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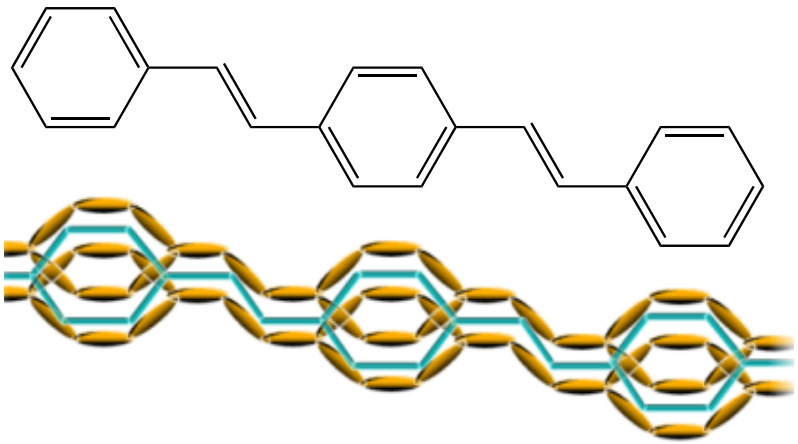
Charge and spin transport physics of organic semiconductors

Henning Sirringhaus

Cavendish Laboratory

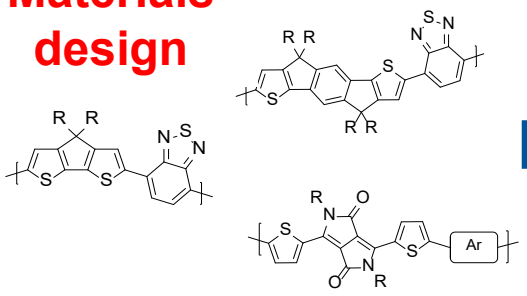
Organic electronics

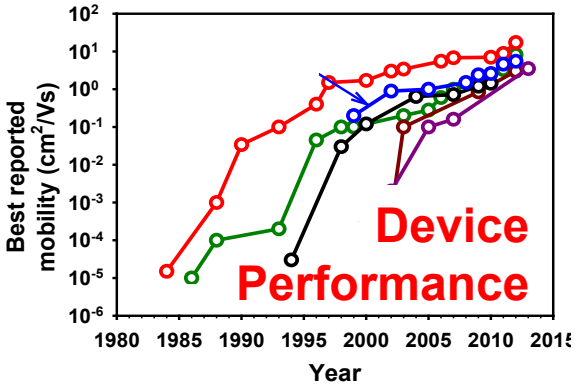
Innovation driven by new materials discovery



- Semiconducting properties imparted by π-electrons
- Earth-abundant, low-temperature, solution-processible optoelectronic materials

Materials design





New Physics & Applications

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Organic opto- and bioelectronics

LG Smart 3D 65"
Curved OLED TV

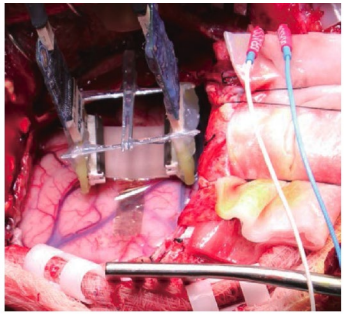
Organic light-emitting diodes

JOLED 21.6”, 4K OLED

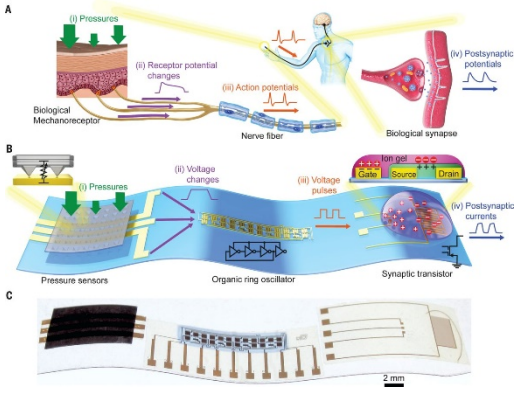
Heliatek BIPV

Organic photovoltaics (18% efficiency)

Implantable / skin electronics



Malliaras, Someya, et al.,
Nature 540, 397 (2016)



Bao et al., Science 360, 998 (2018)

Flexible electronics

FlexEnable/
Novares

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Thin film transistor technologies - Overview

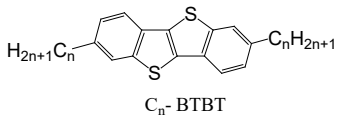
Property	Amorphous Si TFT	Polycryst. Si TFT (low T)	Oxide TFT	Organic TFT
Mobility [cm^2/Vs]	< 1	50-100	10-50	1-10
Leakage current [A]	10^{-12}	10^{-12}	10^{-12}-10^{-13}	10^{-12}-10^{-13}
TFT reliability	Moderate	High	High	Moderate
Process temperature	250-350°C	<500°C	< 250°C	RT-100°C
Manufacturing cost	Low	High	Potentially low	Potentially low
Yield	High	Medium	High	High
Flexibility	Moderate	Low	Moderate	High

- Charge carrier mobilities “good enough” for many large-area applications
- Low-cost manufacturing and mechanical properties driving adoption

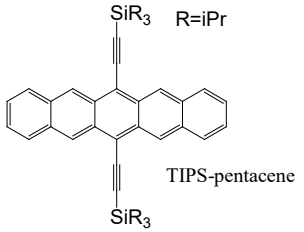
Charge transport physics of high mobility organic semiconductors

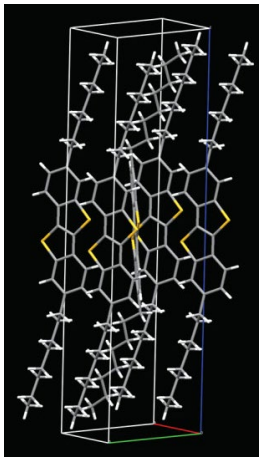
Fused-ring, small molecule semiconductors

- Highly ordered, polycrystalline microstructure
- High mobility > 1-10 cm^2/Vs



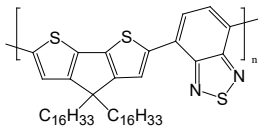
C_n- BTBT

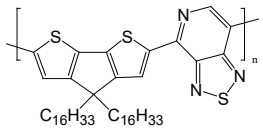


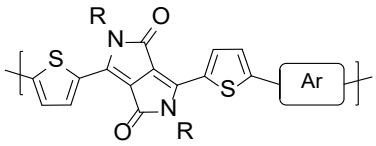


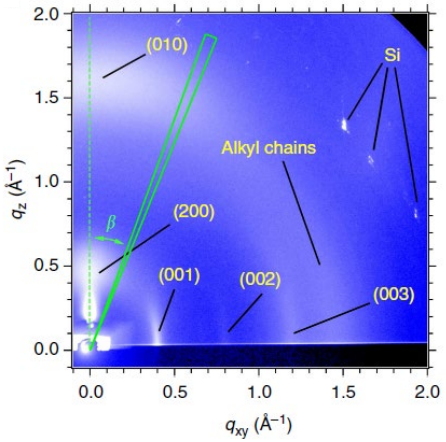
Donor-acceptor conjugated polymers

- Disordered, in some cases near-amorphous microstructure
- Mobility 1 - 5 cm^2/Vs









⇒ Transport physics considered to be quite different

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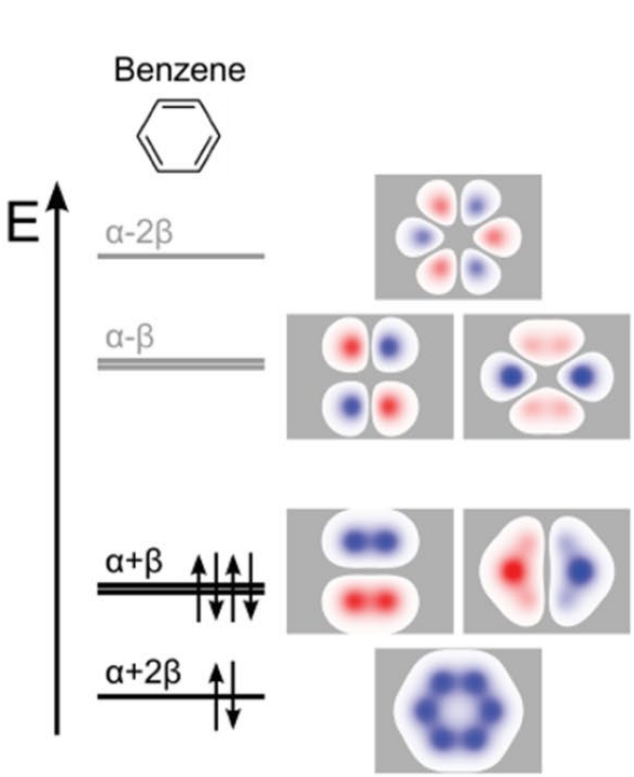
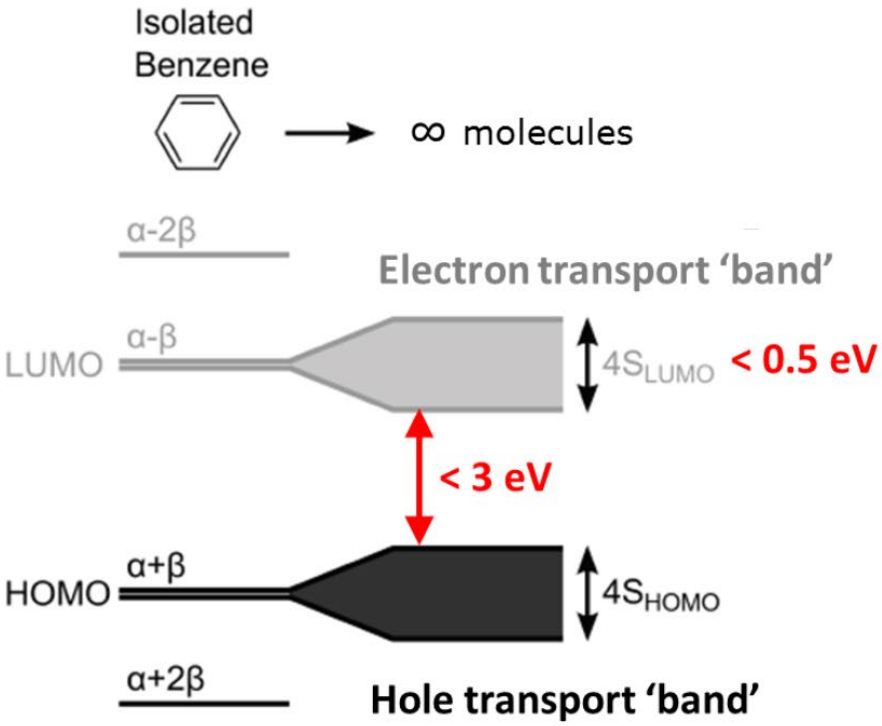
Electronic structure of organic semiconductors



