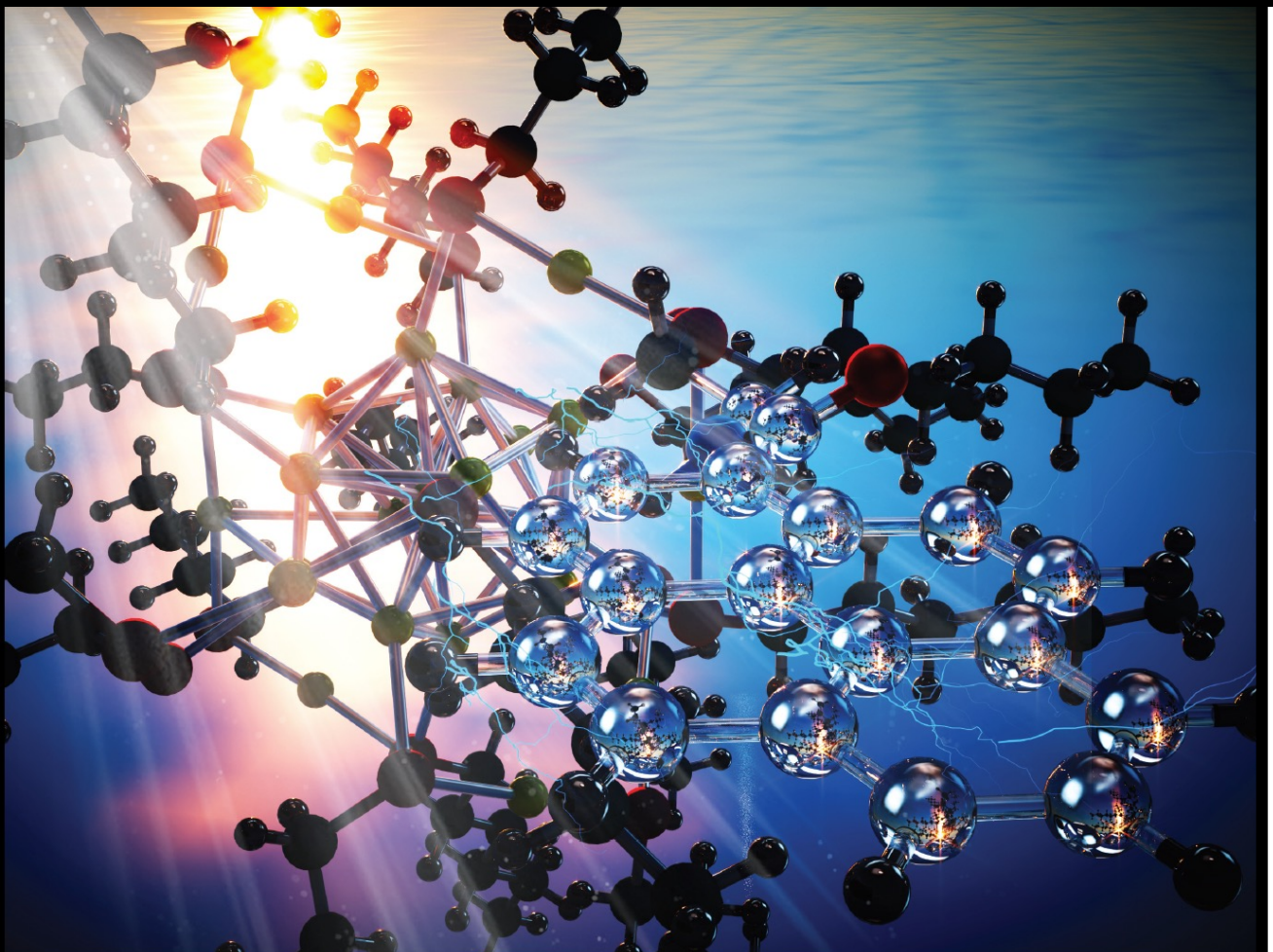
Quantum description of nano-objects for solar thermal energy storage



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Corentin Poidevin
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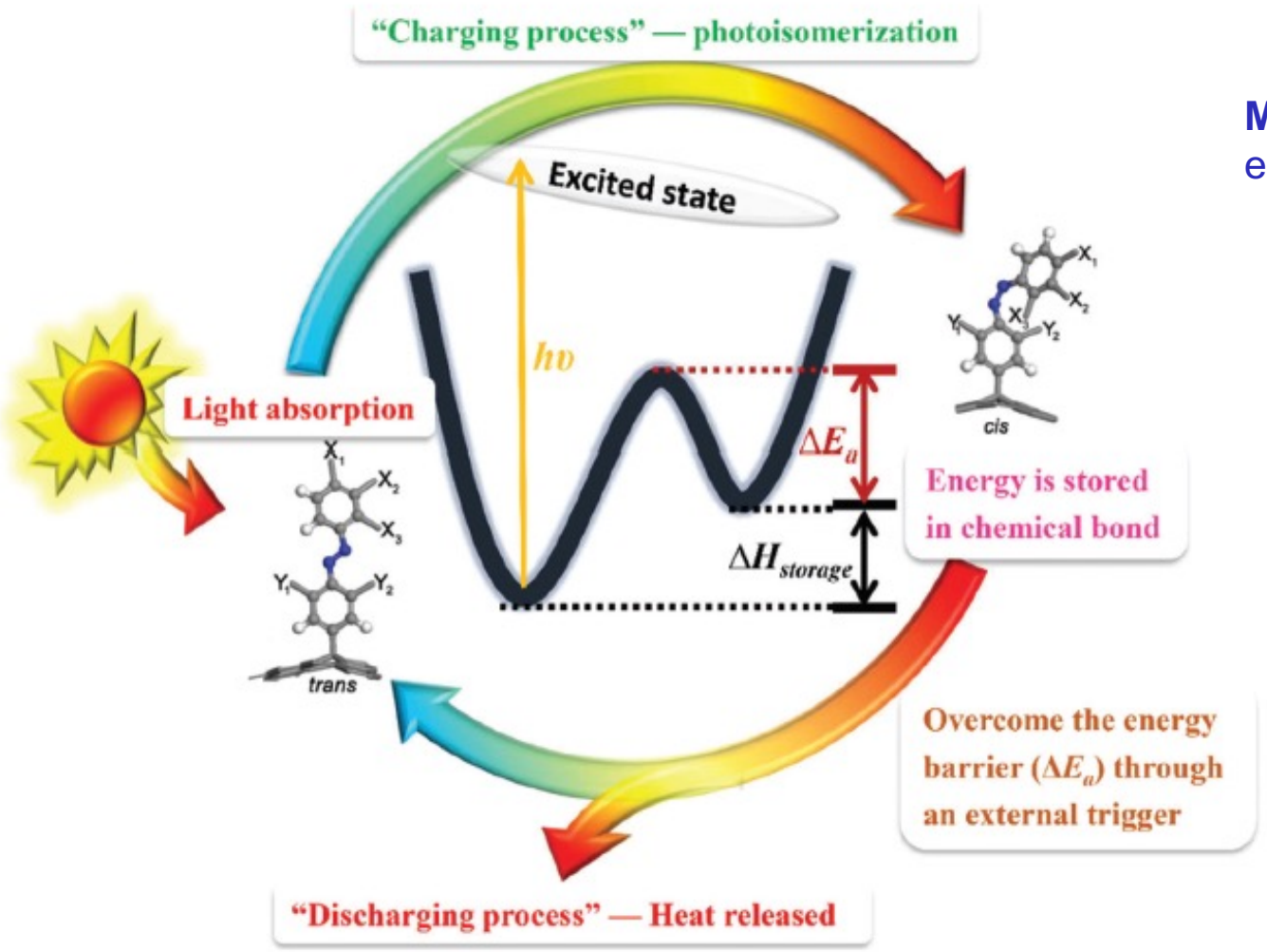
(IPEST, Faculty of science of Bizerte)

Adrian Domiguez-Castro,
Carlos R. Lien-Medrano,
Thomas Frauenheim
(BCCMS, Bremen University)

GDR NAME symposium, Rennes
November 10th 2023

Scientific context

❑ Organic photochromes for solar energy storage:



MOlecular **S**olar **T**hermal (**MOST**) energy storage systems

Chem. Rev., **2004**, *104*, 293-346.

Scientific context

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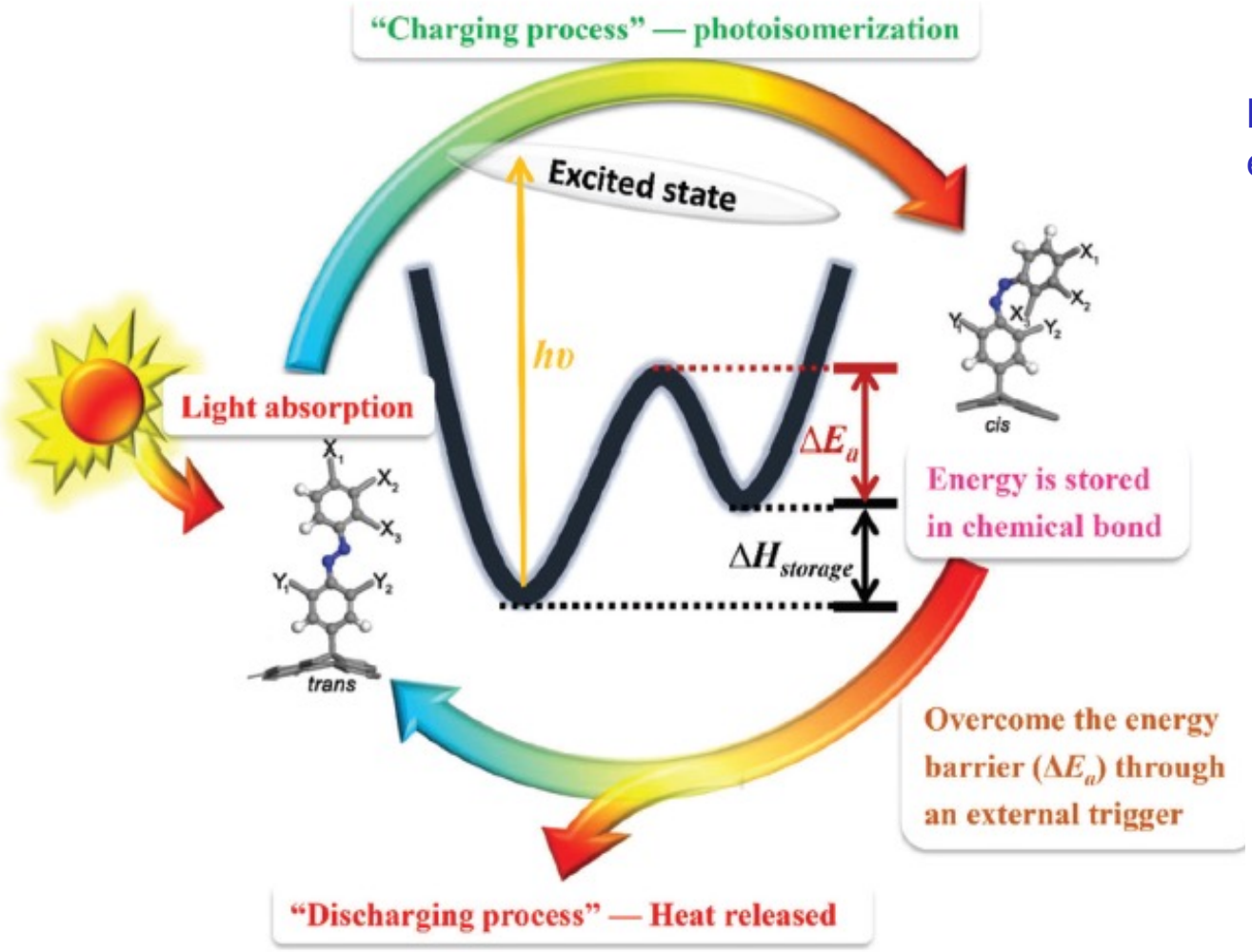

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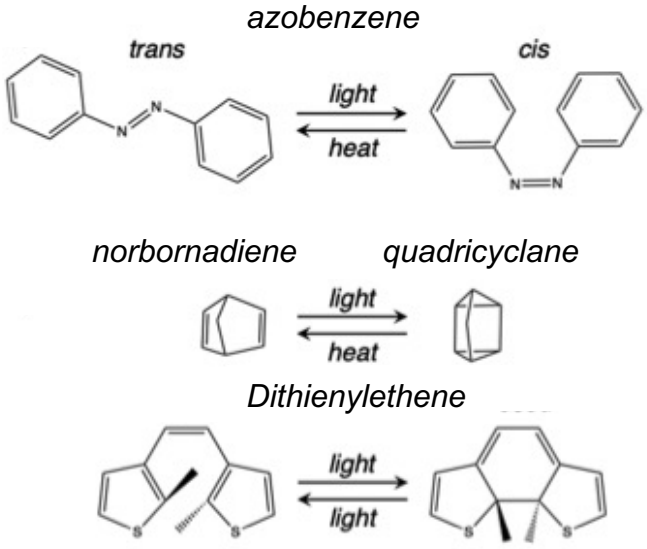

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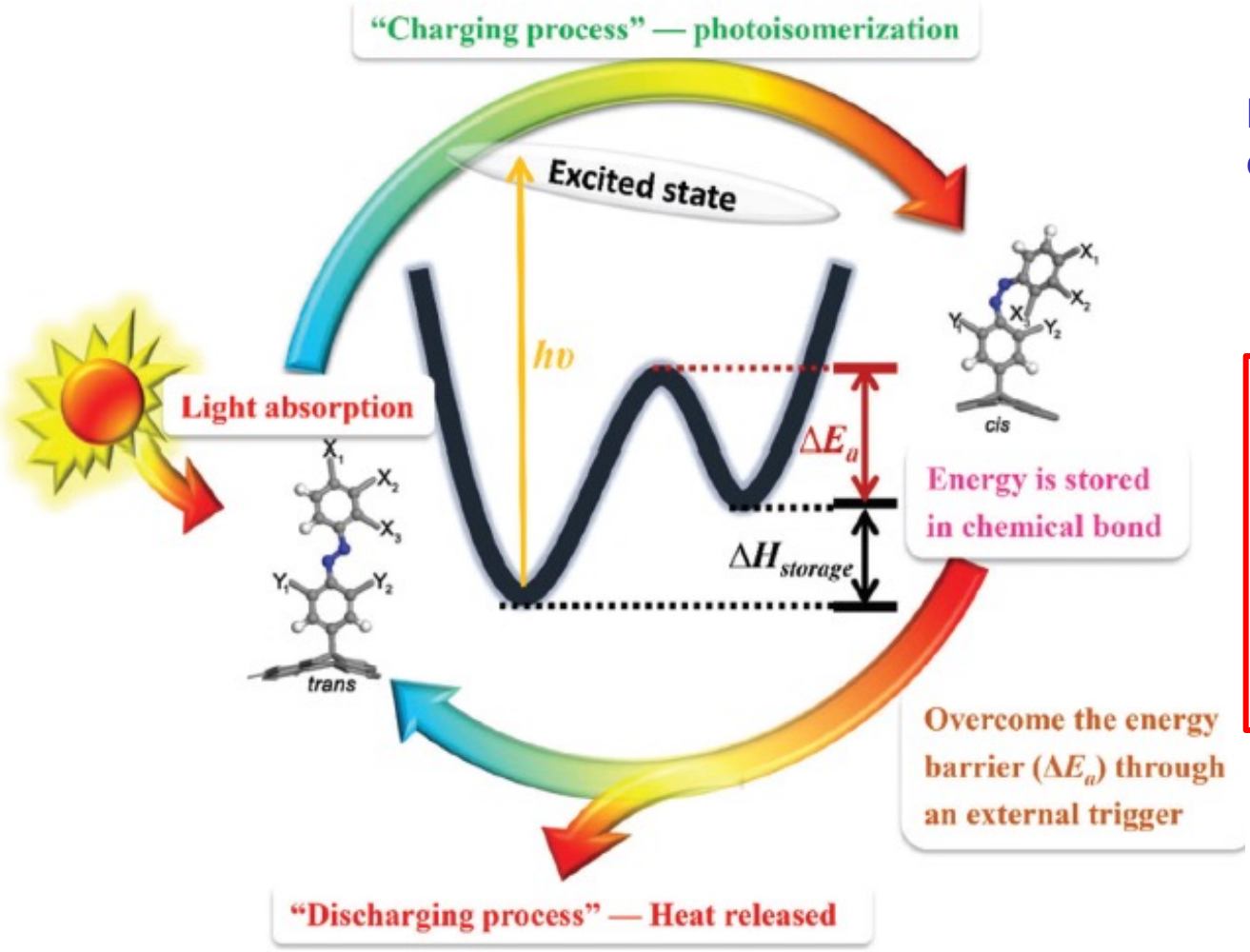
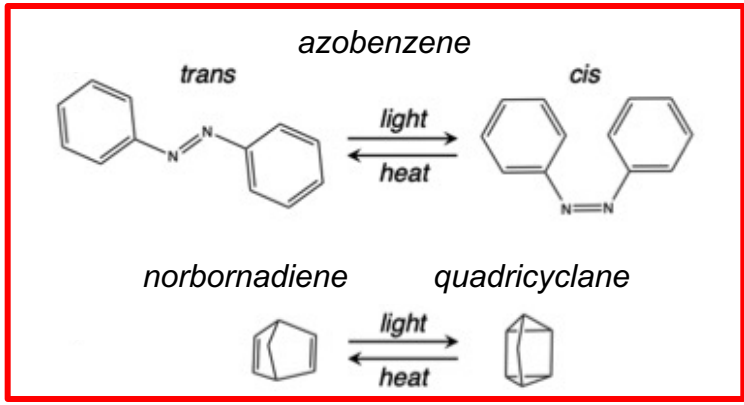
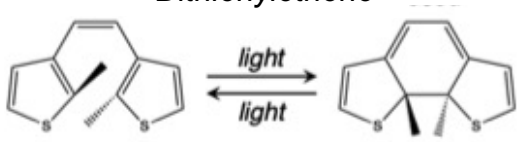


MOlecular **S**olar **T**hermal (**MOST**) energy storage systems

Thermal back isomerization



Dithienylethene



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Scientific context

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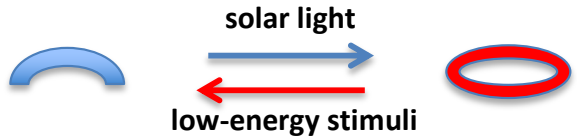
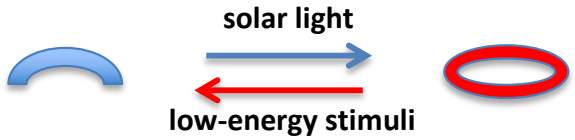


more stable isomer *less stable isomer*

MOST process in solution:
Energy stored = 10 - 100 KJ/mol.

