Center of Excellence for Science and Technology
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Molecular Engineering of DSSC Sensitizers: A DFT Study

Margarita Bužančić Milosavljević

CompChem SPLIT

Bio-Nano

Fluorescence QY

Bioimaging

Photochemistry

Protein Docking

Dye Aggregates

DSSC

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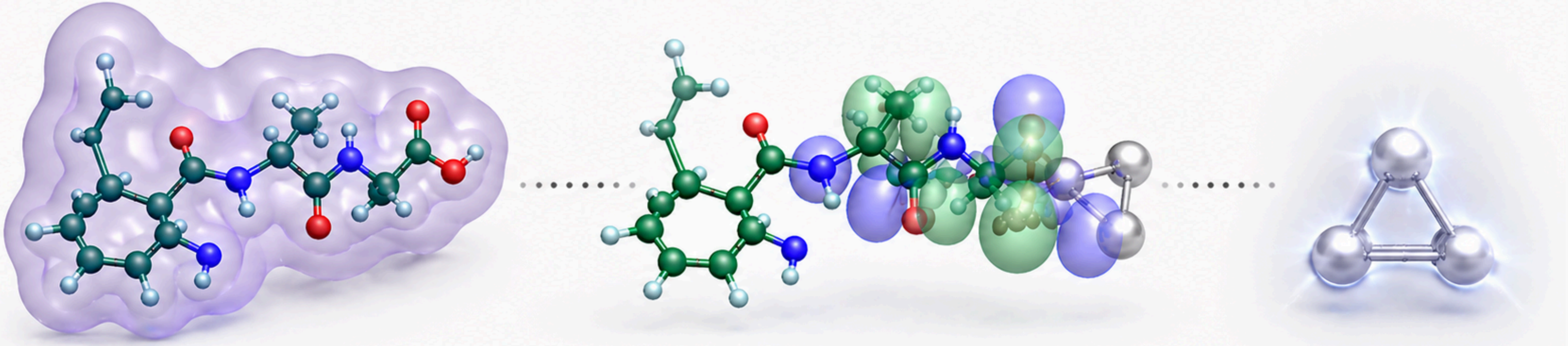
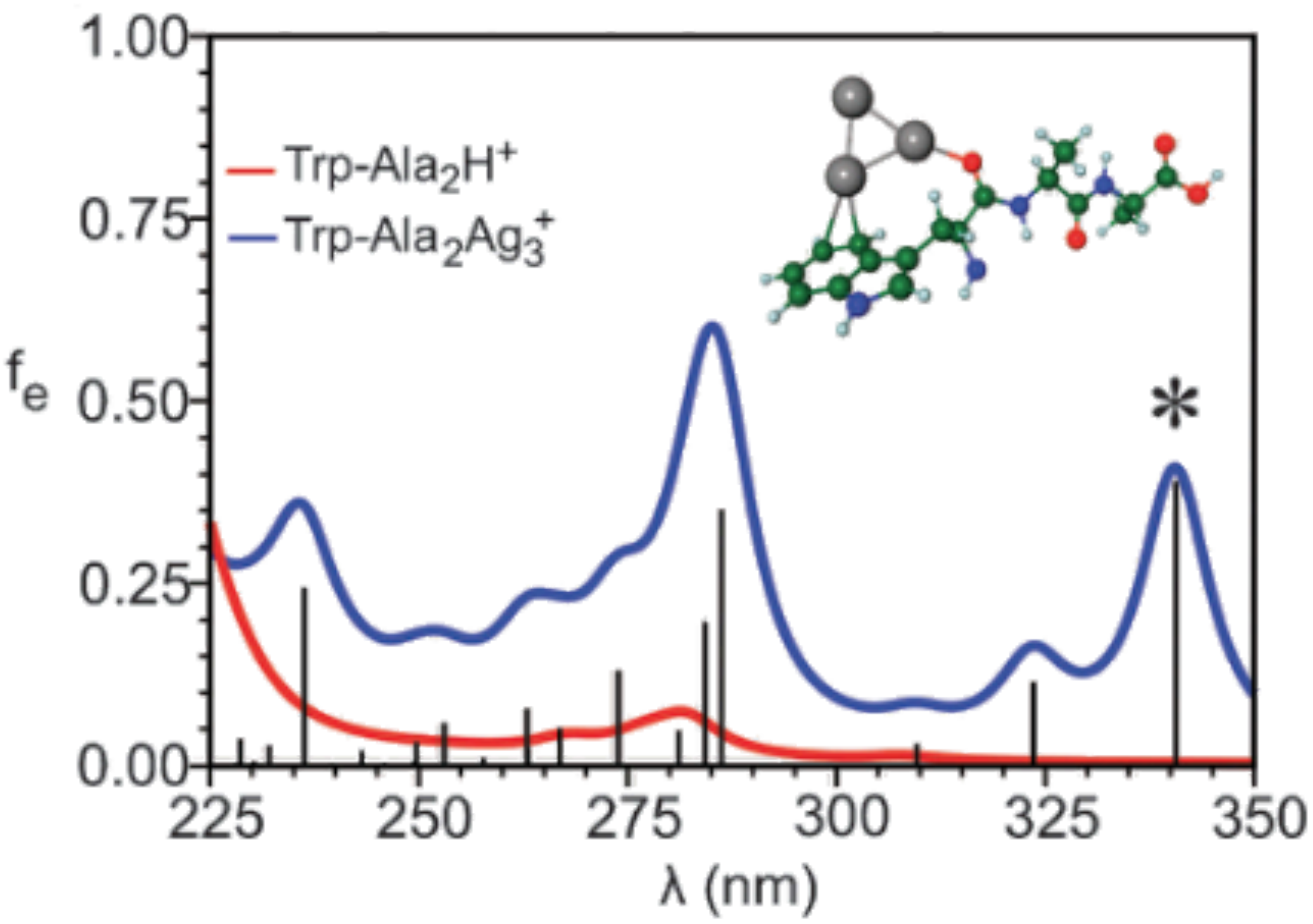
Bio-Nano design properties (new biosensing materials)

