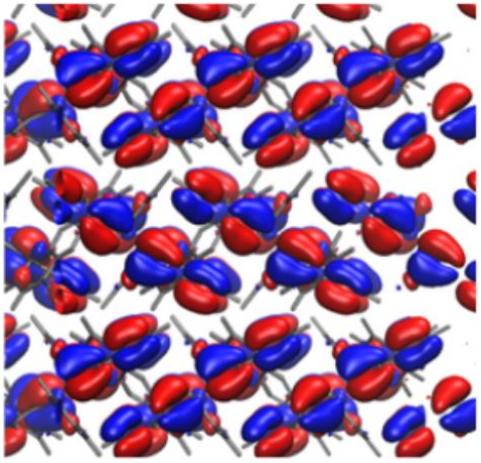

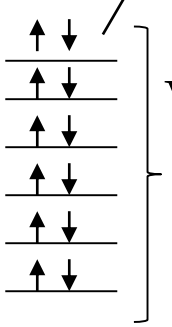

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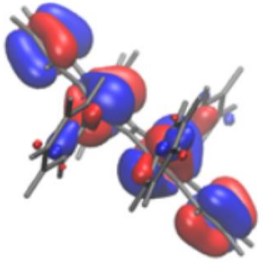

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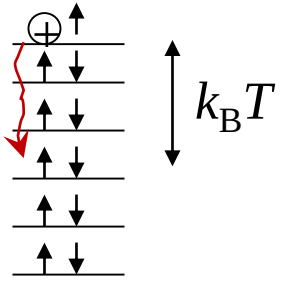
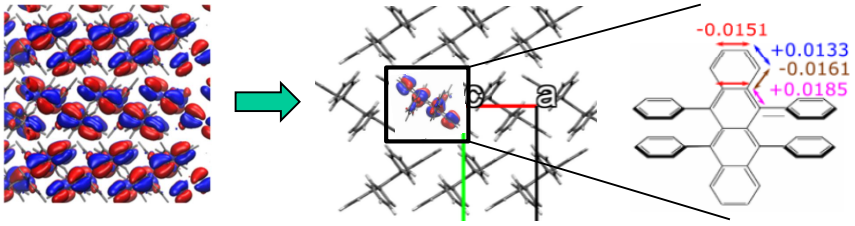


Band Transport?
End of Story?

Important effects to be included

- Nuclear relaxation: reorganization energy (λ)
  (diagonal electron-phonon coupling)



→ Charge localization, small polaron formation

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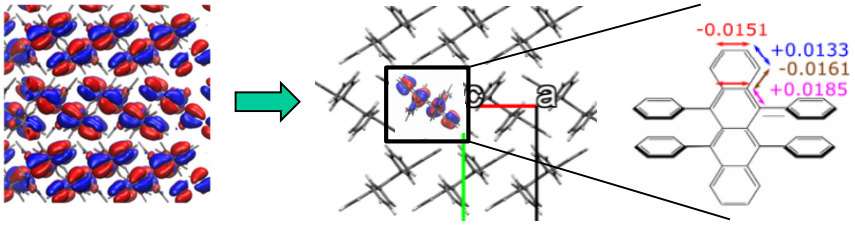

→ Charge localization, small polaron formation

- Thermal fluctuations of electronic coupling (H_{ab})
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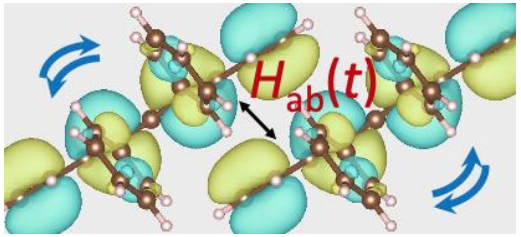

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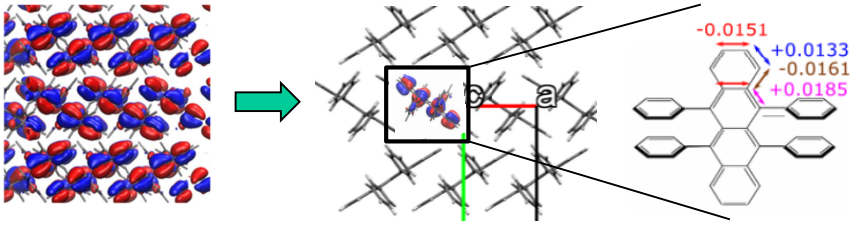

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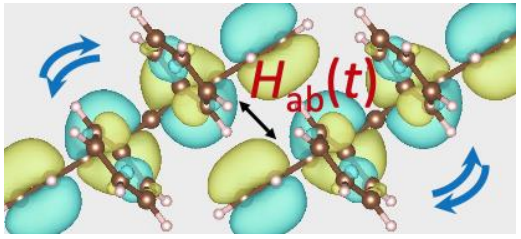
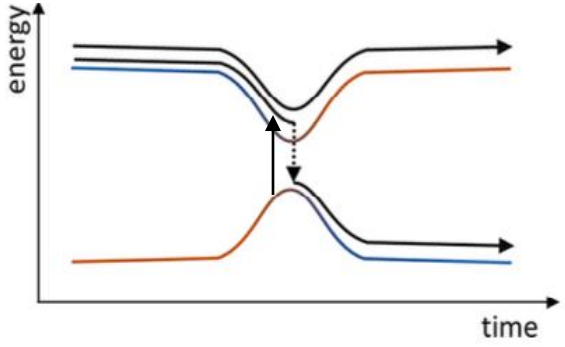


→ Charge localization, polaron formation

- Non-adiabatic (non-Born-Oppenheimer) effects
  between band electronic states
  (Non-adiabatic coupling vectors ($\boldsymbol{d}_{kl}$))



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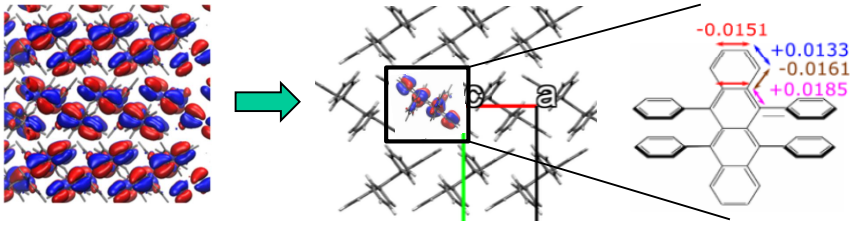

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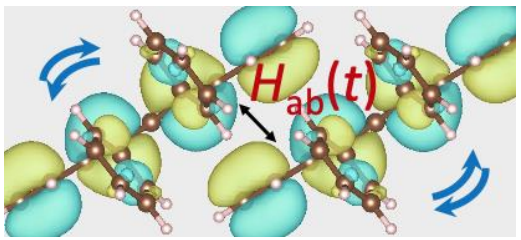

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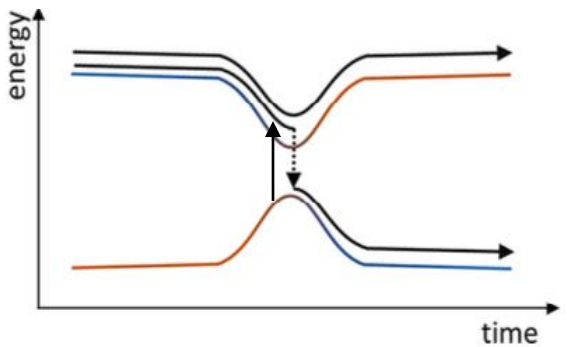
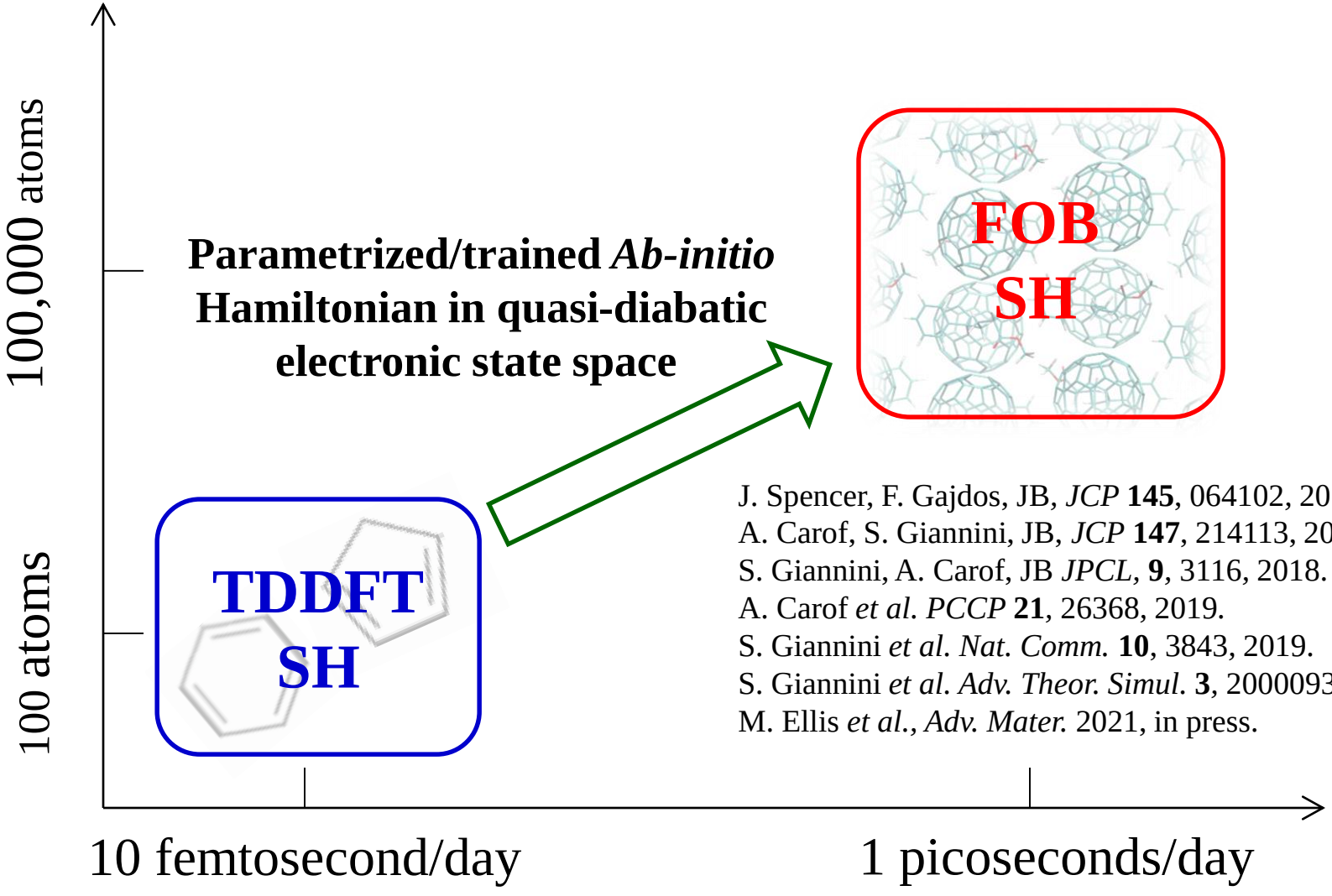


Needed: Coupled electron-nuclear = non-adiabatic dynamics of charge carrier in valence band at finite temperature for truly nanoscale systems

Fragment Orbital-Based Surface Hopping (FOB-SH)




A Carof S Giannini J Spencer F Gajdos



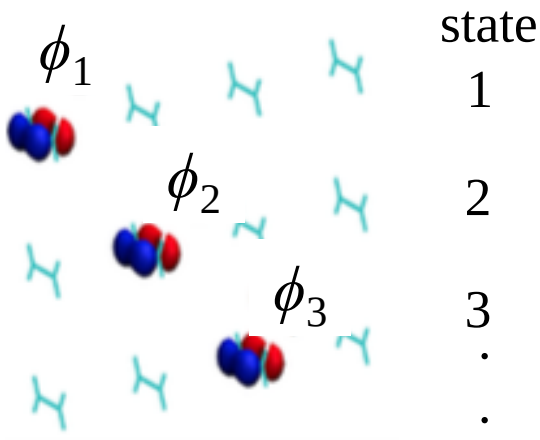
J. Spencer, F. Gajdos, JB, *JCP* **145**, 064102, 2016.
A. Carof, S. Giannini, JB, *JCP* **147**, 214113, 2017.
S. Giannini, A. Carof, JB *JPCL*, **9**, 3116, 2018.
A. Carof *et al. PCCP* **21**, 26368, 2019.
S. Giannini *et al. Nat. Comm.* **10**, 3843, 2019.
S. Giannini *et al. Adv. Theor. Simul.* **3**, 2000093, 2020.
M. Ellis *et al., Adv. Mater.* 2021, in press.

FOB-SH in a nutshell

JCP **145**, 064102 (2016), *JCP* **147**, 214113 (2017), *JPCL* **9**, 3116 (2018), *PCCP* **21**, 26368 (2019)

excess hole or electron

State basis of SOMO orbitals



Hole wavefunction:

$$\psi(\mathbf{r},t) = \sum_k u_k(t) f_k(\mathbf{r}, \mathbf{R}_I(t))$$

Electronic Schrodinger equation:

$$i\hbar \dot{u}_k = \sum_l u_l \left(H_{kl} - i\hbar \left\langle \phi_k \middle| \dot{\phi}_l \right\rangle \right)$$

nuclei

Classical nuclear dynamics

$$\mathbf{F}_{I,i} = -\frac{\partial}{\partial \mathbf{R}_I} E_i \qquad E_i = H_{ii}^{diag}$$

*i*th adiabatic electronic state

Stochastic hopping from surface $E_i \rightarrow E_j$ with probability

$$p_{j \leftarrow i}(u_k, H_{kl}, d_{kl})$$


Antoine Carof


Jacob Spencer

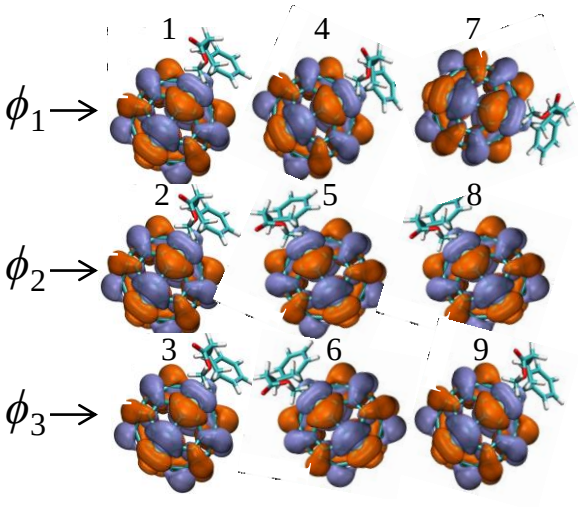

F. Gajdos

1. Fast calculation of Hole Hamiltonian

J. Spencer, F. Gajdos, JB, *JCP* **145**, 064102, 2016.

Hole Hamiltonian (``Tight binding"):

