COMPUTATIONAL CHEMISTRY DAY 2025

NOBLE METAL NANOCLUSTERS: TINY STRUCTURES, BIG IMPACT

June 7th, 2025
Botanical Garden Fran Kušan
Faculty of Pharmacy and Biochemistry, Zagreb

Martina Perić Bakulić
doc. dr. sc.

(martinapb@ktf-split.hr)

KTF
FACULTY OF CHEMISTRY AND TECHNOLOGY
Department of Physics
University of Split

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CENTER OF EXCELLENCE FOR SCIENCE AND TECHNOLOGY-STIM
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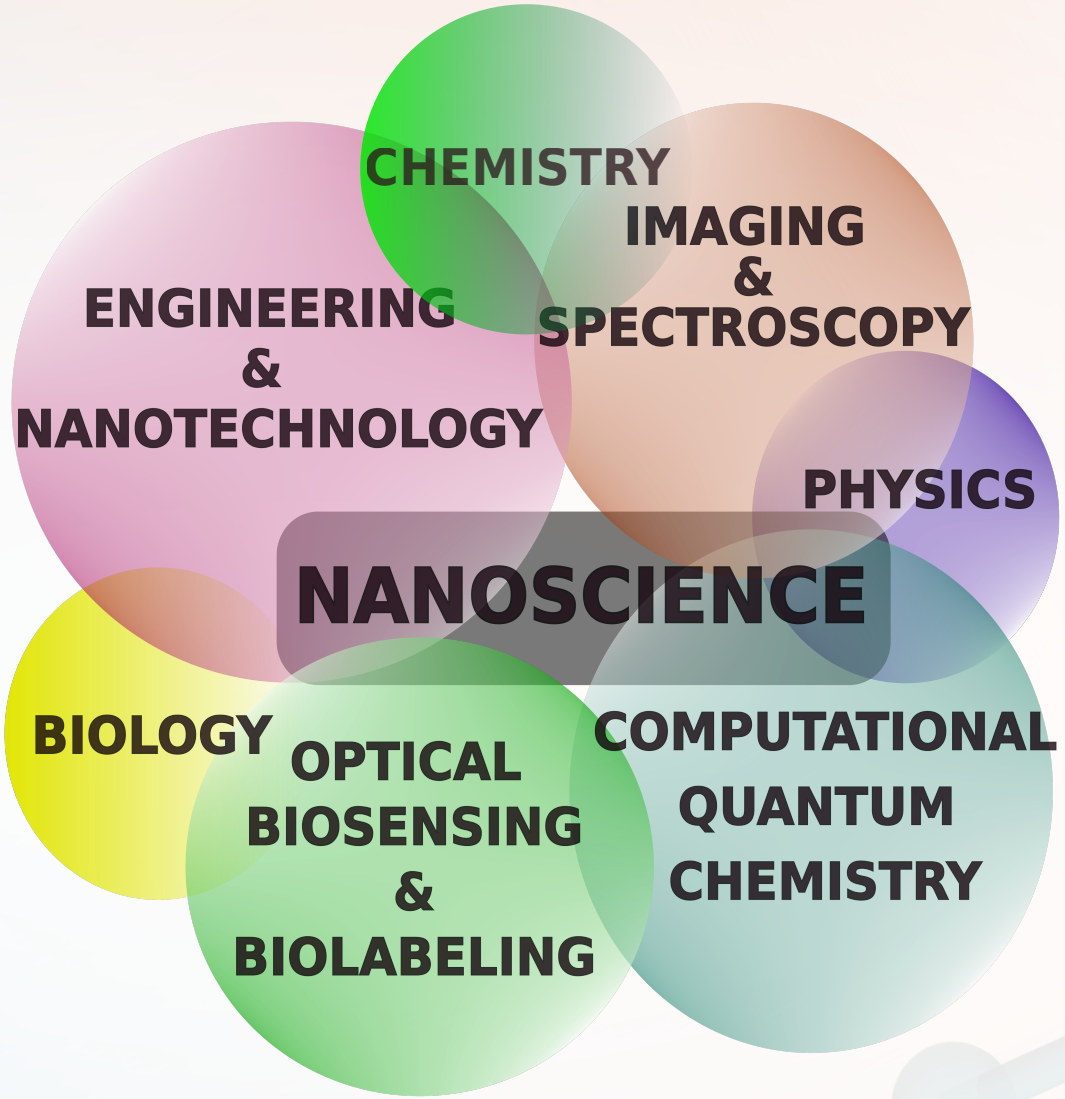
Is there plenty of room at the bottom?

Richard Feynman

American theoretical physicist (1918 – 1988)



"But I am not afraid to consider the final question as to whether, ultimately, in the great future, we can arrange the atoms the way we want; the very atoms, all the way down! What would happen if we could arrange the atoms one by one the way we want them?" R.F. 1959.

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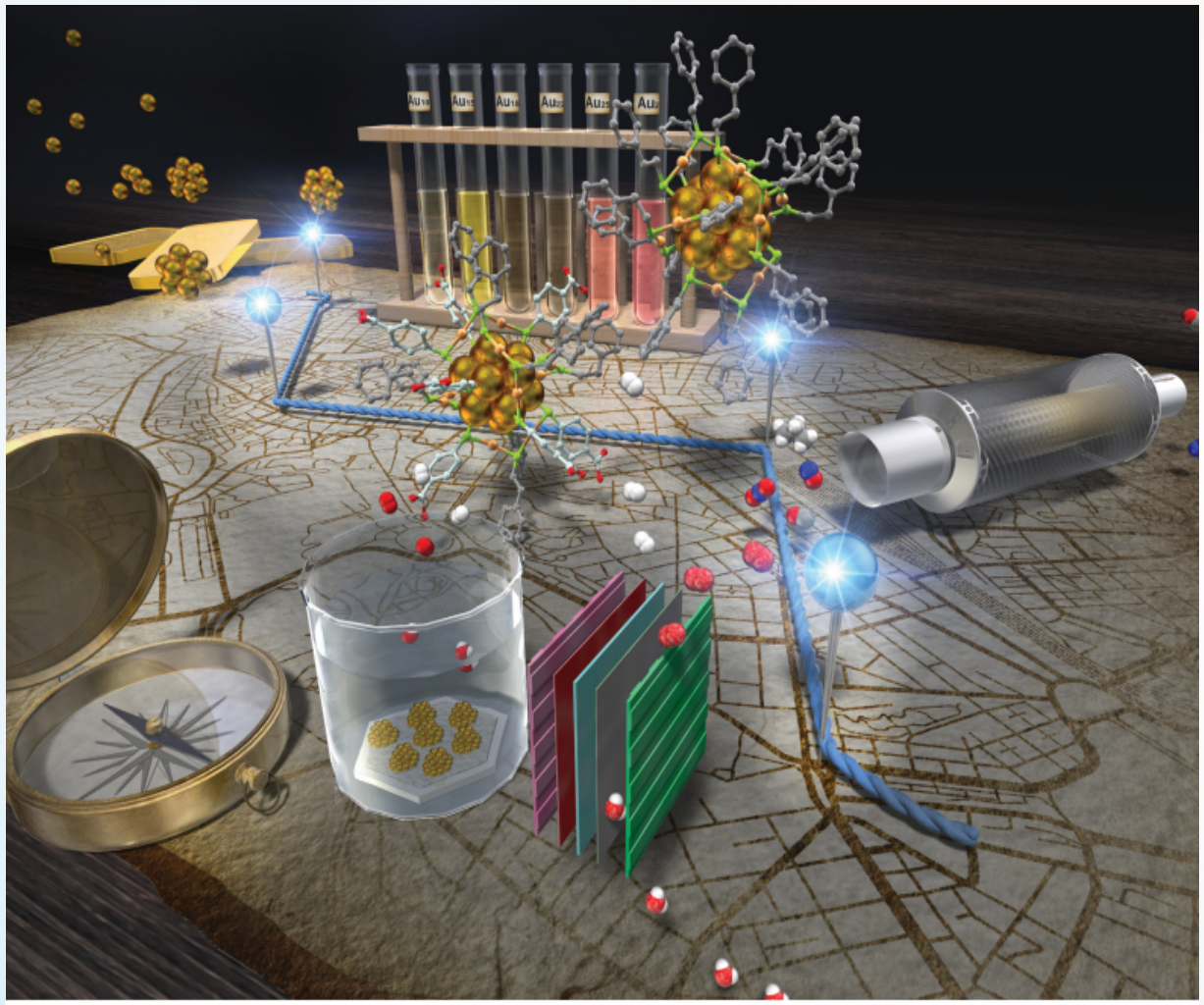
Atomically precise metal clusters - nanoclusters NCs

From Feynman's Vision to Negishi's Lab



ROYAL SOCIETY OF CHEMISTRY

PERSPECTIVE
Yuichi Negishi
Metal-nanocluster science and technology: my personal history and outlook

Phys. Chem. Chem. Phys., 2022, 24, 7569

one of the leading targets in research of nanoscale materials

In the nanoscale range (few to ~100 atoms), metal NCs exhibit discrete electronic states, unlike bulk metals.

Gas-phase NC studies - foundational knowledge about electronic properties and geometric structures without environmental effects

Ligand-protected NCs are chemically stable and tunable - applications in catalysis, optics, and electronics..

