# Temperature-dependent transient charge delocalization in high-mobility organic molecular semiconductors

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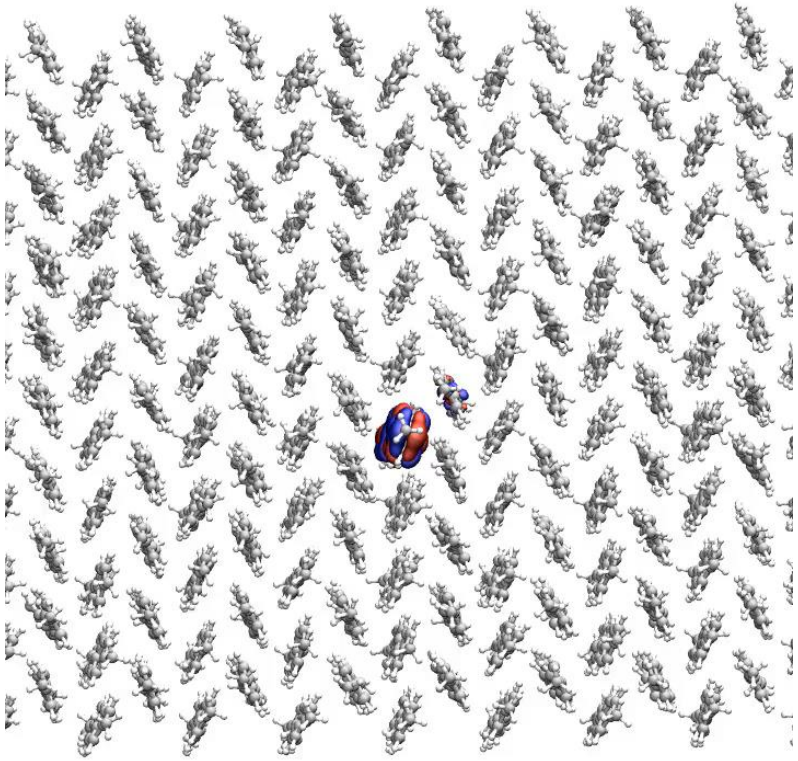
# Transient Localisation

S. Ciuchi et. al., *Phys. Rev. B* (2011 & 2012)
S. Fratini et. al., *Adv. Funct. Mat.* (2016)
S. Fratini et. al., *Nature Materials* (2017)

**pMSB (low mobility OS)**:
Hopping-like transport

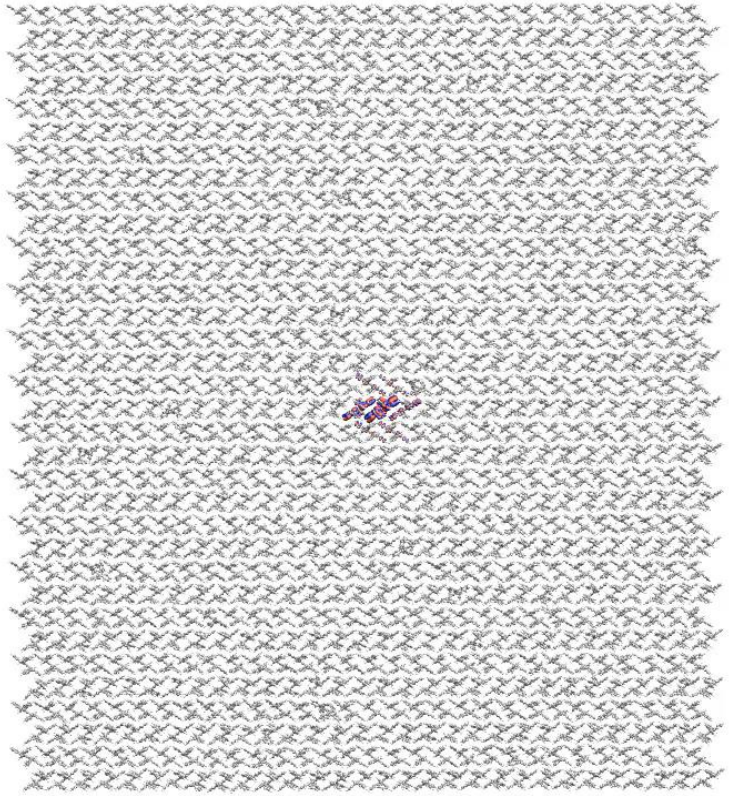


$$\mu = \frac{e}{k_B T}\frac{L_\tau^2}{2\tau}$$

Transient Localisation Length

Relaxation Time

**RUBRENE (high mobility OS):**
Delocalized polaron transport



Giannini, S. *et al.* Quantum localization and delocalization of charge carriers in organic semiconducting crystals. *Nat. Commun.* **10,** 3843 (2019).

