1st year report

Università degli Studi di Perugia
Dipartimento di Fisica e Geologia
PhD in Physics, XXXVII Cycle
28/10/2022

PON-PhD in

Surface physics for green technologies

Mattia Bassotti

Tutors
Dr. Alberto Verdini
Prof. Giovanni Carlotti

Outline

Why surfaces?

Research topics

Ongoing research:

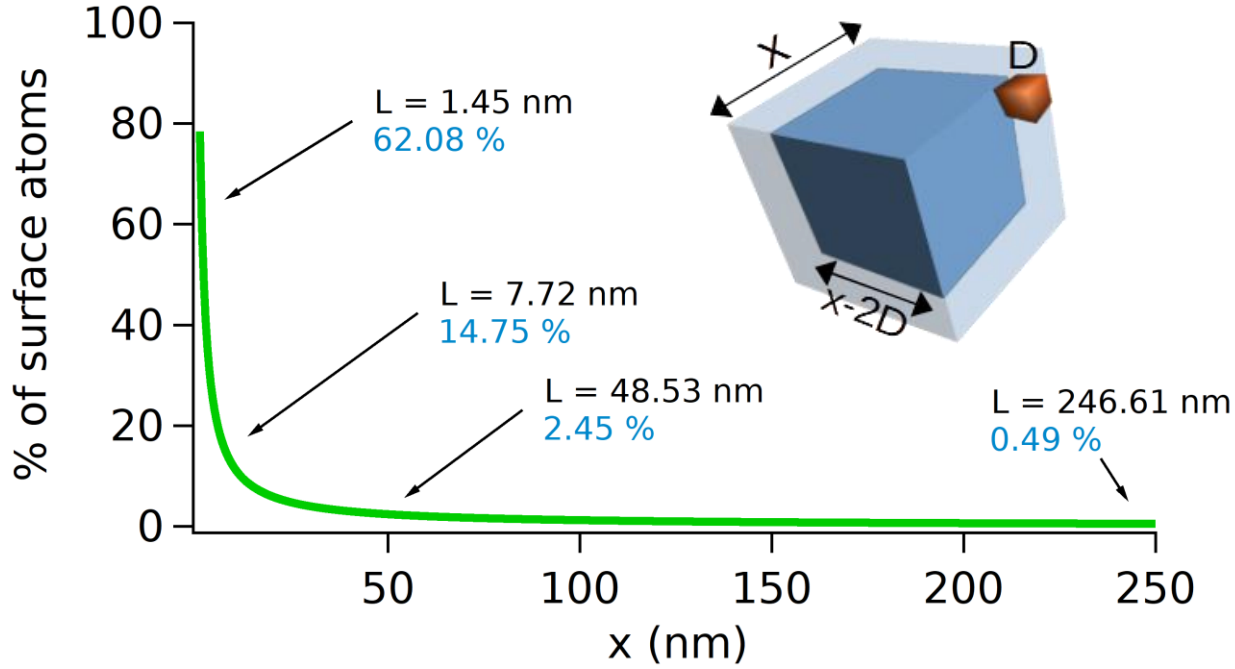
- Decoupling porphyrins
- Tetrapyrroles metalation