Scientific context

❑ Organic photochromes for solar energy storage:



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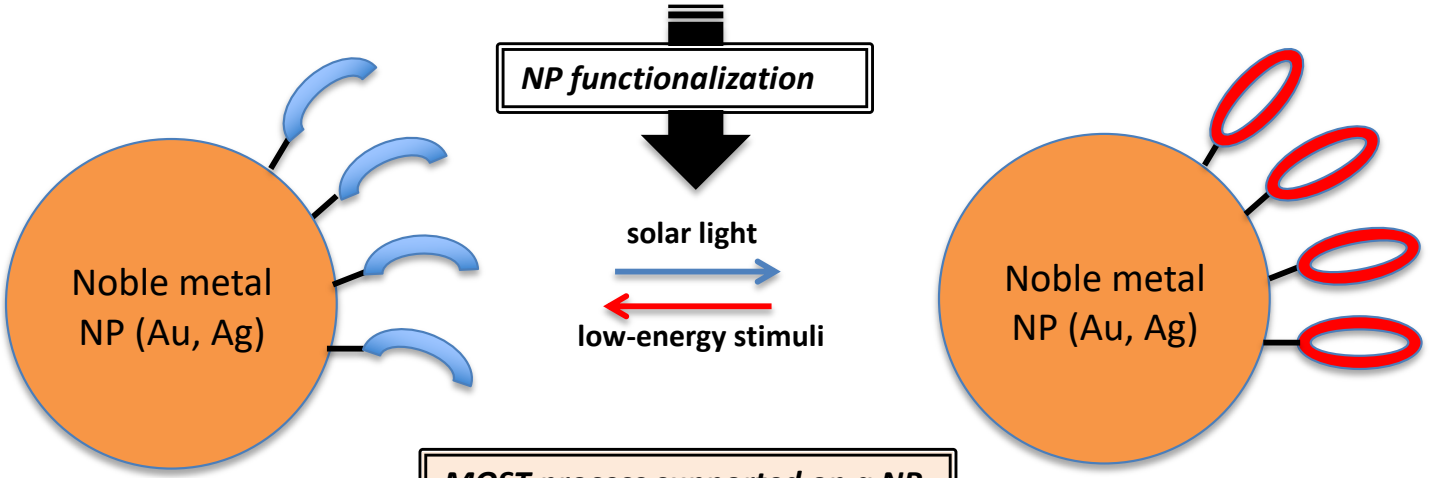


MOST process supported on a NP

Energy stored = ??? KJ/mol | ***Search of efficient NP-Photochromes devices***

FALCON project:
COMPUTATIONAL DESIGN

anr agence nationale de la recherche
AU SERVICE DE LA SCIENCE

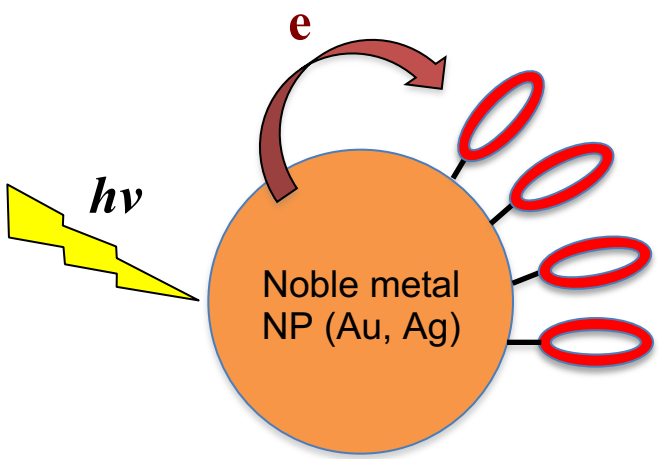
ANR Falcon (2020- 2024)

Scientific context

❑ Nanoparticles (NPs) functionalized with photoactive molecules:

- Photochemical functions within the molecules can be combined and interact with the metallic part properties: **enhanced or emerging properties**.

- Potential **photoinduced electron/ energy transfer** between the NP/molecules.



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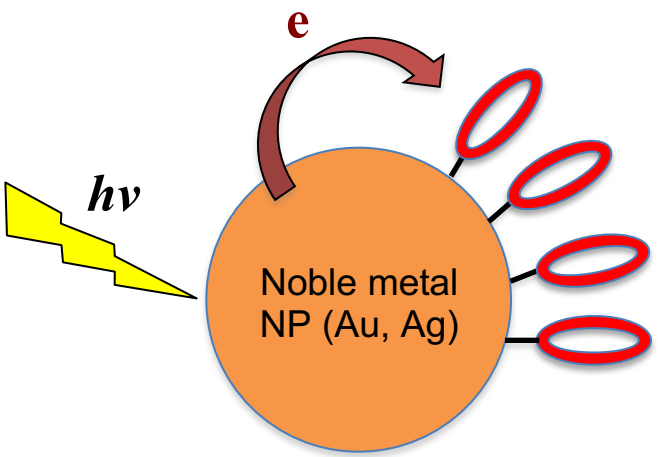
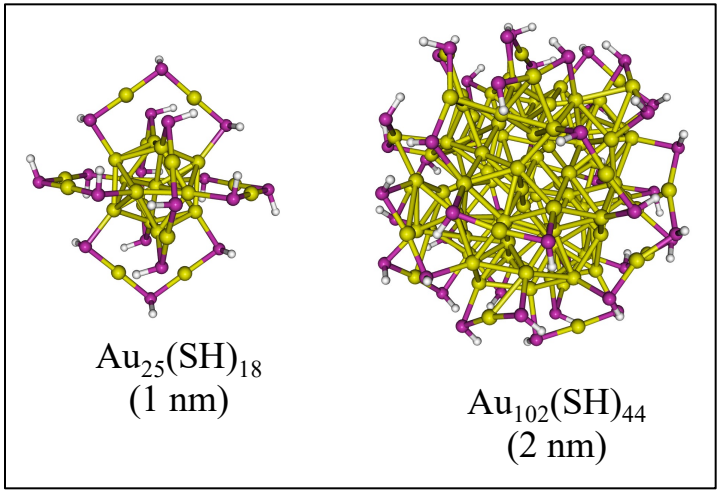
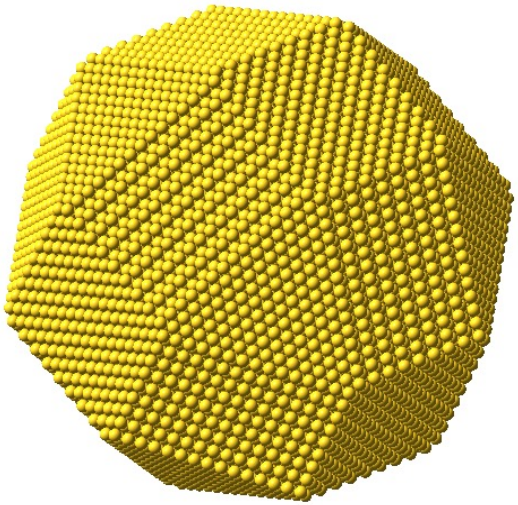


- Potential **photoinduced electron/ energy transfer** between the NP/molecules.

- NP properties are size and shape-dependent (molecular to metallic/**plasmonic**)

Gold Nanoclusters (GNC)



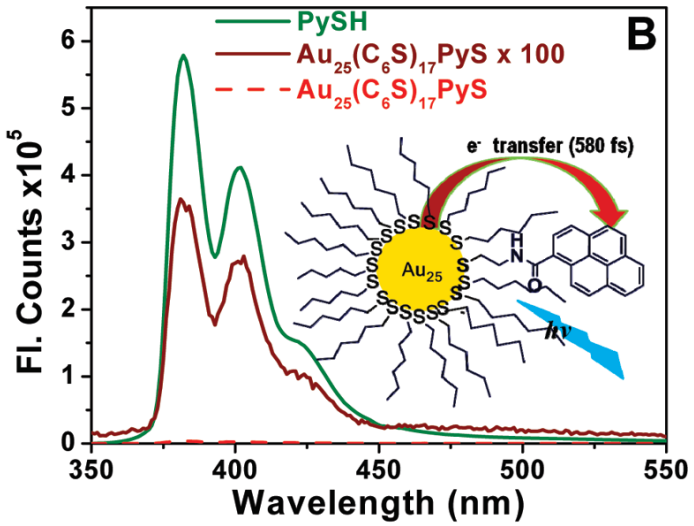


Au_{30211} (10 nm)

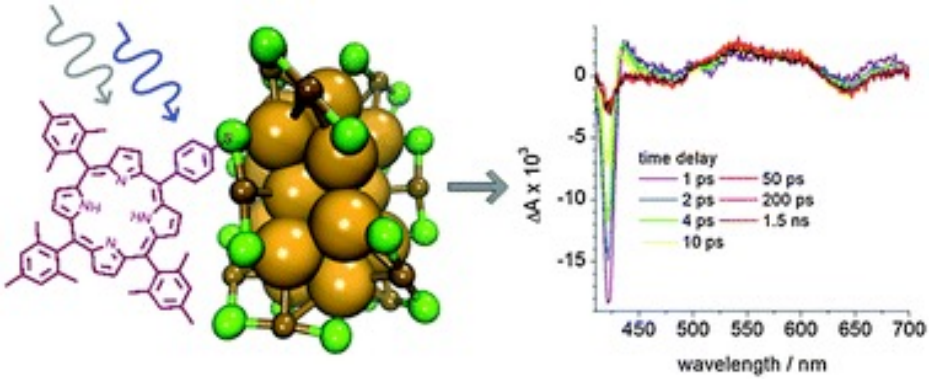
Scientific context

❑ Nanoclusters as the smallest functionalized NPs:

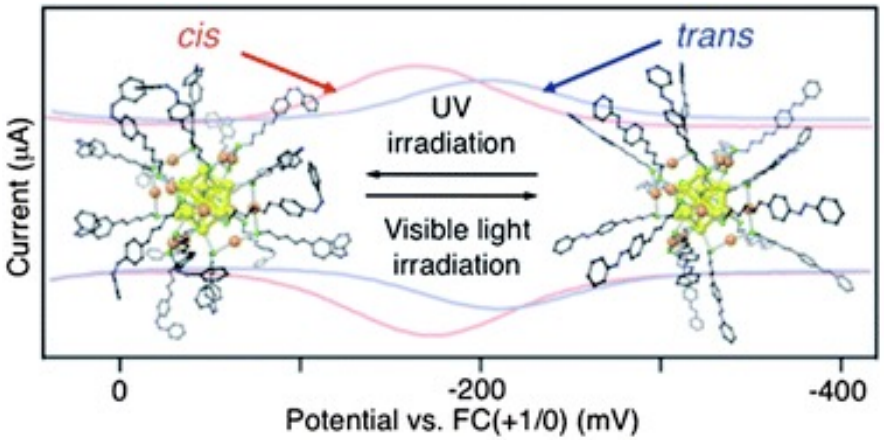
☐ Some experimental examples of functionalized GNC:



J. Phys. Chem Lett., **2010**, *1*, 1497-1503.



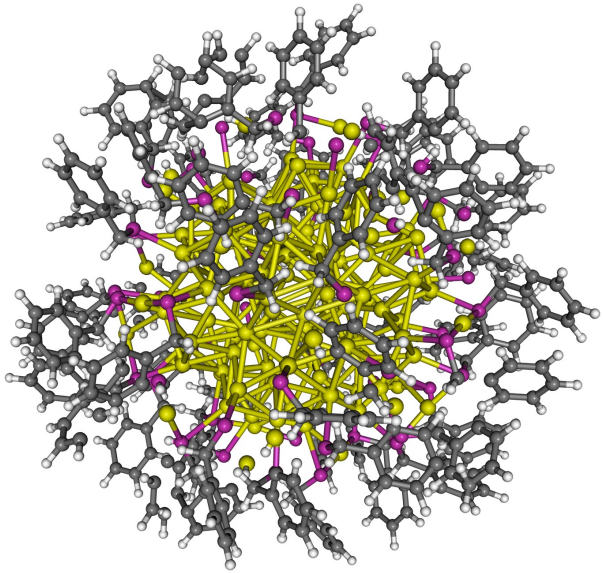
J. Phys. Chem C, **2014**, *118*, 4444-4453.



Nanoscale, **2012**, *4*, 4263-4268.

