Design of magneto-plasmonic heterostructures formed by Au decorated on magnetic Prussian Blue-type nanocrystals

Roger Sanchis Gual

Instituto de Ciencia Molecular

Small Chem 2021 Online International Conference

17/02/2021

VNIVERSITAT DE VALÈNCIA

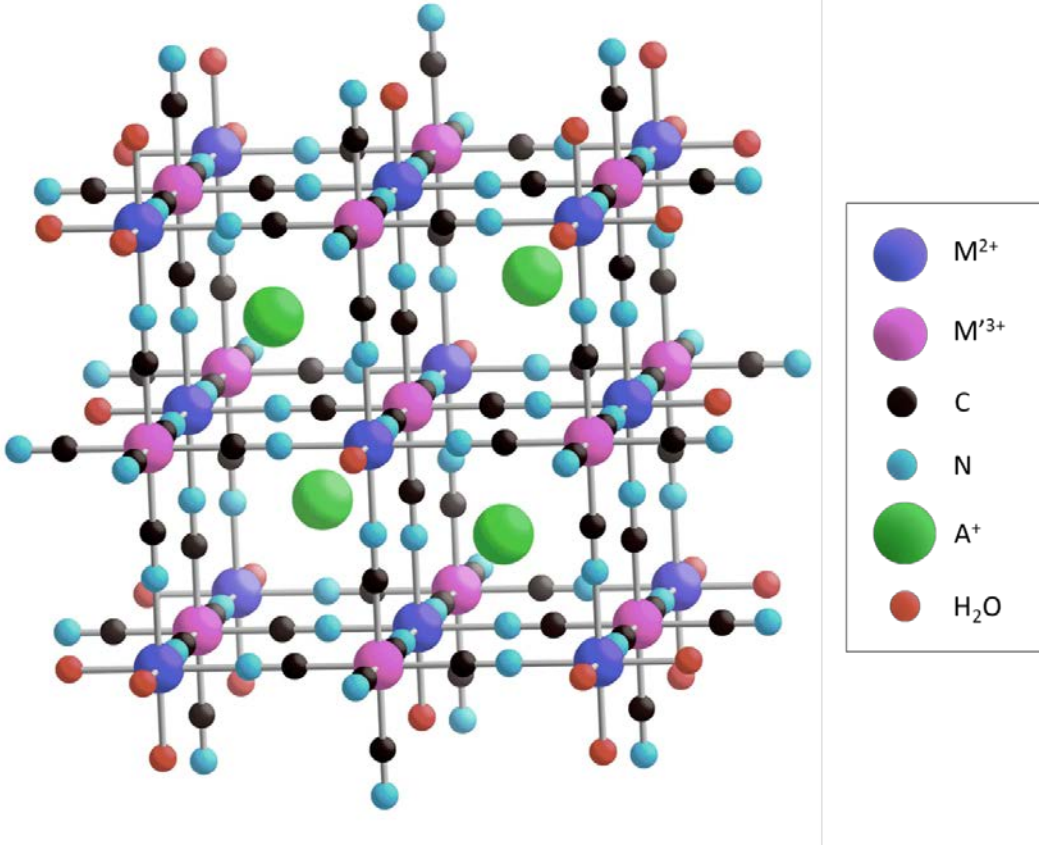
ICMOL
Institut de Ciència Molecular

Prussian Blue Analogue (PBA)

$A_aM_b[M'(CN)_6]_c \cdot nH_2O$

M^{II} and M^{III} = transition metal
A = alkali cation

- Chemical versatility
- Tunability of the properties
- Optical transparency
- Charge transfer properties
- Magnetic properties

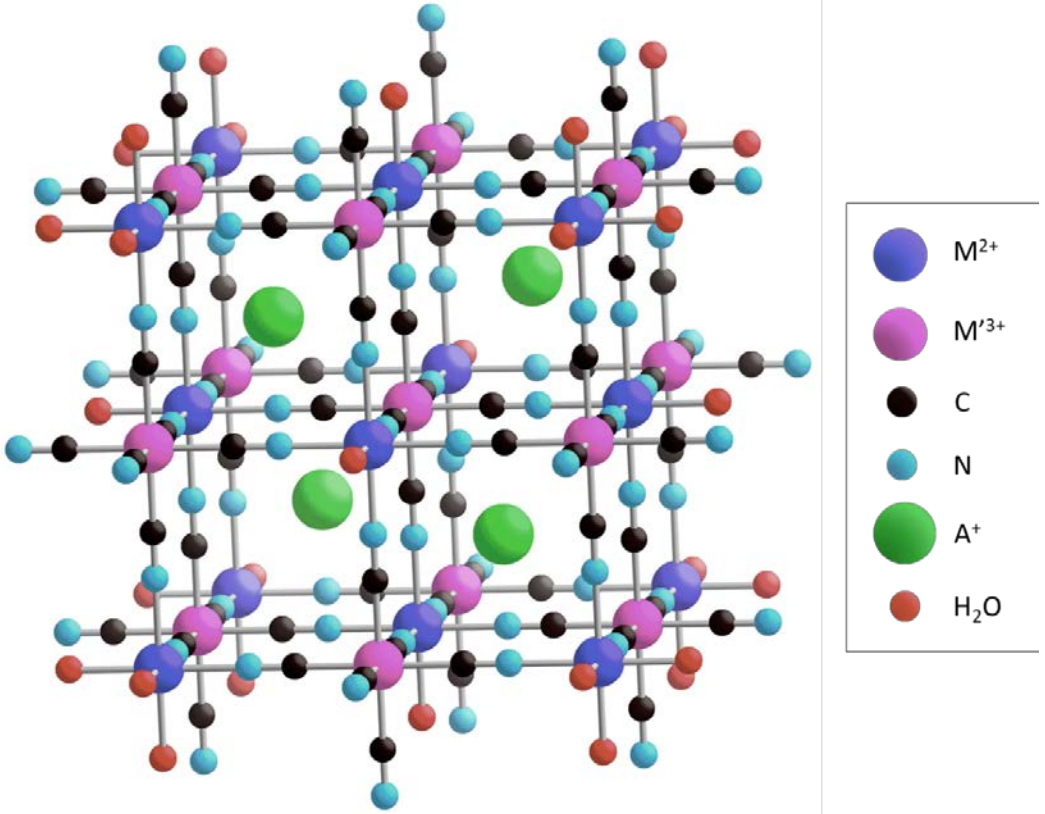


Prussian Blue Analogue (PBA)

$A_aM_b[M'(CN)_6]_c \cdot nH_2O$

M^{II} and M^{III} = transition metal
A = alkali cation

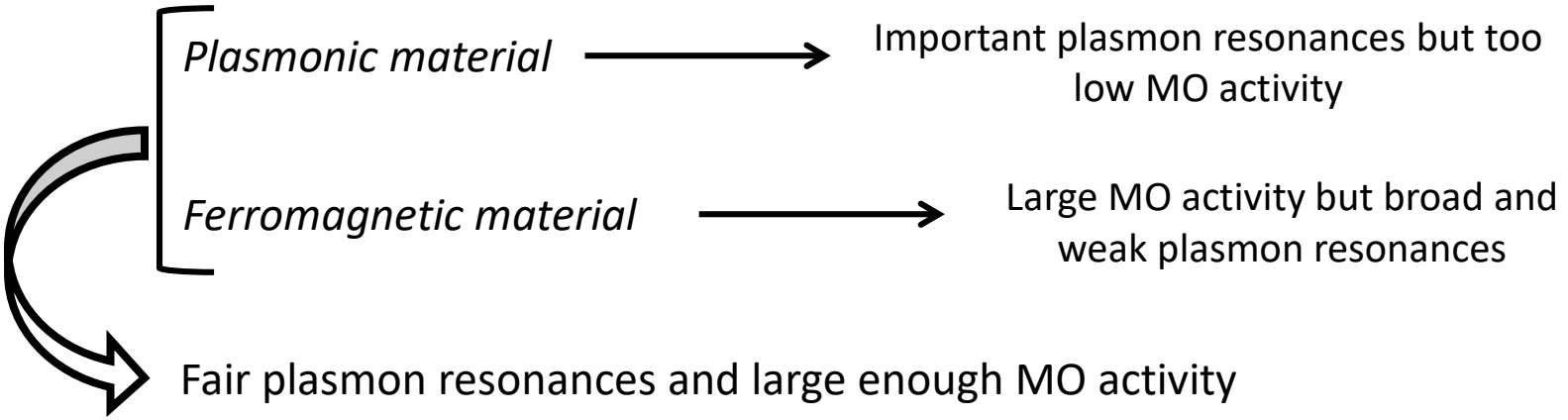
- Chemical versatility
- Tunability of the properties
- Optical transparency
- Charge transfer properties
- Magnetic properties



Magneto-optics are based on the interaction between the light and magnetically ordered materials → PBAs have potential used in magneto-optical devices