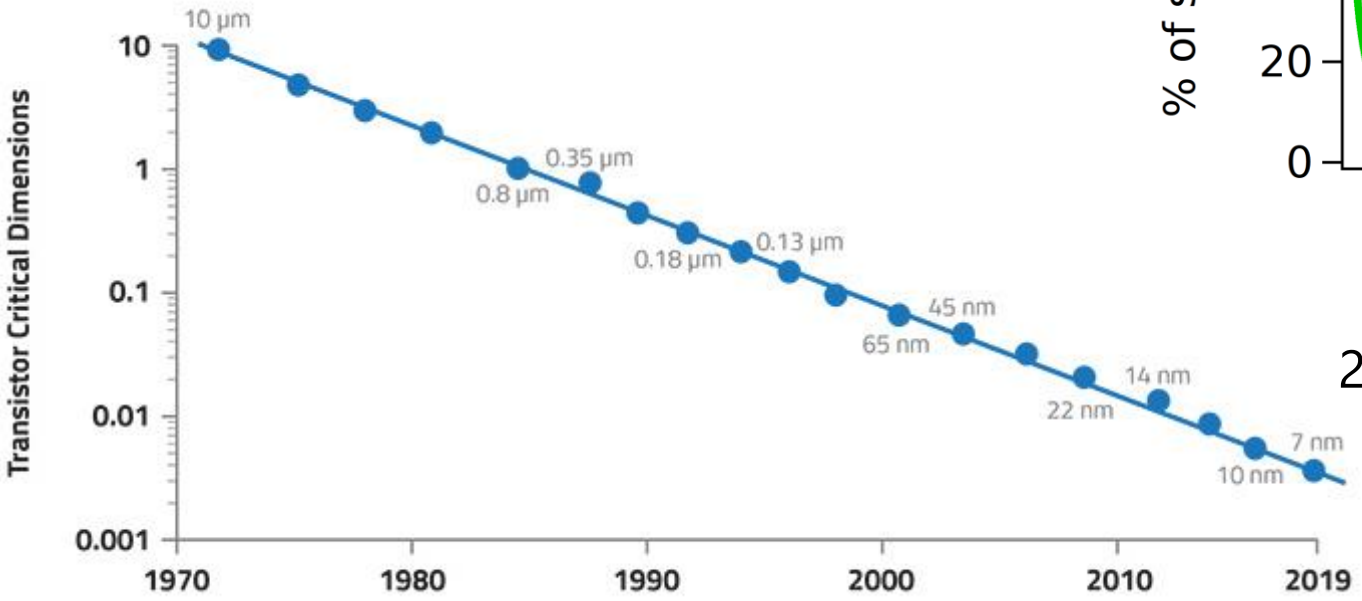
Future outlook

Why surfaces?

- They are more important at the nanoscale, and we are at the nanoscale!

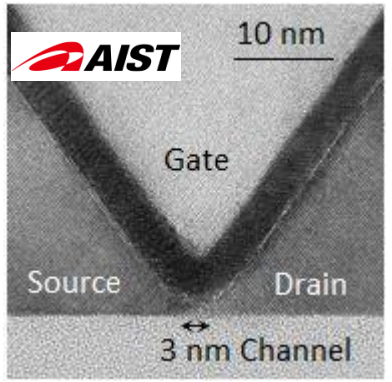
$$Fraction\ of\ surface\ atoms = \frac{x^3 - (x - 2D)^3}{x^3}$$





https://semiengineering.com/scaling-up-and-down/

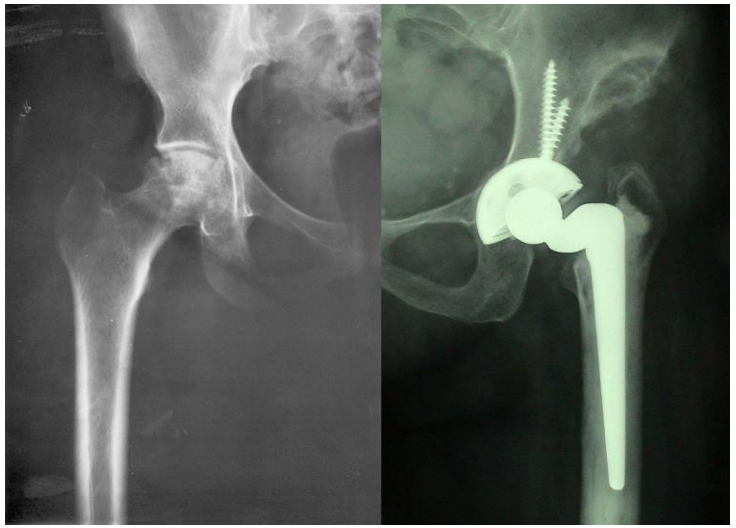
2022 →



2025 → 2 nm
2027 → 1.4 nm

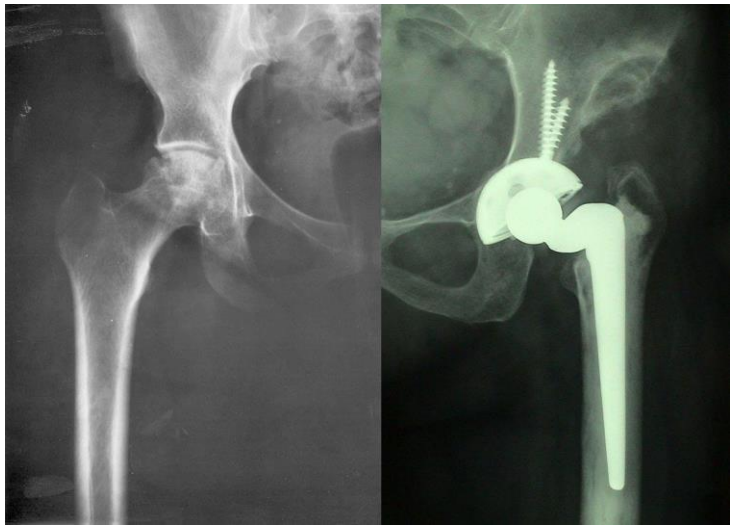
Why surfaces?