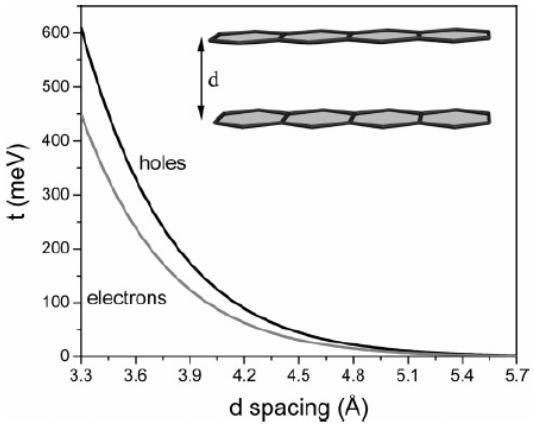


Band transport in molecular crystals

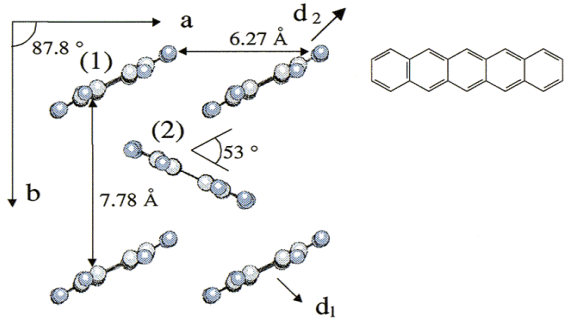
- Extended Bloch electrons expected if electron-phonon coupling and disorder could be neglected – Bandwidth on the order of 100 meV

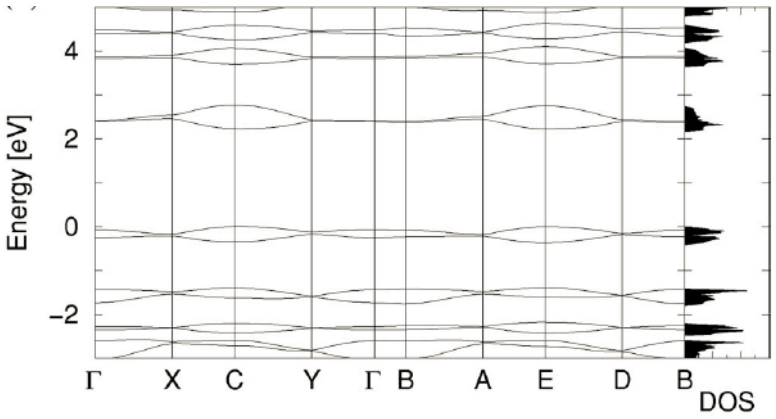
$$H_e = \sum_i \varepsilon_i a_i^+ a_i + \sum_{i,j} J_{ij} a_i^+ a_j$$

$$J_{ij} = \left\langle \phi_i\left(r - R_i\right) \middle| H_e \middle| \phi_j\left(r - R_j\right) \right\rangle$$



Cornil, Chem. Rev. 107, 926 (2007)

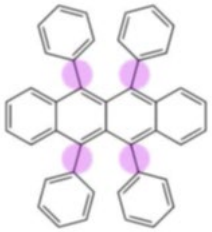




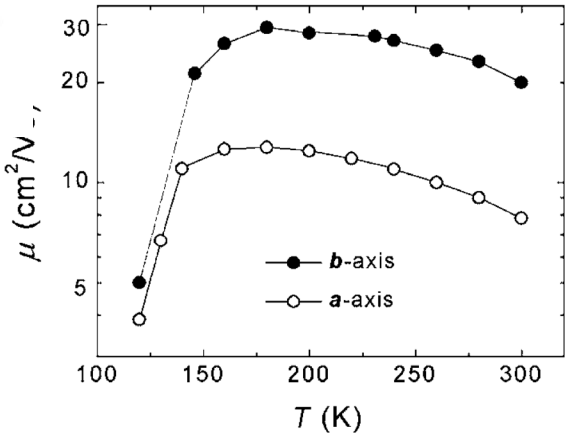
Louie, et al., PRB 67, 115212 (2003)

- But: $m^* = \dfrac{2\hbar^2}{Wa^2}$ $\lambda = \dfrac{\mu}{e}\left(3m^* k_B T\right)^{1/2} < 0.5nm$

Charge transport physics of molecular semiconductors

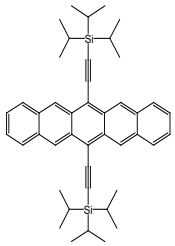


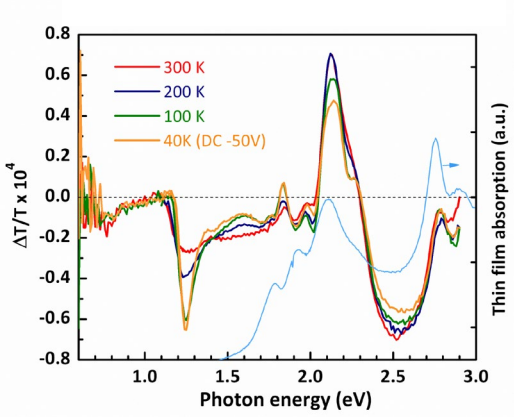
Band-like temperature dependence of mobility



Podzorov, Rev. Mod. Phys. 78, 973 (2003)

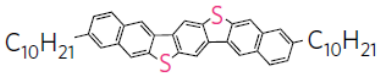
Charge induced optical absorptions resembling radical cations in solution



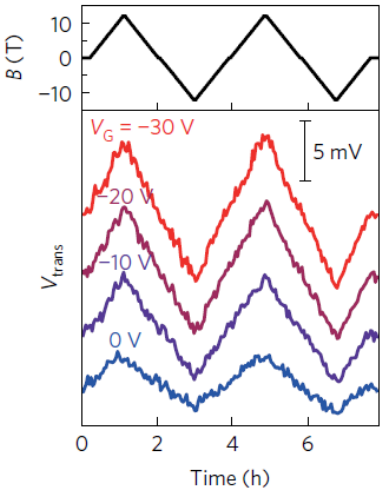


Sirringhaus, et al., Phys. Stat. Solidi B (2012)

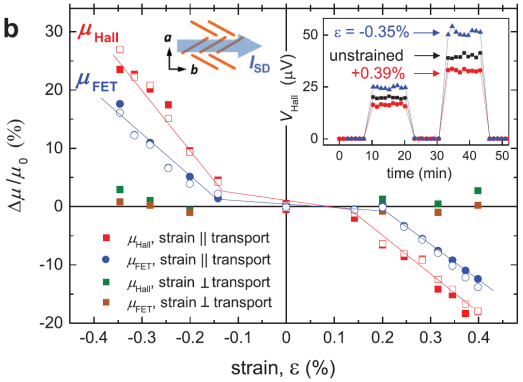
Simple, ideal Hall effect

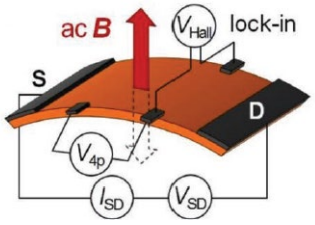


Takeya et al., Nat. Phys. 13, 994 (2017)



Large mobility modulation with mechanical strain





Podzorov, et al., Adv. Sci. 7, 1901824 (2020)

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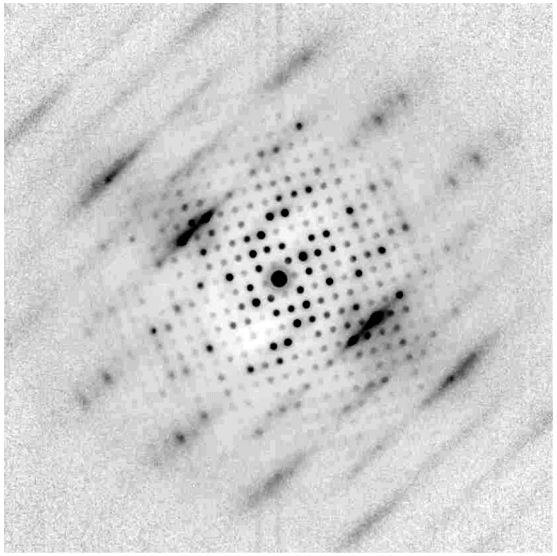
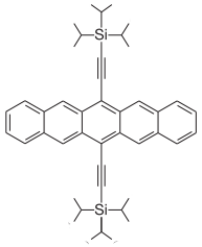
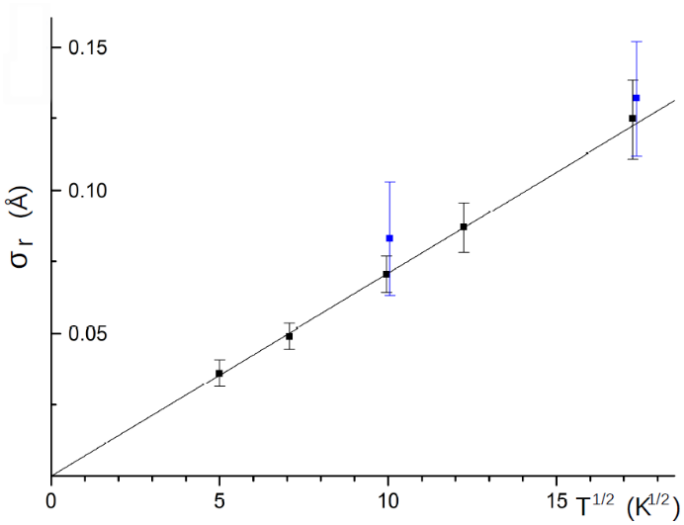
Structural dynamics in soft molecular crystals

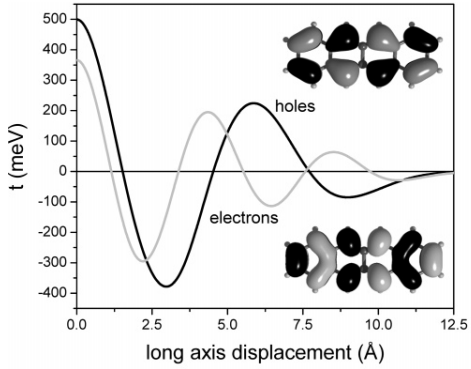


Eggeman, Illig et al., Nat. Mater. 12, 1045-9 (2013)





- Soft bonding causes significant thermal fluctuations on the order of 0.1Å – disorder in transfer integrals and site energies



Bredas, et al., Chem. Rev. 104, 4971 (2004)