Theoretical chemistry in large systems

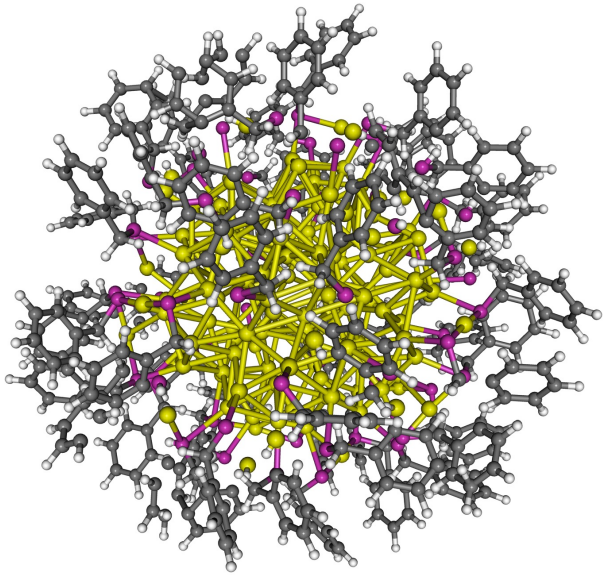
❑ Modeling photoinduced properties in nanosized systems:

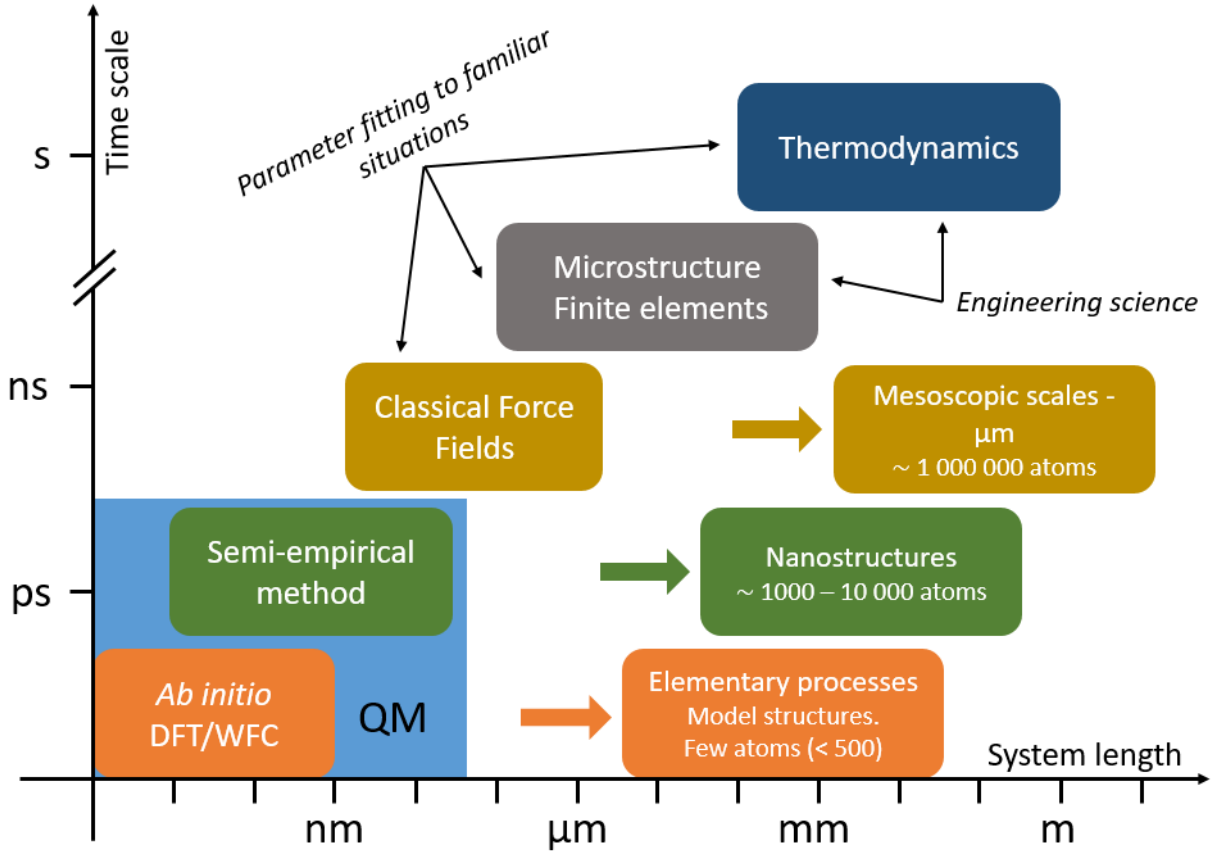


- These objects encompass hundreds of atoms and **too many electrons** for most of the quantum methods.
- In order to model the photoinduced process, we need to explore the **excited-states behavior**, and their evolution during time.
- **We need a fast and cheap quantum method.**

Theoretical chemistry in large systems

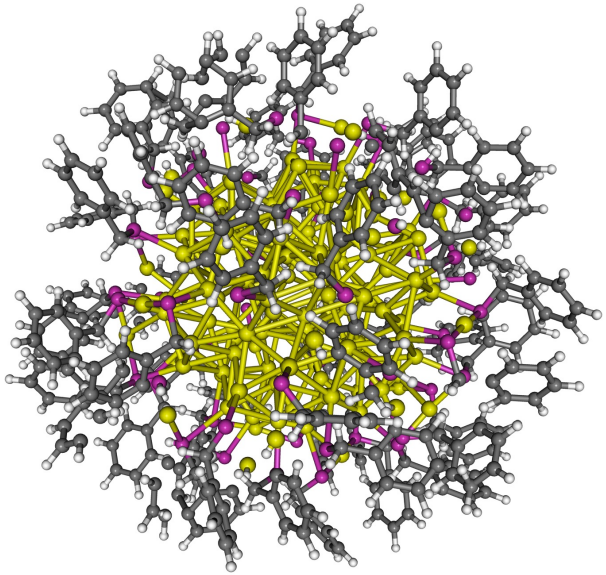
❑ Choice of the method:

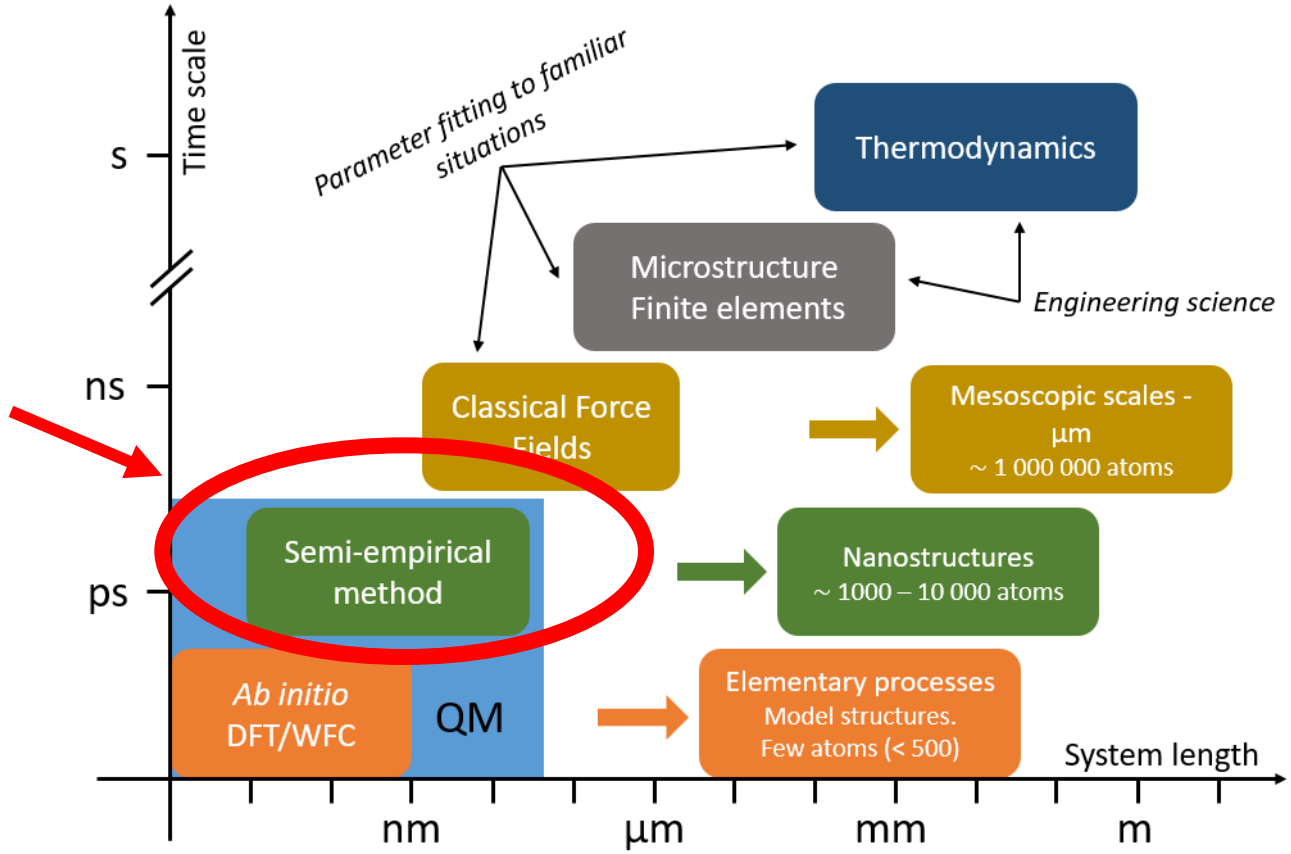




Theoretical chemistry in large systems

❑ Choice of the method:





Theoretical chemistry in large systems

Pr. T. Frauenheim
BCCMS, Bremen

❑ Density Functional Tight Binding (DFTB)

- The basics of DFTB used today appears in 1998 (Frauenheim *et al.*), to model hydrocarbons.
- The main idea behind this method is to:
  - ➢ Use with a **minimal atomic-like basis set** (valence electrons only).
  - ➢ replace the Hamiltonian with a **parameterized Hamiltonian matrix**

Phys. Rev. B., **1998**, *58*, 7260-7268.

Theoretical chemistry in large systems

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- The main idea behind this method is to:
  - ➢ Use with a **minimal atomic-like basis set** (valence electrons only).
  - ➢ replace the Hamiltonian with a **parameterized Hamiltonian matrix**

- **A parameterization is necessary (pairwise, A-B), based on DFT.**
- **Thus we do not need any experimental data for this process.**

Calculations are *ca.* 100 times cheaper than with DFT

Phys. Rev. B., **1998**, *58*, 7260-7268.

Theoretical chemistry in large systems

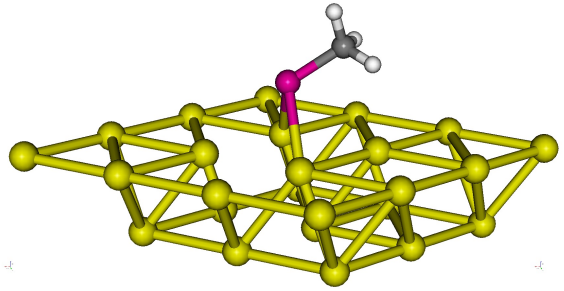
❑ Density Functional Tight Binding (DFTB)

❑ Example: **Au-X** parameterization

Journal of COMPUTATIONAL CHEMISTRY WWW.C-CHEM.ORG FULL PAPER

SCC-DFTB Parameters for Simulating Hybrid Gold–Thiolates Compounds

Arnaud Fihey,*[a] Christian Hettich,[b] Jérémy Touzeau,[a] François Maurel,[a] Aurélie Perrier,*[a] Christof Köhler,[b] Bálint Aradi,*[b] and Thomas Frauenheim[b]



Au_n -SCH_3

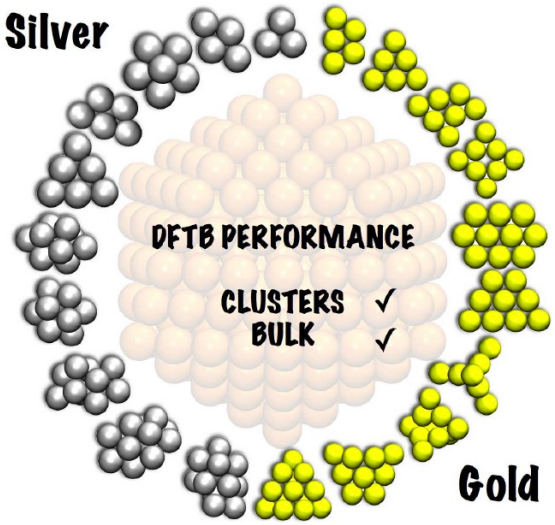
- *"Au-org"* parameters suited to describe organic thiolate molecules adsorbed onto a gold aggregate/surface.
- DFT integrals used are obtained with the **PBE** functional and slater minimal basis sets.

J. Comput. Chem. A, **2015**, *36*, 2075-2087.

Theoretical chemistry in large systems

Density Functional Tight Binding (DFTB)

- DFTB only benchmarked on bare Au/Ag NP of different sizes (formation energy, structure).



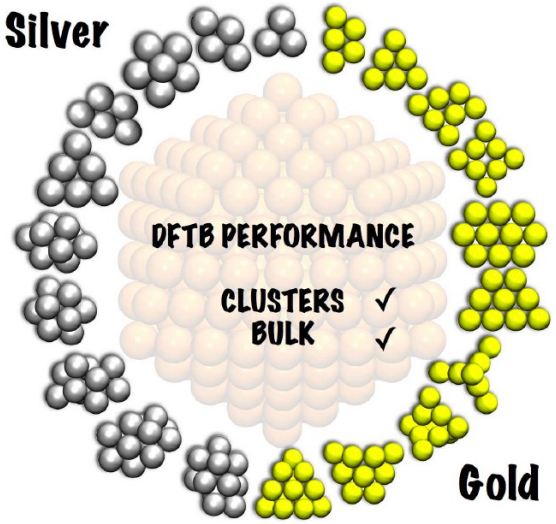
J. Phys. Chem. A, **2016**, *120*, 8469-8483.

Theoretical chemistry in large systems

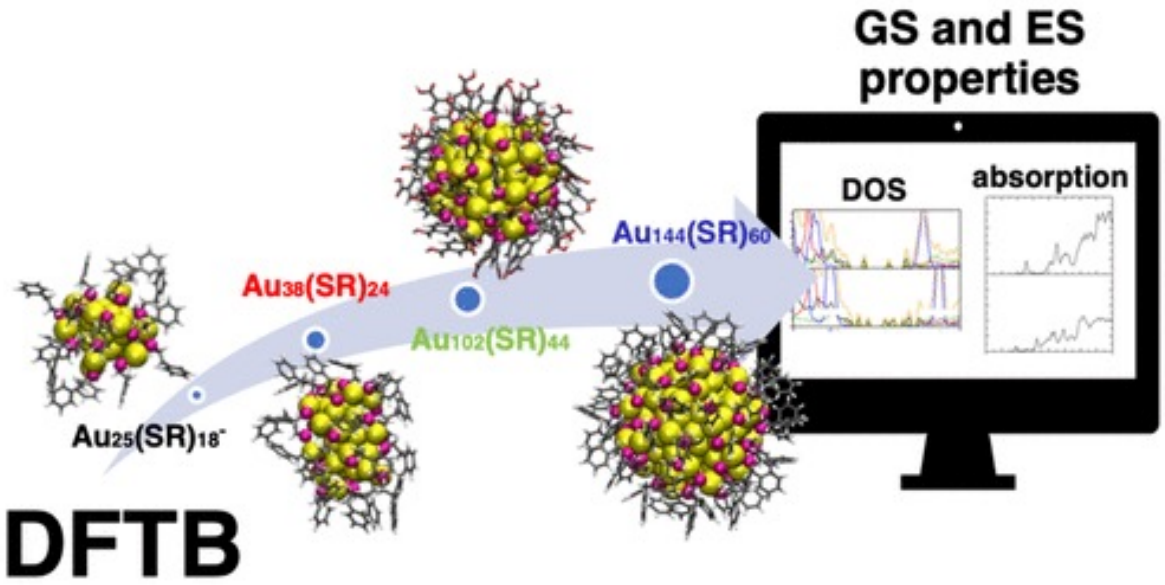
Density Functional Tight Binding (DFTB)

- DFTB only benchmarked on bare Au/Ag NP of different sizes (formation energy, structure).

- Performances for gold nanoclusters (structure, optical properties) ?



