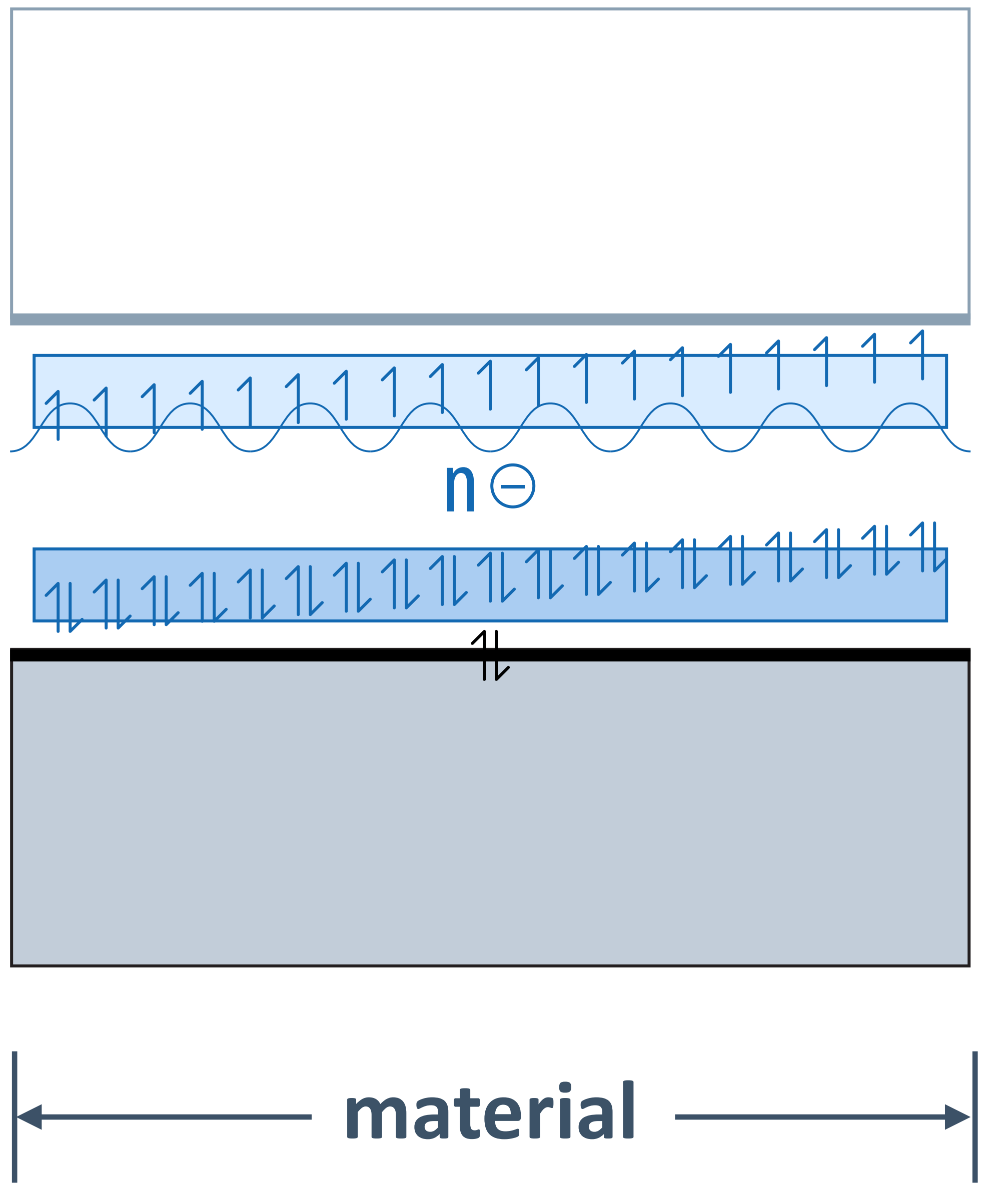
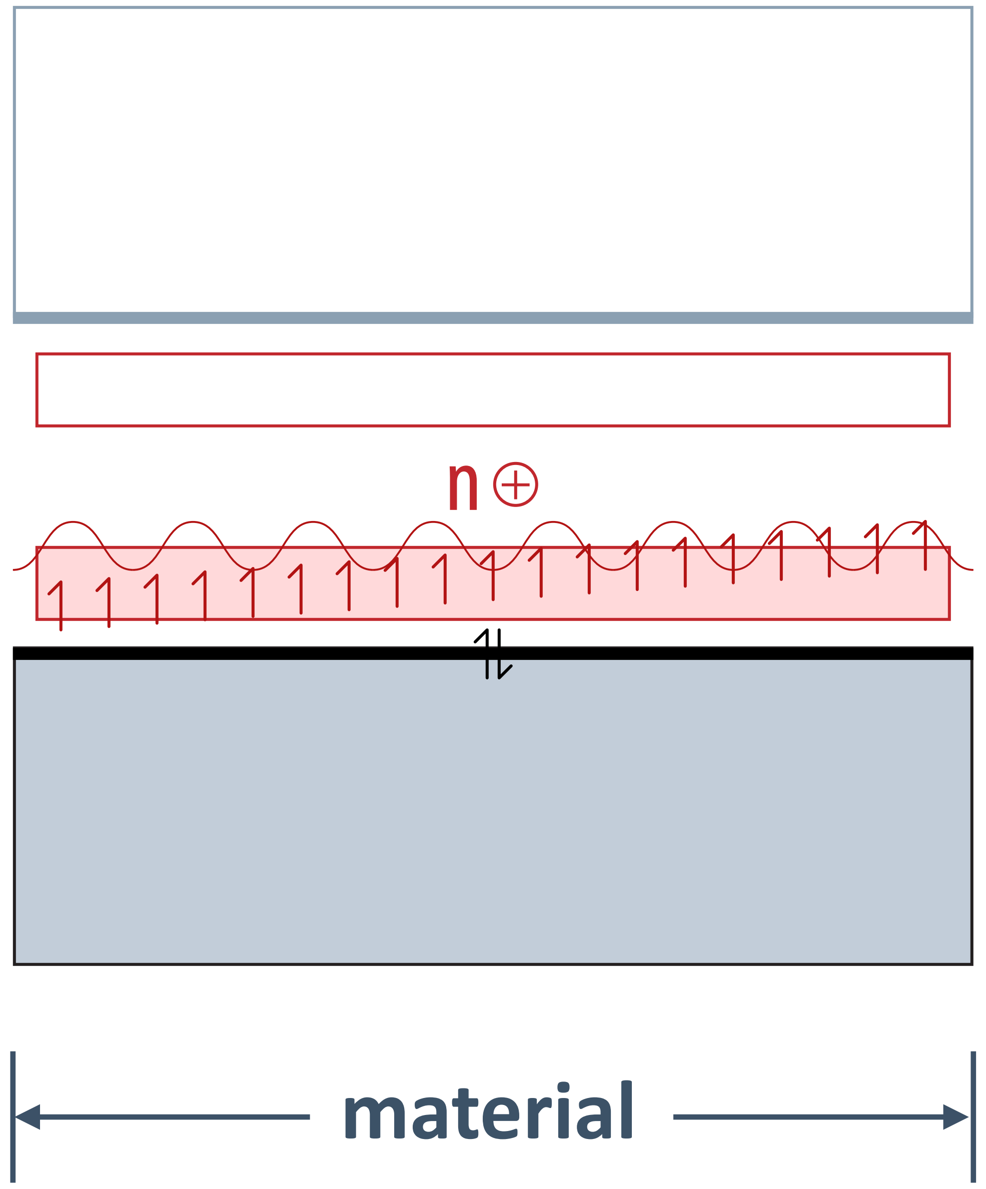
6.2 Band Transport and Transient Localization