Main problem → Magneto-optical effects are usually weak

Magneto-plasmonics



ACS Appl. Mater. Interfaces 2013, 5, 1955−1960

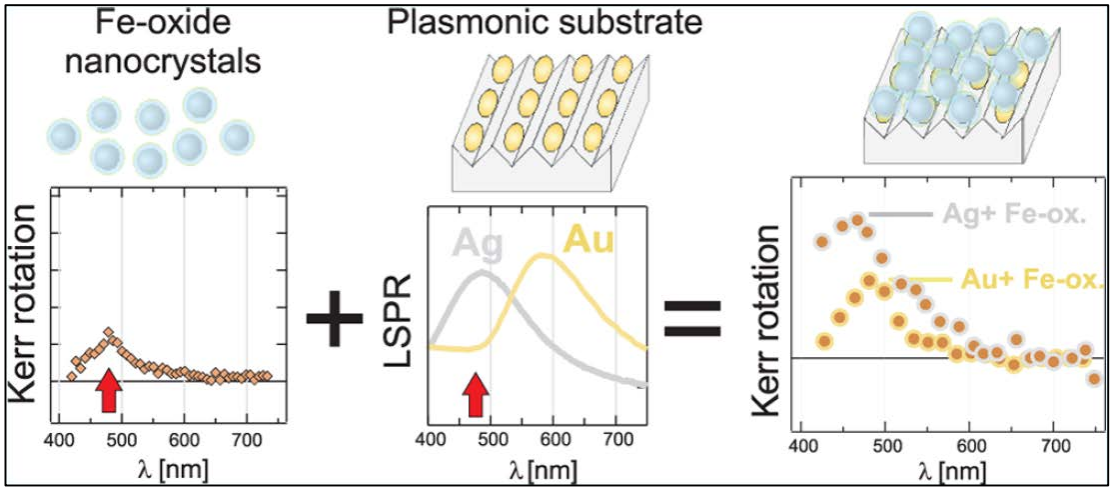
Magneto-plasmonics

Plasmonic material → Important plasmon resonances but too low MO activity

Ferromagnetic material → Large MO activity but broad and weak plasmon resonances

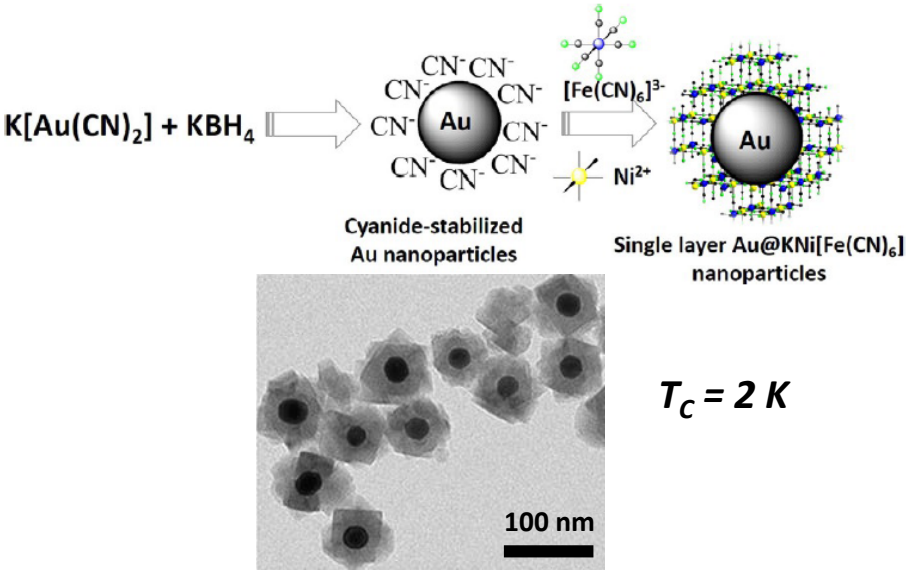
Fair plasmon resonances and large enough MO activity

Magneto-plasmonic materials are heterostructures where ferromagnetic and plasmonic structures are combined in a unique entity



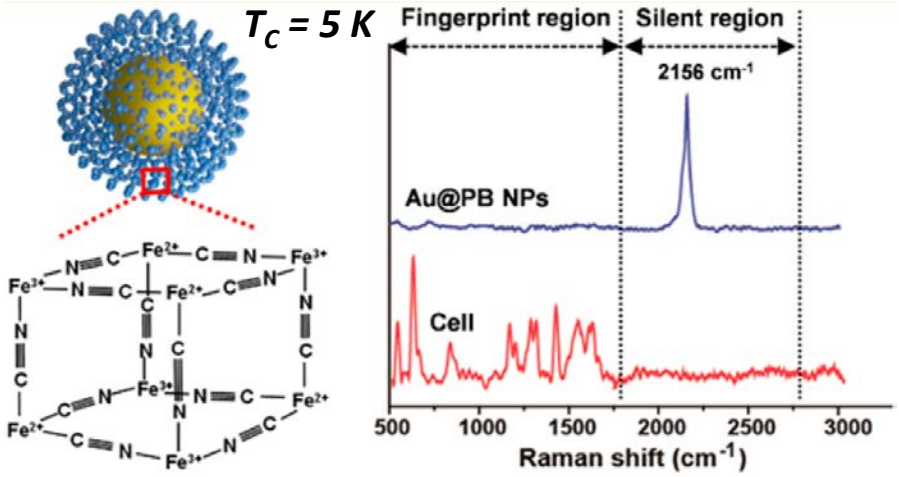
ACS Appl. Mater. Interfaces 2013, 5, 1955−1960

Au-PBA heterostructures

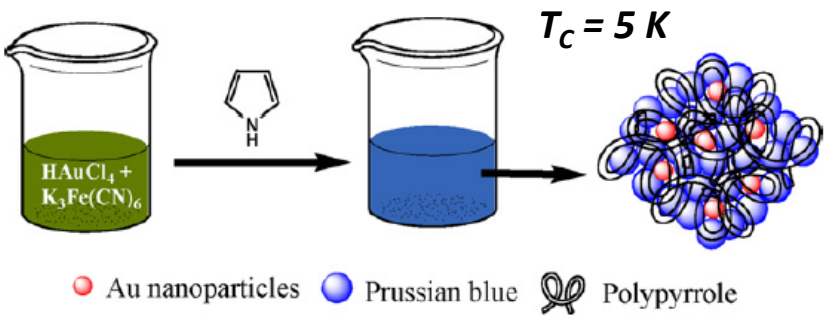


T_C = 2 K

Chem. Eur. J. ***2017***, *23, 7483 – 7496*



Anal. Chem. ***2017***, *89, 1551−1557*

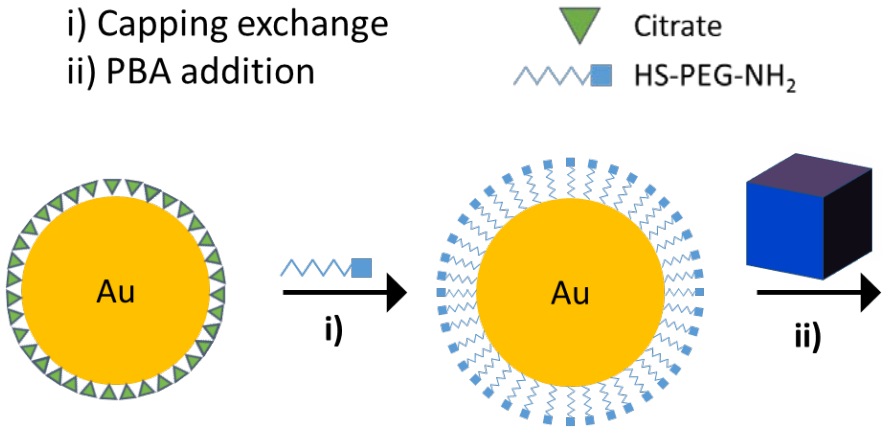


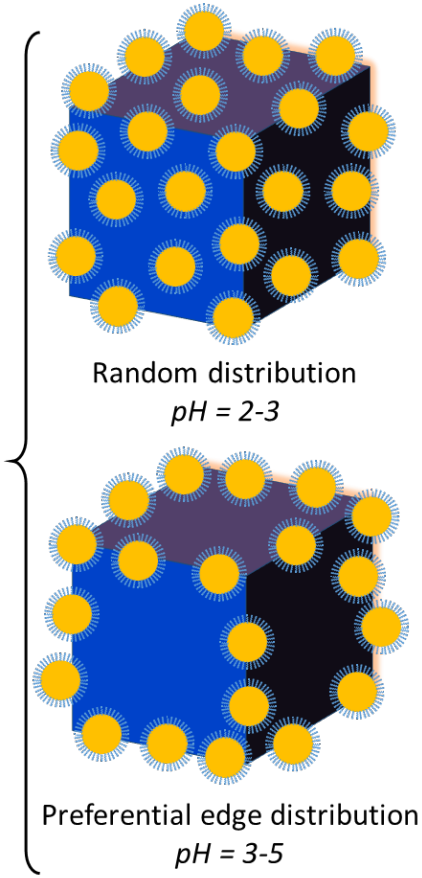
Anal. Chim. Acta ***2012***, *711 40– 45*