$$H_{kl} = \left\langle f_k \middle| H \middle| f_l \right\rangle$$



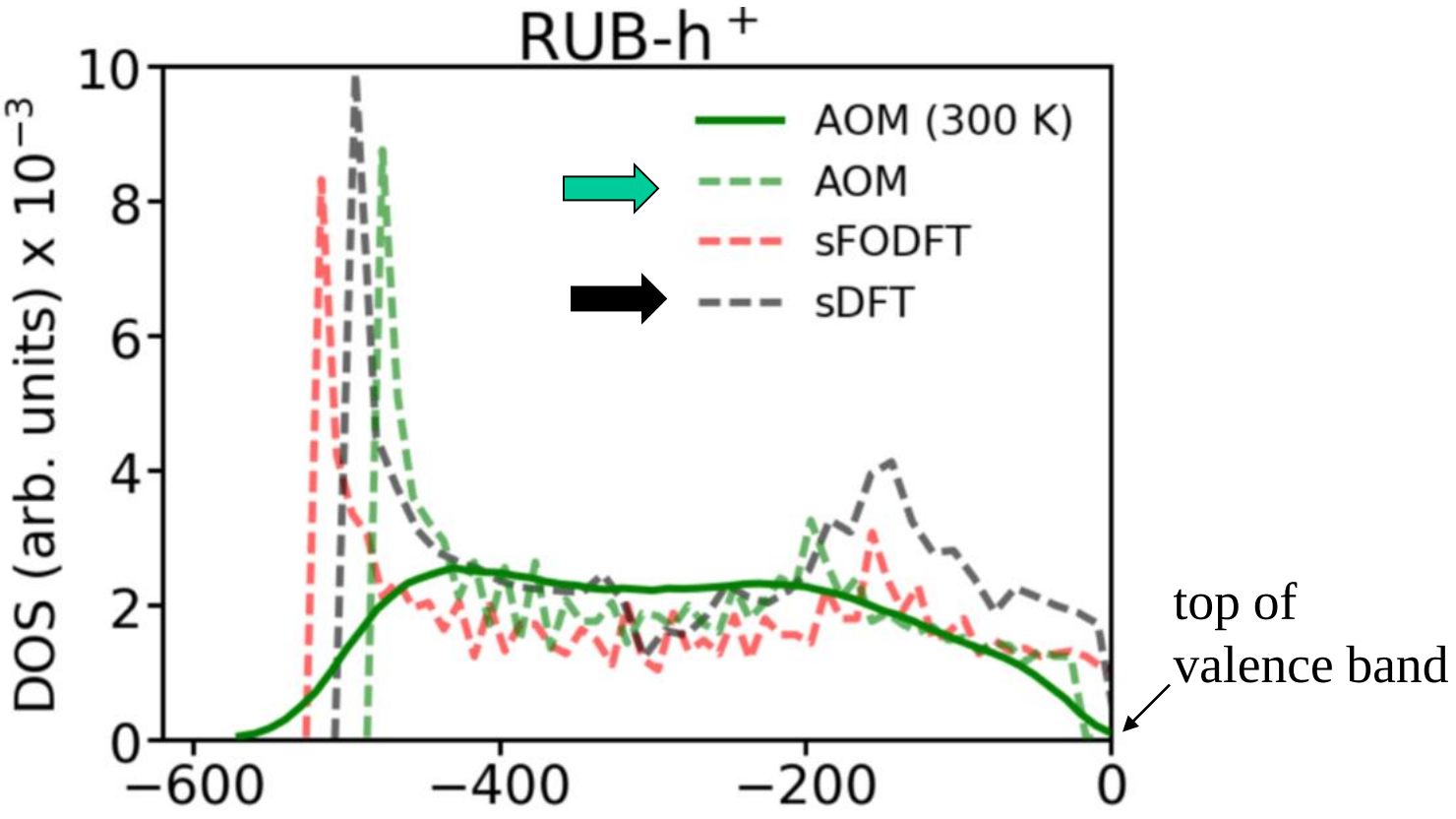
force field

Analytic overlap method (AOM)

$$H_{kl} = \bar{C}\,\bar{S}_{kl}$$

$$H = \begin{pmatrix} H_{11} & H_{12} & 0 & H_{14} & 0 & 0 & 0 & 0 & 0 \\ H_{21} & H_{22} & H_{23} & 0 & H_{25} & 0 & 0 & 0 & 0 \\ 0 & H_{32} & H_{33} & 0 & 0 & H_{36} & 0 & 0 & 0 \\ H_{41} & 0 & 0 & H_{44} & H_{45} & 0 & H_{47} & 0 & 0 \\ 0 & H_{52} & 0 & H_{54} & H_{55} & H_{56} & 0 & H_{58} & 0 \\ 0 & 0 & H_{63} & 0 & H_{65} & H_{66} & 0 & 0 & H_{69} \\ 0 & 0 & 0 & H_{74} & 0 & 0 & H_{77} & H_{78} & 0 \\ 0 & 0 & 0 & 0 & H_{85} & 0 & H_{87} & H_{88} & H_{89} \\ 0 & 0 & 0 & 0 & 0 & H_{96} & 0 & H_{98} & H_{99} \end{pmatrix}$$

Density of states rubrene valence band



→ Good agreement AOM vs sDFT for peak position and band width (0.5 eV)

2. Fast calculation of nuclear gradients

J. Spencer, F. Gajdos, JB, *JCP* **145**, 064102, 2016
A. Carof, S. Giannini, JB, *JCP* **147**, 214113, 2017

$$\boldsymbol{F}^{ad}_{I,i} = -\sum_{kl} U^{T*}_{ik} \nabla_I H_{kl} U_{li}$$

nuclear force on adiabatic PES *i*

$$\boldsymbol{d}^{ad}_{I,ij} = \frac{1}{E_j - E_i} \sum_{kl} U^{T*}_{ik} \nabla_I H_{kl} U_{lj} + \ldots$$

NACV between PESs *i,j*

$$\nabla_I H_{kl} = C \nabla_I S_{kl}$$

off-diagonal gradients in HOMO basis
(diagonal gradient from force field)

$$\nabla_I S_{kl} = \boldsymbol{d}_{I,kl} + \boldsymbol{d}^{*}_{I,lk}$$

overlap gradients in HOMO basis

$$\boldsymbol{d}_{I,kl} = \left\langle j_k \middle| \nabla_I j_l \right\rangle$$

NACV in HOMO basis
(finite difference)

Antoine Carof

3. Making surface hopping work

- **Decoherence correction:** damping of inactive states using frozen Gaussian approximation

$$c_i \to c_i \exp(-\tau_{ia}^{-1}\Delta t) \qquad \tau_{ia}^{-1} = \sum_I \frac{\left|\boldsymbol{F}_{I,i}(t) - \boldsymbol{F}_{I,a}(t)\right|}{2\hbar a_I^{1/2}}$$

Schwartz, Bittner, Prezhdo, Rossky, *JCP* 104, 5942 (1996)

- **Detection of trivial crossing:** (i) State tracking algorithm

Giannini, Carof, JB *JPCL* (2018) similar to Tretiak's algorithm

(ii) Enforcing sum rule: $\sum_i g_{ia} = -\frac{d\left|c_a\right|^2}{dt}\left|c_a\right|^{-2} dt \qquad g_{ja} = \sum_i g_{ia} - \sum_{i \neq j} g_{ia}$

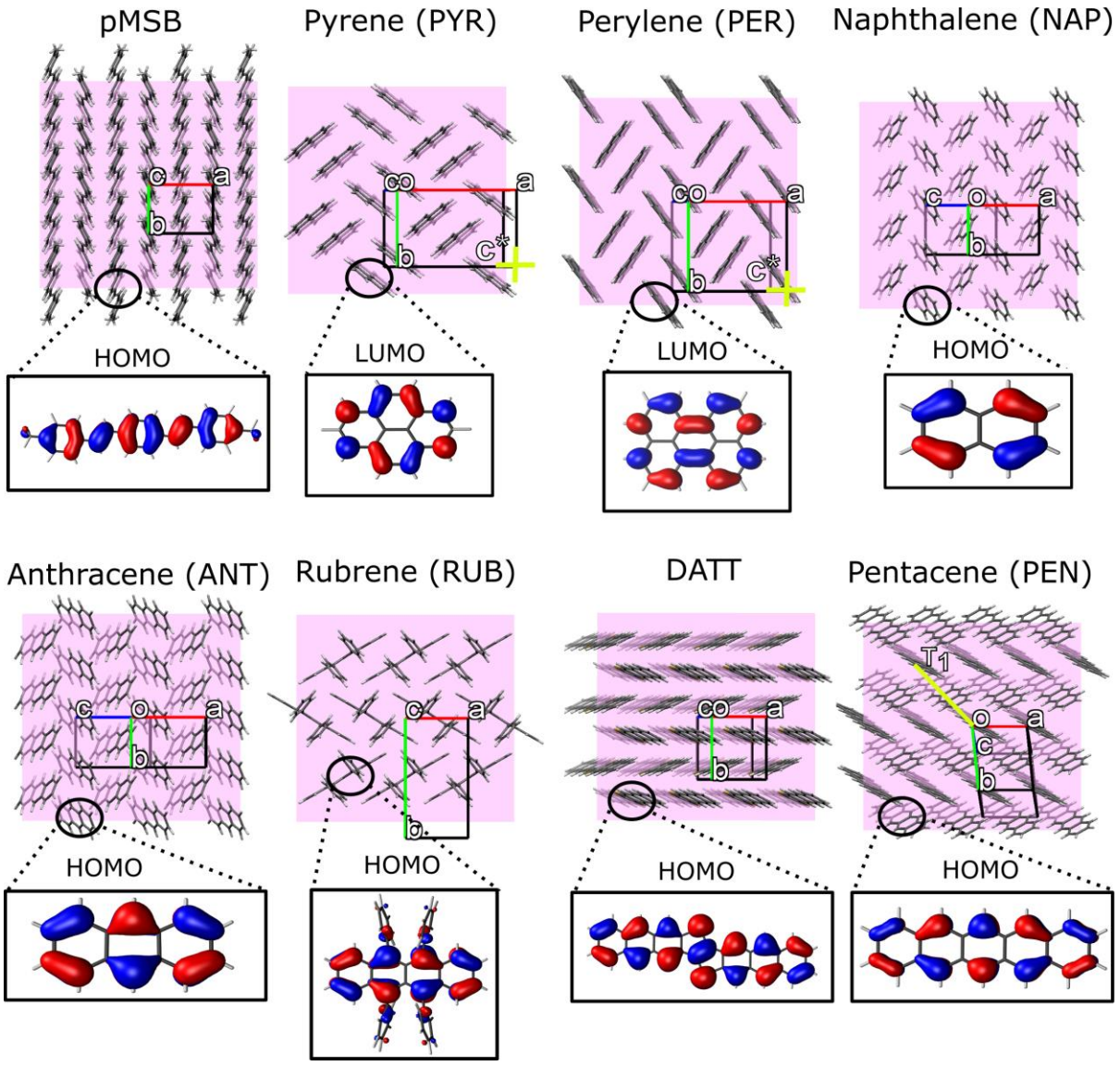
Wang and Prezhdo, *JPCL* 5, 713 (2014)

- **Removal of decoherence-correction induced artificial long-range CT** via projection of wavefunction in moving active region

Giannini, Carof, JB *JPCL* (2018)

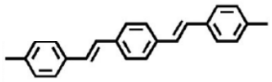
Organic Single Crystals

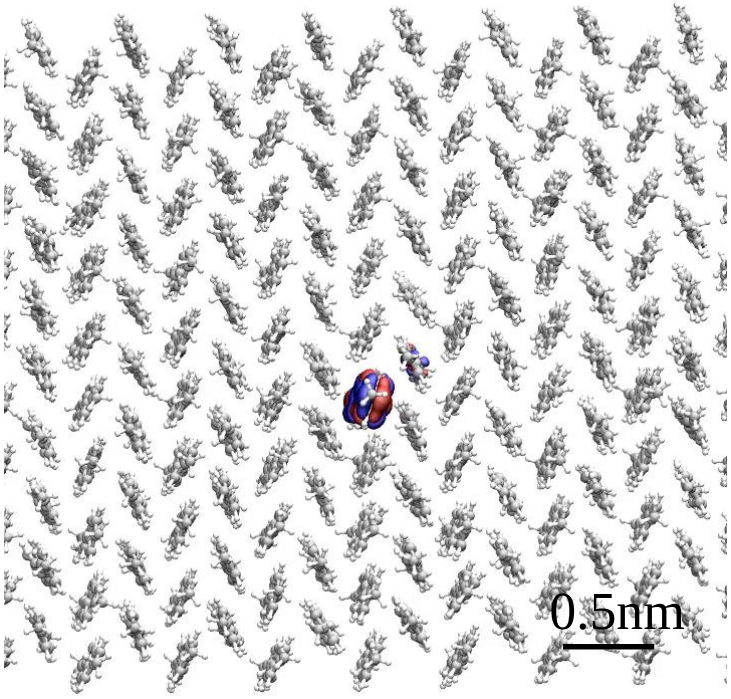
Samuele Giannini



FOB-SH hole transport in conductive plane at 300K

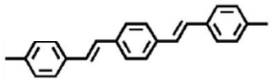
Giannini *et al*. *Nature Comm.* **10**, 3843, 2019; *Adv. Theor. Simul.* **3**, 2000093, 2020.

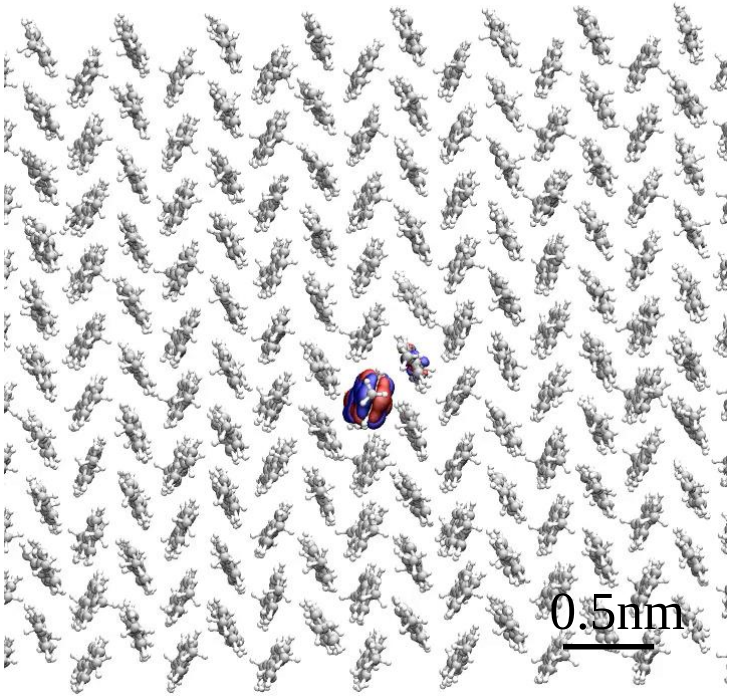
pMSB 



FOB-SH hole transport in conductive plane at 300K

Giannini *et al*. *Nature Comm.* **10**, 3843, 2019; *Adv. Theor. Simul.* **3**, 2000093, 2020.

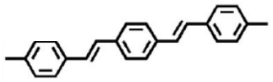
pMSB 

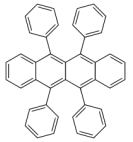


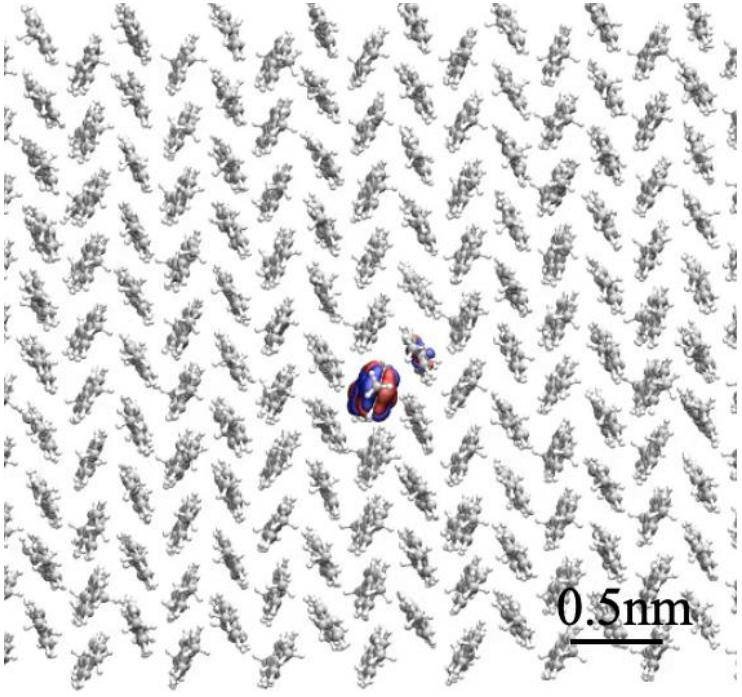
~small polaron hopping

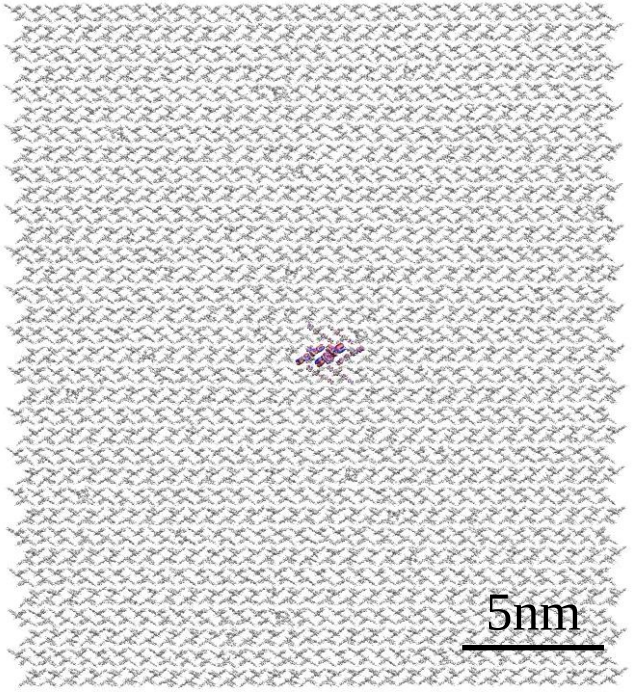
FOB-SH hole transport in conductive plane at 300K

