

**B6 (May): Theory of transfer processes
and optical spectra of molecule,
inorganic semiconductor, and
metal nanoparticle hybrid systems**

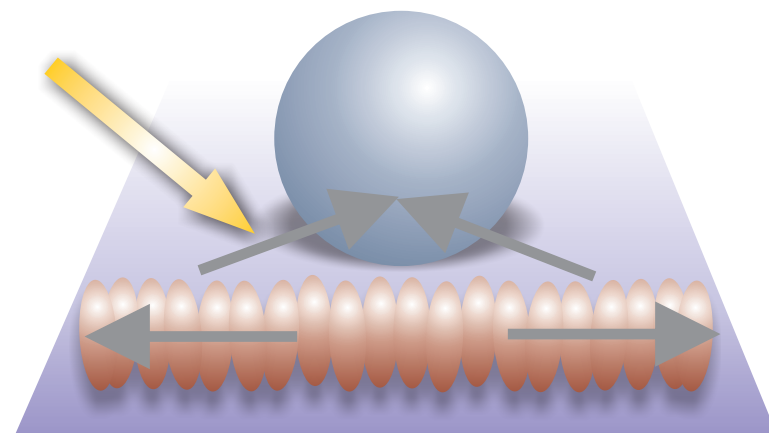
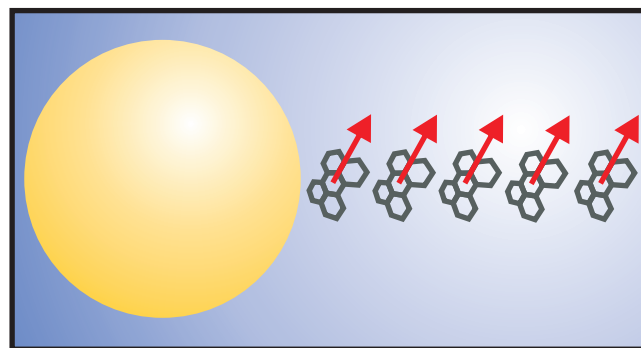
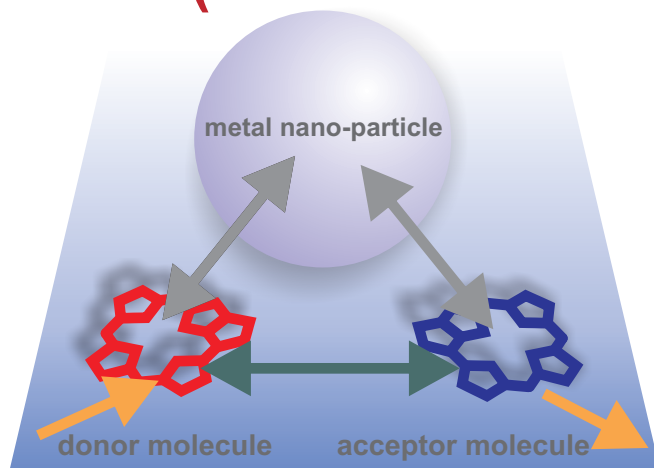
**Volkhard May, Institute of Physics
Humboldt-University at Berlin**



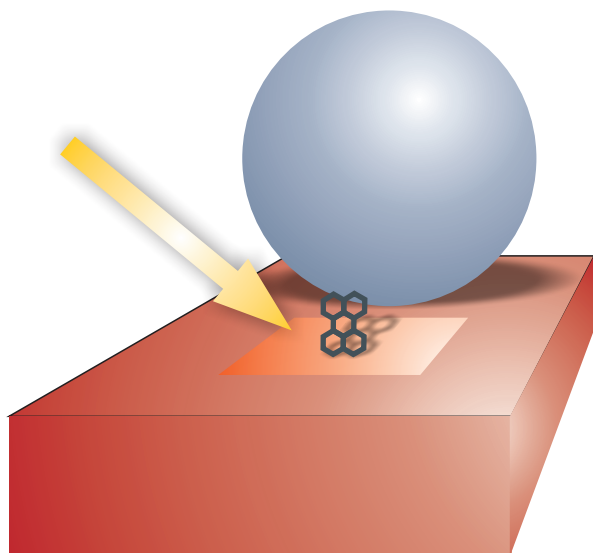
**Sub-project 1: Charge transfer kinetics at the HIOS
interface**

