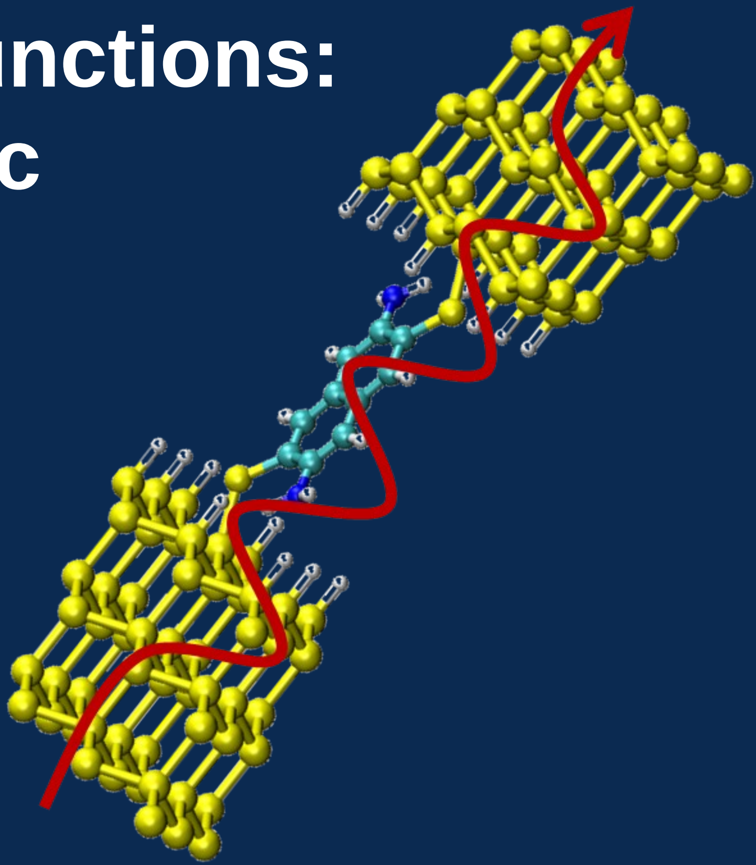
TECHNISCHE UNIVERSITÄT DRESDEN

Institute for Materials Science and Max Bergmann Center of Biomaterials

Engineering the thermopower in semiconductor-molecule junctions: towards high thermoelectric efficiency at the nanoscale



D. Nozaki, H. Sevinçli,
W. Li,R. Gutierrez, and G. Cuniberti

Phys. Rev. B 81, 235406 (2010)

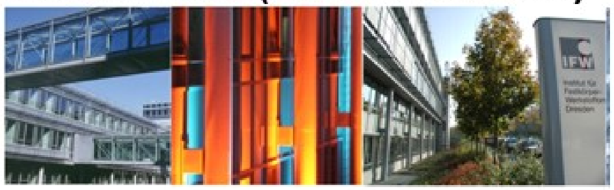
Workshop - Orsay, 10 - 12.10.2011

Dresden

Germany

Research centers in Dresden

IFW Dresden (Leibniz Institute)



FZD (Helmholtz center)

Namlab

Max-Planck Institute (MPI-PKS)

Max-Bergmann Center

Max-Planck Institute (MPI-CPFS)

Fraunhofer Institute

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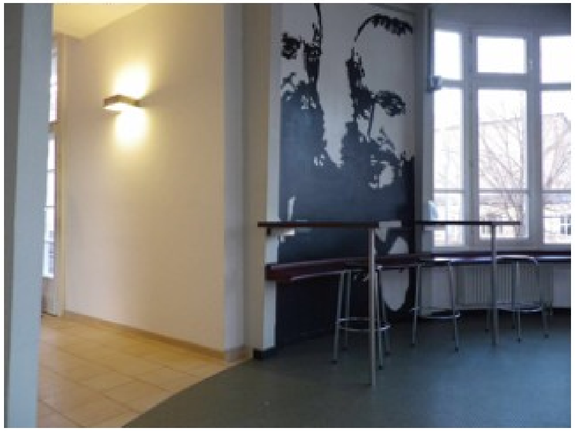
TU Dresden

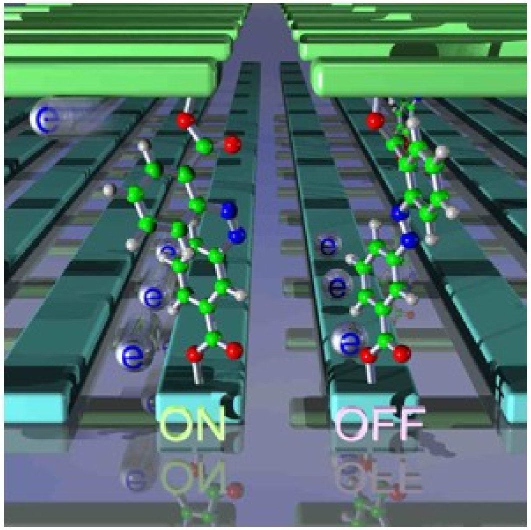




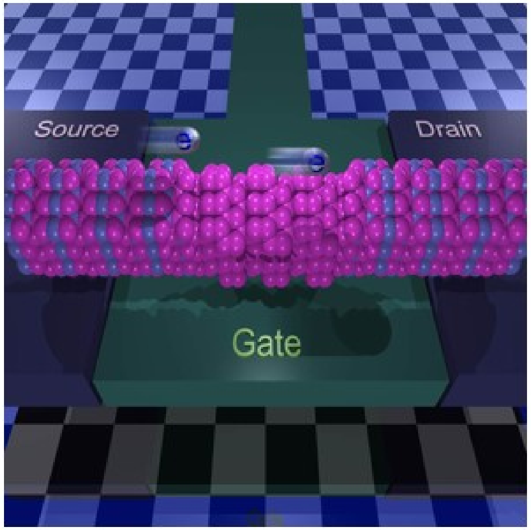



Research at TU Dresden

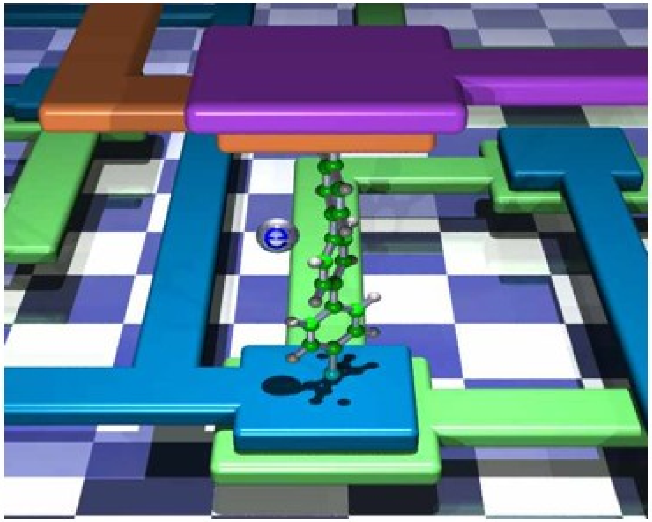
Nozaki *et al.* Nano Res. (2009)



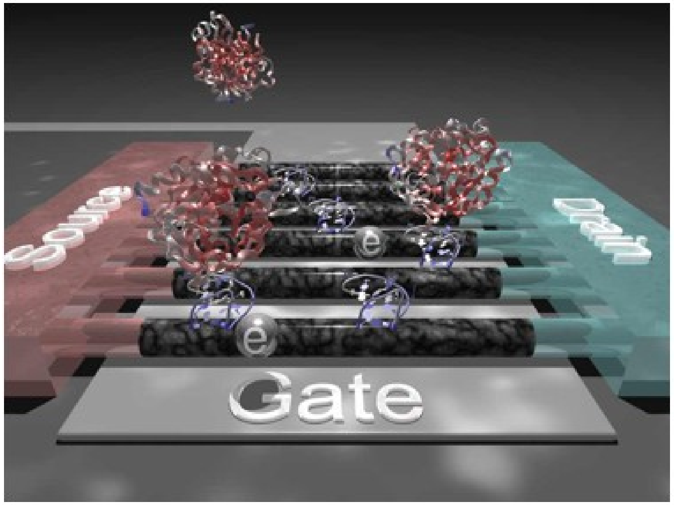
Nozaki *et al.* Nanotech. (2011)



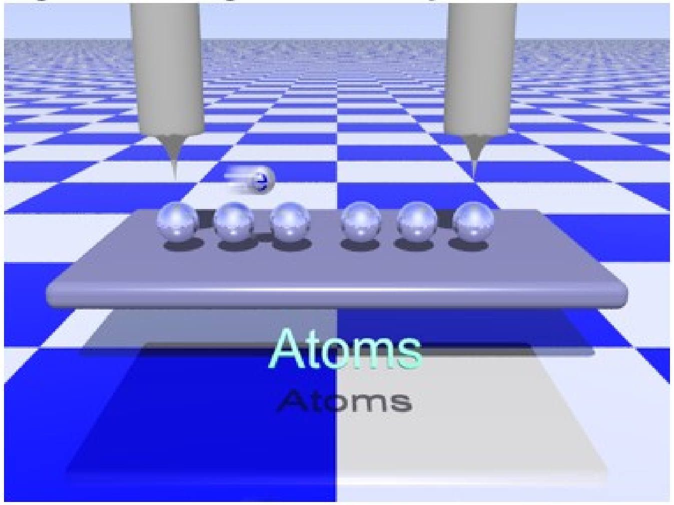
Dulic *et al.* Angew. Chem. Int.. (2010)



SiNW biosensors (ongoing)



Nozaki *et al.* New J. Phys. (2010)



All images by D. Nozaki

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(TU Dresden & POSTECH)

Mr. Wu Li

Dr. Haldun Sevincli

Dr. Rafael Gutierrez
(TU Dresden)

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- Sächsiche AufbauBank (SAB)
- Namlab (Dr. Weber *et al.*)

Outline

1. **Introduction** - **thermoelectric effects, history, applications**
2. **Motivation – recent experiments**
3. **Toy model and application to molecular systems**
4. **Results**
5. **Summery**

Heat is wasted as byproducts in many situations.

(ex. CPUs, industries, combustion etc.)