J. Phys. Chem. A, **2016**, *120*, 8469-8483.

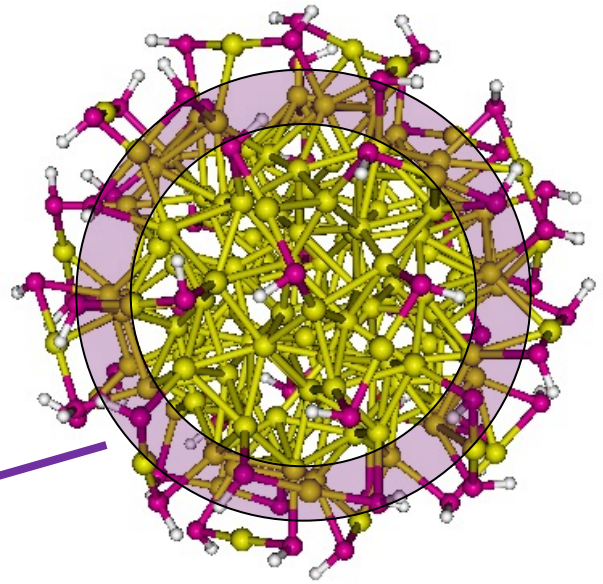


J. Phys. Chem. C, **2023**, 127, *39*, 19675–19686

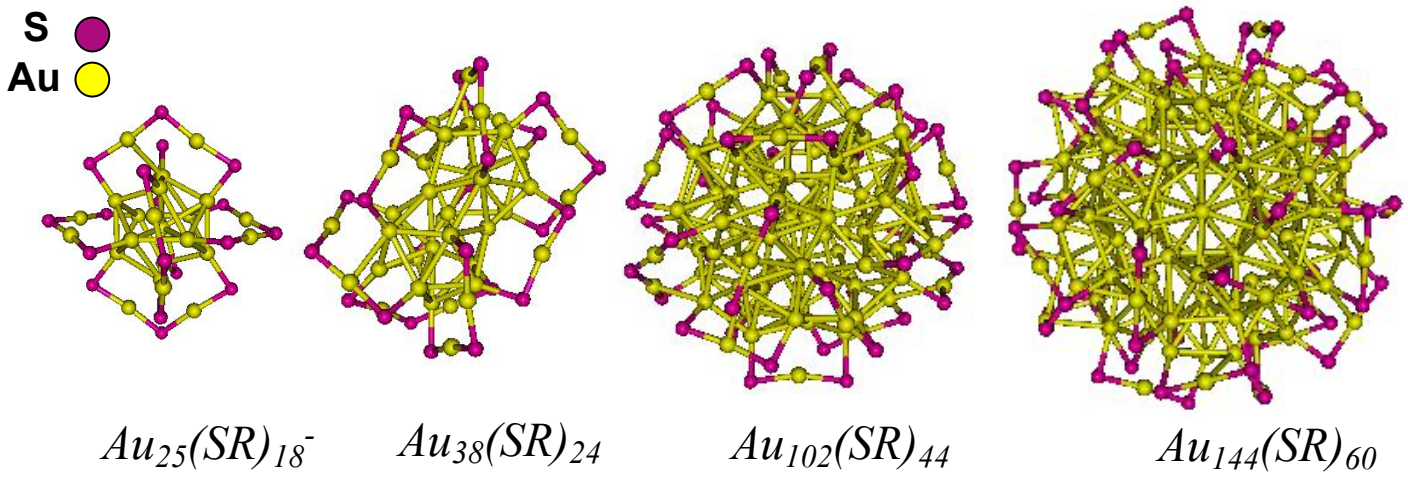
Modeling gold nanoclusters with DFTB

❑ Geometry:

- Experimental structure (X-Rays) of the GNC are all retrieved along the series.
- Errors on bond distances depend on the bond type:



Au(core) – S(shell)
Au(core) –Au(shell)
Overestimated (ca. 10%)



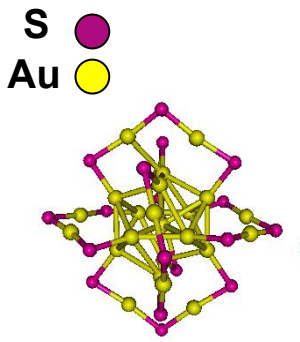
$Au_{25}(SR)_{18}^-$ $Au_{38}(SR)_{24}$ $Au_{102}(SR)_{44}$ $Au_{144}(SR)_{60}$

J. Phys. Chem. C, **2023**, 127, *39*, 19675–19686

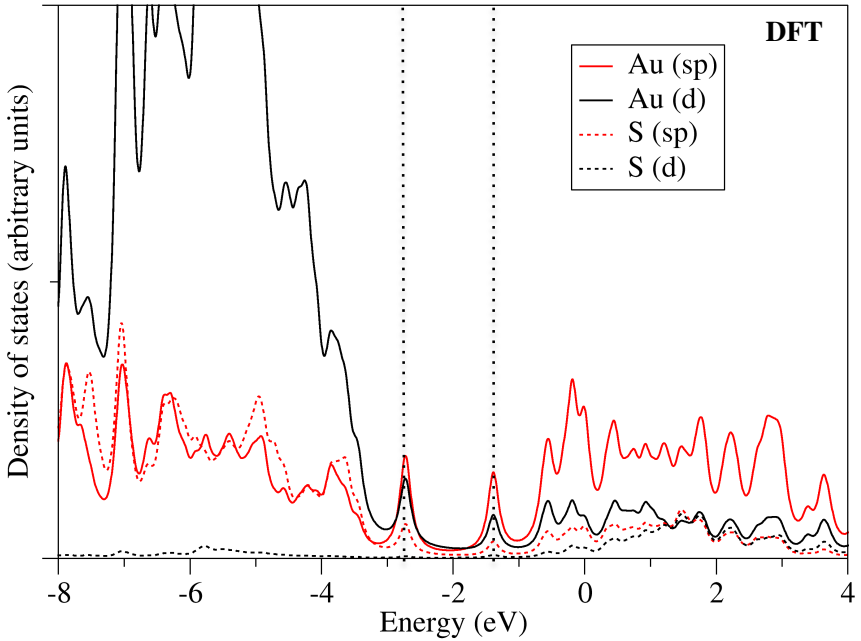
Modeling gold nanoclusters with DFTB

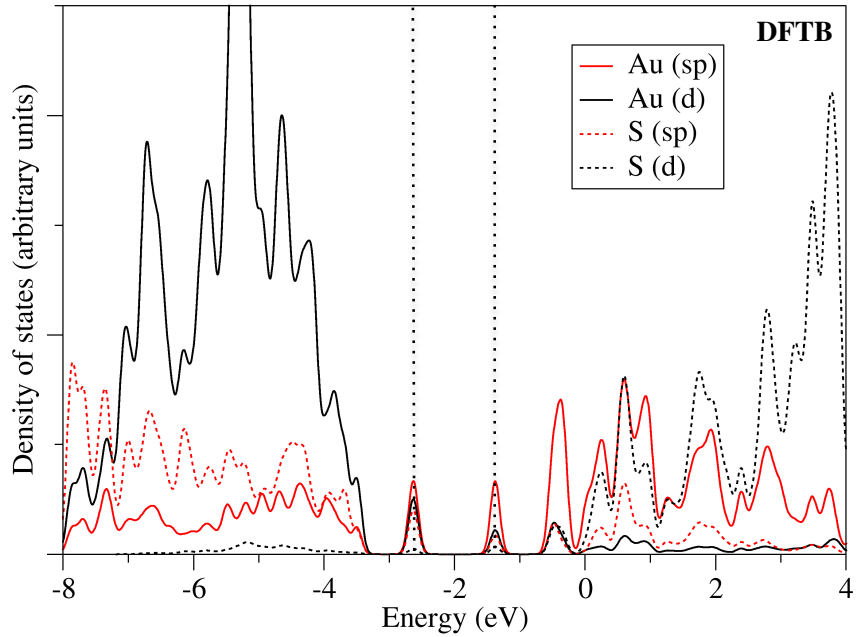
❑ Electronic structure:

- ❑ Electronic structure : comparison between DFT and DFTB:
  - ➢ Electronic gap correctly reproduced.
  - ➢ Positions of the band accurate, except for high energy bands of S.



$Au_{25}(SH)_{18}^-$



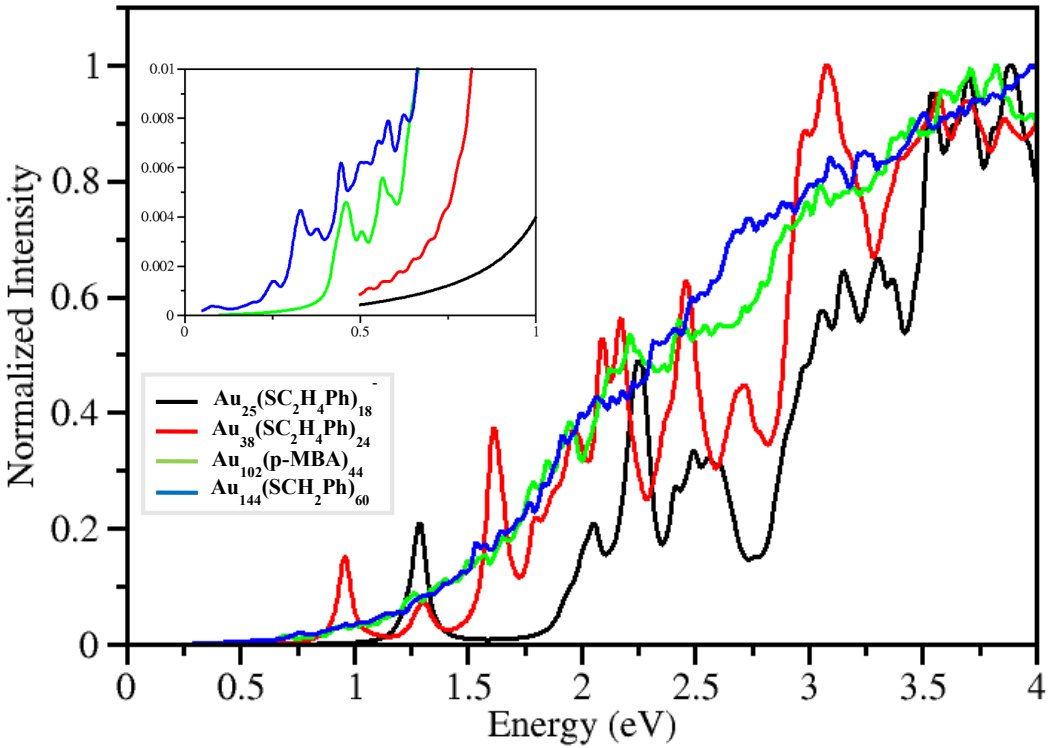


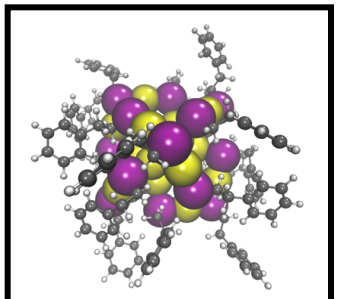
J. Phys. Chem. C, **2023**, 127, *39*, 19675–19686

Modeling gold nanoclusters with DFTB

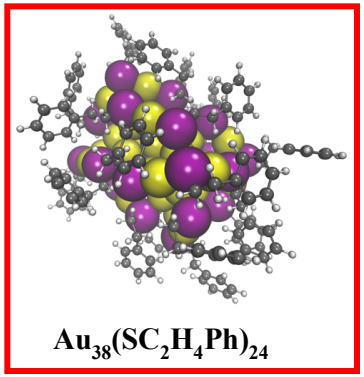
❑ Optical properties:

Real-Time-TD-DFTB absorption spectrum:





$Au_{25}(SC_2H_4Ph)_{18}^-$



$Au_{38}(SC_2H_4Ph)_{24}$

- Satisfying agreement with experiment and reference TD-DFT calculations.

J. Phys. Chem. C, **2023**, 127, *39*, 19675–19686

Modeling gold nanoclusters with DFTB

❑ Optical properties:

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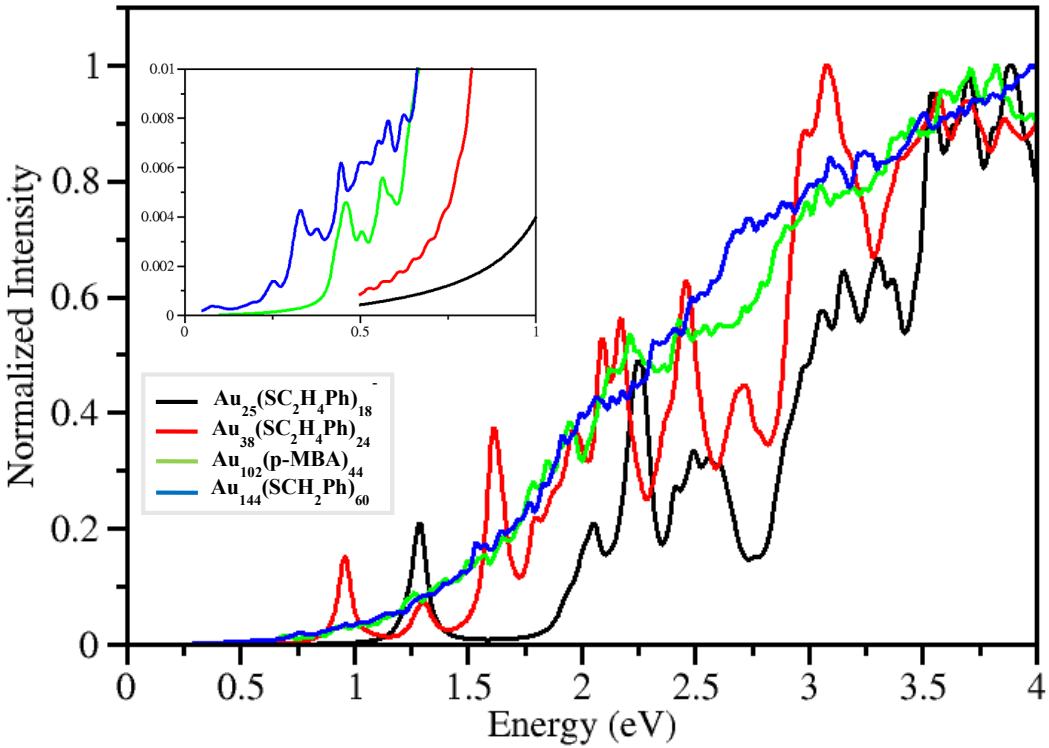
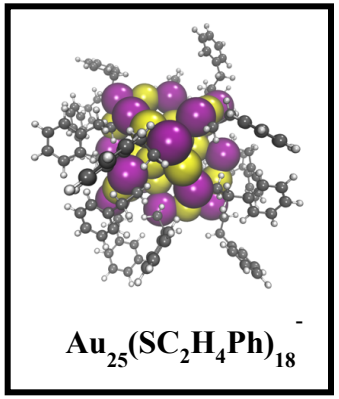
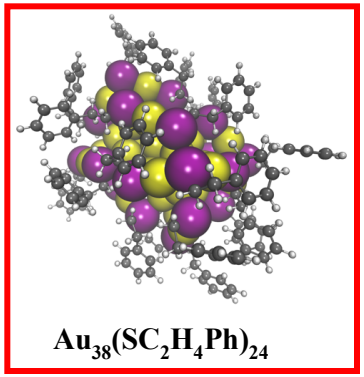
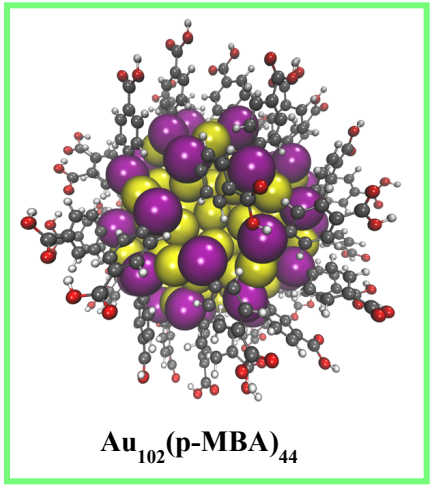




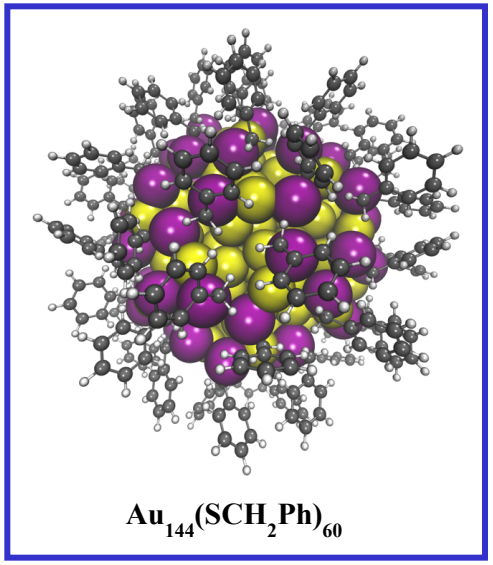
$Au_{25}(SC_2H_4Ph)_{18}^-$



$Au_{38}(SC_2H_4Ph)_{24}$



$Au_{102}(p\text{-}MBA)_{44}$



$Au_{144}(SCH_2Ph)_{60}$

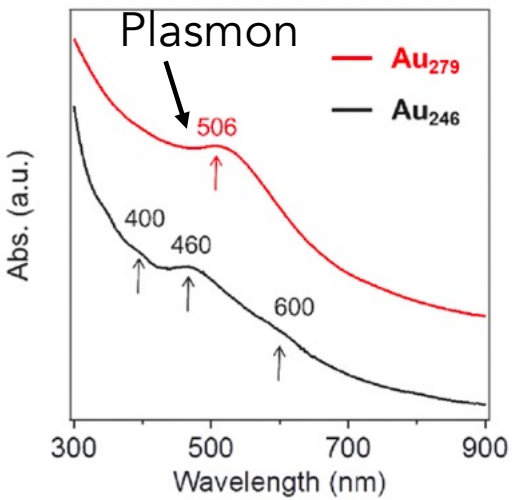
- Satisfying agreement with experiment and reference TD-DFT calculations.
- Evolution from molecular to semi-conductor like behavior with growing size.

