Ultrashort laser/electron pulse facility for the study of charge and exciton dynamics in functional materials

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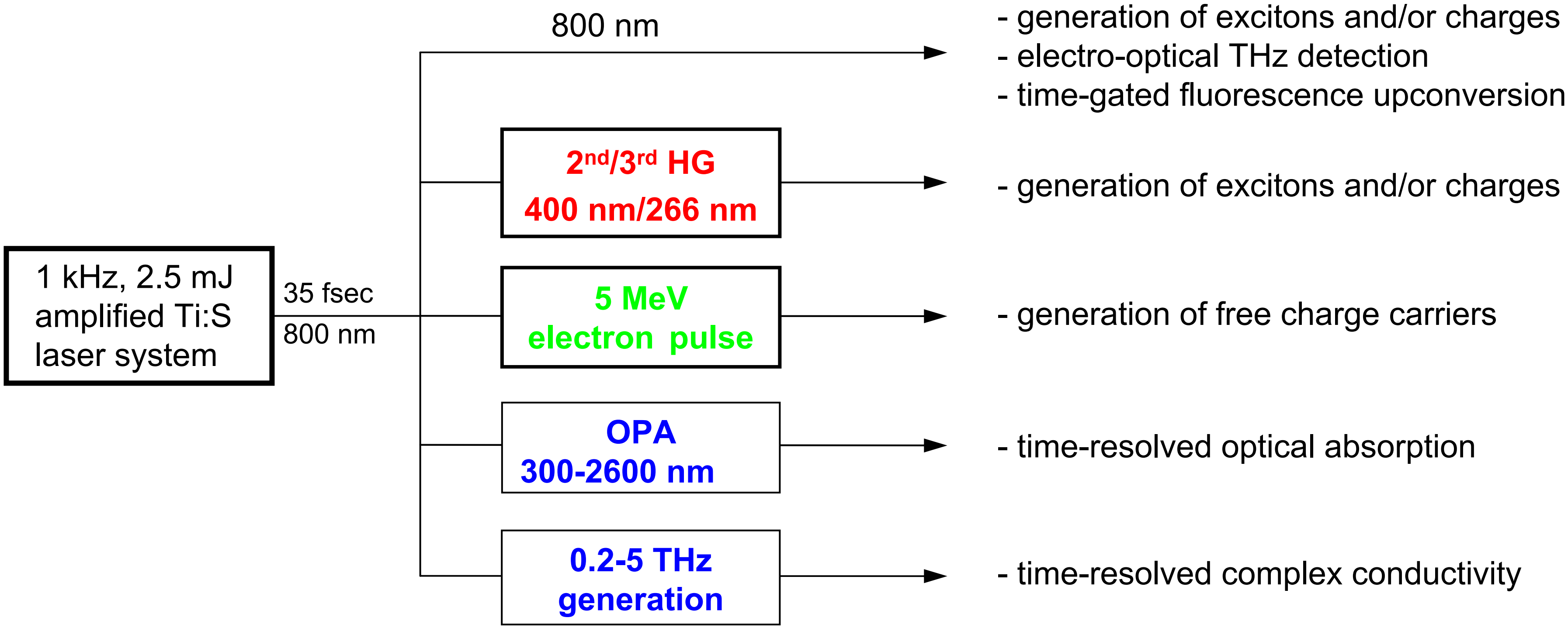