Thermoelectric devices

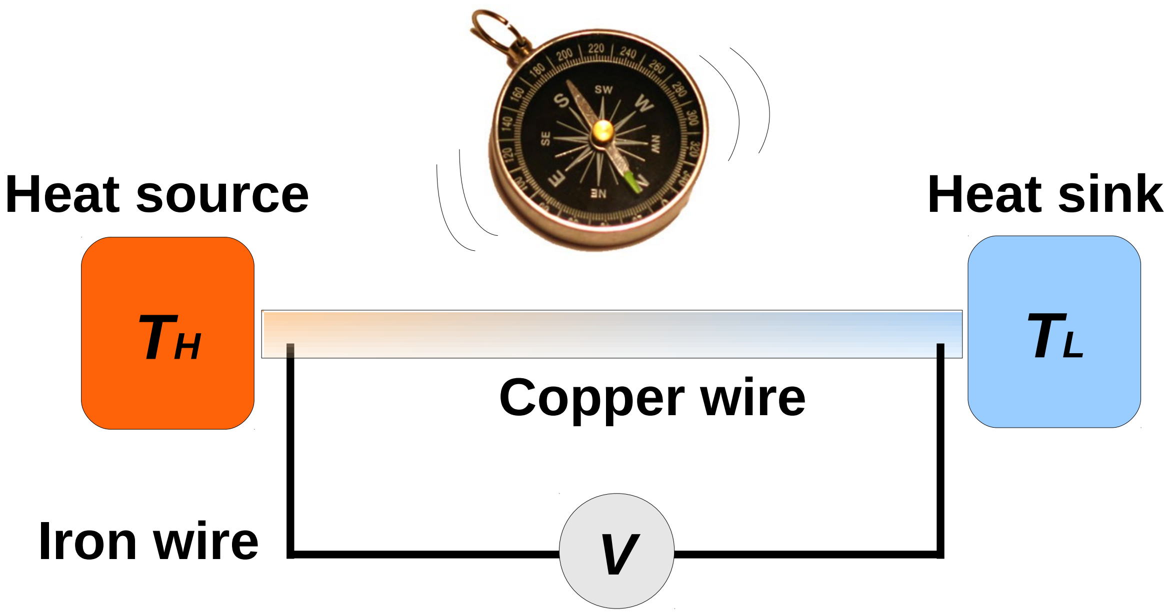
Merit: static, no motion, thin,

shape can be changed

Demerit: low efficiency, low voltage

Introduction – Seebeck effect

1821 – He found deflection of compass when circuit made by two different metals was placed in a heat gradient.



Thomas Jhon Seebeck
(1770-1831)

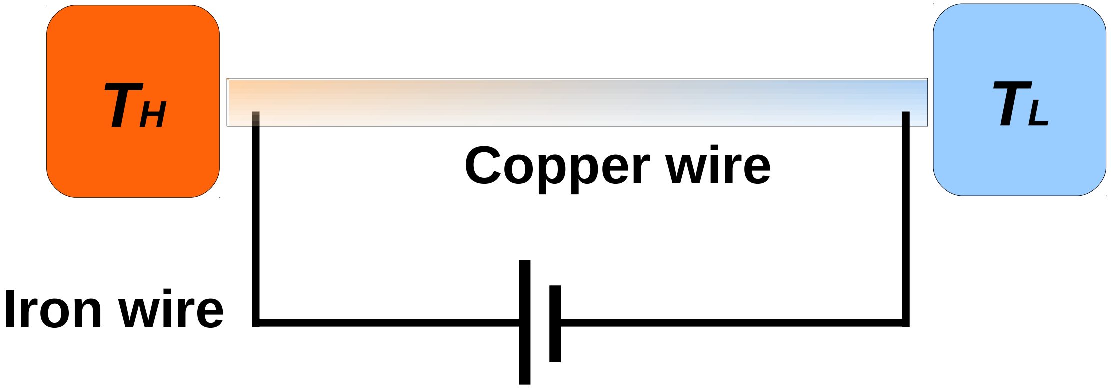
Thermopower

$$S = V/\ T\ (\mu V/K)$$

Heat gradient → Electric current

Introduction – Pelitier effect

1834 – He found temperature gradient was created when current was driven through circuit made by two different metals.

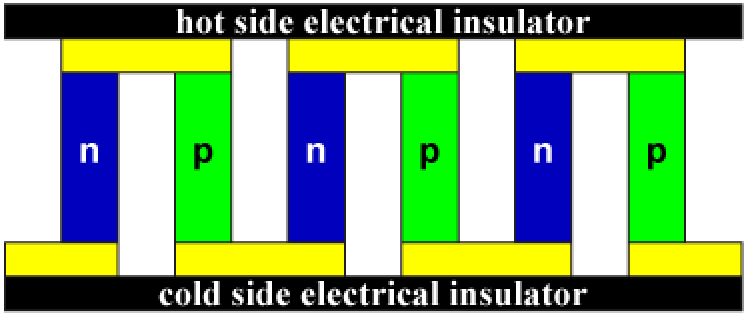


Jean Charles Athanase Peltier
(1785-1845)

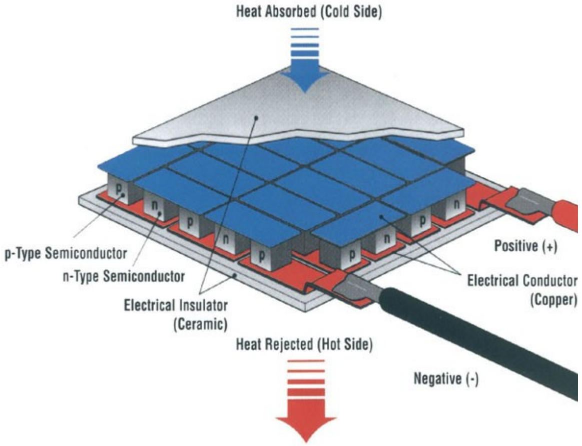
Heat gradient ⟵ Electric current

Thermoelectric devices

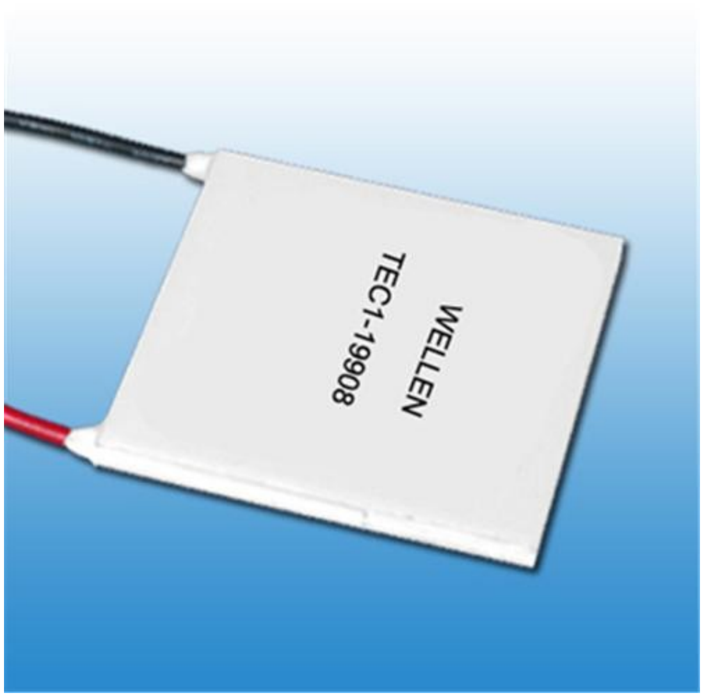
Side view



D. J. Paul, Univ. Glasgow



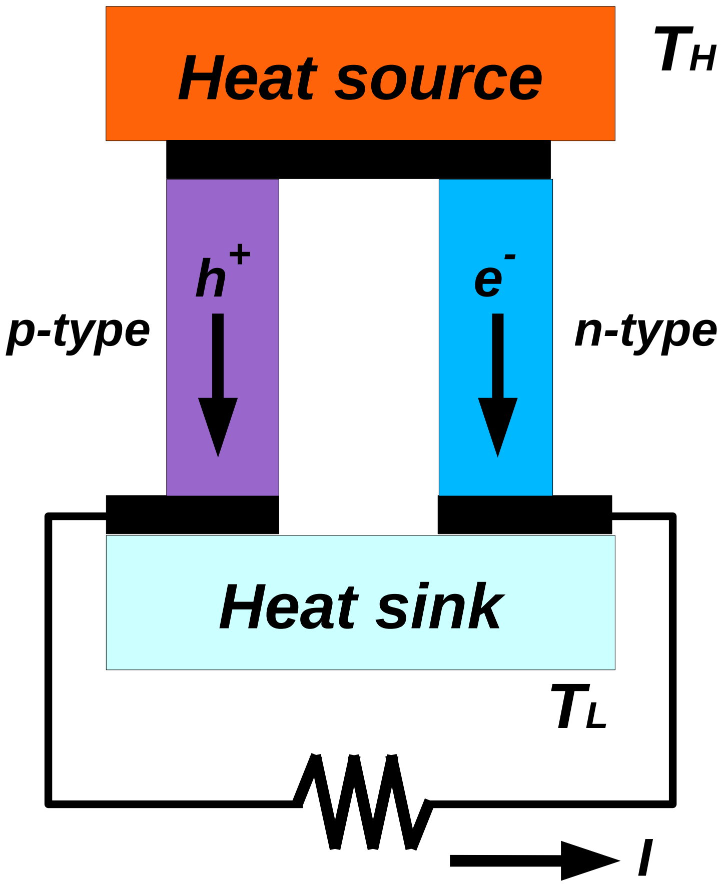
Thermoelectric module



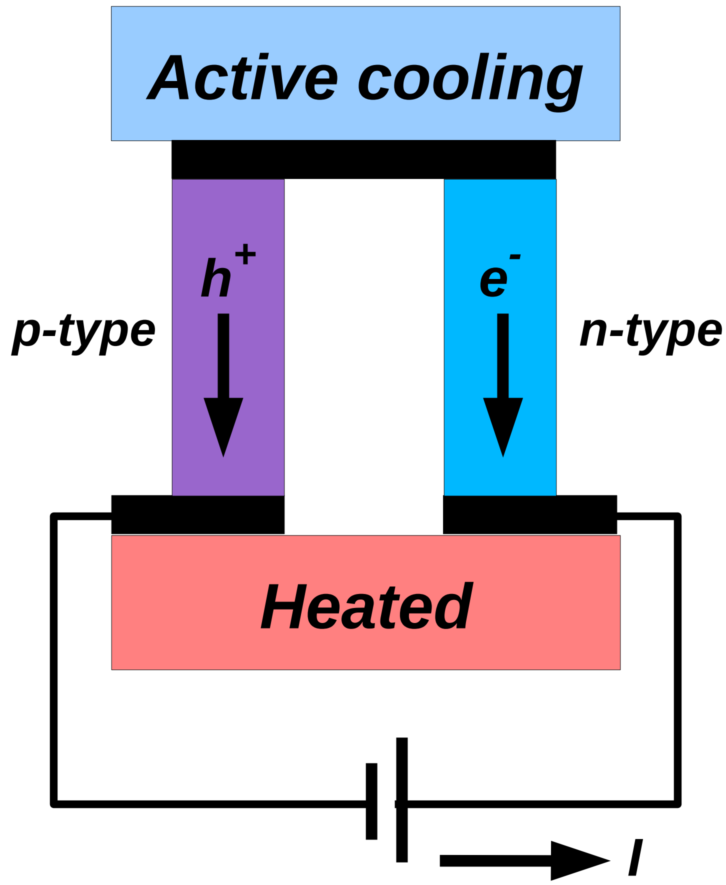
Thermoelectric Modules Tec1-19908
Wellen Technology Co. Ltd