Giannini *et al*. *Nature Comm.* **10**, 3843, 2019; *Adv. Theor. Simul.* **3**, 2000093, 2020.

pMSB 

rubrene 





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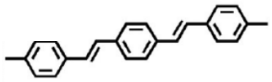
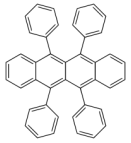
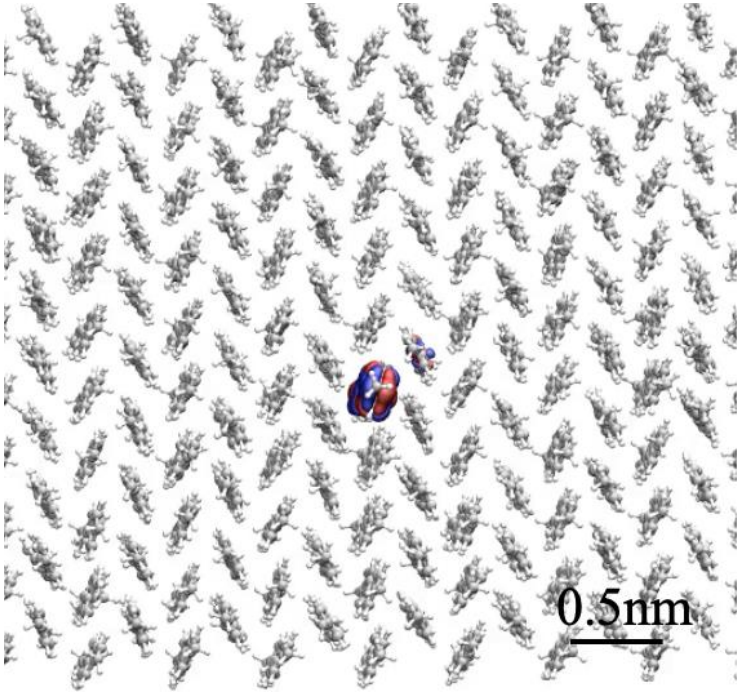
pMSB 

rubrene 



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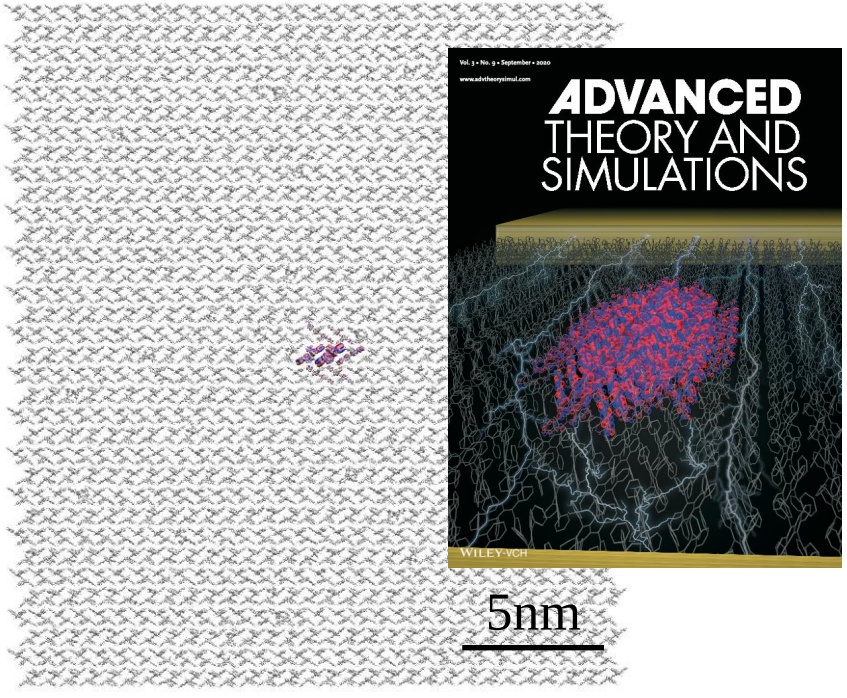
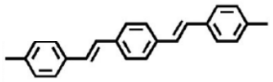
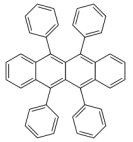


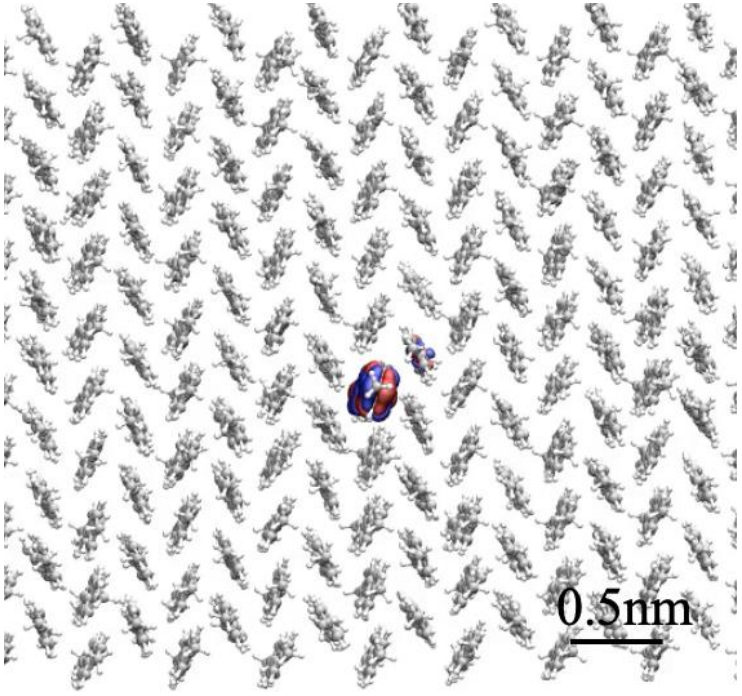
large (``flickering") polaron diffusion

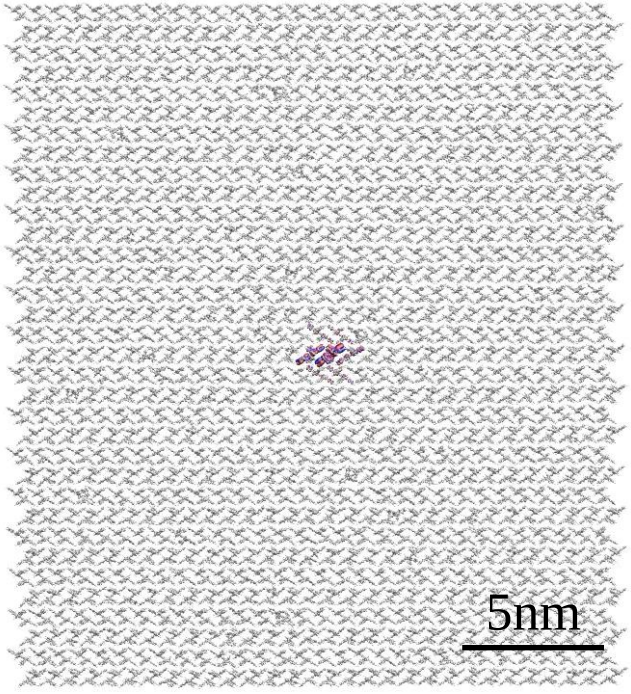
Why no band transport? What limits polaron size?

Giannini *et al*. *Nature Comm.* **10**, 3843, 2019; *Adv. Theor. Simul.* **3**, 2000093, 2020.

pMSB 

rubrene 





~small polaron hopping

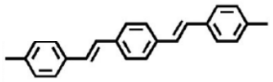
large polaron diffusion

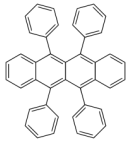
$$\xi = \frac{2\langle|H_{ab}|\rangle}{\lambda} < 1$$

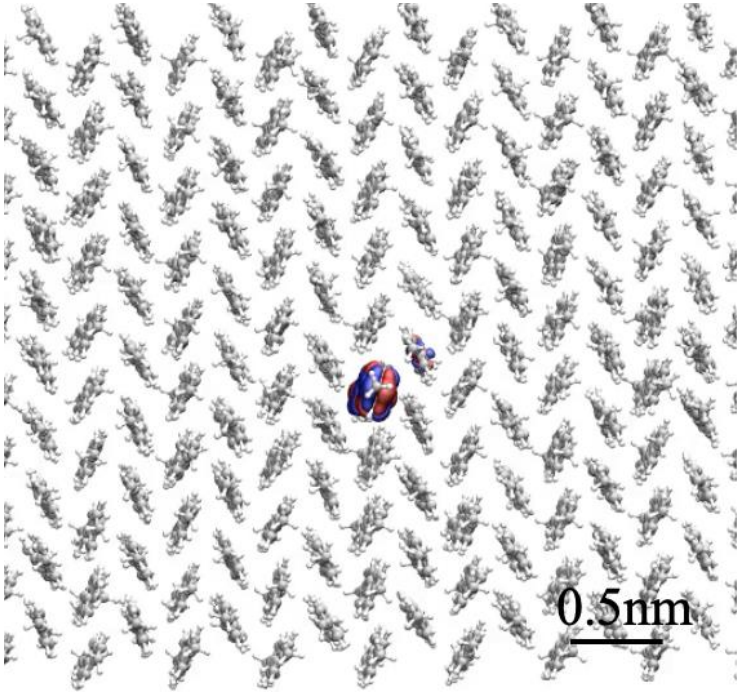
→ polaron localised due to λ (local e-p coupling)

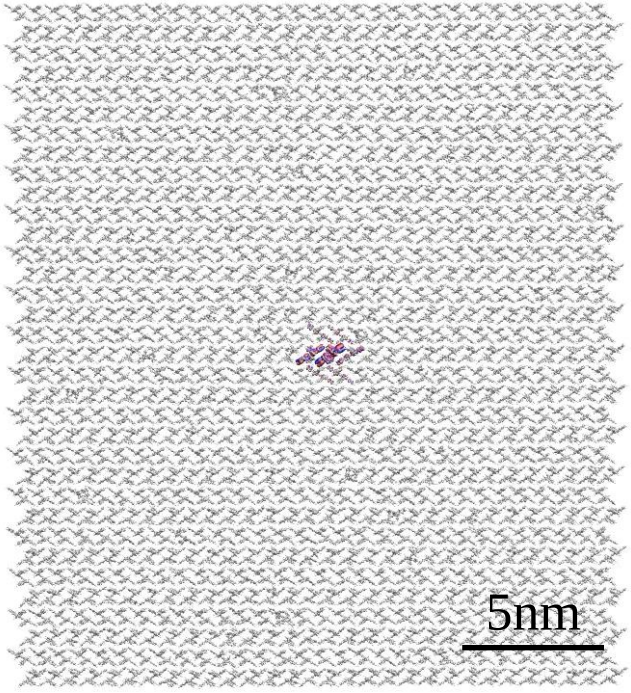
Why no band transport? What limits polaron size?

Giannini *et al*. *Nature Comm.* **10**, 3843, 2019; *Adv. Theor. Simul.* **3**, 2000093, 2020.

pMSB 

rubrene 





~small polaron hopping

$$\xi = \frac{2\langle|H_{ab}|\rangle}{\lambda} < 1$$

→ polaron localised due to λ (local e-p coupling)

large polaron diffusion

$$\xi = \frac{2\langle|H_{ab}|\rangle}{\lambda} > 1$$

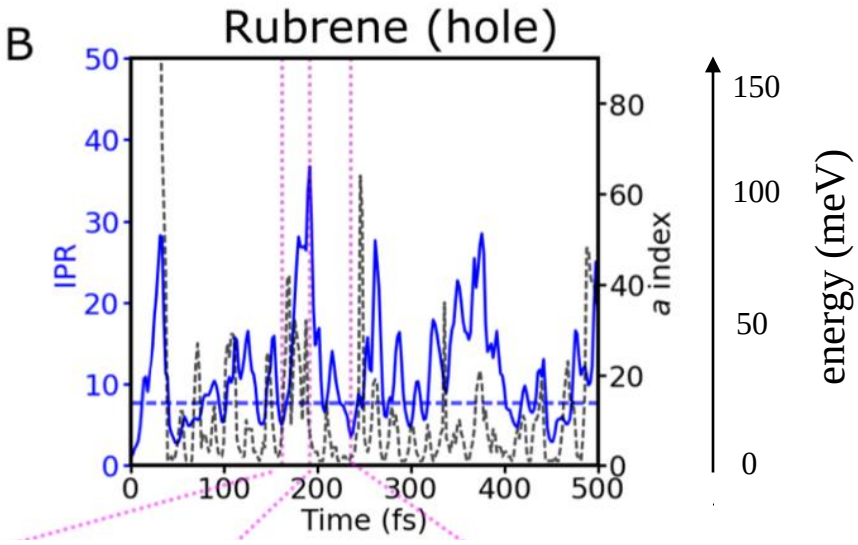
→ polaron size limited by thermal fluctuations of H_{ab} (non-local e-p coupling)

Transport Mechanism from FOB-SH

Giannini *et al*. *Adv. Theor. Simul*. **3**, 2000093, 2020.

IPR = inverse participation ratio (number of molecules over which charge is delocalized)

a index = active state PES in FOB-SH



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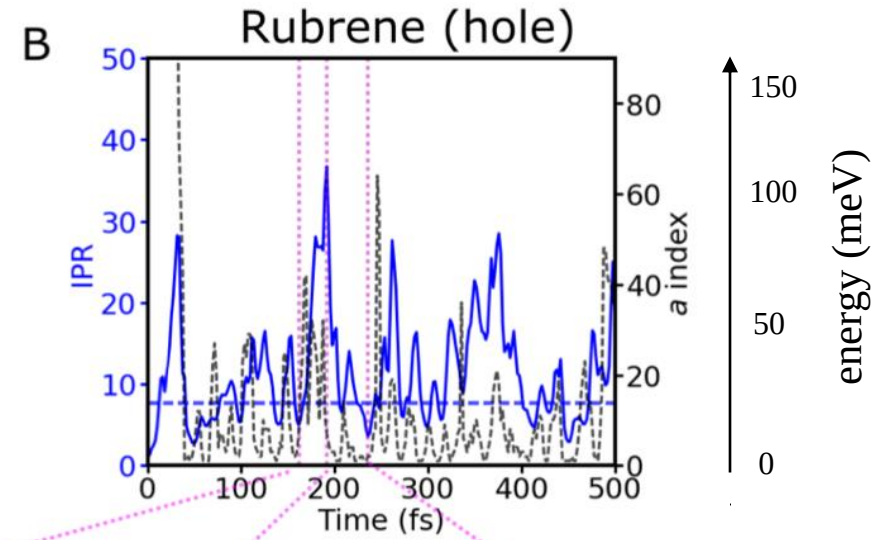

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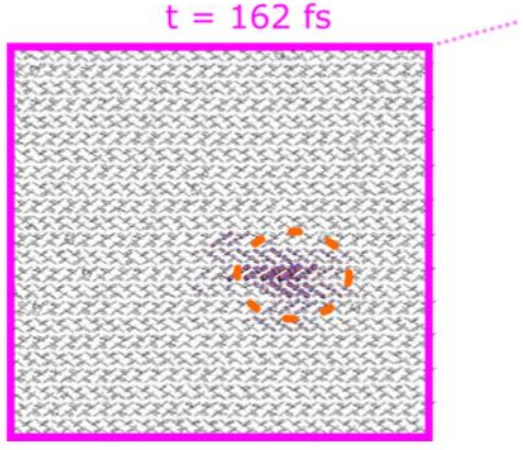