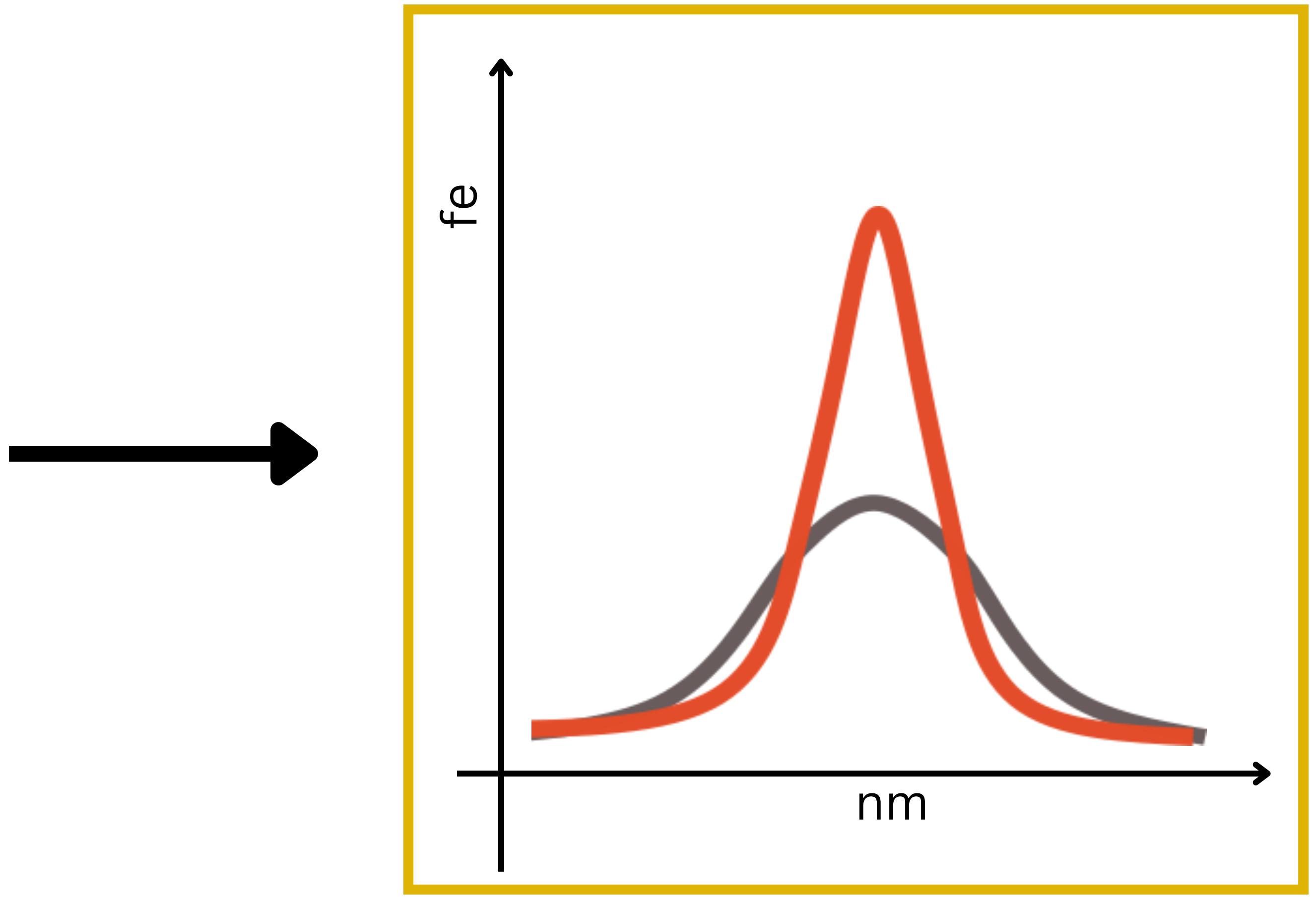


bio-molecule → orbital hybridisation ← nanocluster

Bio-Nano design properties

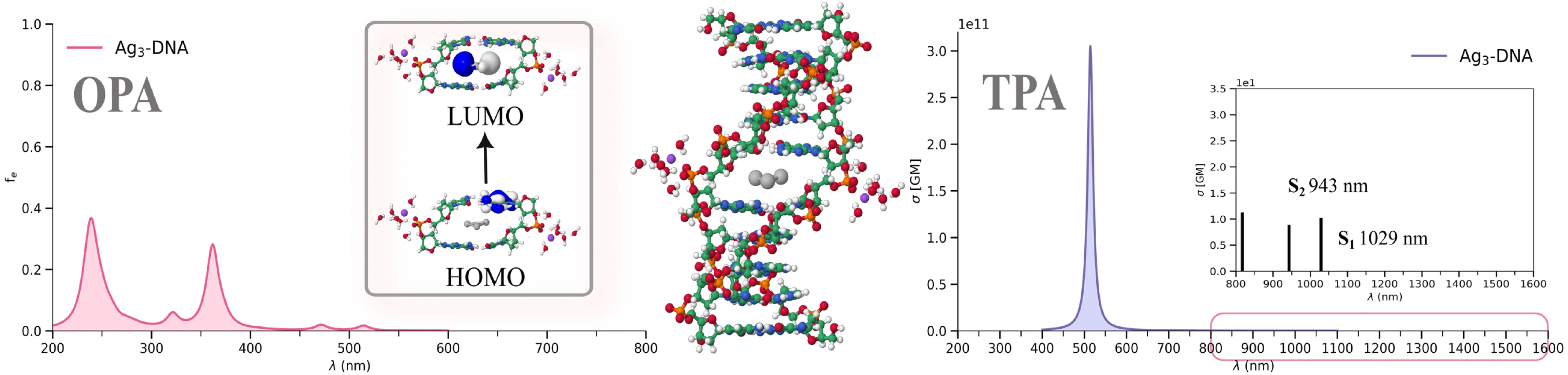


enhancement of absorption intensity



Phys. Chem. Chem. Phys., 2014, 16, 1257

Bio-Nano design properties

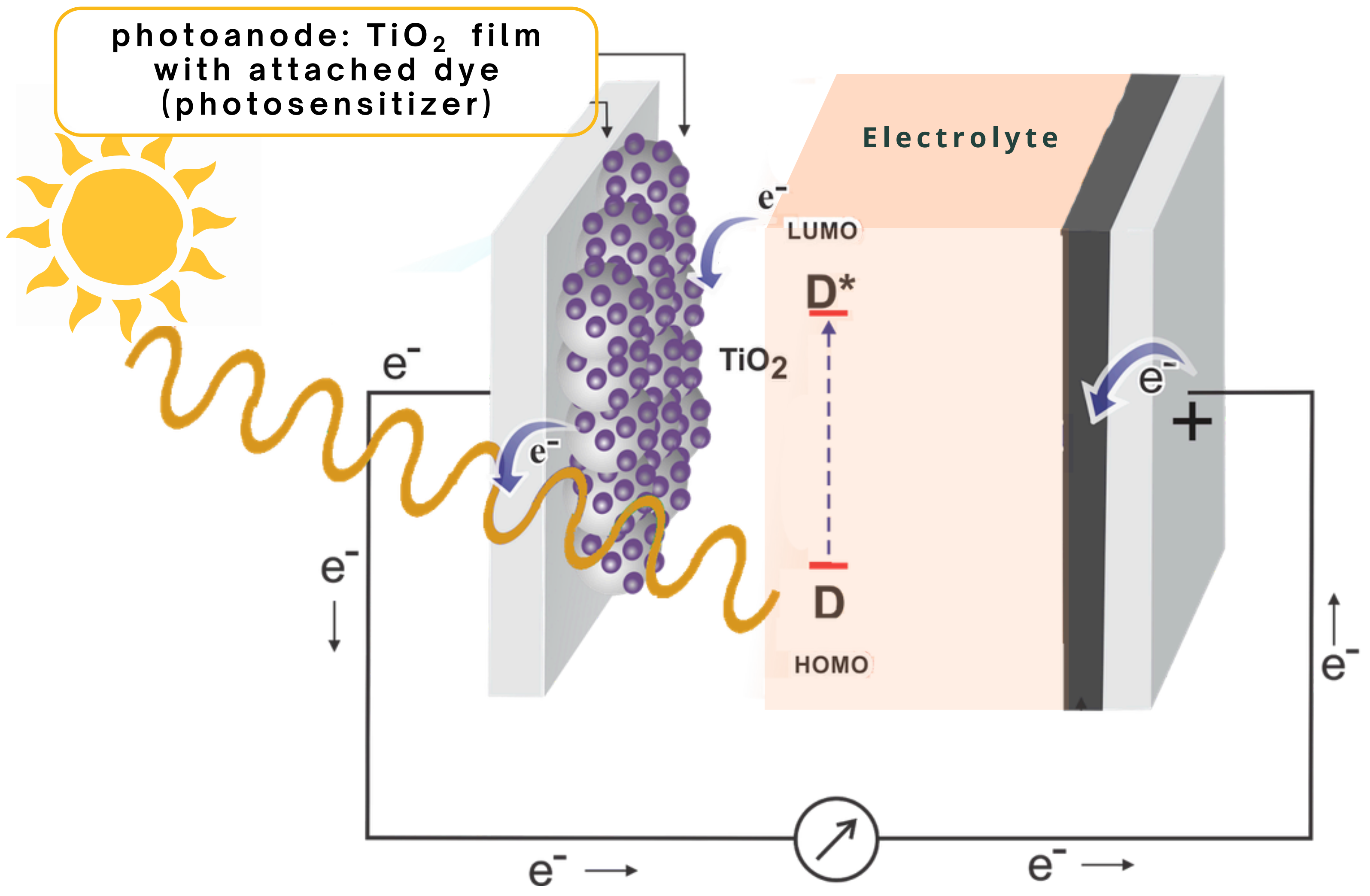


J. Phys.Chem. Lett., 2018, 9, 2584–2589

DSSC?

SOLAR CELLS - DSSC

dye-sensitised solar cell



fluorescent dye - active component

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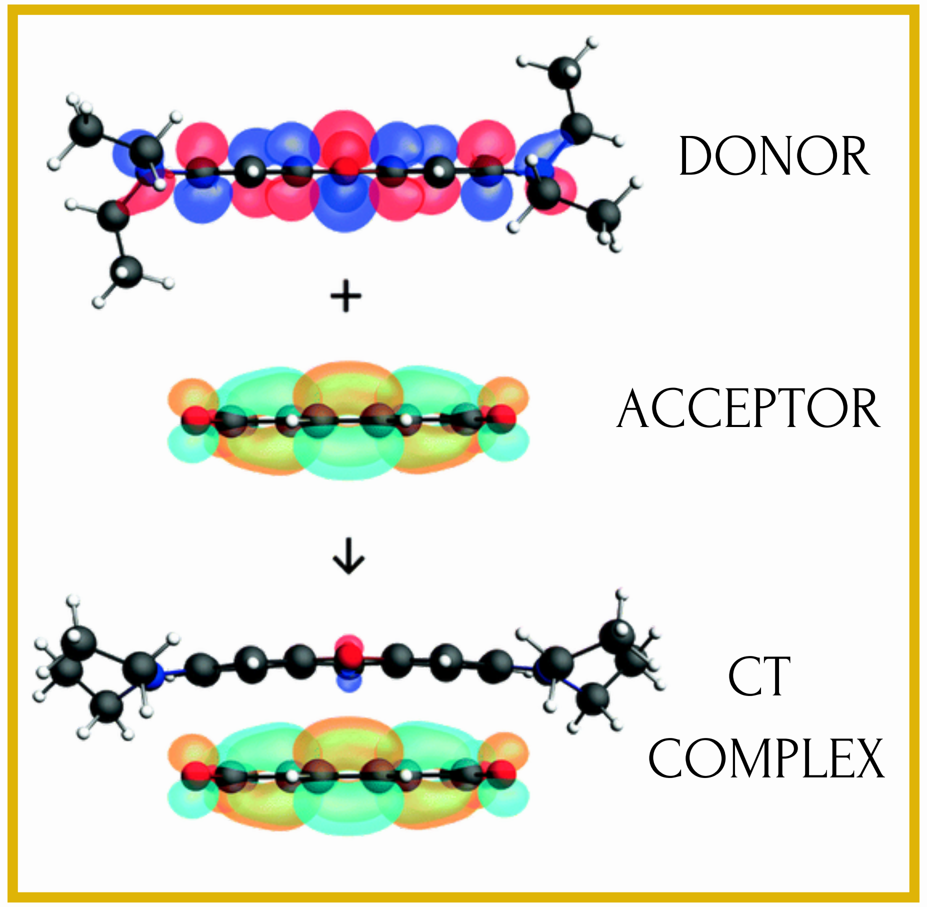
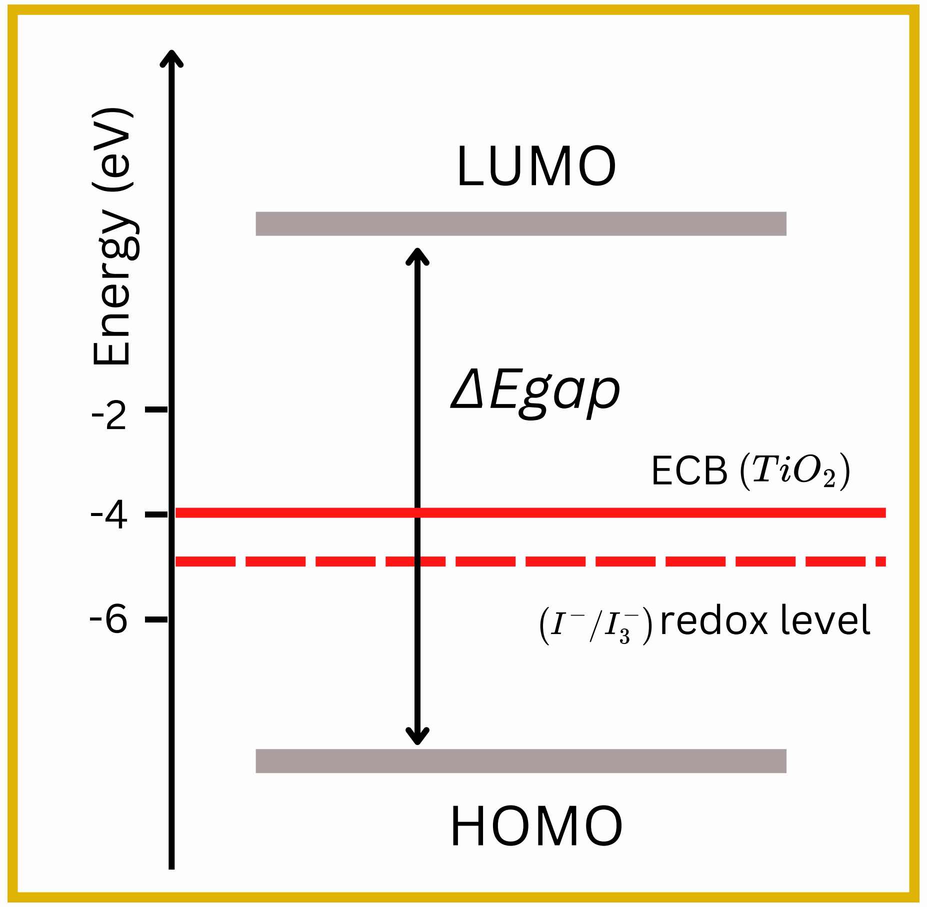
Design requirements