How to understand Seebeck/Pelitier effect

Seebeck effect



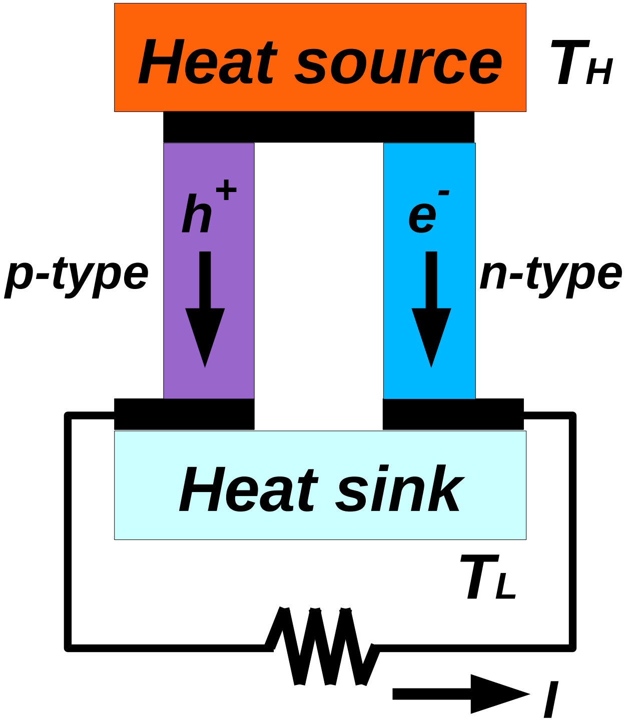
Pelitier effect



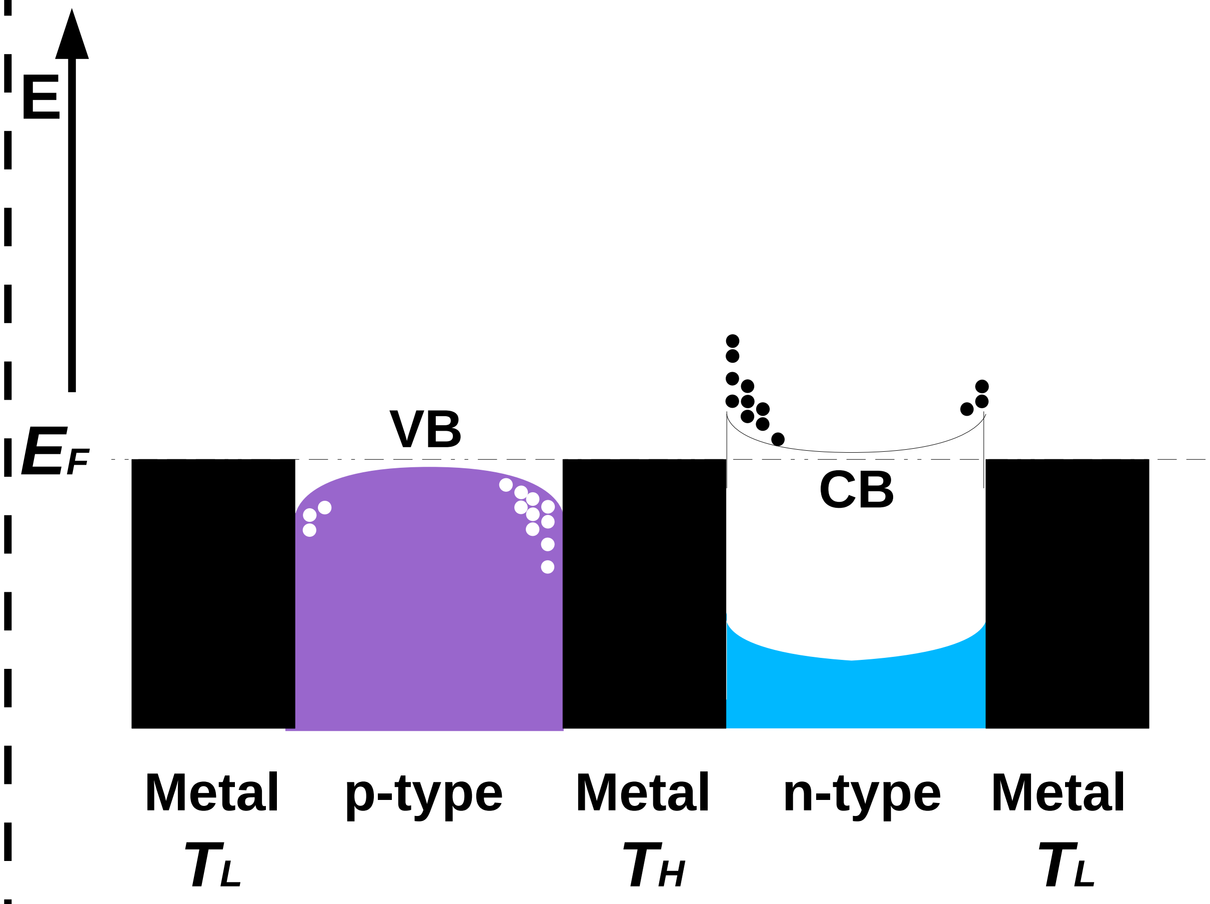
Review: Francis J. DiSalvo, Science 285, 704 (1999)

How to understand Seebeck effect?

Seebeck effect



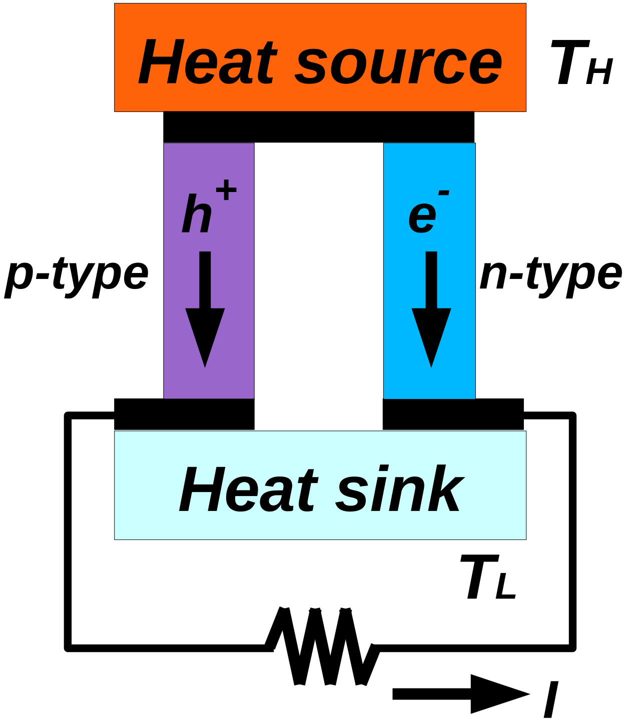
Energy band diagram



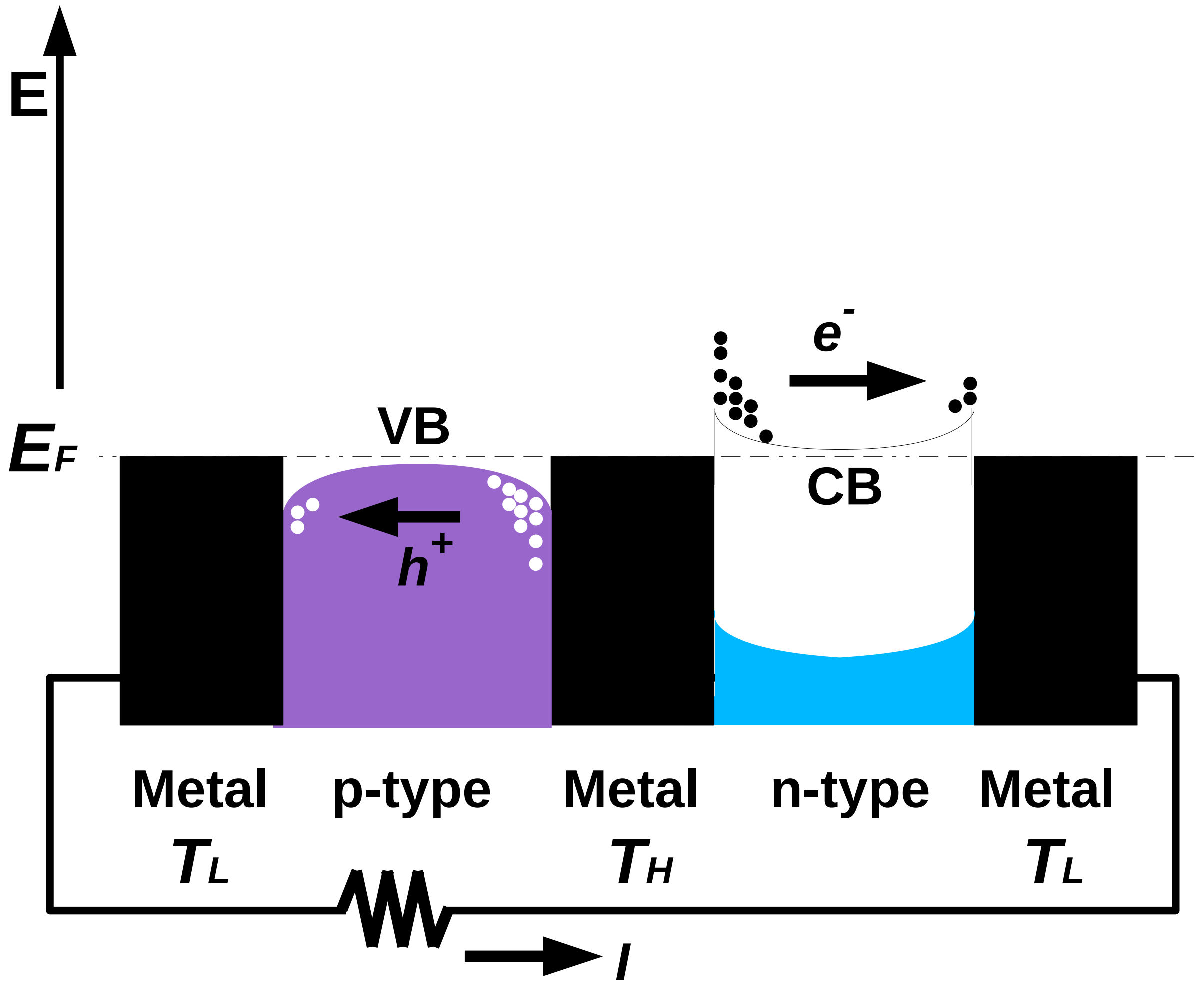
Taylor Sparks's web page

How to understand Seebeck effect?