**Sub-project 2: Excitation energy transfer kinetics
at the HIOS interface: Effects of metal
nanoparticles**

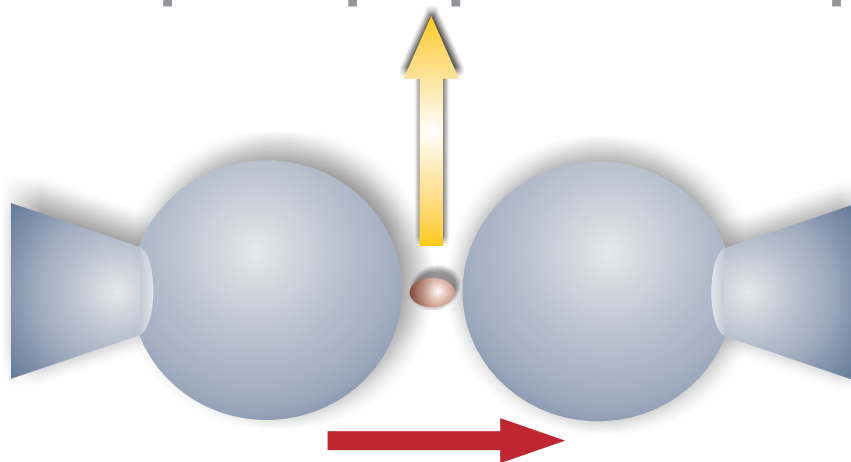
Sub-project 1 (2011-15): Plasmon enhancement of COM-ISC
optical properties and excitation energy transfer
-> B1 (Aichele/Benson)



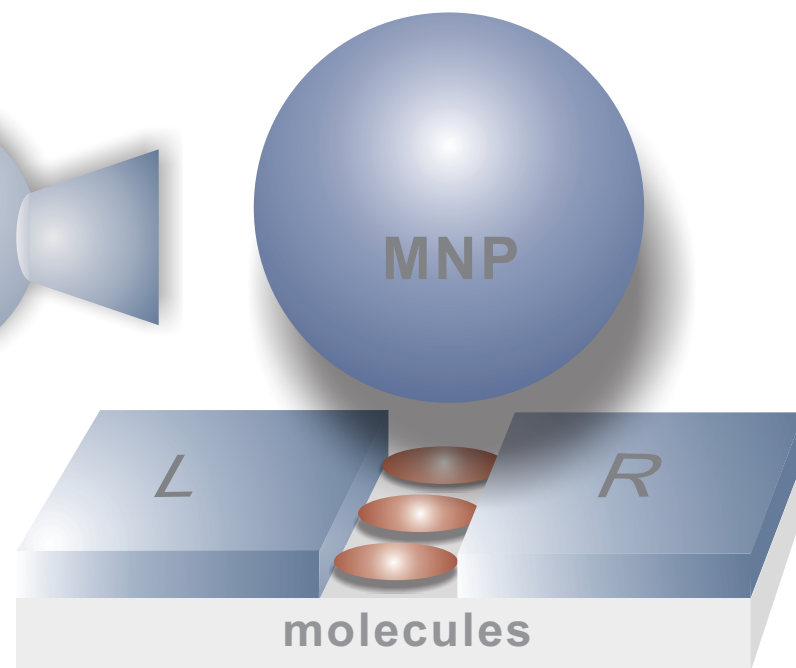
plasmon affected excitation energy transfer
and optical properties of supramolecular systems