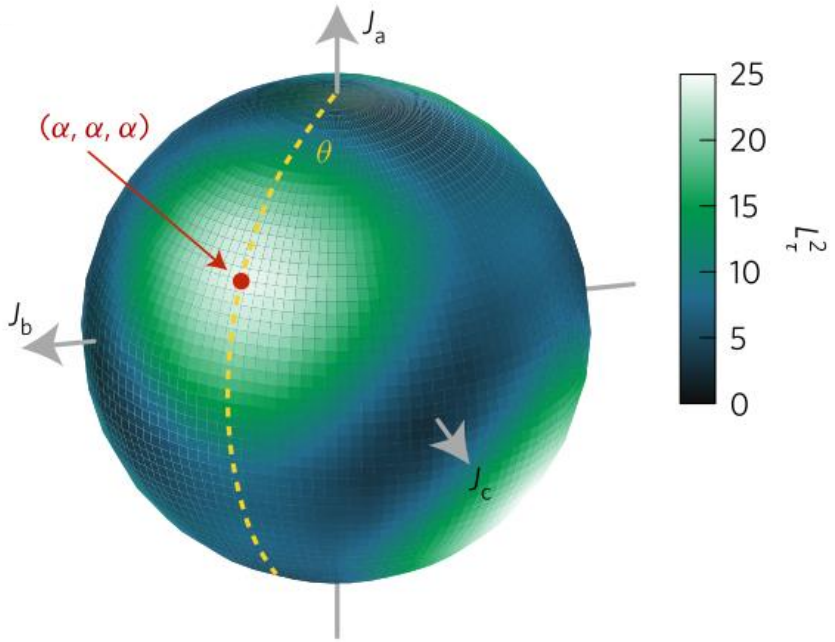
# Transient Localisation

## Mapping the transport space

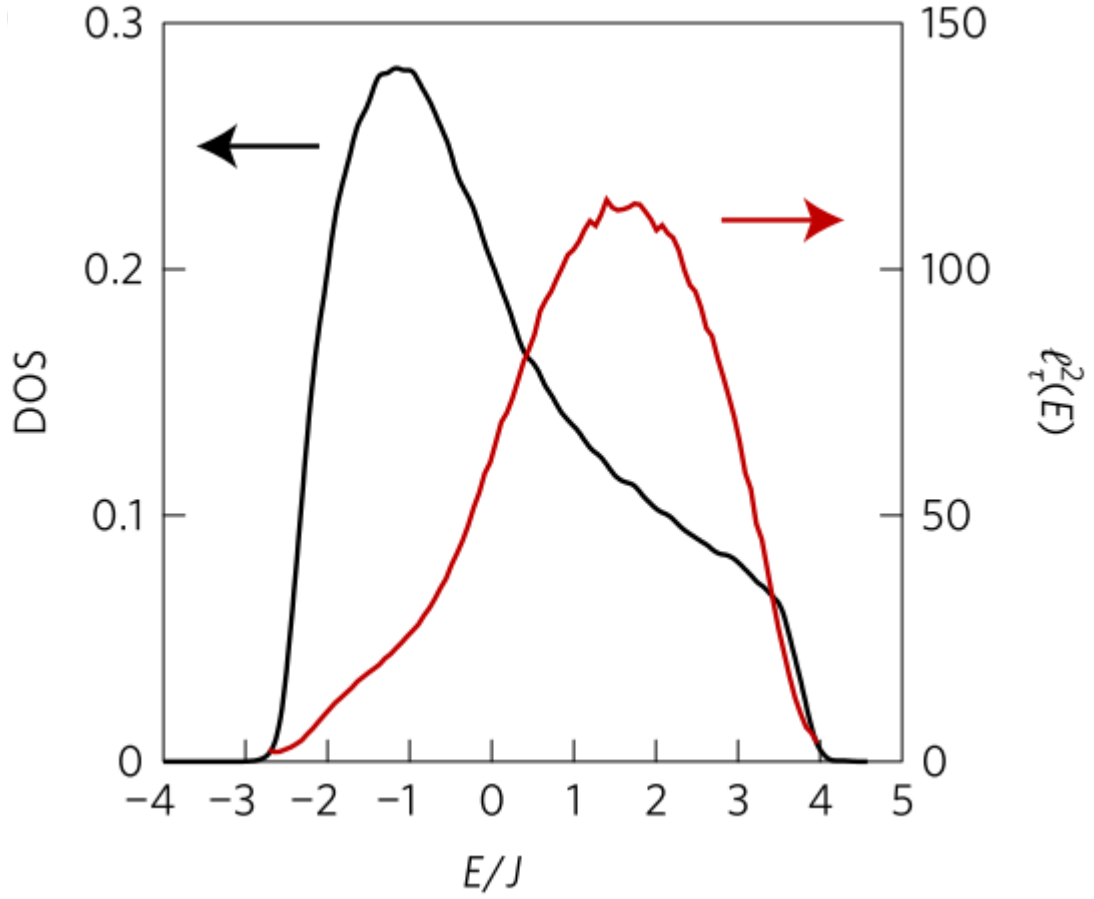
Transient Localisation Length

$$\mu = \frac{e}{k_B T}\frac{L_\tau^2}{2\tau}$$

Relaxation Time




Credit: S. Fratini et. al., *Nature Materials* (2017)




The plot on the right refers to the ideal case, the (α,α,α) point in the sphere (J values isotropic & in phase)

UMONS Université de Mons

UHMOb

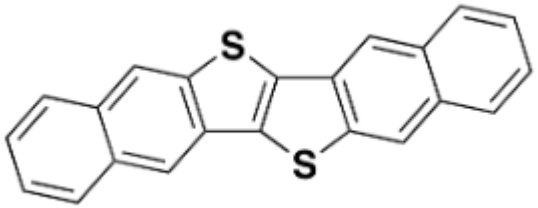
Haas, Takimiya et. al., *Appl. Phys. Letters* (2009)

# Molecules of Interest

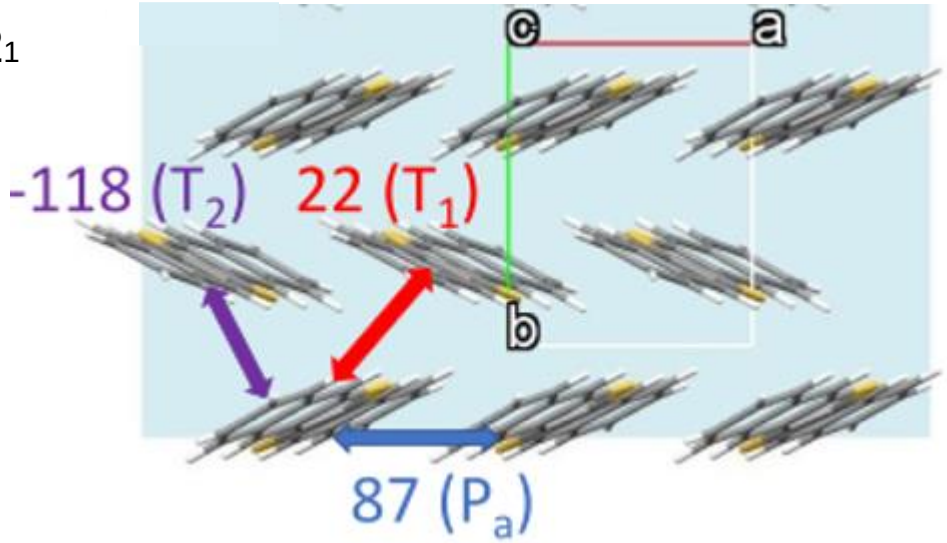
Goal: using T-dependence of transport parameters to probe the charge transport mechanism