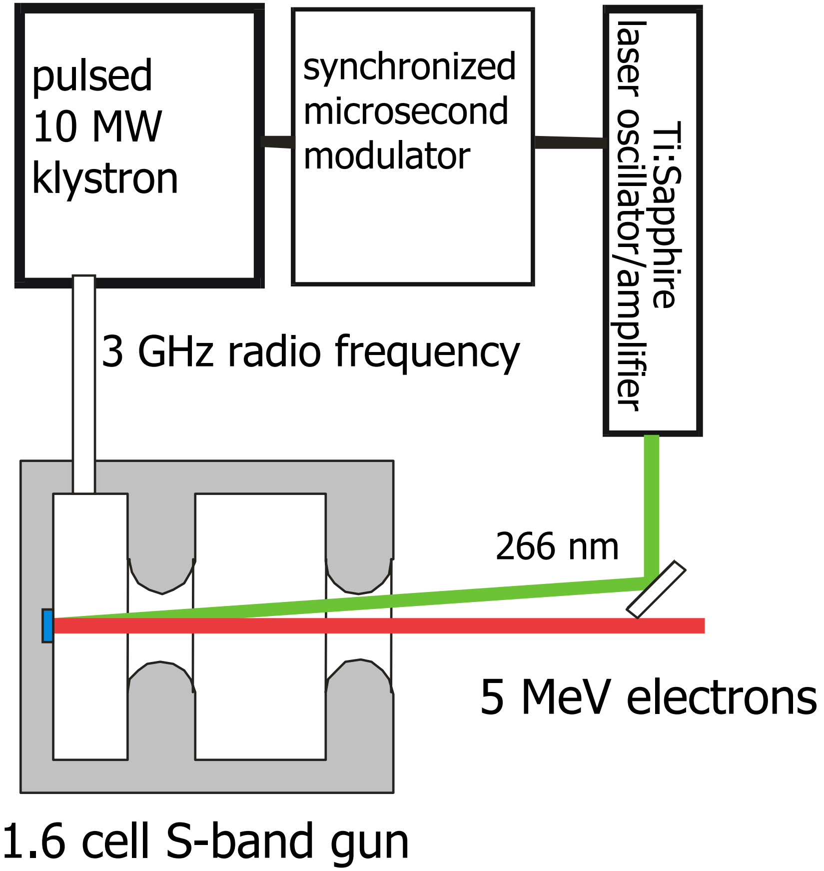
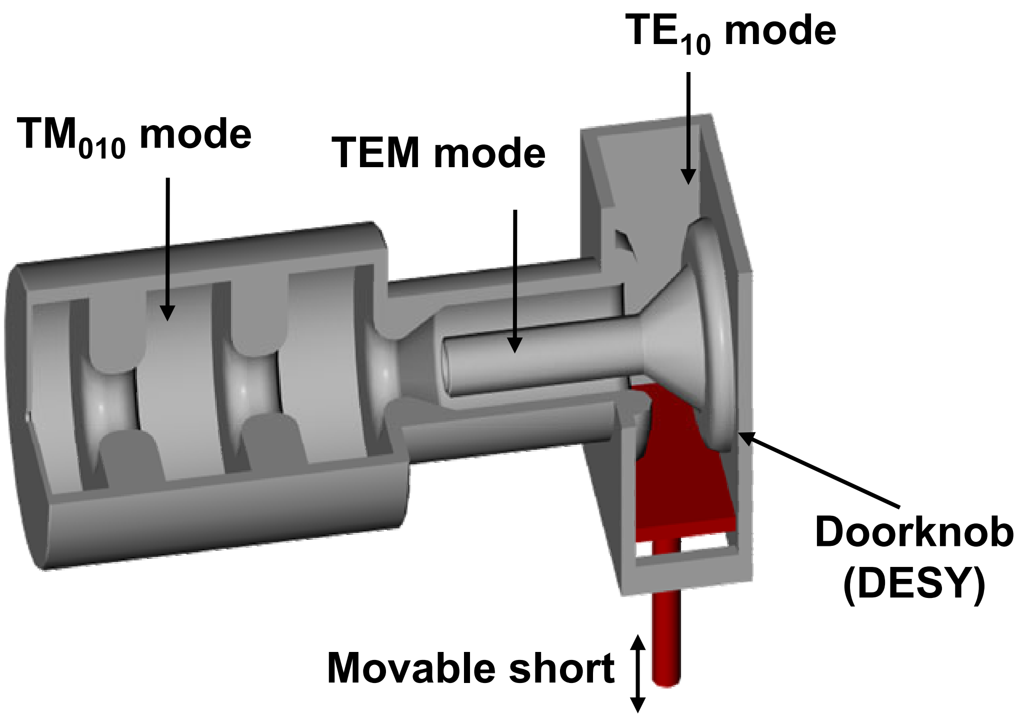
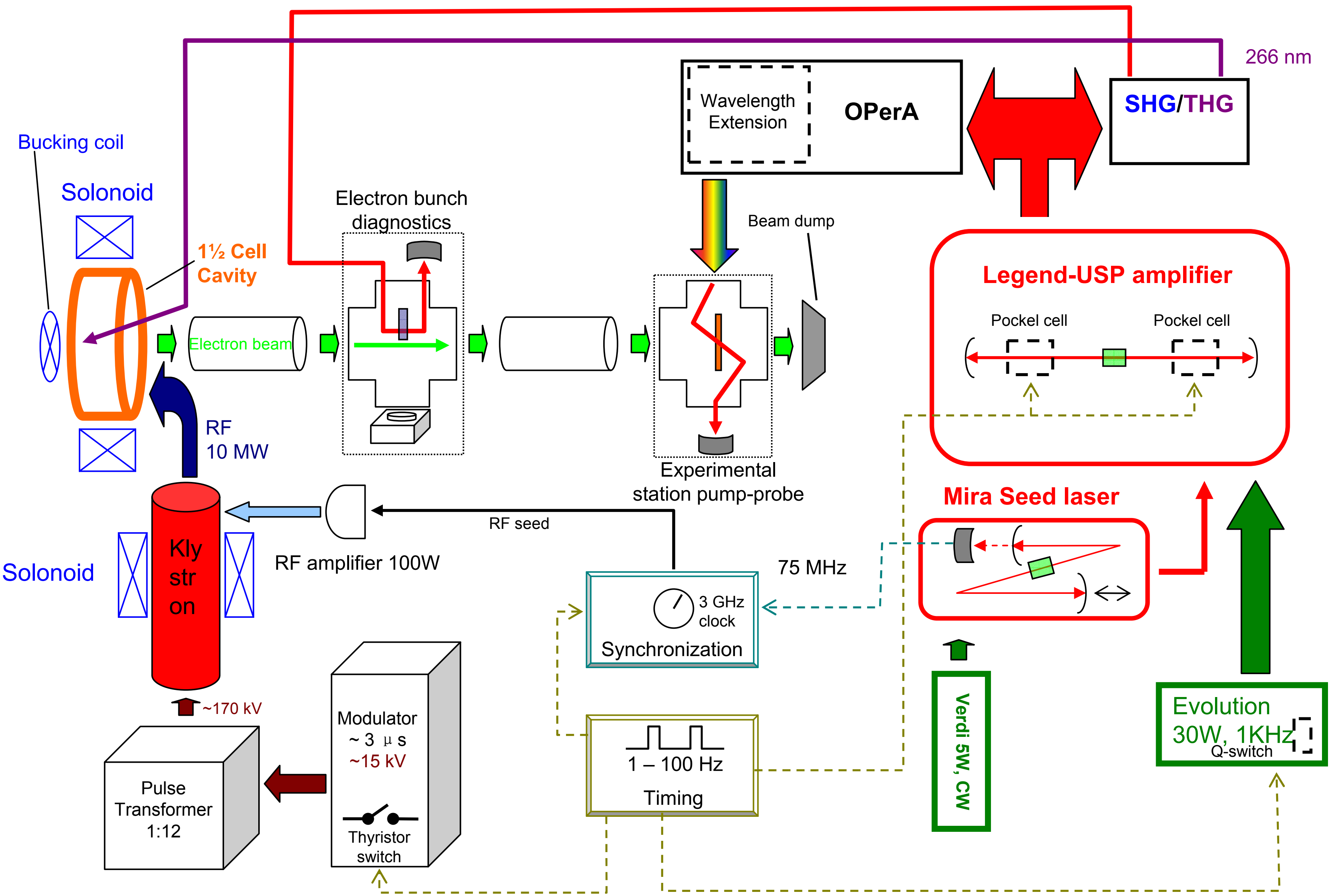
Capabilities of new fsec laser/electron accelerator system