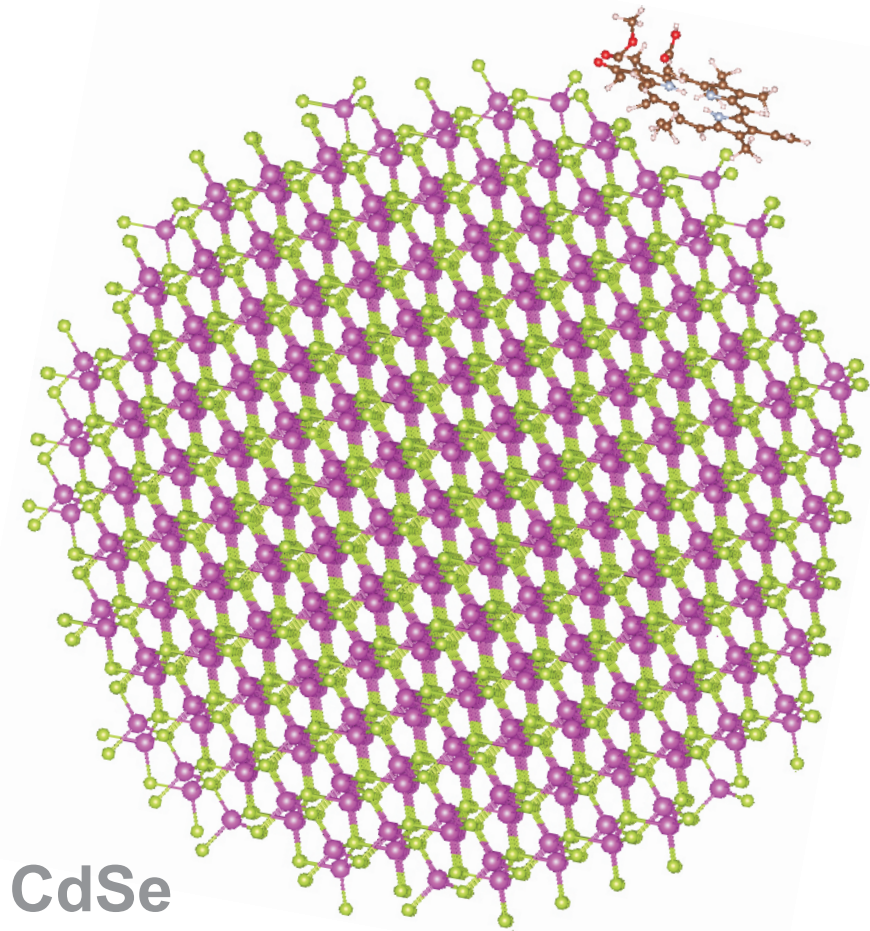
plasmon enhanced
interfacial
electron transfer



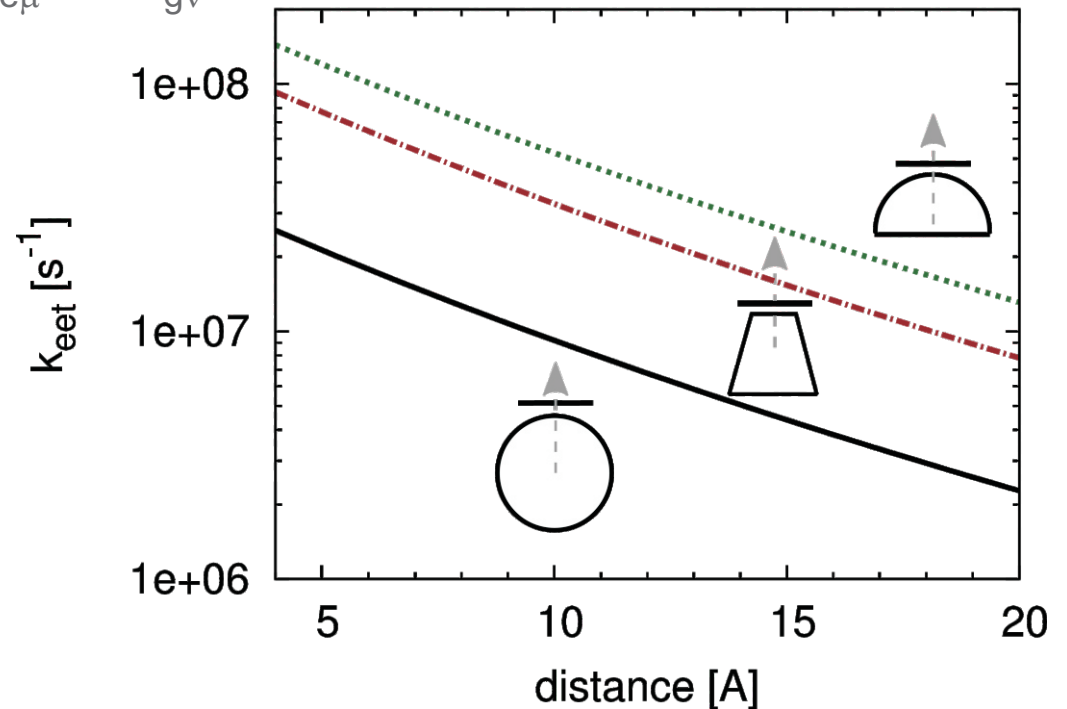
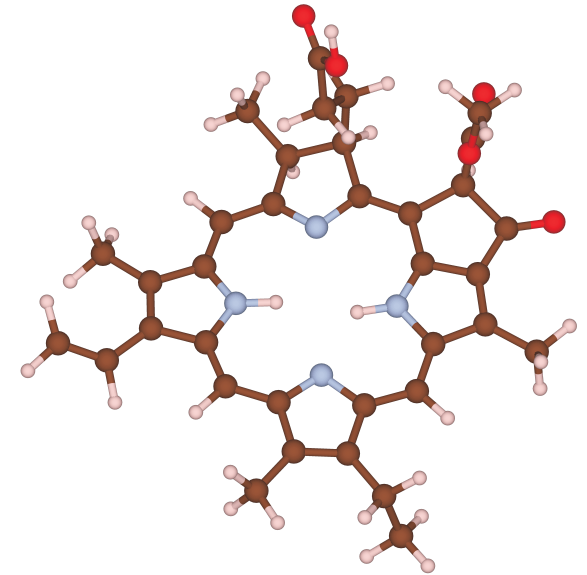
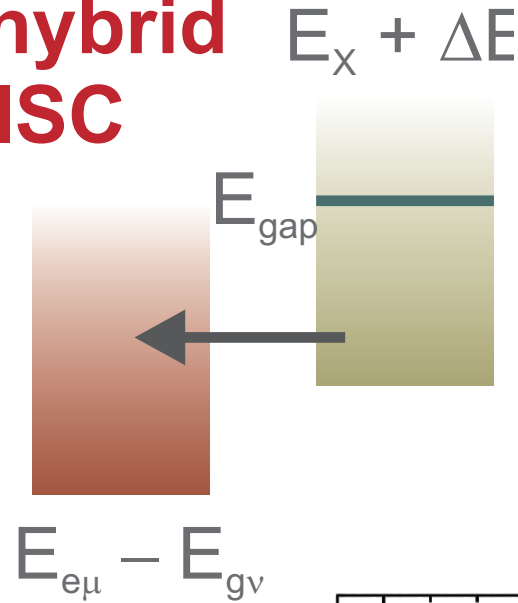
plasmon enhanced
single molecule
electro-luminescence