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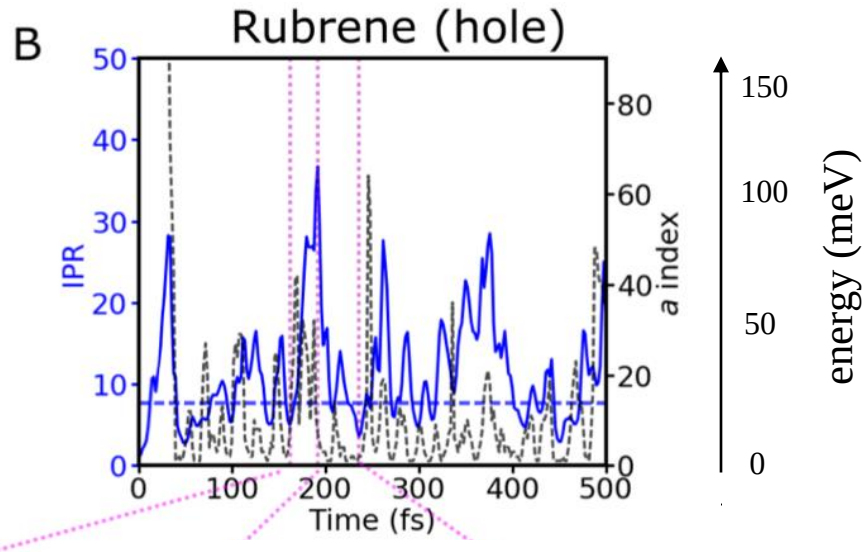

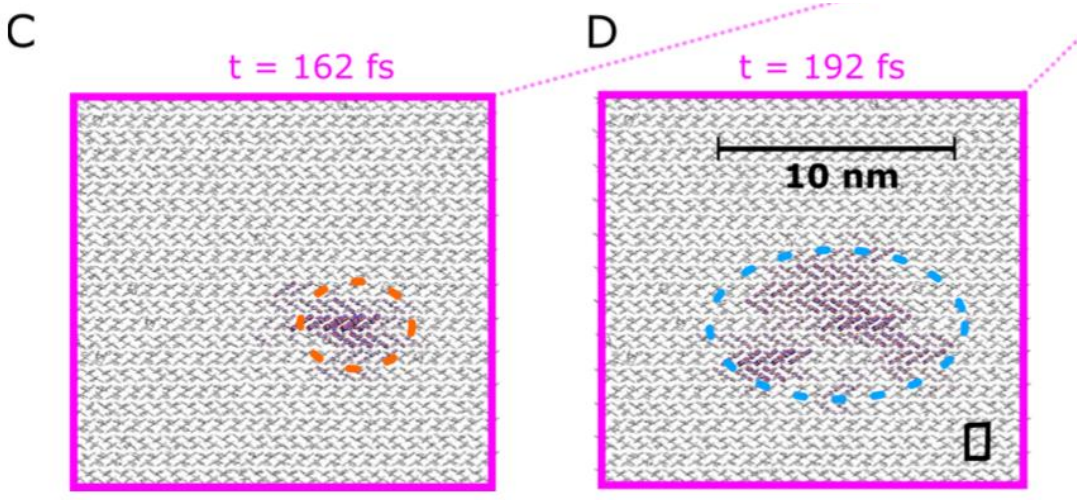

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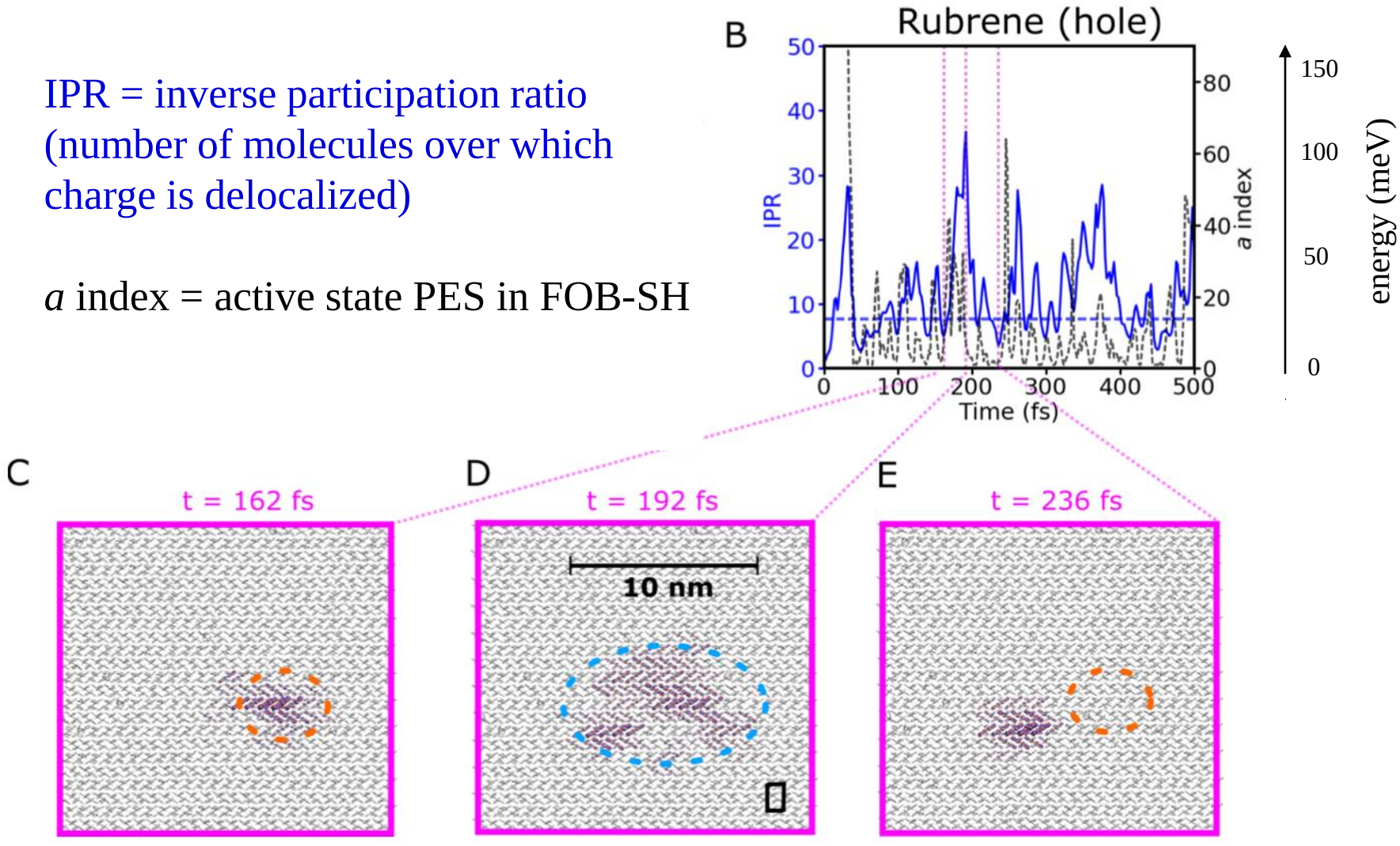


From trajectories to charge mobilities

Mean-Square Displacement

$$MSD(t) = \frac{1}{N_{traj}} \sum_{n}^{traj} \langle \Psi_n(t) | (x - x_0)^2 | \Psi_n(t) \rangle$$

⇩

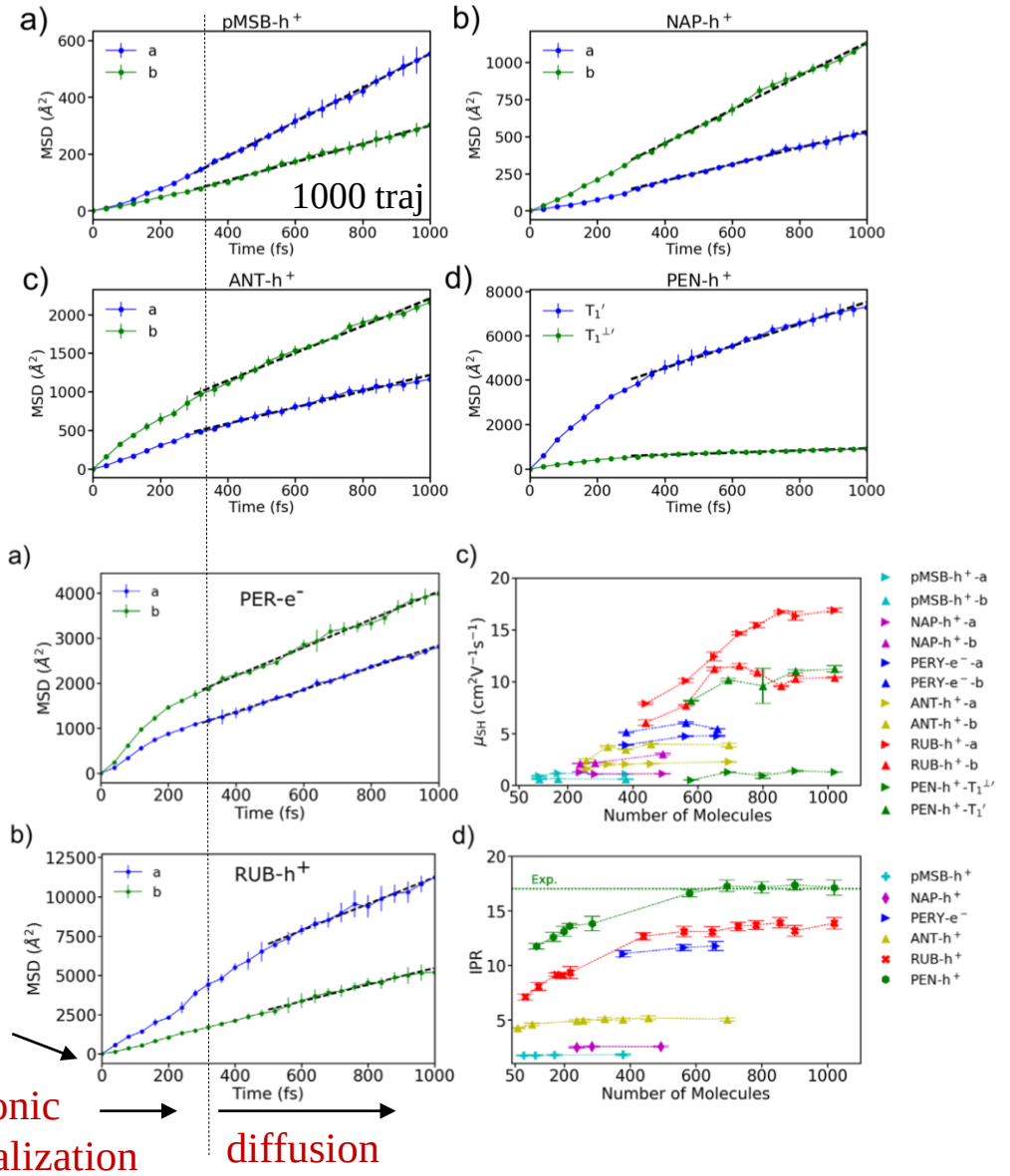
Diffusion coefficient

$$D = \frac{1}{2} \frac{d}{dt} MSD(t)$$

⇩

Charge mobility

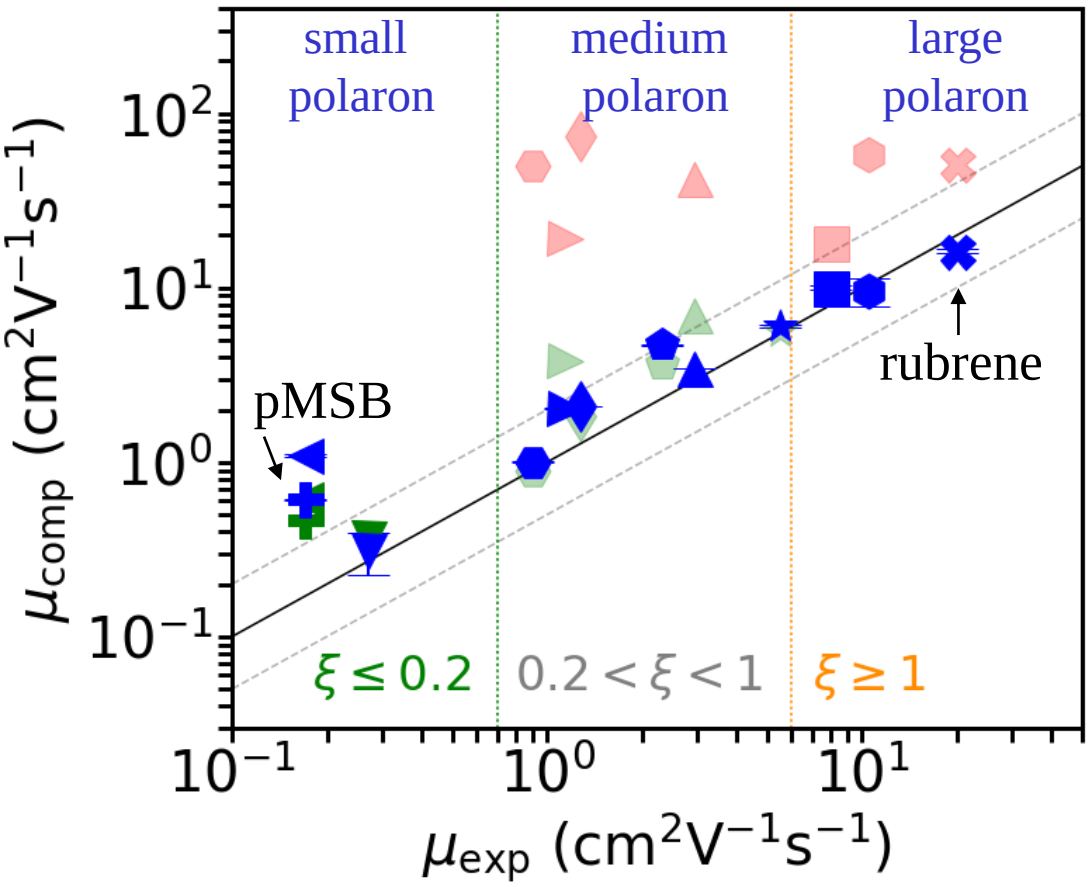
$$m = \frac{eD}{k_B T}$$



Charge mobility: FOB-SH vs Experiment

Giannini *et al. Nature Comm.* **10**, 3843, 2019; *Adv. Theor. Simul.* **3**, 2000093, 2020.

Samuele Giannini

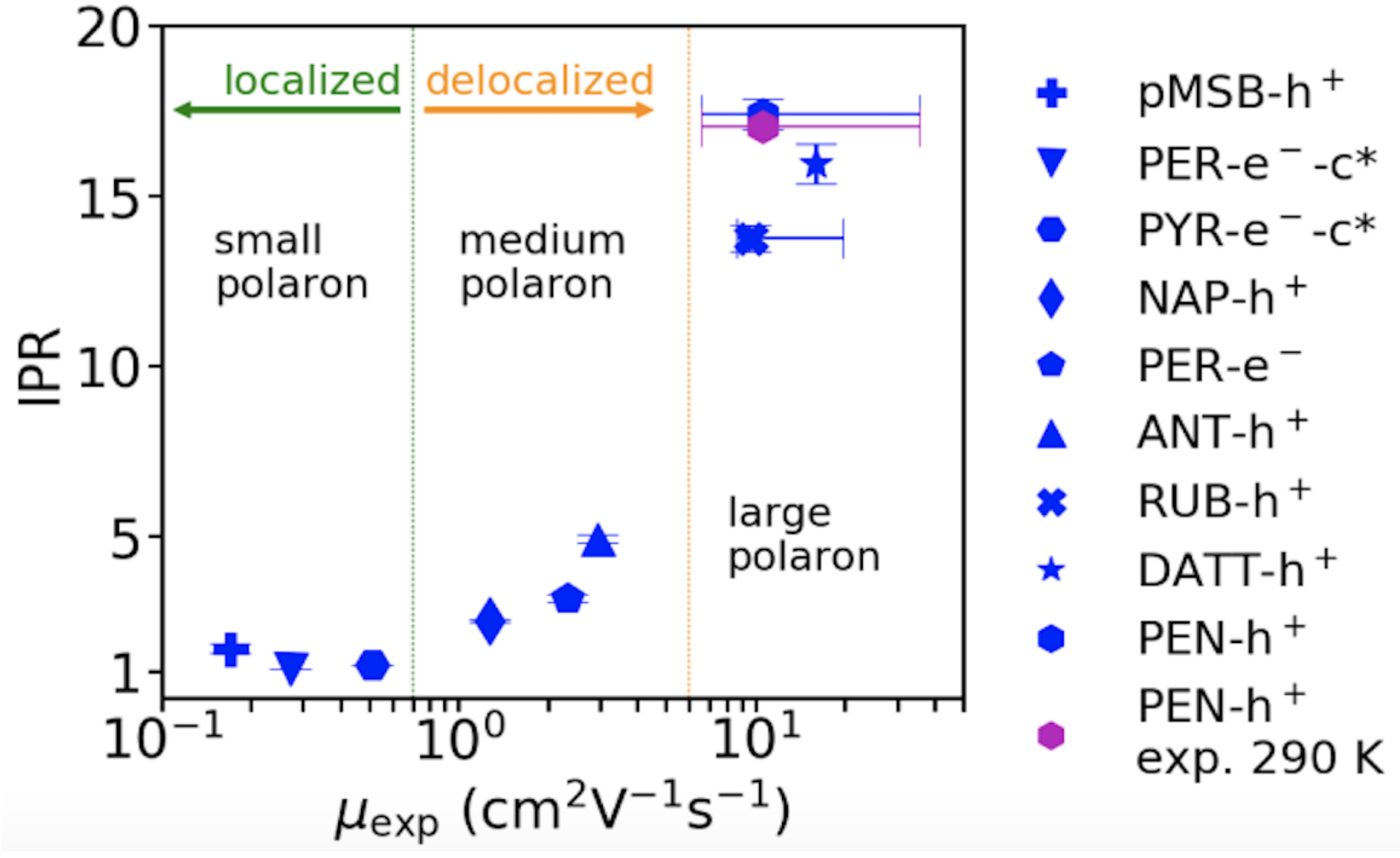


μ_{SH}
μ_{hop}
μ_{band}
PER-e^--c*
pMSB-h^+-a
pMSB-h^+-b
ANT-h^+-a
ANT-h^+-b
NAP-h^+-a
NAP-h^+-b
PER-e^--a
PER-e^--b
RUB-h^+-a
RUB-h^+-b
PEN-h^+-T_1

→ major improvement over band theory!