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Bare noble metal nanoclusters

NANOCLUSTERS:

< 2 nm

discrete energy levels

molecule-like electronic properties

multiple absorption bands

Non-scalable regime

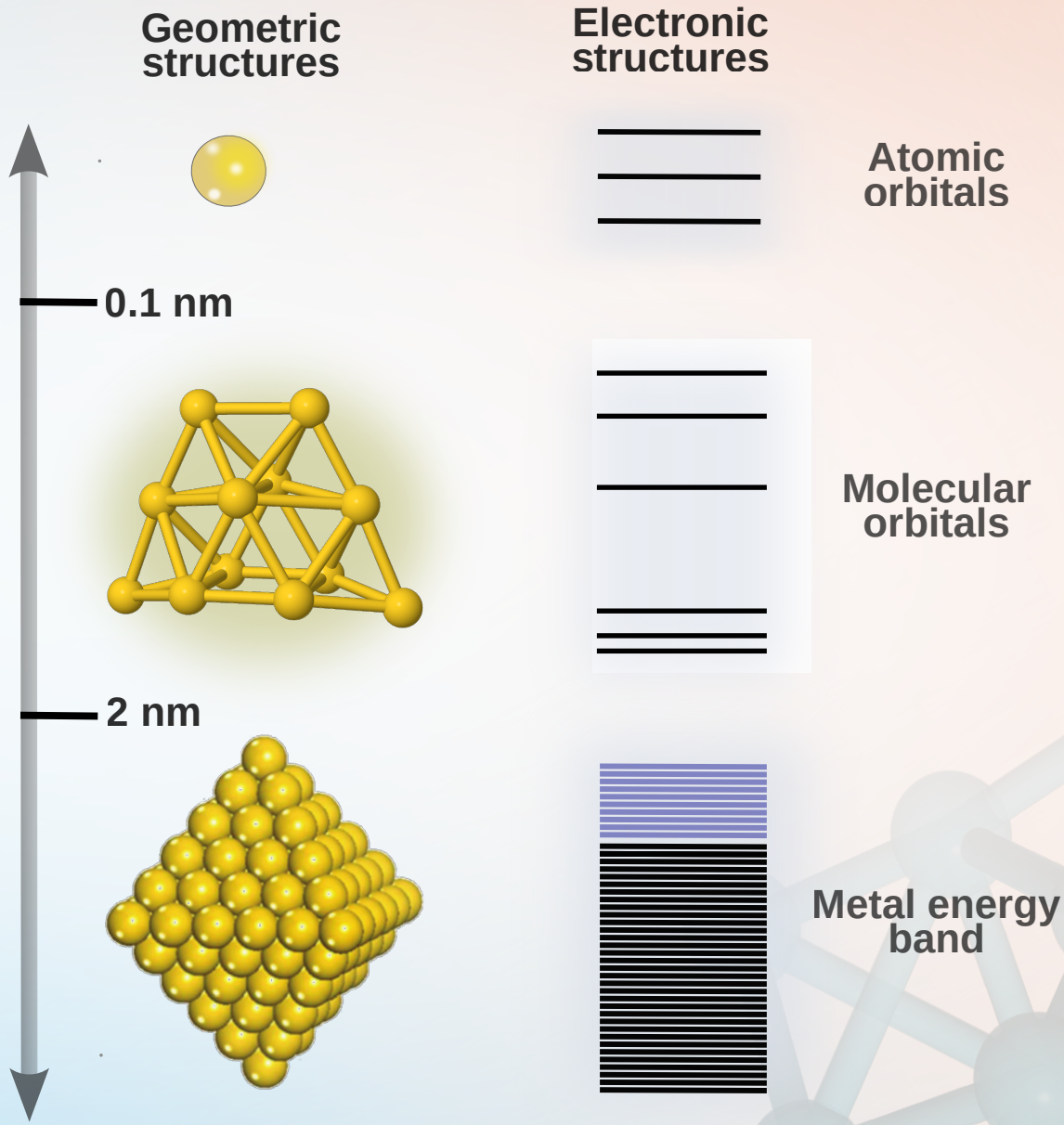
where "each atom counts"

NANOPARTICLES:

> 2 nm

localized surface

plasmons resonances (LSPR)



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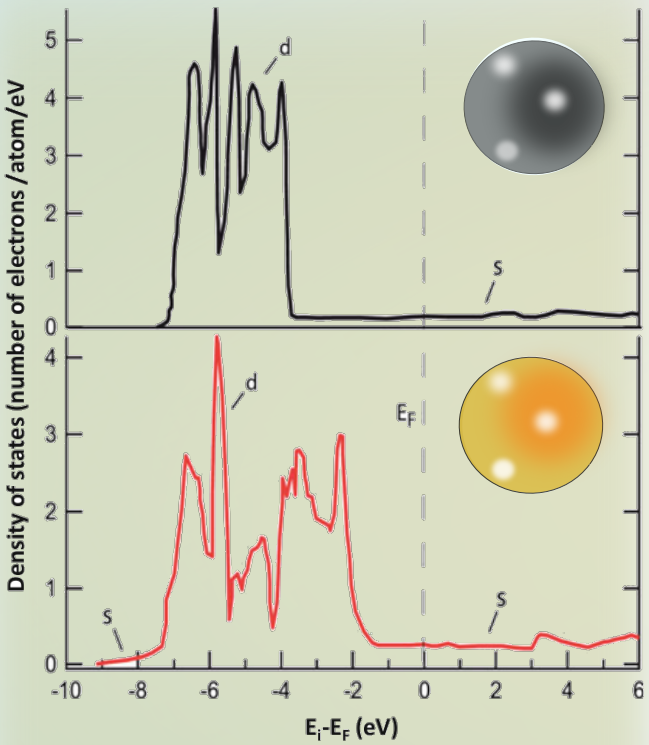
Gold and silver nanoclusters

DIFFERENT ELECTRONIC STATES (s-d gap)



Density of states (DOS) calculated for the noble metals Ag and Au [1]

DIFFERENT OPTICAL PROPERTIES

[2-5]

most extensively studied and commonly used noble metal NCs:

remarkable optical properties
(their outermost valence s electrons are very delocalizable and capable of nondirectional bonding)

High biocompatibility and low toxicity

suitable for **biological applications**, including **imaging** and **therapeutic purposes**.

optical properties of Au and Ag NCs are size-dependent due to quantum size effects

"EACH ATOM COUNTS!"

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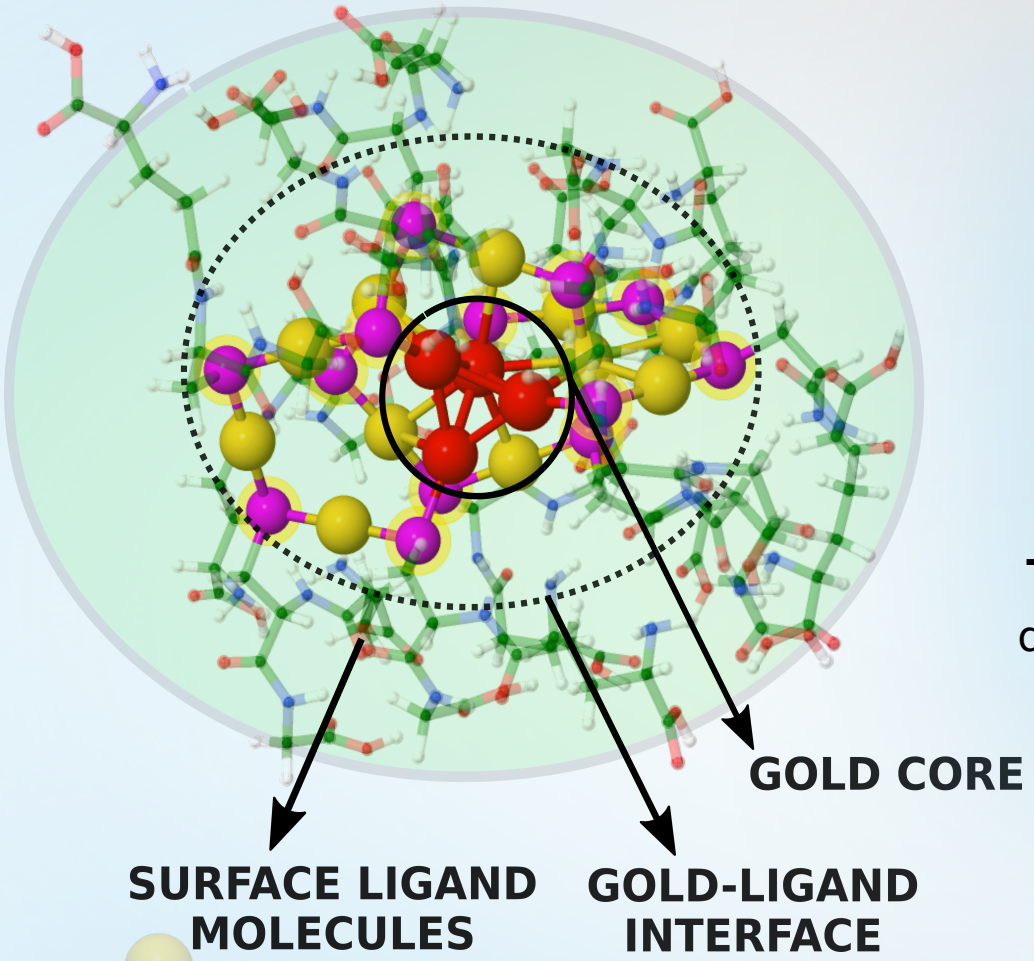
Protected noble metal nanoclusters



ADVANTAGES:

Enhanced Stability: Coating or functionalizing nanoclusters can enhance their stability by protecting them from oxidation or aggregation.

Biocompatibility: Surface modifications can improve the biocompatibility of nanoclusters

Tailored Functionality: Protective layers can be designed to impart specific functionalities, such as targeting ligands for selective binding.

The protective layer influences the optical properties of the nanoclusters.

Careful design is necessary to balance stability with the desired functionality.

