Supramolecular Control of Charge Transport Along Molecular Wires

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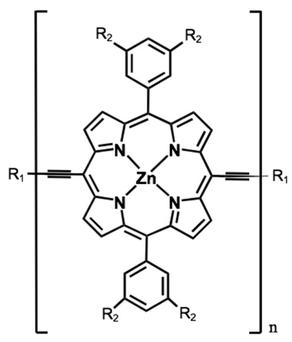
Introduction

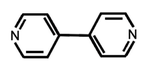
Organic π-conjugated polymers are attractive candidates as wires in molecular-scale electronics. The properties of some polymers can be tuned by non-covalent interactions leading to self-assembly. We experimentally demonstrate the possibility of supramolecular control of the conducting properties of *Zn*-porphyrin polymer wires. Theoretical studies are carried out to get insight into the factors, which govern charge carrier mobility in such molecular wires.

Experimental

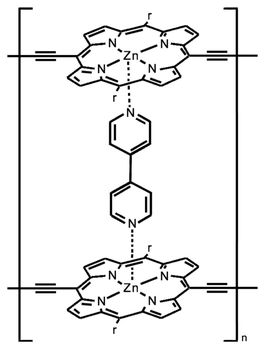
Molecular system studied



Butadiyne-linked *Zn*-porphyrin oligomers form *ladder-like* structures when bidentate ligand (4,4′-bipyridyl) is added



Conjugation length increases

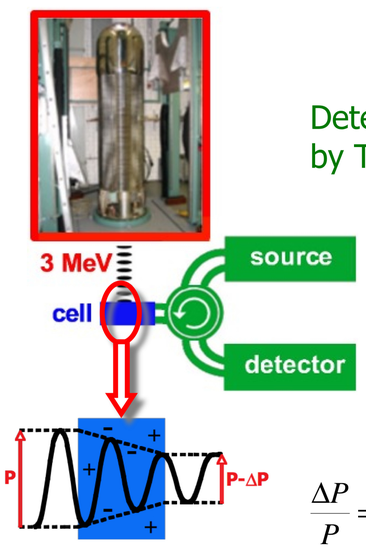


Pulse radiolysis - time-resolved microwave conductivity

Creation of charge carriers by pulse radiolysis
(10 ns pulse of 3 MeV electrons)

Nearly uniform concentration of Bz^+ and e^- produced in O_2-saturated benzene solution of butadiyne-linked *Zn*-porphyrin oligomers (P_n).

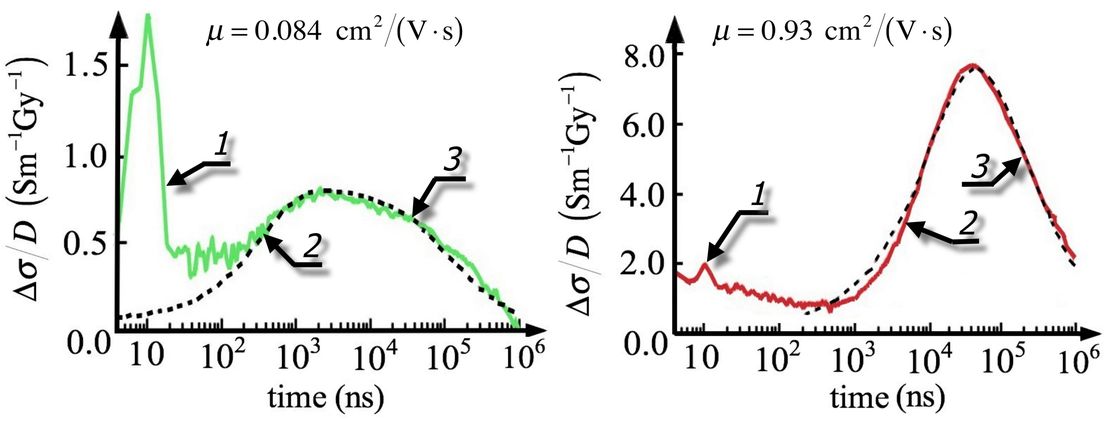
Microwaves are absorbed by mobile charge carriers



Detection by TRMC

$$\frac{\Delta P}{P} = A\Delta\sigma$$

TRMC measurement results

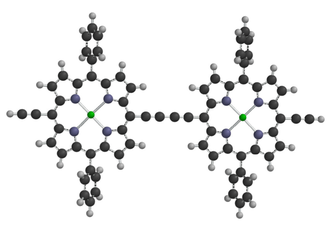


1 $O_2 + e^- = O_2^-$ 2 $Bz^+ + P_n = Bz + P_n^+$ 3 $P_n^+ + O_2^- = P_n + O_2$

Bz — benzene P_n — porphyrin oligomer

Increased conjugation length increases (1*D*) charge carrier mobility from **0.084** to **0.93 cm²/(V·s)**, mobility ***independent of the chain length***.

Dimer parameter calculation



- We obtain the rotation barriers Δ*E* and charge transfer integrals *J'* from calculations on a dimer.
- These parameters are used to simulate charge transport along the polymer chain.