**Sub-project 2 (2011-15):
Exciton formation in nanohybrid
systems of COMs and an ISC
-> B8 Riechert/Grahn**



**CdSe
nano-crystal
Pheophorbide-a
complex**



transfer rate versus NC-molecule distance

Sub-Project 1

Y. Zhang and V. May, *Plasmon-Enhanced Molecular Electroluminescence: Effects of Nonlinear Excitation and Molecular Cooperativity*, Phys. Rev. B 89, 245441 (2014).

L. Wang and V. May, *Plasmon Enhanced Heterogeneous Electron Transfer: A Model Study*, J. Phys. Chem. C 118, 2812 (2014).

J. Megow and V. May, *Plasmon Enhanced Molecular Absorption: A Mixed Quantum-Classical Description of Supramolecular Complexes Attached to a Metal Nanoparticle*, Chem. Phys. 428, 6 (2014).

Y. Zhang, Y. Zelinskyy, and V. May, *Plasmon Enhanced Electroluminescence of a Single Molecule: A Theoretical Study*, Phys. Rev. B 88, 155426 (2013)

Y. Zelinskyy, Y. Zhang, and V. May, *Photoinduced Dynamics in a Molecule Metal Nanoparticle Complex: Mean-Field Approximation Versus Exact Treatment of the Interaction*, J. Chem. Phys. 138, 114704 (2013)

G. Kyas, Y. Zelinskyy, Y. Zhang, and V. May, *Spatio-Temporal Excitation Energy Localization in a Supramolecular Complex Coupled to a Metal-Nanoparticle*, Ann. Phys. (Berlin), 525, 189 (2013), special issue "Ultrafast Phenomena at the Nanoscale"

Y. Zhang, Y. Zelinskyy, and V. May, *Time and Frequency Resolved Emission of Molecular Systems Coupled to a Metal Nanoparticle*, J. Nanophot. 6, 063533 (2012)

Y. Zhang, Y. Zelinskyy, and V. May, *Plasmon Enhanced Single Molecule Electroluminescence*, J. Phys. Chem. C 116, 25962 (2012)

Y. Zelinskyy, Y. Zhang, and V. May, *A Supramolecular Complex Coupled to a Metal Nanoparticle: Computational Studies on the Optical Absorption*, J. Phys. Chem. A 116, 11330 (2012), Joern-Manz-Festschrift

Y. Zelinskyy and V. May, *Photoinduced Switching of the Current through a Single Molecule: Effects of Surface Plasmon Excitations of the Leads*, Nano Lett. 12, 446 (2012)

Y. Zelinskyy and V. May, *Optical Properties of Supramolecular Complexes Coupled to a Metal-Nanoparticle: A Computational Study*, Chem. Phys. Lett. 511, 372 (2011).