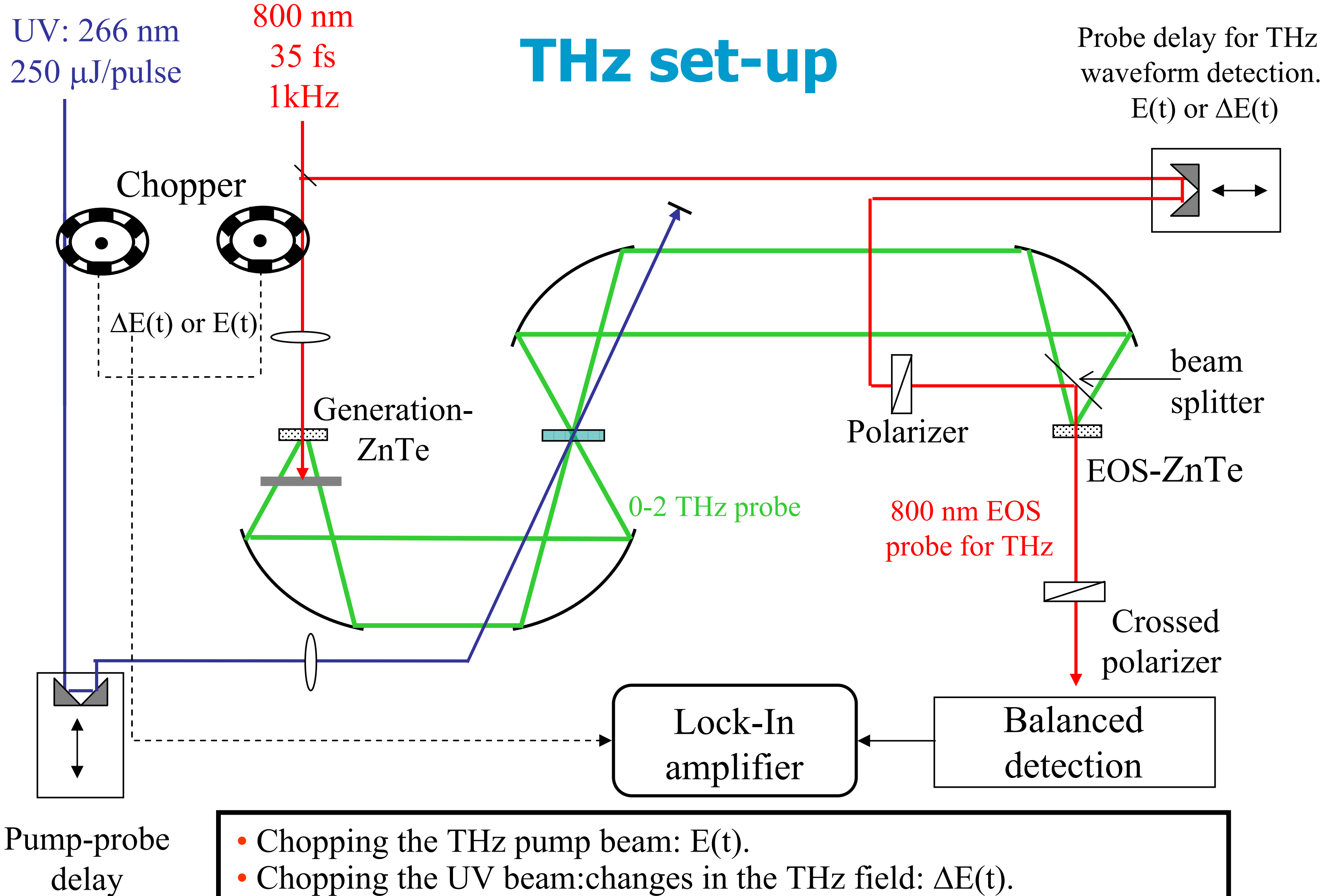

pulsed
10 MW
klystron
synchronized
microsecond
modulator
Ti:Sapphire
laser oscillator/amplifier
3 GHz radio frequency
266 nm
5 MeV electrons
1.6 cell S-band gun


TE10 mode
TM010 mode
TEM mode
Doorknob
(DESY)
Movable short

Ultrafast laser/electron pulse facility in Delft, The Netherlands



THz set-up



- Chopping the THz pump beam: E(t).
- Chopping the UV beam:changes in the THz field: ΔE(t).
- Varying the time delay between the THz UV pump: Dynamics

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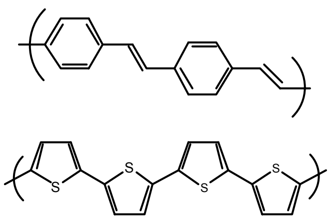
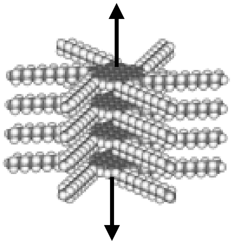
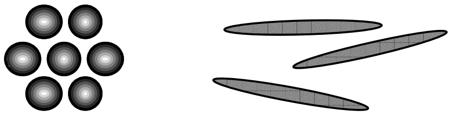
Materials with (potential) opto-electronic applications