Bloch-Boltzmann Transport (Band Transport)





- **band transport occurs via propagating Bloch waves, extended states in a periodic lattice**
  - scattering due to molecular rotations and vibrations, as well as lattice vibrations
  - acceleration in electric field F versus deceleration by scattering due to lattice vibrations
  - injected charge drifts at constant velocity $v = \mu\, F$ (with μ materials property)

Criteria for Band Transport

- **band transport takes place if the interaction energy between neighbouring sites is larger than any other energy present due to dynamic disorder or static disorder**

$$H_1 \gg H_2, H_3, H_4, H_5$$

$$J_{nm} \gg g_{n\lambda}, f_{nm\lambda}, \delta\epsilon_n, \delta J_{nm}$$

- **the probability to fulfill this requirement is high for**
  - intramolecular transport through “lattice” of repeat units in polymers (large H_1)
  - intermolecular transport in highly ordered single crystals (low static disorder, small H_4, H_5)
  - at low temperatures (low dynamic disorder, small H_2, H_3)
  - for large π-systems (large H_1)
- **band width, hence mobility must be large for carrier residence time to be sufficiently small**
  - charge leaves any specific molecular site before geometric relaxation can occur ($<10^{-13}$ s)
  - Bloch wave can “escape” a molecular site before it gets “self-localized” by vibrations