Seebeck effect

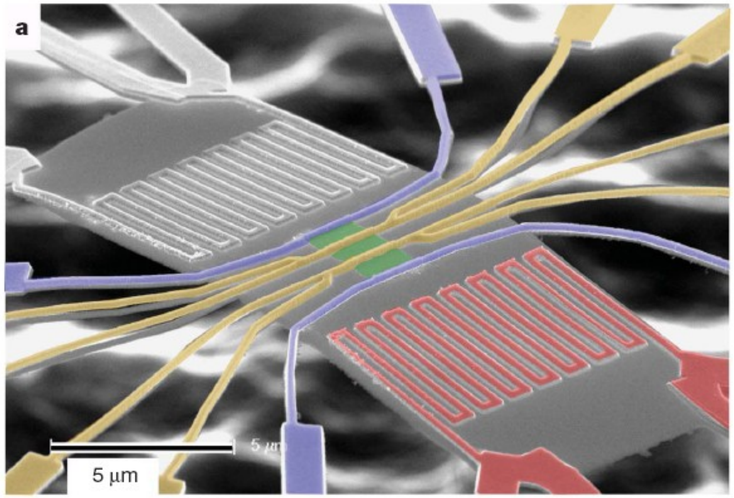


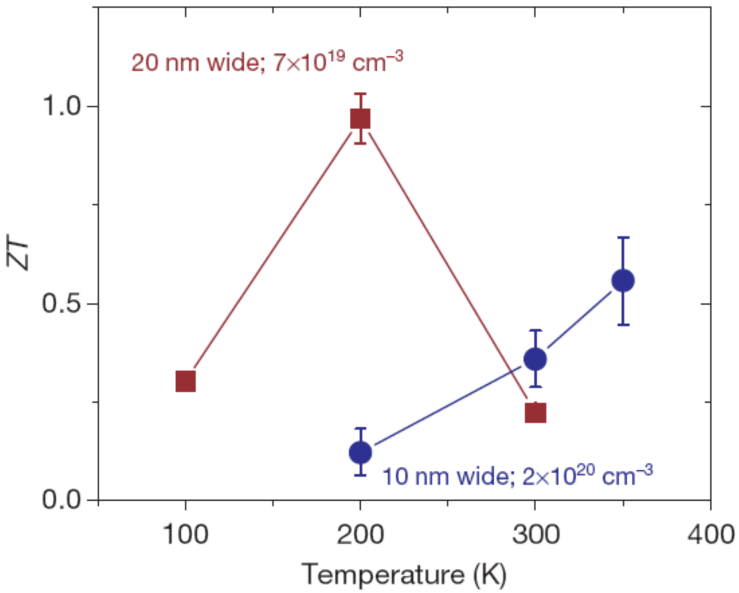
Energy band diagram



Taylor Sparks's web page

Thermoelectricity at the nanoscale





“Silicon nanowires as efficient thermoelectric materials”
A.I. Boukai *et al.,* Nature **451**, 168 (2008)

“Enhanced thermoelectric performance of rough silicon nanowires”
A. I. Hochbaum *et al.,* Nature **451**, 163 (2008)

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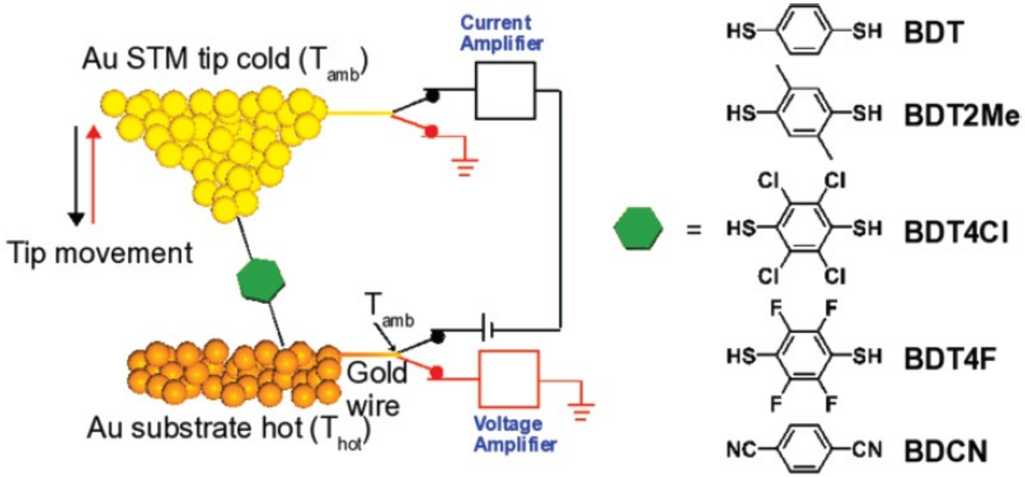
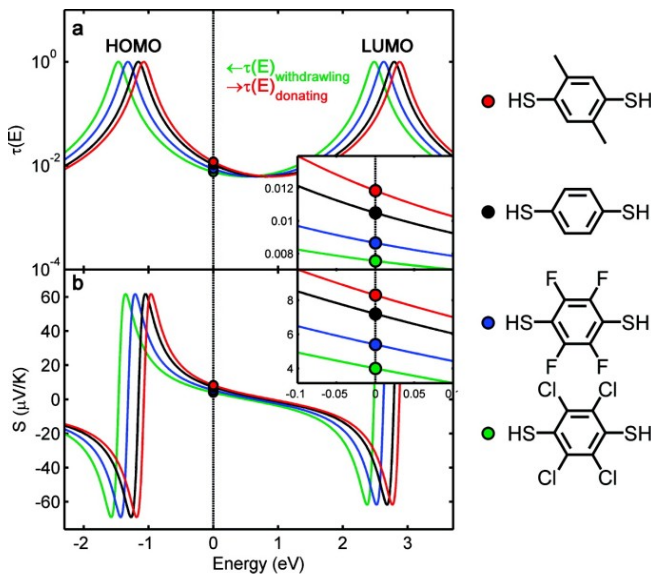
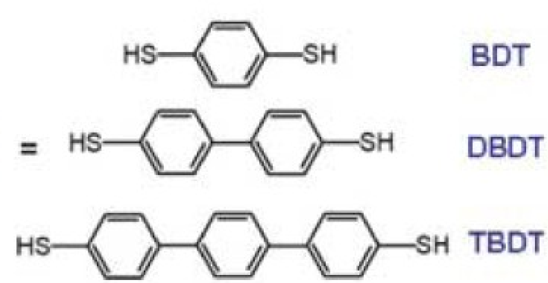
Thermoelectricity in molecular junctions



“Probing the chemistry of molecular heterojunctions using thermoelectricity”
K. Baheti *et al*.,
Nano Letters **8**, 715 (2008)



“Thermoelectricity in molecular junctions”
P. Reddy, et al.
Science **315**, 1568 (2007)



Seebeck coeff. sensitive to position of the Fermi level

How to calculate figure of merit ?

Thermoelectric figure of merit

Seebeck coeff. (µV/K)

Electrical conductivity

$$ZT = S^2 T \frac{\sigma}{\underbrace{\kappa_{\mathrm{el}} + \kappa_{\mathrm{ph}}}}$$

Thermal conductivity

Breakthrough: Nanostructuring

Hicks & Dresselhaus

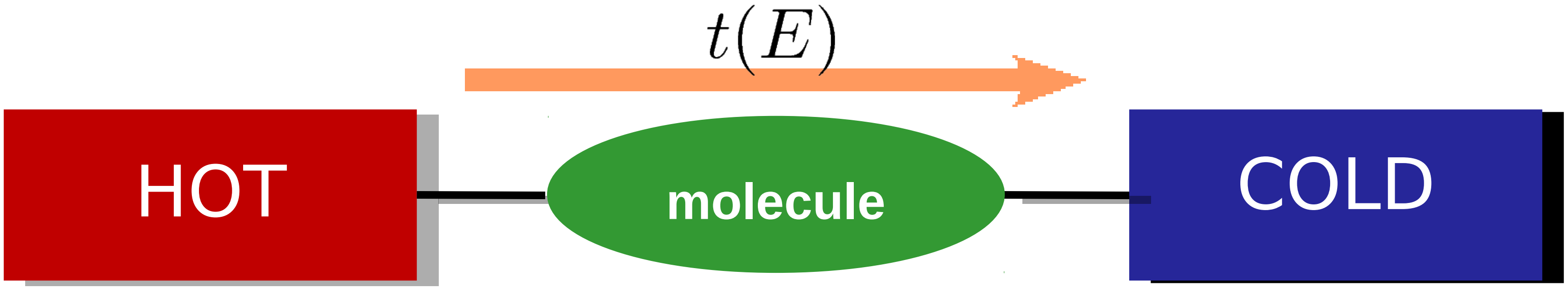
Thermoelectric figure of merit of a 1D conductor

Phys. Rev. B **47**, 16631 (1993)