J. Phys. Chem. C, **2023**, 127, *39*, 19675–19686

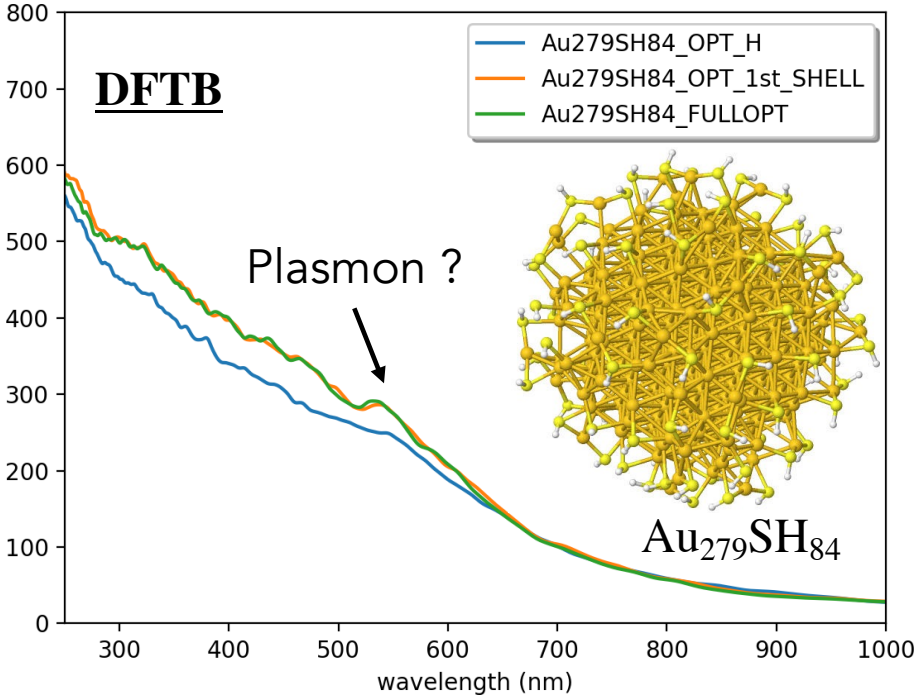
Modeling gold nanoclusters with DFTB

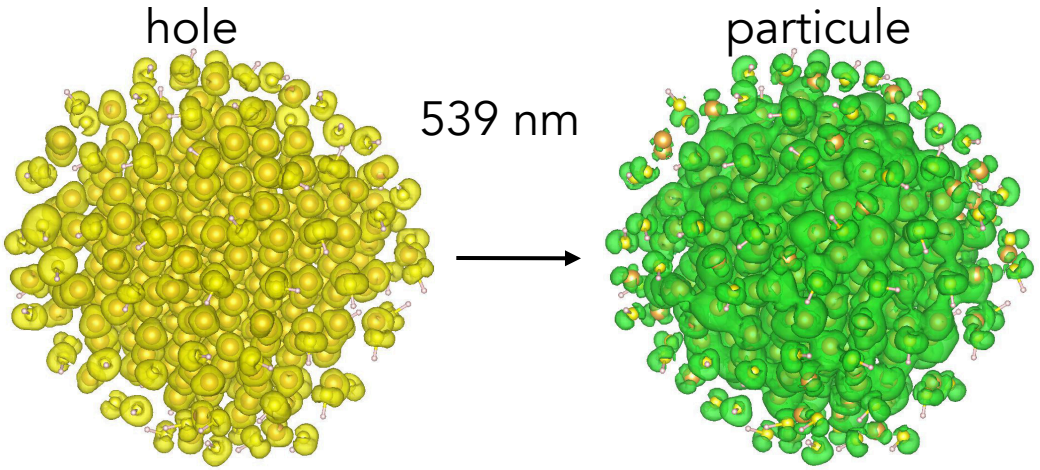
❑ Optical properties:

Experimental



JACS, **2018**, *17*, 5691-5695



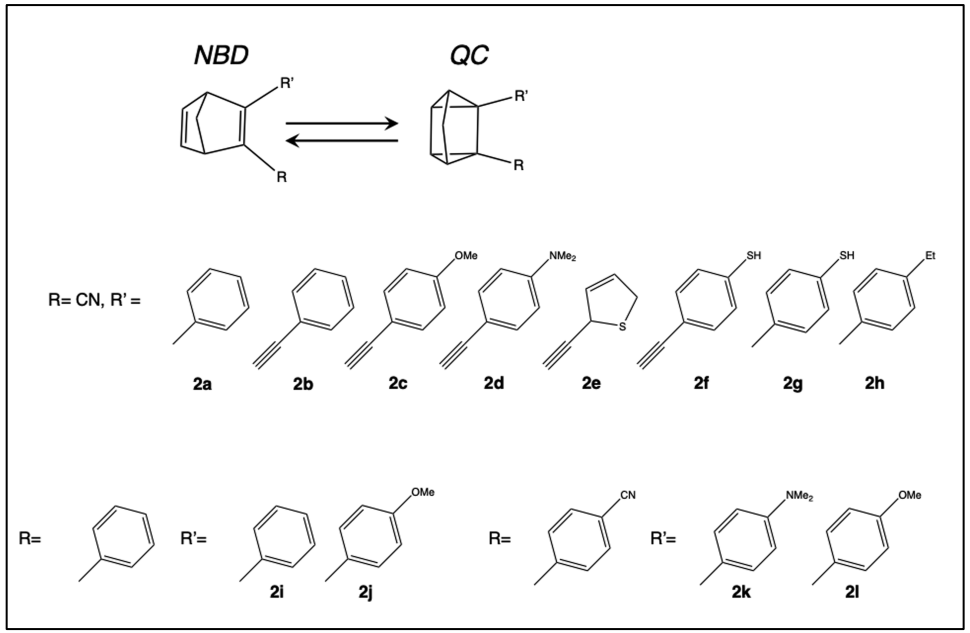


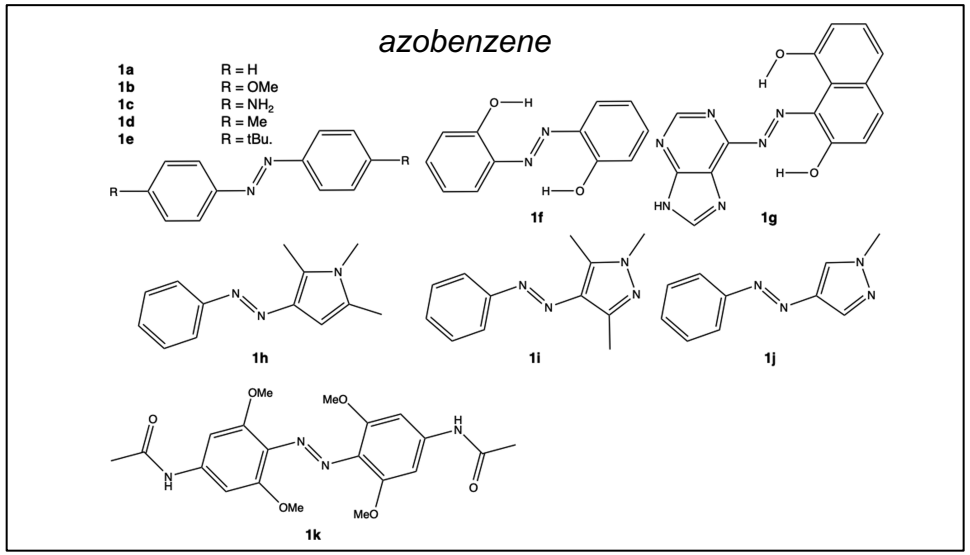
➢ Not an easy task to identify the nature of the transition as a plasmon band …

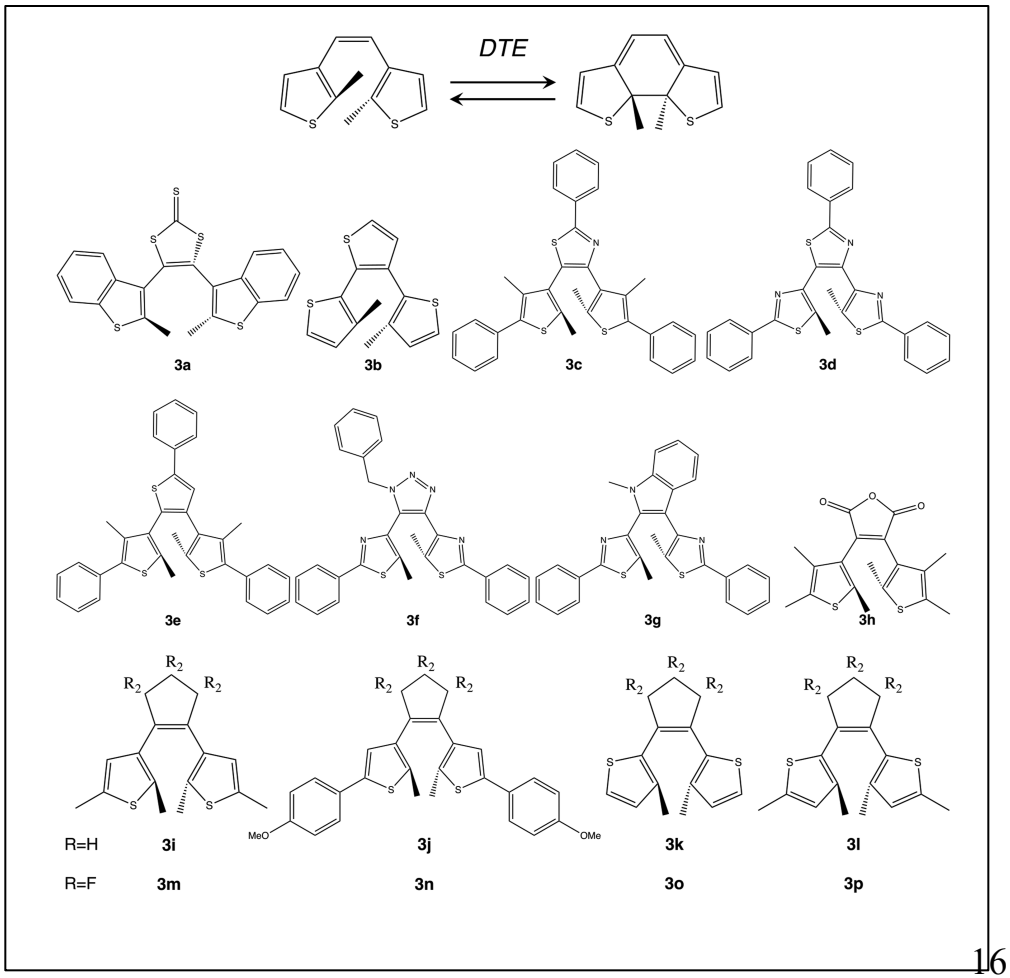
DFTB description of organic photochromes

- **Careful DFTB benchmark on 35 photochromes:**
- ✓ geometries
- ✓ Excitations
- ✓ Energy difference between the two isomers

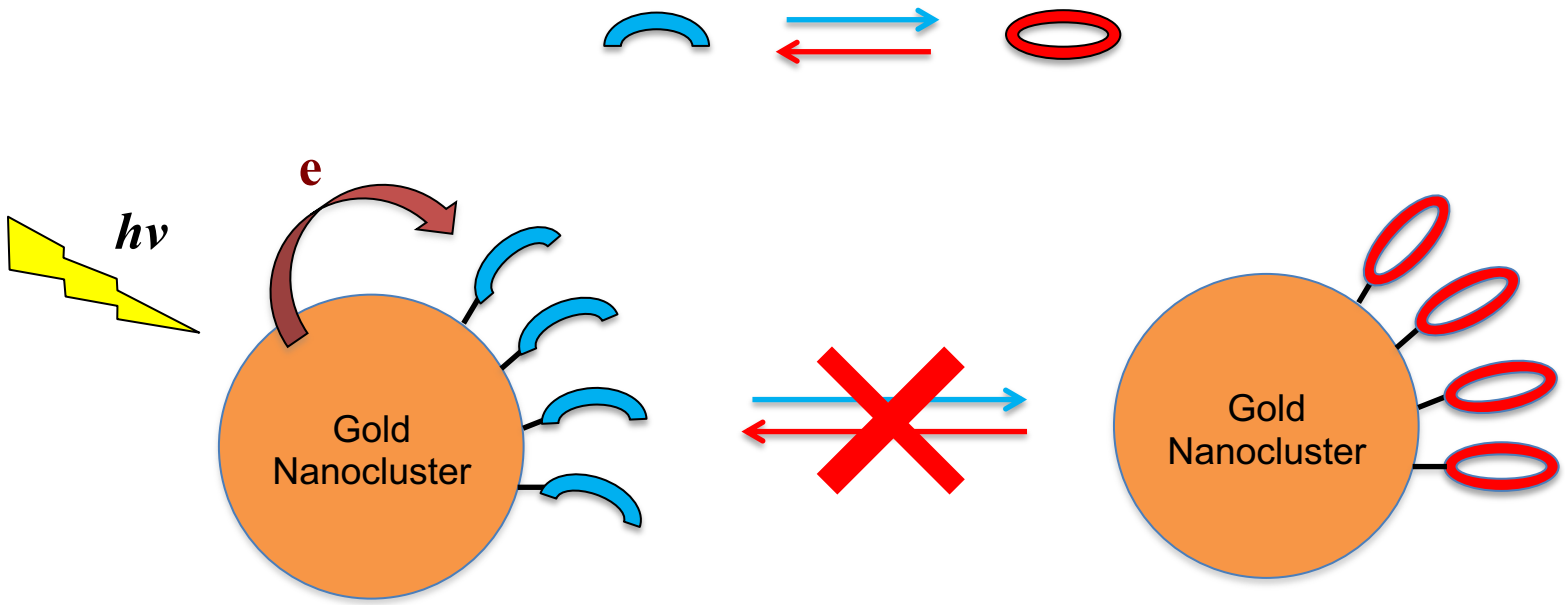
J. Chem. Phys., **2023**, *158*, 074303.







Modelling a photoinduced electron transfer

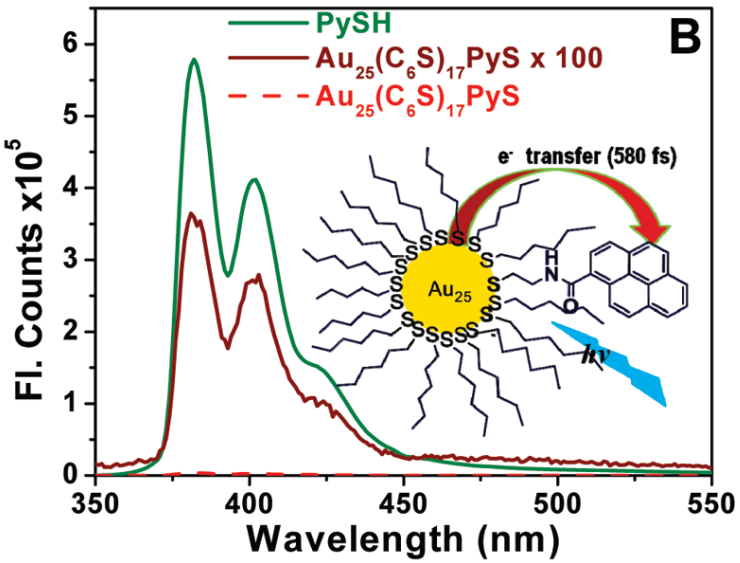


Can we explore the photoinduced processes that could act as a quenching mechanism for the photoactivity ?

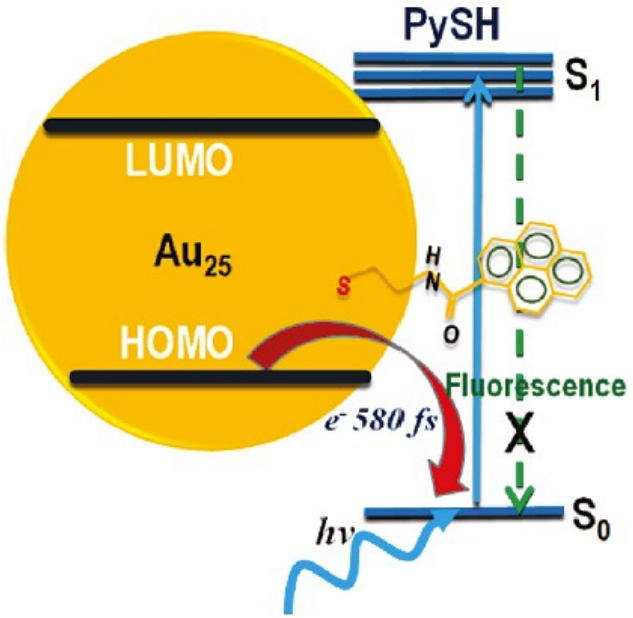
Modelling a photoinduced electron transfer

❑ Systems under study:

- Au_{25} cluster functionalized with a pyrene fluorophore:



J. Phys. Chem Lett., **2010**, *1*, 1497-1503.

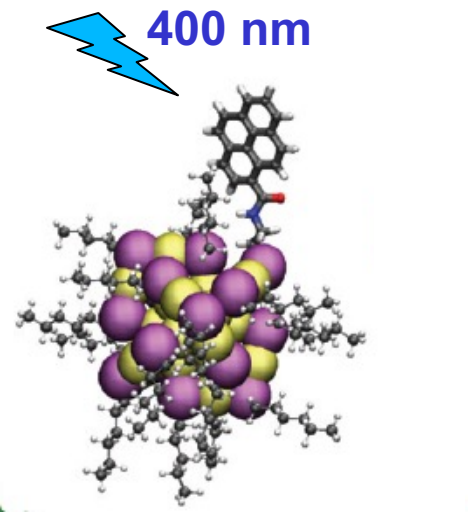


- A photo-induced electron transfer from the cluster to the pyrene is proposed as a quenching mechanism.