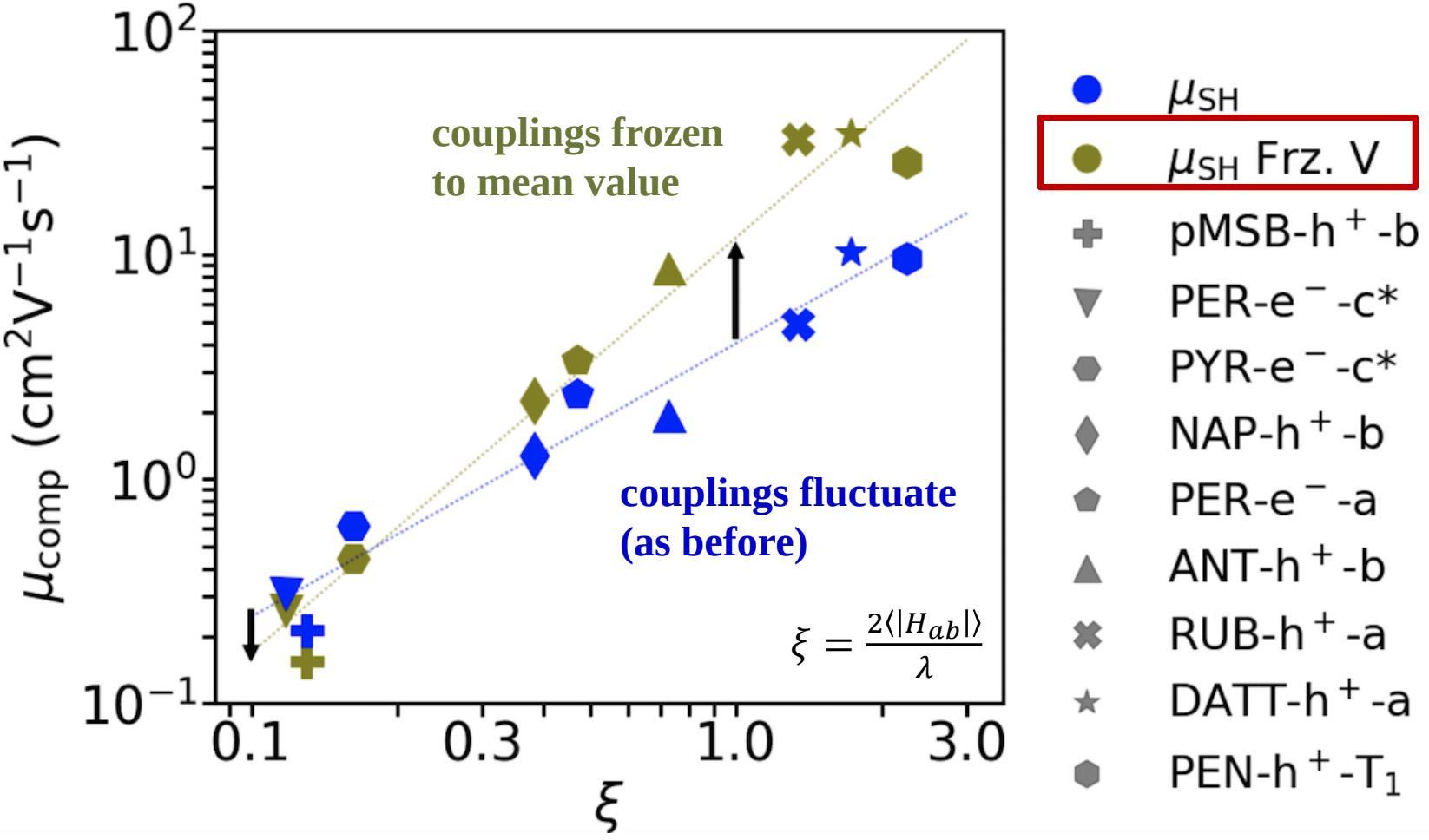
Mobility correlates well with polaron size (as published)

Giannini *et al. Nature Comm.* **10**, 3843, 2019.



What limits charge mobility in organic crystals? Thermal fluctuations of electronic coupling

Giannini *et al. Nature Comm.* **10**, 3843, 2019.



Three ``design rules" for high mobility OS

Ziogos *et al. J. Mater. Chem. C* **8**, 1054, 2020.

Orestis Ziogos

1. $H_{ab} > \lambda/2$

→ to get delocalized polarons, avoid small polaron formation/hopping transport

2. **Isotropic H_{ab} in 2D or 3D + favourable sign combinations**

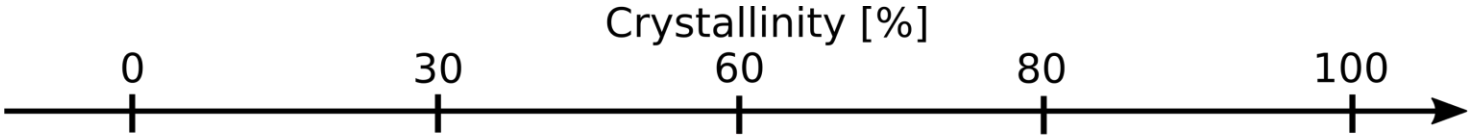
→ to ensure that electronic states at top of valence band are delocalized (at 0 K)

3. **Minimize thermal fluctuations of H_{ab}**

→ to ensure that electronic states remain delocalized (at finite T)

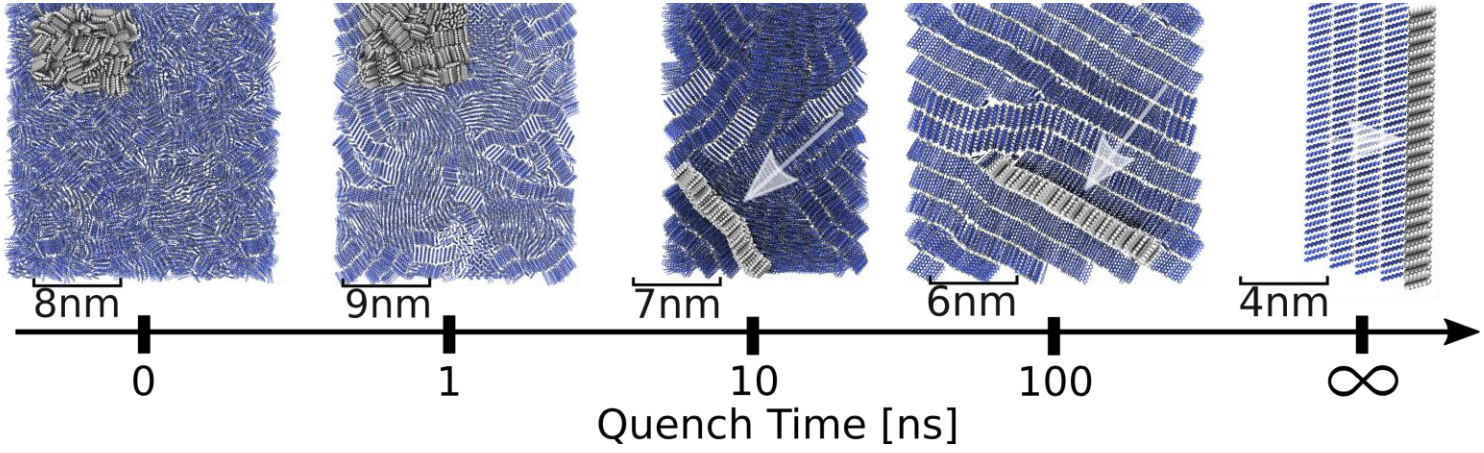
Amorphous, nano- and single crystalline pentacene