Thermoelectric coefficients in molecular junctions

Electronic part of the thermoelectric transport coefficients:

if no inelastic effects → Landauer approach



$$ZT = \frac{S^2 \, \sigma \, T}{\kappa_{el} + \kappa_{ph}}$$

$$\sigma = \frac{e^2}{h} L_0(\mu) \qquad S = \frac{1}{eT} \frac{L_1(\mu)}{L_0(\mu)} \qquad \kappa_{el} = \frac{1}{hT} \left(L_2(\mu) - \frac{L_1^2(\mu)}{L_0(\mu)} \right)$$

$$L_n(\mu) = \int dE \, t(E) \, (E - \mu)^n \frac{\partial f}{\partial E}$$

Electronic contribution to thermal conductivity

Transmission function (Fisher-Lee relation)

$$t(E) = T_{el}(E) = Tr\left[G^R(E)\Gamma_L(E)G^A(E)\Gamma_R(E)\right]$$

Retarded Green's function

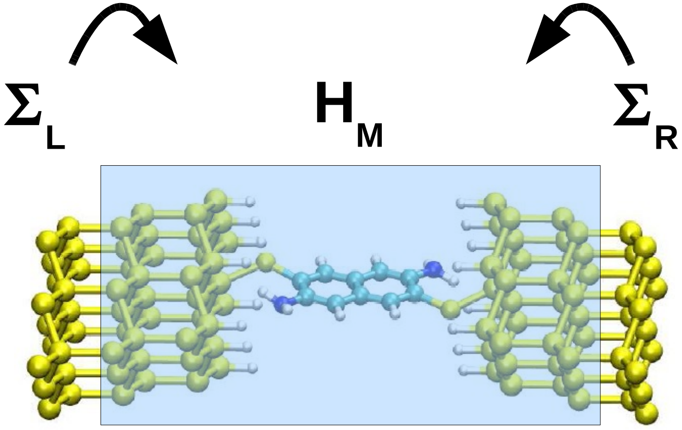
$$G^R(E) = \left[(E+\delta i)S_M - H_M(E) - \Sigma_L(E) - \Sigma_R(E)\right]^{-1}$$

Broadening function

$$\Gamma_{L/R}(E) = i\left[\Sigma_{L/R}(E) - \Sigma_{L/R}(E)^{\dagger}\right]$$

Self-energy

$$\Sigma_{L/R}(E) = (ES_{L/R} - V_{L/R})g_{L/R}(E)(ES_{L/R} - V_{L/R})^{\dagger}$$



- Surface Green function: algorithm by Lopez-Sancho
- Self-consistent NEGF: gDFTB by Alesandro Pecchia

Phononic contribution to thermal conductivity

Transmission function for phonon transport

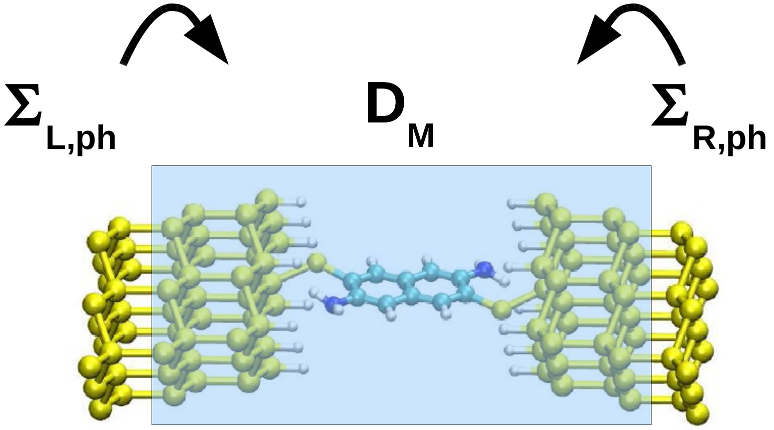
$$T_{ph}(\omega) = Tr\left[G^R_{ph}(\omega)\Gamma_{L,ph}(\omega)G^A_{ph}(\omega)\Gamma_{R,ph}(\omega)\right]$$

Retarded Green's function

$$G^R_{ph}(\omega) = \left[(\omega + \delta i)^2 - D_M(E) - \Sigma_{L,ph}(E) - \Sigma_{R,ph}(E)\right]^{-1}$$

Phonon contribution to the thermal conductance

$$\kappa_{ph}(T) = \int_0^\infty \frac{d\omega}{2\pi}\hbar\omega\frac{\partial f_B(\omega,T)}{\partial T}T_{ph}(\omega)$$



Improving *ZT*

Main goal:

increase thermopower ***S*** and figure of merit ***ZT***

Possible road:

- ***decouple*** electronic and vibronic thermal conductance channels

- ***suppress*** (ideally) vibronic thermal conductance

  T. Markussen, A.-P. Jauho, and M. Brandbyge, PRL **103**, 055502 (2009)

- ***filter*** electron (hole) contribution to ***S***

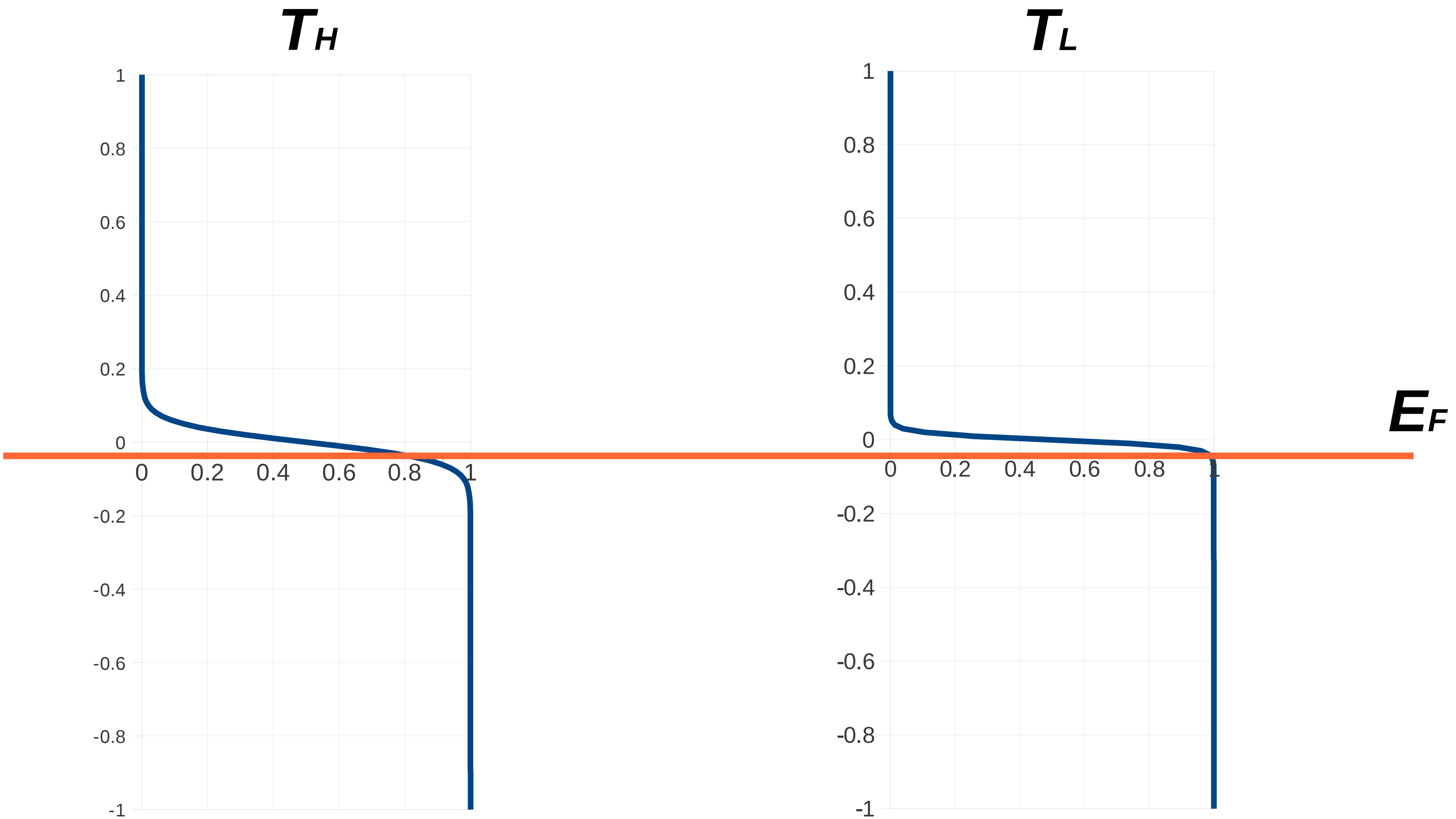
  $$S = S_{\mathrm{elec}} - S_{\mathrm{hole}}$$

- ***resonance*** near Fermi level (log-derivative!)

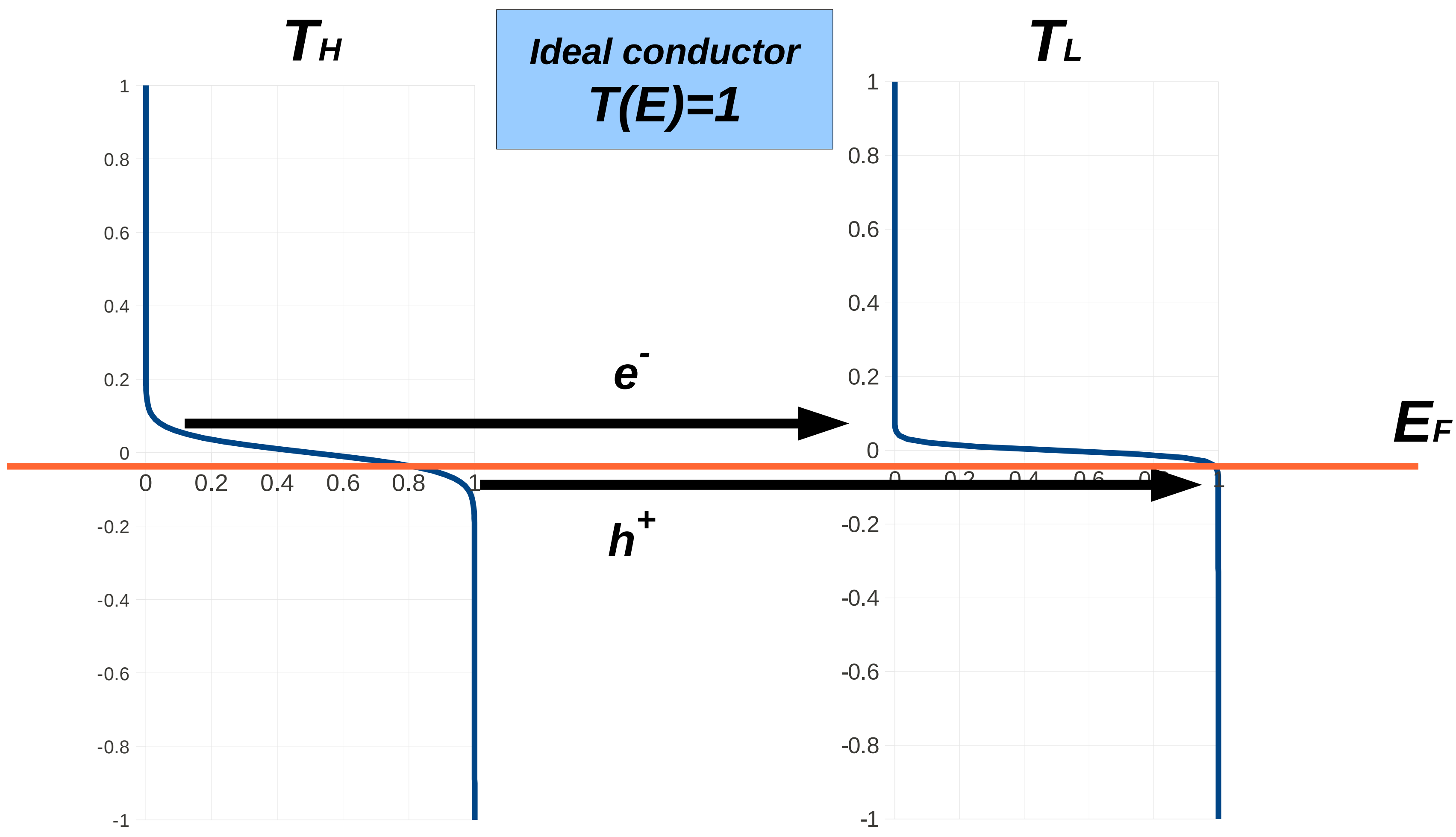
  G. D. Mahan, J.O. Sofo, Proc. Natl. Acad. Sci. **93**, 7436 (1996)

Chemical tuning of thermoelectricity in molecular junctions!?