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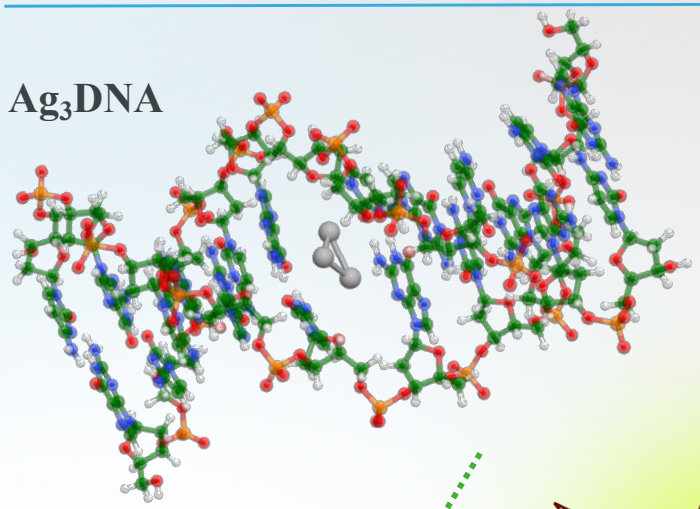
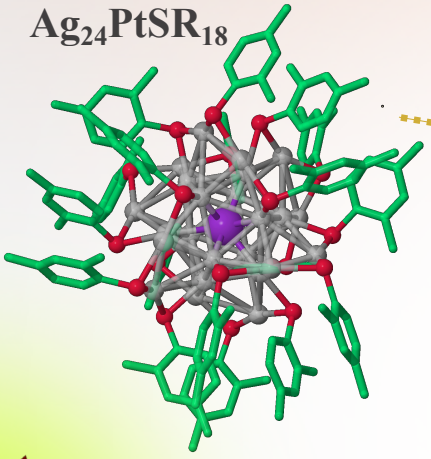
DFT modeling of protected noble metal NCs: Theory meets Experiment

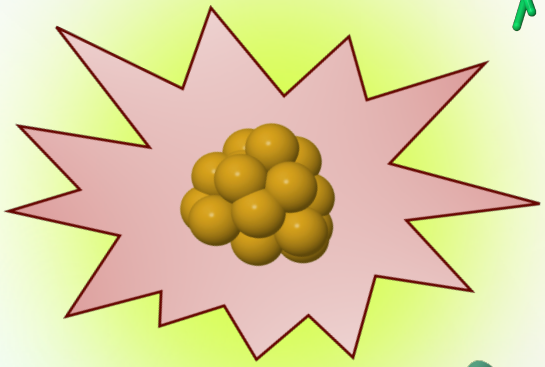


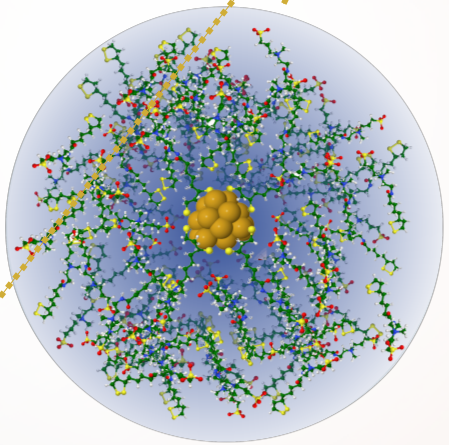
Ag_3DNA



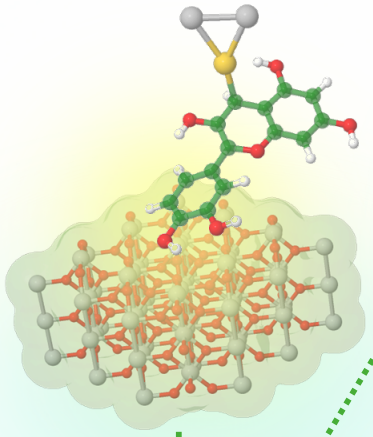
$Ag_{24}PtSR_{18}$

LIGANDED NCs

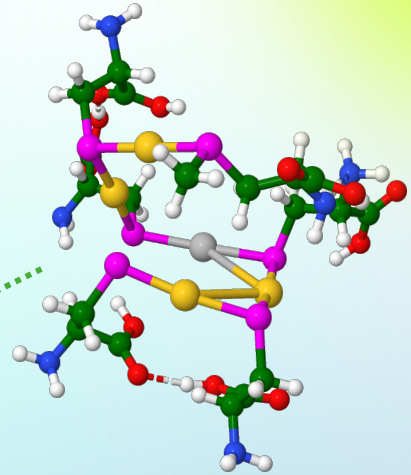




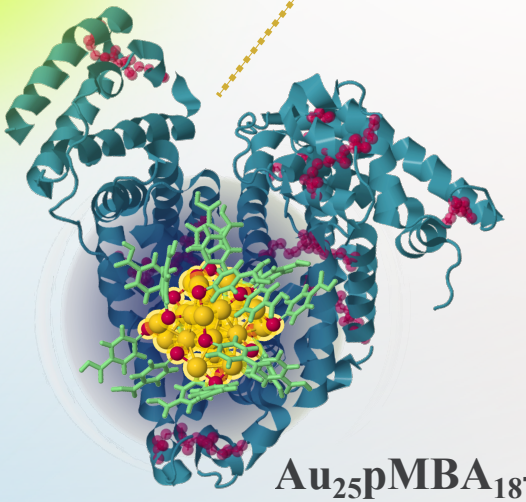
$Au_{12}Zw_4$ in ligand shell



Ag_2Au-Cyanidine-TiO_2



$AgAu_4Cys_6CH_3$



$Au_{25}pMBA_{18}$-BSA

BIO-NANO HYBRIDS

Exploring the photophysics of noble metal NCs

IMAGING & SPECTROSCOPY

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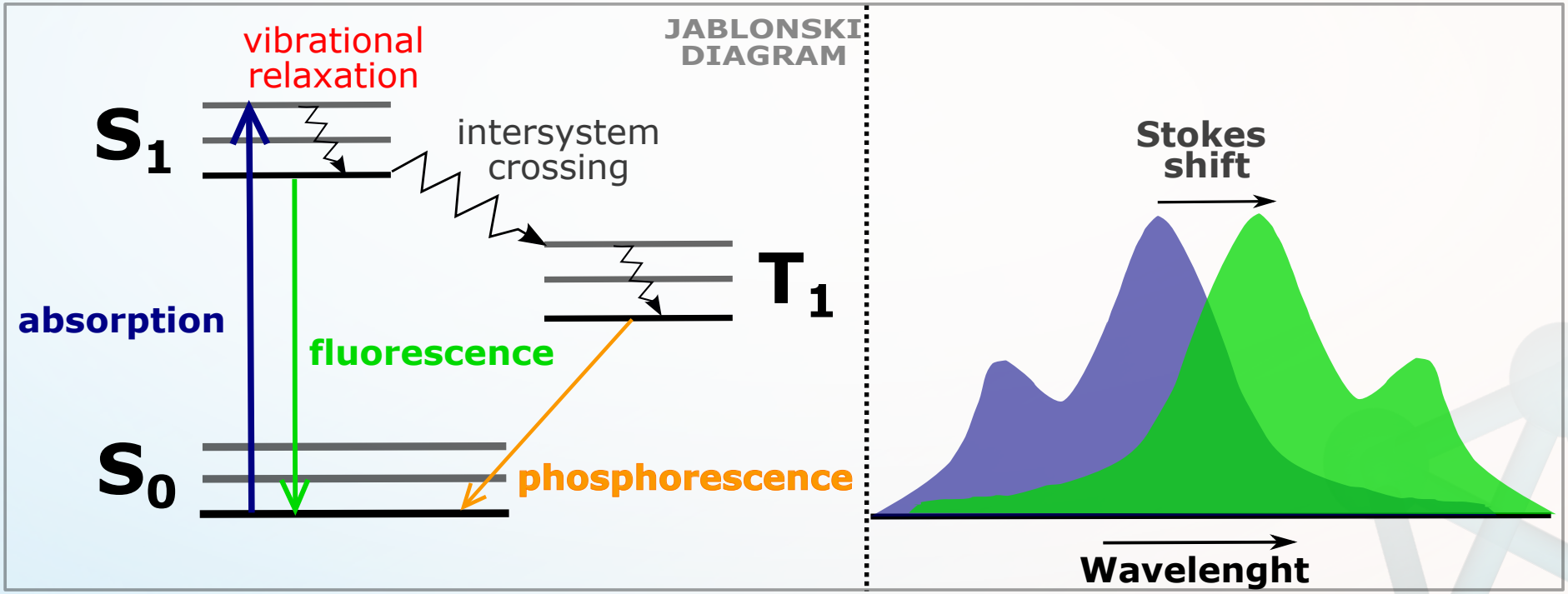
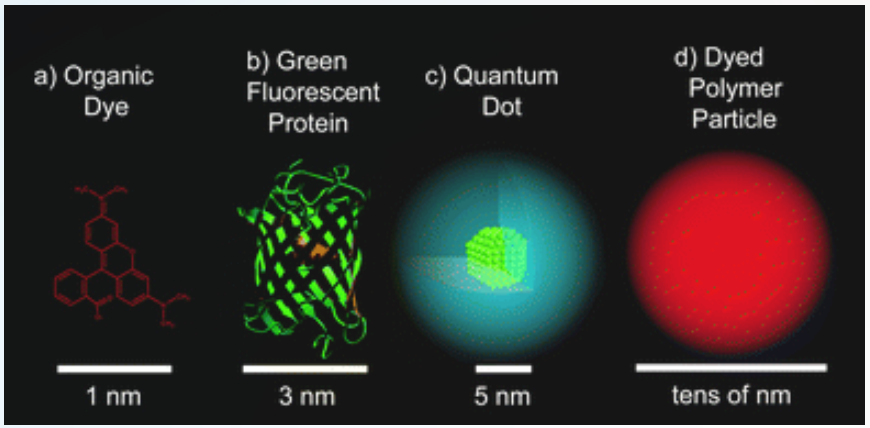
OPTICAL BIOSENSING & BIOLABELING

BIOANALYTICAL PURPOSES - MEDICAL DIAGNOSTICS



Application of noble metal NCs?

Fluorescent probes for bioimaging



Burns, A., Ow, H., & Wiesner, U. Chem. Soc. Rev., 35(11), 1028–1042.

High photostability and tunable fluorescence in the visible to near-infrared (NIR) region make noble metal NCs ideal for imaging biological tissues.

Advantages over organic dyes and quantum dots: lower toxicity, resistance to photobleaching, and better biocompatibility.

Biosensing and Chemical Sensing / Biolabeling

Noble metal NCs can act as turn-on/turn-off fluorescent sensors due to their sensitivity to changes in local environment or interaction with specific molecules.