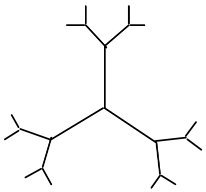
conducting polymers



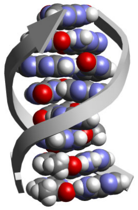
discotic liquid crystals



inorganic nanoparticles, nanorods



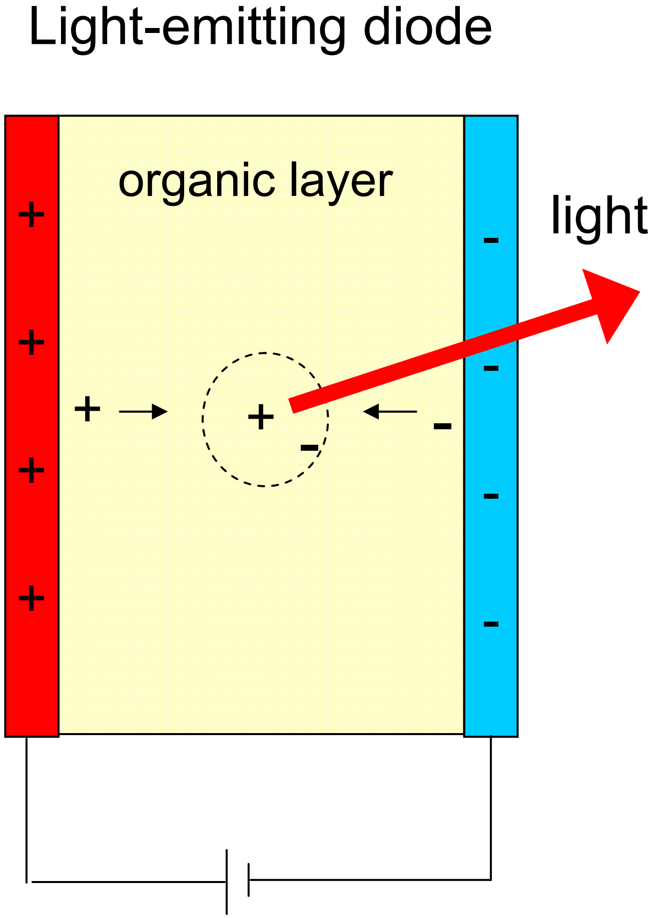
supra-molecular
assemblies

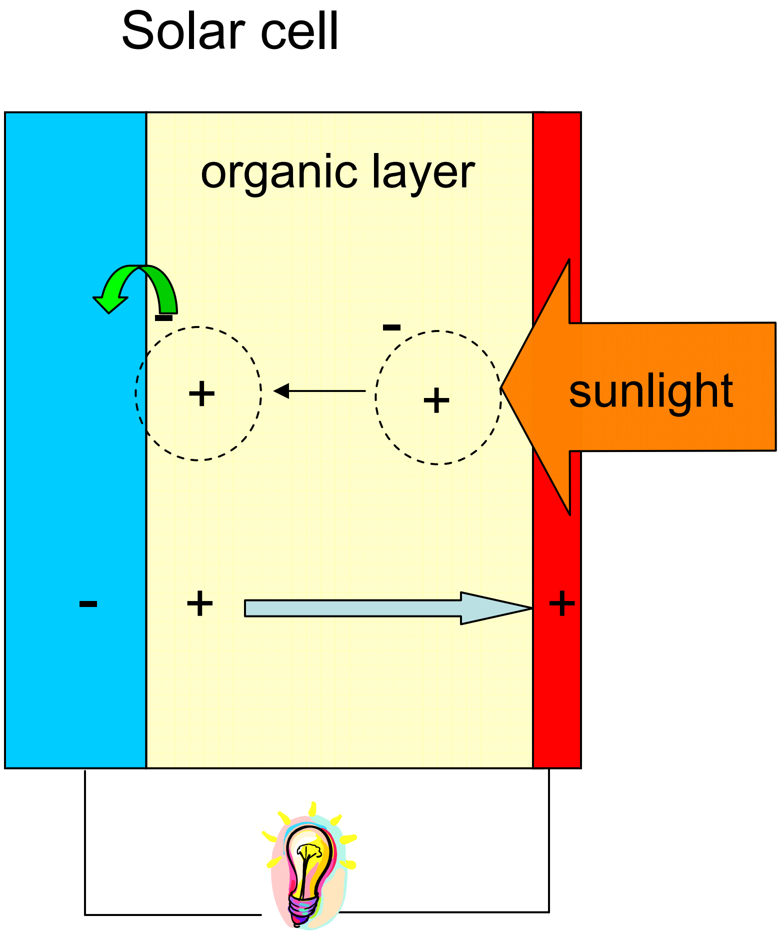


DNA

composite systems

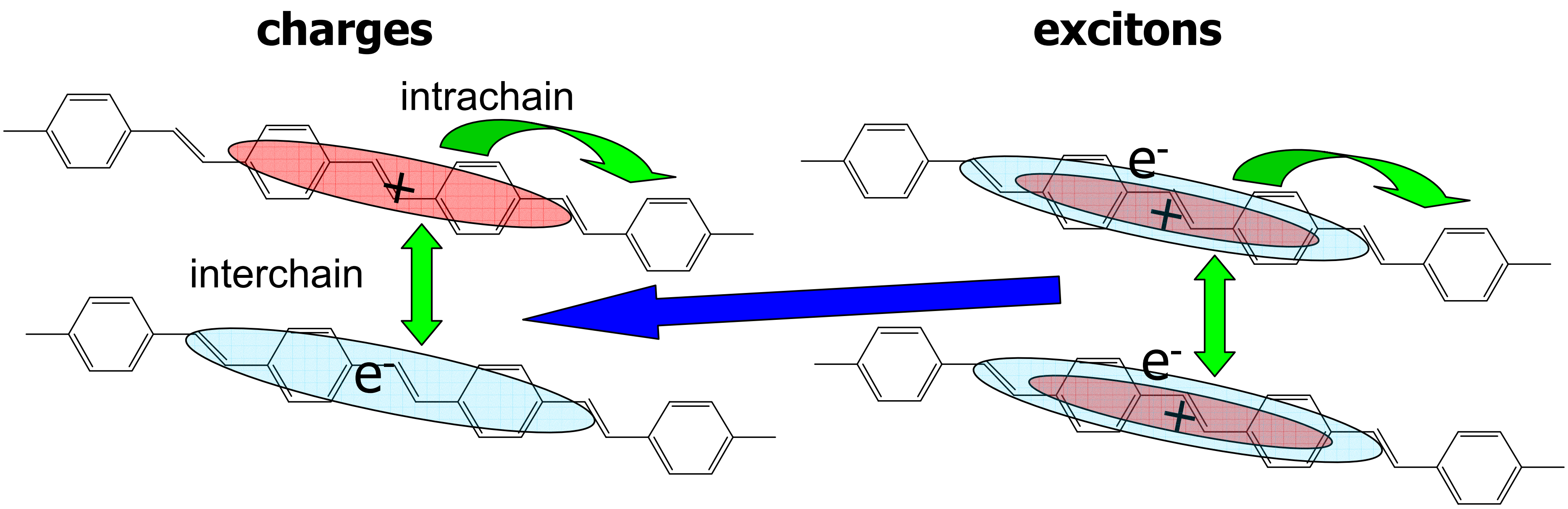
Organic materials in opto-electronic devices