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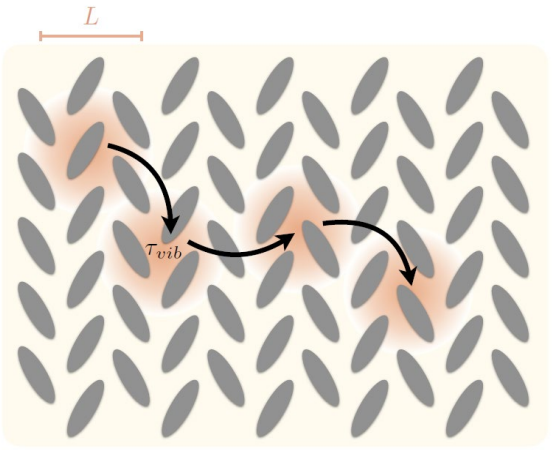
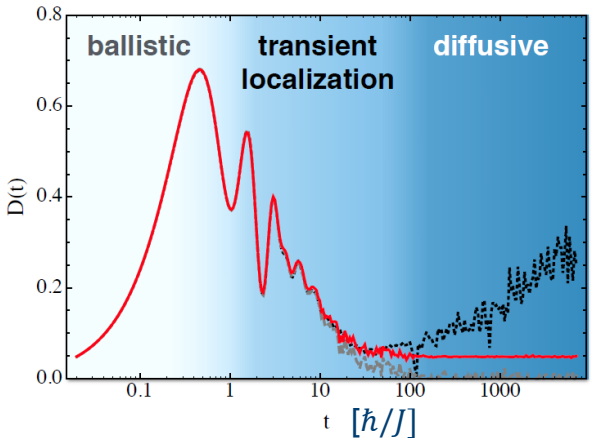
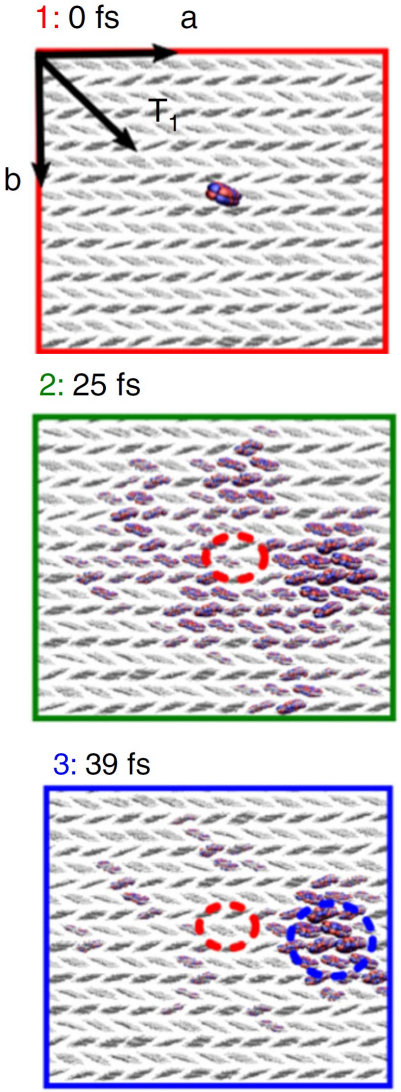
Charge transport - Transient localisation



$$\mu = \frac{e}{k_B T} \frac{L^2 \omega_0}{2}$$



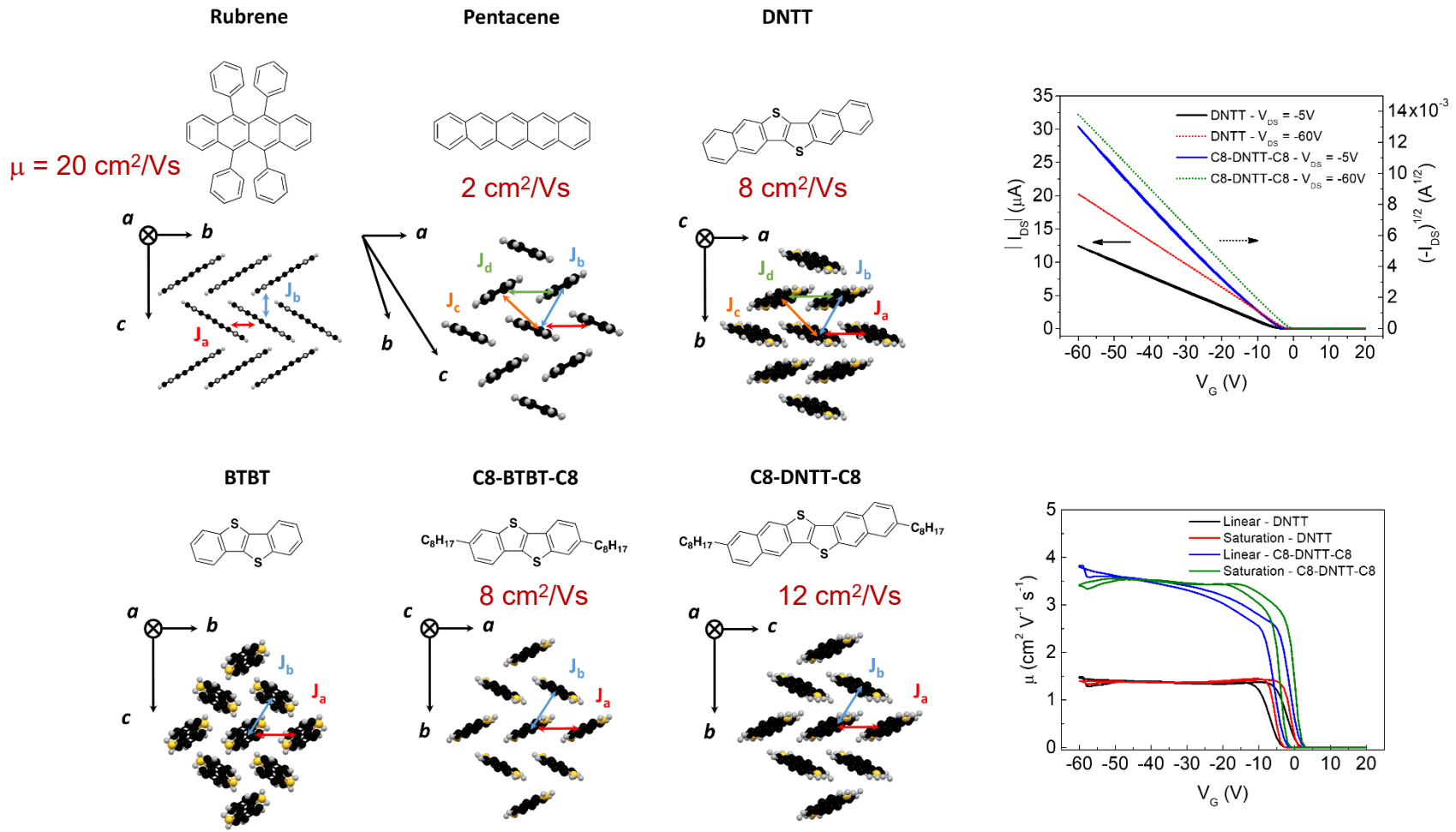
Troisi, et al., Chem. Rev. 40, 2347 (2011)
Fratini, et al., Adv. Funct. Mat 26, 2292 (2016)



Giannini et al., Nat. Comms. 10, 3843 (2019)

Electrons are “surfing on the waves of molecular lattice distortions”

Correlation between crystal packing and in-plane charge carrier mobility



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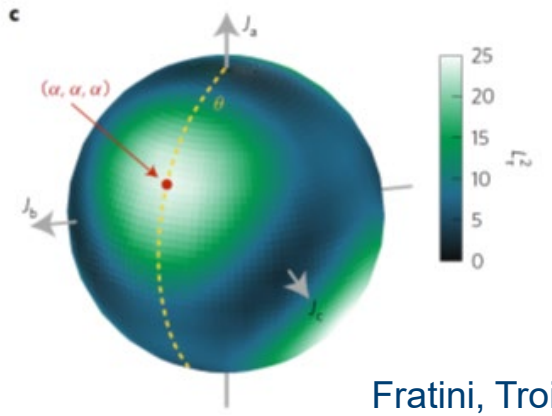
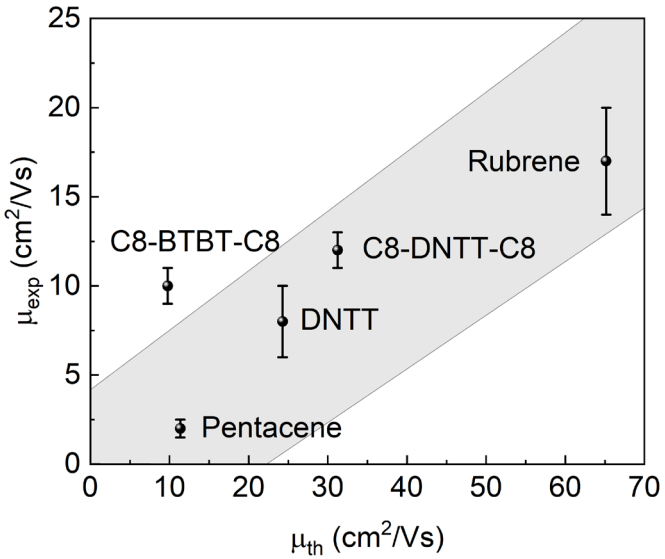
Mobility in transient localisation regime

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



Fratini, Troisi et al., Nature Materials 16, 998 (2017)

- Key parameters:
  - $J_a.J_b.J_c$ - Overall magnitude of J less important than distribution
  - $\Delta J_a/J_a, \Delta J_b/J_b, \Delta J_c/J_c$ - Mobility sensitive magnitude of thermal disorder
  - ω_0 - Influences not just τ, but also strength electron-phonon coupling
- Ability to quantitatively predict charge carrier mobilities



Schweicher, Ruggiero, Davino et al. (2019)

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Unraveling the complexity of the structural dynamics

- Units cells with 100 atoms – Several hundred phonon modes
- Do all these modes couple to the charge motion or are specific modes particularly relevant ?
- Need for low-frequency vibrational spectroscopy probing intermolecular motions

Terahertz time-domain spectroscopy (THz-TDS)

Inelastic Neutron Scattering (INS)