➢ **Are we able to retrieve this outcome with DFTB modeling tool ?**

Electron transfer in pyrene-labelled Au_{25}

❑ DFTB Ehrenfest non-adiabatic molecular dynamics:

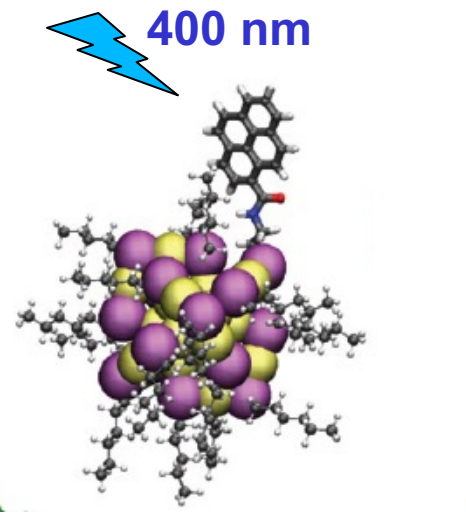


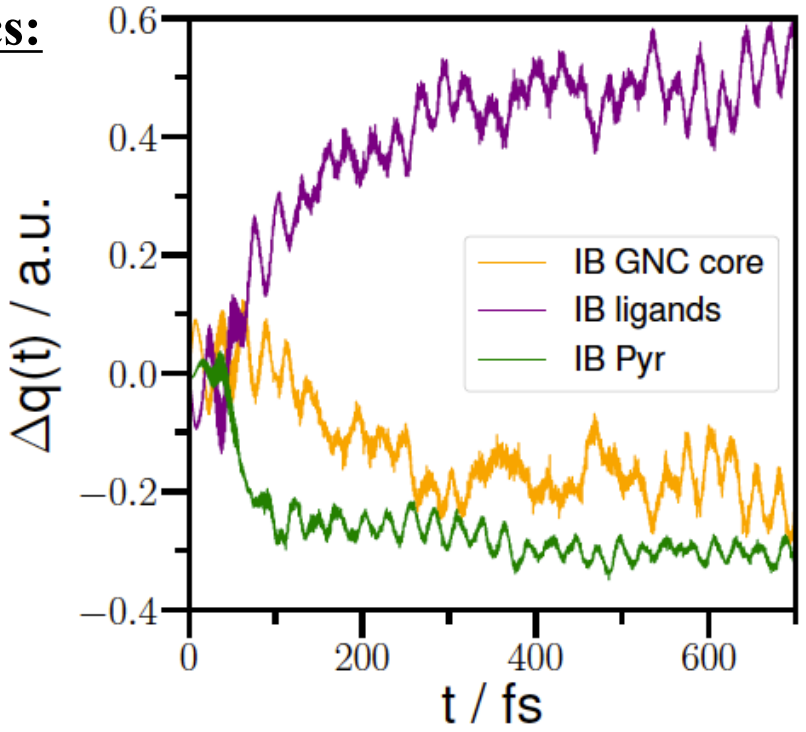
Erhenfest dynamic setup to reproduce exp. measurements:
We use a sinusoid laser pulse in tune with the **Pyrene abs. at 400 nm** (aligned with its trans. dipole moment).
Atoms (classic particles) and electrons (quantum particles) can move.
E_0 in the pulse: 0.1 V. $Å^{-1}$
timestep: 0.0024 fs
700 fs of dynamics

Nanoscale, **2021**, *13*, 6786-6797.

Electron transfer in pyrene-labelled Au_{25}

- **DFTB Ehrenfest non-adiabatic molecular dynamics:**
  - We plot the charge difference over time, under excitation with the laser:

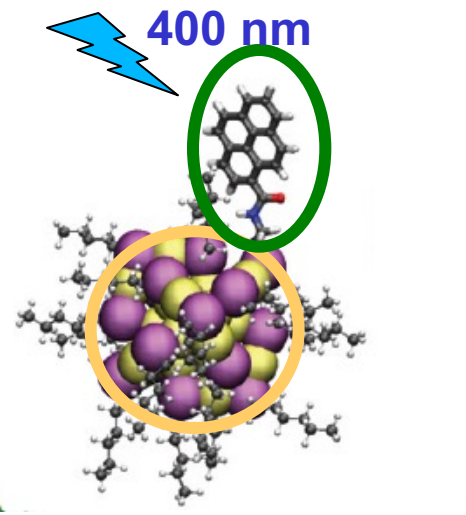




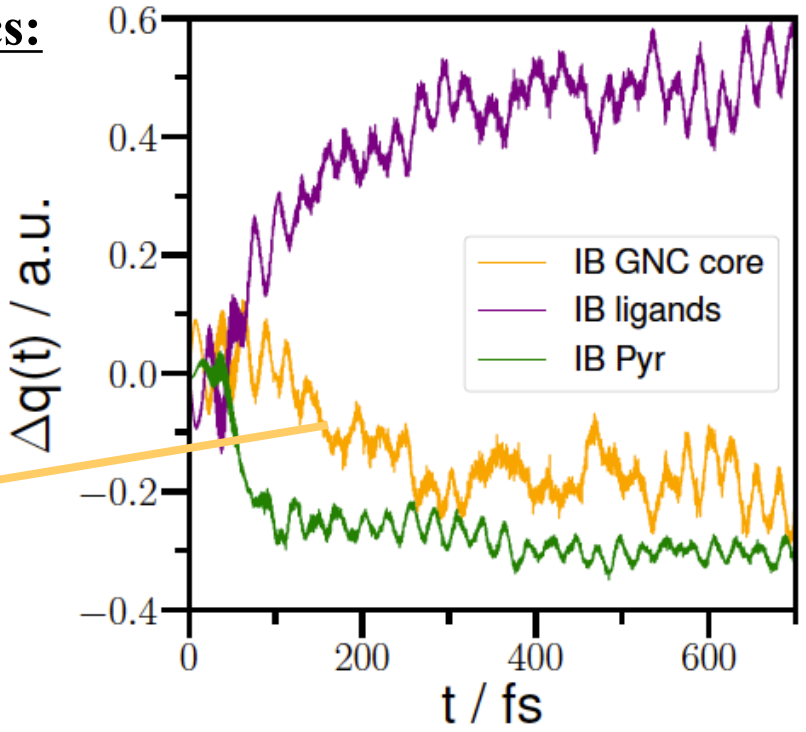
Nanoscale, **2021**, *13*, 6786-6797.

Electron transfer in pyrene-labelled Au_{25}

- **DFTB Ehrenfest non-adiabatic molecular dynamics:**
  - We plot the charge difference over time, under excitation with the laser:



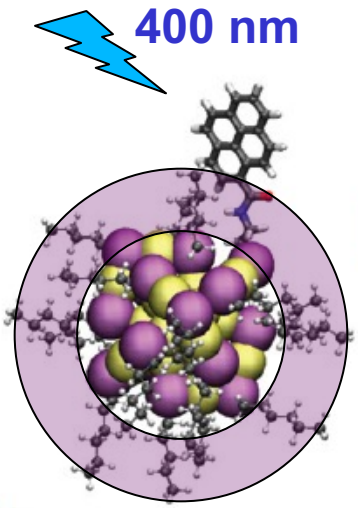
The GNC starts as an electron donor (< 50 fs) before starting accepting electrons.



Nanoscale, **2021**, *13*, 6786-6797.

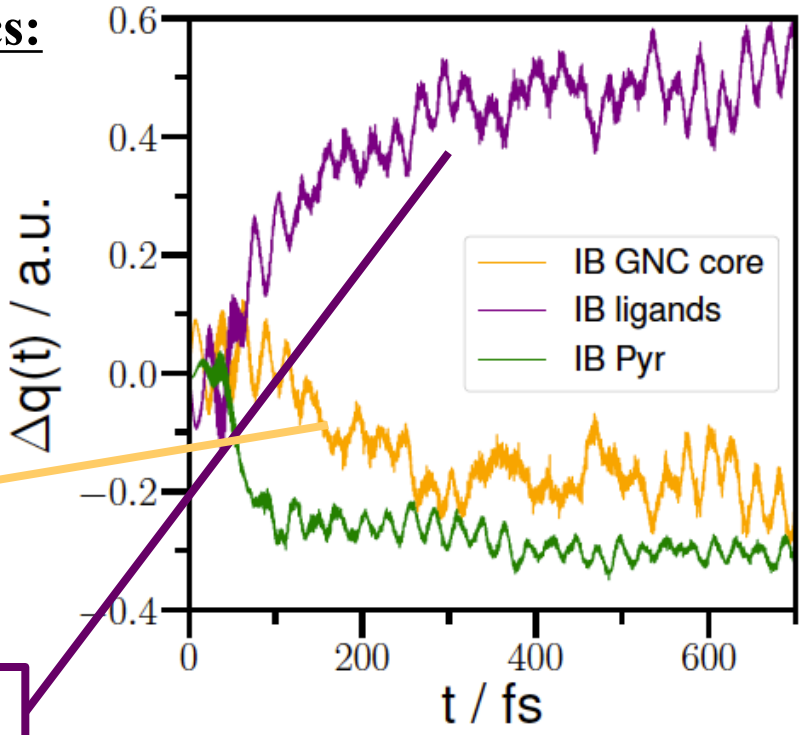
Electron transfer in pyrene-labelled Au_{25}

- **DFTB Ehrenfest non-adiabatic molecular dynamics:**
  - We plot the charge difference over time, under excitation with the laser:



The GNC starts as an electron donor (< 50 fs) before starting accepting electrons.

The C_6H_{13} ligands actually act as the main electron donor after an equilibration period of 100 *fs*.

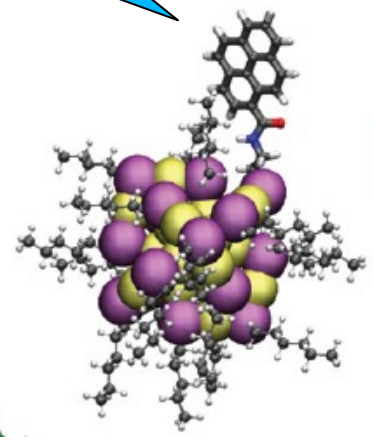


Nanoscale, **2021**, *13*, 6786-6797.

Electron transfer in pyrene-labelled Au_{25}

- **DFTB Ehrenfest non-adiabatic molecular dynamics:**
  - We plot the charge difference over time, under excitation with the laser:

400 nm



The GNC starts as an electron donor (< 50 fs) before starting accepting electrons.

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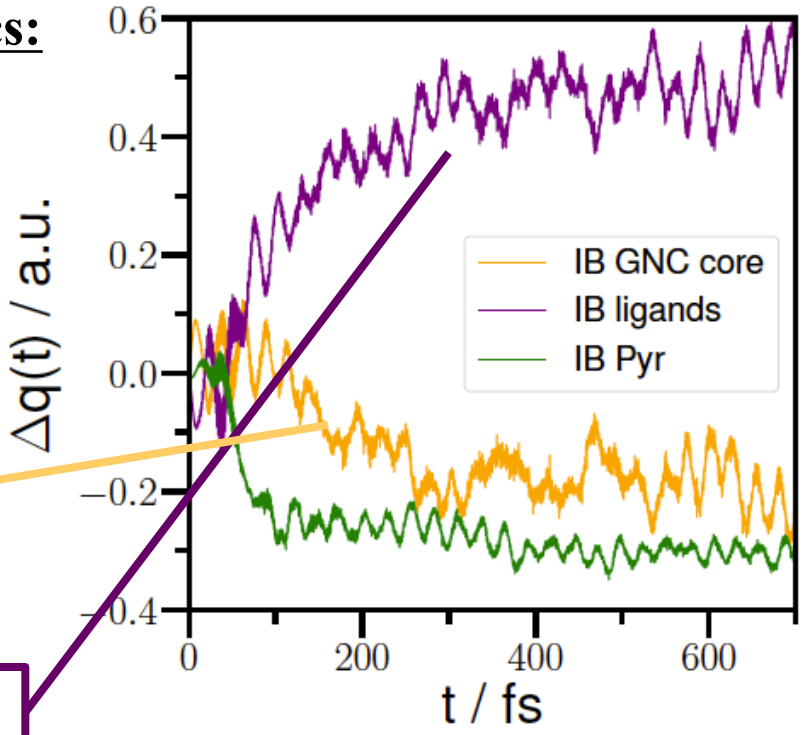


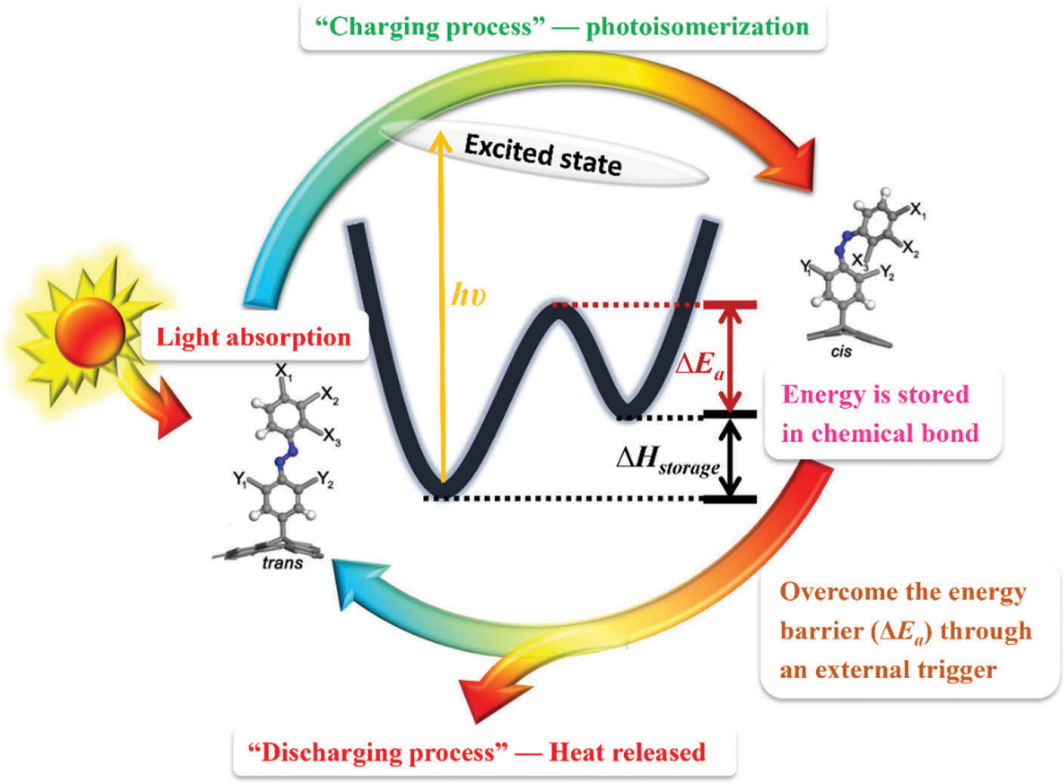
- A clear charge-separated state is obtained after 100-200 *fs* (in agreement with experiments).

➔Taking into account **all** the protecting ligands is necessary to understand the experimental charge transfer mechanism**.**

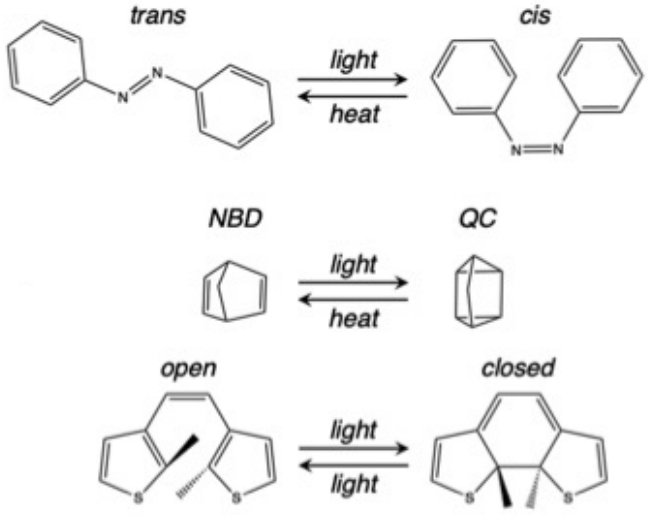
Nanoscale, **2021**, *13*, 6786-6797.