## Thienoacenes

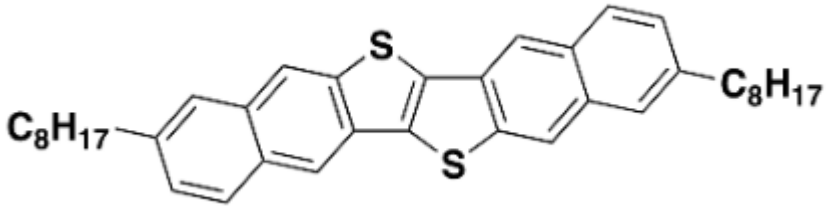
DNTT



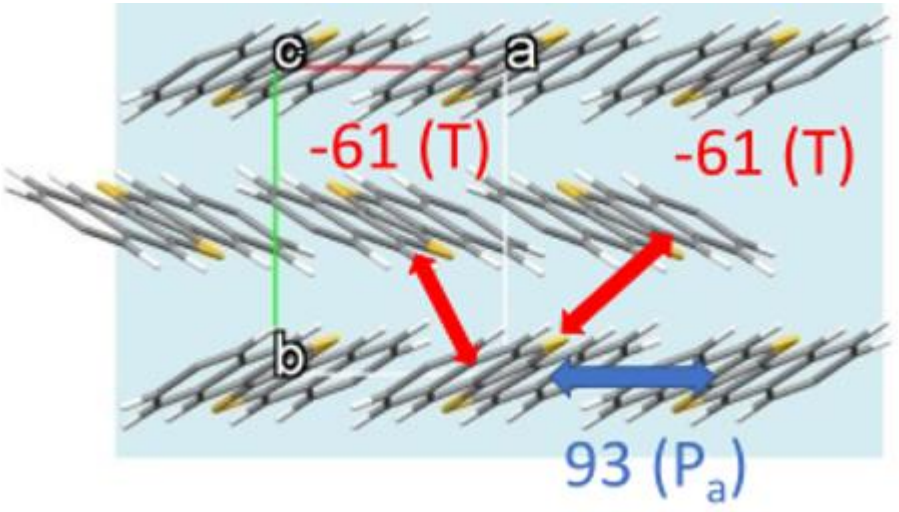

$P2_1$




C8-DNTT-C8




$P2_1/c$



# FOB-SH

## Mixed QM-MD method

$$H(t) = \sum_k \epsilon_k(t)|\phi_k(t)\rangle\langle\phi_k(t)| + \sum_{k\neq l} H_{kl}(t)|\phi_k(t)\rangle\langle\phi_k(t)|$$

- The Hamiltonian is time-dependent (and it depends on the atomic position at each time step): electron-phonon coupling included
- The Hamiltonian is recomputed at each time step using a combination of classical force-fields and ultrafast coupling calculations (the latter is called AOM)

**Excess electron or hole:**

$$\Psi(\mathbf{r},t) = \sum_k u_k(t)\phi_k(\mathbf{r},\mathbf{R}(t))$$

**Time dependent Schrödinger eq. (in the quasi-diabatic orbital basis):**

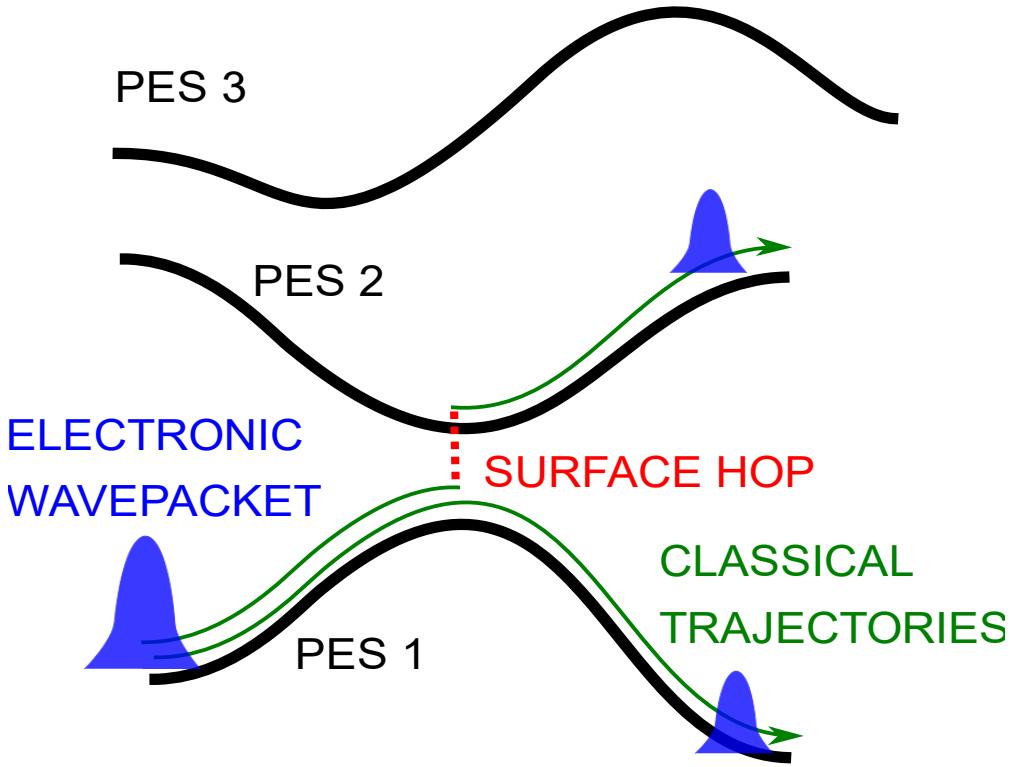
$$i\hbar\dot{u}_k(t) = \sum_{l=1}^{M} u_l(t)\left[H_{kl}(\mathbf{R}(t)) - i\hbar\langle\phi_k|\dot{\phi}_l\rangle\right]$$