Combined experimental and theoretical study

1. THz-TDS (20-80 cm^{-1}) + INS (150-1500 cm^{-1})
2. State-of-the-art fully-periodic quantum mechanical calculations

ISIS Pulsed Neutron & Muon Source
Rutherford Appleton Laboratory, UK

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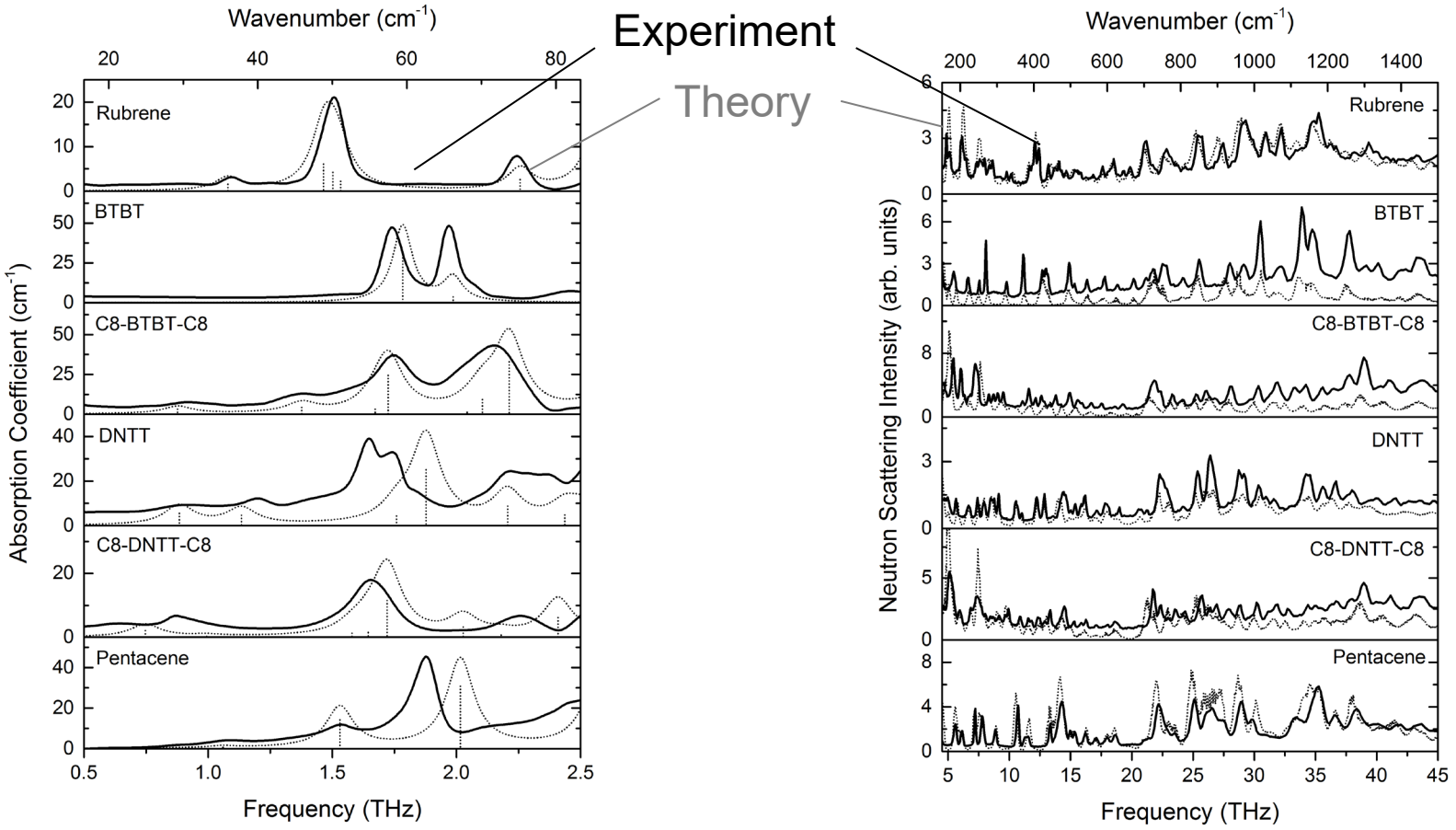
Low frequency vibration spectra



- Good agreement with theory (DFT - CRYSTAL17 Grimme D3-corrected[15,16] PBE with split-valence triple-zeta 6-311G(2d,2p)

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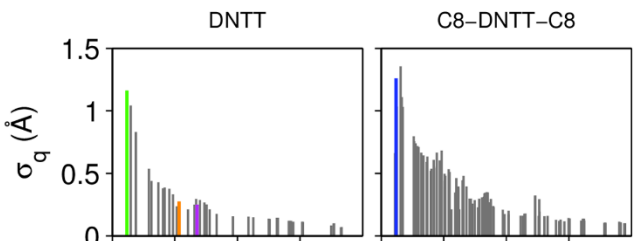
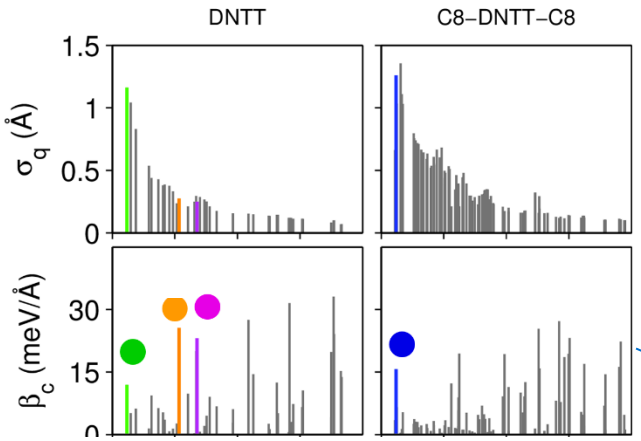
Schweicher, Ruggiero, Davino et al. Adv. Mat. 1902407 (2019)

Mode-resolved non-diagonal electron phonon coupling constants in DNTT and C8-DNTT-C8



$$[\sigma_k^Q(T)]^2 = \frac{k_B T}{m_k \omega_k^2},$$

Mode-resolved non-diagonal electron phonon coupling constants in DNTT and C8-DNTT-C8

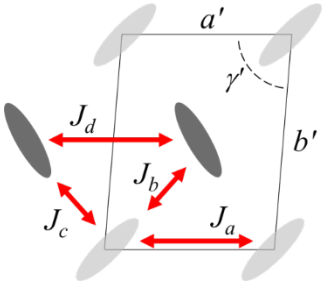


$$[\sigma_k^Q(T)]^2 = \frac{k_B T}{m_k \omega_k^2},$$

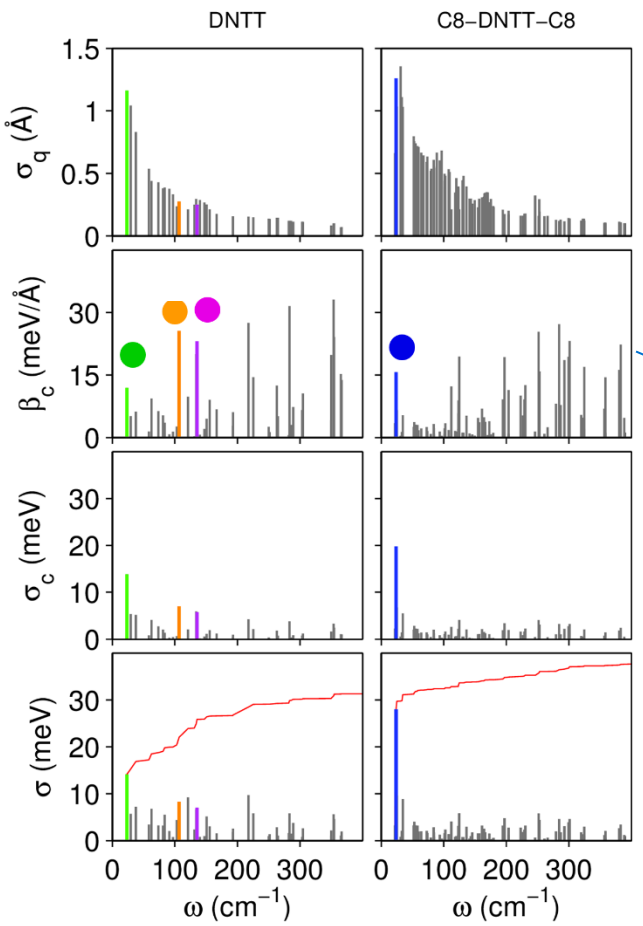
$$H = \sum_i \varepsilon_i \, c_i^\dagger c_i + \sum_{\langle i,j \rangle} J_{ij} \left(c_i^\dagger c_j + H.c. \right)$$

$$J_x = J_x^0 + \sum_k \beta_{xk} \, Q_k$$

$$\beta_{xk} = \left(\frac{\partial J_x}{\partial Q_k} \right)_0$$



Mode-resolved non-diagonal electron phonon coupling constants in DNTT and C8-DNTT-C8



$$[\sigma_k^Q(T)]^2 = \frac{k_B T}{m_k \omega_k^2},$$

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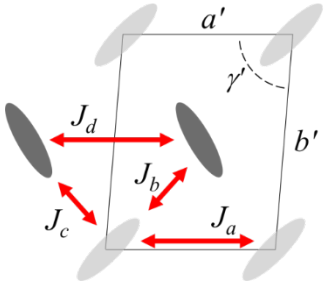
$$\beta_{xk} = \left(\frac{\partial J_x}{\partial Q_k} \right)_0$$



$$(\sigma_x^P)^2 = \sum_k (\sigma_{xk}^P)^2 = \sum_k \left(\beta_{xk} \sigma_k^Q \right)^2$$

- Identification of specific “killer” modes that contribute most strongly to dynamic disorder

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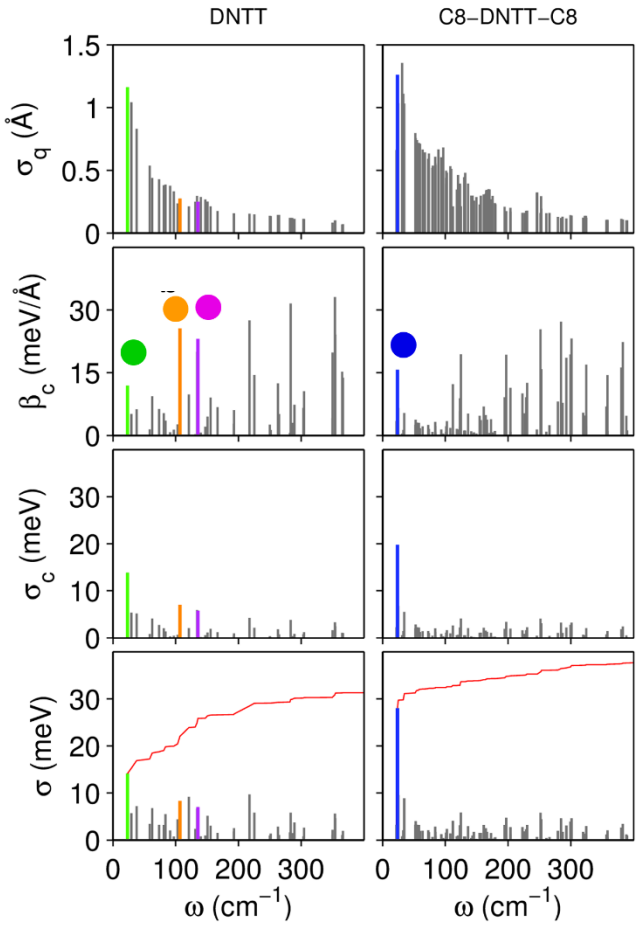
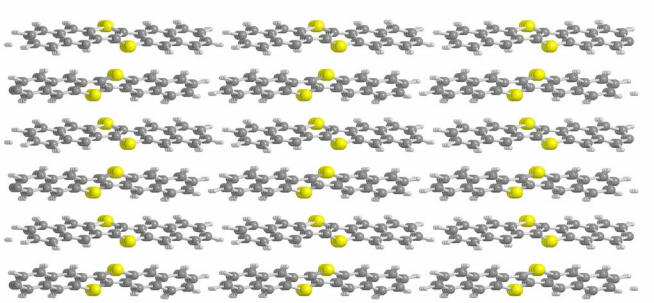
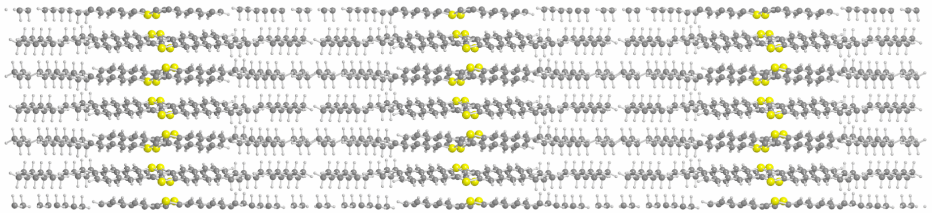
Mode-resolved non-diagonal electron phonon coupling constants in DNTT and C8-DNTT-C8