G. Kyas and V. May, *Density Matrix Based Microscopic Theory of Molecule Metal-Nanoparticle Interactions: Linear Absorbance and Plasmon Enhancement of Intermolecular Excitation Energy Transfer*, J. Chem. Phys. 134, 034701 (2011).

Sub-Project 2

D. Ziemann and V. May, *Distant and Shape Dependent Excitation Energy Transfer in Nanohybrid Systems: Computations on a Pheophorbide-a CdSe Nanocrystals Complex* J. Phys. Chem. Lett. 5, 1203 (2014).

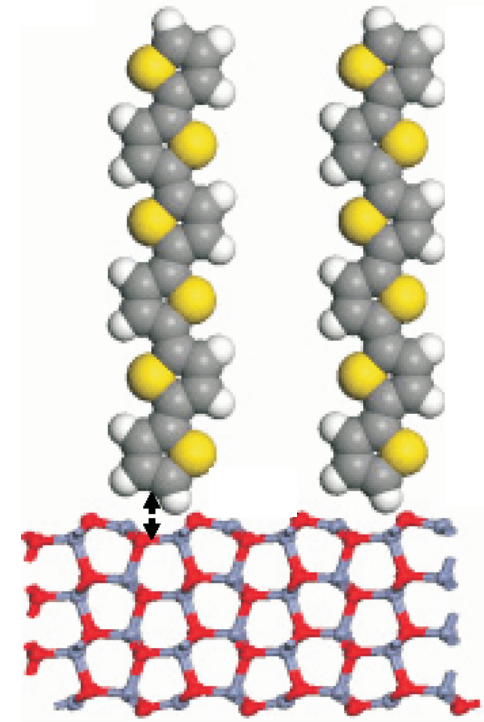
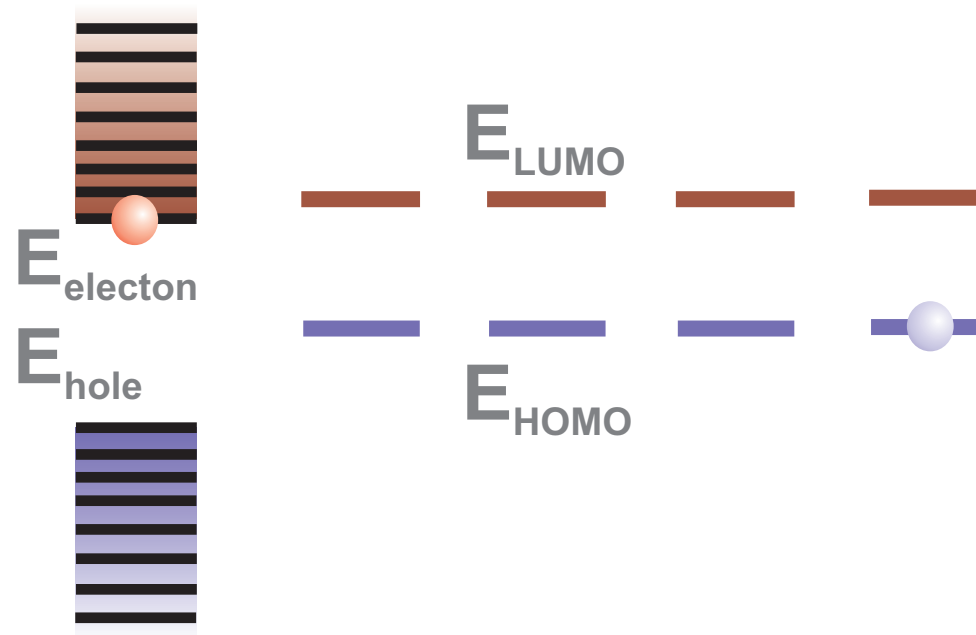
J. Megow, Th. Körzdörfer, Th. Renger, M. Sparenberg, S. Blumstengel, F. Henneberger, and V. May, *Calculating Optical Absorption Spectra of Thin Polycrystalline Films: Structural Disorder and Site-Dependent Electronic Polarization of Molecules* (in preparation)