How to optimize electronic *ZT* ?

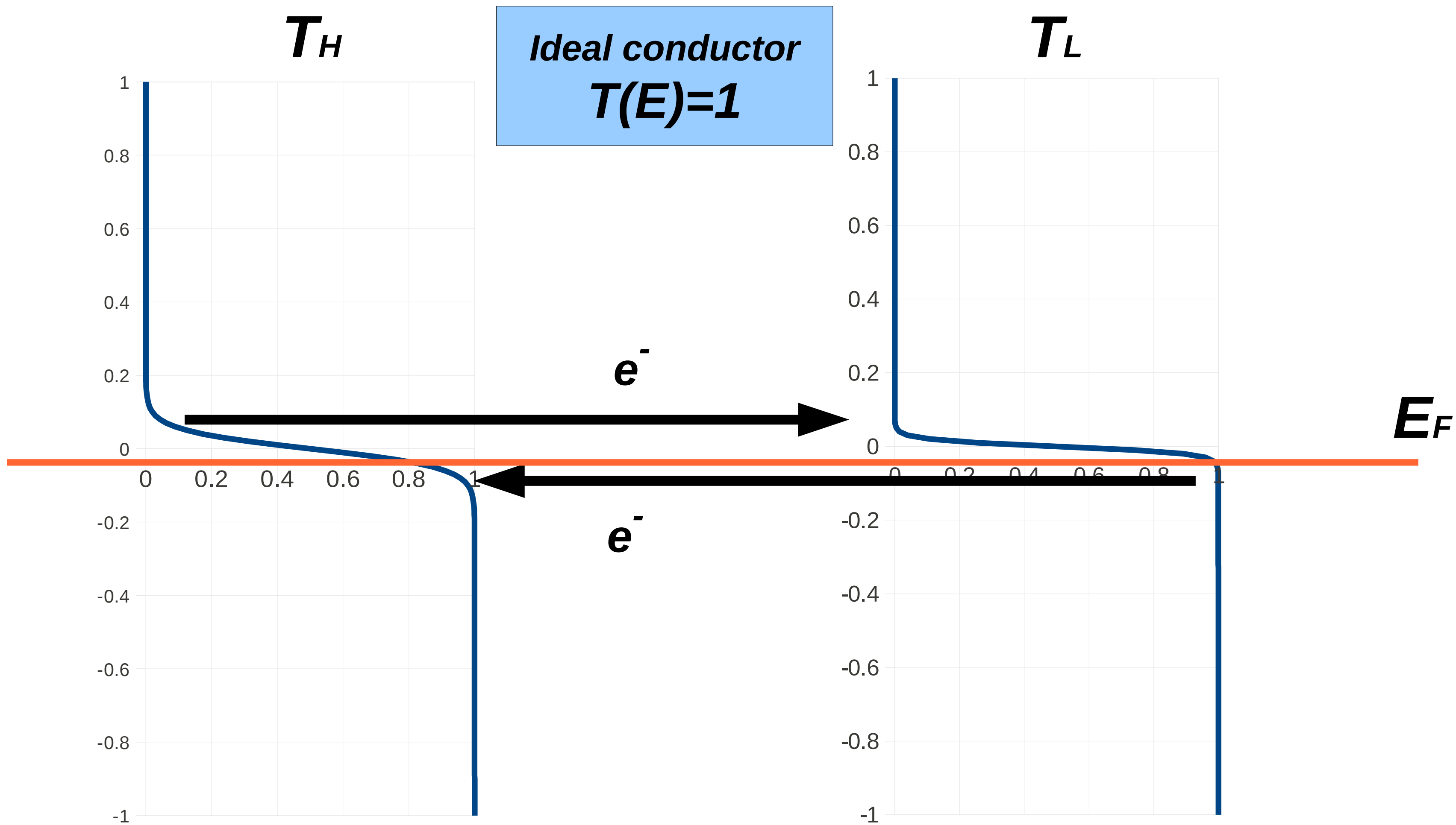


How to optimize electronic *ZT* ?



$N_L(E) = DOS_L(E) * F_L(E)$ $\qquad$ $N_R(E) = DOS_R(E) * F_R(E)$

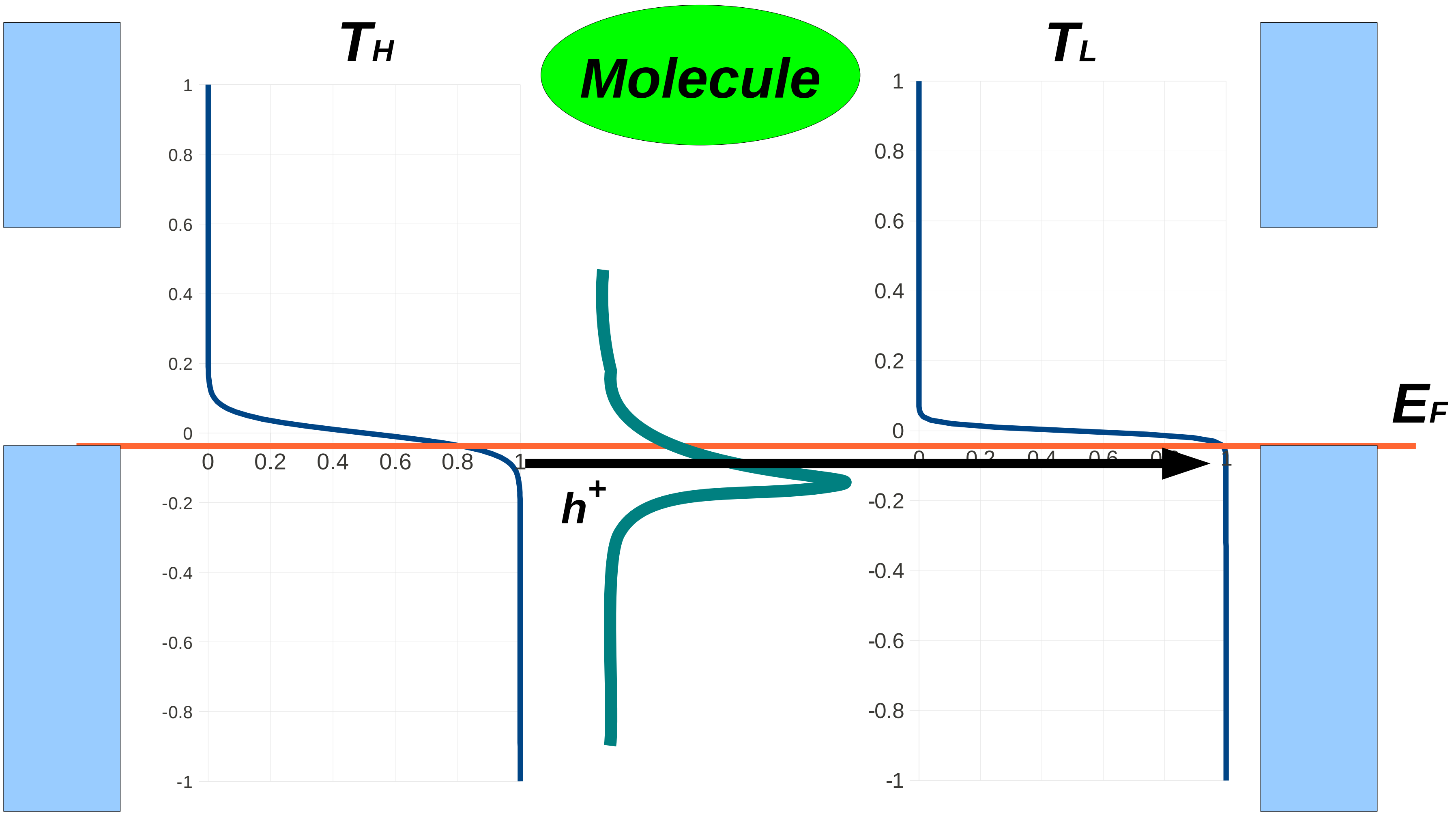
How to optimize electronic *ZT* ?



$$N_L(E) = DOS_L(E) * F_L(E)$$

$$N_R(E) = DOS_R(E) * F_R(E)$$

How to optimize electronic *ZT* ?