KEY CONCEPT: see A. Köhler and H. Bässler, *Electronic Processes in Organic Semiconductors*, p. 215-217

Criterion for Band Transport

- Einstein-Smoluchowski relationship for relation to (charge) diffusion constant D

$$D = \frac{\mu}{q} k_B T$$

- for band transport, the charge diffusion length L_D must be (much) larger than the lattice constant a

$$L_D = \sqrt{D\tau} > a$$

- where the lower limit of the mean free time τ between scattering events is given linked to the band width W by the uncertainty principle

$$W > \frac{\hbar}{\tau}$$

- **lower limit for band transport (Le Blanc condition):**

$$\mu > \frac{qa^2}{\hbar} \frac{W}{k_B T} \approx 5\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$$

for $W \approx 25$ meV at room temperature and $a \approx 5$ Å

Temperature Dependence for Band Transport

- **root mean square thermal charge velocity $\langle v \rangle$ follows Boltzmann statistics**

$$\langle v \rangle = \sqrt{\frac{3k_BT}{m*}}$$

- **mean free time τ (with molecular number density ρ and scattering cross section $\sigma_x \propto T$)**

$$\tau \propto \frac{1}{\rho\sigma_x\langle v \rangle} \propto \frac{m*}{\rho\sigma_x\sqrt{3k_BT}} \propto T^{-\frac{3}{2}}$$

- **since mobility is proportional to mean free time τ :**

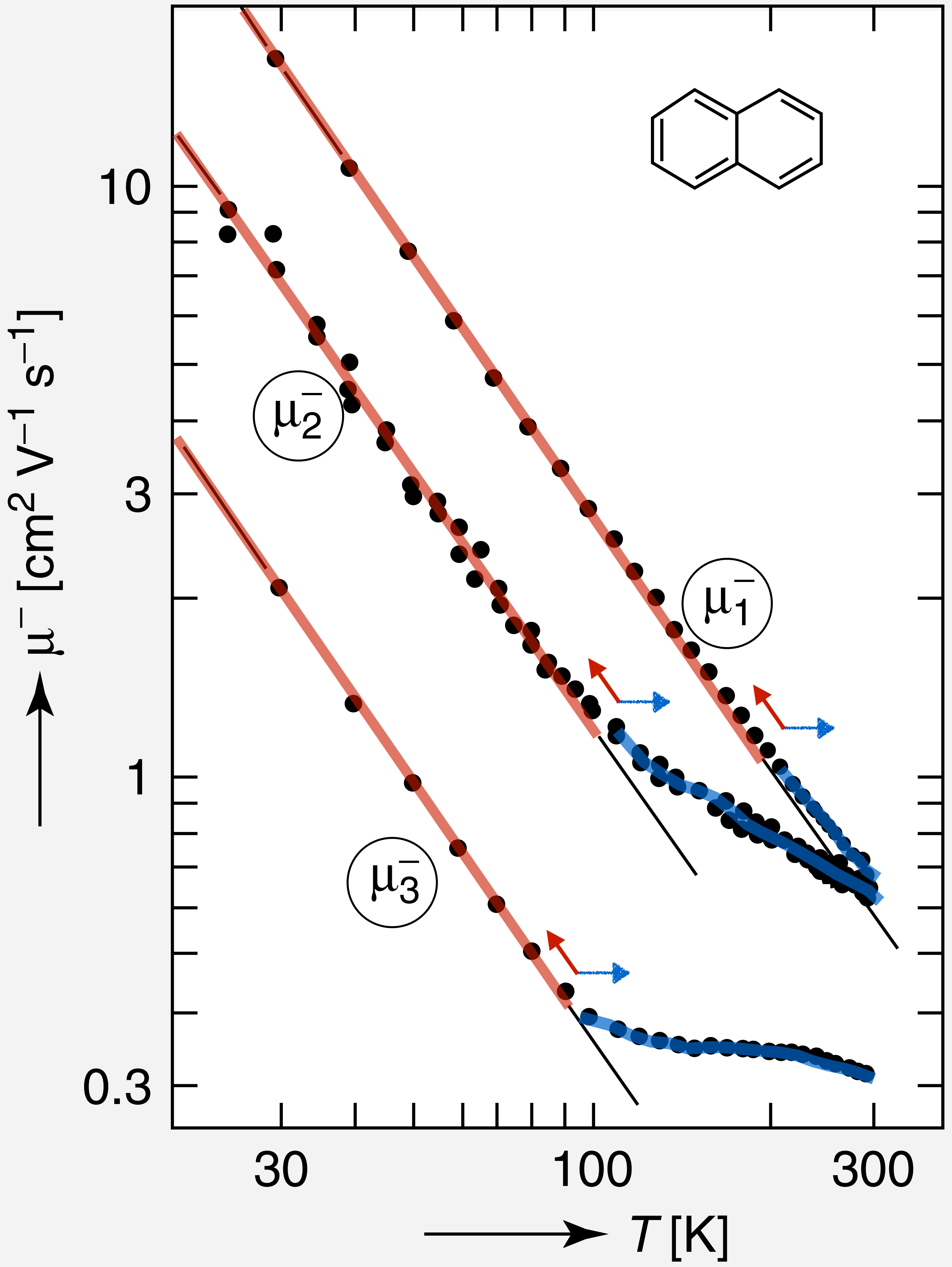
$$\mu = \frac{q\tau}{m*} \propto T^{-\frac{3}{2}} \quad \Leftrightarrow \quad \frac{d\mu}{dt} < 0 \quad \text{and} \quad \ln\mu = -\frac{3}{2}\ln T$$