DNTT 23 cm^{-1}



C8-DNTT-C8 24 cm^{-1}



Schweicher, Davino et al. Adv. Mat. 1902407 (2019)

- Lowest frequency modes in both molecules are long axis intermolecular displacements

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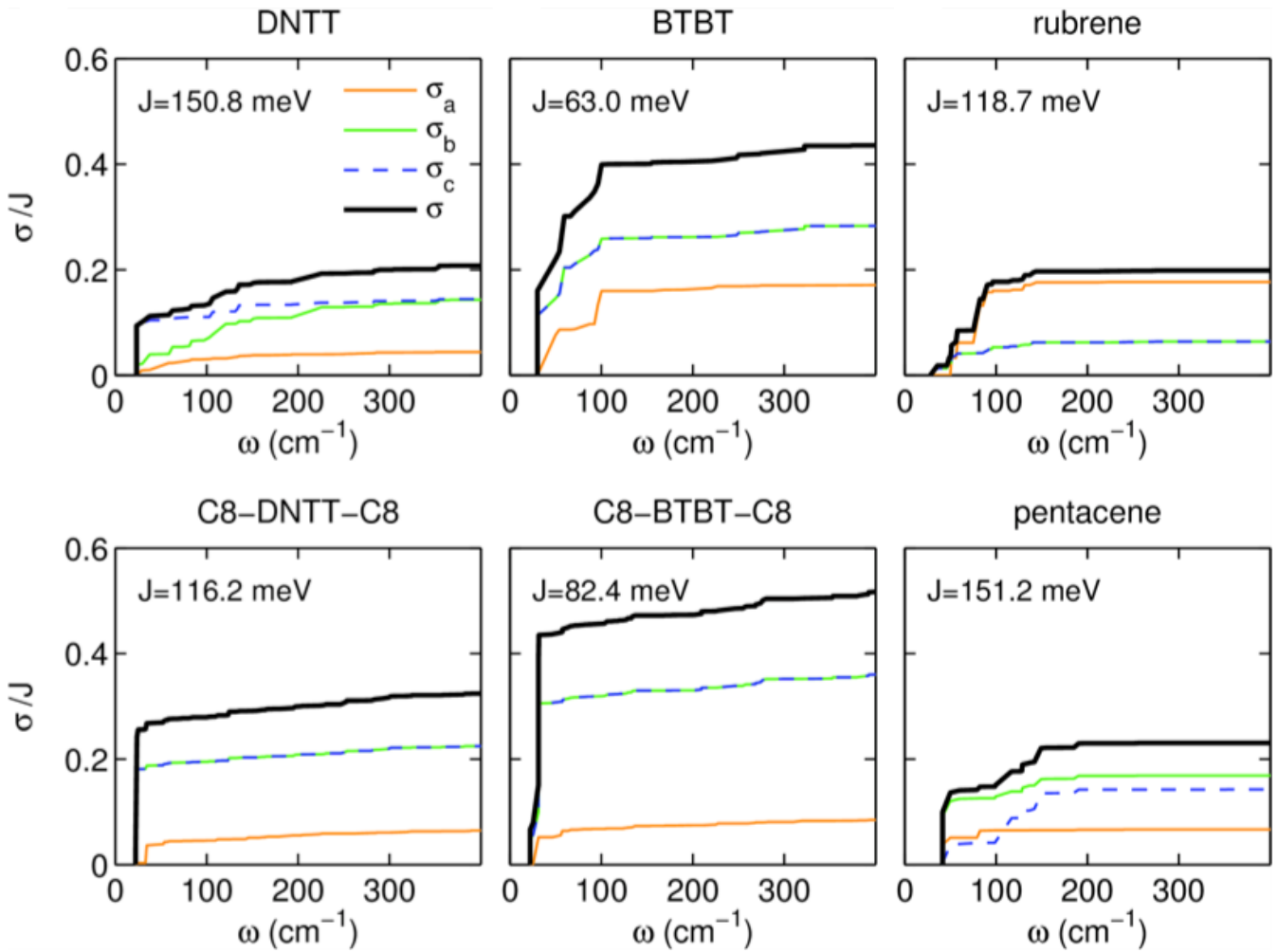
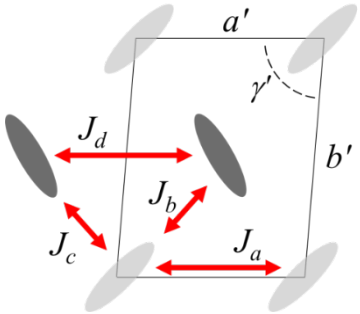
Comparison of dynamic disorder between different molecules





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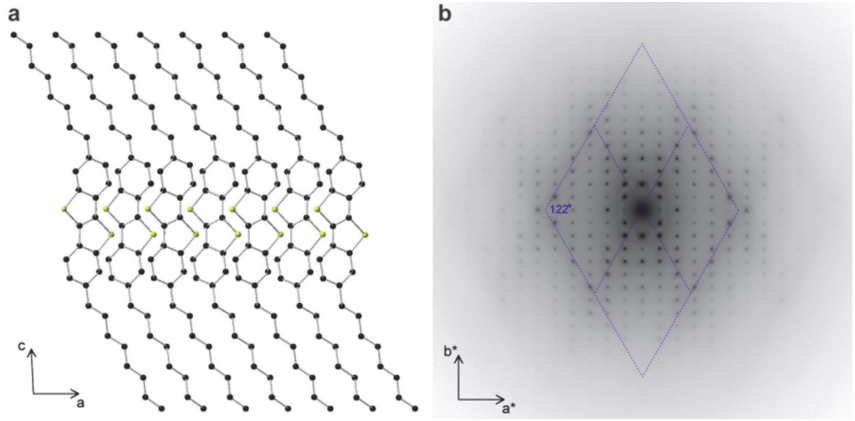
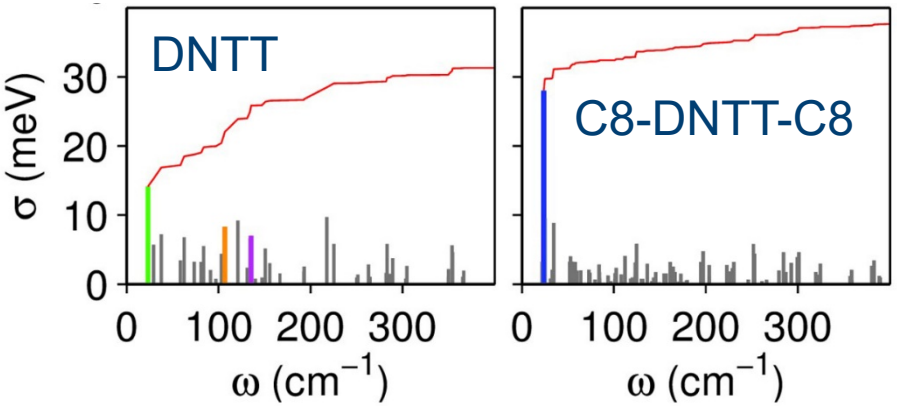
- Significant variations in dynamic disorder between molecules – Key factor for predicting charge carrier mobilities

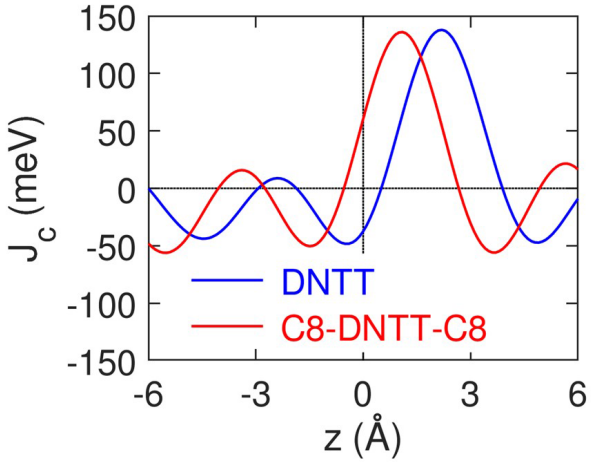
Example of molecular design rules – Effect of side-chain substitution on thermal disorder



Illig et al., Nature Comms 7, 10736 (2016)

- Amplitude of long axis fluctuations suppressed by side chain substitution
- But still, thermal disorder is larger in C8-DNTT than DNTT – How does this arise ?