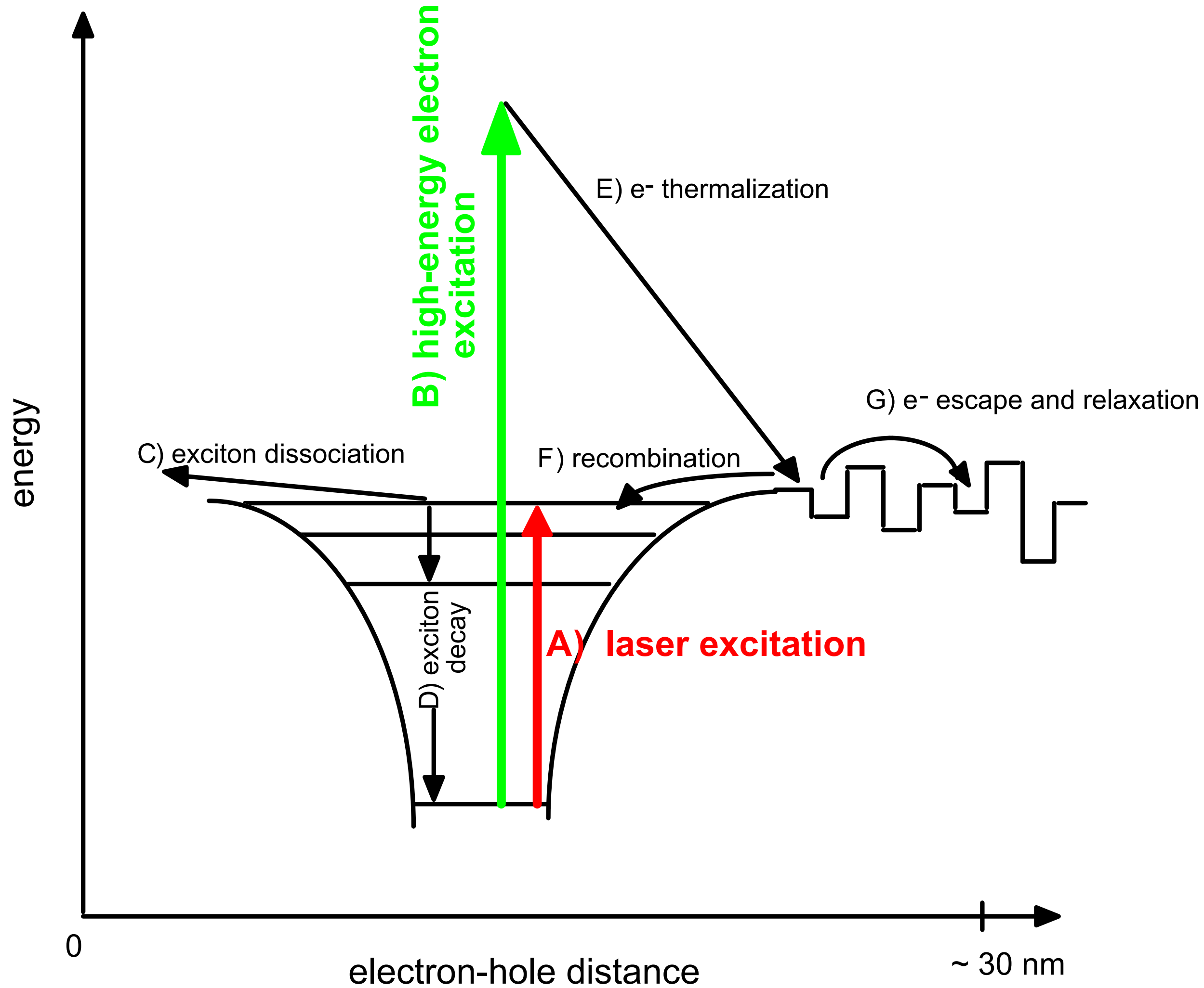


Fundamental knowledge needed for improved device perfomance

- factors governing motion of charges and excitons
- efficiency of charge recombination
- decay channels of excitons: fluorescence, dissociation, annihilation
- quantum yield for photogeneration of charges



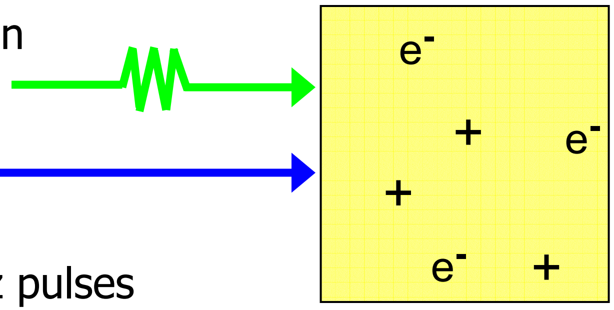
Study of ultrafast processes



Electron versus laser pulses

Formation of charges

5 MeV electron pulses



Detection

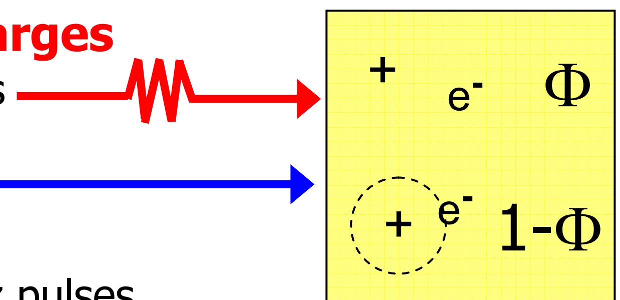
optical or THz pulses

<u>charges:</u>

- concentration on psec timescale known
- *absolute values* of extinction coefficient and THz mobility
- decay mechanism and kinetics

Formation of excitons and/or charges

laser pulses



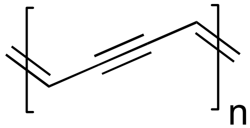
Detection

optical or THz pulses

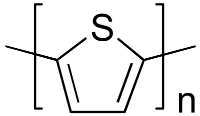
<u>excitons and charges</u>

- quantum yield Φ
- exciton properties and dynamics

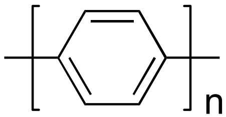
conjugated polymers



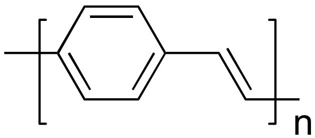
polydiacetylene



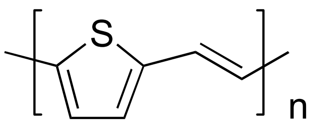
polythiophene



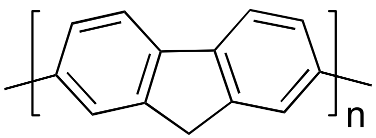
poly(p-phenylene)(PPP)



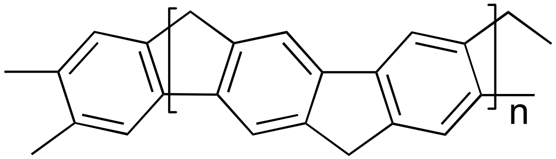
poly(p-phenylene vinylene) (PPV)



poly(thienylene vinylene) (PTV)