M. Ellis *et al*., *Adv. Mater*., 2021, in press.



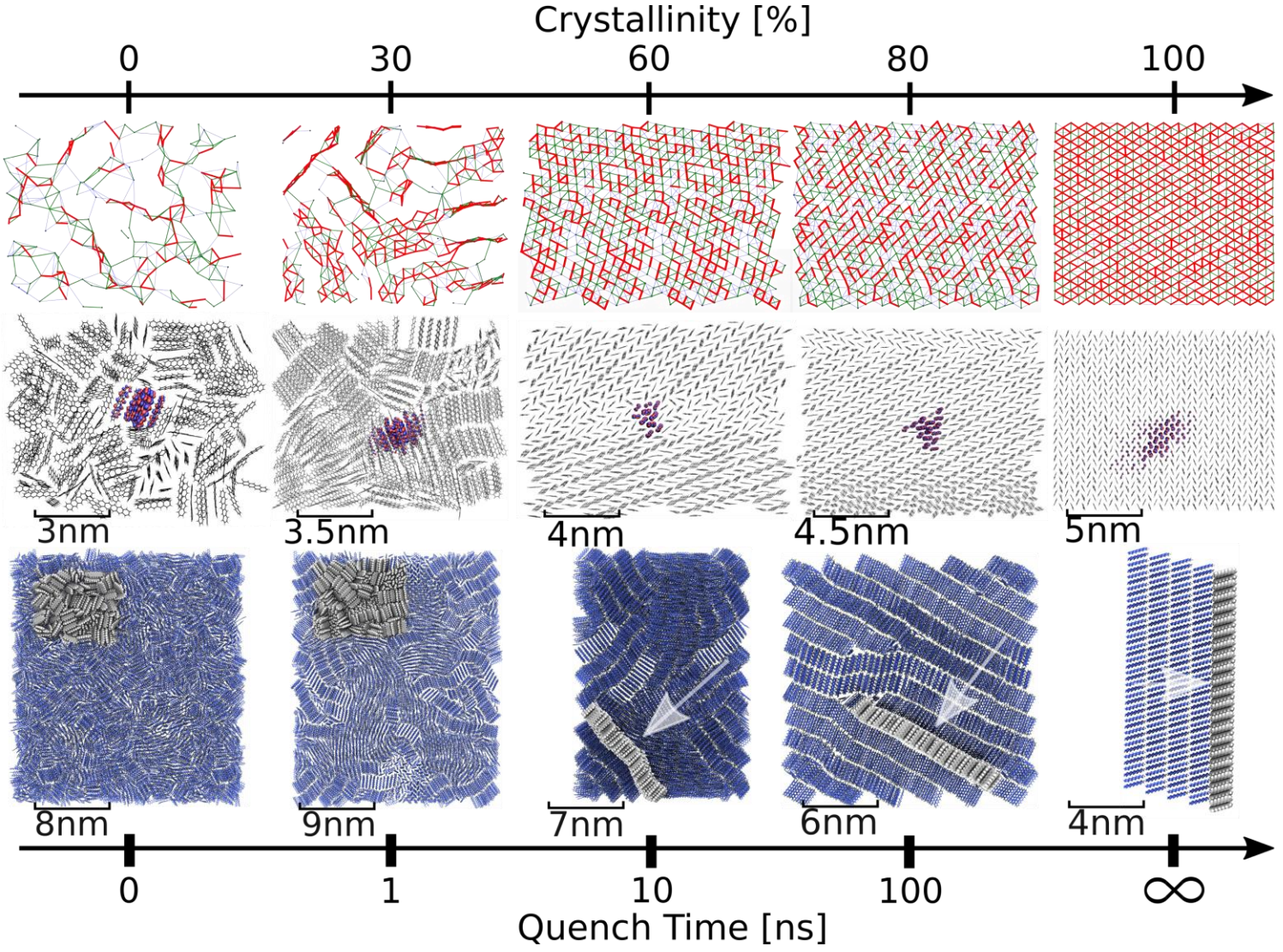
Pentacene samples prepared with MD

1. Melting of crystal at 800 K
2. Quenching to 300 K at different quench times



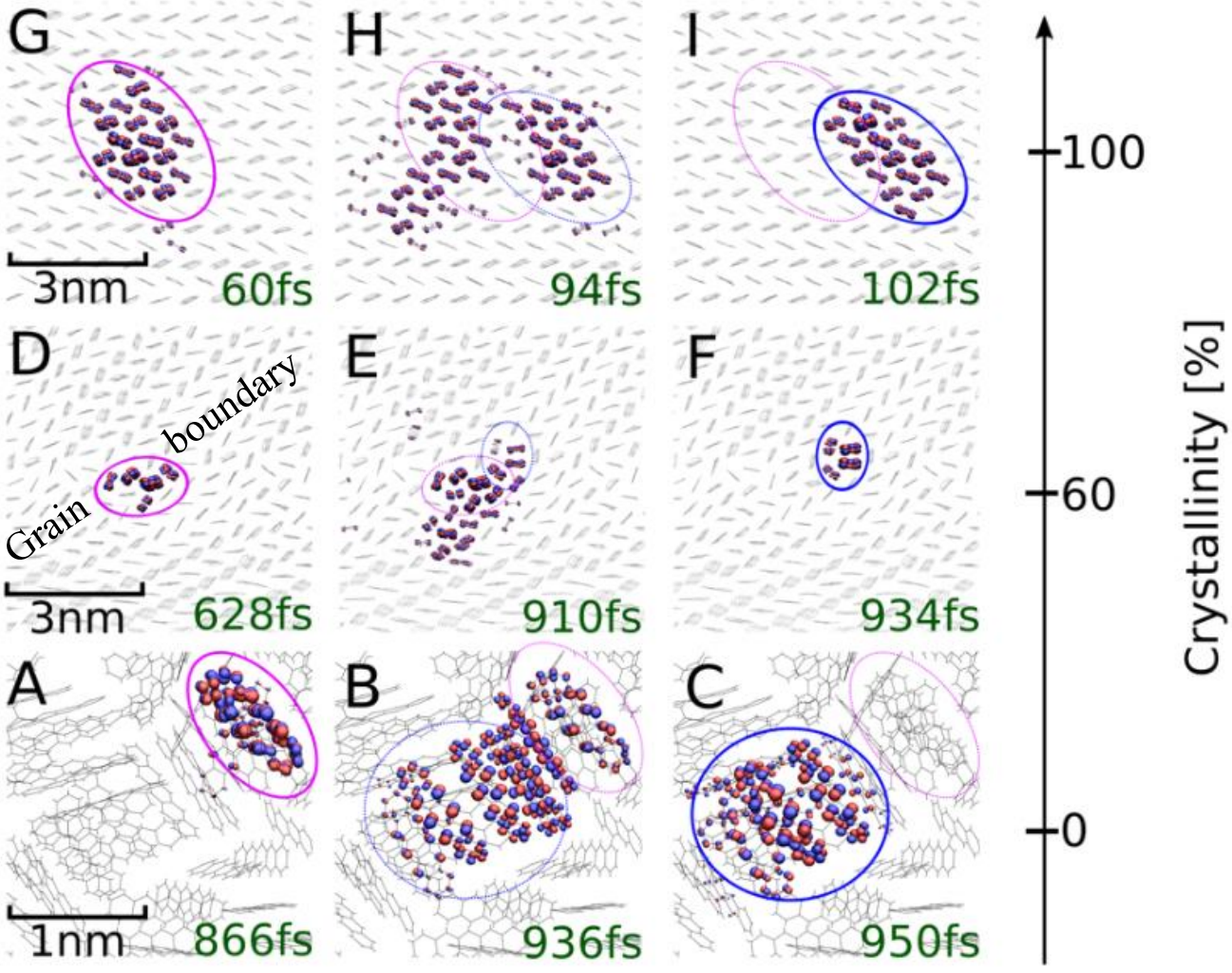
Hole delocalization and crystallinity

M. Ellis *et al.*, *Adv. Mater.*, 2021, in press.



Transport mechanism and crystallinity

M. Ellis *et al*., *Adv. Mater*., 2021, in press.



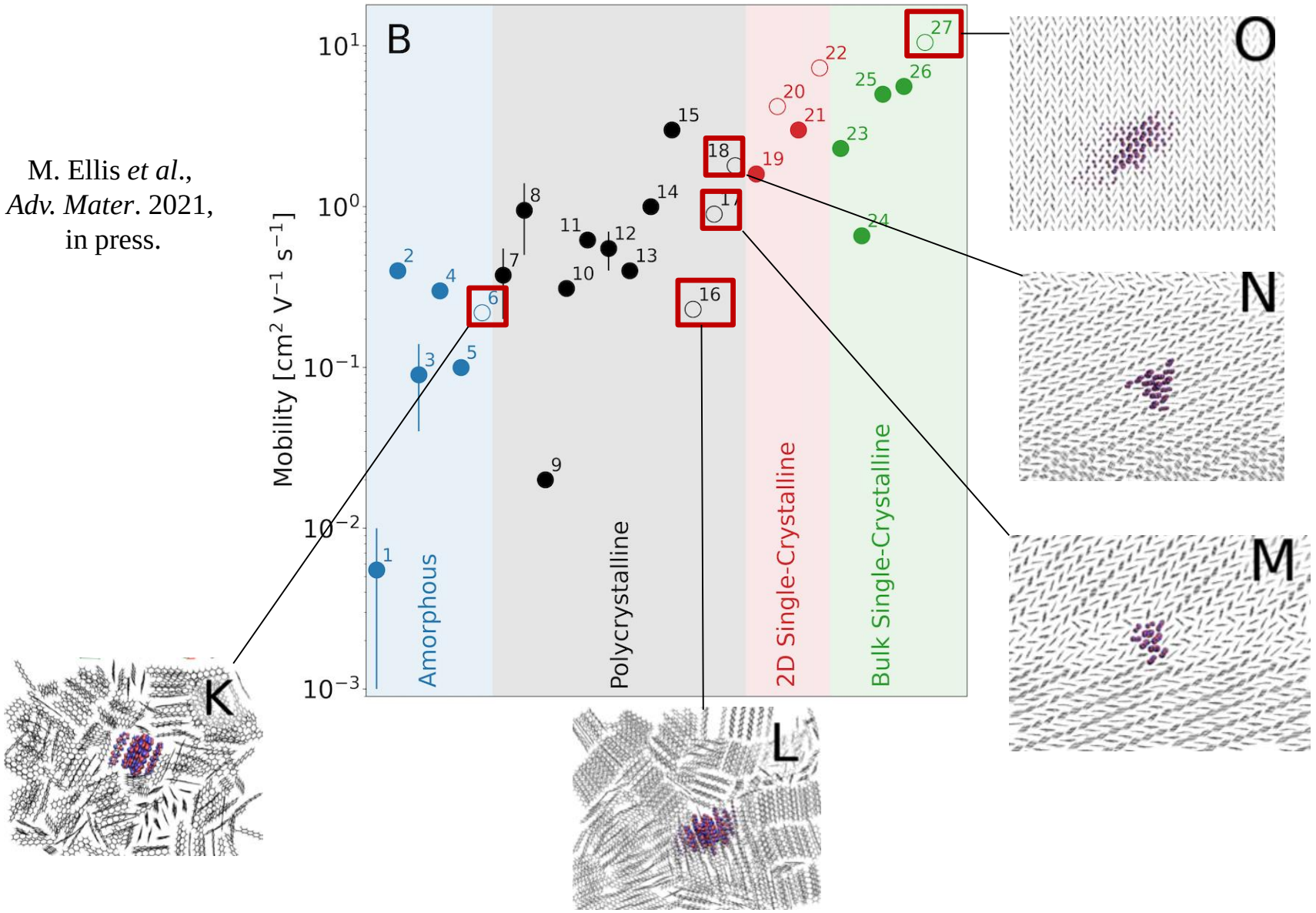
Large polaron diffusion

Trapping/Escape from Grain boundary

Small polaron hopping

FOB-SH vs Experiment

M. Ellis *et al*.,
Adv. Mater. 2021,
in press.



Summary

- Developed a non-adiabatic MD method for real-time propagation of charge carriers and Frenkek excitons in ``soft" materials

- Practical: -large systems (1000 sites $\triangleq 10^5$ valence electrons)
  -convergence: 10^3 trjs 1ps each in 1 day on 10^3 cores

- Predictive: Experimental mobilities/diffusion constants well reproduced

- New picture of charge transport in high mobility molecular materials:
  Large polaron diffusion - distinct from band and small polaron hopping transport

- Provides numerical benchmarks for new theories
  e.g. transient localization theory, stochastic Liouville

- Useful: Prediction of charge mobility in new materials

Outlook

- Extending state space of electronic Hamiltonian in FOB-SH / FE-SH

→ Charge separation and recombination at n-p type interfaces (excitonic solar cells)

→ Exciton dissociation at n-p type interfaces

- Beyond Surface Hopping

→ Classical limit of exact factorisation (Abedi, Gross, Agostini,…)
Ehrenfest + quantum momentum terms
Problem: Divergence of quantum momentum in Eq. S28 of *Min* et al. *JPCL* 2017

→ Surface Hopping with Quantum Nuclei/RPMD (Tully, Shushkov, Miller,…)
Problem: Many beads but only one electronic SE. Expensive.

Acknowledgement

Non-adiabatic dynamics/Organics

Antoine Carof, Samuele Giannini,
Orestis Ziogos, Matt Ellis, Jan Elsner,
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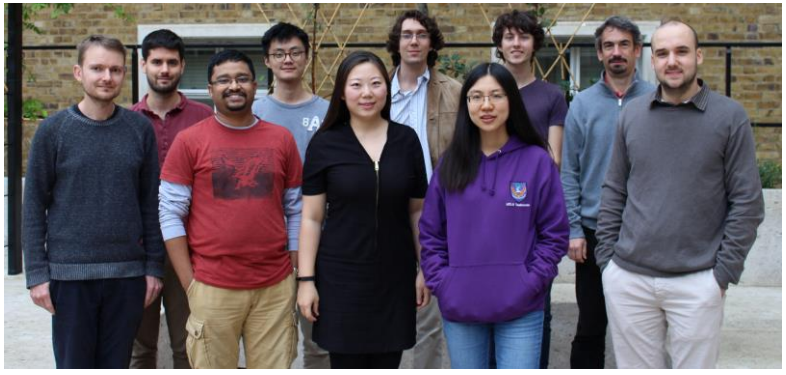
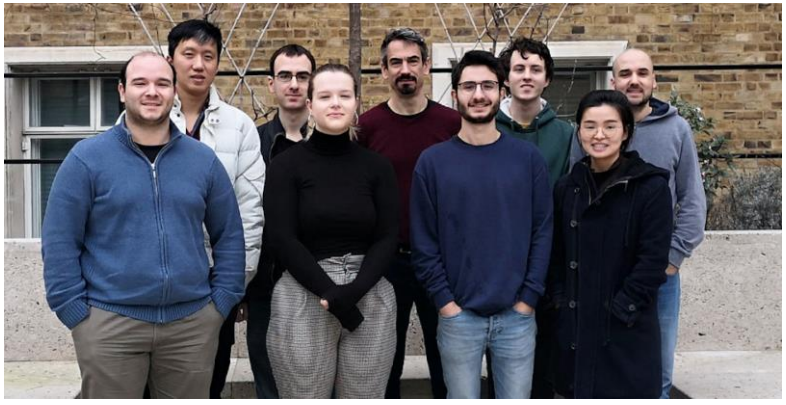
Harald Oberhofer / Karsten Reuter (TUM)
Jenny Nelson FRS, Artem Bakulin (Imperial)
David Beljonne (Mons)
Marcus Elstner (KIT)
Irene Burghardt (Frankfurt)
Henning Sirringhaus FRS (Cambridge)





European Research Council

European Commission

IAS TUM Institute for Advanced Study

EPSRC Engineering and Physical Sciences Research Council

THE ROYAL SOCIETY CELEBRATING 350 YEARS

Pacific Northwest NATIONAL LABORATORY

UCL

Thanks for listening!

Breakdown of traditional transport theories

H. Oberhofer, K. Reuter, JB *Chem Rev.* **117**, 10319, 2017.

Upper speed limit for hopping

$$\mu_{hop} \leq \frac{2\pi c \tilde{\delta} d_{ab}}{k_B T} = \mu_{hop}^{\max}$$

ET rate << vibrational relaxation rate

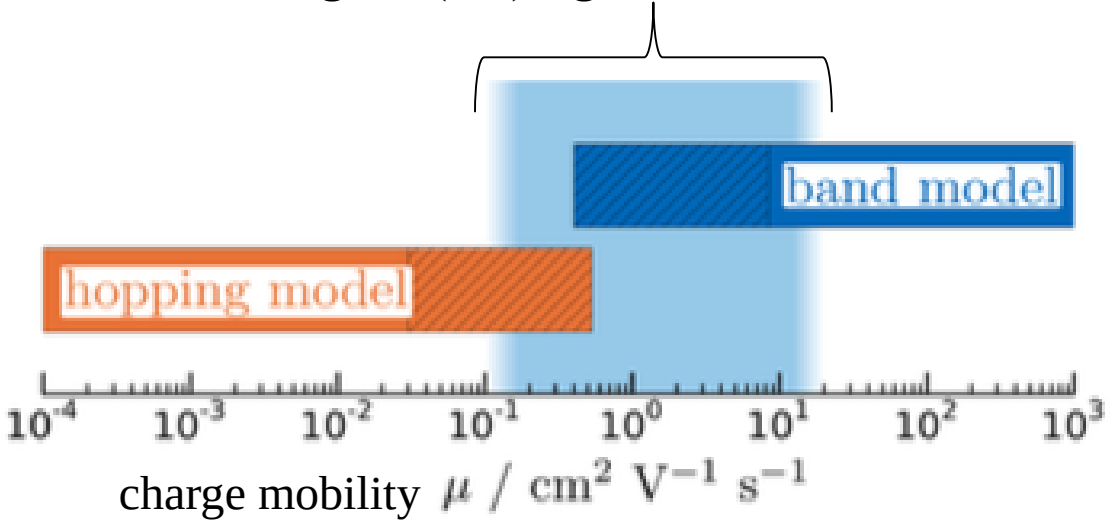
Troisi, Org. Electron. 12, 1988 (2011)

Lower speed limit for band

$$m_{band}^{3} \frac{q d_{ab}}{v_g m^*} = m_{band}^{\min}$$

carrier mean free path > lattice spacing

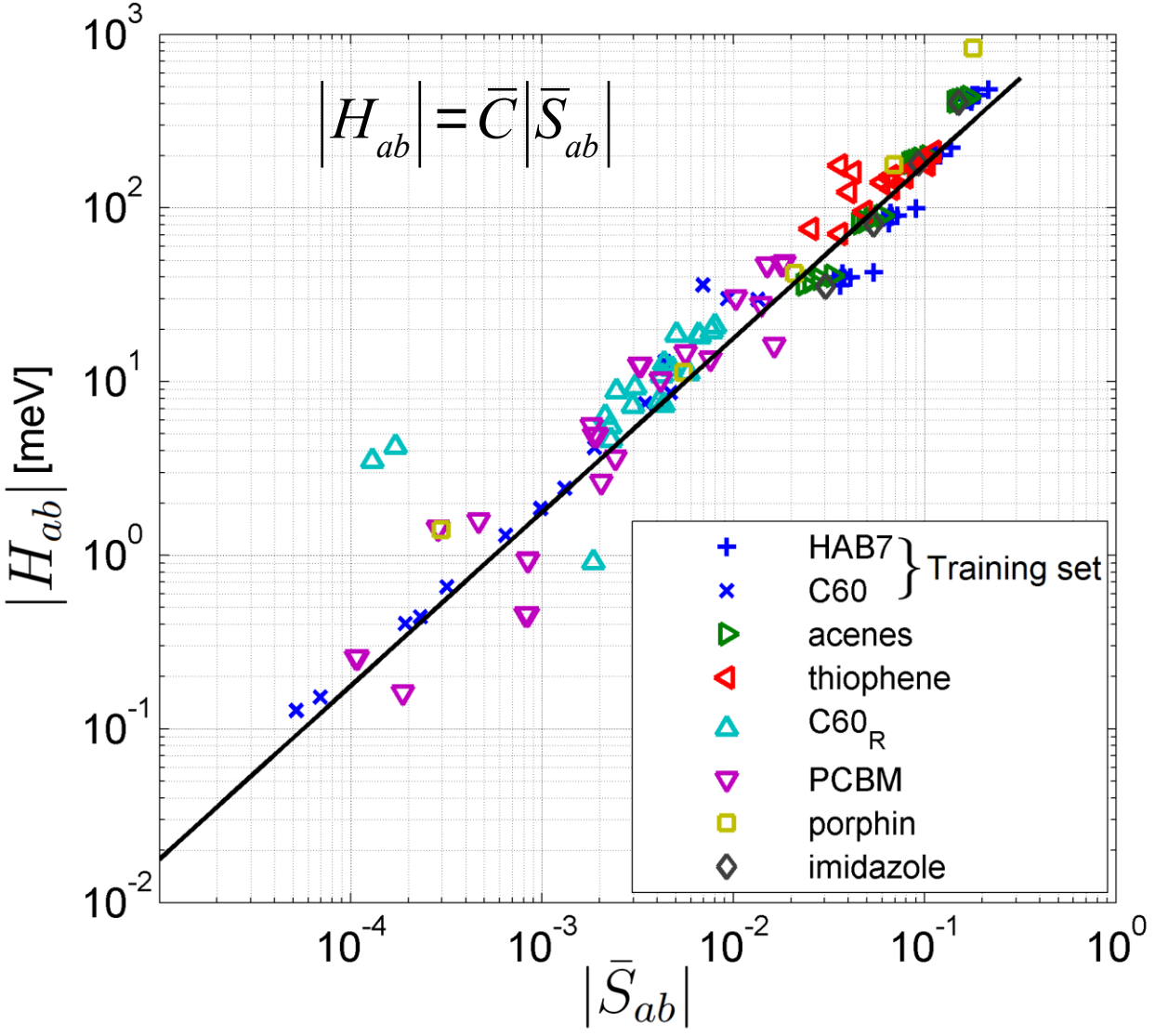
good (bio)organic semiconductors



→ CT in OS ``between" hopping and band transport

Ultrafast estimation of electronic couplings

F. Gajdos, JB *et al. J. Chem. Theor. Comput.* **10**, 4653 (2014).



blue symbols
=
Training set

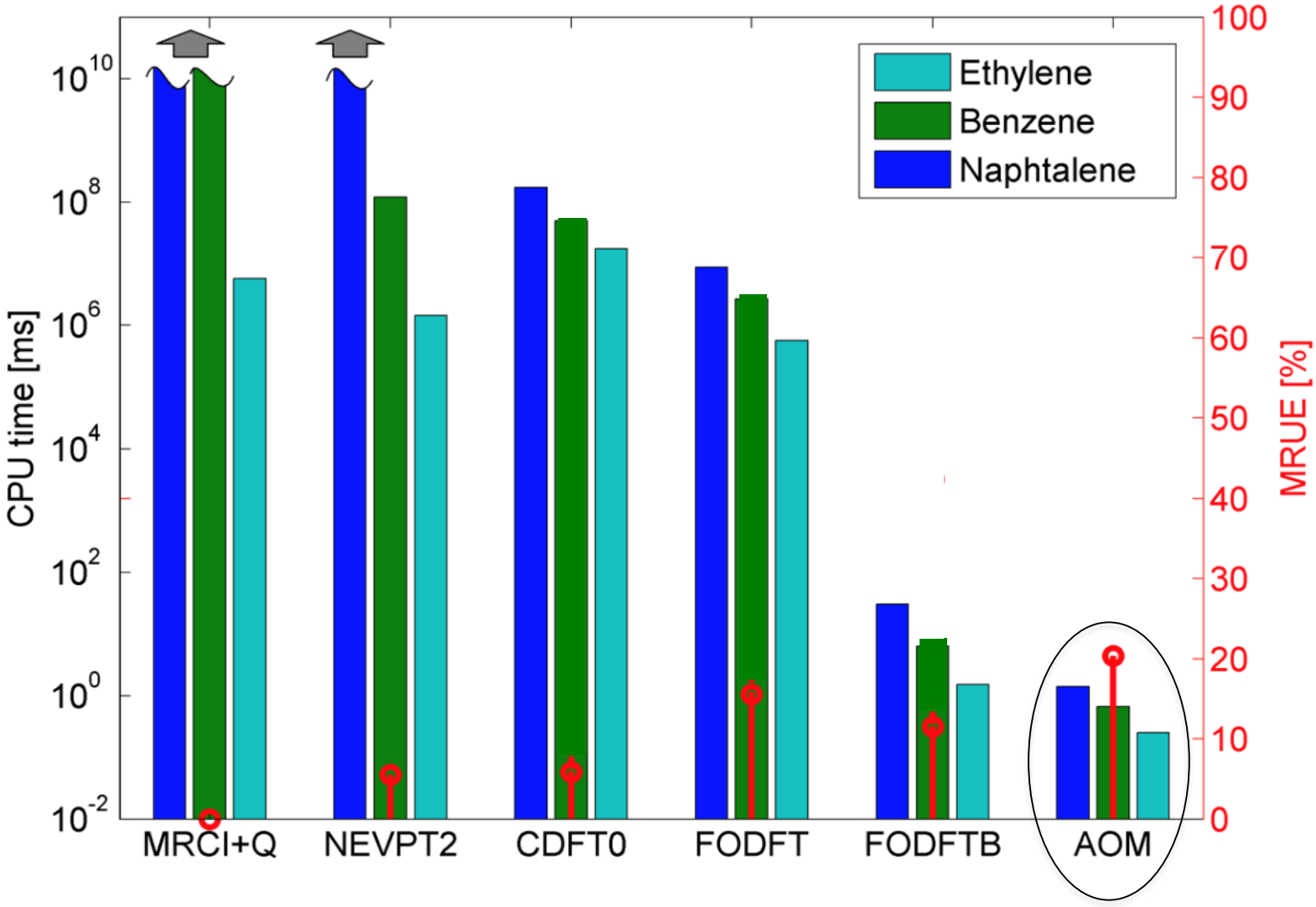
$\bar{C} = 1.819\ \text{eV}\ (R^2 = 0.974)$
(black line)