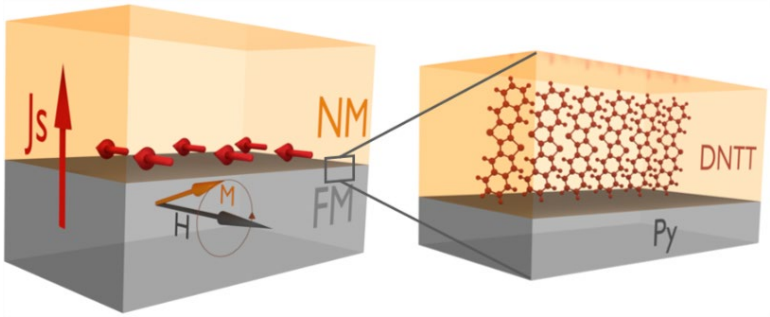


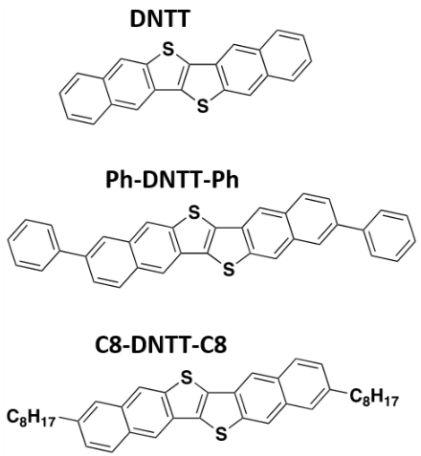
Thermal disorder determined by $^{dJ_c}/_{dz}$

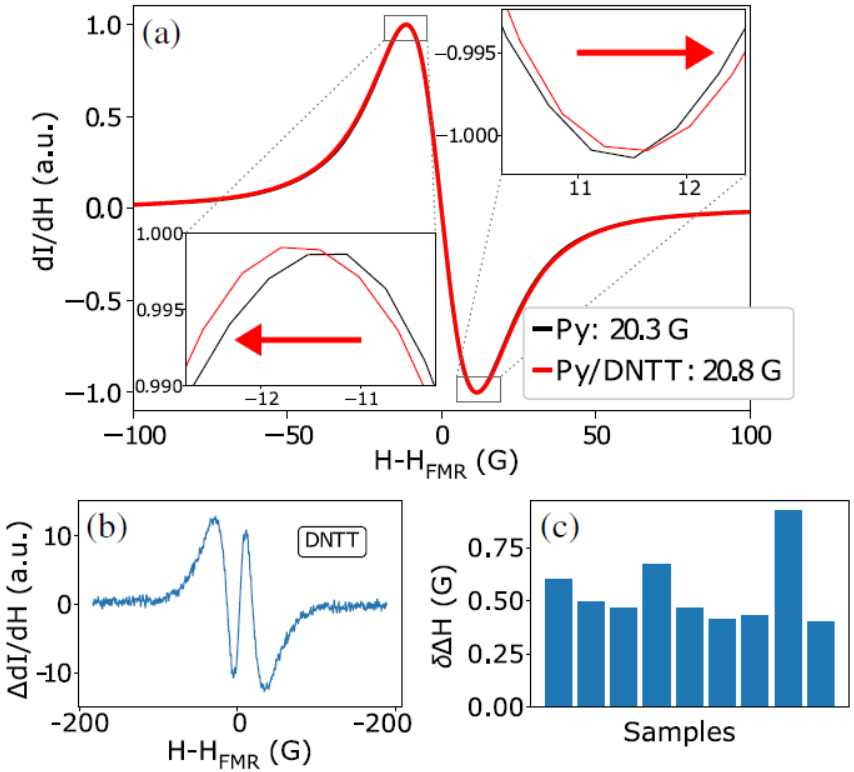
Conclusions I

- Transport physics governed by close coupling between charge and structural dynamics
- Transient localisation - most appropriate framework for describing the unique charge transport physics of molecular semiconductors.
  - Mode-resolved understanding of electron phonon coupling allows identification of “killer” modes that dominate dynamic disorder.
  - Differences in degree of dynamic disorder between molecules are a key factor that needs to be taken into account for quantitative prediction of charge carrier mobilties.
  - Side chain substitution could be an even more effective strategy for reducing thermal disorder if approaches could be found for minimizing $^{dJ_c}/_{dz}$.

Spin transport - Molecular tuning of spin injection detected by line width broadening

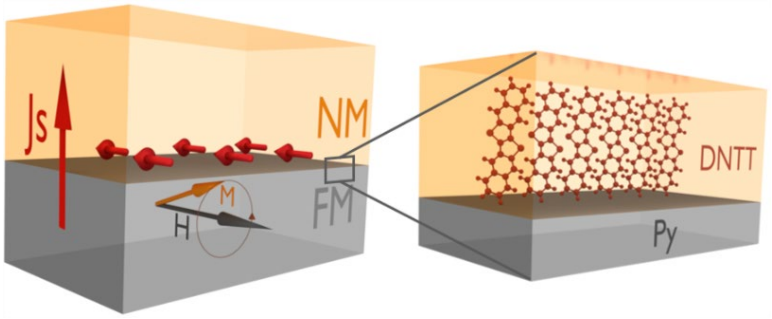


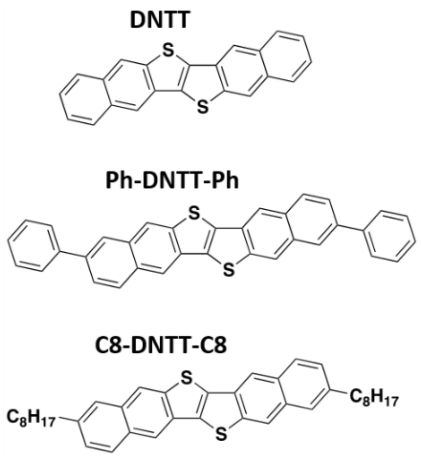


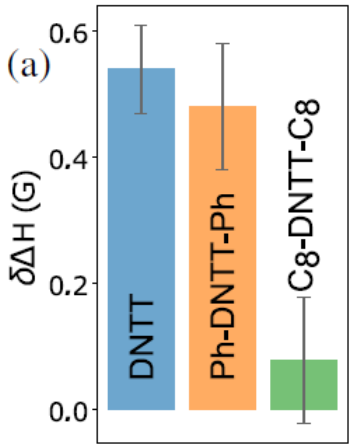


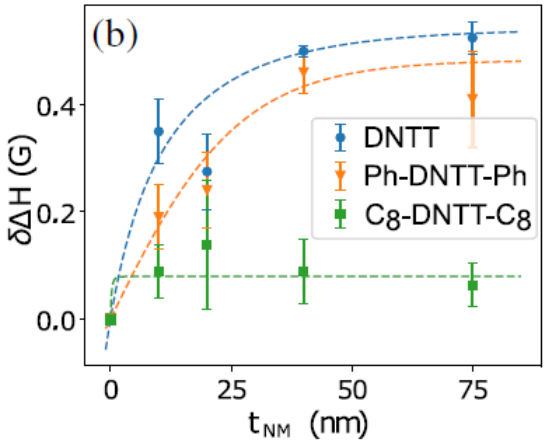
A. Wittmann et al., Phys. Rev. Lett. 124, 027204 (2020)

Spin transport - Molecular tuning of spin injection detected by line width broadening





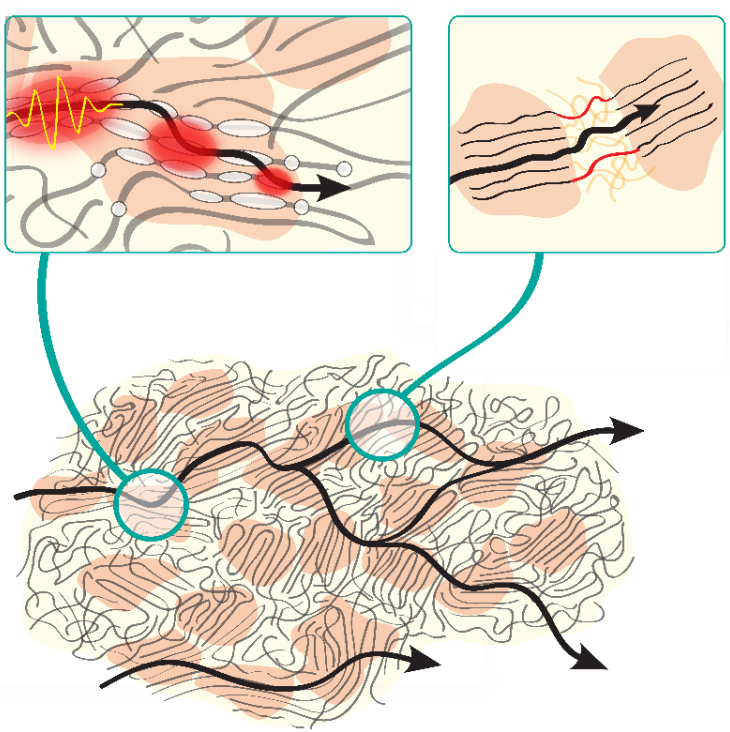




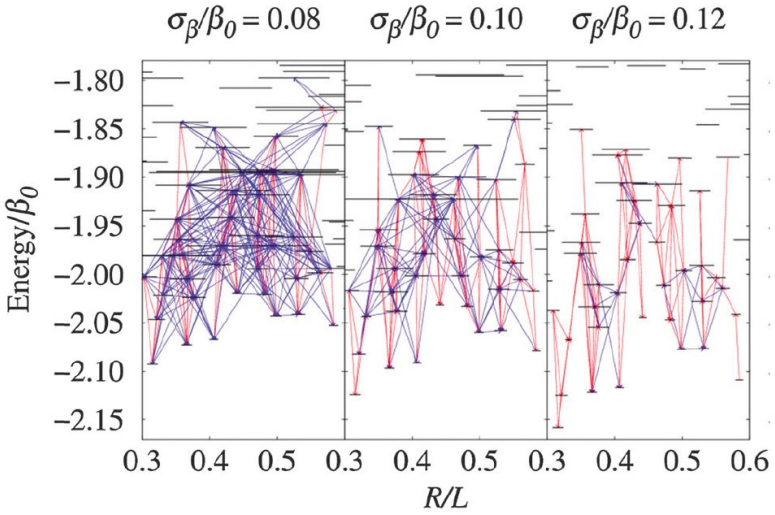
	DNTT	Ph-DNTT-Ph	C_8-DNTT-C_8
$\delta\Delta H$ (G)	0.54 ± 0.05	0.48 ± 0.09	0.10 ± 0.04
$g^{\uparrow\downarrow}$ (m^{-2})	3.35×10^{18}	2.98×10^{18}	6.3×10^{17}
λ_S (nm)	40	30	1

A. Wittmann et al., Phys. Rev. Lett. 124, 027204 (2020)

Charge transport in conjugated polymers – Spatial variations in conformation cause energetic disorder



A. Salleo



Troisi, Phys. Chem. Chem. Phys, 16, 9997 (2014)

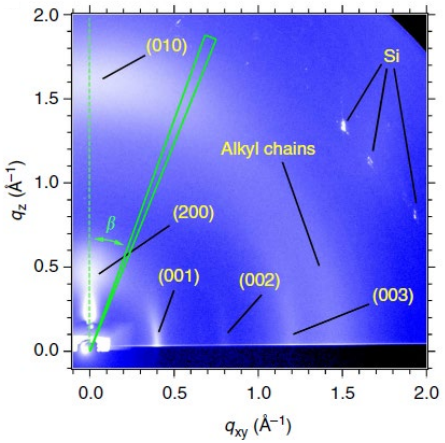
$$H(p_i, x_i) = H_0^{\text{el}} + H^{\text{nucl}} + V^{\text{el-nucl}} + V^{\text{el}}(t)$$

$$= \sum \beta_i |i\rangle\langle i+1| + \sum_{i=1,N} \frac{p_i^2}{2m} + \frac{1}{2} m\omega^2 x_i^2$$