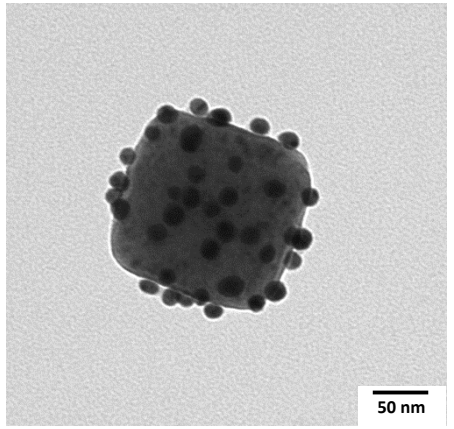
Due to the synthetic routes, these hybrids are restricted to weak magnetic PBAs and isotropic Au cores

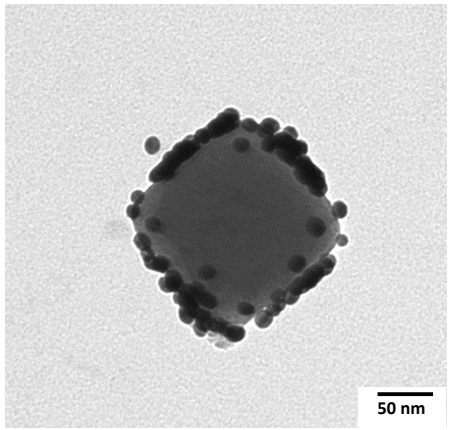
Synthetic protocol

i) Capping exchange
ii) PBA addition





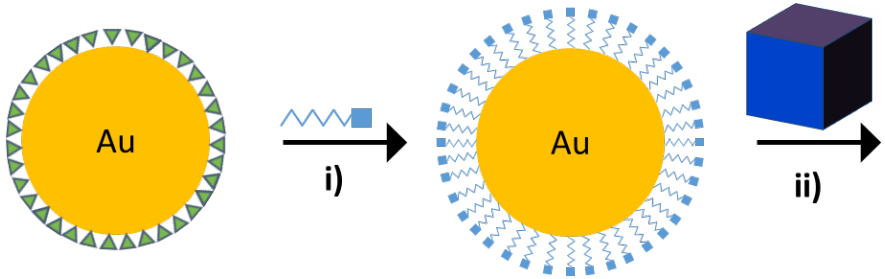


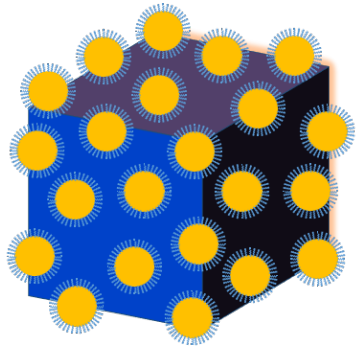


Synthetic protocol

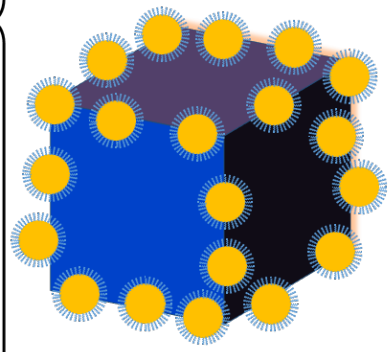
i) Capping exchange
ii) PBA addition

Citrate
HS-PEG-NH_2

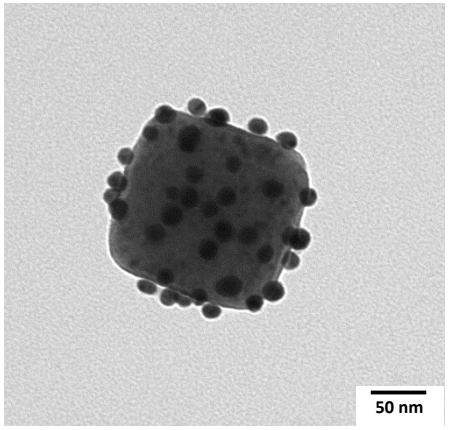


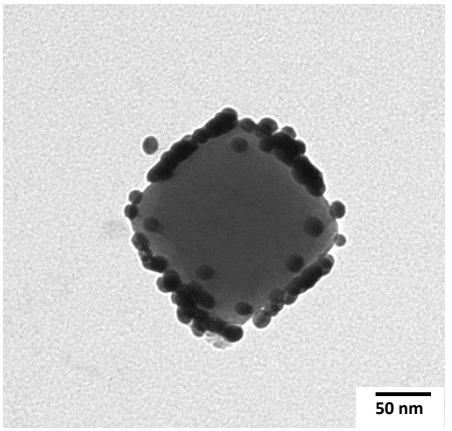


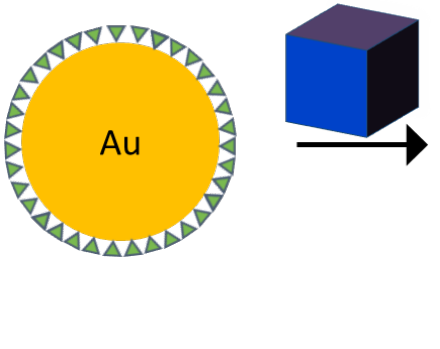
Random distribution
pH = 2-3



Preferential edge distribution