J. Megow, M. Röhr, M. Schmidt am Busch, Th. Renger, R. Mitric, S. Kirstein, J. Rabe, and V. May, *Understanding the Exciton Spectrum of Double-Walled Tubular Dye-Aggregates: Importance of Site-Dependent Excitation Energy Shifts Due to Environmental Polarization* (in preparation)

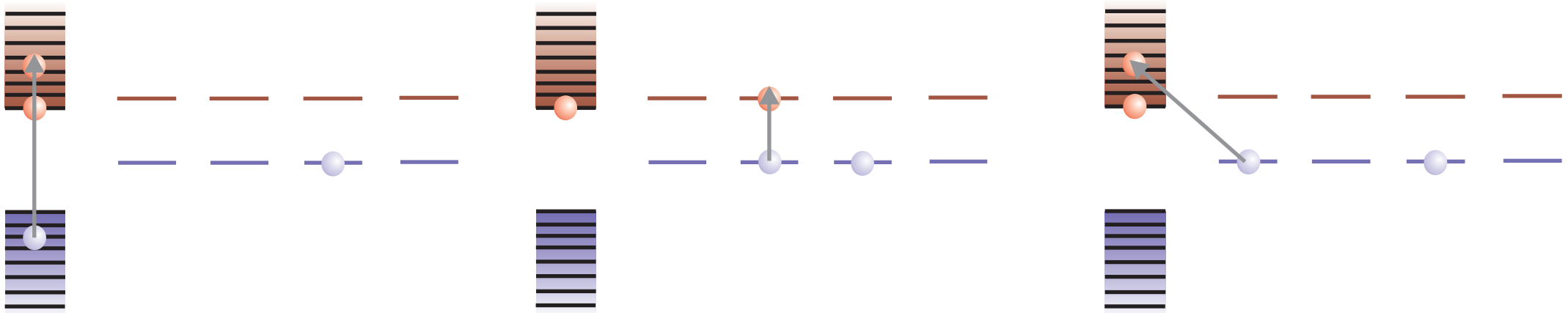
Sub-project 1: Charge transfer kinetics at the HIOS interface

electron hole kinetics at
the interface

- ZnO cluster with thousands of atoms
- complex with 100 molecules
- semiempirical models for the excited states
- photoinduced dynamics



collaboration with A4 (Heimel), B3 (Blumstengel), B7 (Neher),
B11 (Draxl), B12 (Knorr/Richter)



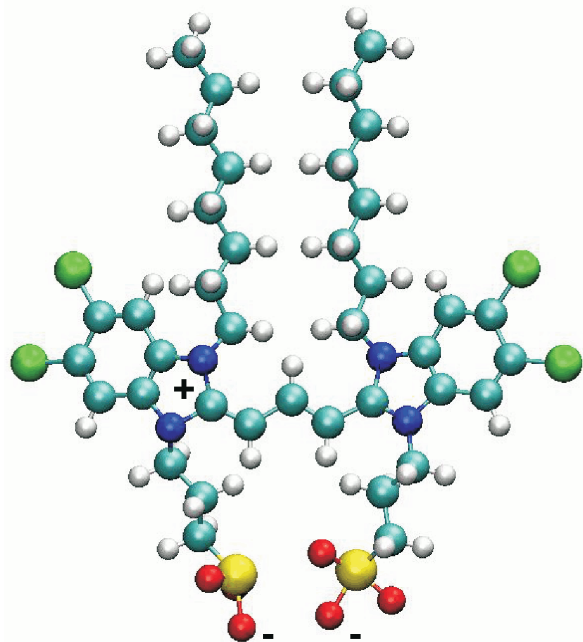
two electron-hole pair motion in a transient absorption experiment

Sub-project 2: Excitation energy transfer kinetics at the HIOS interface: Effects of Metal Nanoparticles