- **negative temperature coefficient of mobility (decrease of mobility with temperature) following a power law with slope –3/2 (in double-logarithmic representation**
- **these are commonly criteria required but not sufficient (!) to argue for band transport**

KEY CONCEPT: see A. Köhler and H. Bässler, *Electronic Processes in Organic Semiconductors*, p. 215-217

Example of Band Transport at Low Temperature

- aromatic molecules can exhibit band transport in single crystals at low temperatures



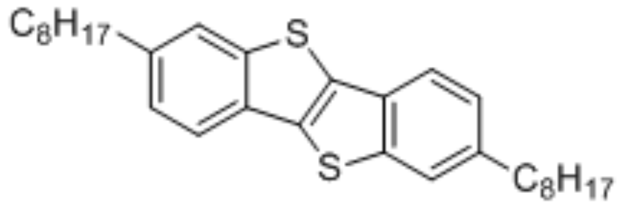
- **band transport occurs at T < 100 K, in all lattice directions, indicated by a temperature dependence $\mu(T) \propto T^{-n}$**
- **different mobilities in different lattice directions reflect the anisotropy of the interaction energy J_{nm} inferred by DFT calculations**
- **the smaller the mobility, the earlier $\mu(T)$ deviates from the band-like temperature dependence**
- **this is a signature of the breakdown of the band concept**
- **at room temperature, incoherent transport in two lattice directions becomes equal**

- **very few other examples because a crucial element was the extreme care of excluding impurities**

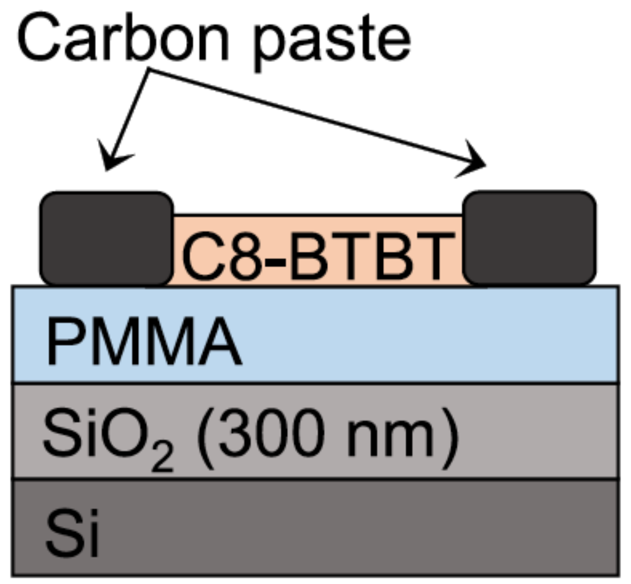
Karl, Varta, *Mol. Cryst. Liq. Cryst.* **1989**, *171*, 31; *Charge-Carrier Mobility in Organic Crystals*, Springer, Germany, **2001**.