Solar energy conversion

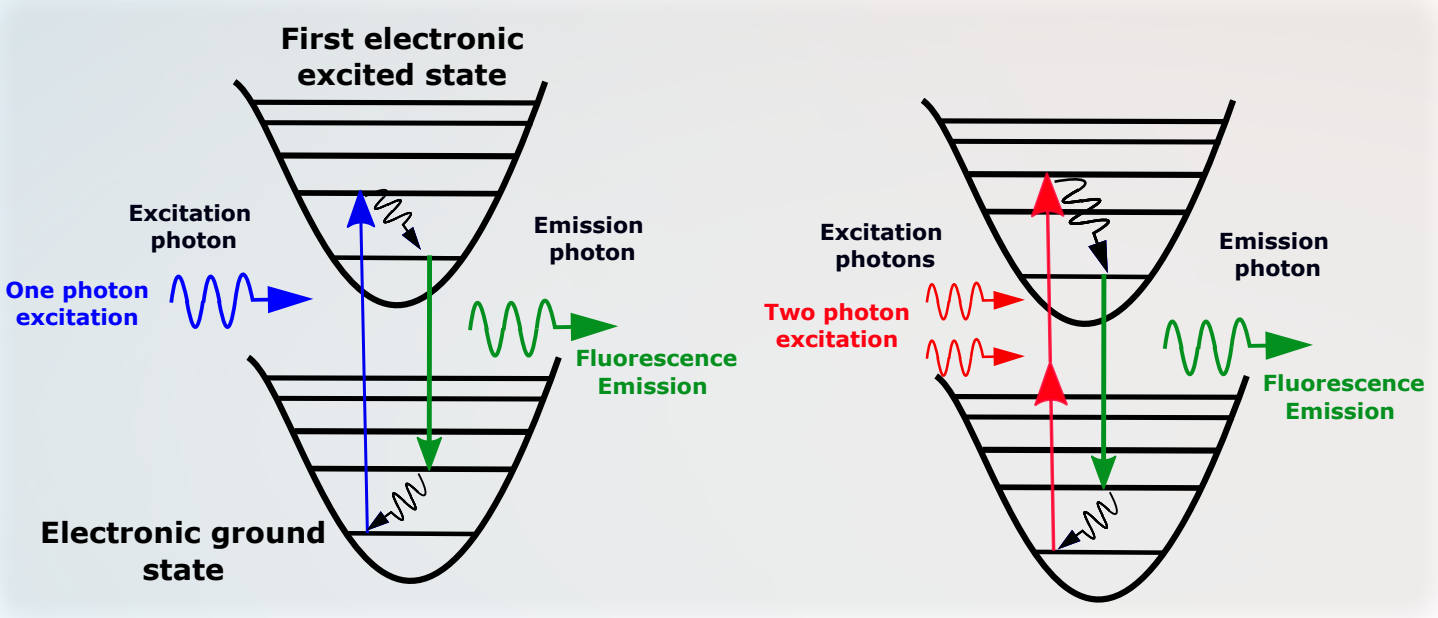
Au and Ag NCs are used as light-harvesting sensitizers due to their tunable optical absorption.

Their discrete HOMO - LUMO levels enable them to inject electrons into TiO_2 conduction bands efficiently.

What about nonlinear optical properties?

Non-linear optics dates back from 1930.:

optical absorption process involving two photons



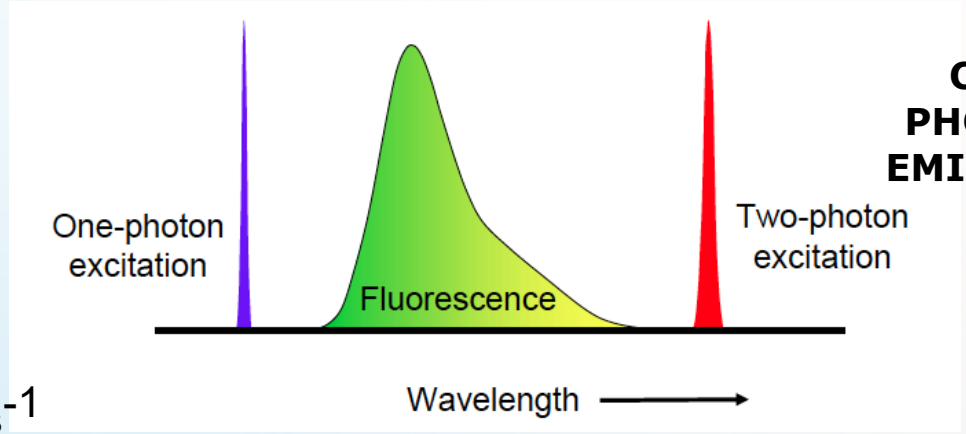
Maria Goeppert-Mayer
(1906-1972)
Nobel Prize in Physics
(1963.)

TPA cross section

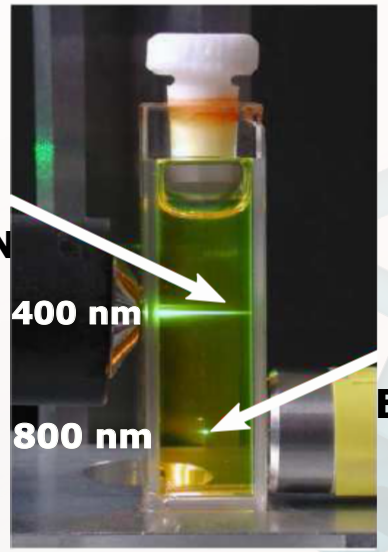
$$I_{TPA} = \sigma_{TPA} I^2$$

1 GM

10^{-50} cm^4 * s * photons^{-1}



ONE PHOTON EMISSION



TWO PHOTON EMISSION

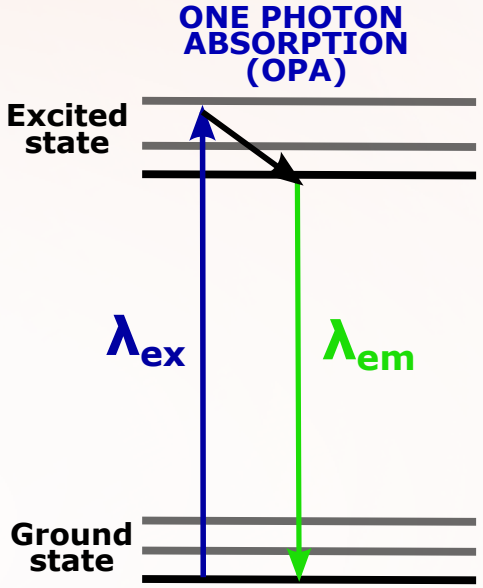
property of SpectroBio Lab, Lyon, France

TD-DFT: predicting linear/nonlinear optical properties

TD-DFT is based on the response of one-electron density matrix to an external field:

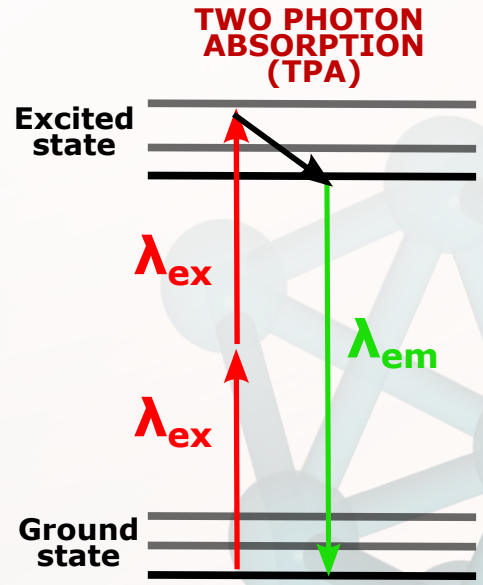
LINEAR RESPONSE (LR)

The solution of equations of motions in the first order in an external field yields the excitation energies and ground to excited state dipole moments.



NONLINEAR (QUADRATIC) RESPONSE

Inclusion of terms describing response up to the second-order in the external field (QR) yields permanent dipole moments of excited states as well as the state-to-state transition dipoles.



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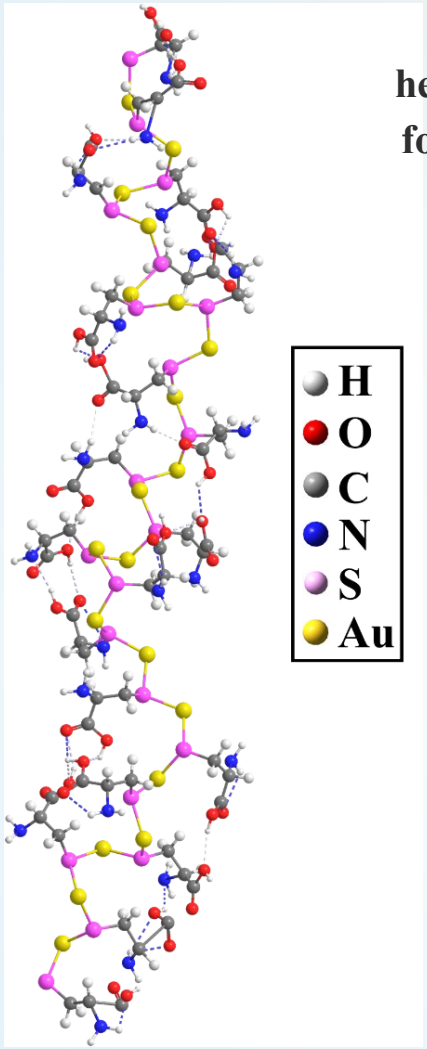
SILVER DOPED GOLD CYSTEIN NANOWIRE

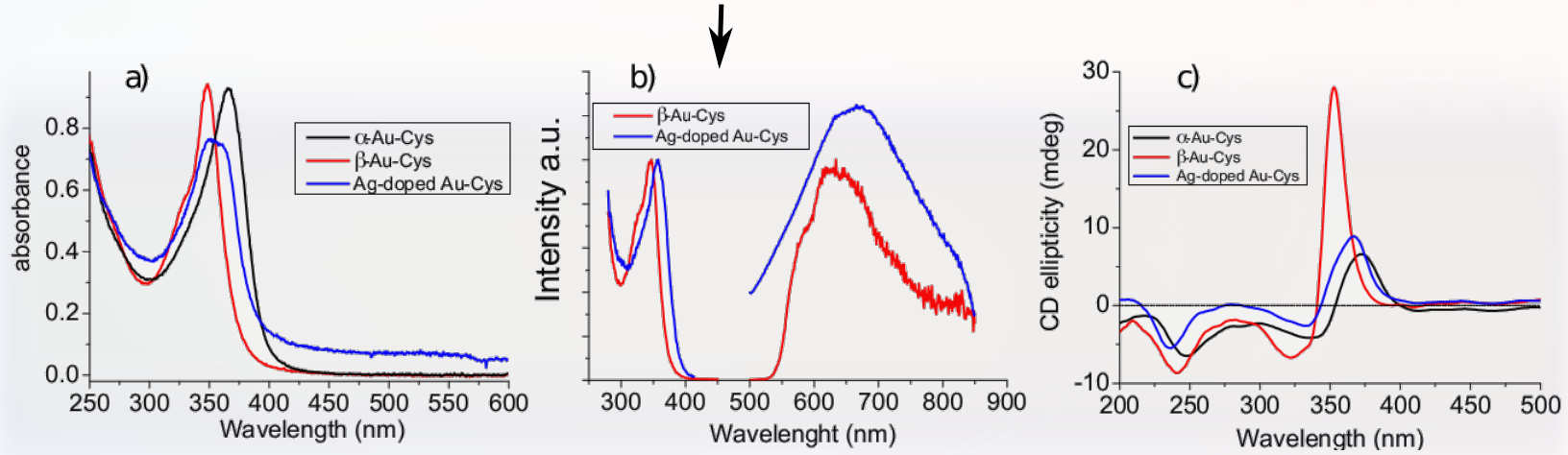
BIO-NANO HYBRID EXAMPLE



Langmuir, 27(1), 481–486 [13]