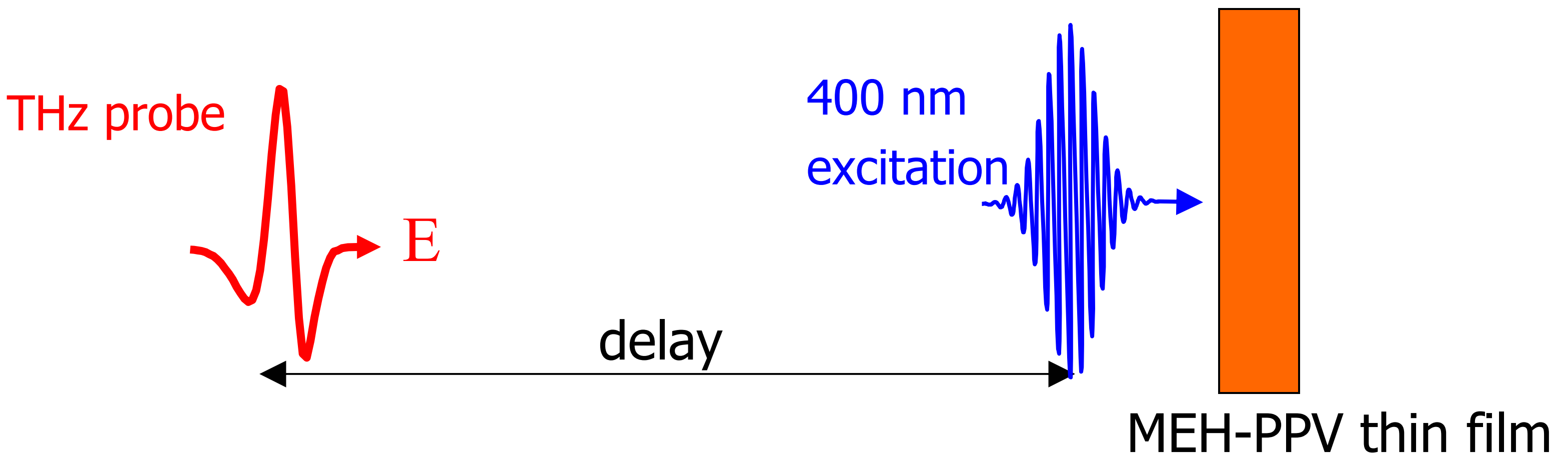
polyfluorene



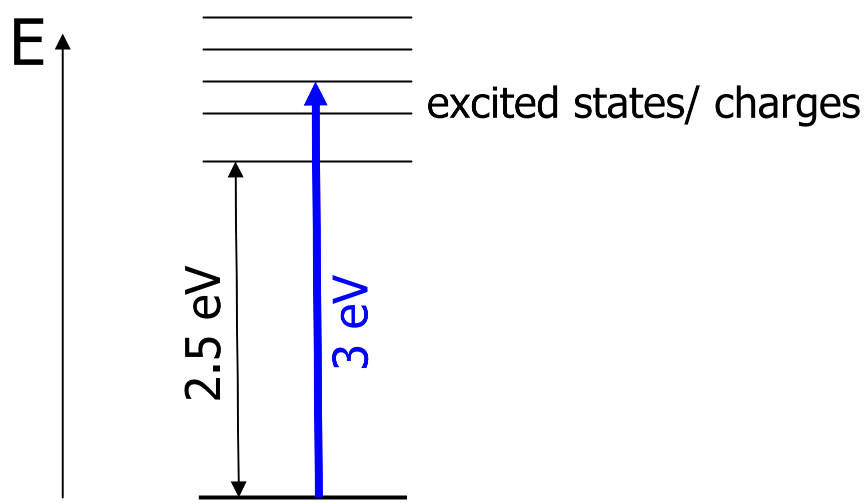
ladder-type PPP

<u>Effects of:</u> backbone, substituents, defects, temperature, morphology (dilute solution, thin films, bulk) spin-coating, annealing....

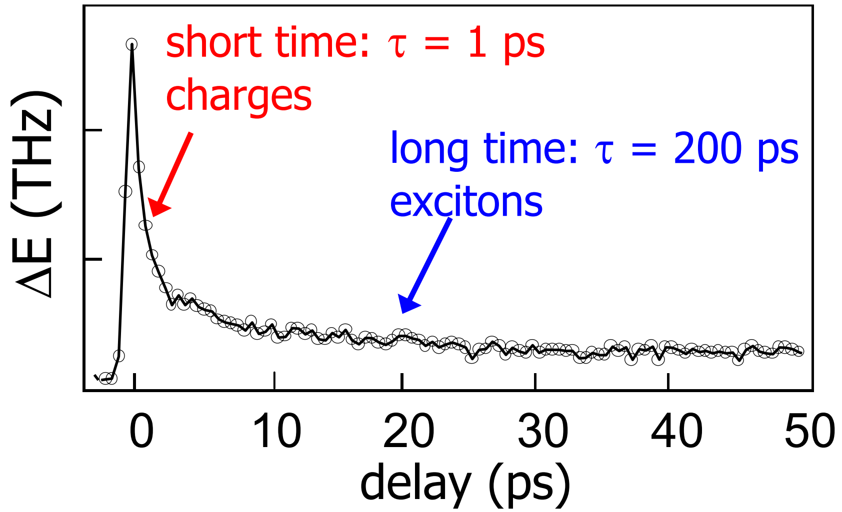
Photogeneration efficiency of charges in MEH-PPV