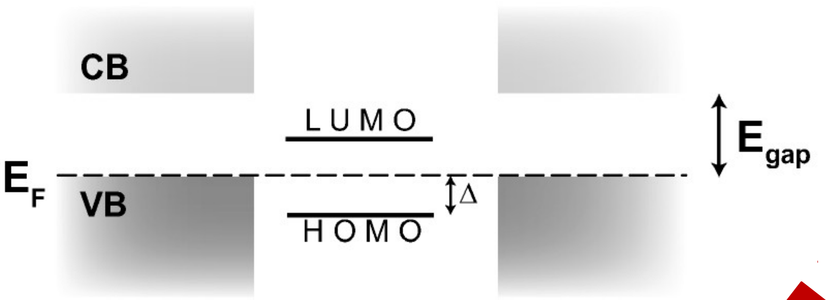


$N_L(E) = DOS_L(E) * F_L(E)$

$N_R(E) = DOS_R(E) * F_R(E)$

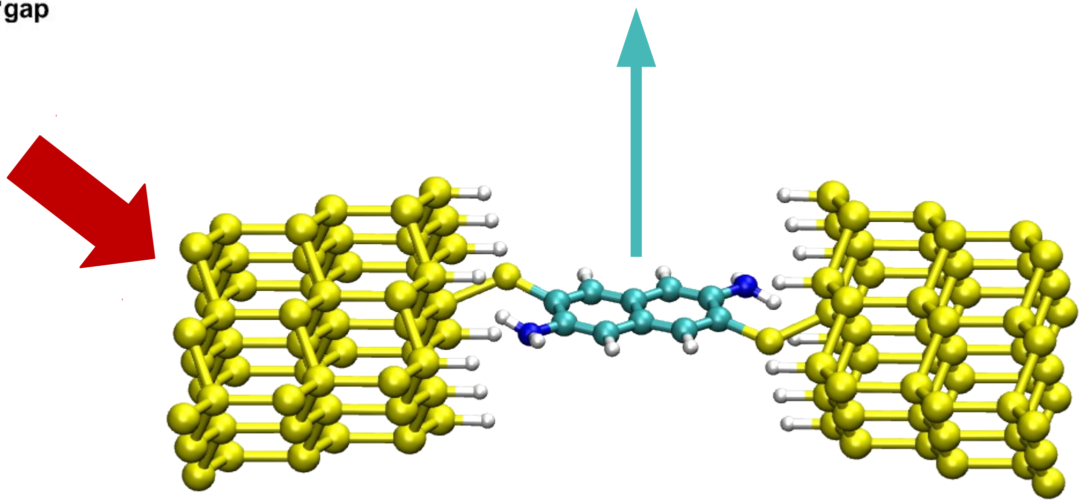
Si electrodes+polyacene molecules

Si(111) electrodes are used in order to increase the thermopower to ***filter out* the negative contribution of electrons.**



Toy model

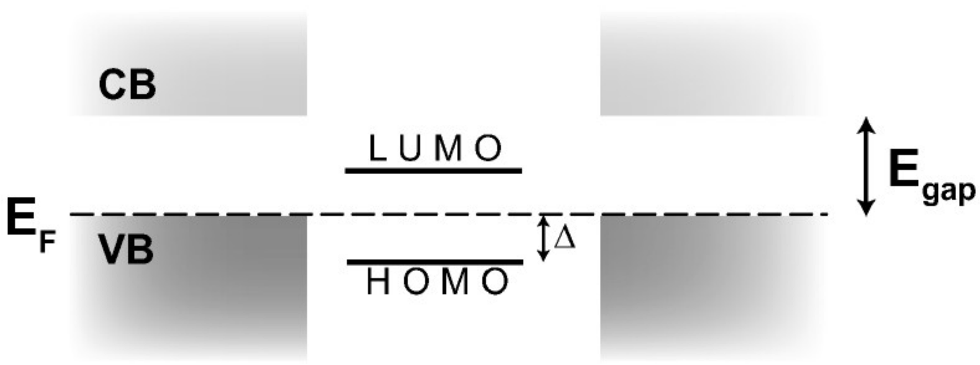
benzene, naphtalene, and anthracene with NH_2 side groups