Proposed helical structure for cystein-gold polymer nanoparticle

NON-FLUORESCENT…
but highly chiral!
Russier-Antoine et al, (2016)
PNS: Materials International [14]



SILVER DOPING STRATEGY PROPOSED FOR ENHANCING FLUORESCENCE

IMPORTANT TO GAIN THEORETICAL INSIGHT ON THE ORIGIN OF OPTICAL LINEAR AND NONLINEAR PROPERTIES!

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SILVER DOPING STRATEGY PROPOSED FOR ENHANCING FLUORESCENCE OF BIO-NANO HYBRID

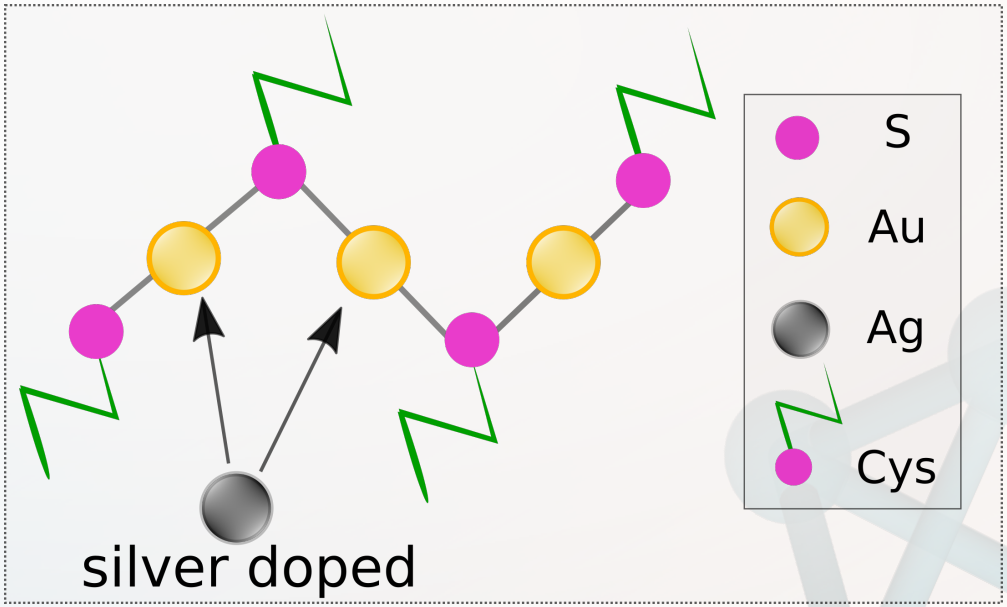
Fakhoury, H., Perić, M., Bertorelle, F., Dugourd, P., Dagany, Xavier, Russier-Antoine, I., ... Antoine, R. (2019). Sub-100-nanometer Silver Doped Gold-Cysteine Supramolecular Assemblies with Enhanced Nonlinear Optical Properties. Physical Chemistry Chemical Physics.

THEORETICAL APPROACH: new class of nonlinear nano-bio hybrids

investigate structural properties at DFT level

calculate optical properties (OPA&TPA)

Au/Ag: different relativistic effects
different Au-S affinity?



Elongate the proposed model to confirm structural and optical properties

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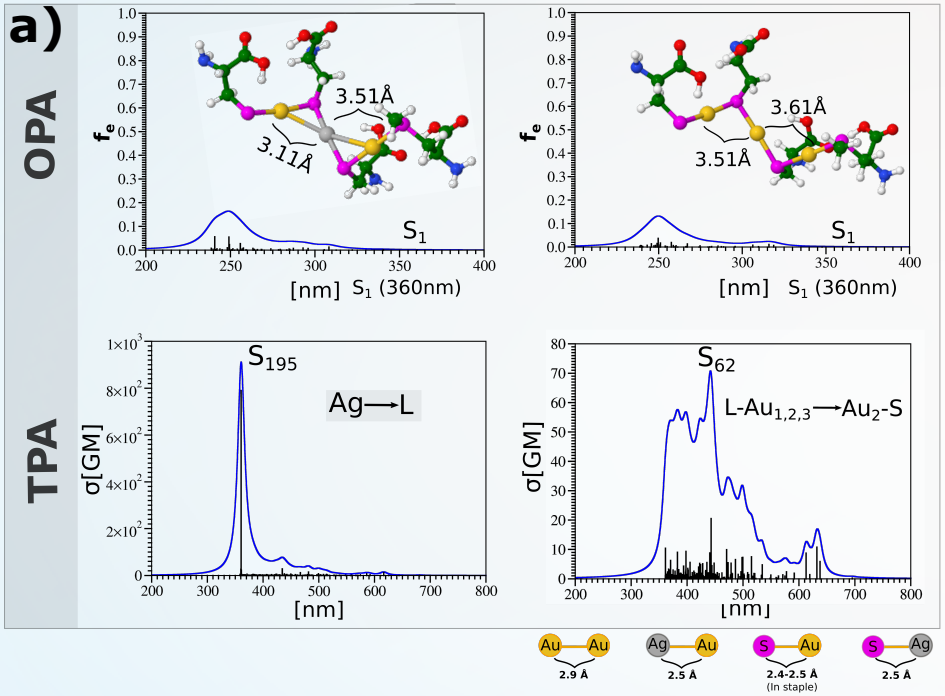
SILVER DOPING STRATEGY PROPOSED FOR ENHANCING FLUORESCENCE OF BIO-NANO HYBRID

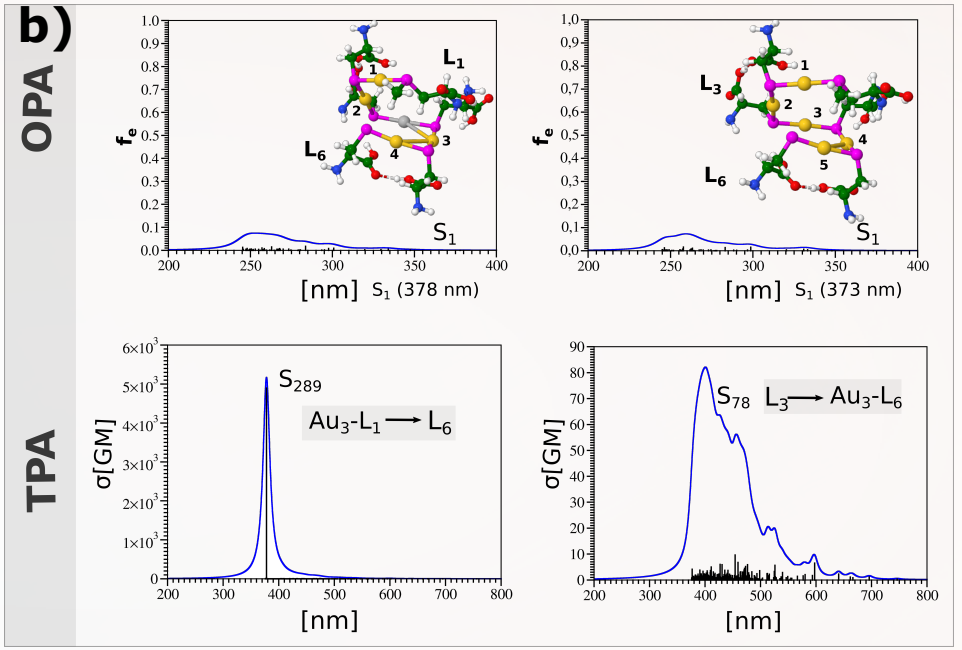
Two model systems have been considered:

a) M_3–Cys_4–CH_3 ($M=Au_3$ and $Ag–Au_2$)

b) M_5–Cys_6–CH_3 ($M=Au_5$ and $Ag–Au_4$) (Helical form!)