pH = 3-5

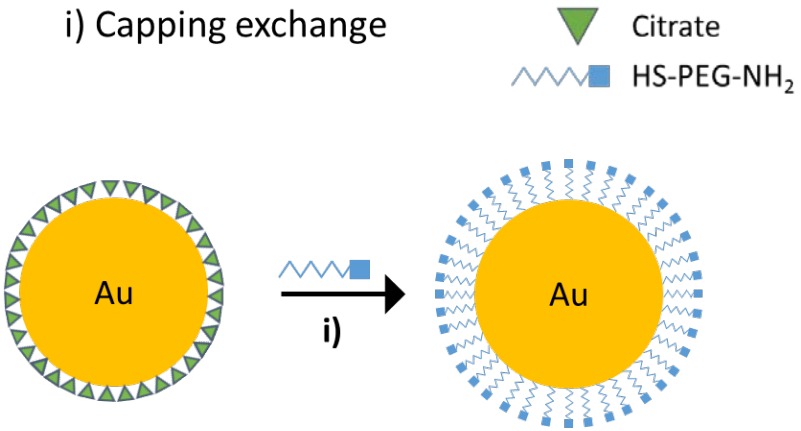


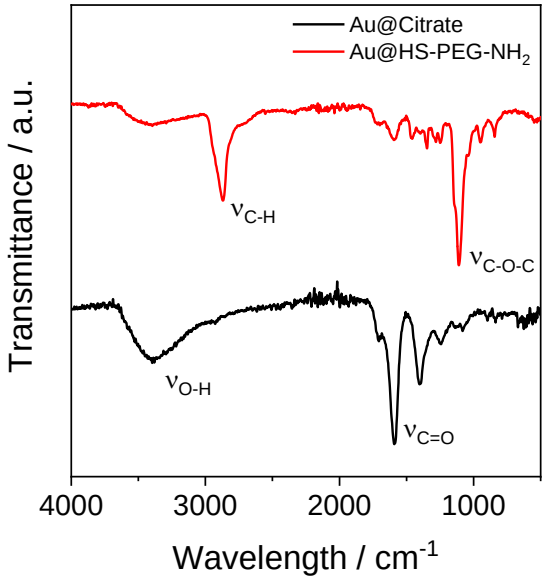




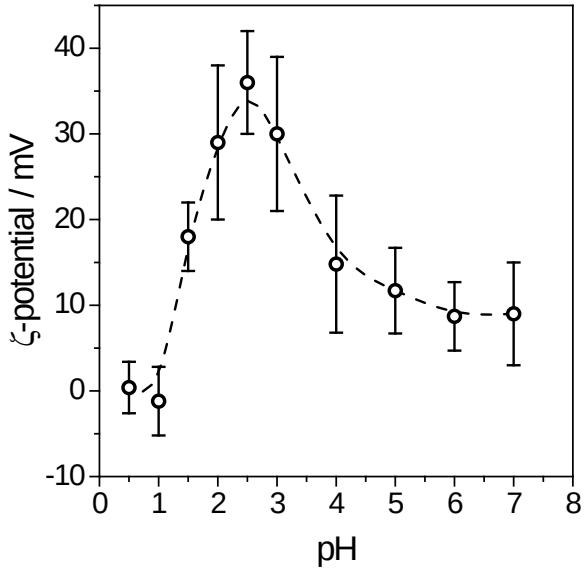
No interaction

Synthetic protocol

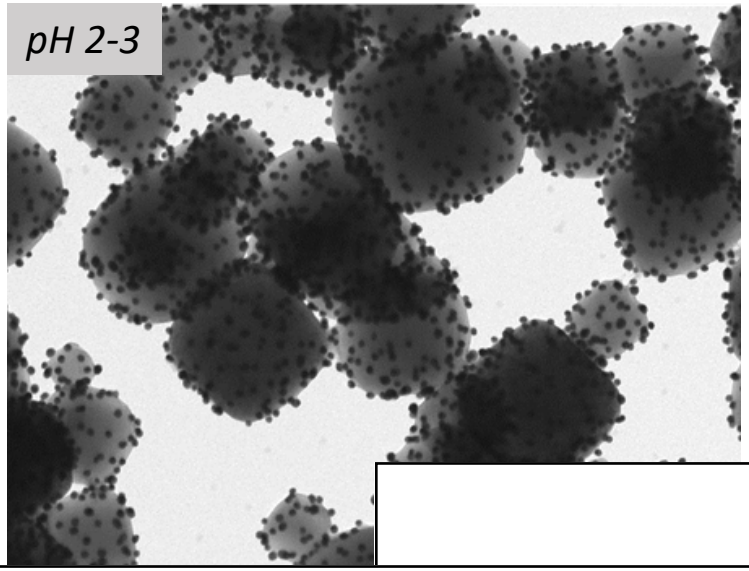


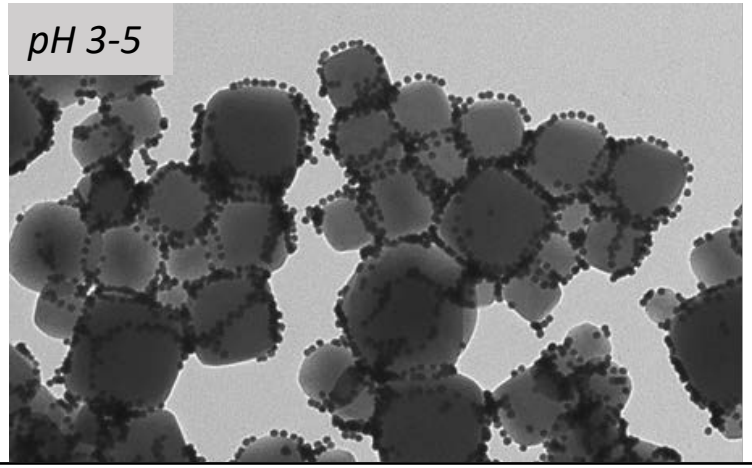


NP	*ζ-potential / mV*		
	Citrate	CTAB	HS-PEG-NH_2
Au NPs	-40 ± 6	/	9 ± 6
Au NRs	/	35 ± 7	12 ± 4
Au NSs	/	/	12 ± 4
Ag NPs	-35 ± 2	/	11 ± 5



Synthetic protocol

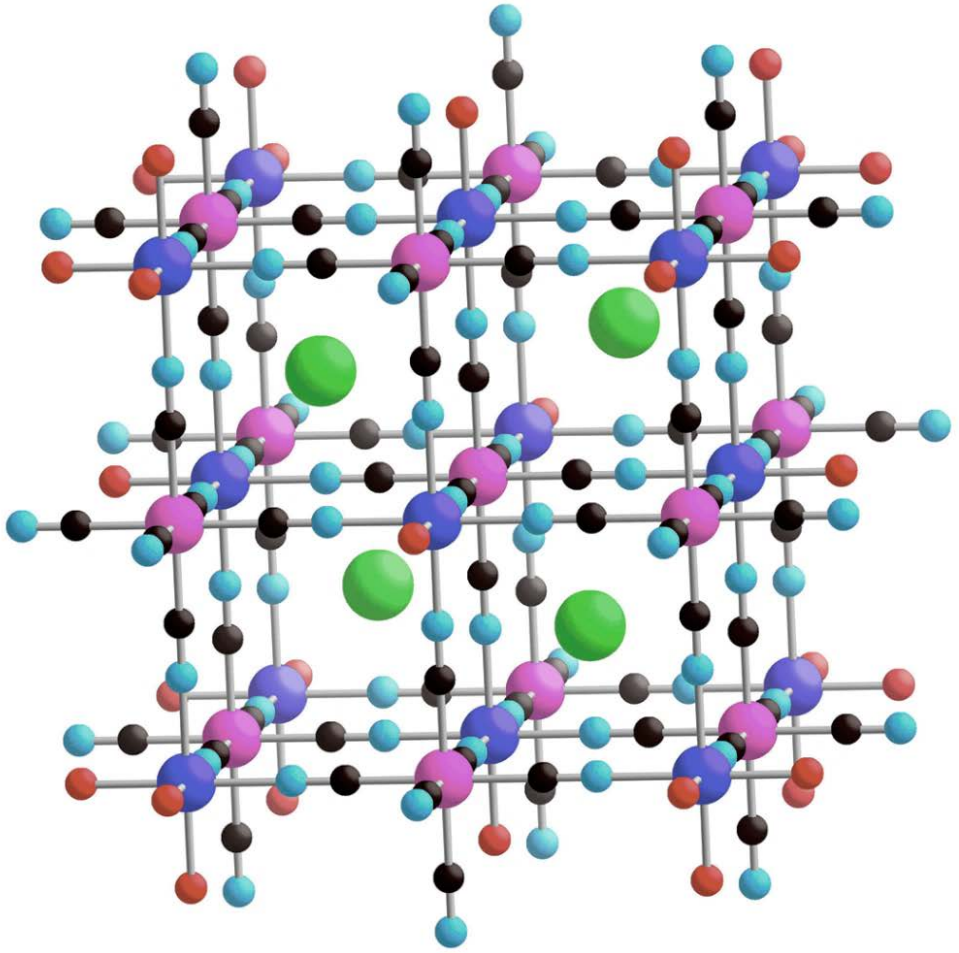




Synthetic protocol

Edge:
$M(CN)_6^{3-}$ surrounded by **4** metallic centers

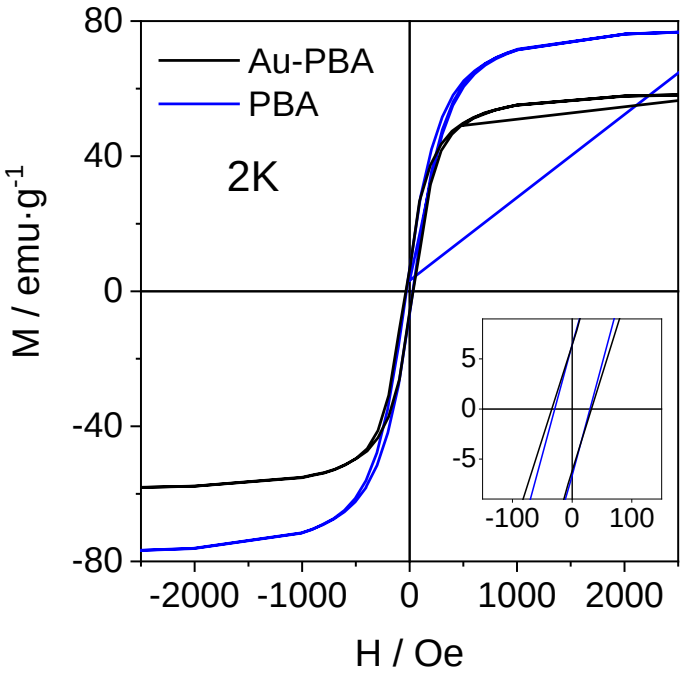
Face:
$M(CN)_6^{3-}$ surrounded by **5** metallic centers