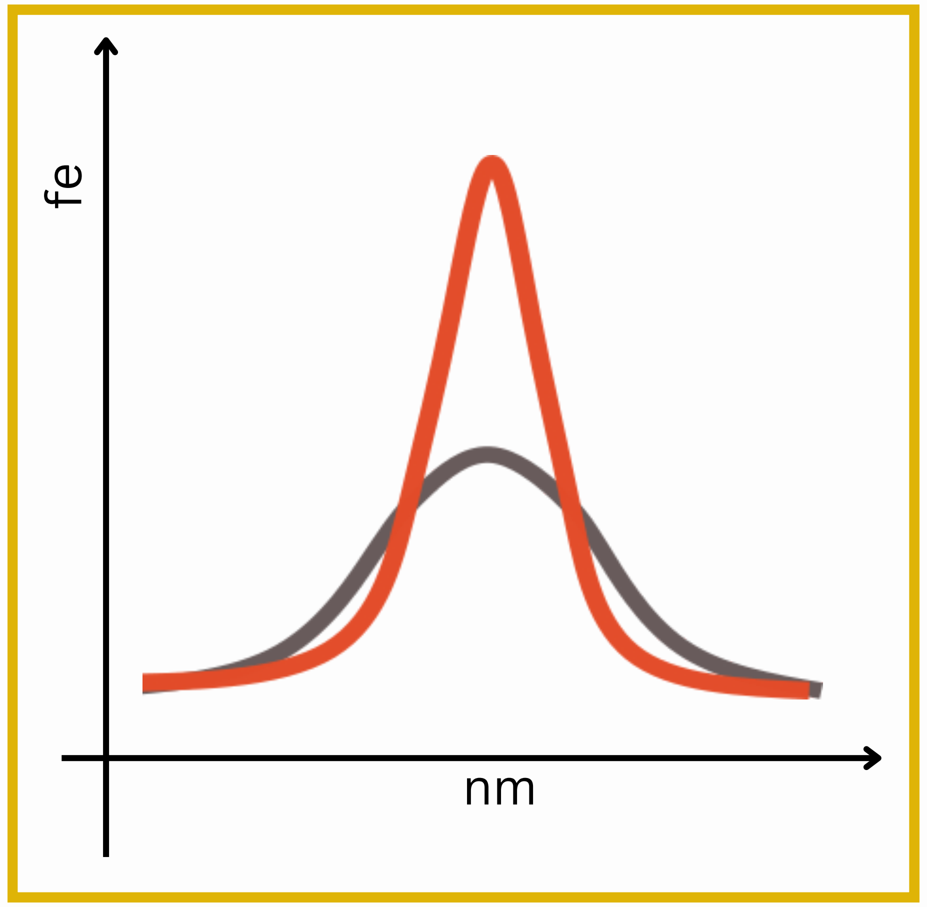
- efficient charge transfer complex



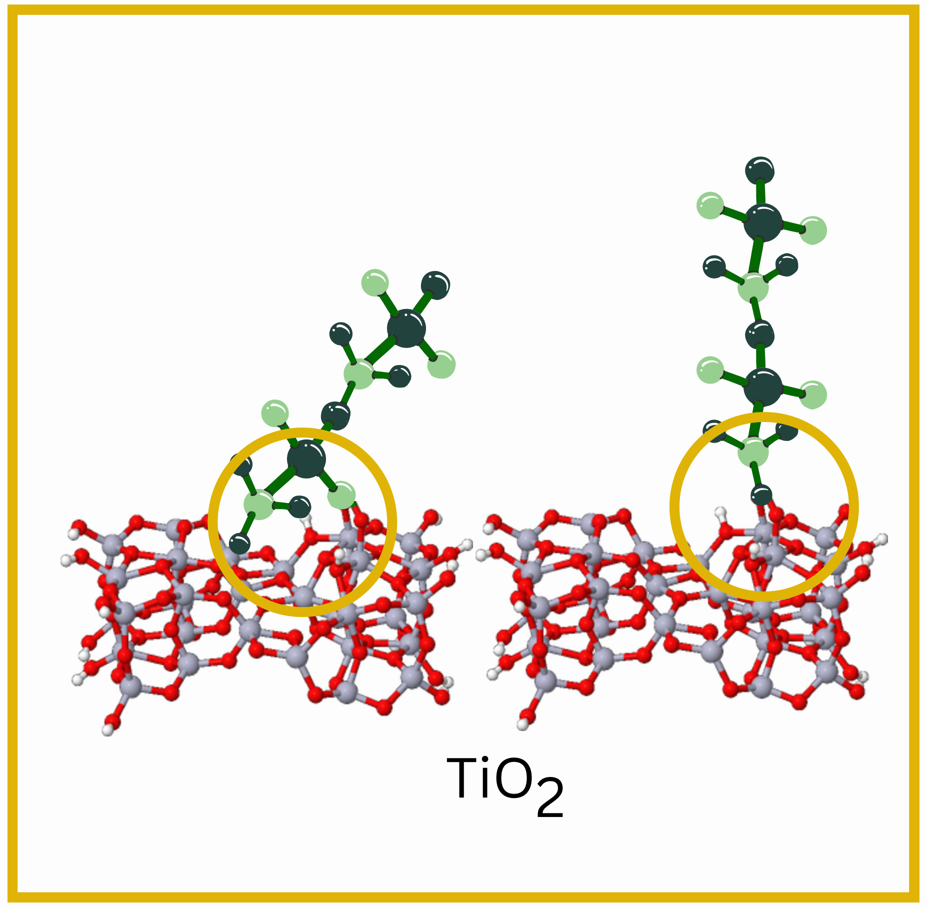
- effective photo-induced electron transfer



- enhancement of absorption intensity



- anchoring to the semiconductor surface



- high photon conversion efficiency

$$IPCE = LHE \cdot \Phi_{injec} \cdot \eta_c$$

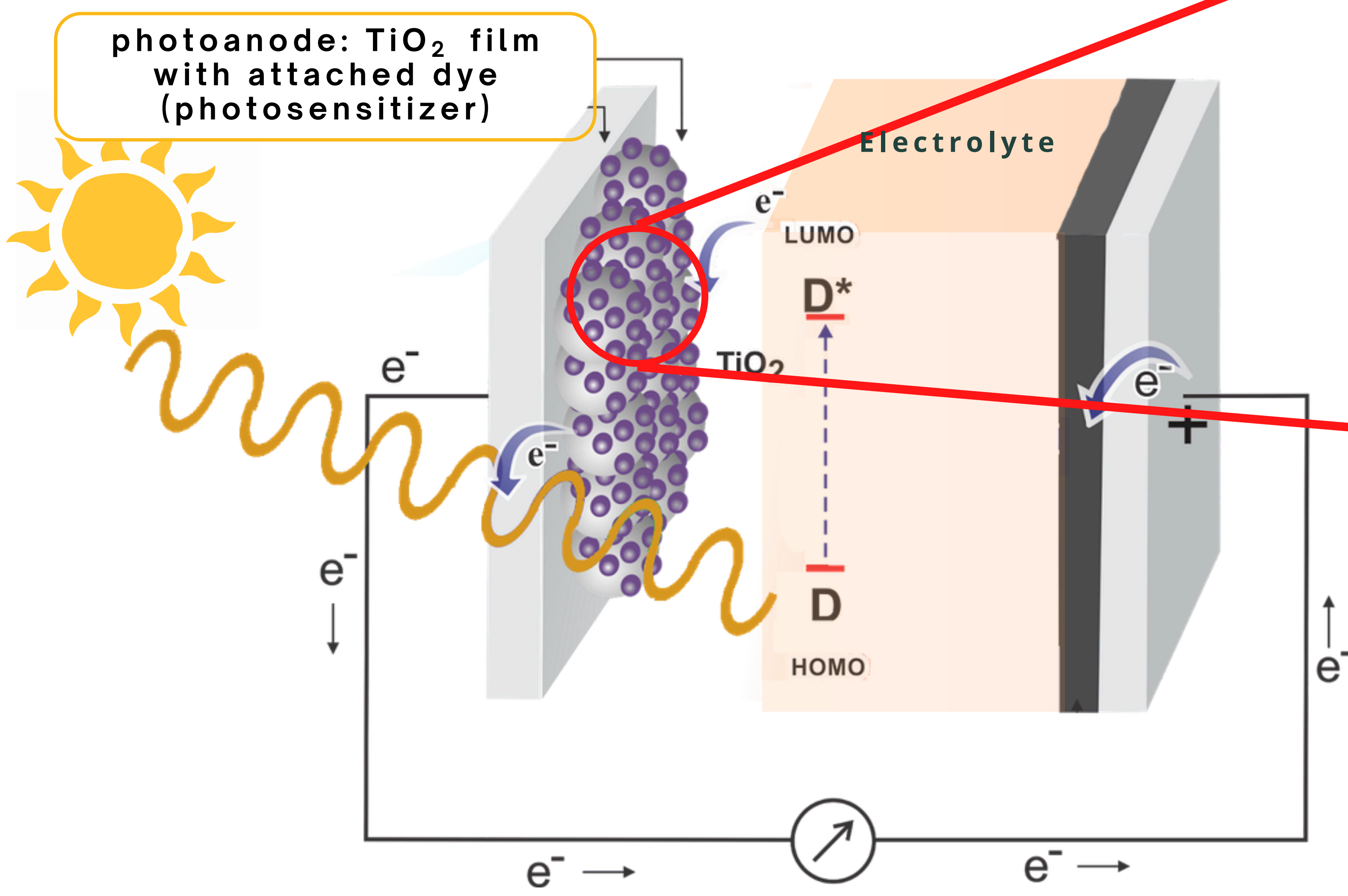
$$LHE = 1 - 10^{-f}$$

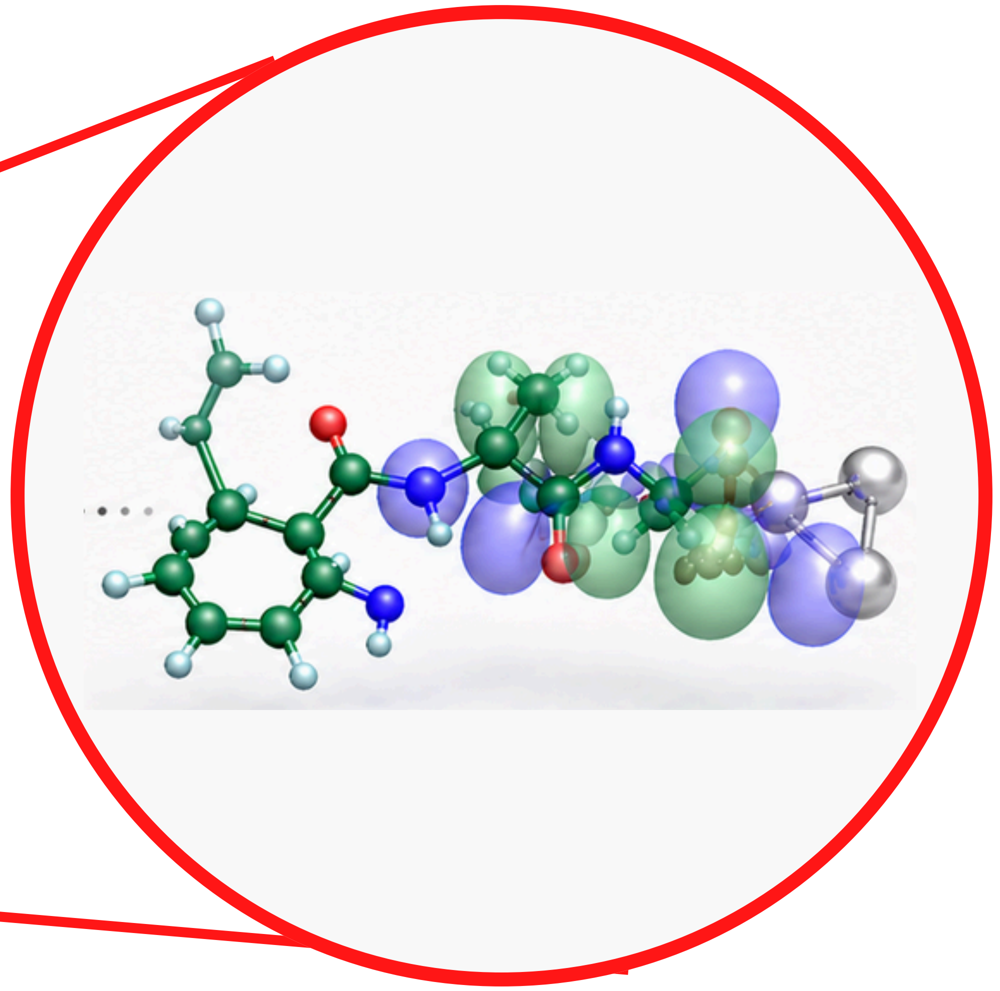
$$\Phi_{inject} \sim -\Delta G^{inject}$$