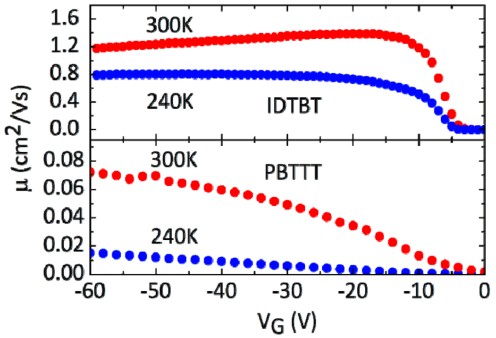
$$+ \sum_{i=1,N} \alpha x_i |i\rangle\langle i| + \sum \gamma_i(t) |i\rangle\langle i+1| + h.c.$$

Vibrational dynamics induces coupling between localized eigenstates of the static, disordered chain Hamiltonian

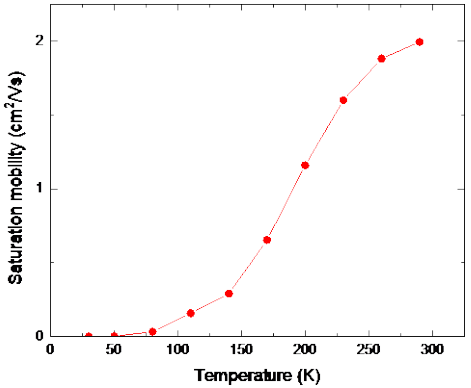
Polymers with low degree of energetic disorder due uniform / torsion-free backbone conformation



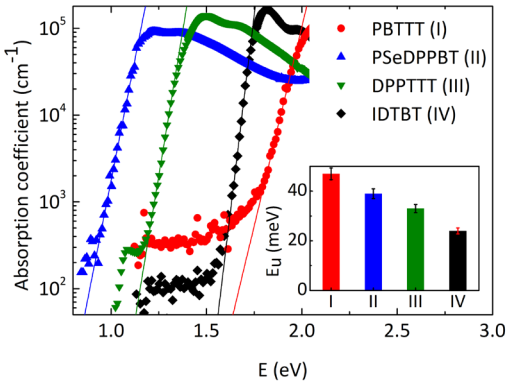
High, gate voltage independent mobility of 1.5- 2.5 cm^2/Vs

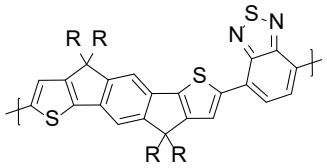


Temperature activated mobility

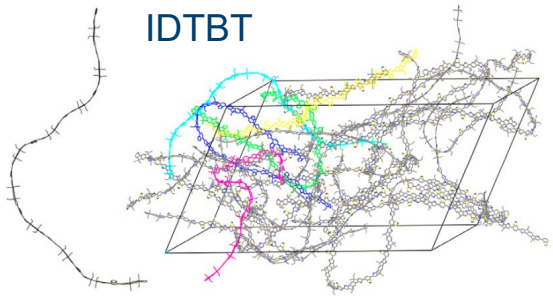


Low energetic disorder due to well-defined backbone conformation

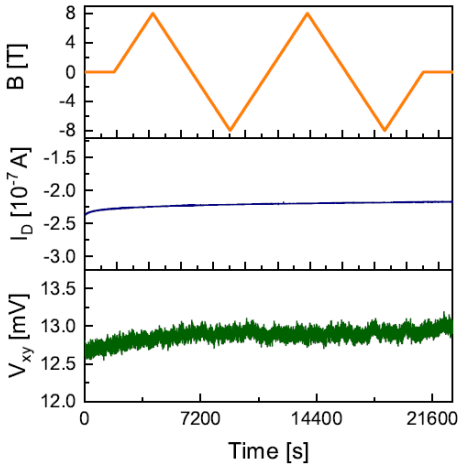




IDTBT



No Hall effect



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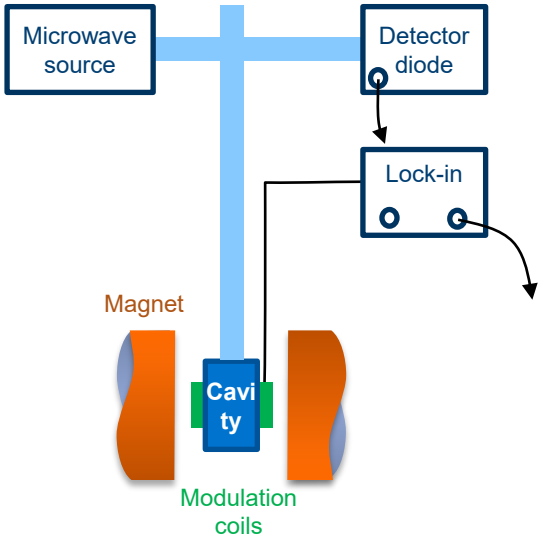
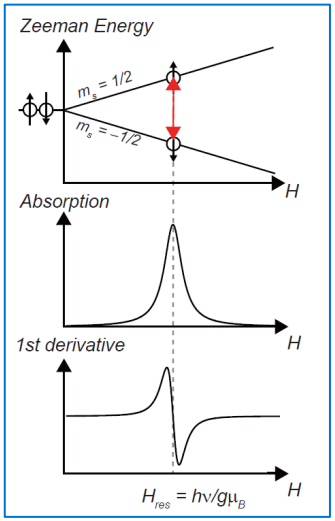
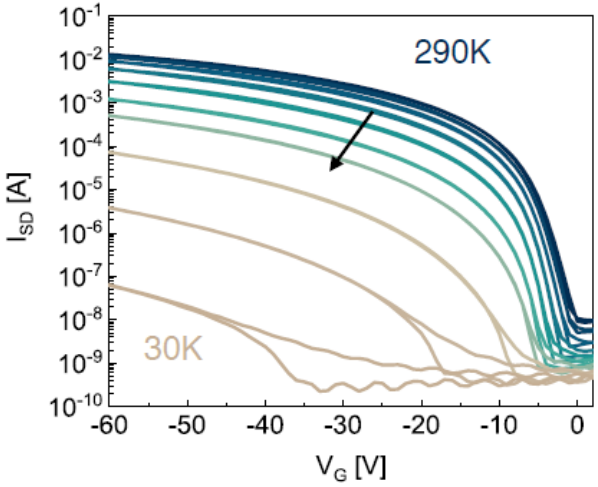
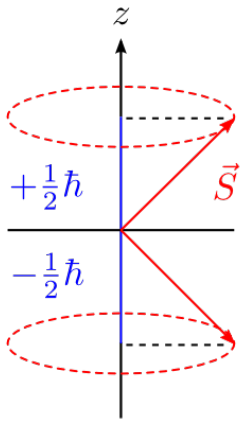
Venkateshvaran, Nikolka *et al.* Nature 515, 384 (2014)

Investigation of charge transport and spin relaxation physics by field induced electron spin resonance



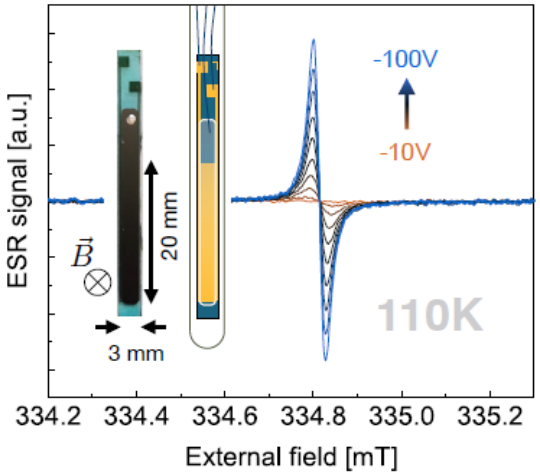






$$T_2 = \left(\frac{g\mu_B}{\hbar} \Delta B_{1/2} \right)^{-1}$$

$$A \propto B_m / \sqrt{1 + \gamma_e^2 T_1 T_2 B_m^2}$$



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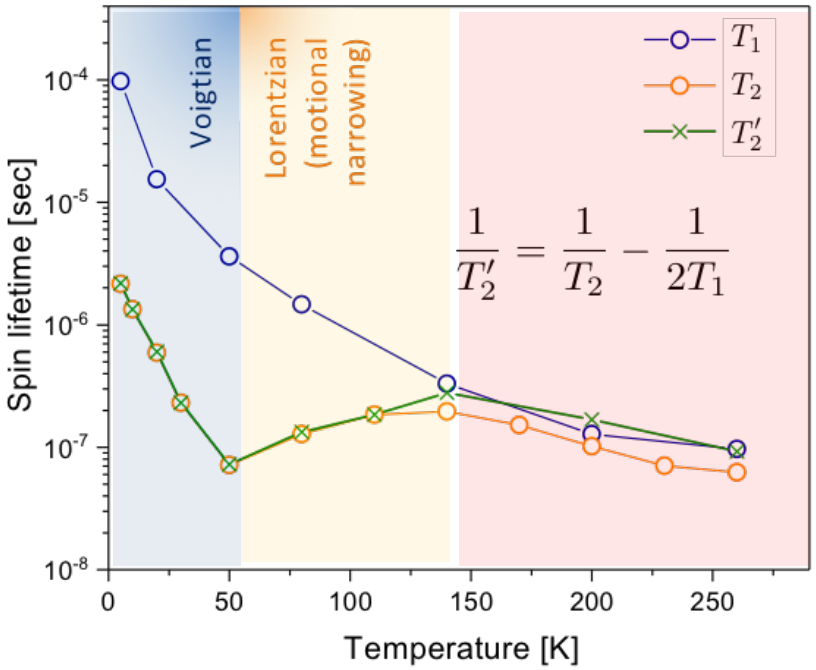
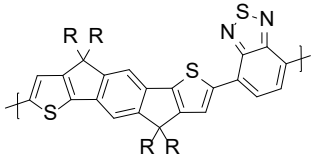
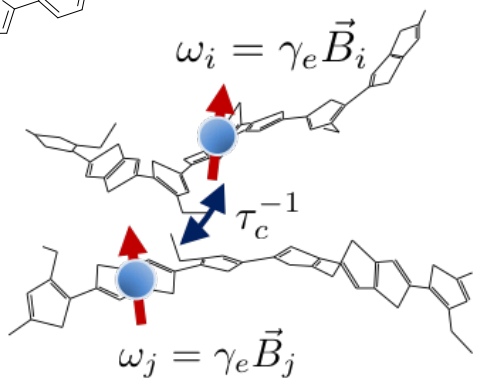
Temperature dependence of spin relaxation times in IDTBT FETs







$$T_2' = \tau_c + \frac{1}{\gamma B_{\mathrm{rms}}} + \frac{1}{\gamma^2 B_{\mathrm{rms}}^2 \tau_c}$$

dephasing by hopping[1] — motional narrowing

- Regime I (4 – 50K): Spin dephasing by slow hopping
- Regime II (50-150K): Motional narrowing
- Regime III (150 – 270K): $T_2 = T_1$ decreasing with increasing temperature