B3LYP/ def2-SVP/19e-RECP

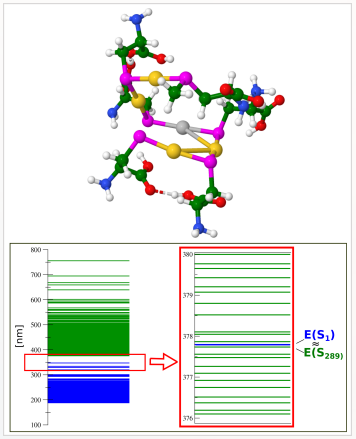




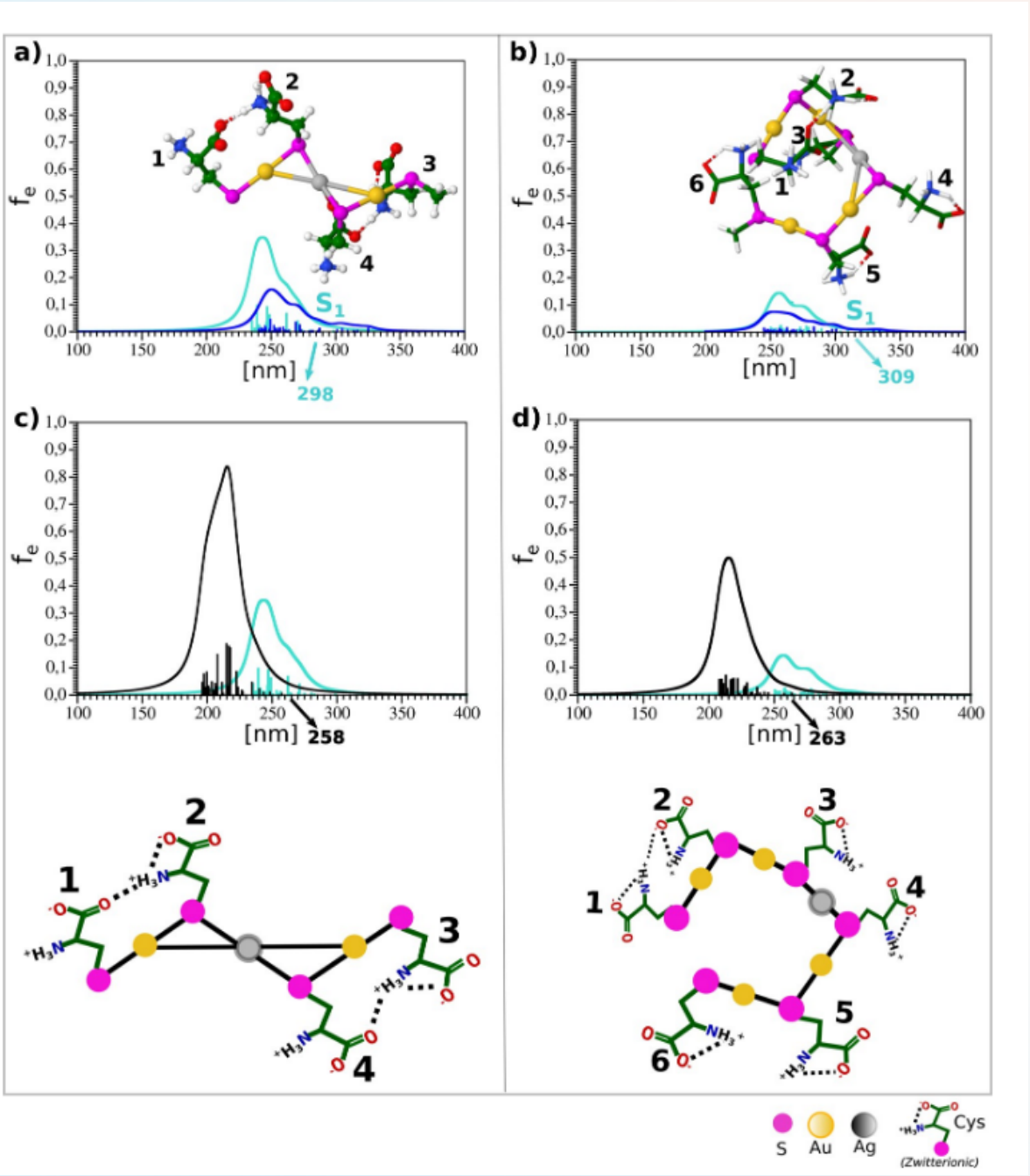
Doping with silver atoms does not influence the linear absorption properties (OPA)

Silver atoms play a key role in the nonlinear properties (TPA):

due to large transition dipole moments (TDM), different Au/Ag relativistic effects and affinity to sulfur.



Resonance between OPA & TPA states



Comparison of OPA spectra obtained for optimized structures of two model systems: a)Au_2-Ag-Cys_4-CH_3 and b) Au_4-Ag-Cys_6-CH_3 in gas phase (blue) and in water (turquoise) using TDDFT with B3LYP functional and SMD approach for solvent.

Comparison of functional CAM-B3LYP (black) with B3LYP (turquoise) of OPA spectra, c) and d), for two model systems including solvent with SMD approach.

Schematic illustration of interacting cysteine pairs within solvent is shown in lower part.

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DOPING STRATEGY - INSPIRED NEW RESEARCH ON LIGANDED NOBLE METAL NANOCLUSTERS!

Angewandte Chemie

GDCh Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Forschungsartikel

Gold-Doping Effect on Two-Photon Absorption and Luminescence of Atomically Precise Silver Ligated Nanoclusters

Anna Pniakowska, Krishnadas Kumaranchira Ramankutty, Patryk Obstarczyk, Martina Perić Bakulić, Željka Sanader Maršić, Vlasta Bonačić-Koutecký, Thomas Bürgi, Joanna Olesiak-Bańska

First published: 25 August 2022 | https://doi.org/10.1002/ange.202209645 | Citations: 2

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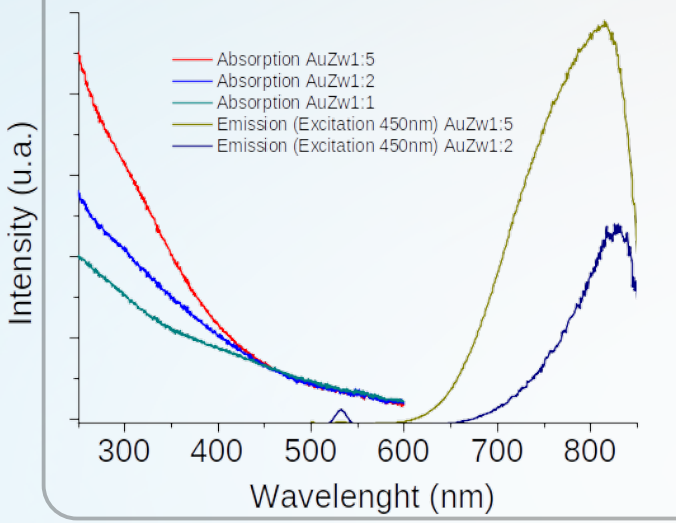
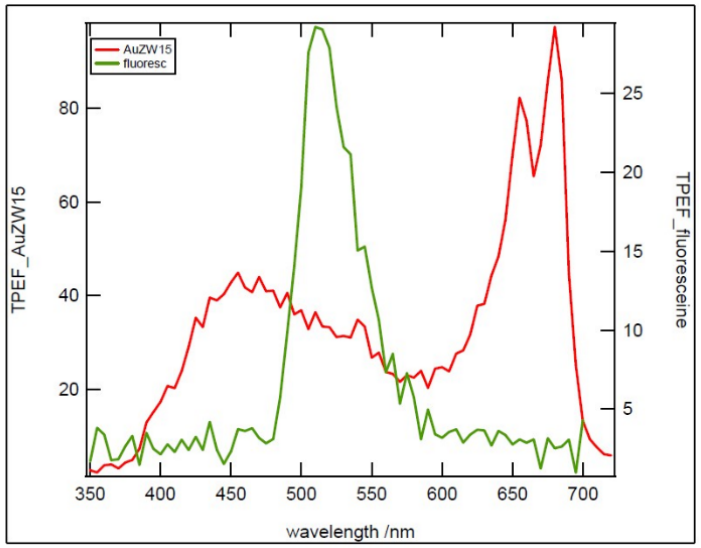
Zwitterion functionalized gold NCs

Experimental optical spectra, one-photon absorption/emission



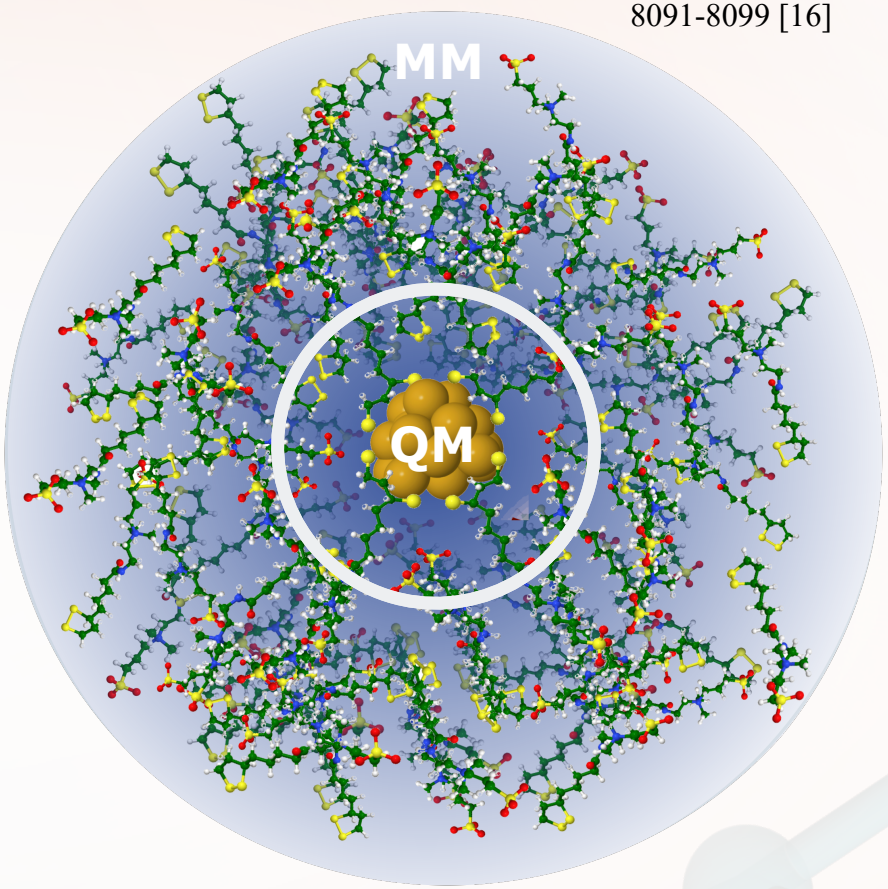


TPEF for Au:Zw ratio 1:5

enhancement of emission for Au:Zw ratio 1:5

CONCEPT
Au:Zw ratio
1:1
1:5

Xavier Le Guevel et al, Nanoscale, 2014,6, 8091-8099 [16]



Zwitterionic form of the tails of ligands creates strong intermolecular electrostatic interactions.

The formation of **different ligand shells** on the surface of the AuNCs occurs.