- Medicine, Prosthesis coating

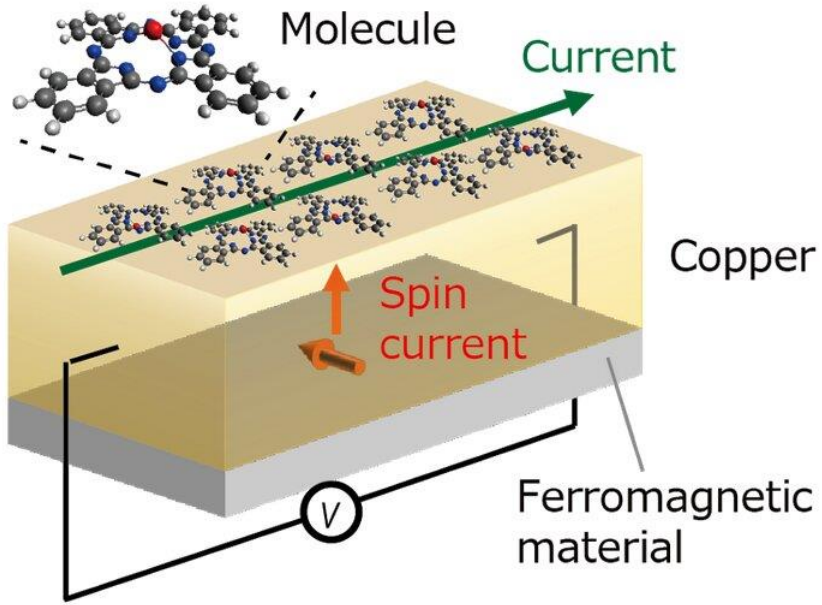


Why surfaces?