Effective charge transfer integral (electronic structure calculation in terms of *molecular fragment orbitals* φ_i, φ_j): $J_{ij}'(t) = 0.27\cos\theta \ \text{eV}$

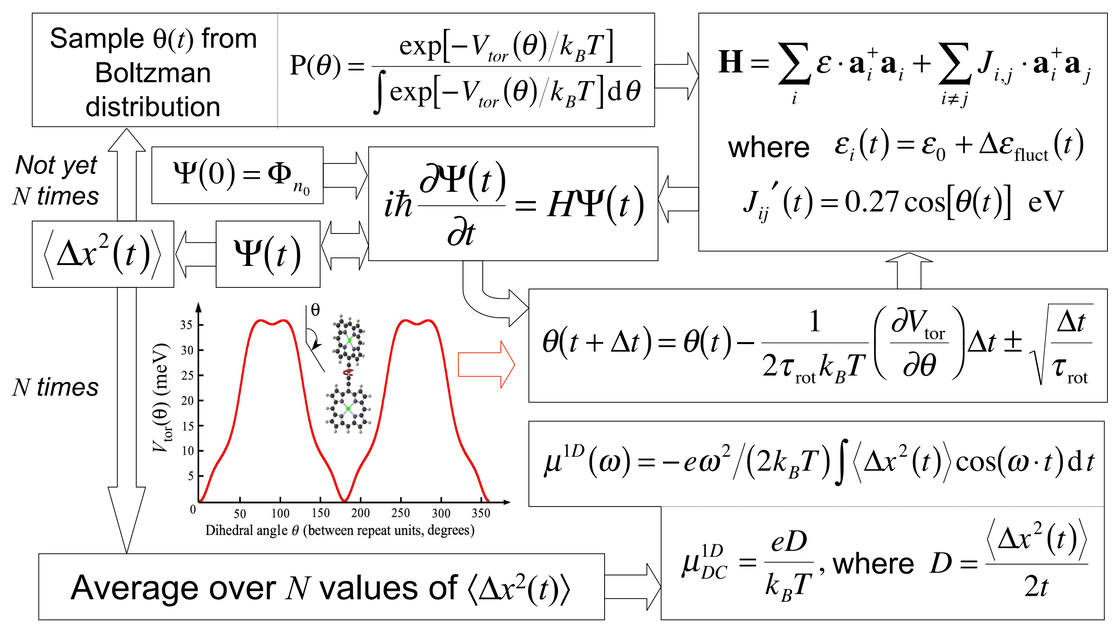
Rotation barrier is quite low: $\Delta E_{\max} \approx 35$ meV (about $1.4kT$ at *RT*)

Reorganization energy: $\lambda = 0.36 \ \text{eV}$

Mobility calculation

Band-like transport simulation

Band-like transport simulation algorithm

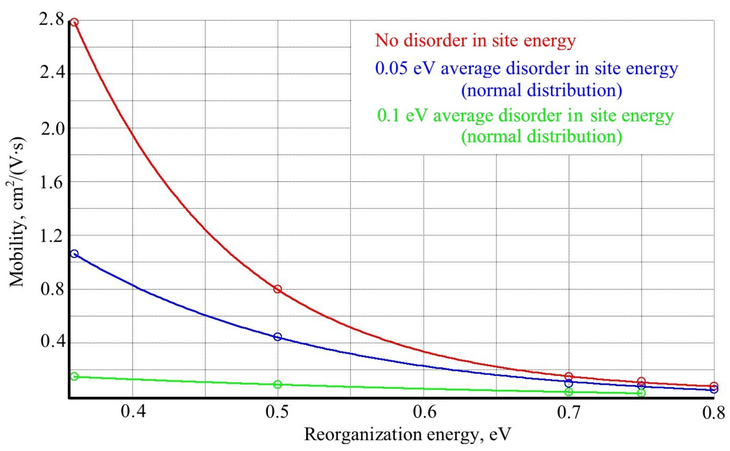


Main results of the simulation

- Mobility of holes on an infinite chain ~ **4.5 cm²/(V·s** (*much higher than the experimental value*)
- Mobility strongly chain length-dependent
- Taking into account the effects of disorder, geometry relaxation and polymer chain length distribution does not cause the mobility to decrease significantly

Polaron hopping simulation

Mobility as a function of reorganization energy



Calculated reorganization energy: $\lambda = 0.36 \ \text{eV}$

Relative stability: ~0.3 eV

$$\Delta = E^{+1,\ \text{localized}}_{(\text{Oxidized})-(\text{Neutral})} - E^{+1,\ \text{delocalized}}_{(0.5\,\text{Oxidized})-(0.5\,\text{Oxidized})}$$

"Hopping time":

$$\tau_s = \frac{e\delta^2}{\pi\mu k_BT} \sim 2.5 \ \text{ps}$$

Geometry relaxation time: $\tau_{\text{relax}} \sim 50$ fs

Marcus hopping mobility:

$$\mu = \frac{e\delta^2 J_{\text{eff}}^2}{\hbar k_BT}\sqrt{\frac{\pi}{\lambda k_BT}}\exp\left(-\frac{\lambda}{k_BT}\right)$$

δ — monomer unit length, J_{eff} — effective charge transfer integral

Since $\Delta > 0$, $\tau_s > \tau_{relax}$ — we can expect localized charges on polymer chain.

Hopping mobility of charges on a *freely rotating chain* with *small site energy disorder* is close to experimentally measured value.

Conclusions

It has been shown experimentally, that the mobility of charges on porphyrin wires can be strongly enhanced by inducing chain planarity. Simulations of band-like charge transport provide significantly overestimated values of the charge carrier mobility. Simulations of hopping transport based on Marcus theory lead to mobility values that are close to experimental results.

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