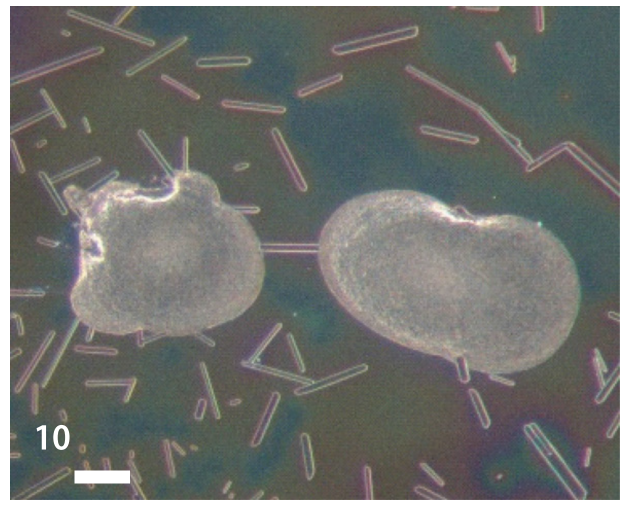
Example of Band Transport in Organic Field-Effect Transistors

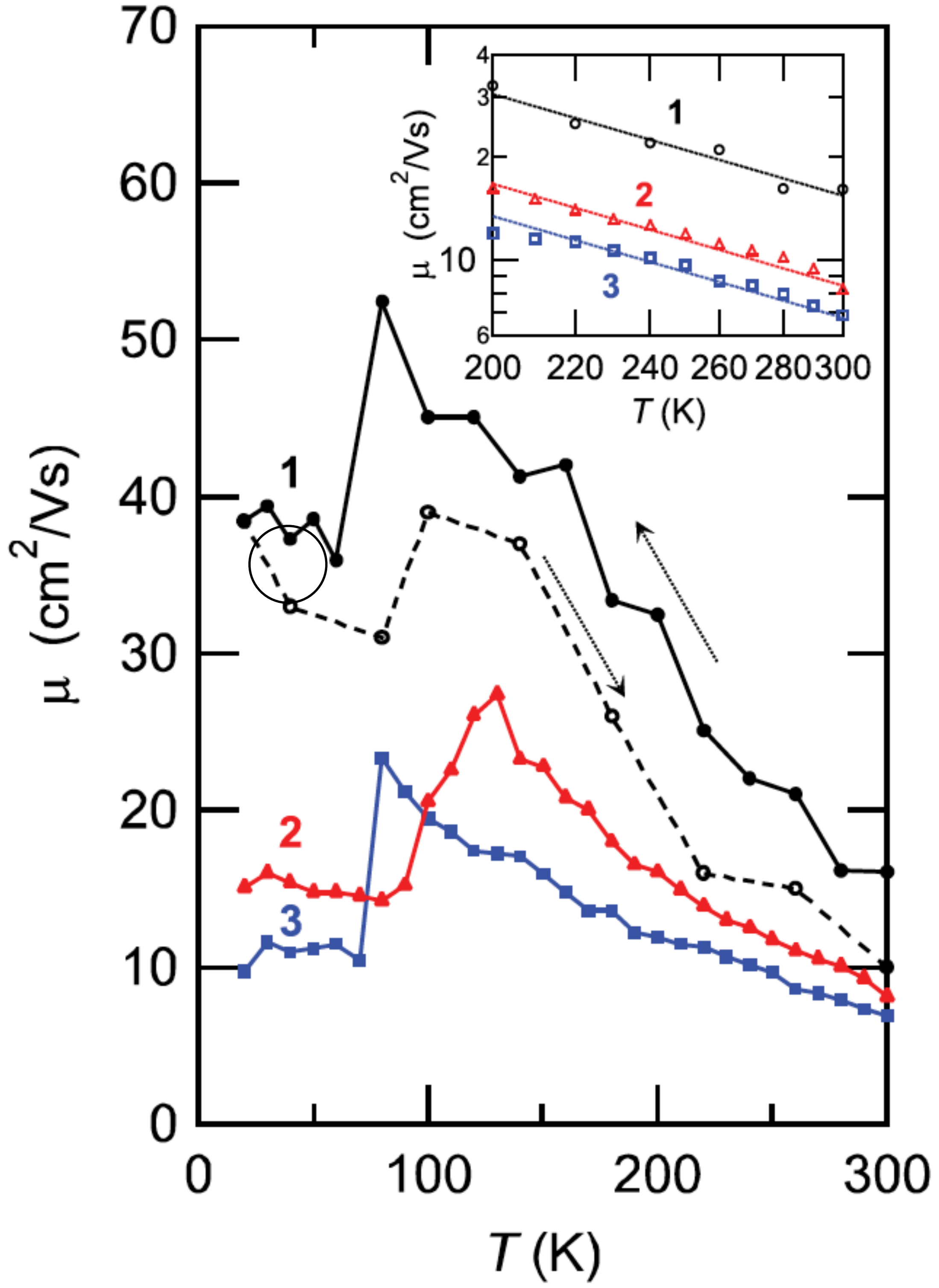
- band transport observed in solution-processed single-crystal transistors from C8-BTBT