FLUORESCENT DYE - ACTIVE COMPONENT

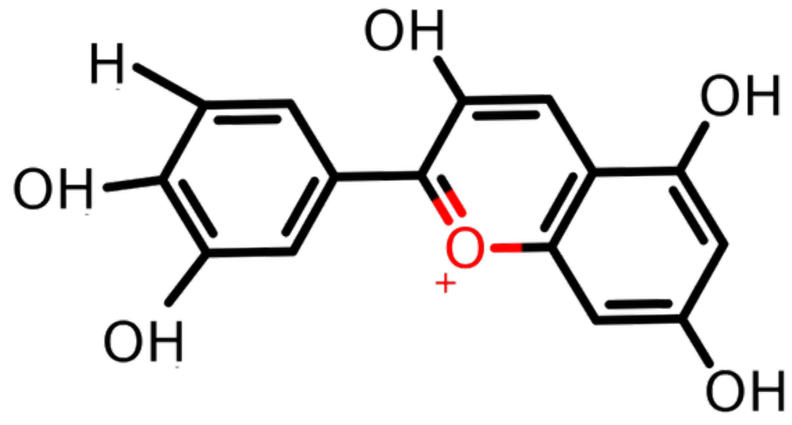
SOLAR CELLS - DSSC

dye-sensitised solar cell





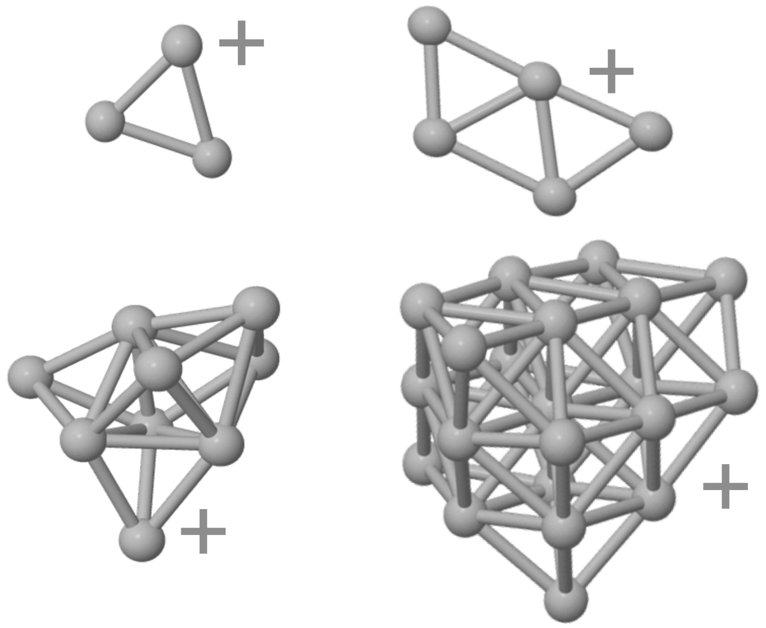
Natural dyes



cyanidin

- non-toxic
- easy to extract
- extensively researched for DSSC
- low efficiency (max. 4%)

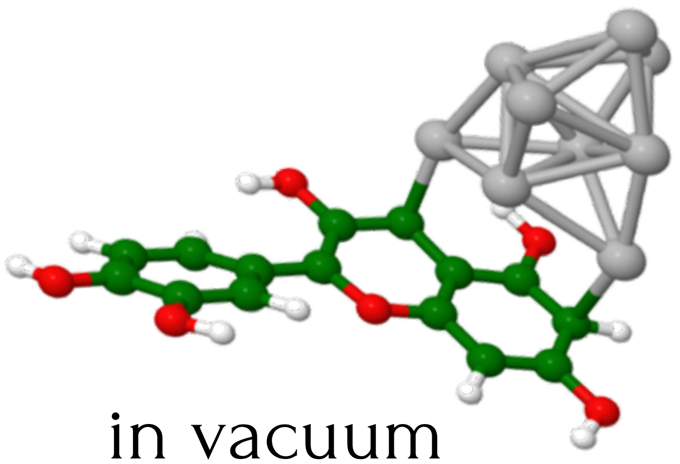
Nanoclusters



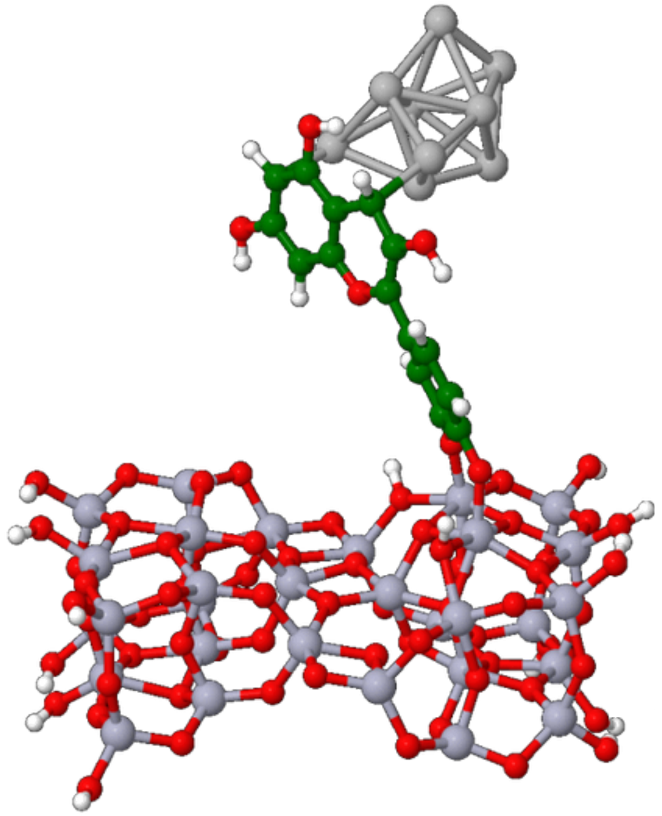
Ag_n^+

- strong intensity
- easily bound to organic molecules
- size regime < 2nm - each atom counts (discrete quantum states)
- specific properties depend on the number of atoms

Bio-Nano Hybrid Sensitizer



in vacuum



on the surface

DSSC

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Model systems for dye-sensitized solar cells: cyanidin-silver nanocluster hybrids at TiO_2 support†

Margarita Bužančić Milosavljević, [a] Antonija Mravak, [a] Martina Perić Bakulić [*a] and Vlasta Bonačić-Koutecký [*abc]

Theoretical study of structural, optical, and photovoltaic properties of novel bio-nano hybrids (dye-nanocluster), as well as at TiO_2 surface model support is presented in the context of the application for dye-sensitized solar cells (DSSC). A group of anthocyanidin dyes (pelargonidin, cyanidin, delphinidin, peonidin, petunidin, and malvidin) represented by cyanidin covalently bound to silver nanoclusters (NCs) with even or odd number of valence electrons have been investigated using DFT and TDDFT approach. The key role of nanoclusters as acceptors in hybrids cyanidin-NC has been shown. The nanoclusters with an even number of valence electrons are suitable as acceptors in hybrids. The interaction of bio-nano (cyanidin-NC) hybrid with the TiO_2 surface model has been investigated in the context of absorption in near-infrared (NIR) and charge separation due to donor and acceptor subunits. Altogether, the theoretical concept serves to identify the key steps in the design of novel solar cells based on bio-nano hybrids at TiO_2 surface for DSSC application.

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DSSC

cyanidin-silver NC hybrids

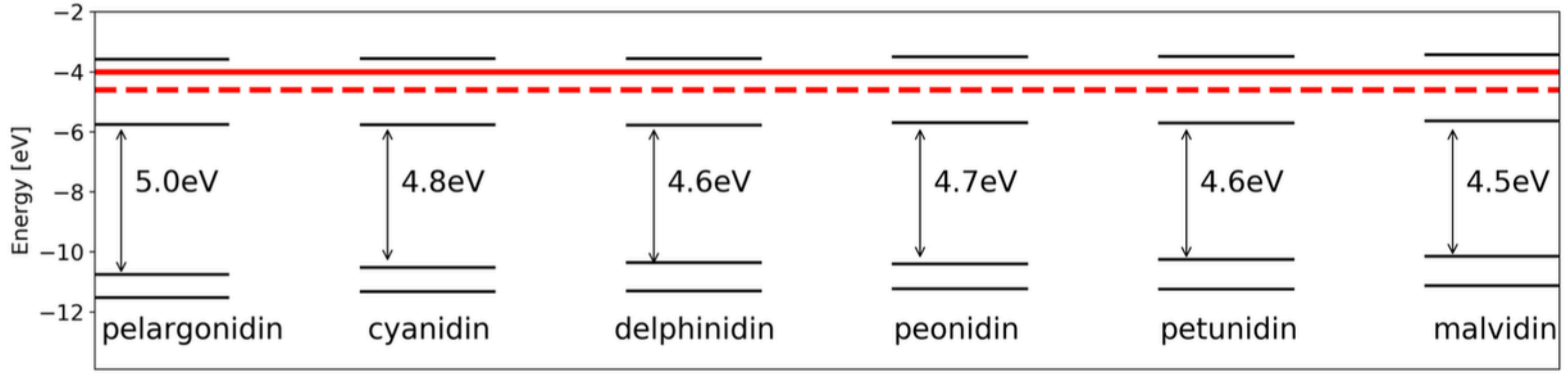


Figure S1: DFT calculated HOMO–LUMO (and HOMO-1, LUMO+1) energy gaps versus vacuum[eV] for the anthocyanidin dyes in comparison with the experimental TiO_2 conduction band edge (red line) and I^-/I_3^- redox level (dashed red line).

anthocyanidin dye-class

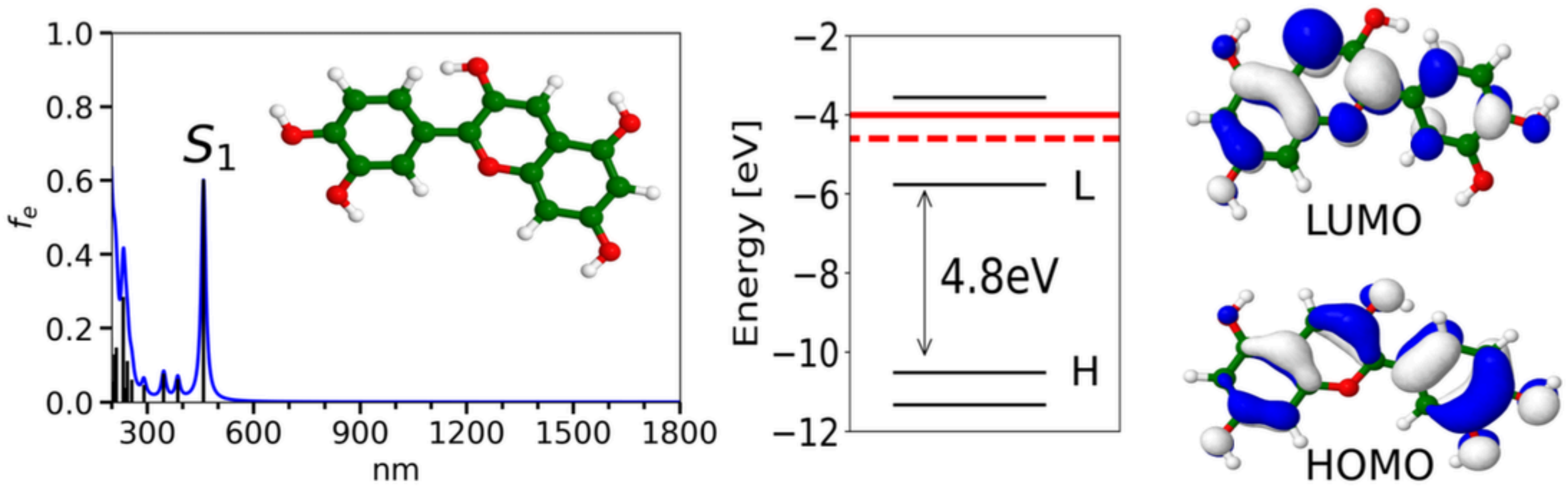
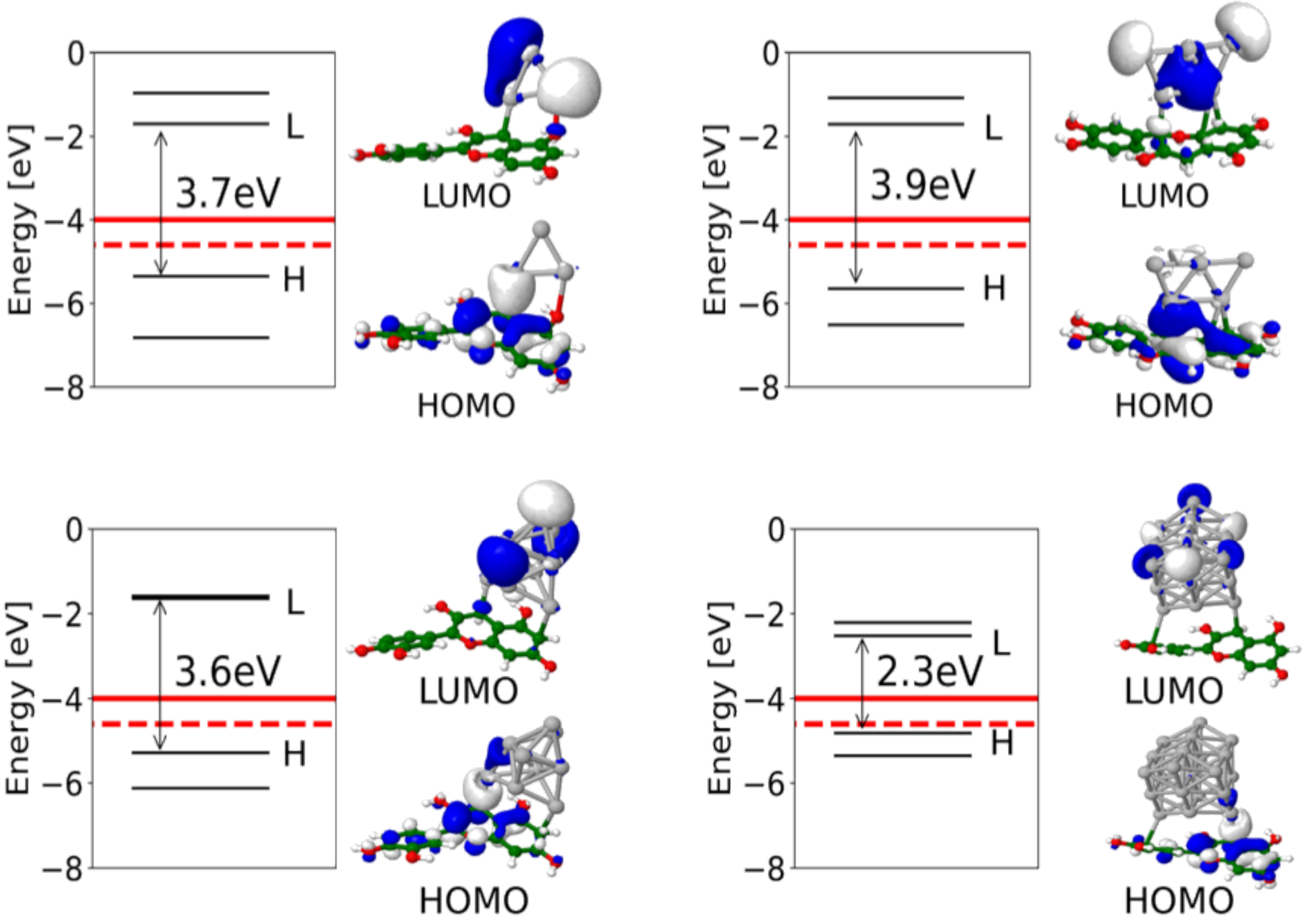