other symbols
=
Test sets

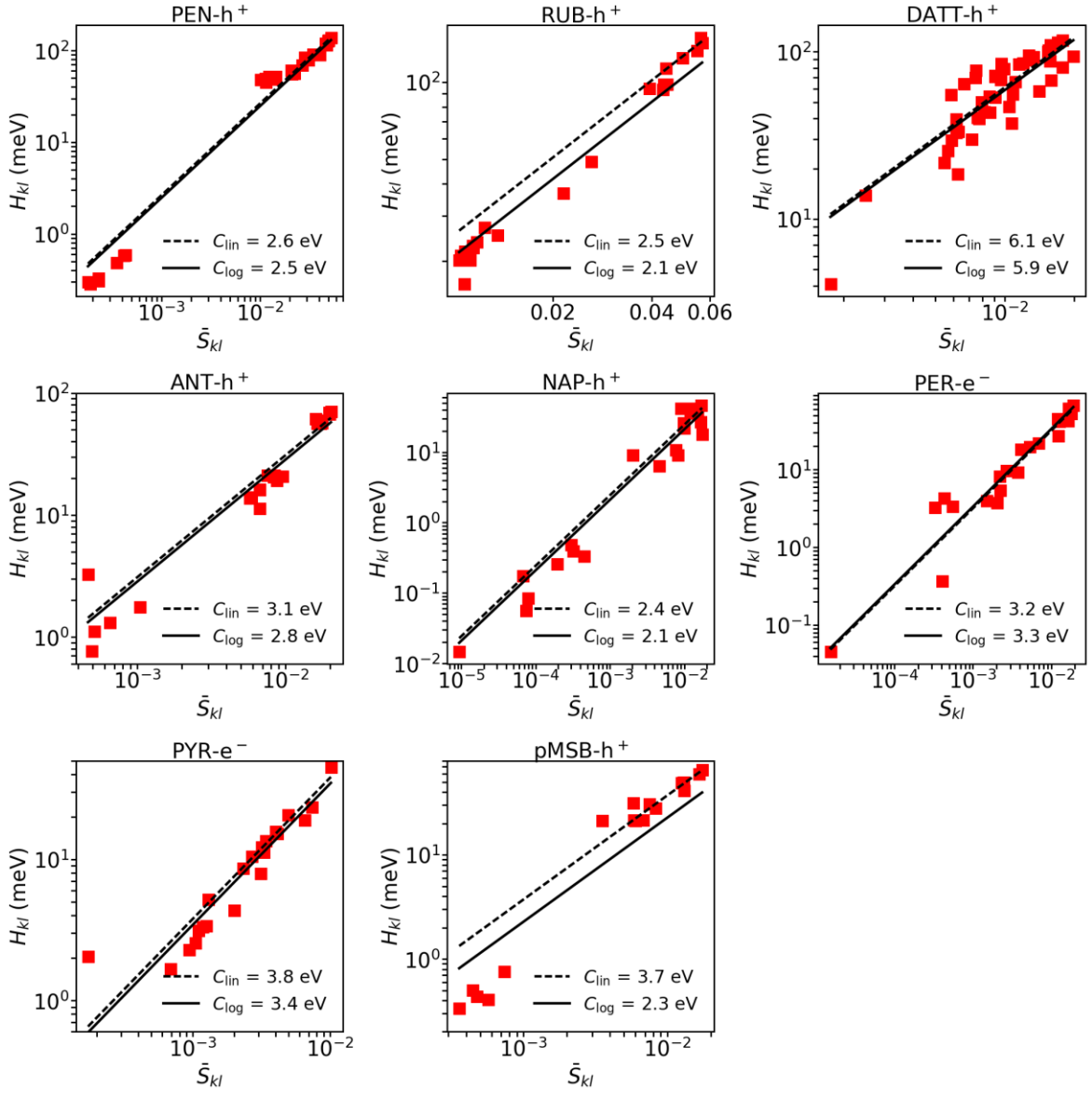
mean error = factor 1.9
over 5 decades!

Speed-up of 6 orders of magnitude, 20% loss of accuracy

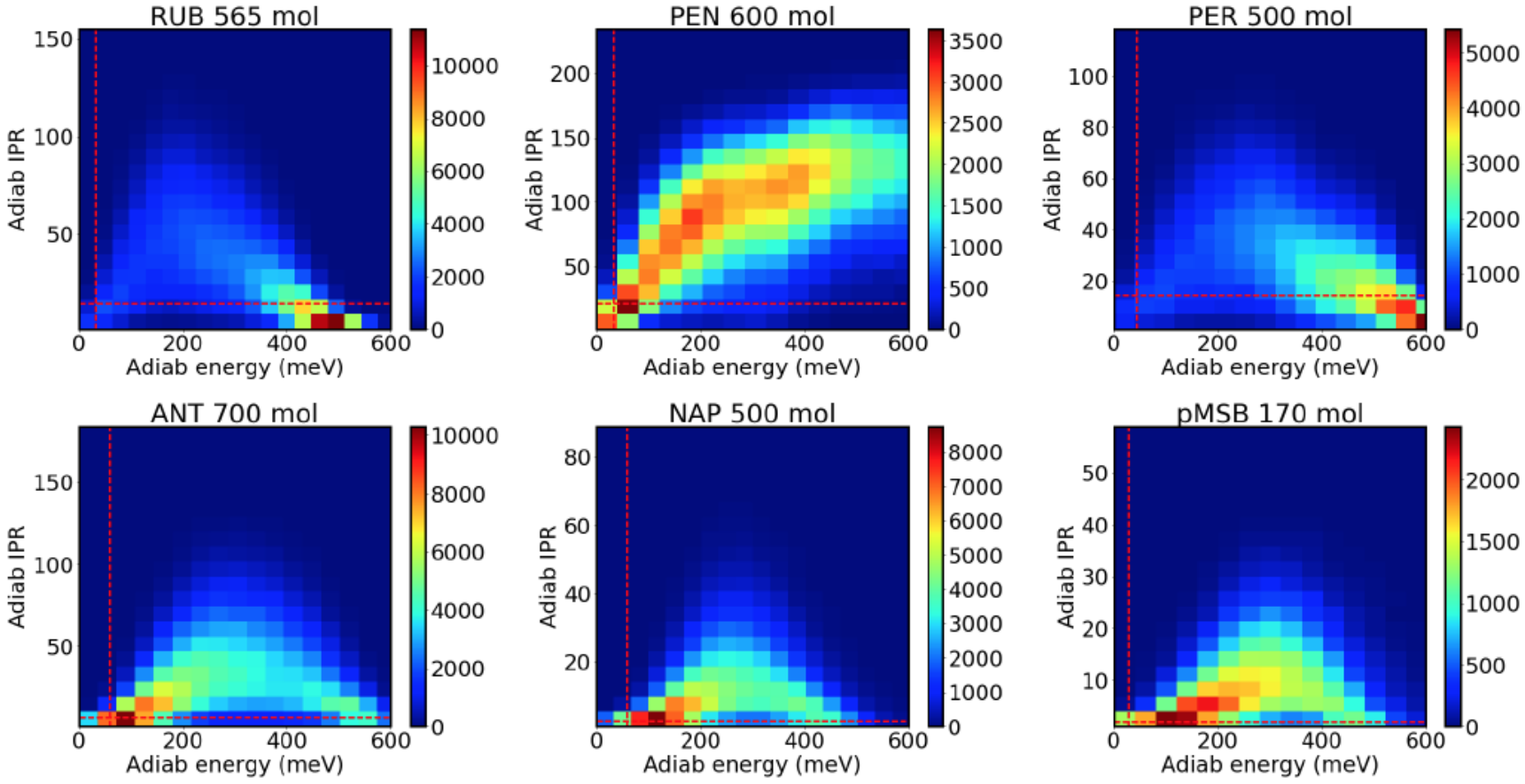
F. Gajdos, JB *et al. J. Chem. Theor. Comput.* **10**, 4653 (2014).



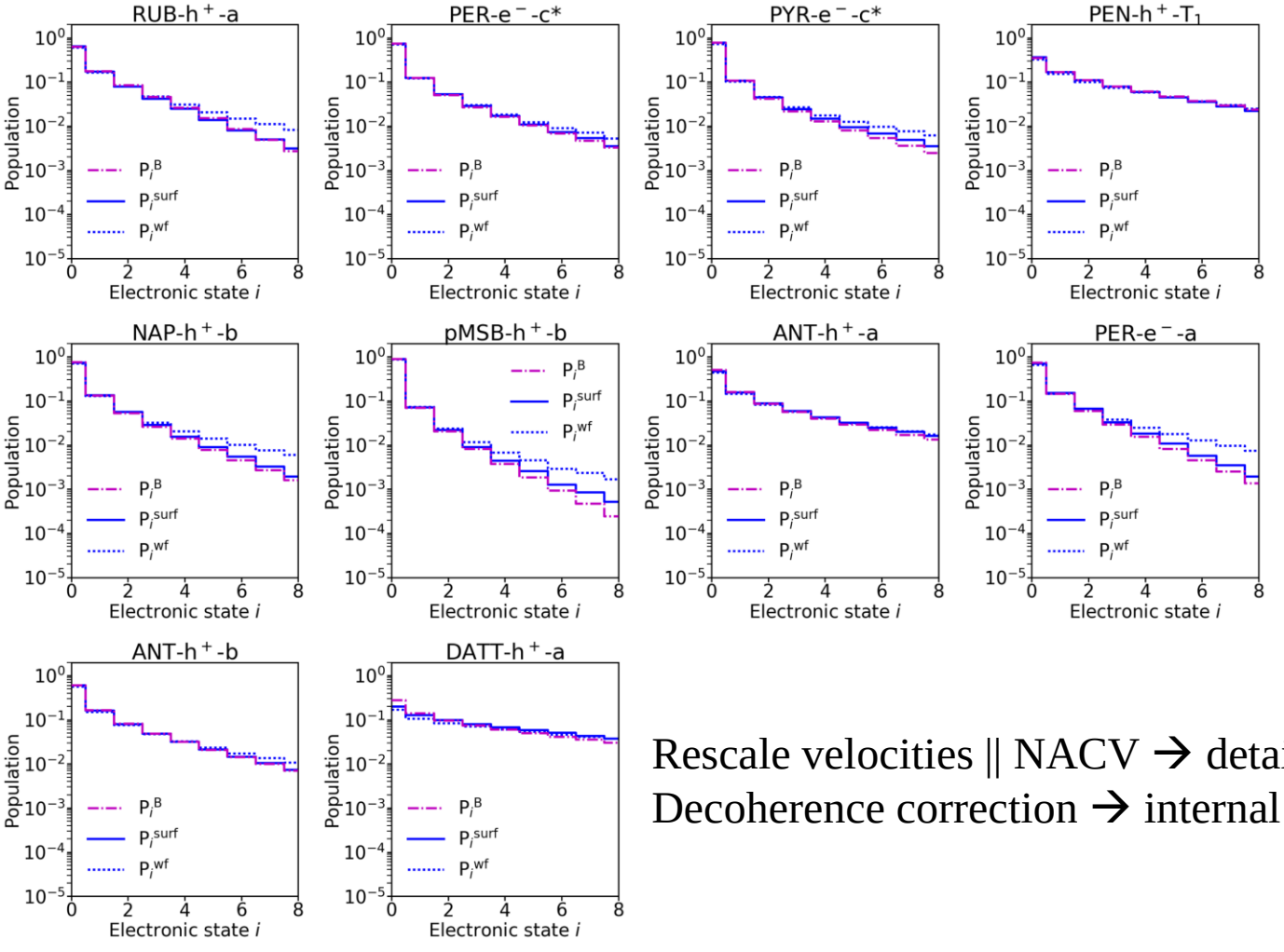
Analytic Overlap Method (AOM) for electronic couplings H_{kl} (as published)



Density of states and IPR (new data)



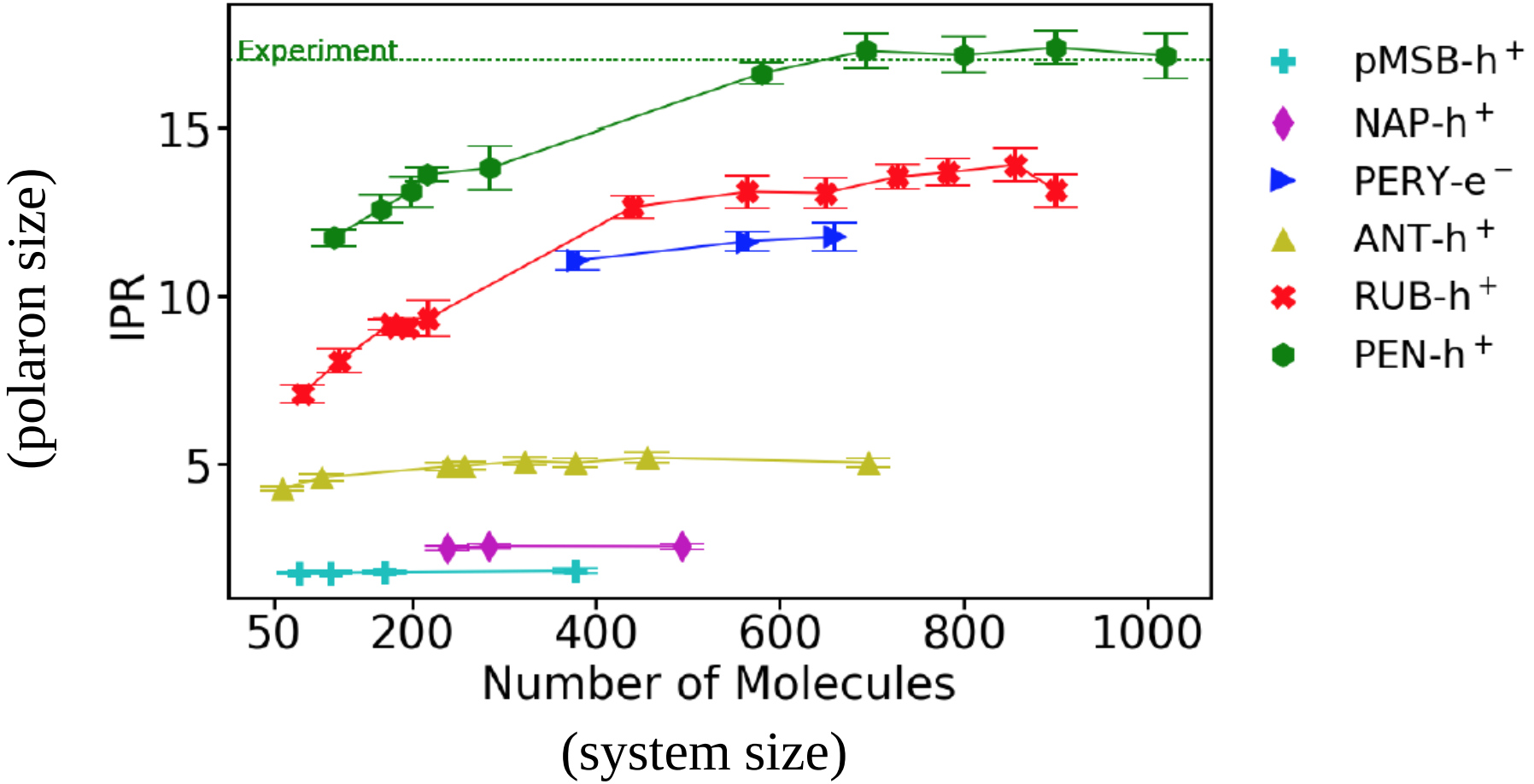
Detailed balance and internal consistency