C8-BTBT







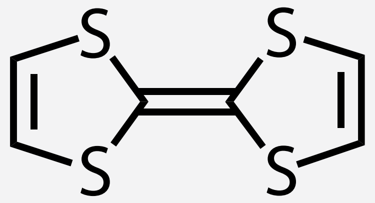
$$\mu(T) \propto T^{-n}$$

- **mobility increases from 16 to 52 cm²/(Vs) with decreasing temperature, with a power law (*n* = –1.6)**
- **mobility and temperature dependence indicate band transport**
- **the abrupt mobility drop observed at around 80 K is attributed to a "discrete trap state"**

Appl. Phys. Lett. **2015**, *106*, 193303.

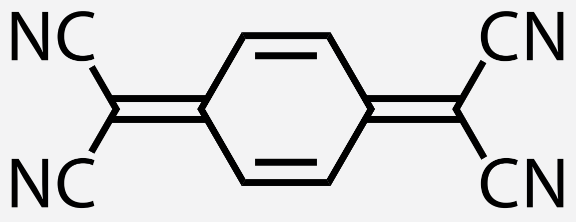
Charge Transfer Salt of TTF and TCNQ

Tetrathiafulvalene (TTF)



$\sigma \approx 10^{-5}$ S cm^{-1}

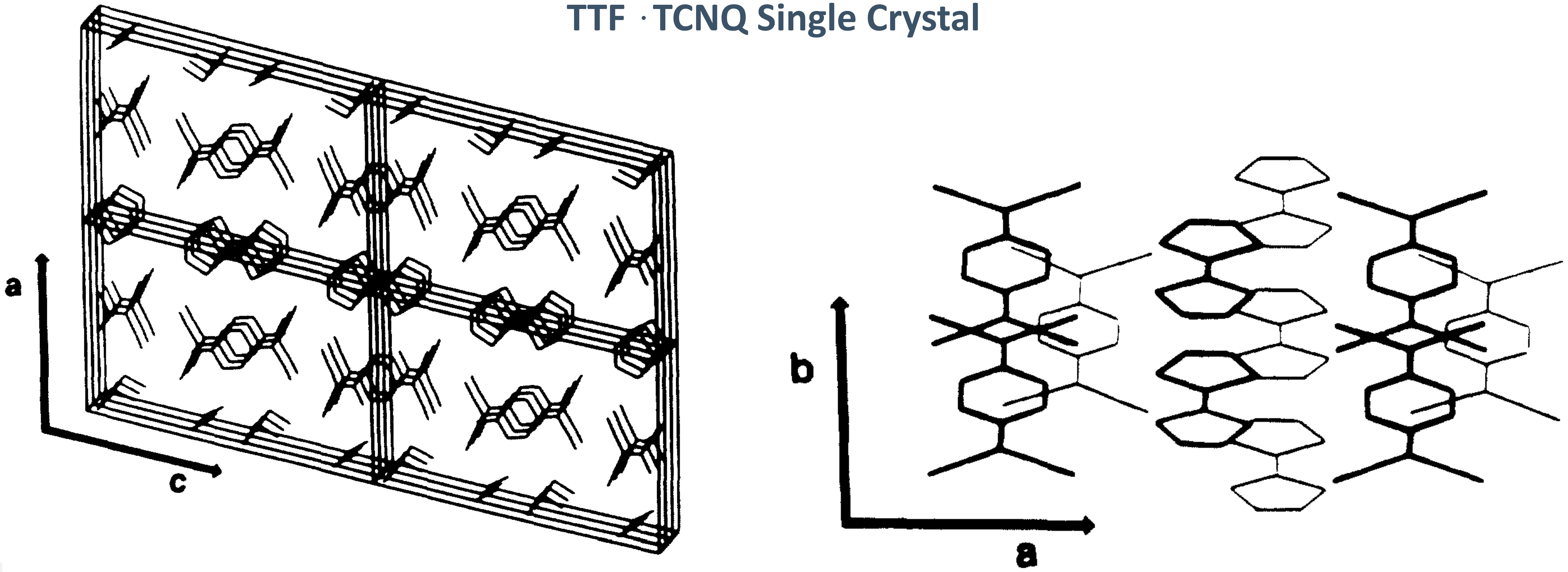
Tetracyanoquinodimethane (TCNQ)