Figure S2: TDDFT calculated absorption spectrum for cyanidin dye employing CAM-B3LYP/def2-SVP method. The structure has been optimized at PBE/def2-SVP level of theory.
DFT HOMO, LUMO orbitals, and HOMO, LUMO, HOMO-1 and LUMO+1 energy gaps versus vacuum. Experimental TiO_2 conduction band edge (full red line) and I^-/I_3^- redox level (dashed red line).

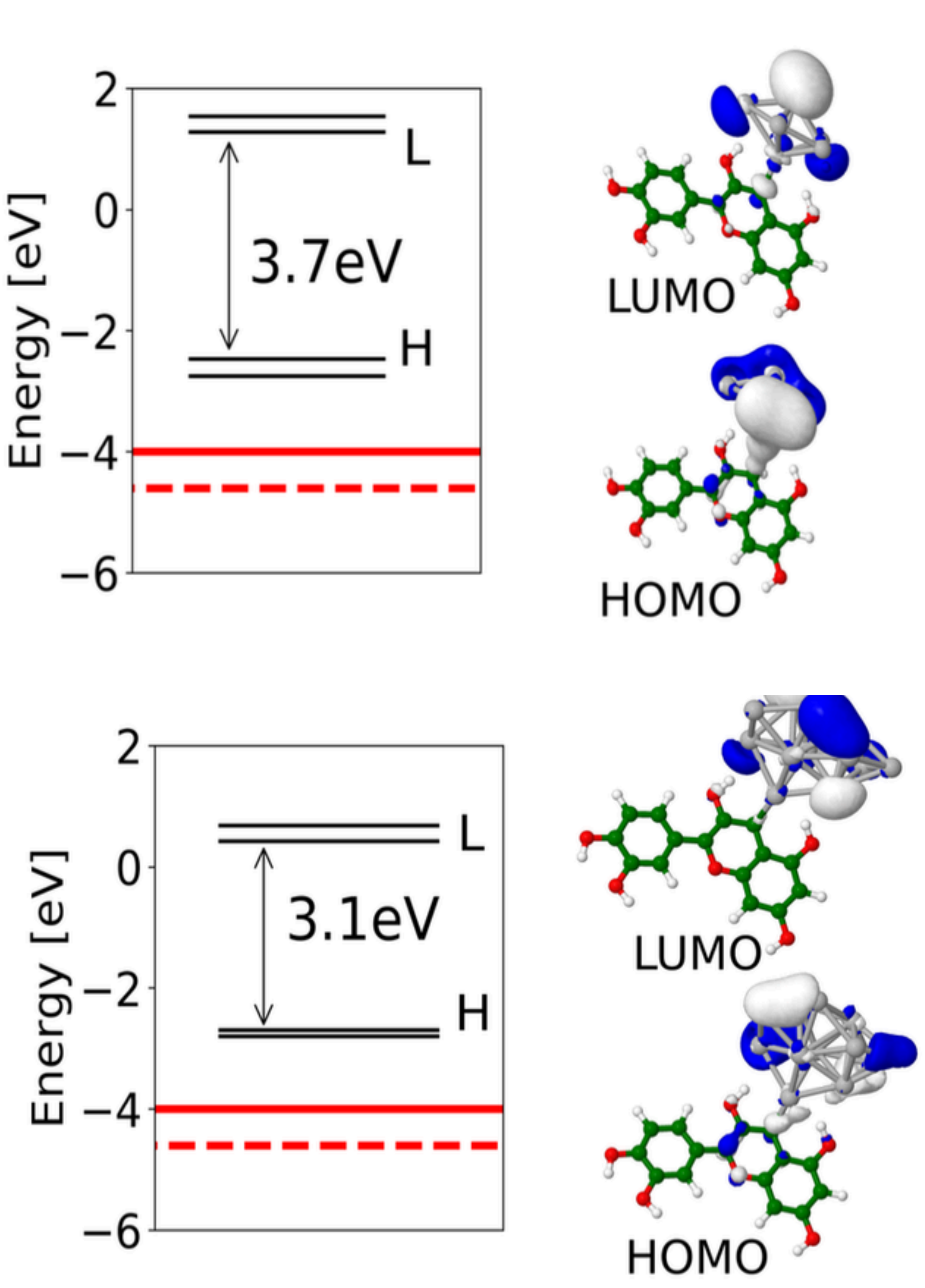
odd

cyanidin-Ag_n (n=3,5,9,21)



even

cyanidin-Ag_n (n=6,12)



- **effective photo-induced electron transfer**

injecting photons into the conduction band

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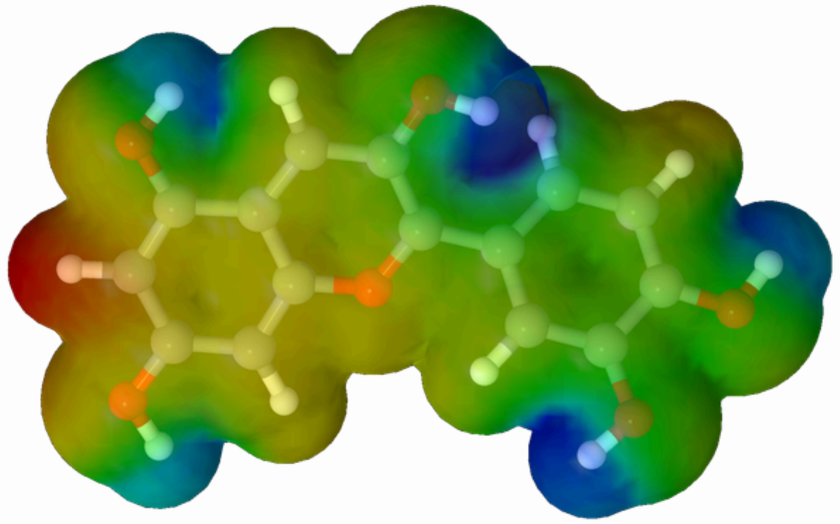
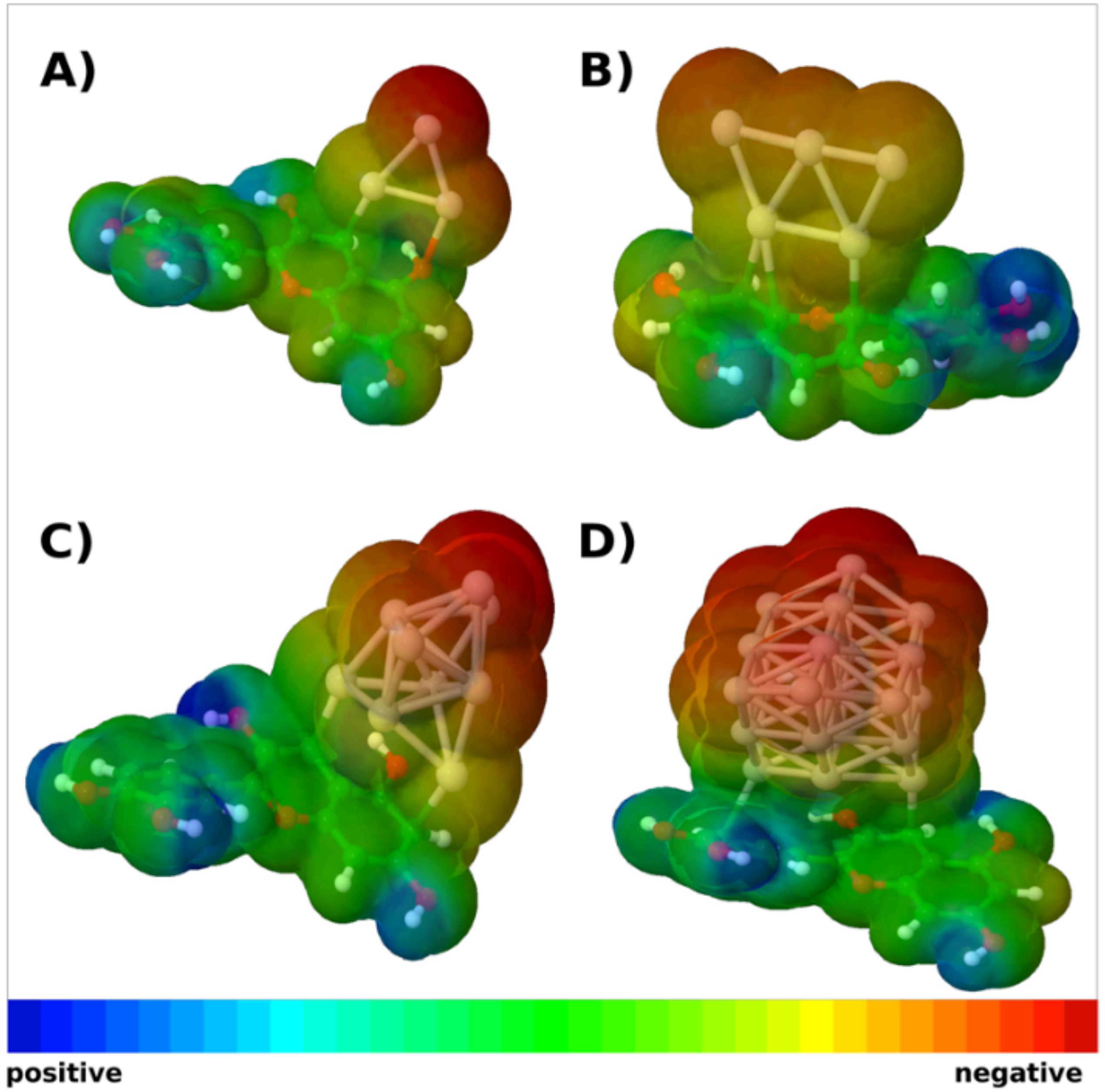
MODELING of cyanidin-silver NC hybrids