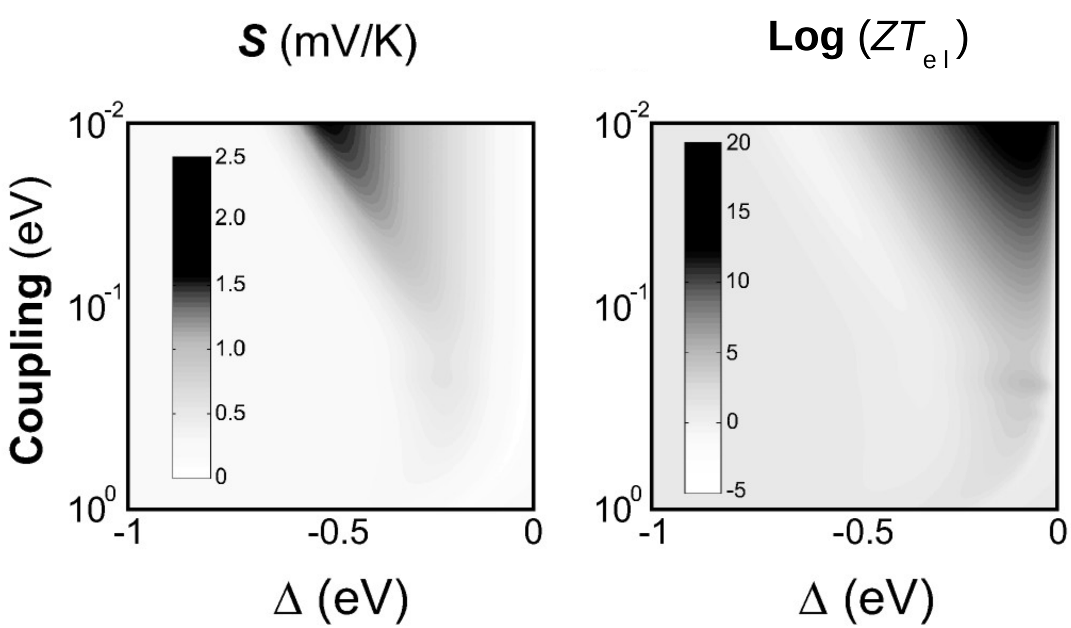
Atomistic model

Methodology: DFT-based approach (DFTB) + Green's function approach

strategy: semiconducting electrodes

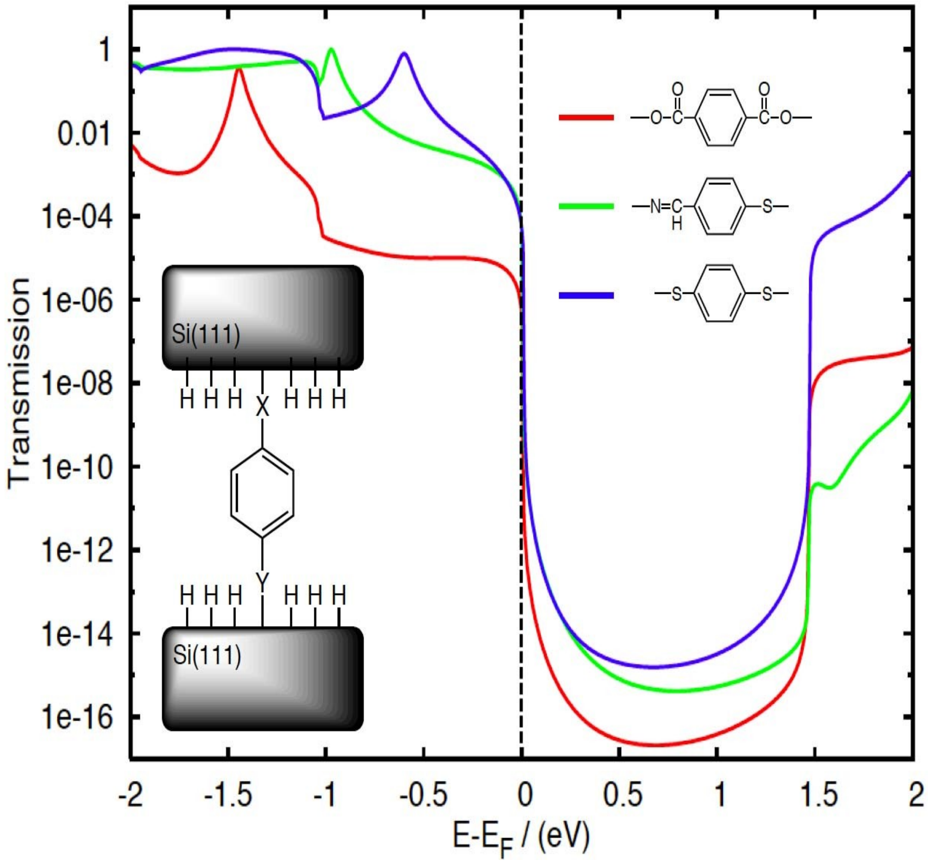


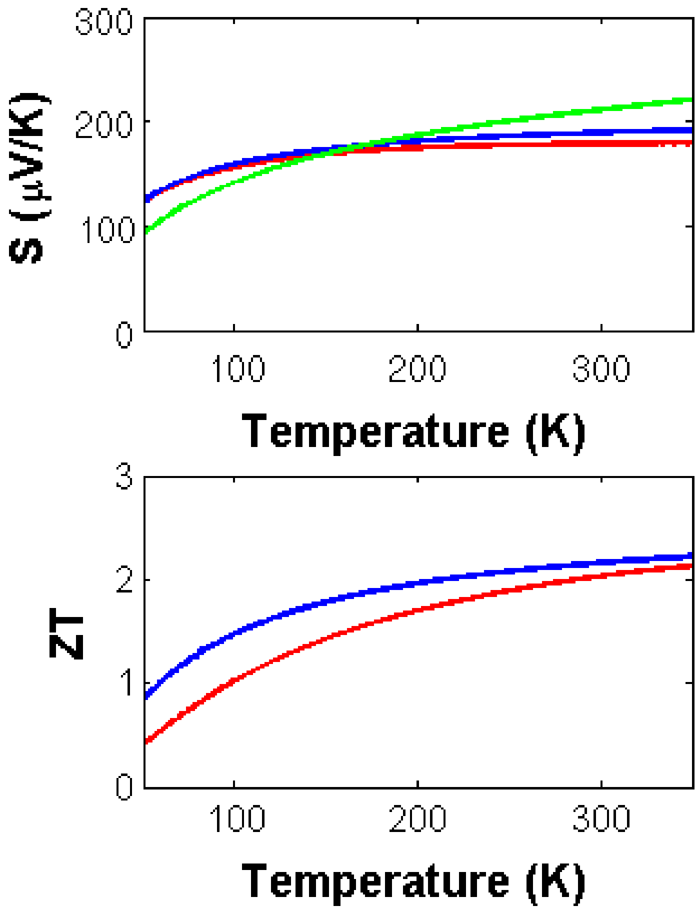
toy model



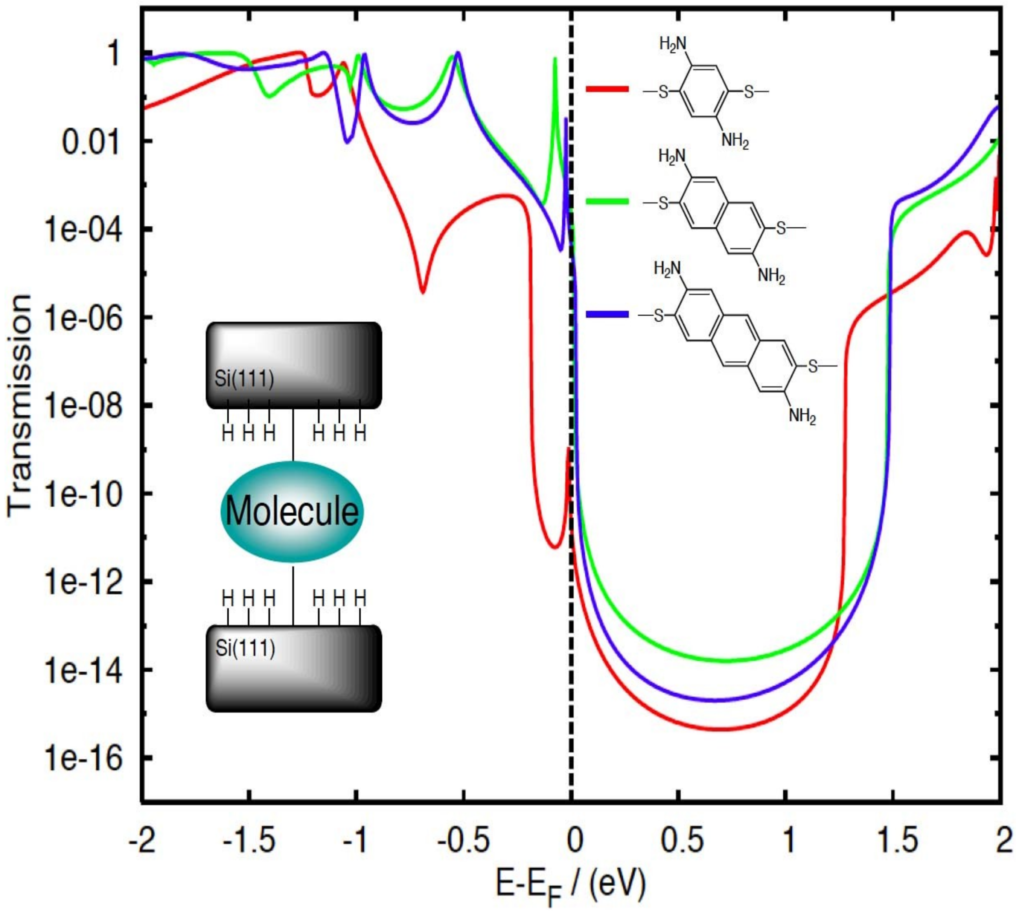
S and ZT are maximized for ***weak coupling*** and when the ***HOMO*** level is close to the ***Fermi level***

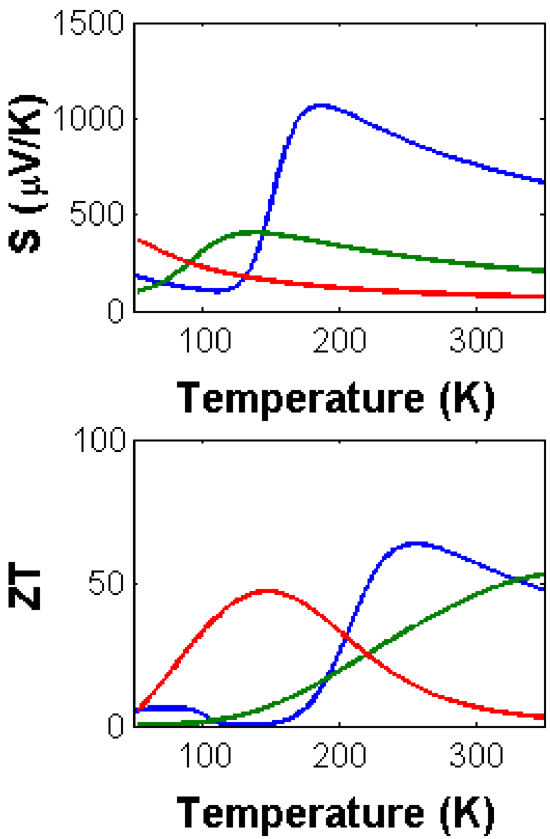
influence of the linkers



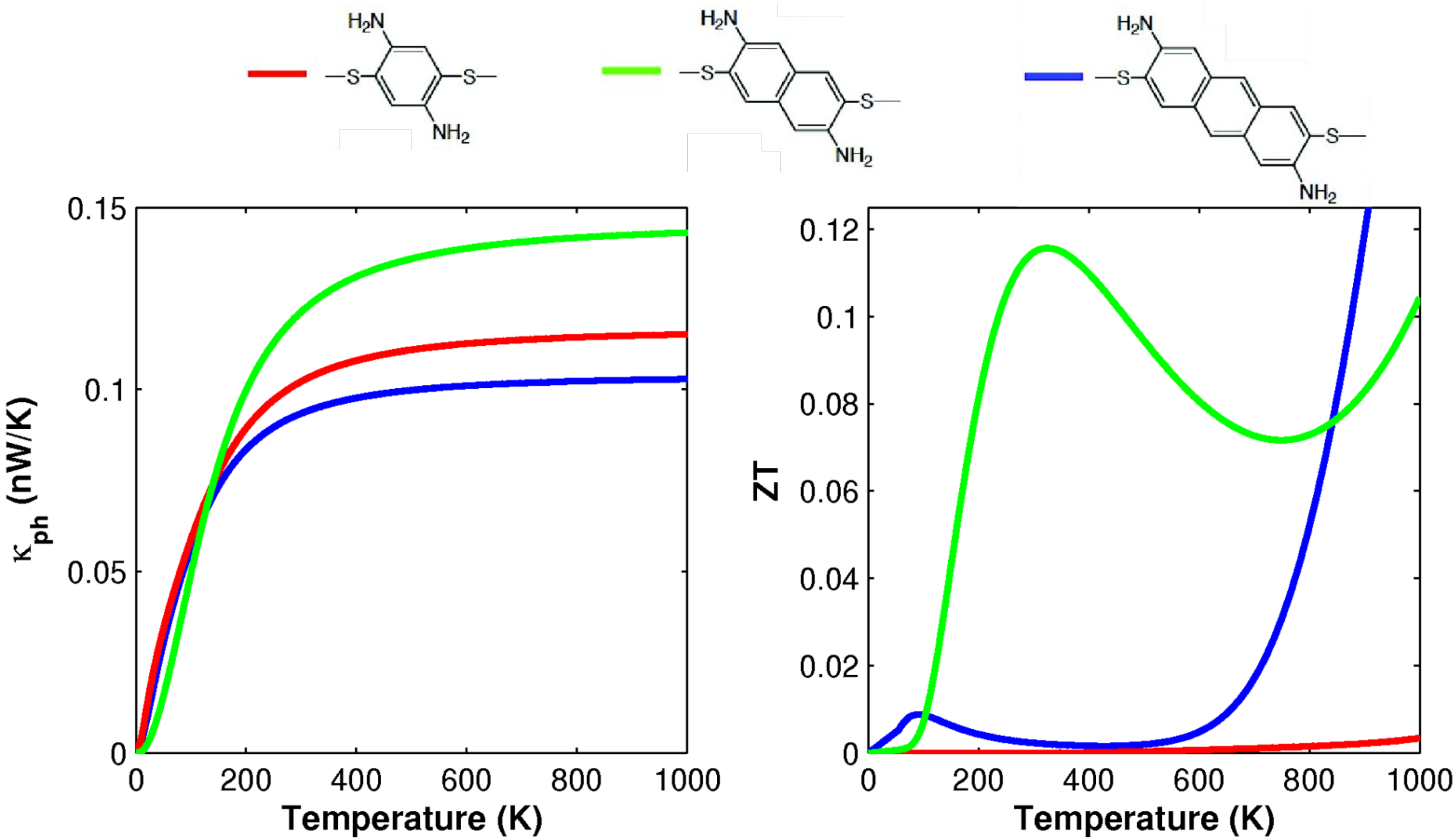


electronic *ZT* for polyacenes





vibrational effects and *ZT*



Vibrational thermal conductance (**naphtalene**), around **150 pW/K** @ RT

ZT$_{max}$ is reduced to about **0.11** @ RT

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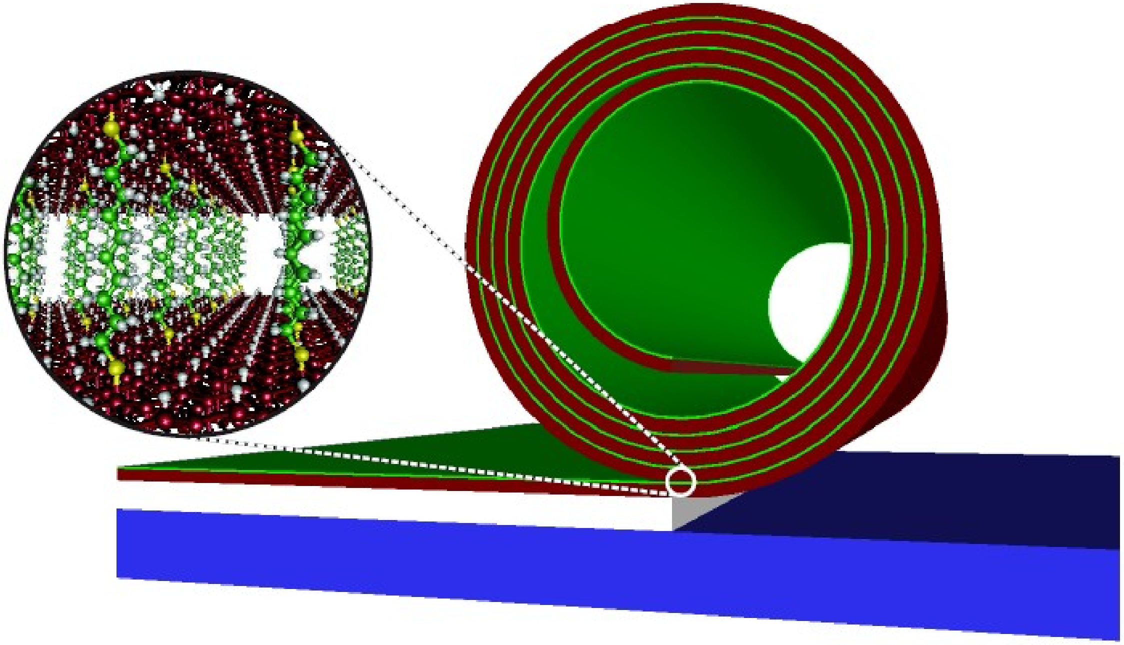
outlook

Thermoelectricity in rolled-up functionalized Si-nanostructures



In cooperation with
Oliver Schmidt (IFW Dresden)
Within SPP 1386 *Nanostrukturierte Thermoelektrika: Theorie, Modellsysteme und kontrollierte Synthese*