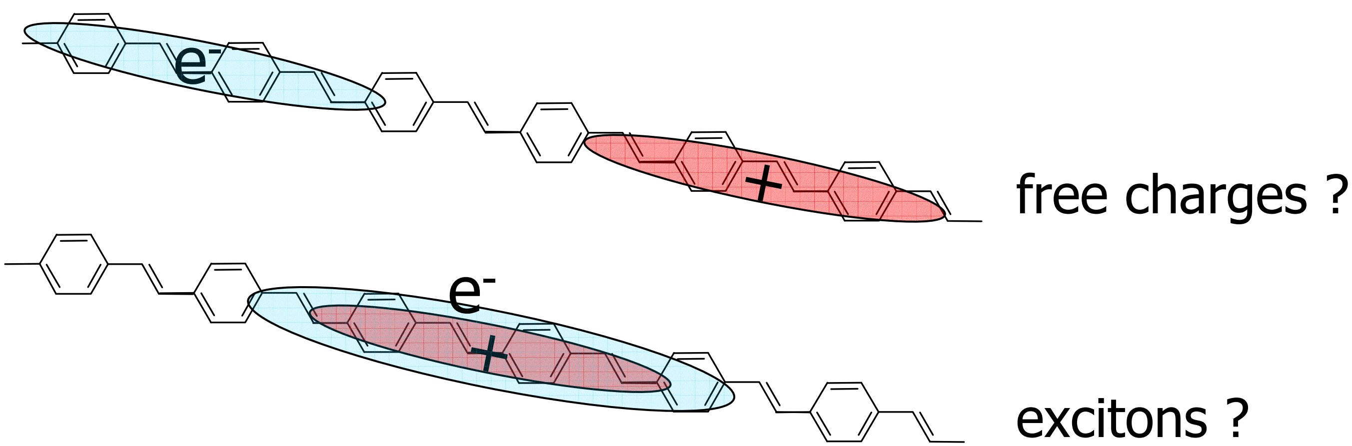


1 THz = 10^{12} Hz = 4 meV

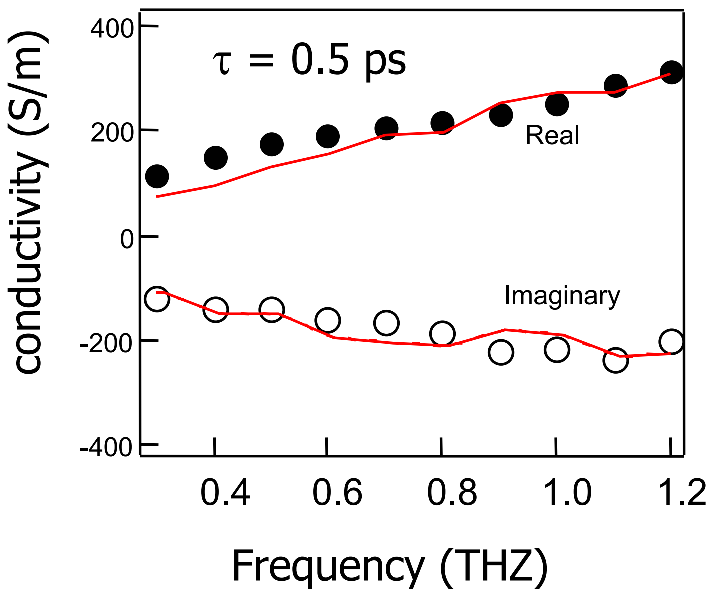


Time resolved information



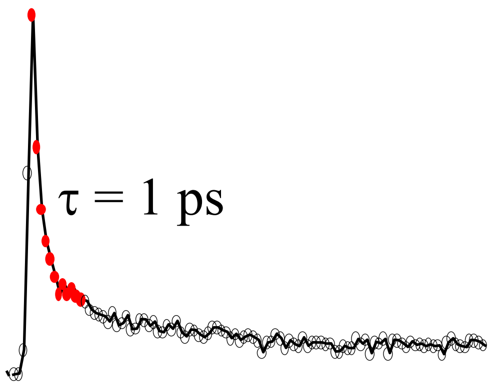


Frequency resolved information at 'short' times



Real and imaginary parts to conductivity: Free charges

Increase with frequency due to torsional disorder as predicted by theory for infinite static PPV chains



lower limit to μ(30 GHz)=10^{-3} $cm^2V^{-1}s^{-1}$: Free charge generation < 1%

Hendry et al., Phys. Rev. Lett. **92**, 196601, 1-4, (2004)

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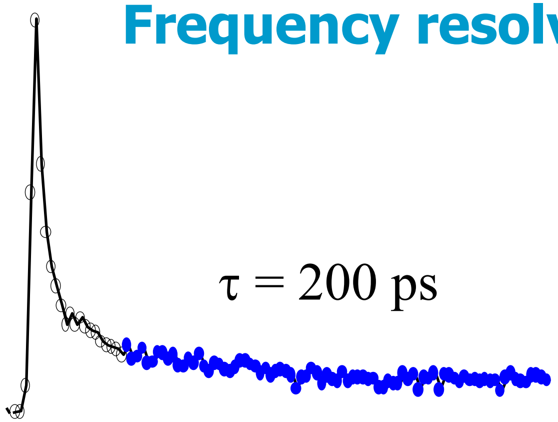
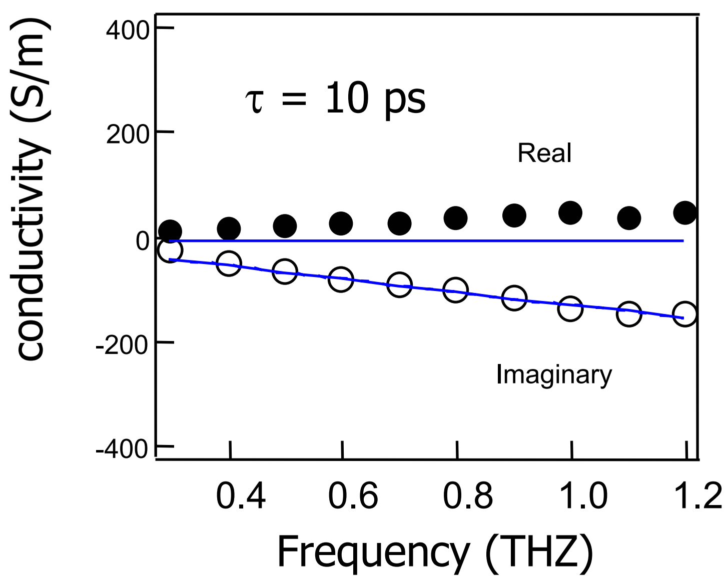
Frequency resolved information at 'long' times





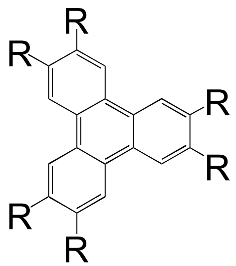
Mainly imaginary conductivity;

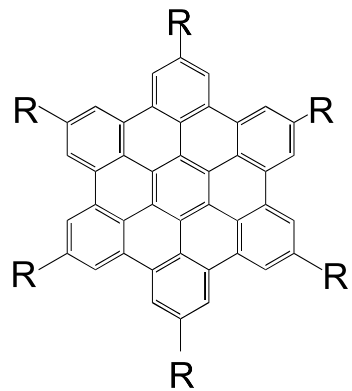
temporary displacement of bound charges: **Excitons**

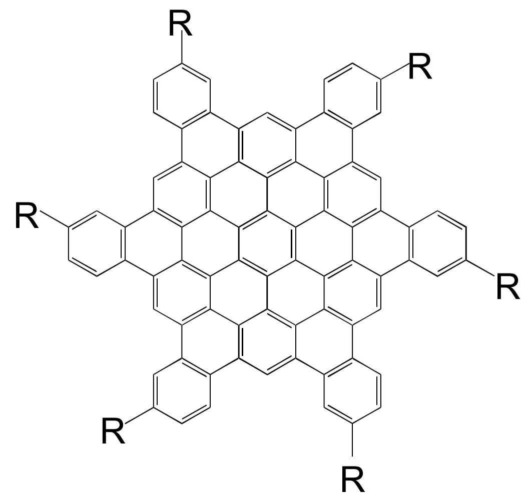
Clausius-Mossoti $\sigma=-i\omega n\varepsilon_0$ describes