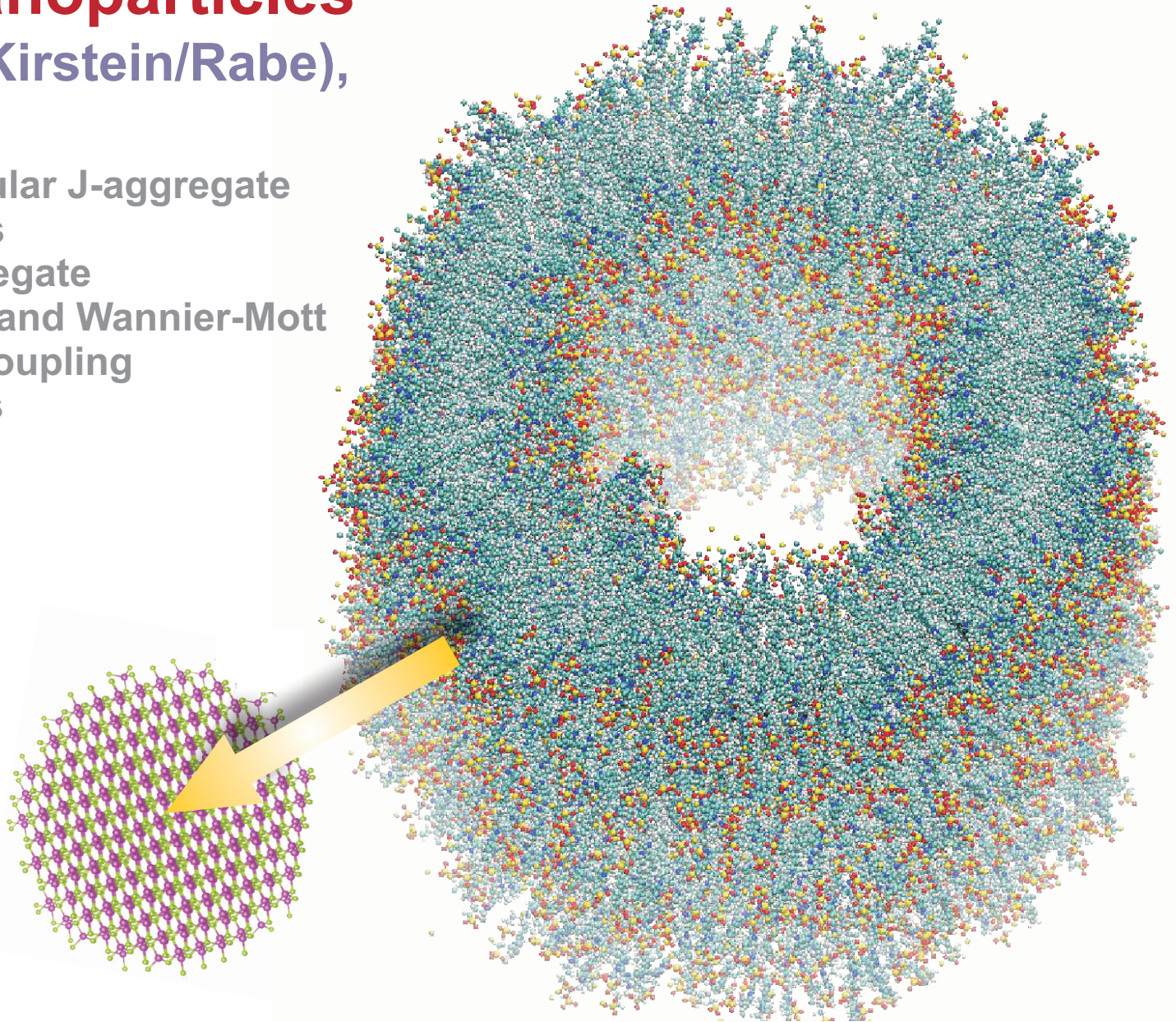
collaboration with A6 (Kirstein/Rabe),
B12 (Knorr/Richter)