On-going work

❑ Solar energy storage with photochromic nanodevices:



Chem. Soc. Rev, **2018**, *47*, 7339-7368.



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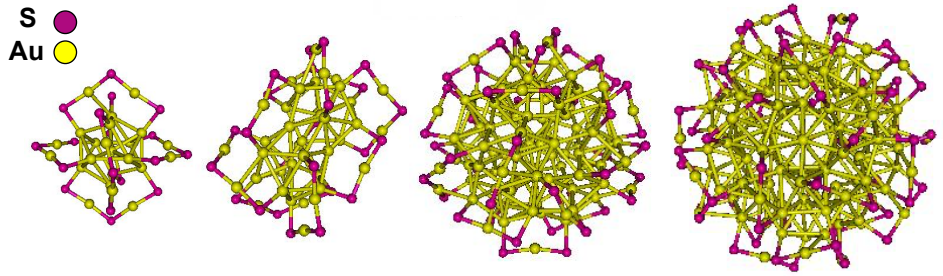
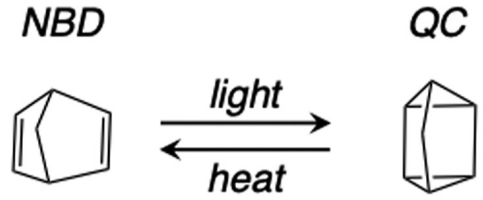
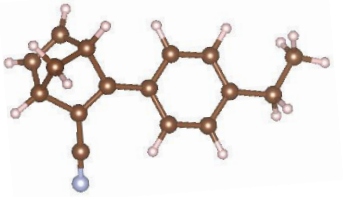


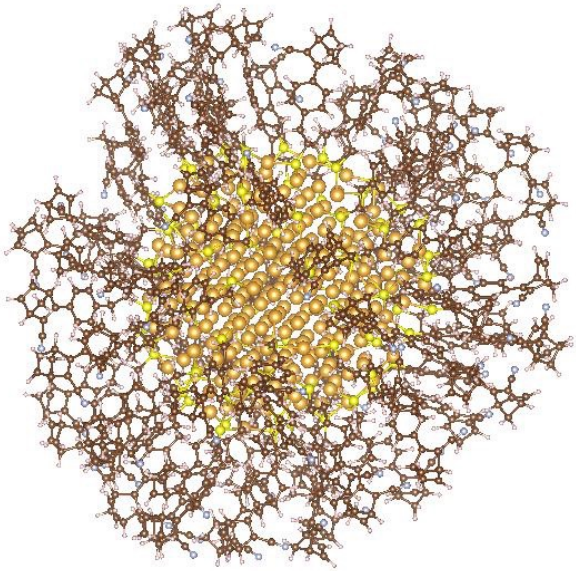
On-going work

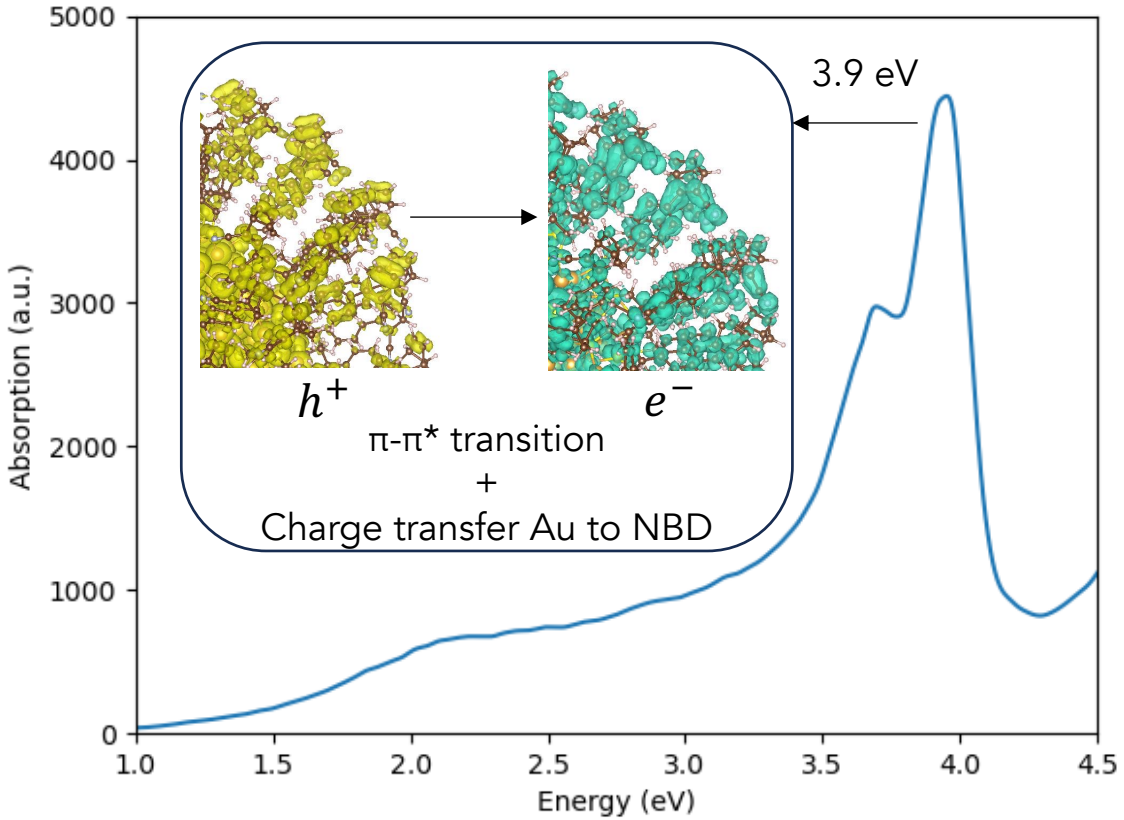
❑ Solar energy storage with photochromic nanodevices:



84 NBD @ $Au_{279}S_{84}$







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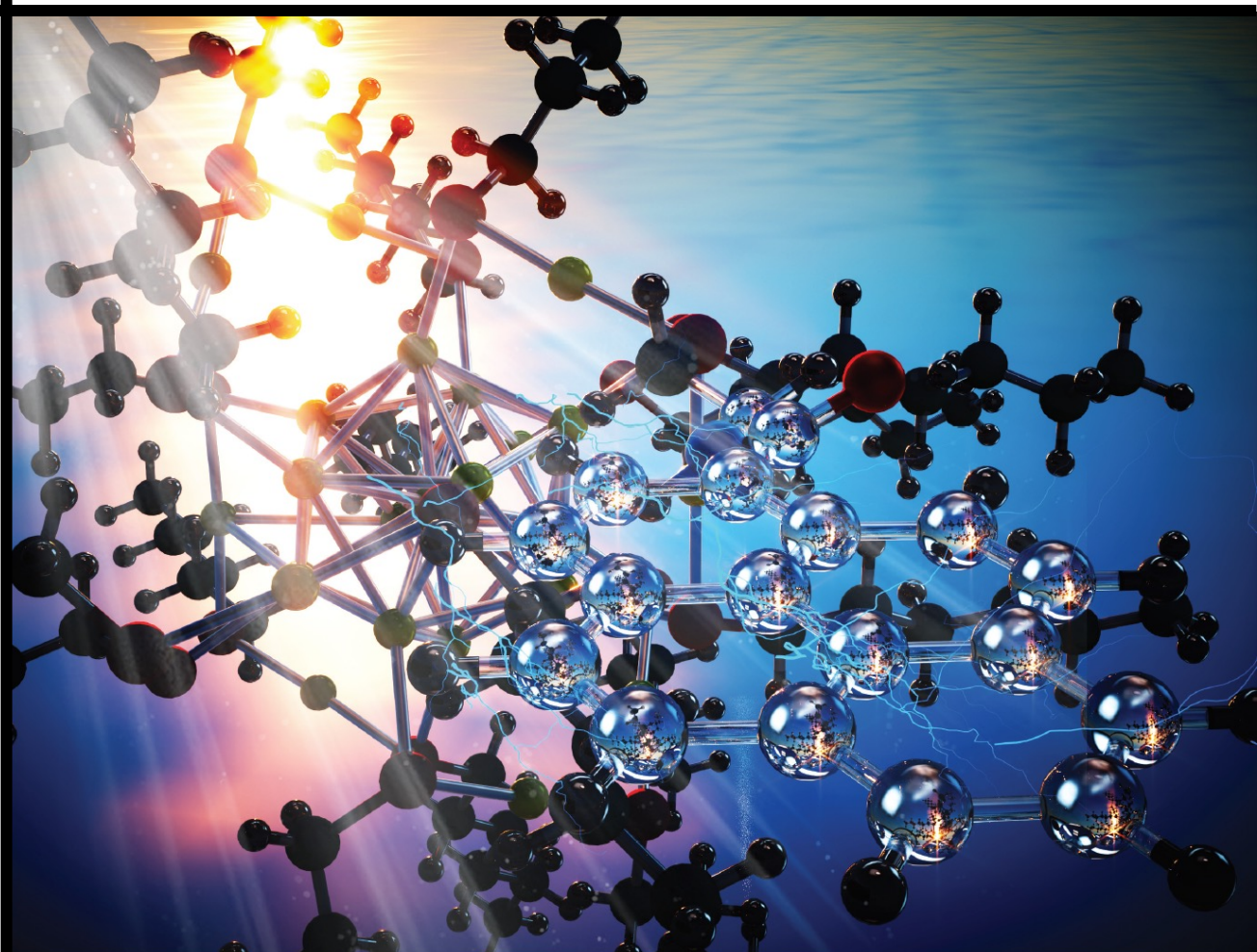
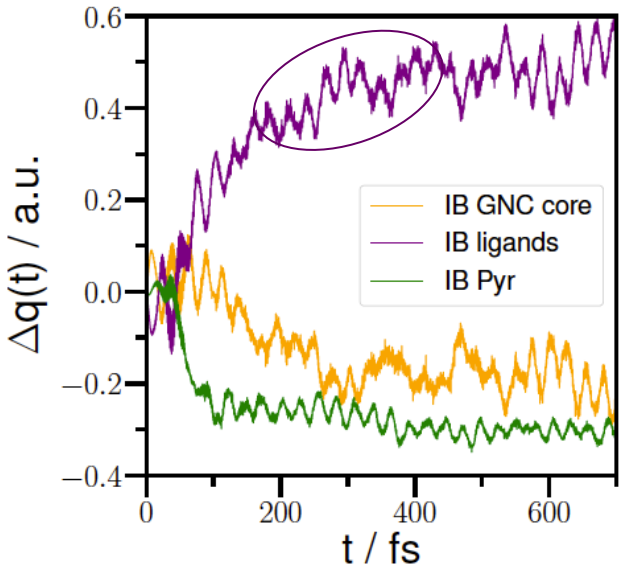
Thomas Frauenheim
(BCCMS, Bremen University)

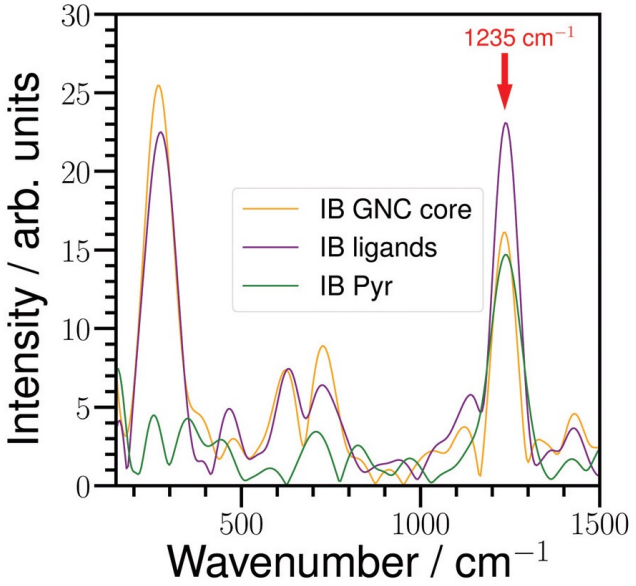


On-going work

❑ Deeper look into the photoinduced electron transfer:

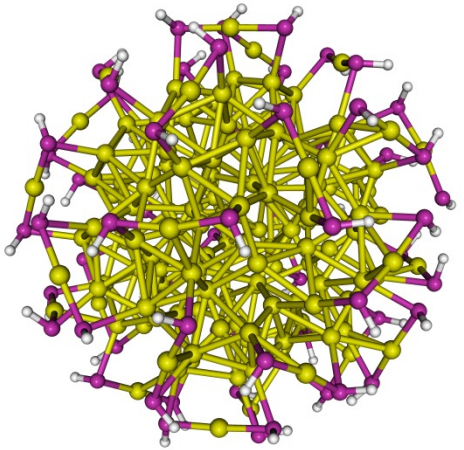


fourier transformed



- Role of the vibronic couplings ? (C-C stretching of the ligands).

- Larger functionalized NCs.
- Different photoactive molecules

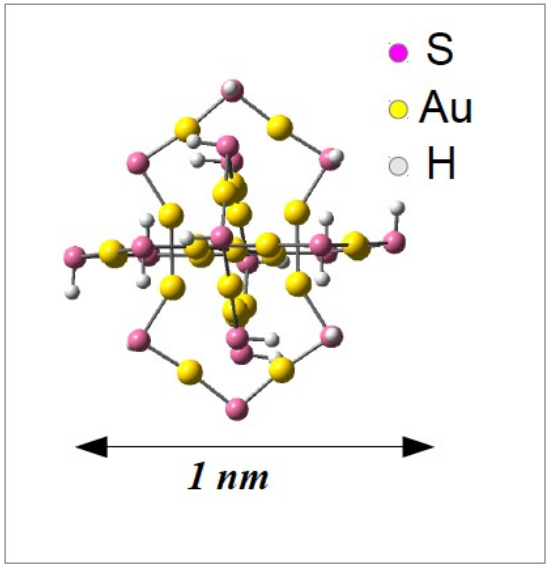


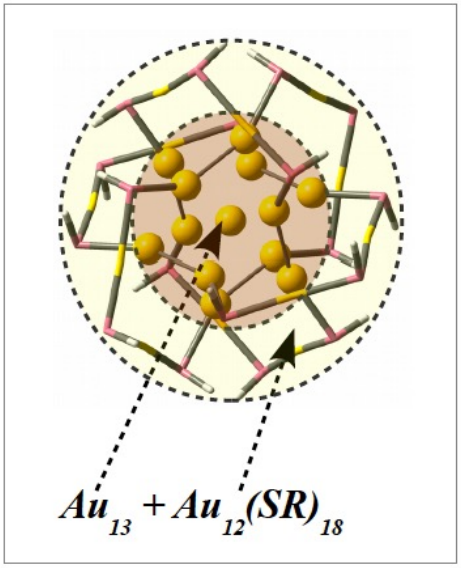
$Au_{144}(SH)_{60}$

Table 1 Comparison of the average distances (in Angströms) and angles (in degrees) within the GNC

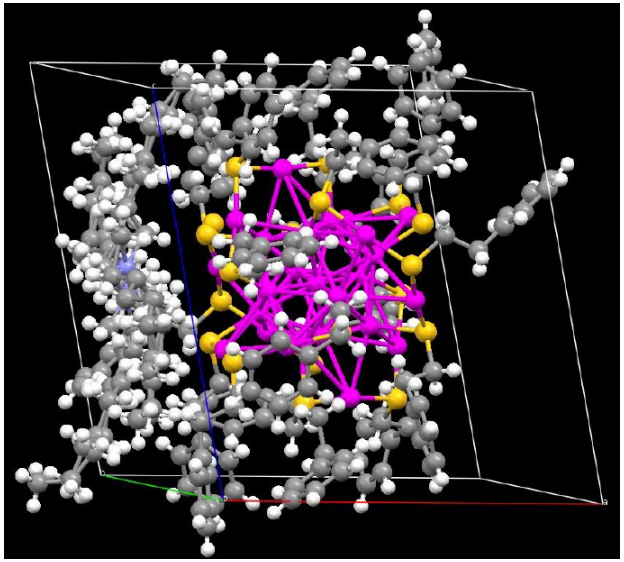
	DFTB ($Au_{25}(SH)_{18}^-$)	DFTB ($Au_{25}(SC_6H_{13})_{18}^-$)	DFT ($Au_{25}(SH)_{18}^-$)	Exp. (ref. 3)
Au(core)–Au(core)	2.77	2.78	2.96	2.88
Au(shell)–S(shell)	2.38	2.39	2.38	2.31
Au(core)–Au(shell)	3.53	3.49	3.29	3.16
Au(core)–S(shell)	2.57	2.60	2.48	2.37
S–Au–S	177.7	174.2	172.7	172.3
Au–S–Au	103.5	101.3	101.5	100.9
Electronic gap	1.22	1.13	1.34	—

The theoretical electronic gaps are also given (in eV).