Giannini, S. et al. *Multiscale Dynamics Simulations* 172-202 (2021) –book chapter

Carof, A., Giannini, S. & Blumberger, J. *Phys. Chem. Chem. Phys.* **21,** 26368–26386 (2019).

# FOB-SH

## Accessing Delocalized States




In SH a swarm of classical trajectories with associated wavefunction mimics the evolution of a full quantum wave-packet

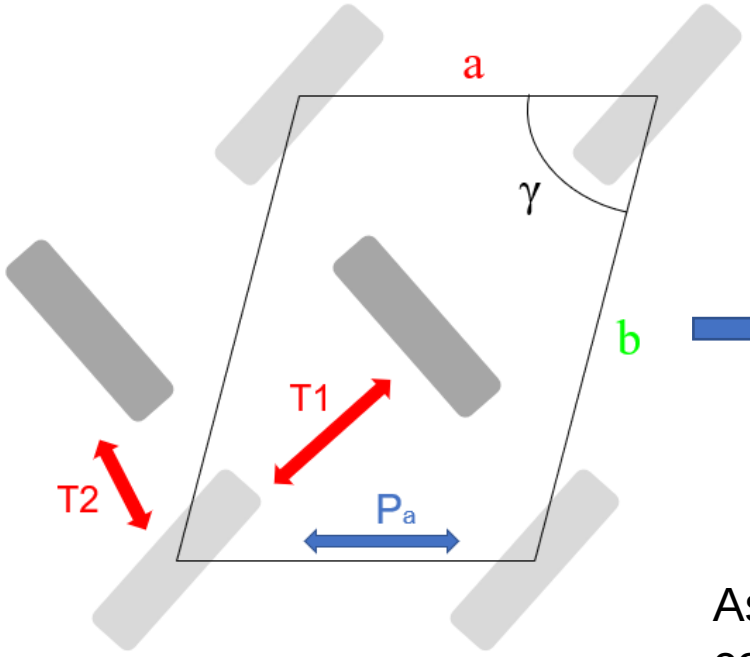
- Non-adiabatic process: Electron PES and nuclear motion are coupled

Giannini, S. et al. *Multiscale Dynamics Simulations* 172-202 (2021) –book chapter

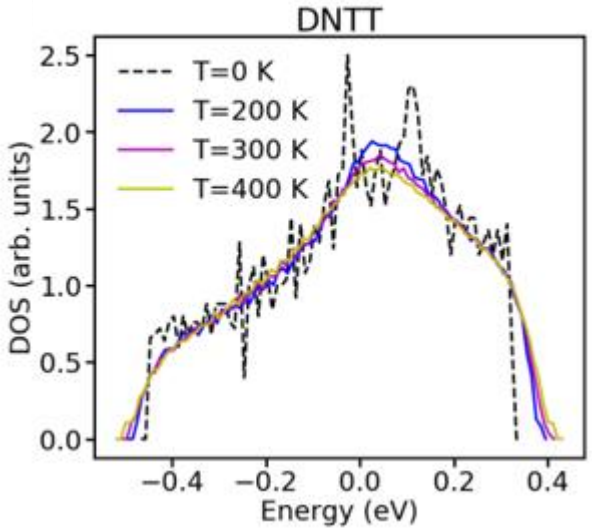
Carof, A., Giannini, S. & Blumberger, J. *Phys. Chem. Chem. Phys.* **21,** 26368–26386 (2019).

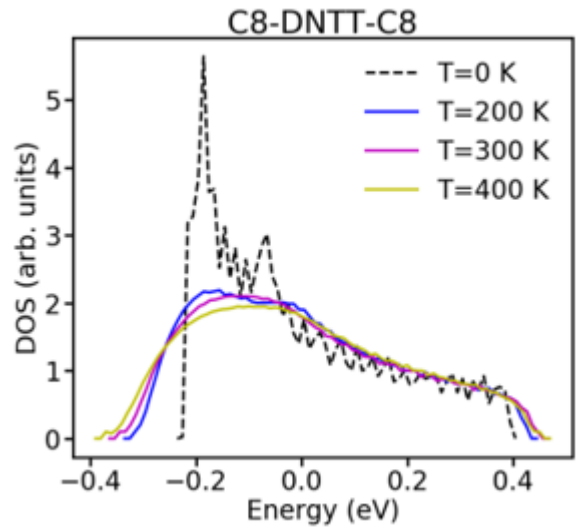
# FOB-SH

## Coupling phase and DOS




| | T1 | T2 | Pa | Results |
|---|---|---|---|---|
| Case 1 | + | + | + | + |
| Case 2 | - | + | + | - |
| Case 3 | - | - | + | + |




As outlined in Slide 2 the phase of the couplings can predict the shape of the DOS, which in the FOB-SH framework has precise consequences