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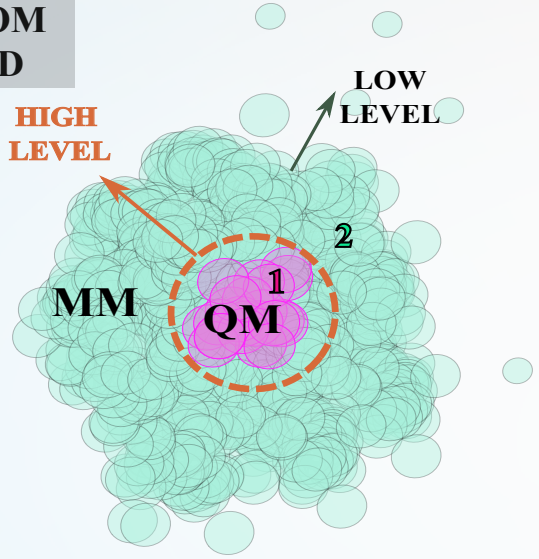
Zwitterion functionalized gold NCs - Theoretical approach?

GOAL: TO APPLY QM/MM METHOD TO INVESTIGATE STRUCTURAL, LINEAR AND NONLINEAR OPTICAL PROPERTIES OF NANOSTRUCTURED MATERIALS

THE ONIOM METHOD



Maseras and Morokuma, 1995;
Ryde, 1996b;
Svensson et al., 1996

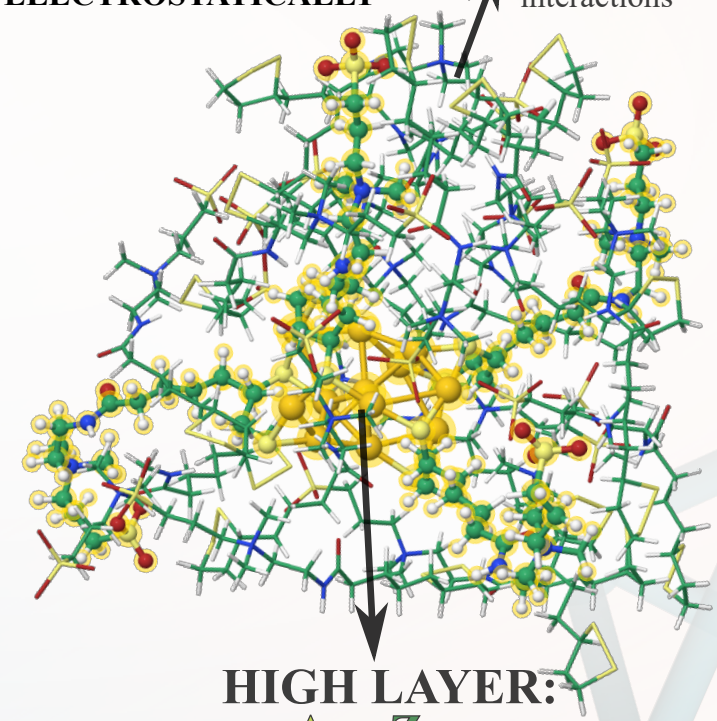
QM/MM method (two layer ONIOM [b3lyp/UFF])

Employ TDDFT calculations (DALTON PEQM): determine OPA and TPA properties for both ratios to confirm experimental result

Model explicit water effect to explain "quenching" in experimental two photon emission spectrum

NO QM-MM COVALENT BONDS: NO LINK ATOMS LIGANDS INTERACTING ELECTROSTATICALLY

LOW LAYER:
Zw18
electrostatic interactions



HIGH LAYER:
$Au_{12}Zw_4$
Zwitterion functionalized gold NC

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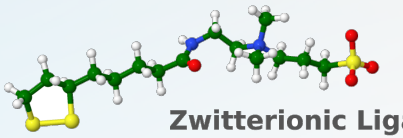
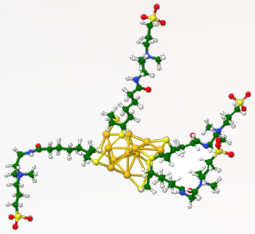
Ligand shell size effects on one- and two-photon excitation fluorescence of zwitterion functionalized gold nanoclusters

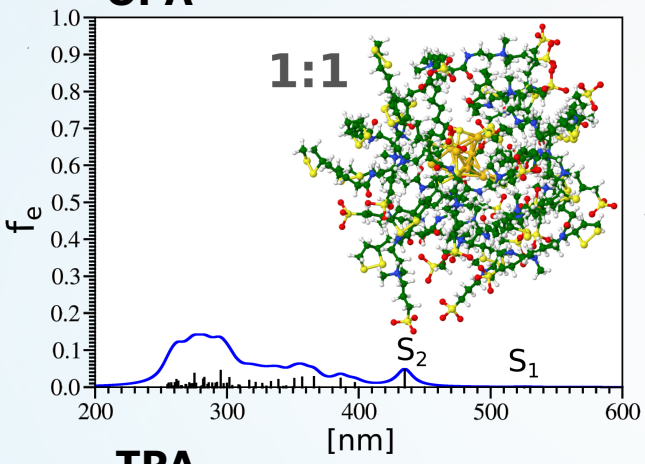


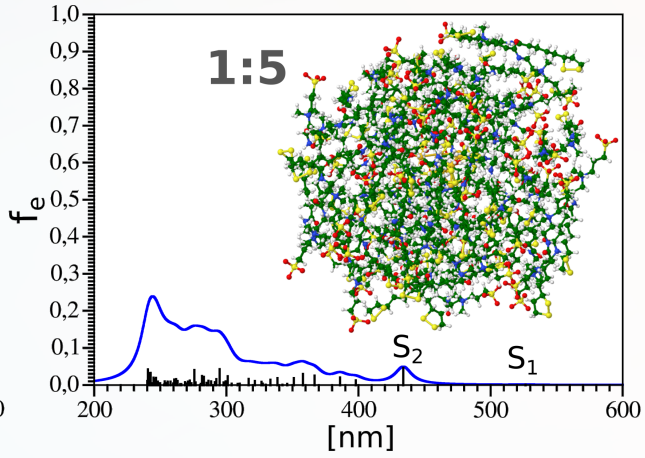
Zwitterionic Ligand
(Bidendate Thiol)



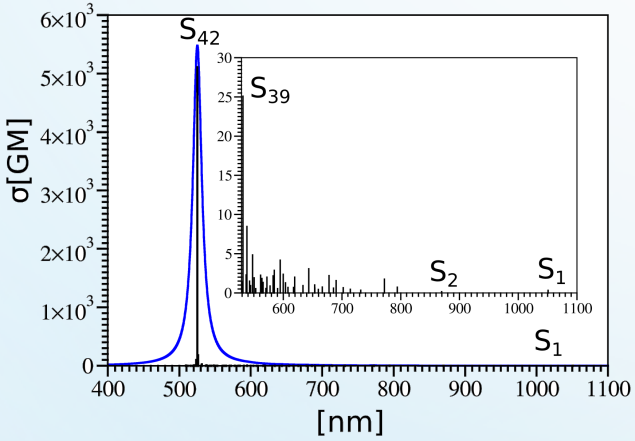
QM

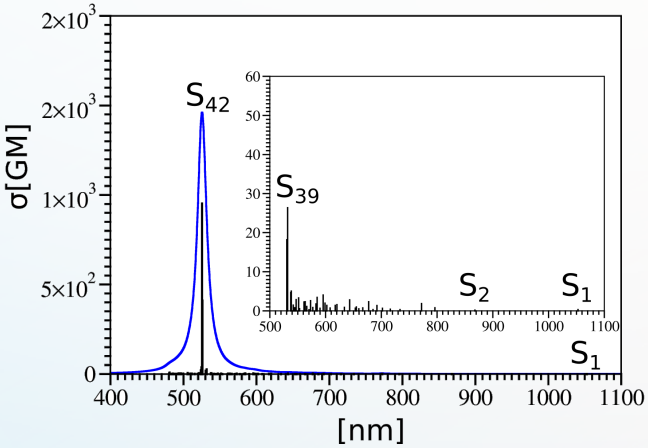
OPA





TPA





Perić, M., Sanader, Z., Russier-Antoine, I., Fakhoury, H., Bertorelle, F., Brevet, P.-F., ... Bonačić-Koutecký, V. (2019). Physical Chemistry Chemical Physics.

OPA spectra:

located between 550 and 350 nm,
independent on the ligand shell size
(good agreement
with experimental findings)

TPA spectra:

huge TPA cross sections
due to resonance S_1 OPA and S_{42} TPA state,

independent on the ligand shell size?

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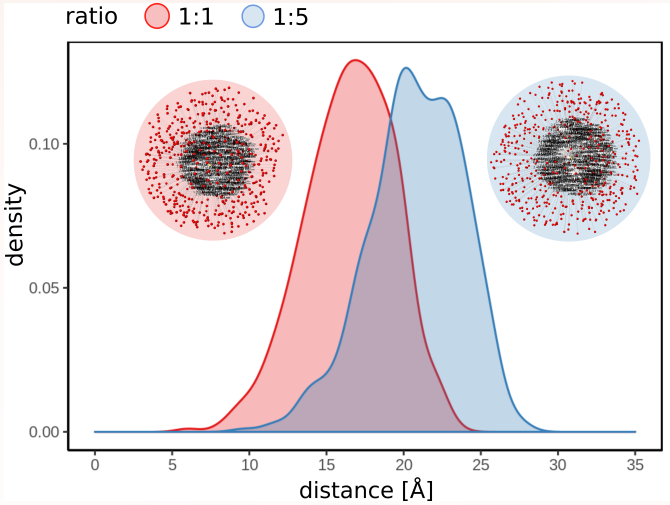
Possible explanation on the origin of the effect of ligand shell size on emission?

1. Rigidification effect brought by the ligand shell on the gold kernel.
(key factor for future design of liganded AuNCs!)