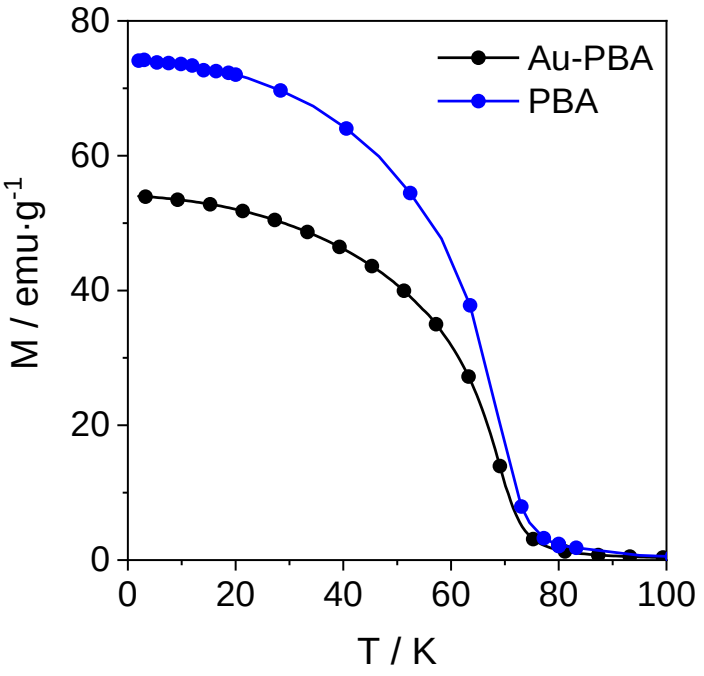


Larger negative charge density on (and near) the edges than on their faces

Higher interaction with the amino group

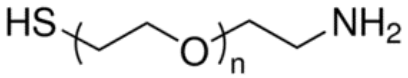
Magnetic properties

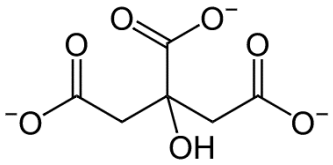


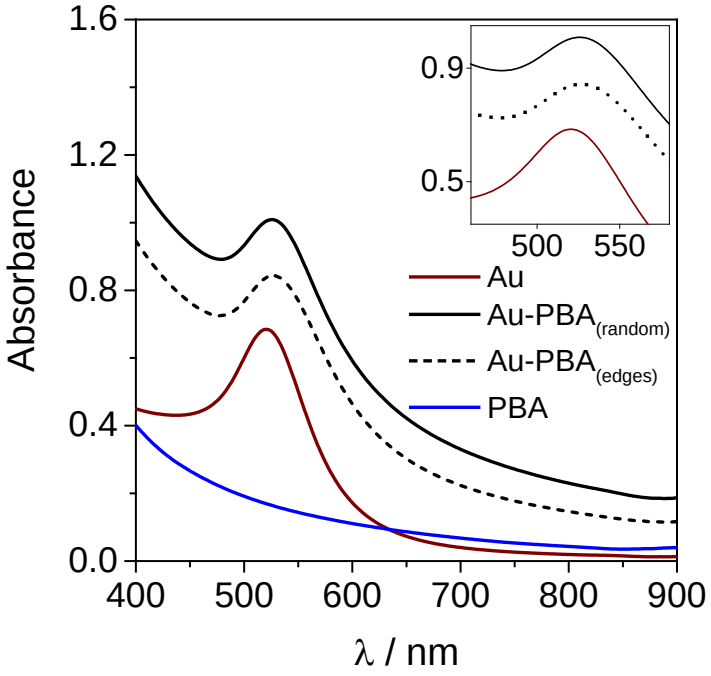


The magnetic properties of the hybrid are almost identical to those measured for pristine NiCr PBA NPs

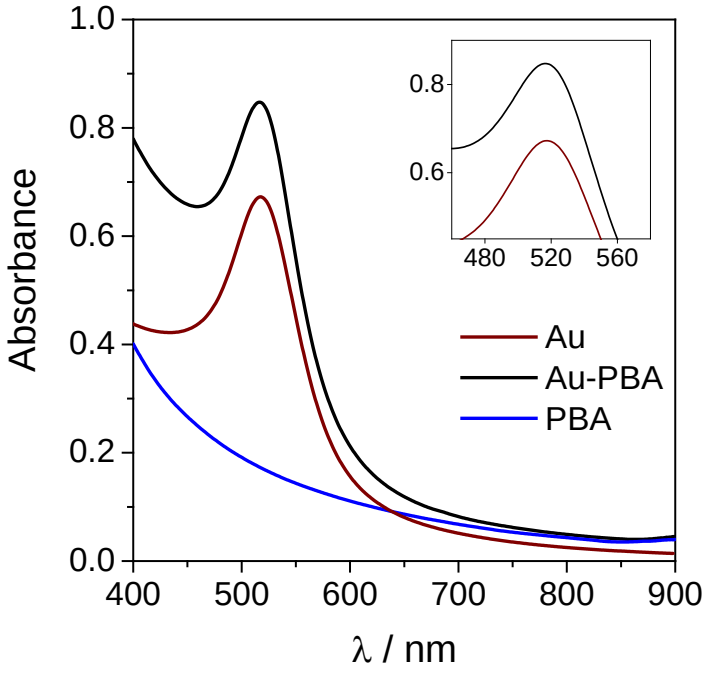
Plasmonic properties







Δλ = 6 nm



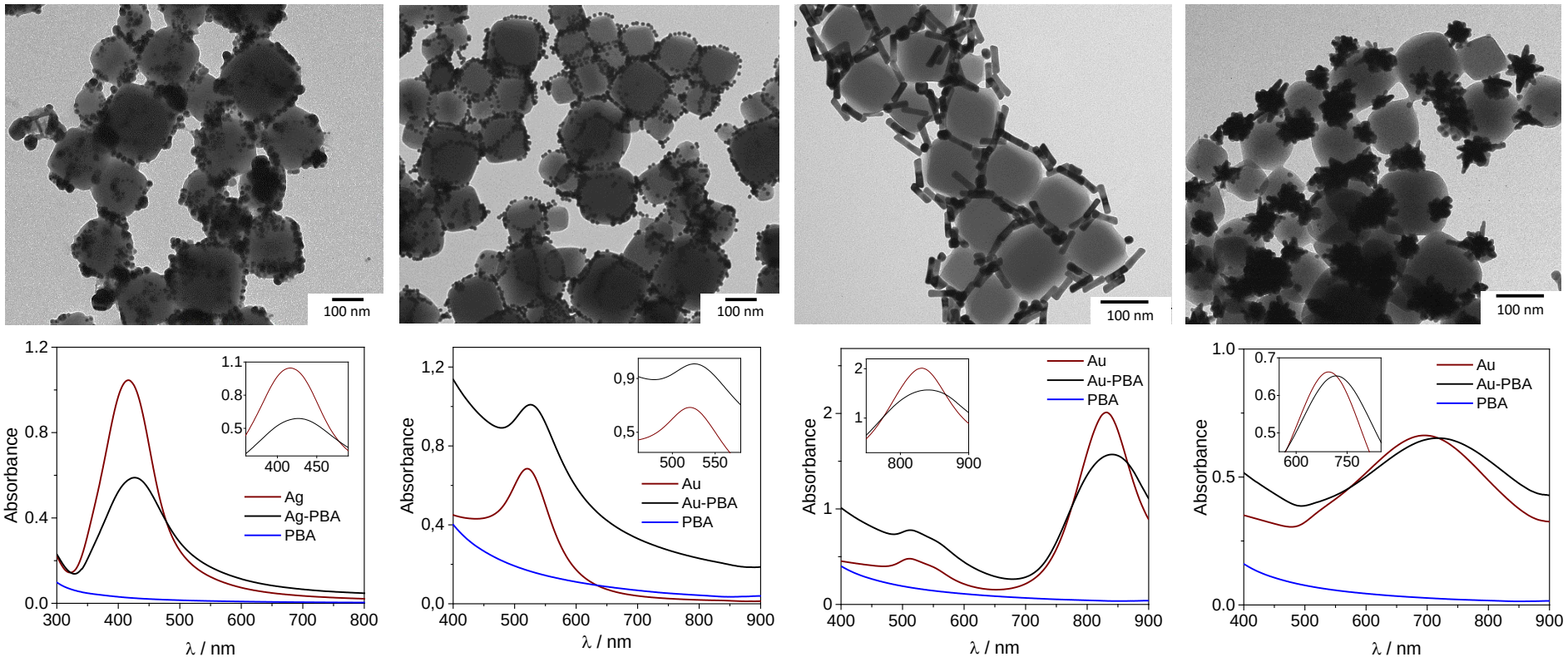
Δλ = 0 nm

Plasmon shift → Modification of the local refractive index at the surface of the Au NPs