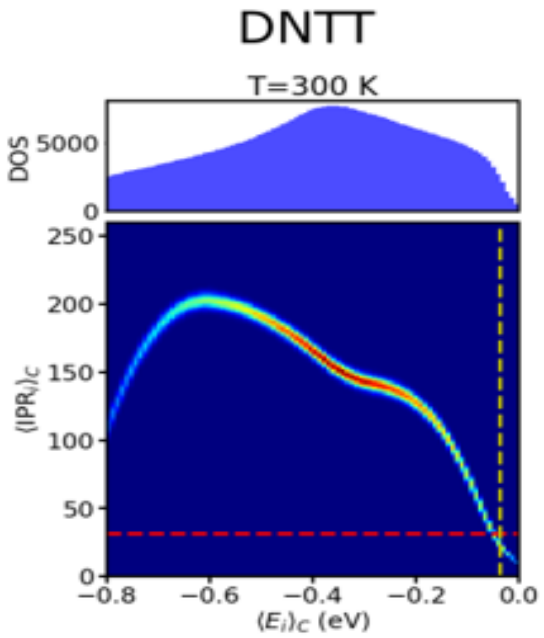
# FOB-SH

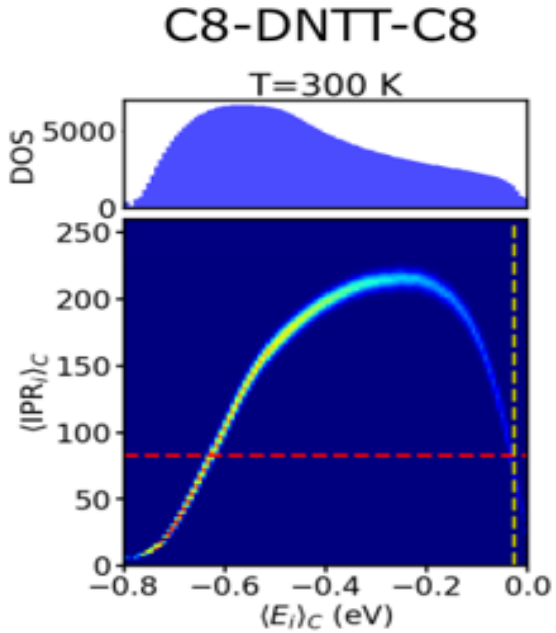
## Inverse Participation Ratio (IPR)

$$\mathrm{IPR}_i(t) = \frac{1}{N_{\mathrm{traj}}} \sum_{n=1}^{N_{\mathrm{traj}}} \frac{1}{\sum_{k=1}^{M} |U_{ki,n}|^4(t)},$$

IPR: Counts how many molecules participate in a delocalized state, i.e. degree of transient delocalization

In FOB-SH, the shape of the DOS is a reliable qualitative predictor of the delocalization of thermally accessible states near the band edge

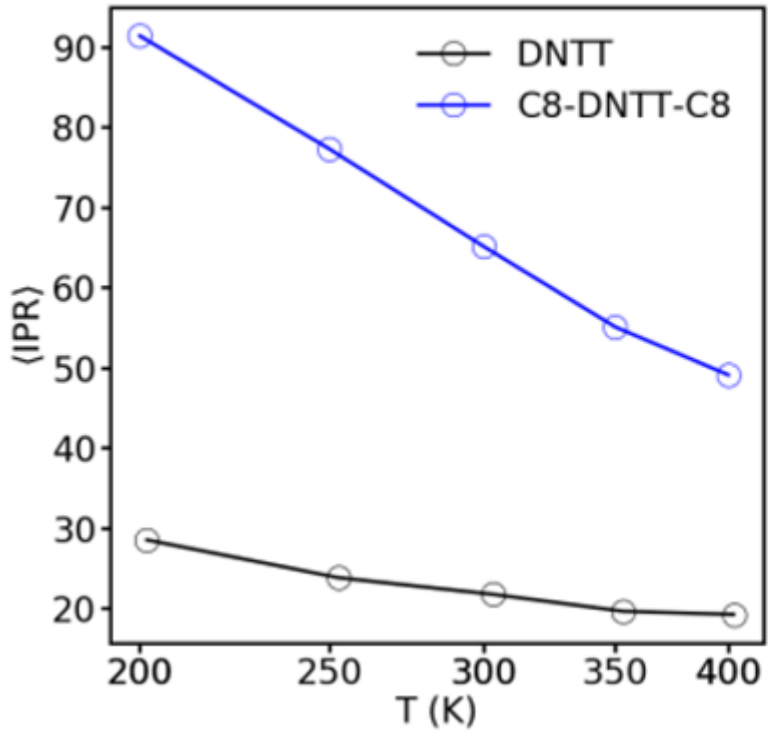


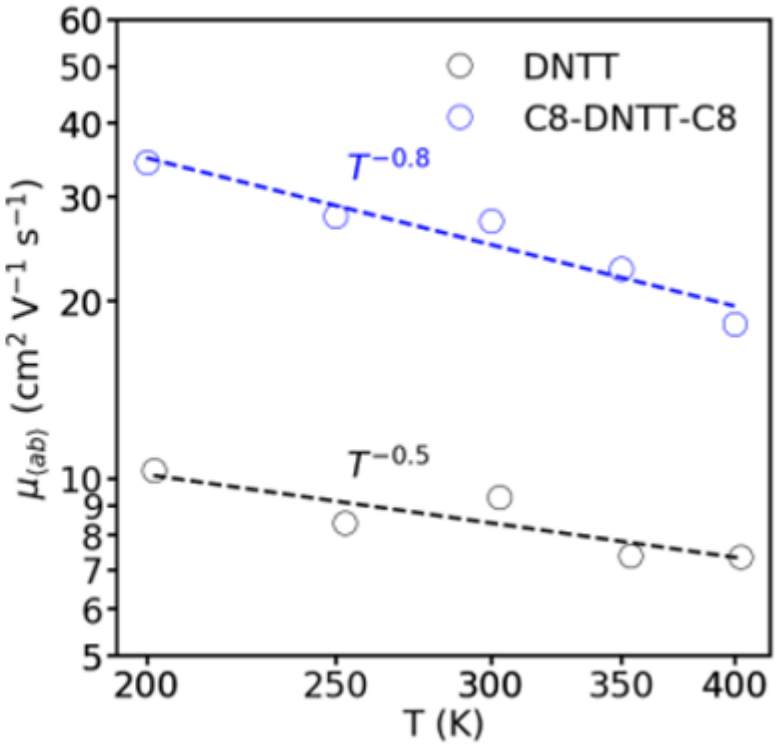
# FOB-SH

Mobility is the key parameter in evaluating intrinsic charge transport, and it tracks well with IPR at variable T