$\sigma \approx 10^{-5}$ S cm^{-1}

$\mu = 2$ cm^2/V·s

TTF · TCNQ Single Crystal



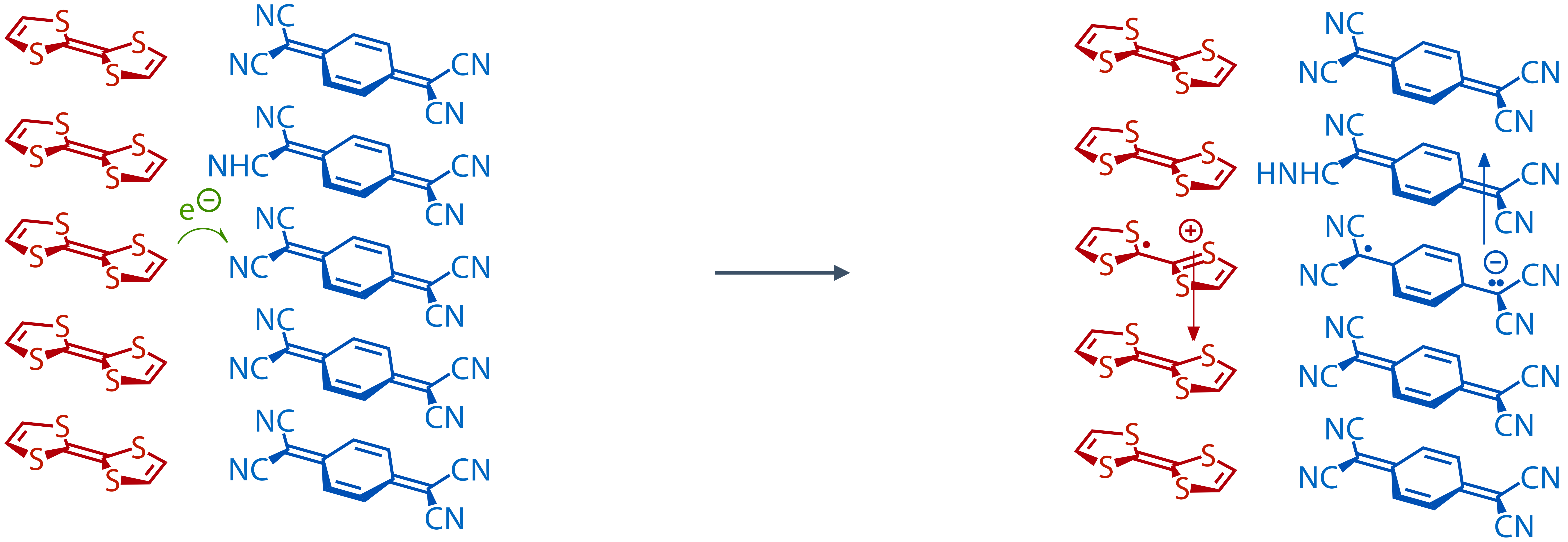
$\sigma = 500$ S cm^{-1}, metallic at $T < 54$ K

Phys. Rev. Lett. 1988, 60, 1418.

Charge Transfer Complexes between Electron Donor and Acceptor Materials

- if electron donors / acceptors crystallized in pairs, electron transfer would yield localized charges
- ‘charge transfer complex’ with poor conductivity

Charge Transfer Salts between Electron Donor and Acceptor Materials



- electron donors and acceptors crystallize in segregated stacks, charge transfer between stacks
- electron transfer yields strongly delocalized charge carriers
- ‘charge transfer complex’ with high (even metallic) conductivity

Transient Localization Regime ("Band-Like" Transport)

- transient localization regime if the interaction energy between neighboring sites is comparable to the off-diagonal disorder and both are on the order of the thermal energy