cyanidin

cyanidin-Ag_n (n=3,5,9,21)



donor-acceptor character

- **efficient charge transfer complex**

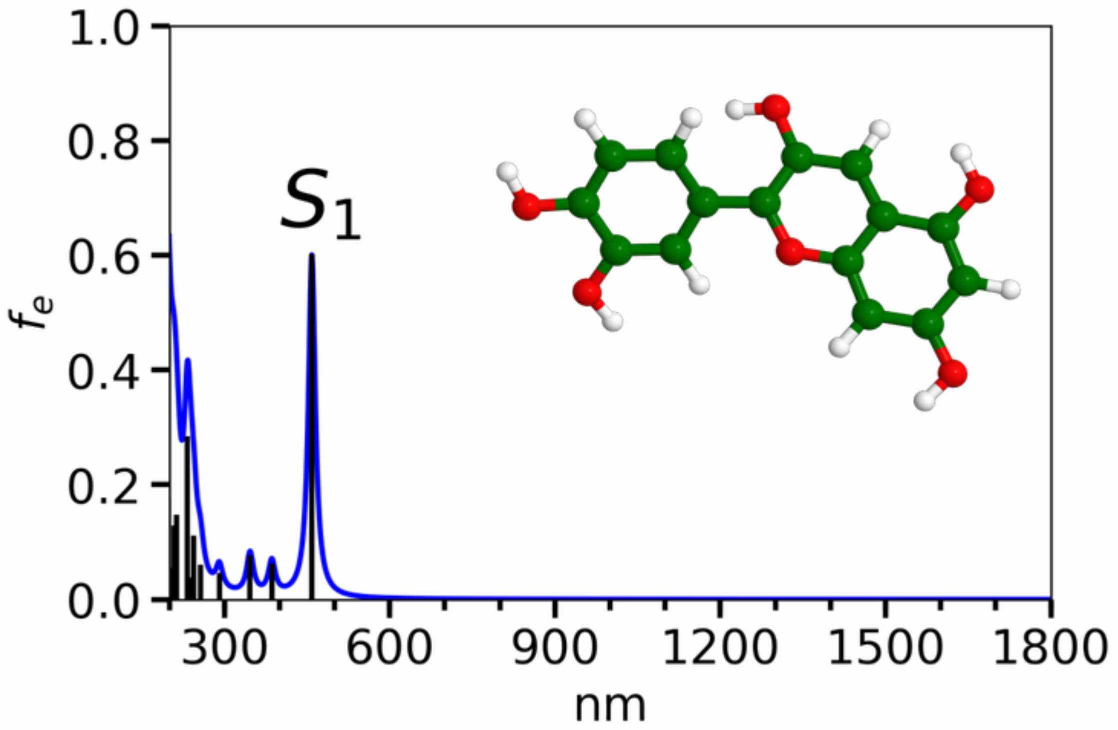
DSSC

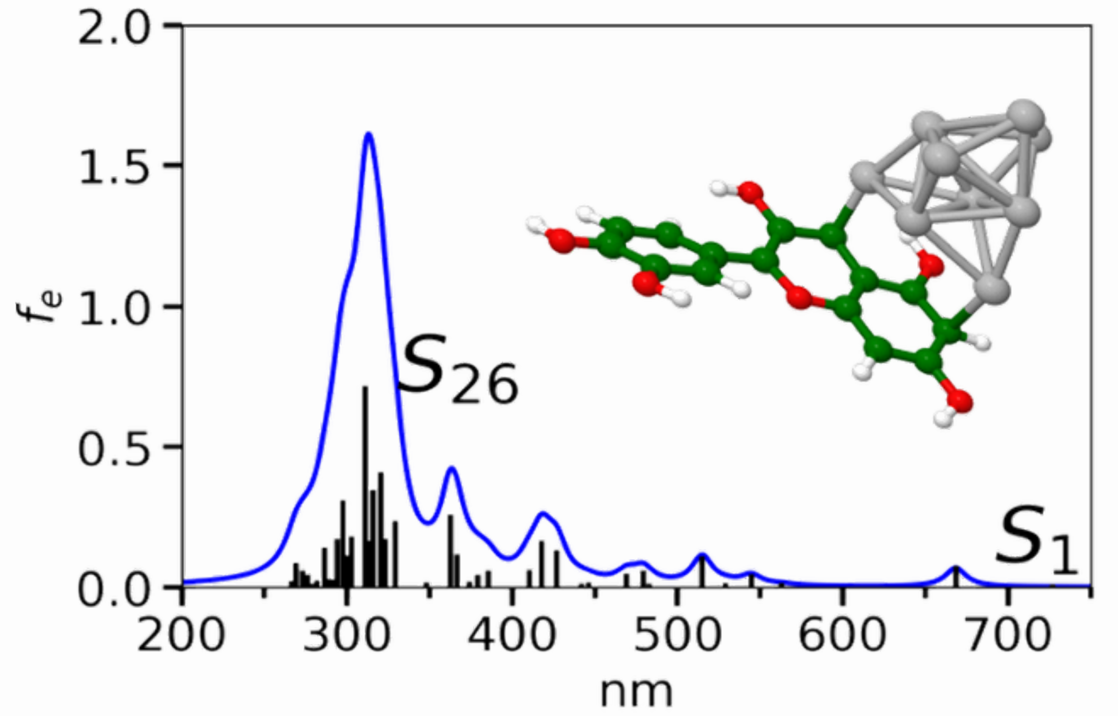
cyanidin-silver NC hybrids

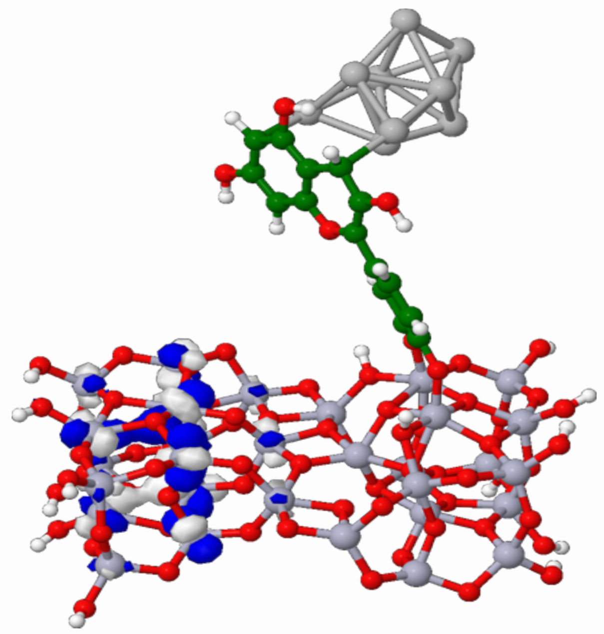
number of valence electrons impacts stability (**even** - odd)

$$IPCE = LHE \cdot \Phi_{injec} \cdot \eta_c$$

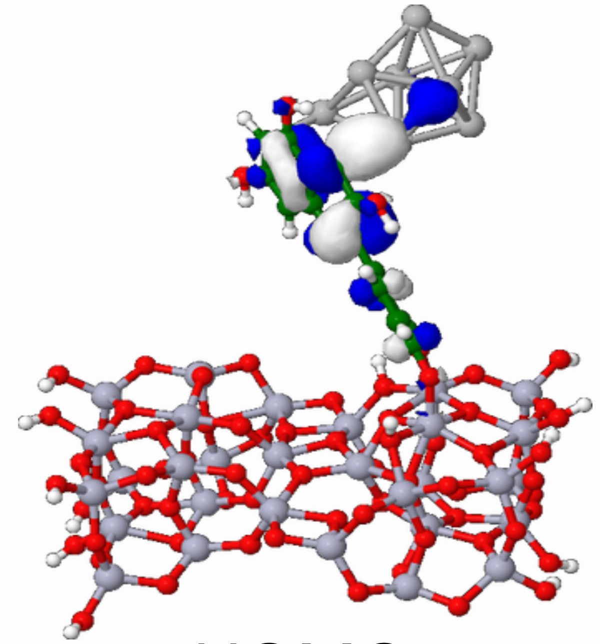
	LHE	ΔG^{inject} [eV]	E_b [eV]
Cyanidin$^+$	0.75	3.815	
Cyanidin-Ag_3	0.73	−1.304	−12.45
Cyanidin-Ag_5	0.55	−1.730	−12.56
Cyanidin-Ag_9	0.80	−2.706	−11.73
Cyanidin-Ag_{21}	0.79	−2.908	−11.07
(Cyanidin-Ag_6)$^-$	0.68	−4.683	−8.26
(Cyanidin-Ag_{12})$^-$	0.79	−4.750	−8.97







LUMO



HOMO

- **high photon conversion efficiency**

- **enhancement of absorption intensity**

- **anchoring to the semiconductor surface**

DSSC

cyanidin-silver NC hybrids

Bio-nano hybrids as sensitizers for DSSC?

YES!

DSSC

nanomaterials

MDPI

Article

Enhancing Efficiency of Dye Sensitized Solar Cells by Coinage Metal Doping of Cyanidin-Silver Trimer Hybrids at TiO_2 Support Based on Theoretical Study

Margarita Bužančić Milosavljević [1], Martina Perić Bakulić [2], Željka Sanader Maršić [3], Antonija Mravak [3,*] and Vlasta Bonačić-Koutecký [1,4,5,*]

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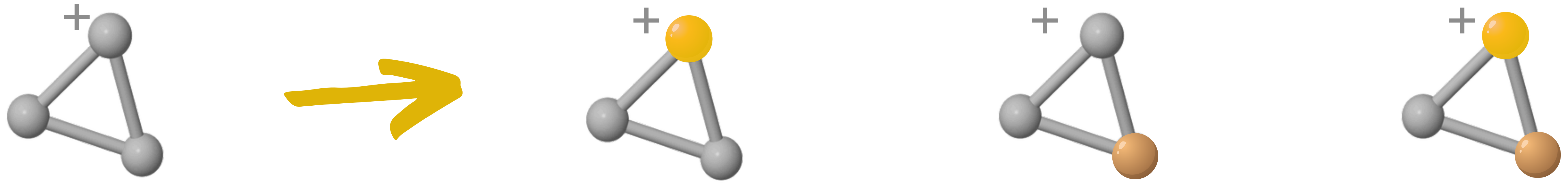
Abstract: Identification of a natural-based sensitizer with optimal stability and efficiency for dye-sensitized solar cell (DSSC) application remains a challenging task. Previously, we proposed a new class of sensitizers based on bio-nano hybrids. These systems composed of natural cyanidin dyes interacting with silver nanoclusters (NCs) have demonstrated enhanced opto-electronic and photovoltaic properties. In this study, we explore the doping of silver nanocluster within a cyanidin-

DSSC

doping of cyanidin-silver NC hybrids with Cu and/or Au atoms

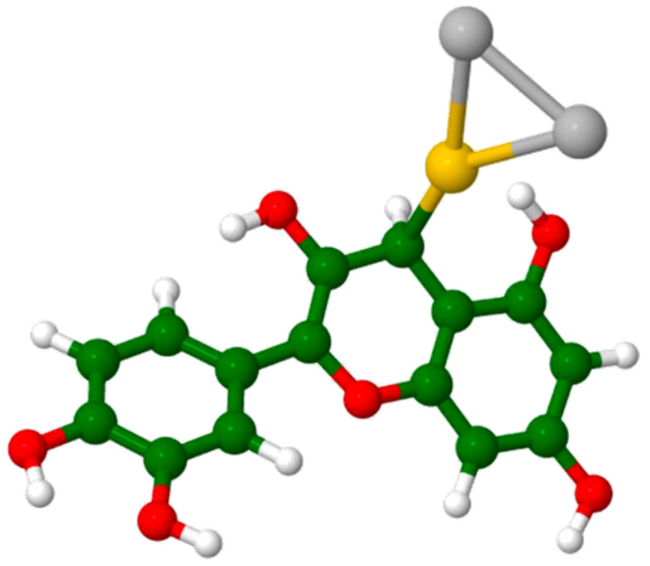
modification of NCs by doping:

- tune the geometric and electronic properties
- improve their stability

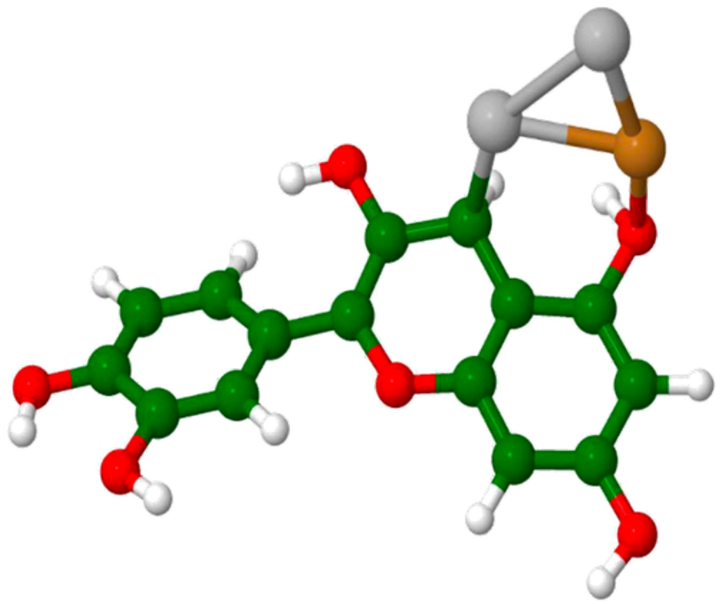


Ag_3^+ Ag_2Au^+ Ag_2Cu^+ $AgAuCu^+$

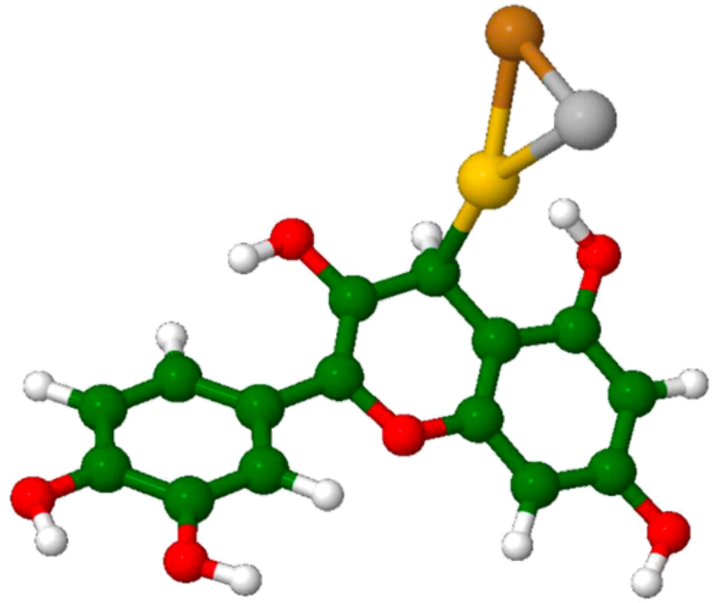
doping of bio-nano hybrids



cyanidin-Ag_2Au



cyanidin-Ag_2Cu

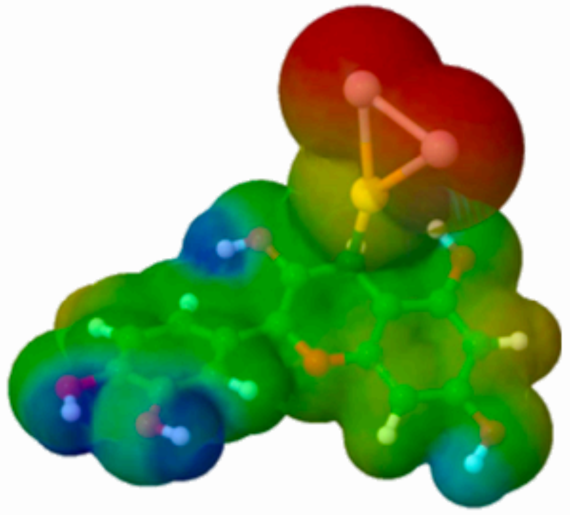


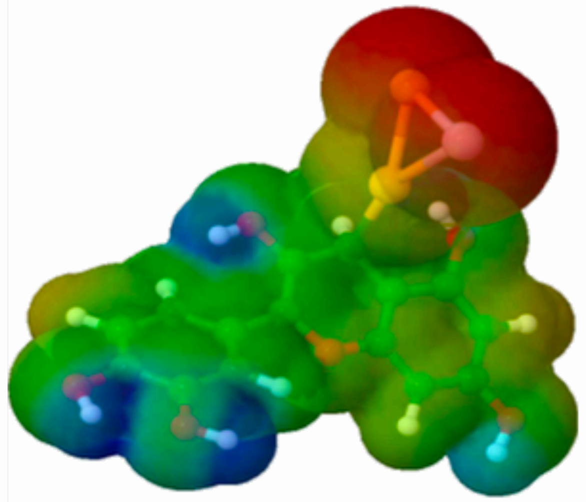
cyanidin-AgAuCu

DSSC

doping of cyanidin-silver NC hybrids with Cu and/or Au atoms

	HOMO [eV]	LUMO [eV]	λ_{max} [nm]	f_e	LHE	ΔG^{inject} [eV]
cyanidin-Ag_3 *	−5.35	−1.65	467	0.57	0.73	−1.30
cyanidin-Ag_9 *	−5.28	−1.68	311	0.71	0.80	−2.71
cyanidin-Ag_{21} *	−4.82	−2.52	332	0.68	0.79	−2.91
cyanidin-Ag_2Au I	−5.58	−2.08	463	0.81	0.85	−1.10
cyanidin-Ag_2Au II	−5.52	−1.71	435	0.52	0.70	−1.33
cyanidin-Ag_2Au III	−5.29	−2.53	518	0.46	0.65	−1.10
cyanidin-Ag_2Cu I	−5.51	−1.84	440	0.37	0.57	−1.31
cyanidin-Ag_2Cu II	−5.30	−0.98	444	0.52	0.70	−1.49
cyanidin-Ag_2Cu III	−5.29	−1.72	457	0.51	0.69	−1.42
cyanidin-AgAuCu I	−5.68	−1.96	449	0.23	0.41	−0.26
cyanidin-AgAuCu II	−5.42	−2.12	228	0.27	0.46	−4.01
cyanidin-AgAuCu III	−5.51	−0.86	425	0.45	0.65	−1.41
cyanidin-AgAuCu IV	−5.53	−1.06	419	0.62	0.76	−1.43
cyanidin-AgAuCu V	−5.54	−1.89	468	0.72	0.81	−1.11





effective photo-induced electron transfer (-ΔG^{inject})

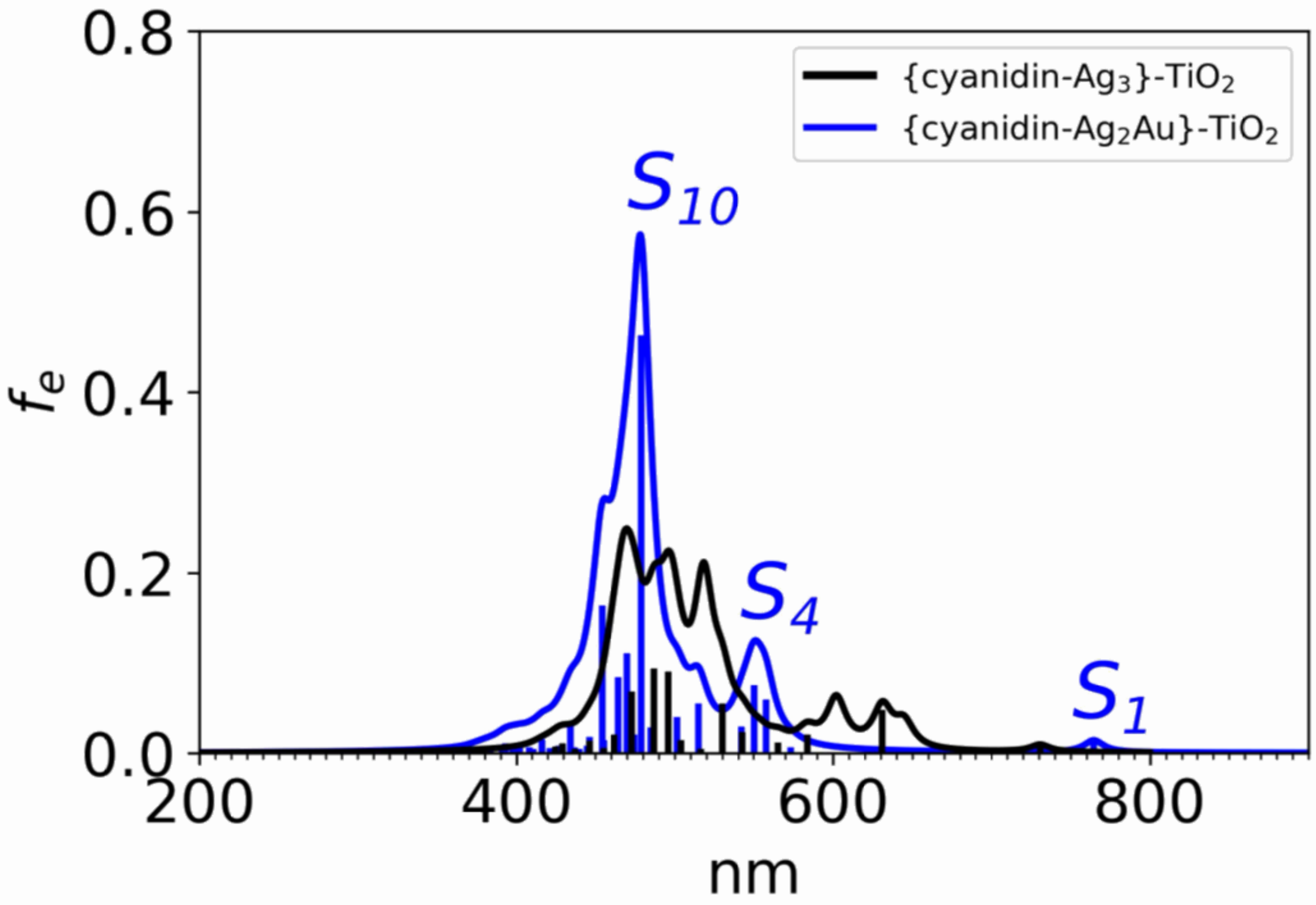
high photon conversion efficiency

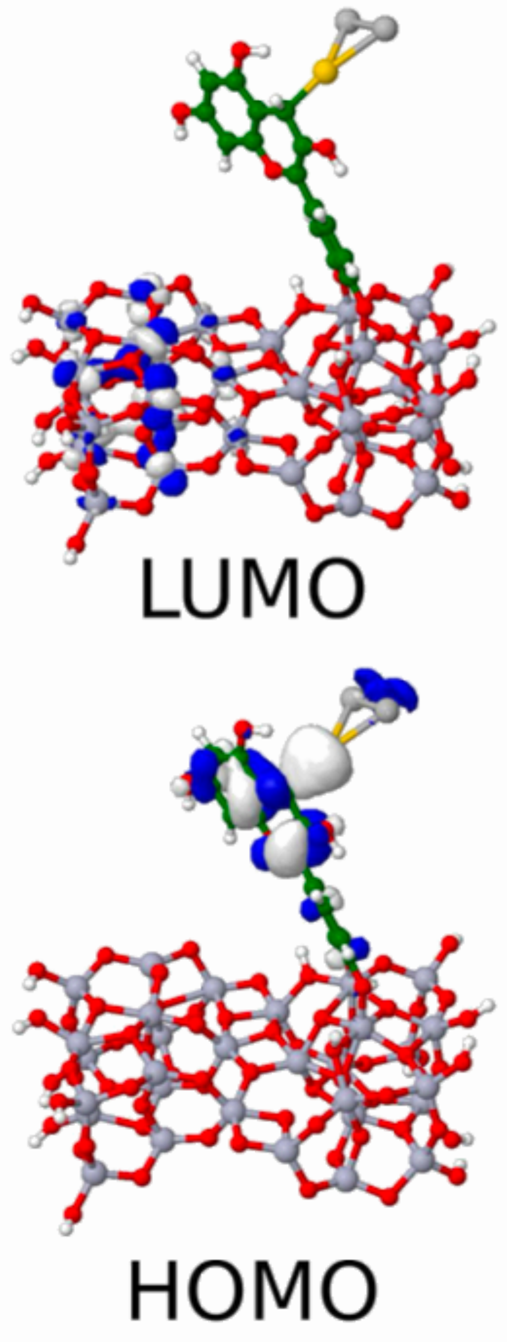
further enhancement of absorption intensity

efficient CT complex

DSSC

doping of cyanidin-silver NC hybrids with Cu and/or Au atoms





anchoring to the semiconductor surface

DSSC

cyanidin-silver NC hybrids

Replacing larger Ag NCs with smaller doped trimers → new bio-nano-based sensitizers with improved stability and light harvesting efficiency