## T and delocalized states




Boltzmann average IPR change with an increase in T

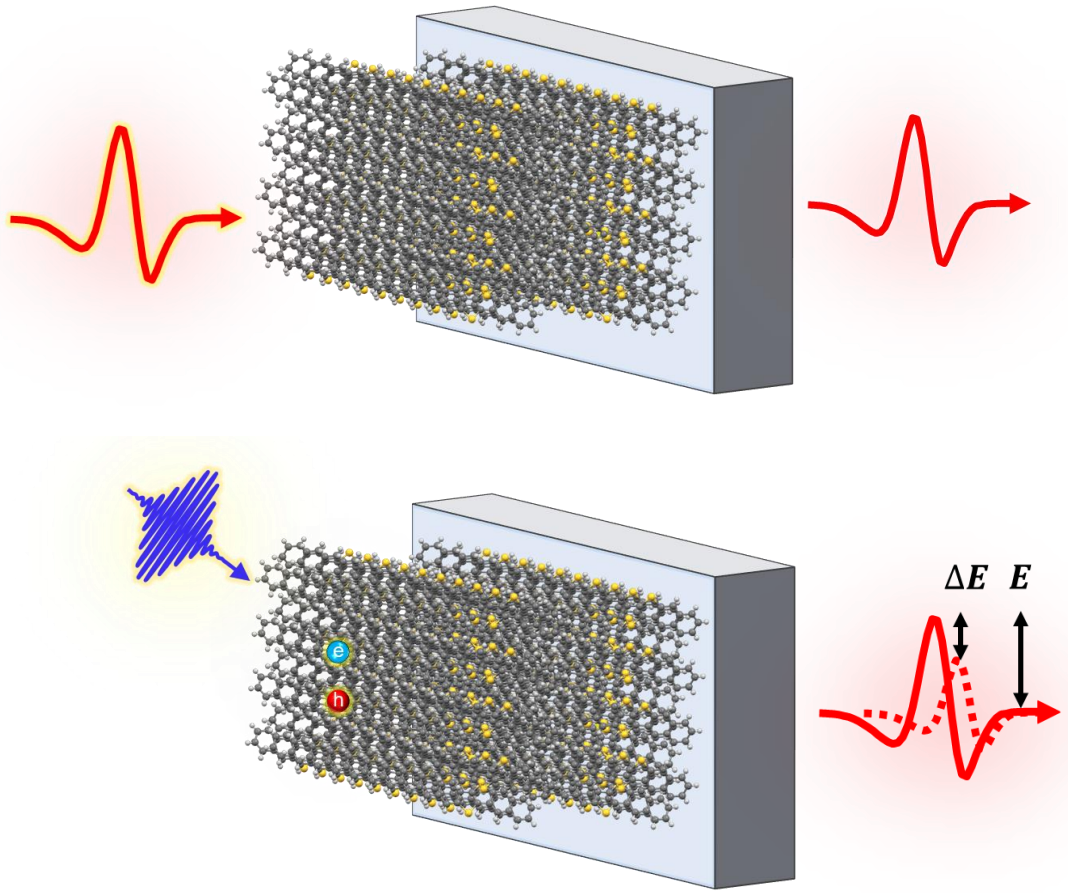


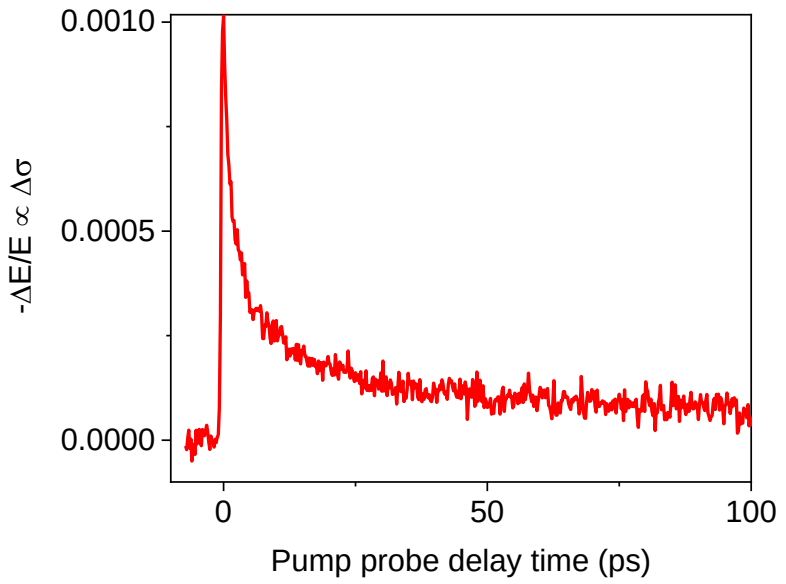

Mobility in HB plane and its variation with an increase in T

# Terahertz Spectroscopy

## Pump-Probe Setup

Credit to Lucia di Virgilio, Max Planck Institute for Polymer Chemistry



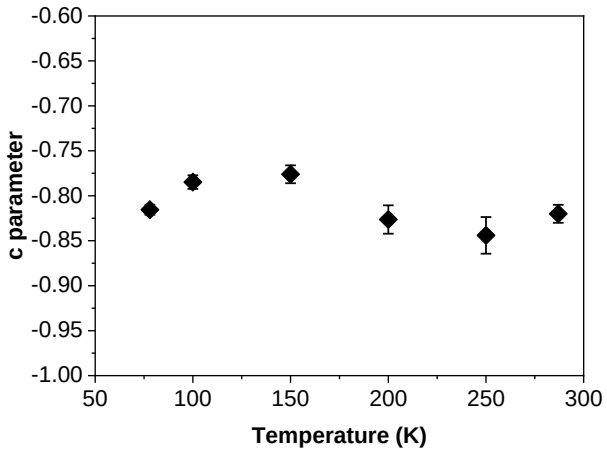



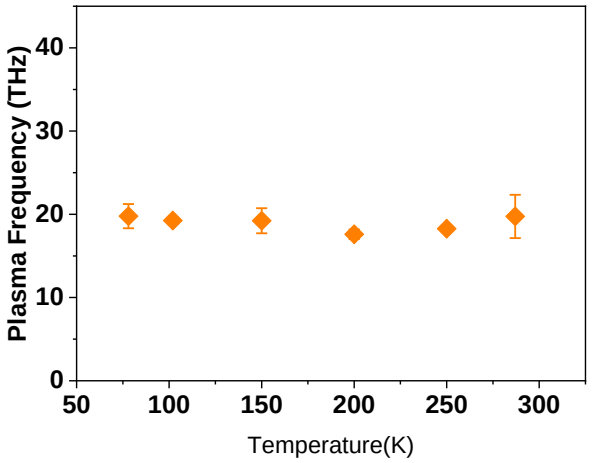

$$-\Delta E(t)/E_{ref} \propto \sigma_{pumped} - \sigma_{unpumped} = N e \mu$$

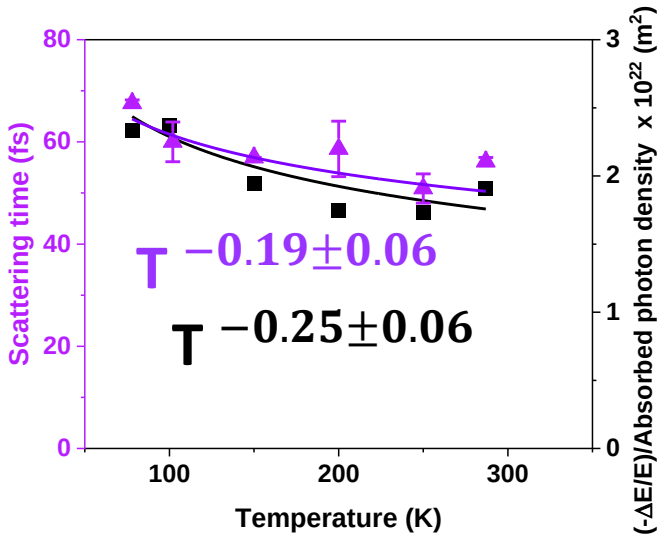
# Terahertz Spectroscopy

## Dependence on T

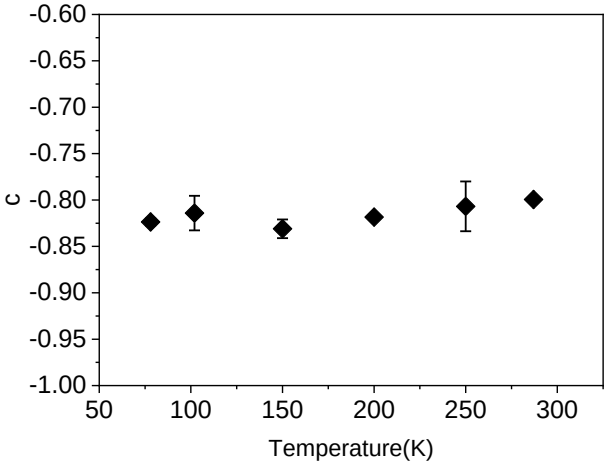