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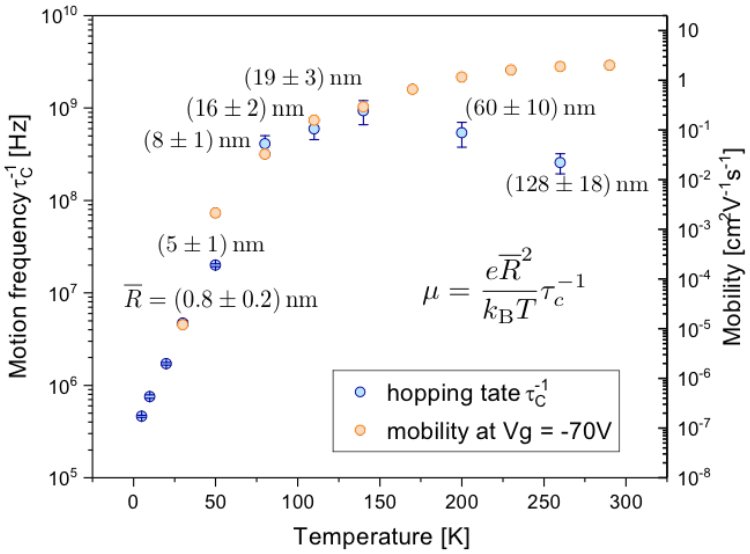
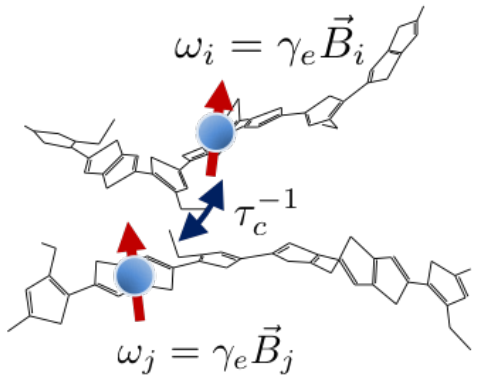
Schott et al., Nature Physics 15, 814 (2019)

Motional narrowing regime - Extraction of motion frequencies and hopping lengths





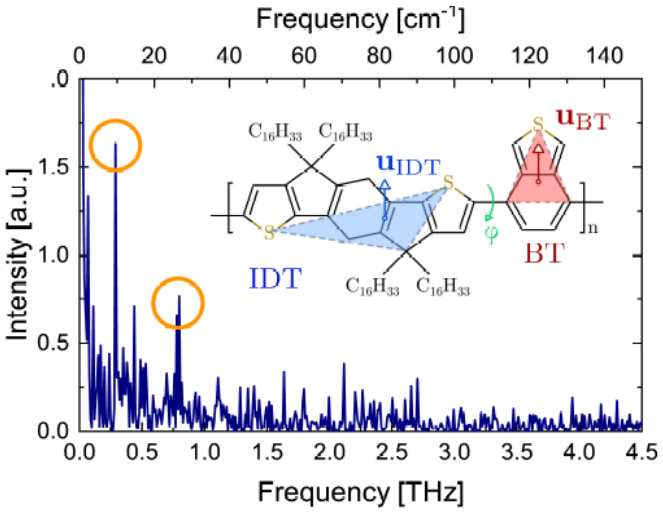
$$\mu = \frac{eR^2}{k_B T}\tau_c^{-1}$$

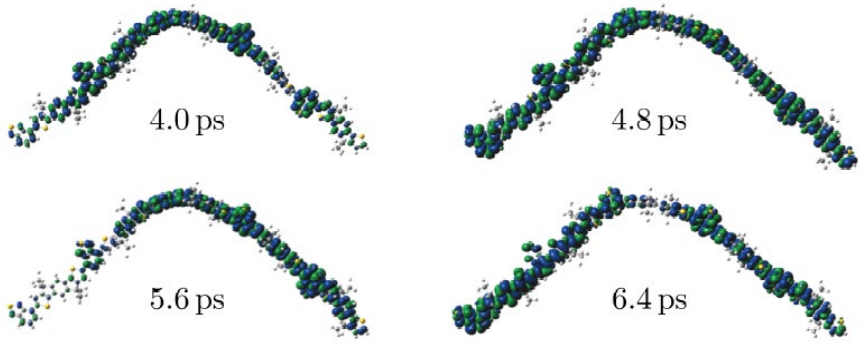
$$T_2' = \tau_c + \frac{1}{\gamma B_{\mathrm{rms}}} + \frac{1}{\gamma^2 B_{\mathrm{rms}}^2 \tau_c}$$

dephasing by hopping[1] motional narrowing

- Assumption: Equate time scale for field fluctuations τ_c with hopping frequency.
- Calculated motion frequencies τ_c^{-1} from 0.3 MHz at 5K to 1 GHz at 150K
- Long hopping lengths on the order of 20 nm at 150K.
- **Motional narrowing model breaks down above 150K.**

High-temperature regime – Coupling between spin and structural dynamics

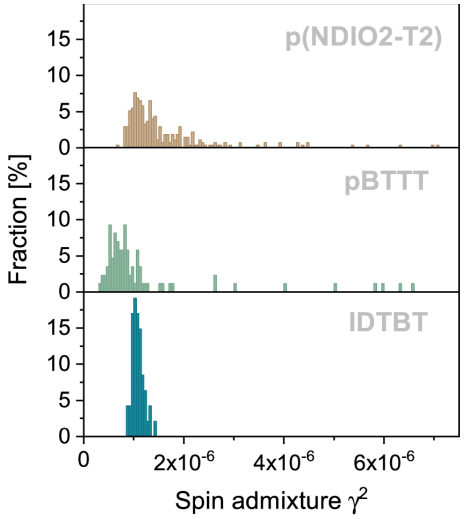




- Vibrational modes drive oscillations of carrier wavefunctions along polymer backbone (infrared active vibrational modes).
- Model – Elliott Yafet type spatial scattering: small probability of spin flip whenever wavefunction moves in real space:

$$1/T_1 = 1/T_2 = 8/3\,\gamma^2\bar{v} = 8/3\,(\Delta g)^2\bar{v}$$

γ – spin admixture; $\bar{v}$ - hopping rate



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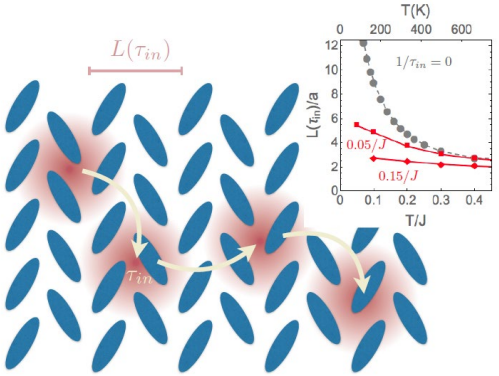
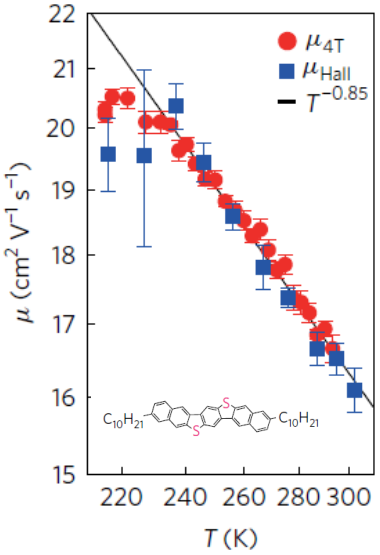
Schott, McNellis, Lemaur et al., Nature Physics 15, 814 (2019)

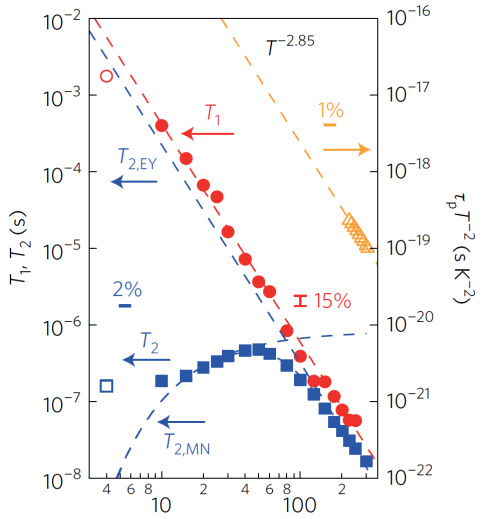
Conclusions II

- Electron spin resonance provides sensitive probe of charge and spin dynamics in high mobility conjugated polymers.
- Quantification of long hopping lengths and fast hopping times in motional narrowing regime (20 nm and 1GHz in IDTBT at 150 K)
- Near room temperature spin relaxation in conjugated polymers is determined by similar transient localisation processes than those that govern spin relaxation in molecular crystals.
- Fascinating and unique transport regime in which structural, charge and spin dynamics are intimately coupled.

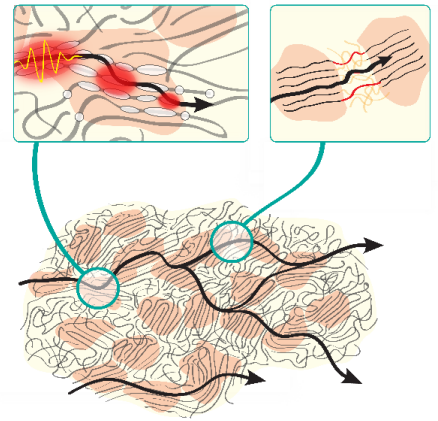
Intimate coupling between structural, charge and spin dynamics

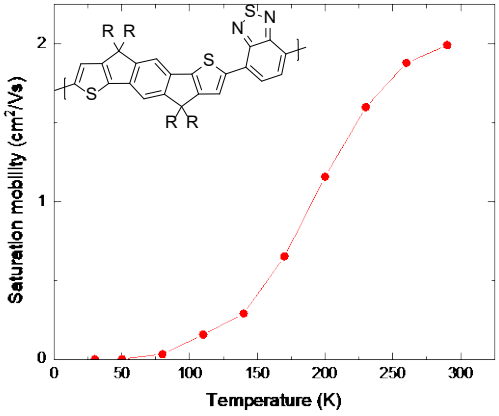


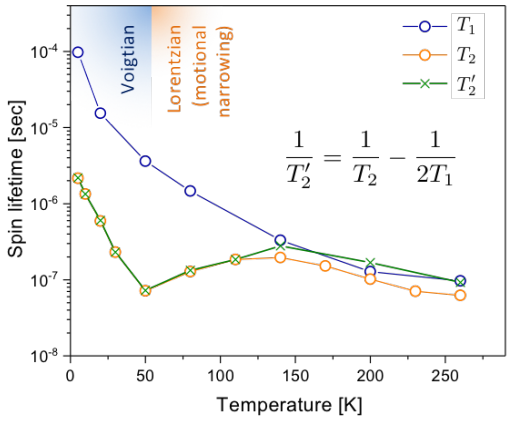




Takeya et al., Nat. Phys. 13, 994 (2017)







Schott et al., Nature Physics 15, 814 (2019)

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UMONS Université de Mons

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