DSSC

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Beyond traditional photosensitizers in DSSCs: harnessing the optical properties of noble metal nanoclusters

Antonija Mravak,[a] Margarita Bužančić Milosavljević[b] and Martina Perić Bakulić*[a]

In an effort to reduce the carbon footprint, green alternative technologies such as dye sensitized solar cells (DSSCs) are being developed. In this evolving field, the search for efficient photosensitizers that can enhance light harvesting, charge transfer, and interfacial stability remains a central challenge. One promising direction for their development includes nanostructured materials, in particular, atomically precise noble metal bio-nanoclusters (bio–NCs). Because of their unique properties that can bridge the gap between classical bulk and quantum systems, they offer great potential as novel, non-traditional photosensitizers. In this Perspective, a computational chemistry-driven outlook is provided, developed in close collaboration with experimental insights, on recent advances in the study of noble metal bio–NCs. Emphasis is placed on their nonlinear optical (NLO) properties – an aspect crucial for DSSC performance, yet often overlooked. Three proposed photosensitizer systems are addressed: cyanidin–Ag_3 hybrid, Ag_3–DNA, and liganded Ag_{25}. Furthermore, heterometal atom doping has been discussed as a strategy to tune the electronic structure of NCs, thereby influencing their stability, catalytic properties, and photoluminescence. Additionally, as interactions with the semiconductor surface play an important role in charge separation, the anchoring modes of these systems on a TiO_2 model are proposed. By integrating insights from time-dependent density functional theory (TDDFT) with emerging experimental perspectives, this work aims to provide a deeper understanding of noble metal bio–NC properties towards revival in solar energy research.

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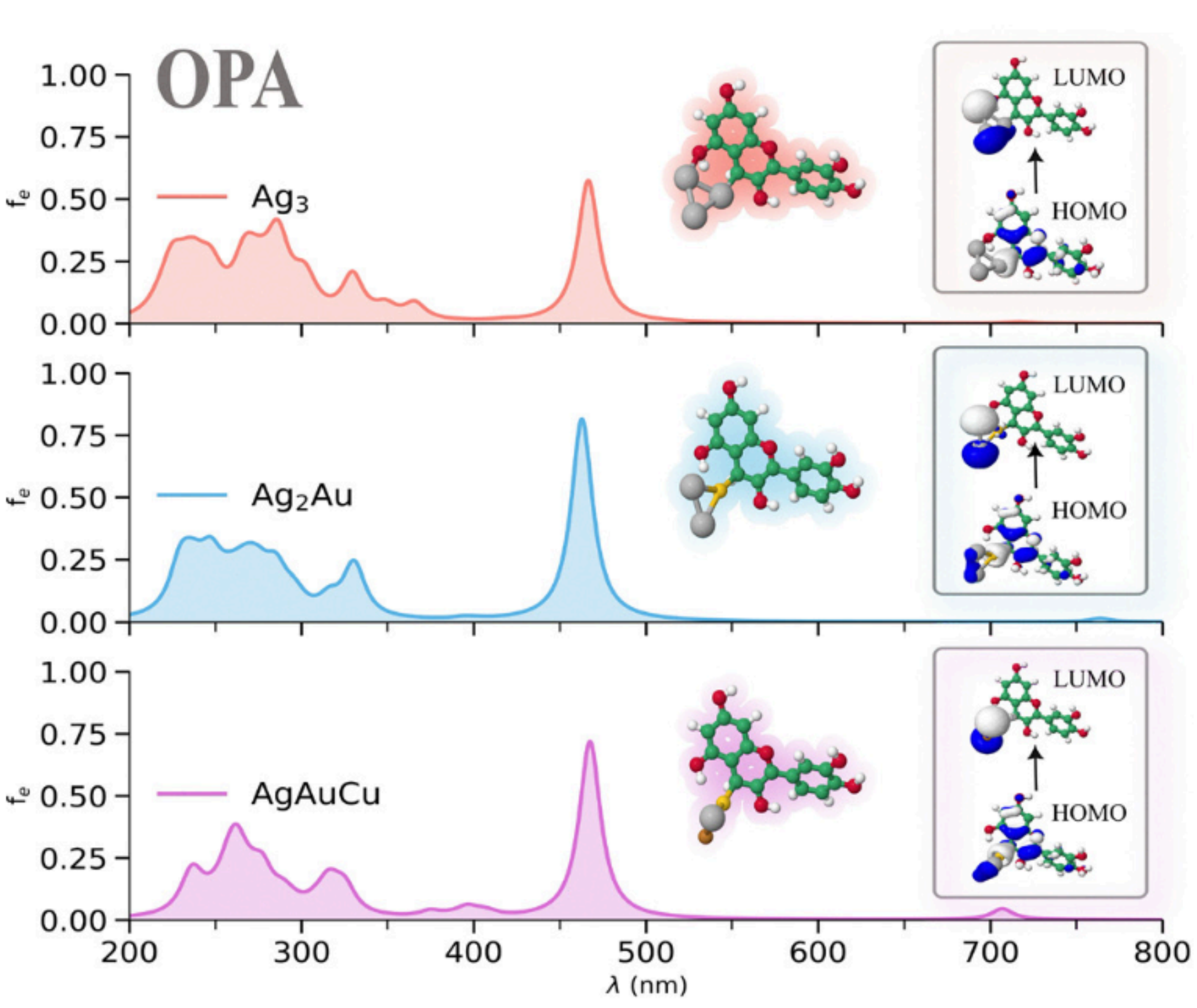
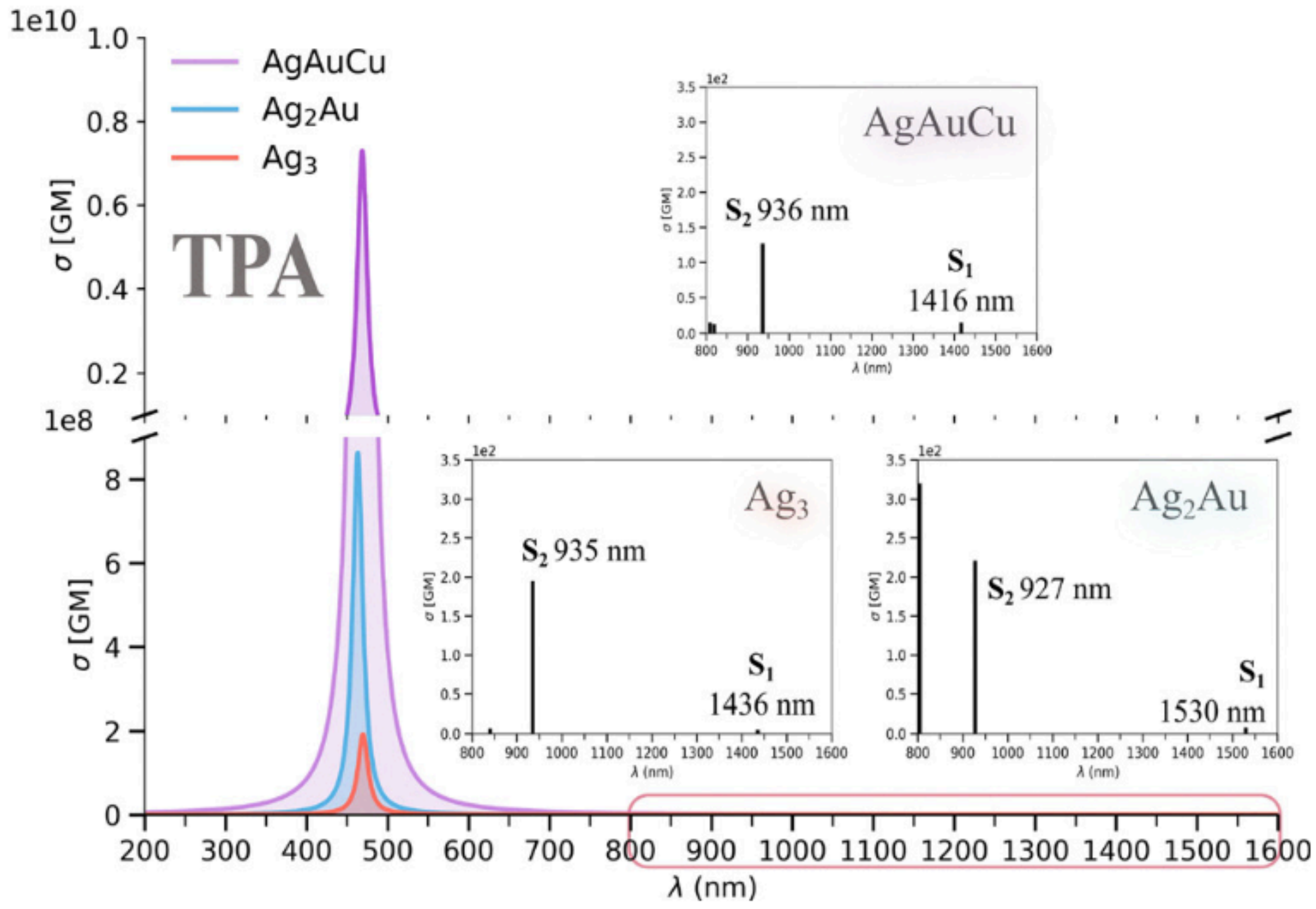


OPA
Ag3
Ag2Au
AgAuCu
LUMO
HOMO
f_e
λ (nm)



TPA
AgAuCu
Ag2Au
Ag3
1e10
1e8
σ [GM]
λ (nm)
S2 936 nm
S1 1416 nm
S2 935 nm
S1 1436 nm
S2 927 nm
S1 1530 nm

DSSC

conclusions and future perspectives

bio-nano hybrid sensitisers:

- enhanced opto-electronic properties
- increased light-harvesting and photocurrent efficiency

- have not been previously investigated as DSSC sensitisers

doping of bio-nano hybrid sensitizers:

- doping by single Au/Cu atoms, and combined Au-Cu -> more stable trimer - hybrid structure (smaller s-d gap)

- influence of doping on the larger NCs needs to be investigated - future

- the findings highlight the potential of bio-nano hybrids as DSSC sensitisers with improved efficiency

- experimental research is needed

Thank you!

University of Zagreb
University Computing Centre

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