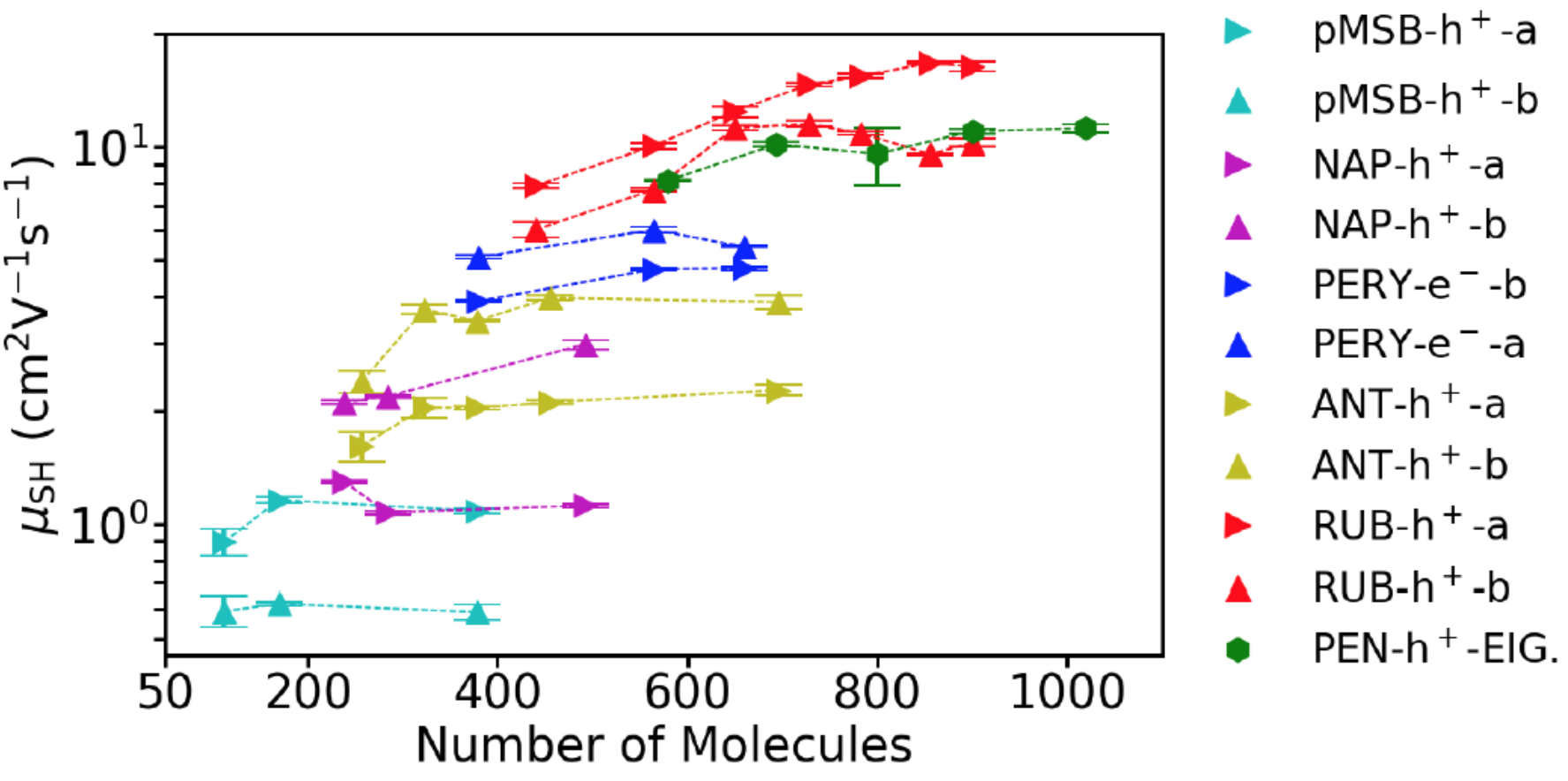
Rescale velocities || NACV → detailed balance

Decoherence correction → internal consistency

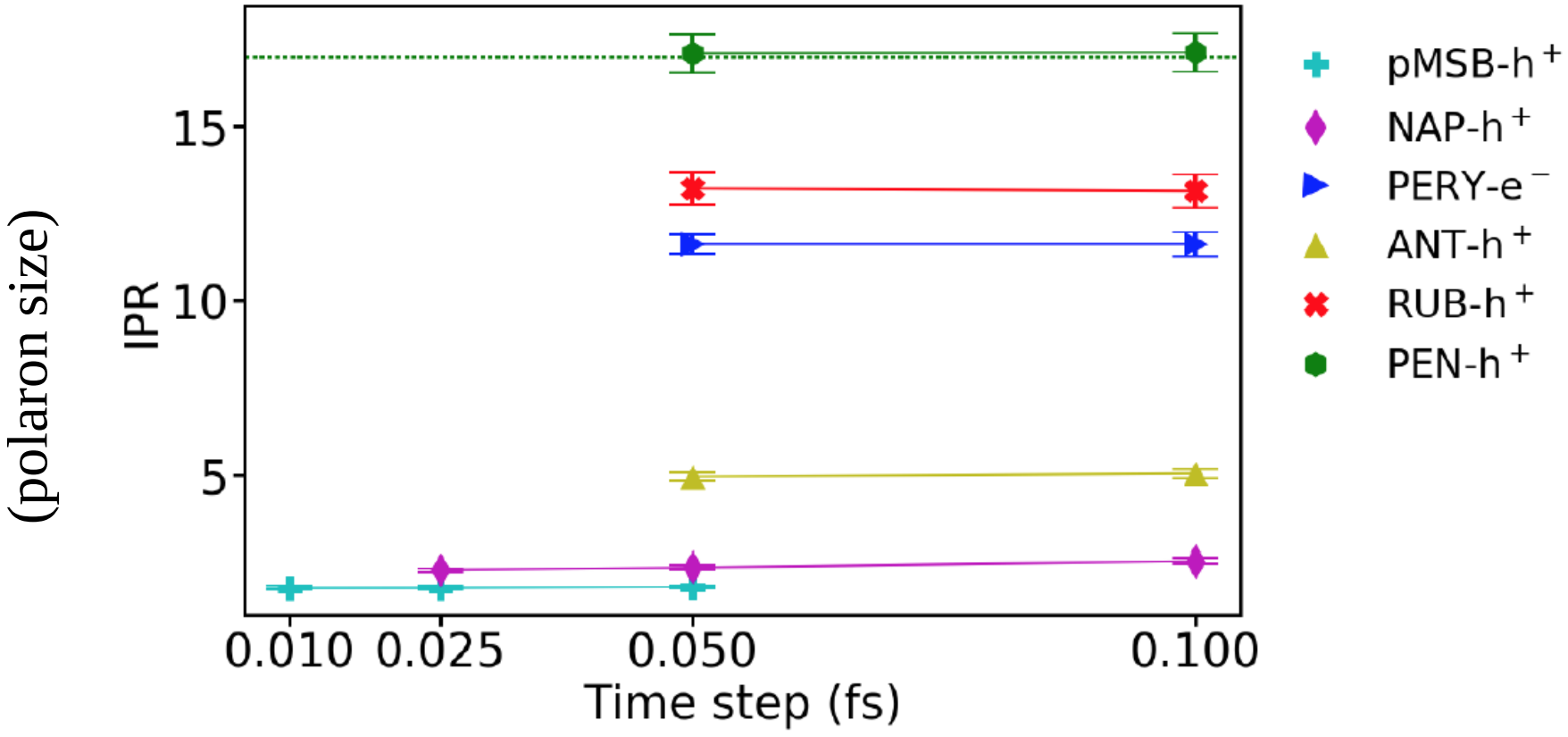
Convergence IPR wrt system size (new data)



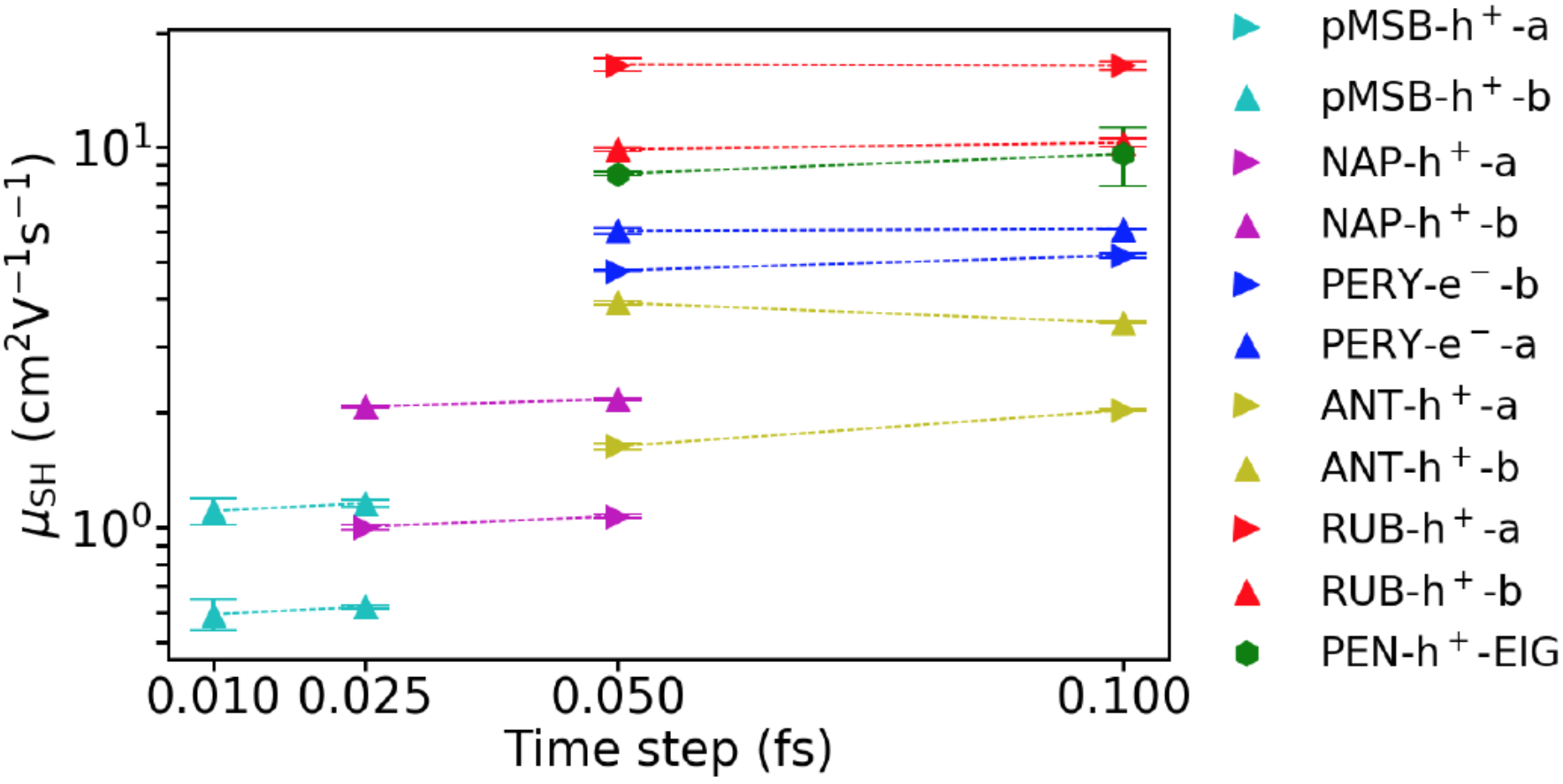
Convergence 2D mobility wrt system size



Convergence IPR wrt time step (new data)

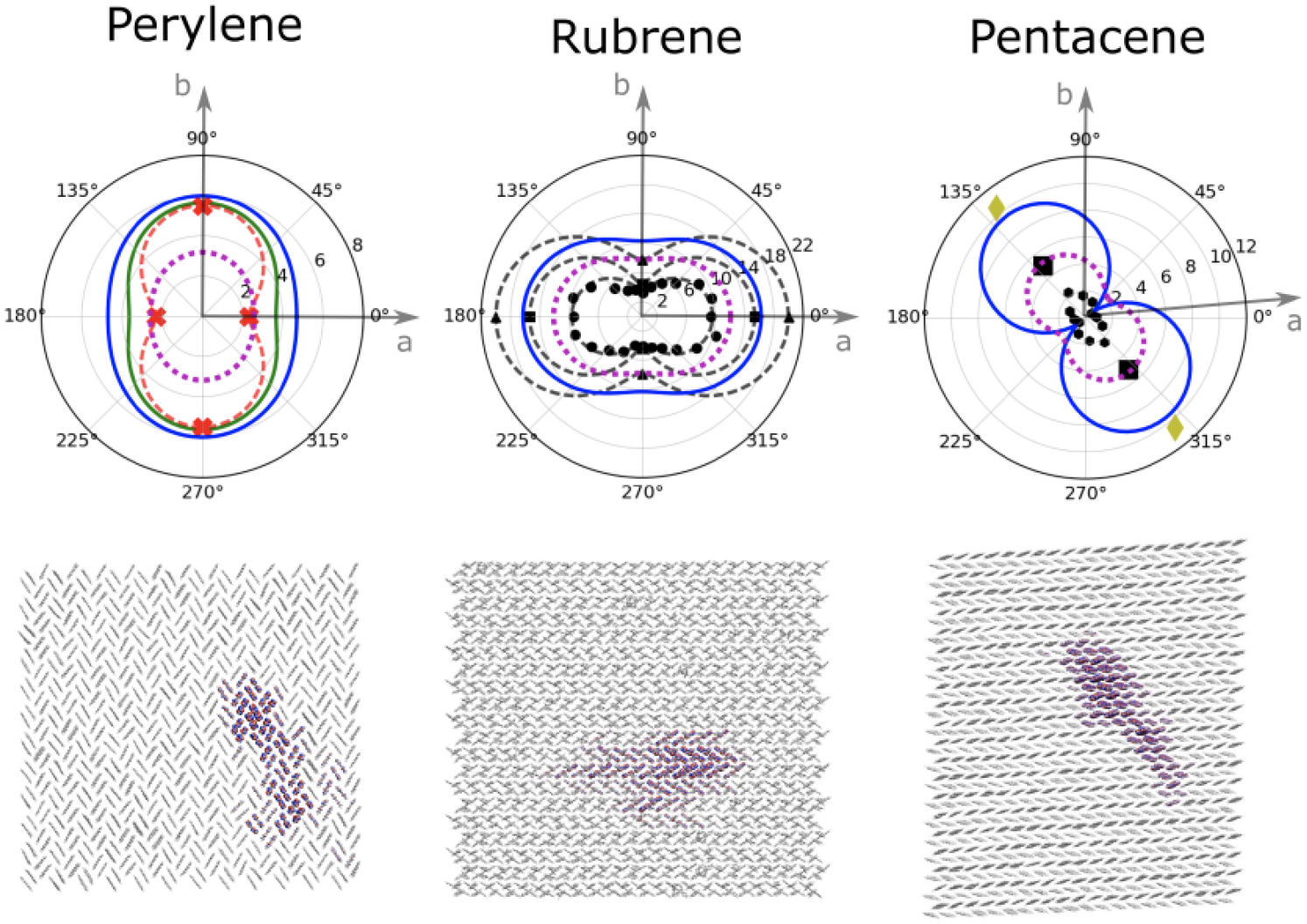


Convergence 2D mobility wrt time step (new data)



Summary: Nature of holes in OS crystals

Giannini *et al. Nature Comm.* **10**, 3843, 2019.



Summary: Nature of holes in OS crystals

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