Synthesis versatility

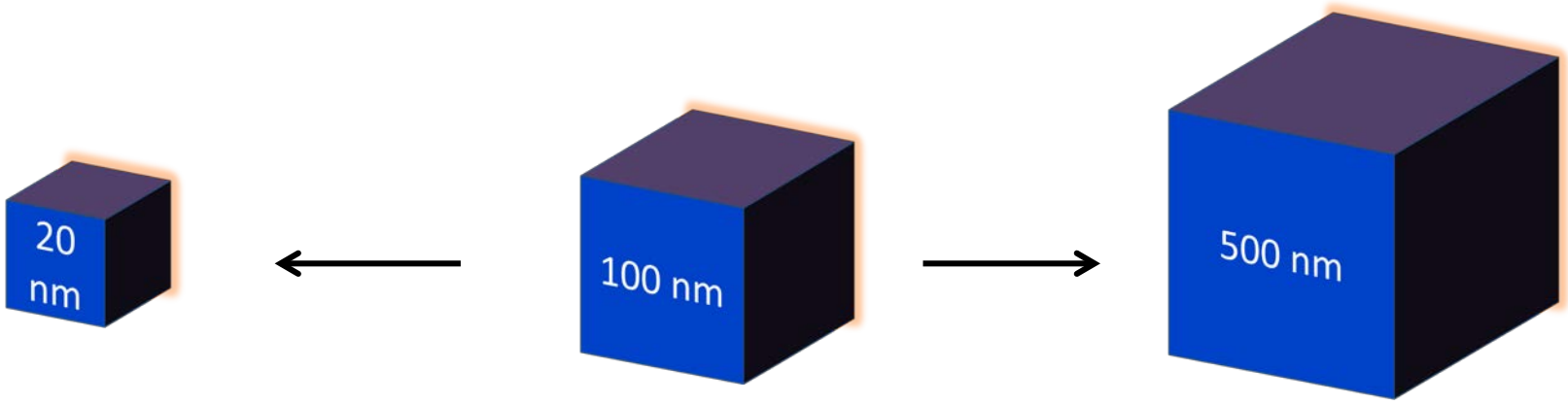
ICMol
Institut de Ciència Molecular

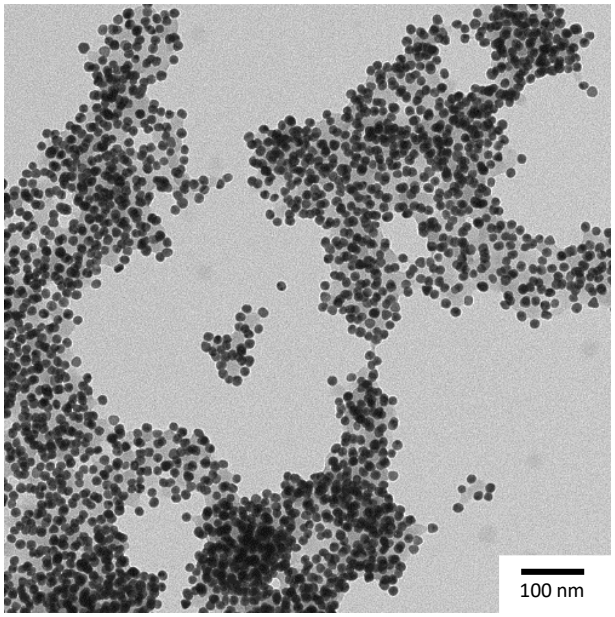
Ag NPs *Au NPs* *Au NRs* *Au NSs*

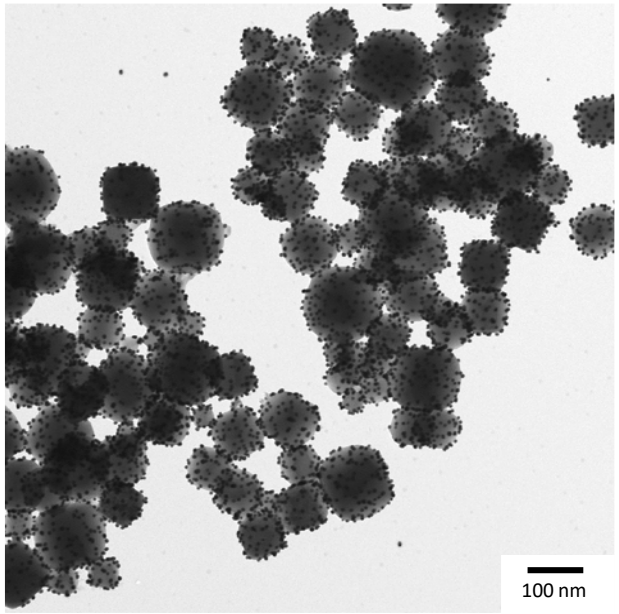


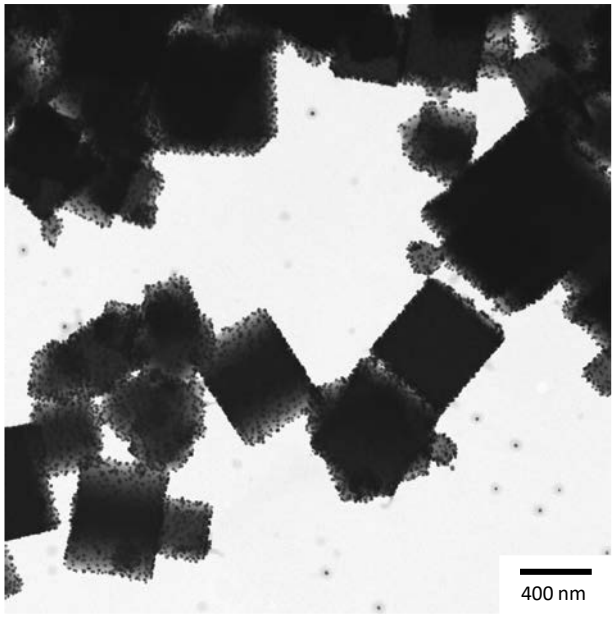
It is possible to tune the plasmonic properties of the hybrids in the whole visible spectrum

Synthesis versatility

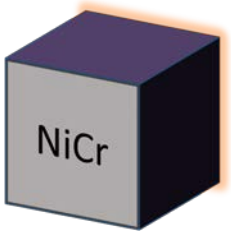


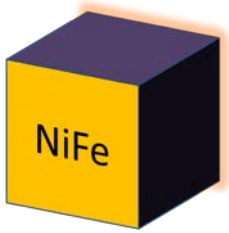


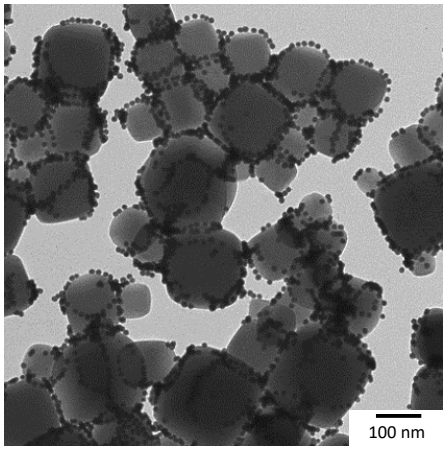


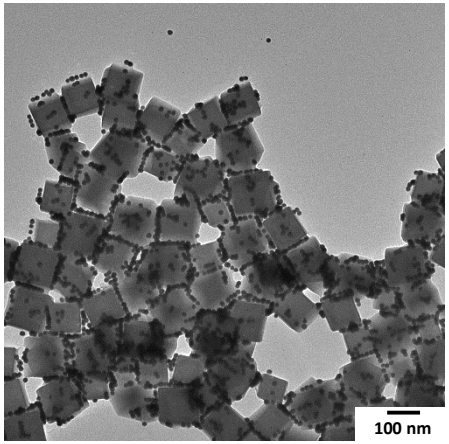


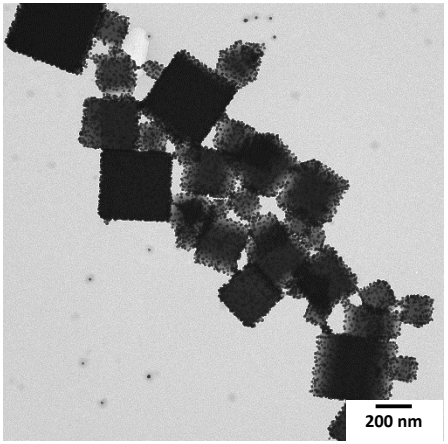
Synthesis versatility

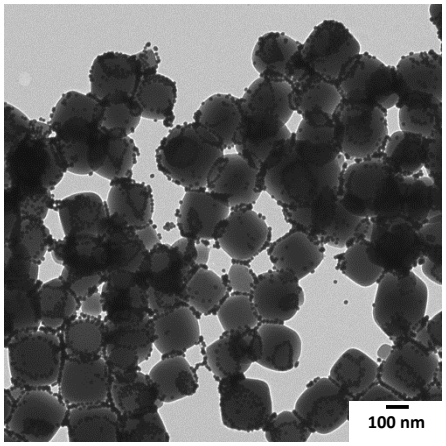


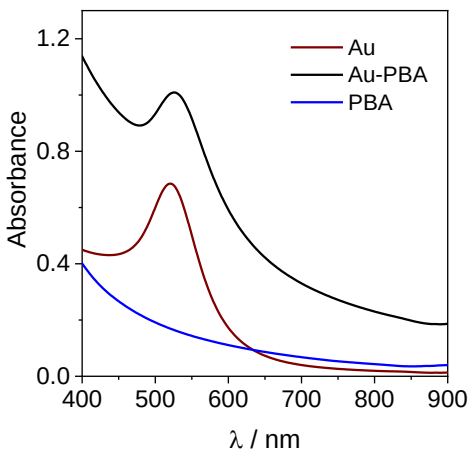


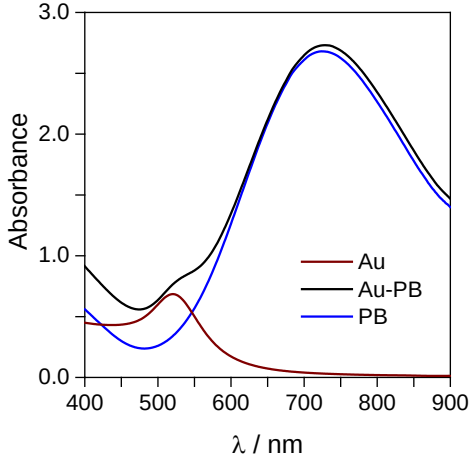


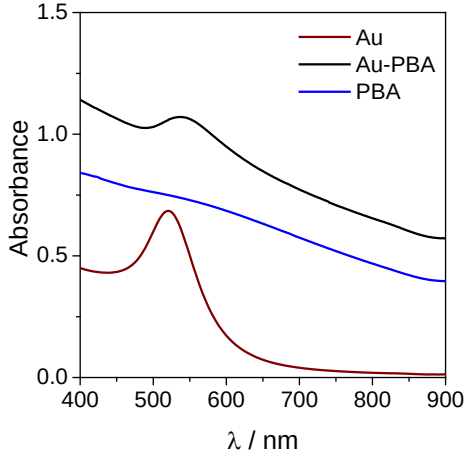


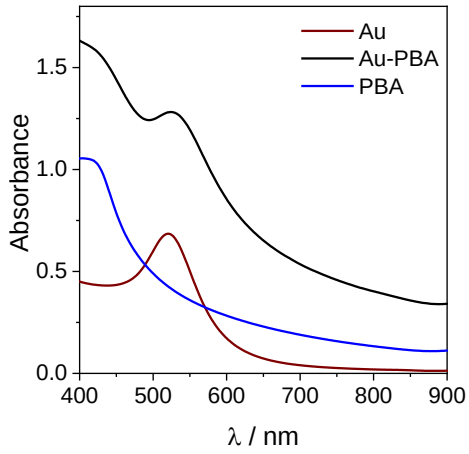












Conclusions

- This synthetic procedure permits to prepare hybrid magneto-plasmonic nanostructures formed by metallic NPs decorating PBA.