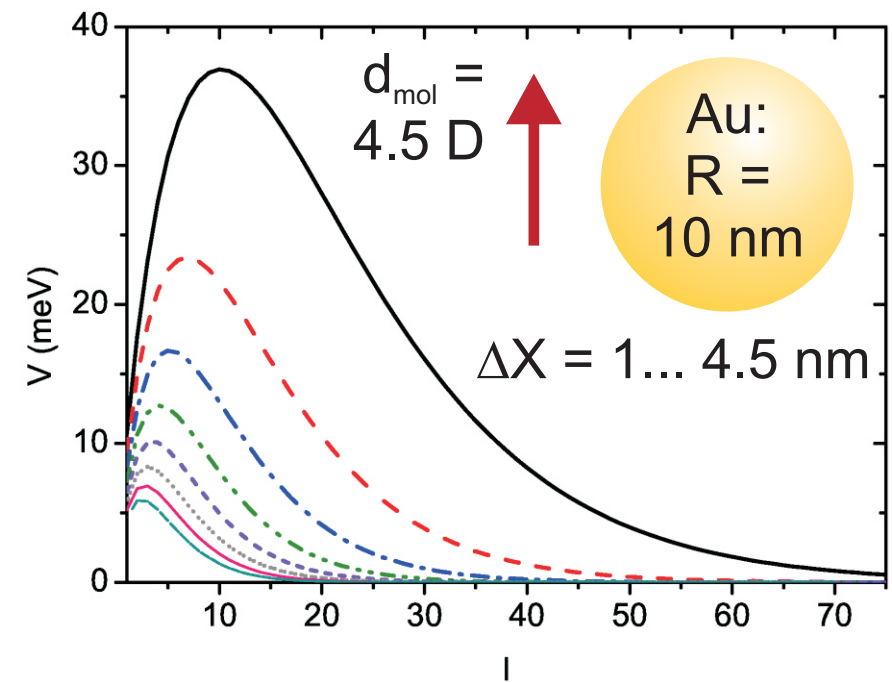
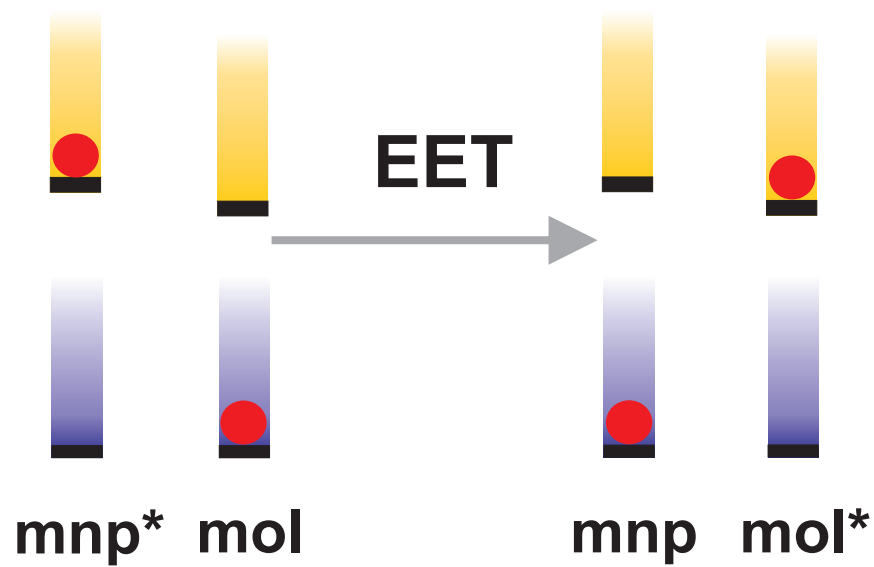
energy transfer between a tubular J-aggregate
and CdSe (CdTe) nano-crystals

- MD simulations of the J-aggregate
- determination of Frenkel like and Wannier-Mott like exciton levels and their coupling
- effects of metal nanoparticles



C8S3 cyanine dye





Molecule–MNP Coulomb Interaction

**m-averaged molecular dipole
MNP multipole coupling**

excitation energy exchange coupling (excitonic coupling)

$$V_{e0,kg} = \langle \varphi_e \psi_0 | \sum_{j,u} \frac{e^2}{|\mathbf{x}_j - \mathbf{y}_u|} | \psi_k \varphi_g \rangle = \int d^3\mathbf{x} d^3\mathbf{y} \frac{\rho_{k0}^*(\mathbf{x}) \rho_{eg}(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|}$$

transition density $\rho_{k0}(\mathbf{x}) = eN_{\text{el}} \int dx \delta(\mathbf{x} - \mathbf{x}_1) \psi_k^*(x) \psi_0(x)$

coupling to multipole plasmon excitations of a spherical MNP

$$V_{e0,lmg} = \sqrt{\frac{4\pi}{2l+1}} e q_{lm}^* [\mathbf{d}_{\text{mol}} \nabla \mathbf{x}] \frac{Y_{lm}(\vartheta, \varphi)}{X^{l+1}}$$