### DNTT

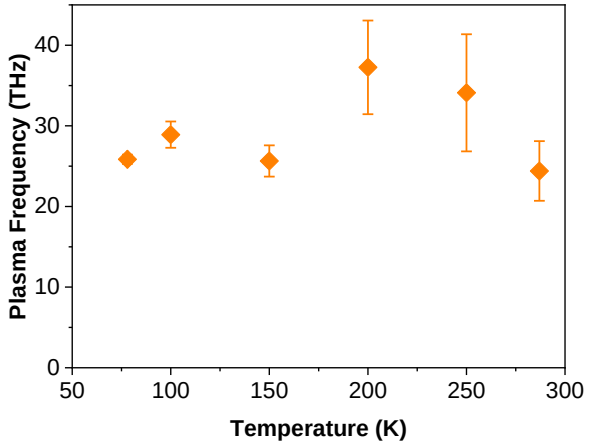


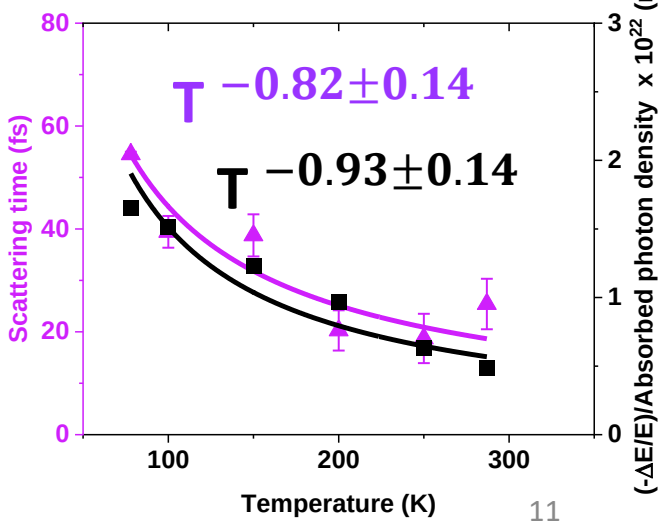




### C8-DNTT-C8



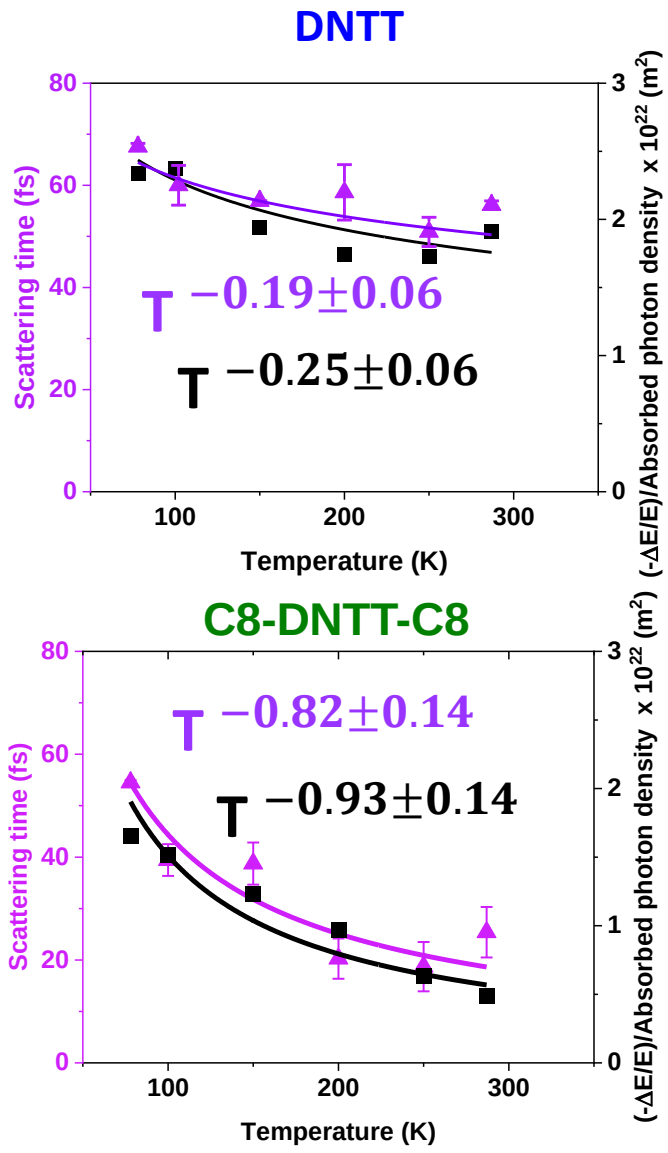



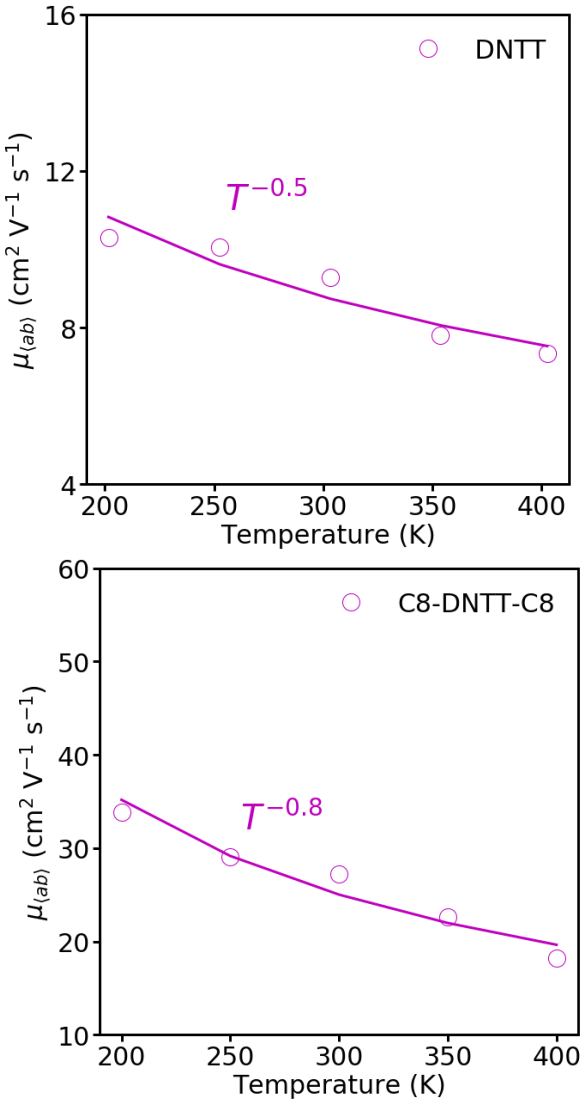




All parameters point to phonons as the primary factor for mobility decay at increasing T

# Dependence on T

## Theory and Practice




Qualitative agreement between theory and experiment on T-dependent power law, DNTT performs worse but C8-DNTT decays more rapidly

# Conclusions

- The first element to evaluate when computationally describing OSCs are static properties at low temperature, but resilience to thermal disorder is also highly desirable. The relative sign of the transfer integral becomes a key parameter, and so C8-DNTT-C8 performs much better than DNTT, while being less resilient to T increases

- Maximizing mobility implies increasing the delocalization (IPR, TL Length) of the thermally accessible states in a given material, which in turn implies a positive phase relationship and isotropic $J_i$ values

- Ongoing work aims to refine these results further and improve our understanding of how low-frequency phonons cause charge transport decay with increasing T

# Thank you for your attention!

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