- We can control the location of the metallic NPs on the PBA: randomly over the whole cubic surface or preferentially on the edges.

- It is possible to anchor anisotropic metallic NPs allowing to tune the optical properties in a wide range of the visible spectrum.

- It provides a versatile platform to investigate the enhancement of the magneto-optical properties thanks to the coupling with the plasmons.

"The design of magneto-plasmonic nanostructures formed by magnetic Prussian Blue-type nanocrystals decorated with Au nanoparticles" *Chem. Comm.* **2021**

Acknowledgments

University of Valencia

Isidora Susic

Ramón Torres-Cavanillas

Dr. Marc Coronado-Puchau

Prof. Eugenio Coronado

University of Antwerp

Dr. Daniel Arenas-Esteban

Prof. Sara Bals

Universitey of Paris-Saclay

Prof. Talal Mallah

Thanks for your attention!

Design of magneto-plasmonic heterostructures formed by Au decorated on magnetic Prussian Blue-type nanocrystals

Roger Sanchis Gual

Instituto de Ciencia Molecular

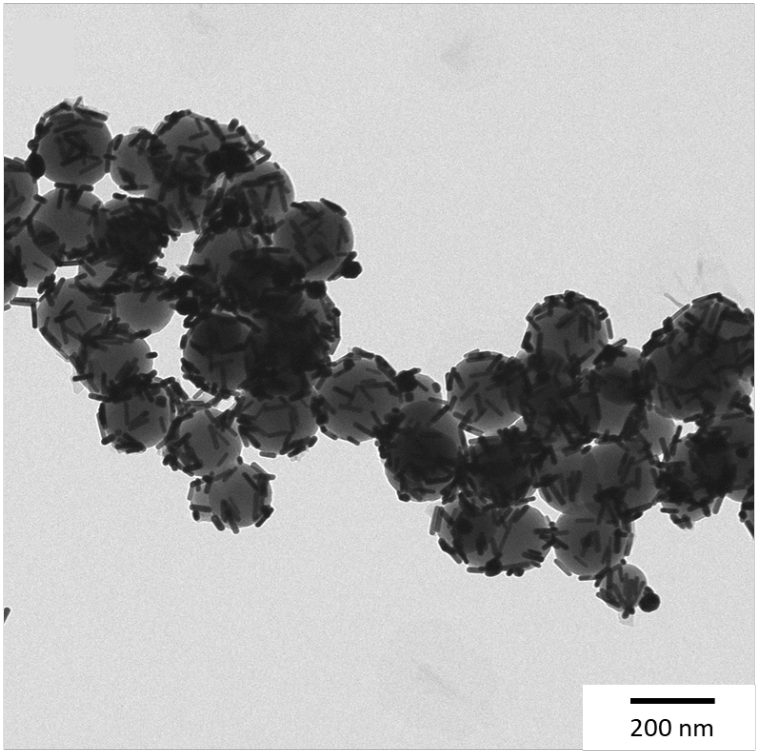
Small Chem 2021 Online International Conference