XR crystallographic structure*:

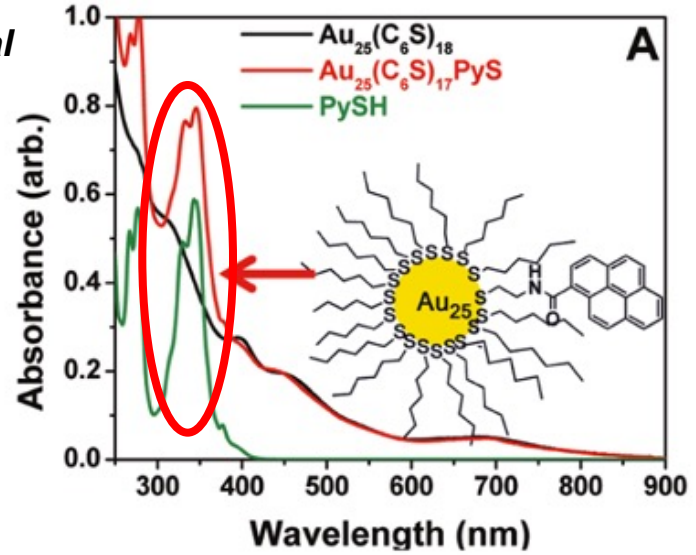


*J. Am. Chem. **Soc**,* **2008**, *130*, 5883-5885.

Electron transfer in pyrene-labelled Au_{25}

❑ Vertical optical properties:

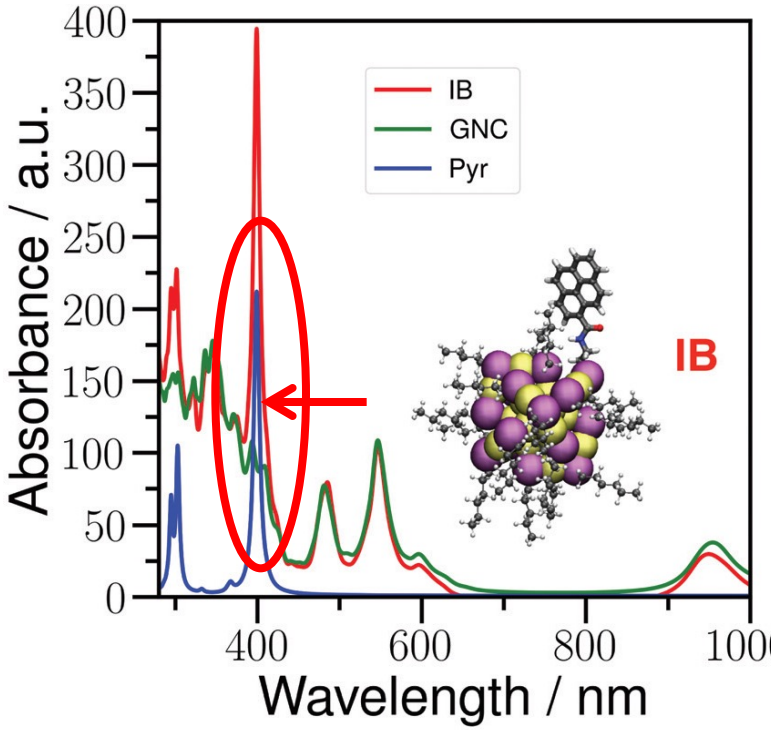
experimental spectrum (CH_2Cl_2)



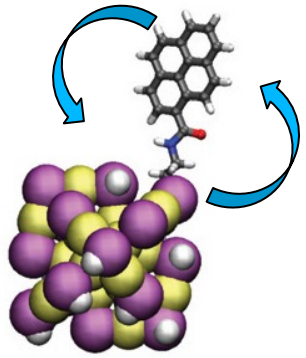
- We compute UV-Vis spectrum with a Real Time domain TD-DFTB electron dynamics run:

We use a brief Dirac pulse polarized in all directions, then the system evolves freely. **The atoms do not move**.
Intensity of the pulse: 0.001 V. Å^{-1}
timestep: 0.0024 fs
ca. 200 fs of dynamics

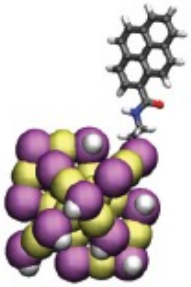
DFTB (gas phase)

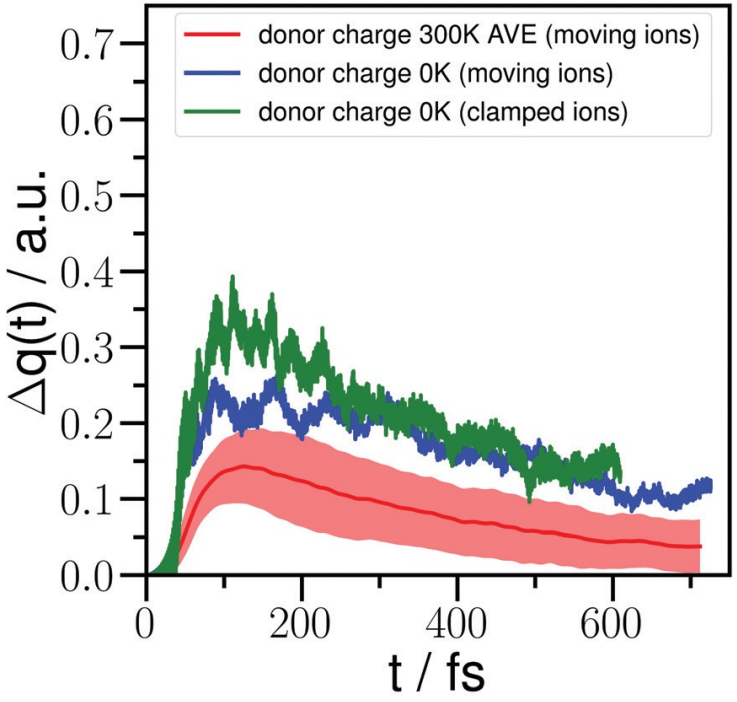


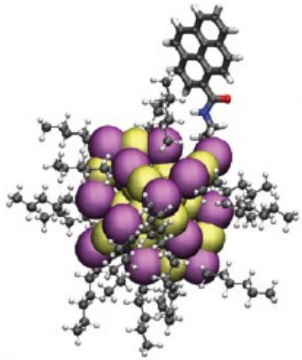
❑ Ehrenfest non-adiabatic molecular dynamics for several conformations :

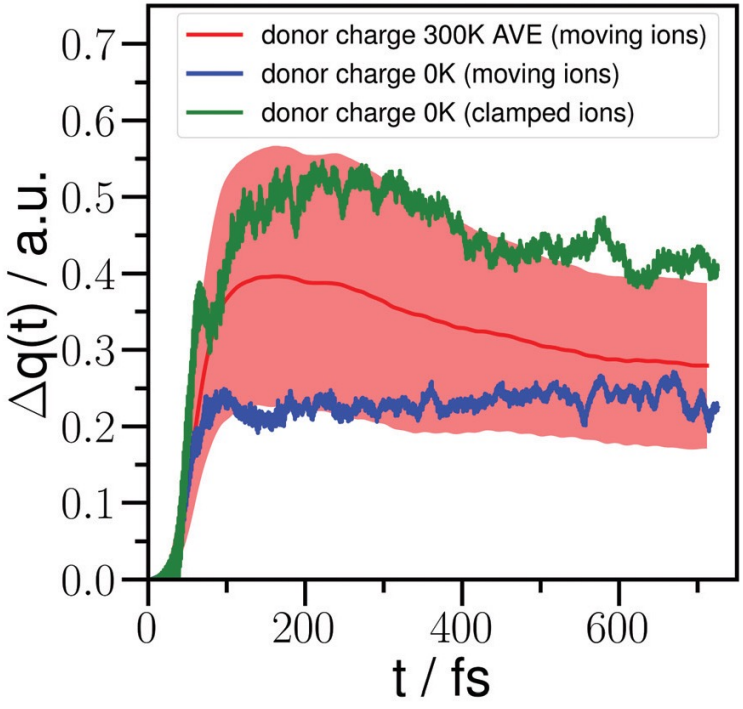


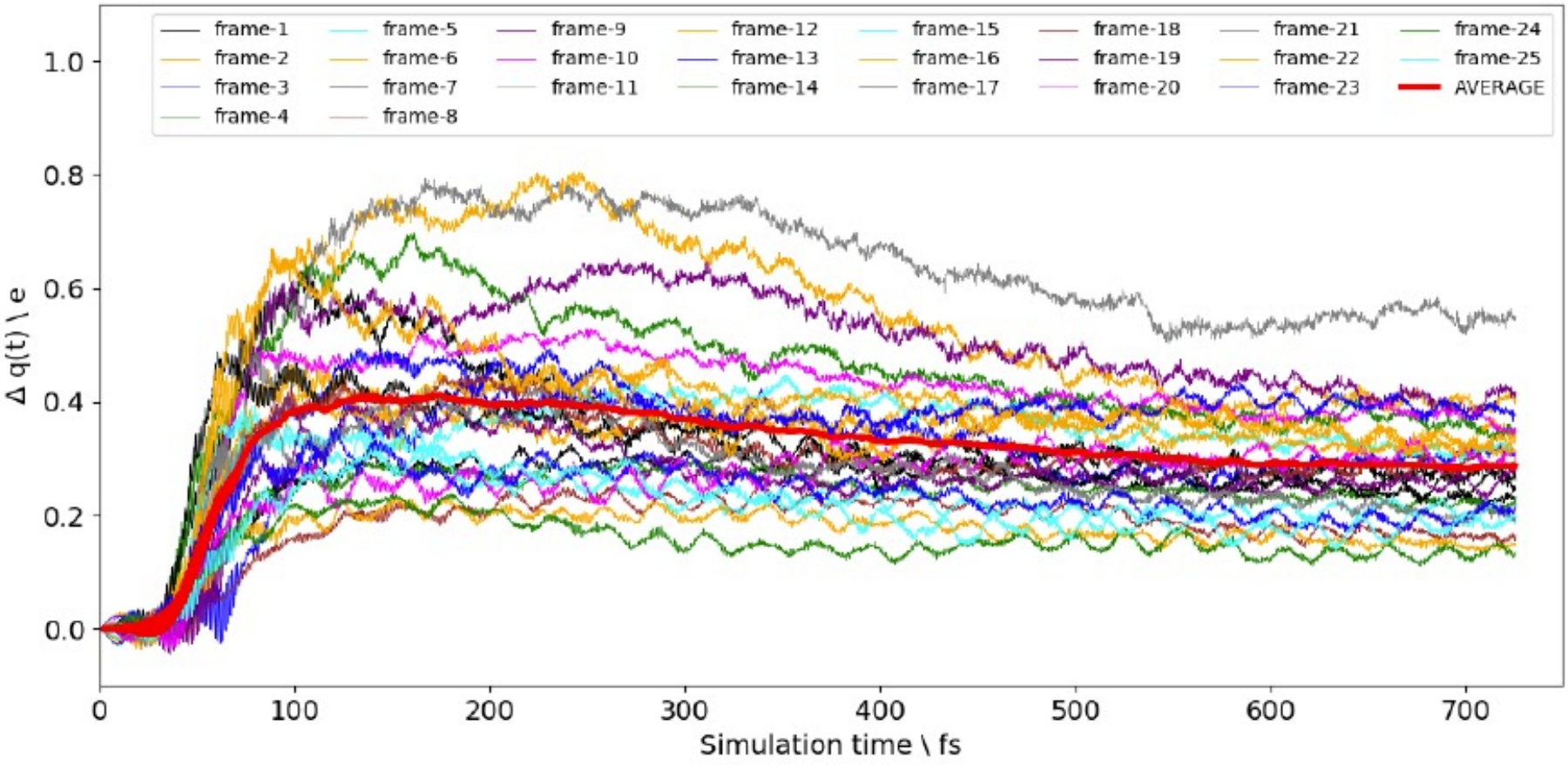
□ We perform in addition a molecular dynamic run (NVT ensemble, 25 *ps*, 0.25 *fs* timestep) and for a batch of conformation, we run Ehrenfest electron dynamics calculations. The average change in density is :










frame-1
frame-2
frame-3
frame-4
frame-5
frame-6
frame-7
frame-8
frame-9
frame-10
frame-11
frame-12
frame-13
frame-14
frame-15
frame-16
frame-17
frame-18
frame-19
frame-20
frame-21
frame-22
frame-23
frame-24
frame-25
AVERAGE
1.0
0.8
0.6
0.4
0.2
0.0
Δ q(t) \ e
0
100
200
300
400
500
600
700
Simulation time \ fs

Density Functional Tight-Binding (DFTB)

❑ Summary of the DFTB models:

- We get, in total, for the third order DFTB3 energy:

$$E^{\mathrm{DFTB3}} = \sum_{iab}\sum_{\mu\in a}\sum_{\nu\in b} n_i c_{\mu i} c_{\nu i} H^0_{\mu\nu} + \frac{1}{2}\sum_{ab}\Delta q_a \Delta q_b \gamma^{\mathrm{h}}_{ab} + \frac{1}{3}\sum_{ab}\Delta q_a^2 \Delta q_b \Gamma_{ab} + \frac{1}{2}\sum_{ab} V^{\mathrm{rep}}_{ab}.$$

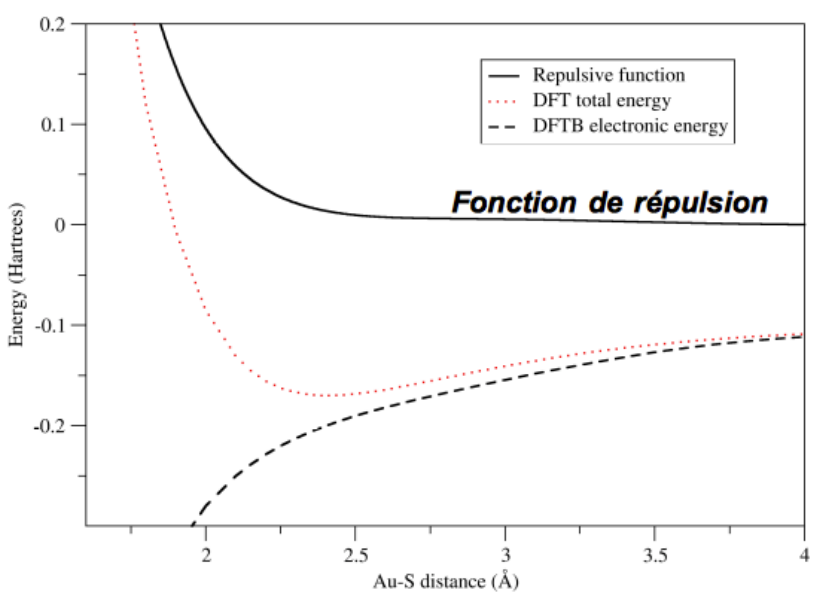
$$\downarrow \qquad\qquad \downarrow \qquad\qquad \downarrow \qquad\qquad \downarrow$$

$$E^1 \qquad\qquad E^2 \qquad\qquad E^3 \qquad\qquad E_{\mathrm{Rep}}$$

DFTB parametrization

❑ Repulsive energy:

$$E_{\text{rep}} = \frac{1}{2} \sum_{\mathcal{AB}}^{N_{\text{atom}}} U_{\mathcal{AB}}$$



☐ Time-consuming part of parameterization : U_{AB} depend on the environnement, thus on the chemical system of interest.

☐ For a dimer A-B, U_{AB} is computed for different A-B distances (1 to 10 a.u):

$$U_{AB} = U_{DFT} - U_{elec}$$

☐ A repulsive polynomial function is interpolated with these points.

☐ Contains the effect neglected by the different approximations (no core electrons,…).

☐ By adding the repulsive part to the parameters, we can now access relative energies and forces.