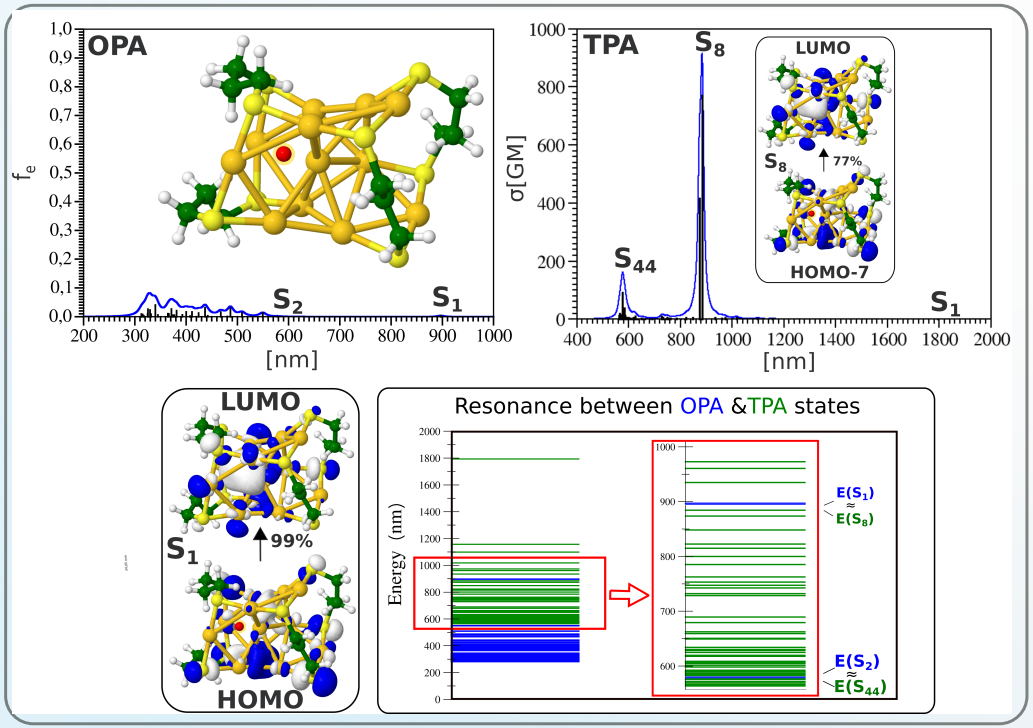
2. Quenching effect due to water penetration through the ligand shell

DIFFERENT WATER PENETRATION DUE TO VARIOUS RIGIDITY of 1:5 and 1:1 ratio

Density of water molecules as a function of radial distance from central Au atom within ligated gold clusters for ratio 1:1 (red) and 1:5 (blue) (R-studio software)



REACHING THE NIR REGIME:



Due to external charge +, the shift from ~535 nm to ~897 nm (NIR regime) occurs (experimentally accessible wavelengths) due to the lack of one electron

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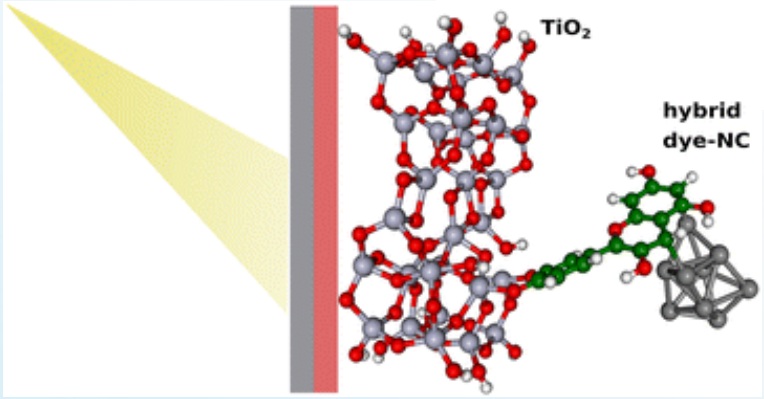
CONCLUSIONS AND FUTURE ASPECTS

Linear and nonlinear optical properties of noble metal NCs can be tailored via controlling the ligands and functional groups. (which are also important for selectivity)

Diversity of bio-scaffolds for design of bio-nano hybrids offers enhanced nonlinear optical properties: application in biosensorics and medical diagnostics.

FUTURE: to investigate light harvesting properties of noble metal NCs - demonstrates versatile application of NCs optical properties



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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]

Martina Perić Bakulić
Assistant Professor
Faculty of Chemistry and Technology,
Department of Mathematics Physics, UNIST, Split,
Croatia

Antonija Mravak
Senior Assistant
Faculty of Chemistry and Technology,
Department of Mathematics and Physics, UNIST, Split, Croatia

Margarita Bužančić
Research Assistant
STIM, UNIST, Split, Croatia

Željka Sanader Maršić
Associate Professor
(Faculty of Science,
Department of Physics
UNIST, Split, Croatia)

EXPERIMENTAL AND THEORETICAL COLLABORATION:

NANO-BIO MED

Dr. Vlasta Bonačić Koutecky, Center of Excellence for Science and Technology, STIM

Wroclaw University of Science and Technology (WUST), Wroclaw, Poland
(Dr. Joanna Olesiak-Bańska)

Universite Lyon 1, Institute Lumiere Matiere, Lyon, France
(Dr. Rodolphe Antoine)

McGill University, Montreal, Canada
(Dr. Dušica Maysinger)

NANO-BIO ENERGY

Faculty of Chemistry and Technology, Split, Croatia,
(Dr. Marina Tranfić Bakić, Dr. Ante Prkić, Dr. Ita Hajdin,
Dr. Sanja Radman)

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LITERATURE

[1] Antoine, R.; Bonačić-Koutecký, V. Liganded Silver and Gold Quantum Clusters: Towards a New Class of Nonlinear Optical Nanomaterials, 2018., SpringerBriefs in Materials https://doi.org/10.1007/978-3-319-64743-2

[2] Alvarez, M. M., Khoury, J. T., Schaaff, T. G., Shafigullin, M. N., Vezmar, I., & Whetten, R. L. (1997). Optical Absorption Spectra of Nanocrystal Gold Molecules. The Journal of Physical Chemistry B, 101(19), 3706–3712. doi:10.1021/jp962922n

[3] Bonačić-Koutecký, V., Pittner, J., Boiron, M., & Fantucci, P. (1999). An accurate relativistic effective core potential for excited states of Ag atom: An application for studying the absorption spectra of Ag_n and Ag_n^+ clusters. The Journal of Chemical Physics, 110(8), 3876–3886. doi:10.1063/1.478242

[4] Bonačić-Koutecky, V., Veyret, V., & Mitrić, R. (2001). Ab initio study of the absorption spectra of Ag_n (n=5–8) clusters. The Journal of Chemical Physics, 115(22), 10450. doi:10.1063/1.1415077

[5] Bonačić-Koutecký, V., Mitrić, R., Bürgel, C., Noack, H., Hartmann, M., & Pittner, J. (2005). Tailoring the chemical reactivity and optical properties of clusters by size, structures and lasers. The European Physical Journal D, 34(1-3), 113–118. doi:10.1140/epjd/e2005-00098-4

[6] Peyser-Capadona, L., Zheng, J., González, J. I., Lee, T.-H., Patel, S. A., & Dickson, R. M. (2005). Nanoparticle-Free Single Molecule Anti-Stokes Raman Spectroscopy. Physical Review Letters, 94(5). doi:10.1103/physrevlett.94.058301

[7] Bonačić-Koutecký, V., Kulesza, A., Gell, L., Mitrić, R., Antoine, R., Bertorelle, F., … Dugourd, P. (2012). Silver cluster–biomolecule hybrids: from basics towards sensors. Physical Chemistry Chemical Physics, 14(26), 9282. doi:10.1039/c2cp00050d

[8] Bonačić-Koutecký, V., Mitrić, R., Bürgel, C., & Schäfer-Bung, B. (2006). Cluster properties in the regime in which each atom counts. Computational Materials Science, 35(3), 151–157. doi:10.1016/j.commatsci.2004.12.075

[9]Russier-Antoine, I., Bertorelle, F., Calin, N., Sanader, Ž., Krstić, M., Comby-Zerbino, C., … Antoine, R. (2017). Ligand-core NLO-phores: a combined experimental and theoretical approach to the two-photon absorption and two-photon excited emission properties of small-ligated silver nanoclusters. Nanoscale, 9(3), 1221–1228. doi:10.1039/c6nr07989j

[10] Groenhof, G. (2012). Introduction to QM/MM Simulations. Biomolecular Simulations, 43–66. doi: 10.1007/978-1-62703-017-5_3

[11] Steinmann, C., Reinholdt, P., Nørby, M. S., Kongsted, J., & Olsen, J. M. H. (2018). Response properties of embedded molecules through the polarizable embedding model. International Journal of Quantum Chemistry, e25717. doi:10.1002/qua.25717

[12] Buceta, D., Busto, N., Barone, G., Leal, J. M., Domínguez, F., Giovanetti, L. J., … López-Quintela, M. A. (2015). Ag2and Ag3Clusters: Synthesis, Characterization, and Interaction with DNA. Angewandte Chemie International Edition, 54(26), 7612–7616. doi:10.1002/anie.201502917

[13] Shen, J.-S., Li, D.-H., Zhang, M.-B., Zhou, J., Zhang, H., & Jiang, Y.-B. (2011). Metal−Metal-Interaction-Facilitated Coordination Polymer as a Sensing Ensemble: A Case Study for Cysteine Sensing. Langmuir, 27(1), 481–486. doi:10.1021/la103153e

[14] Russier-Antoine, I., Bertorelle, F., Kulesza, A., Soleilhac, A., Bensalah-Ledoux, A., Guy, S., … Antoine, R. (2016). Chiral supramolecular gold-cysteine nanoparticles: Chiroptical and nonlinear optical properties. Progress in Natural Science: Materials International, 26(5), 455–460. doi:10.1016/j.pnsc.2016.08.008

[15] Bertorelle, F., Russier-Antoine, I., Calin, N., Comby-Zerbino, C., Bensalah-Ledoux, A., Guy, S., … Antoine, R. (2017). Au10(SG)10: A Chiral Gold Catenane Nanocluster with Zero Confined Electrons. Optical Properties and First-Principles Theoretical Analysis. The Journal of Physical Chemistry Letters, 8(9), 1979–1985. doi: 10.1021/acs.jpclett.7b00611

[16] Bertorelle, F., Russier-Antoine, I., Calin, N., Comby-Zerbino, C., Bensalah-Ledoux, A., Guy, S., … Antoine, R. (2017). Au10(SG)10: A Chiral Gold Catenane Nanocluster with Zero Confined Electrons. Optical Properties and First-Principles Theoretical Analysis. The Journal of Physical Chemistry Letters, 8(9), 1979–1985. doi: 10.1021/acs.jpclett.7b00611