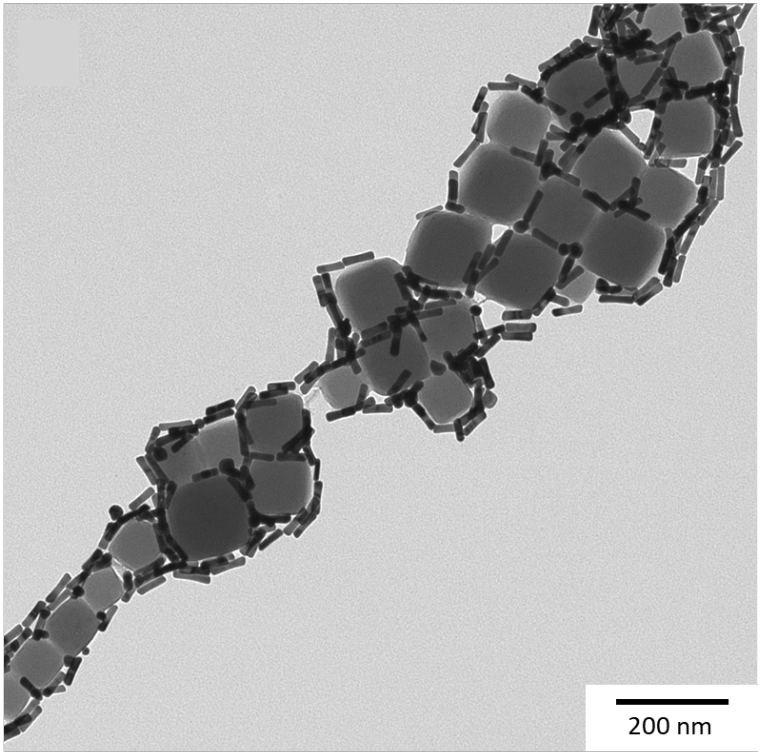
17/02/2021

VNIVERSITAT DE VALÈNCIA

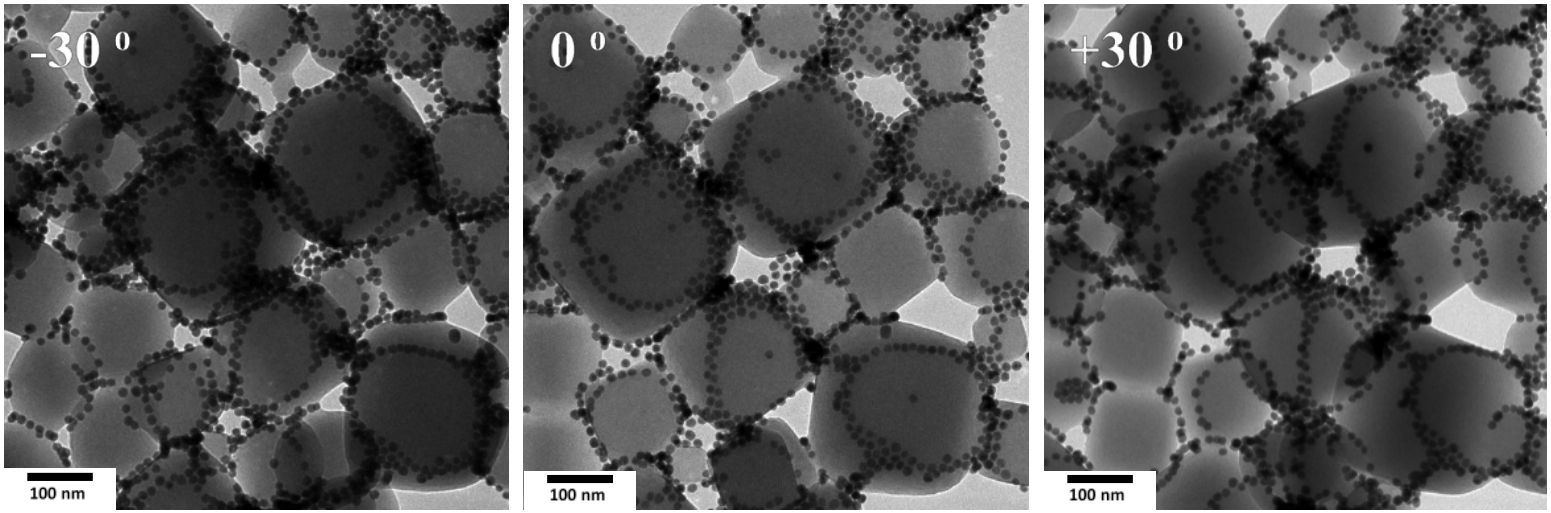
ICMOL
Institut de Ciència Molecular

Supporting: AuNRs decoration

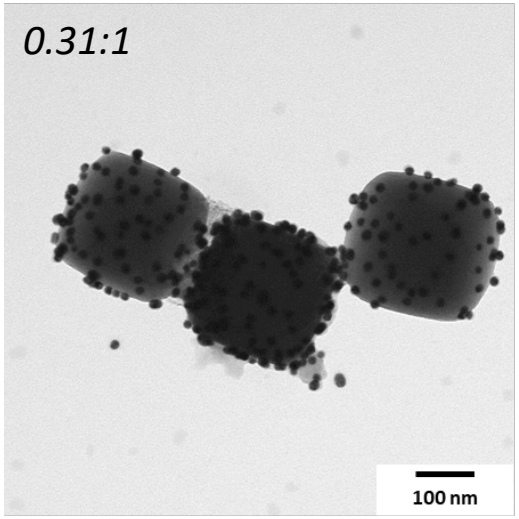


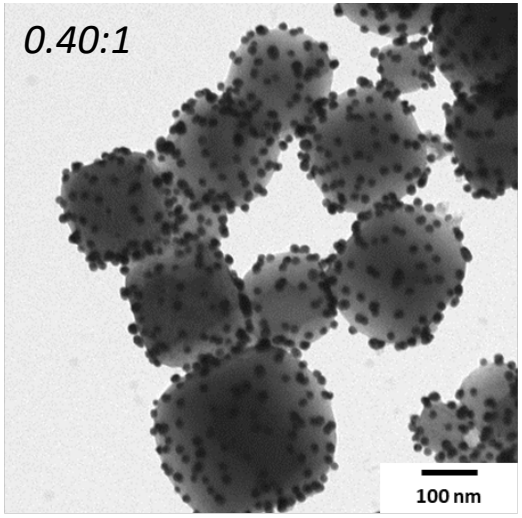


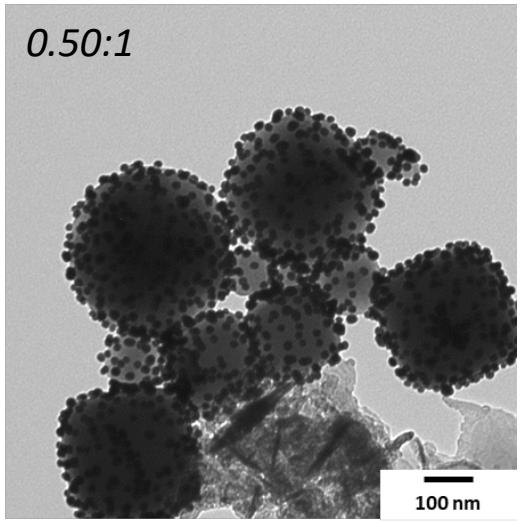
Supporting: Au decoration

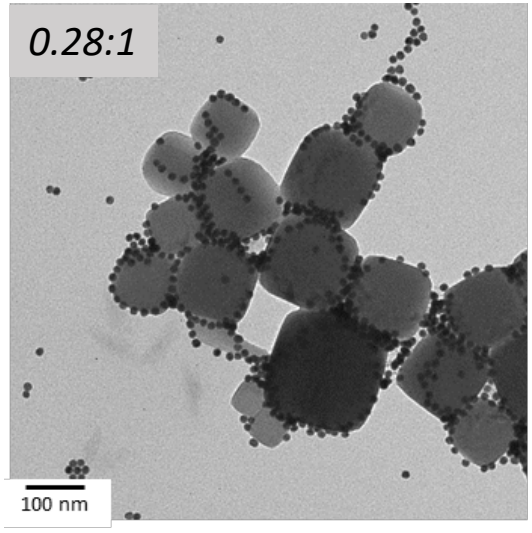


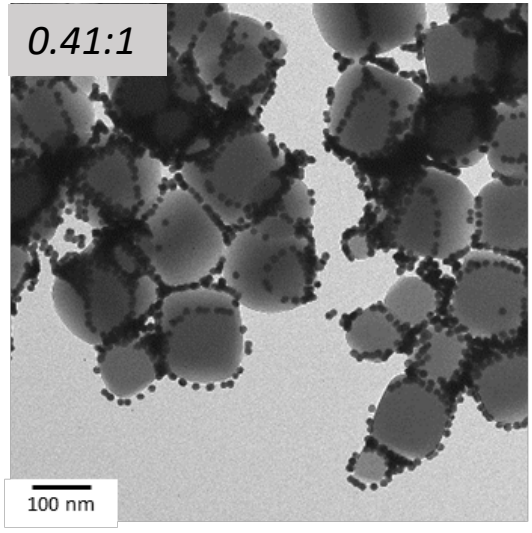
Supporting: Au/PBA molar ratio

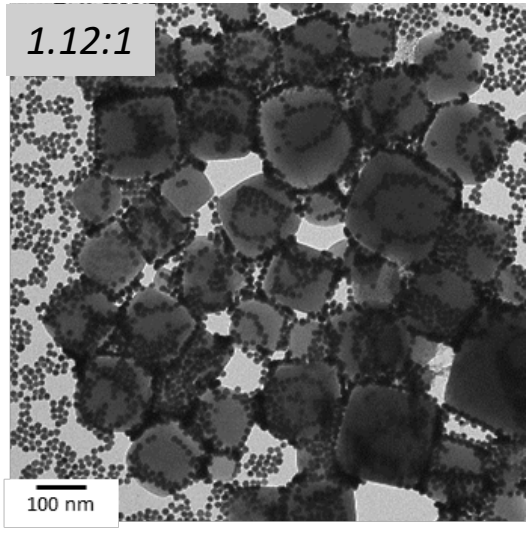




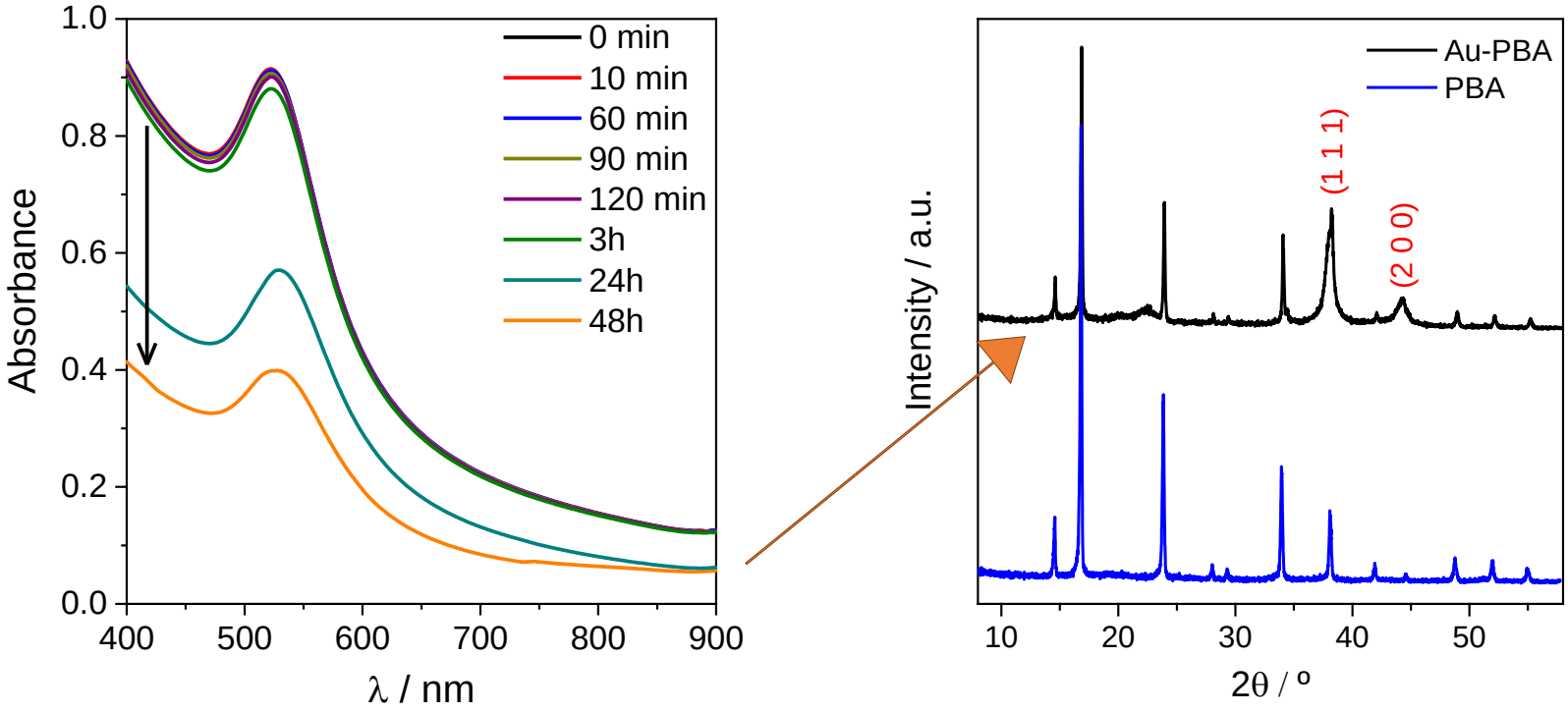








Stability characterization



Aggregation of the heterostructure occurs with time