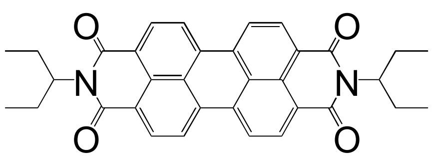
linear increase with frequency

discotic liquid crystalline materials

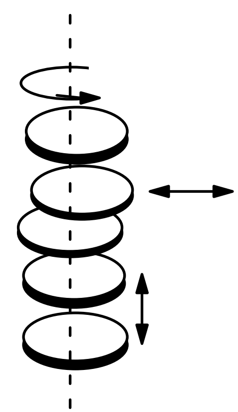






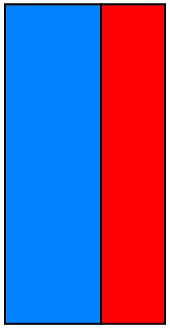


disorder along
the columns

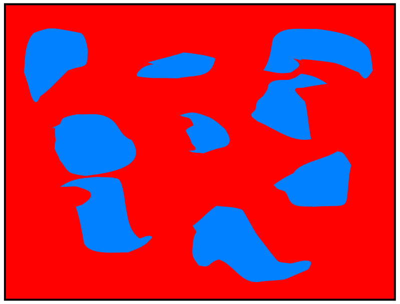


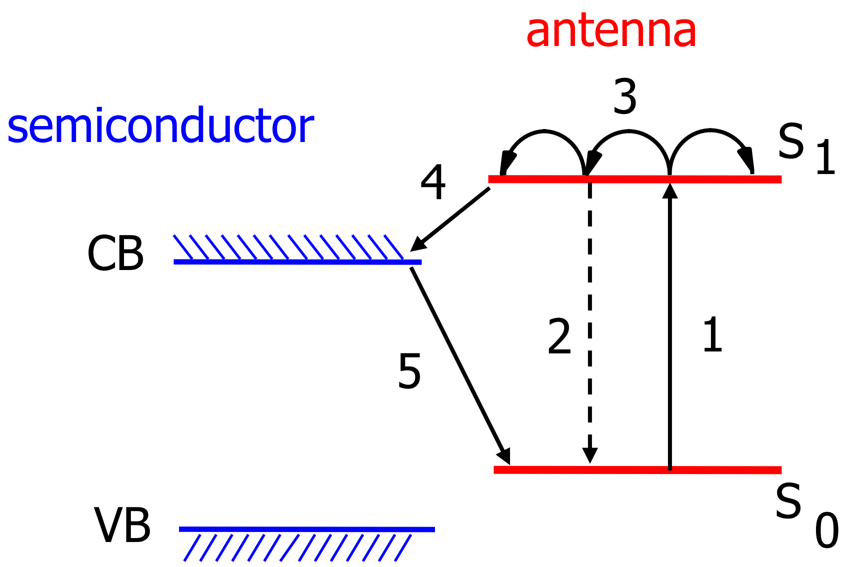
composite systems

bilayer



heterogeneous blend





1: photo-excitation
2: (non)radiative decay
3: exciton diffusion and annihilation
4: interfacial electron transfer
5: interfacial charge recombination

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Conclusion

- **Laser system is expected to be operational early 2005**
- **Electron pulses available 2005/2006**
- **New facility will help to unravel the nature and dynamics of excitons and charge carriers in functional materials**

DNA

How mobile are charges in DNA?

- oxidative damage to DNA (mutations)
- DNA as a molecular wire

--------G G G G--------   --------A A A A--------   --------G A G A--------
--------C C C C--------   --------T T T T--------   --------C T C T--------

Ionization (~ 6 eV needed) with high-energy electron pulse.

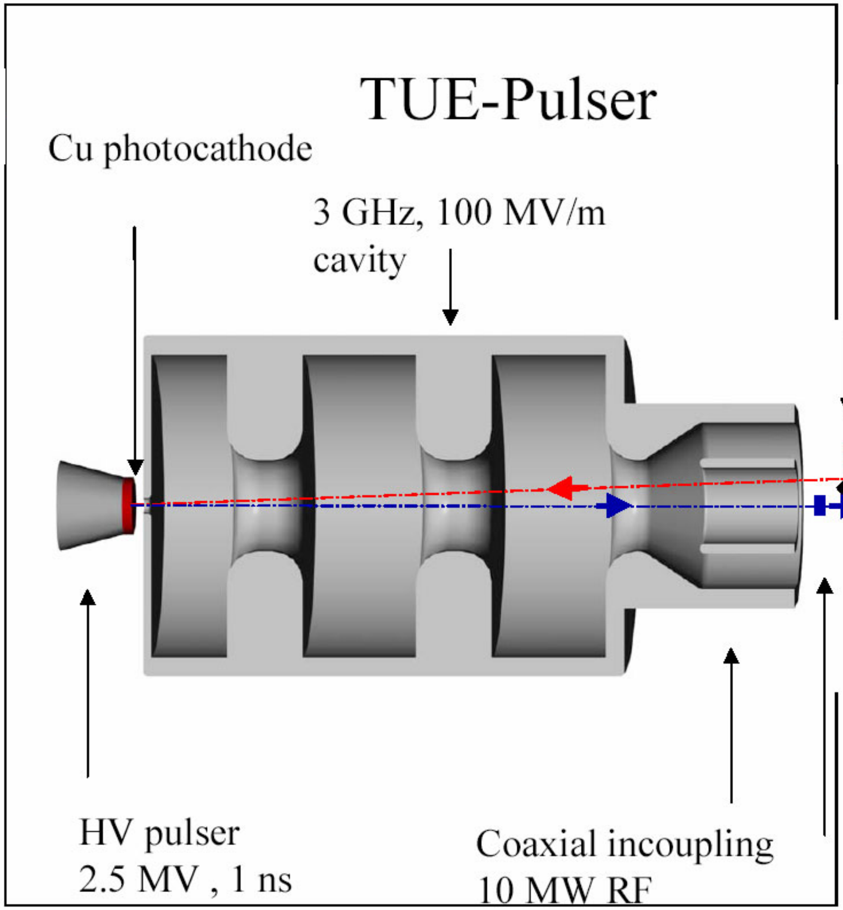
Monitoring of charges by optical absorption and THz conductivity.

Holy Grail

To make an important contribution to the upcoming era of molecular electronics.

To be able to predict the properties of charge carriers and excitons in (not yet existing) materials.

laser driven electron accelerator



FEL 2002, ANL, Chicago

BROOKHAVEN NATIONAL LABORATORY

TU Delft

Motivation

Towards novel electronics based on **organic molecular materials** (instead of e.g. Si) as active component in **opto-electronic devices**.

Advantages include:

- flexible
- easy to process
- tunable properties
- light weight
- cheap

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Clausius-Mossoti $\sigma = -i\,\omega\, n\,\varepsilon_0 \varepsilon$

The product of the exciton density (*n*) and the polarizabiliy (α) determine the imaginary conductivity (σ) .

Literature: $\alpha = 800\text{–}3000\ \mathring{A}^3$ (Gelinck et al. Phys Rev B **62**, 1489 (2000))

This gives an exciton density corrsponding to a photogeneration quantum yield between 0.3 and 1.

Since few charges are generated $\alpha \sim 800\ \mathring{A}^3$

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Theoretical support

- electronic structure calculations (HF, DFT etc.)
- quantum mechanical calcs. on charge and exciton motion
- Monte Carlo simulations of hopping transport