$$H_1(J_{nm}) \approx H_3(f_{nm\lambda}) \approx k_B T$$

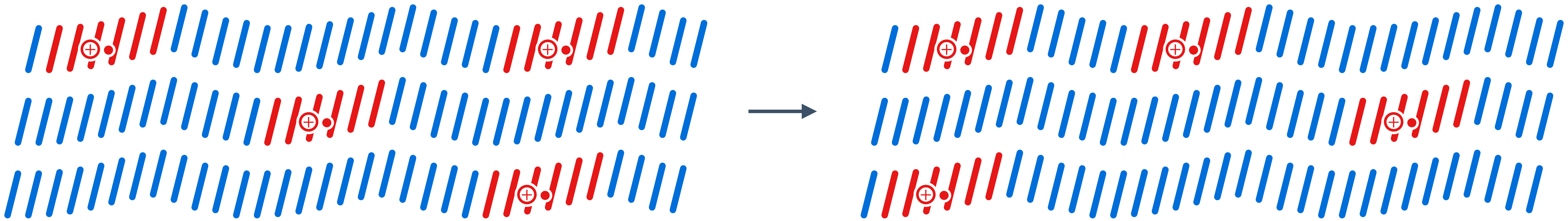
- fluctuation amplitude of the interaction energy similar to its average value; large intermolecular vibrations result in transient localization of the electronic wavefunctions at short times $\lesssim$1 ps, and a sizeable suppression of charge diffusivity

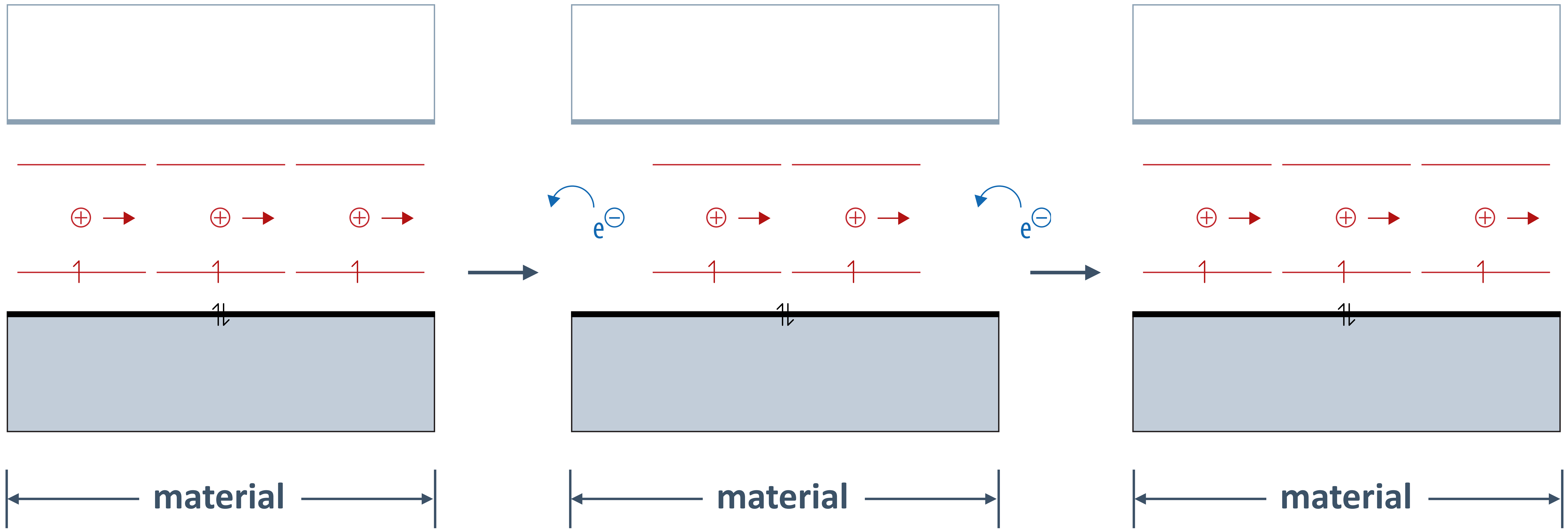
$$\mu = \frac{e}{k_B T} \frac{L^2}{2\tau_{\text{vib}}}$$

- with localization length L and timescale of a certain lattice vibration τ_{vib} (different parameters than those relevant in conventional semiconductors, lattice parameter a and free mean time τ).
- negative temperature coefficient for mobility following a power law (e.g., $n = -2.1$ for rubrene) because dynamic disorder is reduced, which, in turn, increases delocalization and mobility
- mobility $\mu < 5$ cm^2 V^{-1} s^{-1} and mean free path $\lambda \leq a$ (intermolecular distance), so charge carrier relaxes on each molecular site after transfer, hence notion of "band transport" makes no sense

Troisi, *Chem. Soc. Rev.* **2011**, *40*, 2347–2358

Tranient Localization Regime in Highly Ordered Crystalline Solids





- **transport in the transient localization regime "looks like" coherent transport, but is mediated by localized charge carriers, translation coupled with lattice vibrations**