- Medicine, Prosthesis coating



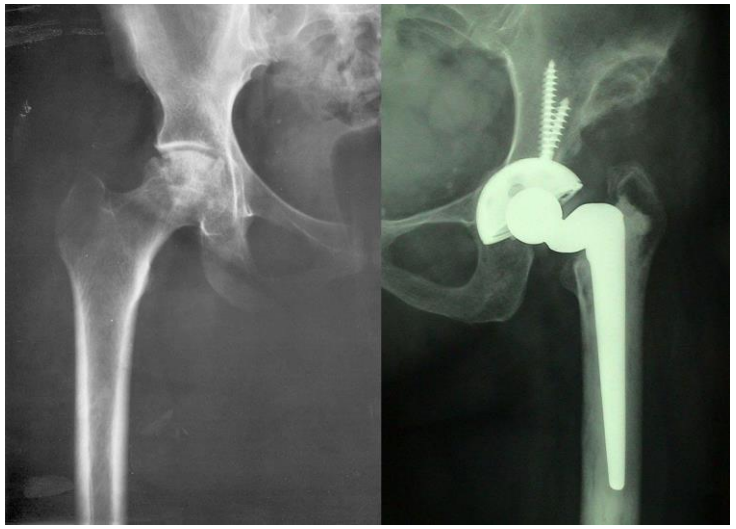
- Spintronics

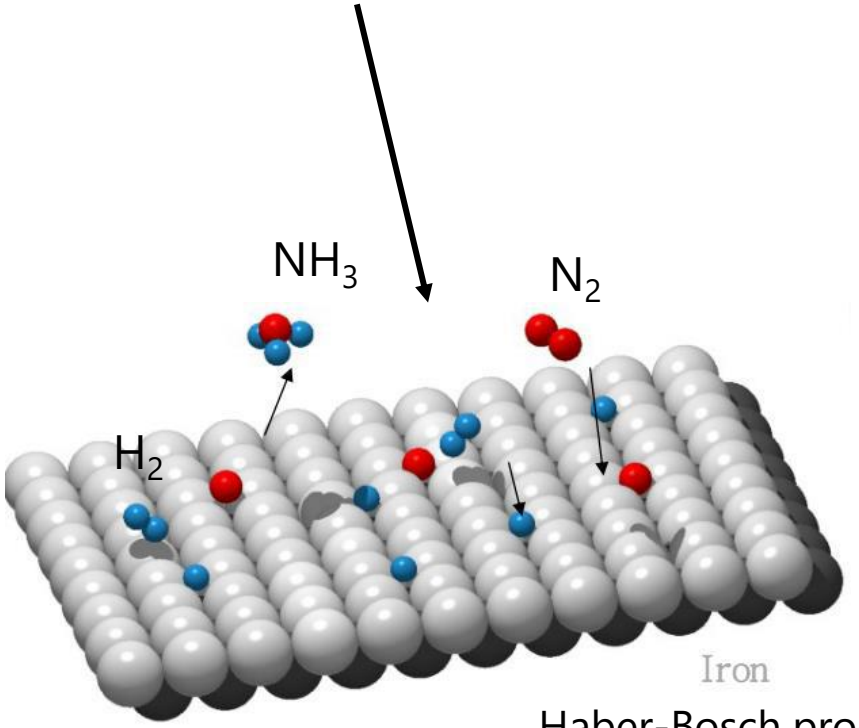


DOI: 10.1021/acs.nanolett.9b02619

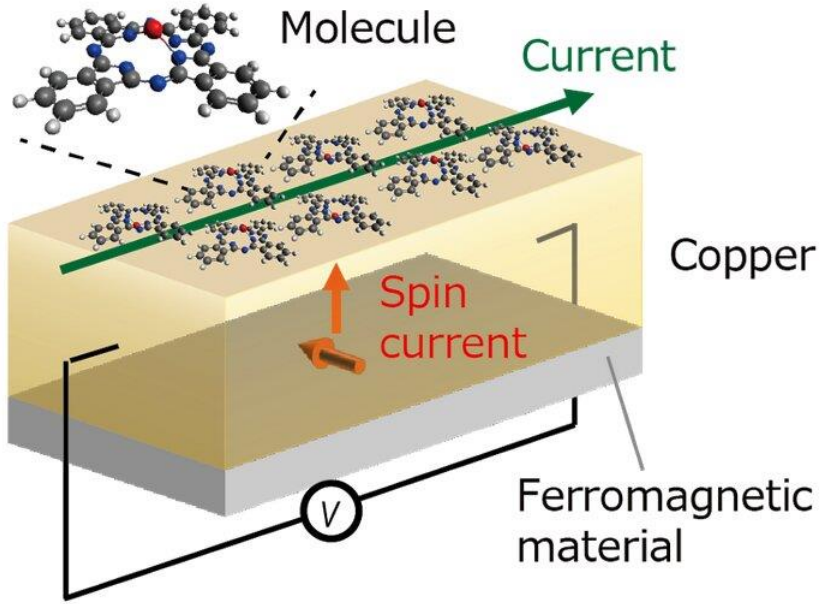
Why surfaces?

- Medicine, Prosthesis coating
- Spintronics
- Heterogeneous Catalysis





Haber-Bosch process (1910)



DOI: 10.1021/acs.nanolett.9b02619

Why surfaces?

- Medicine, Prosthesis coating
- Spintronics
- Catalysis
- Photovoltaics

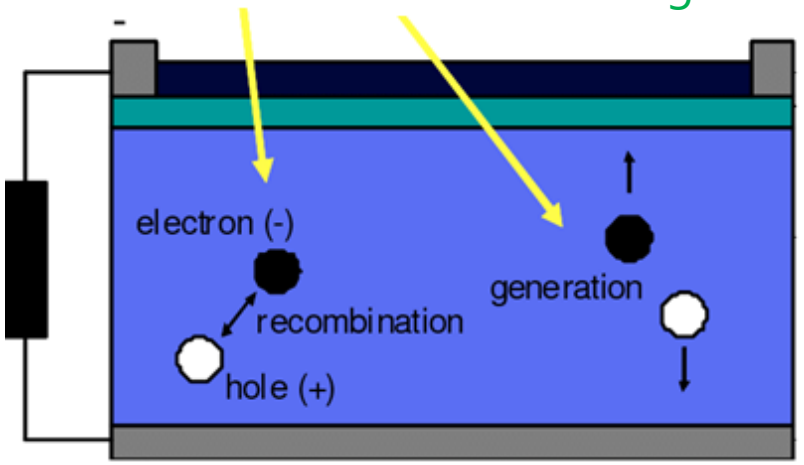
Let's consider:

- Electric energy produced by a 3kW solar panel → 5.5 MWh/year
- Averaged electric cost → 0.5 €/kWh

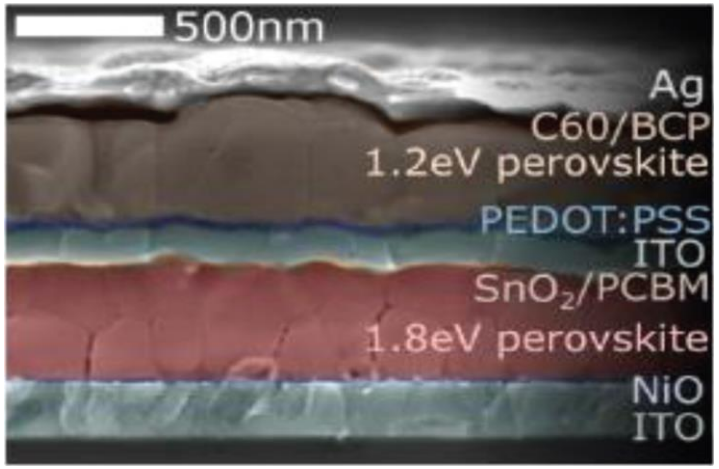
If we raise efficiency of 5%:

+ 275 KWh/year → 140 €/year

Generating an e-h pair isn't enough..



Solar cell section

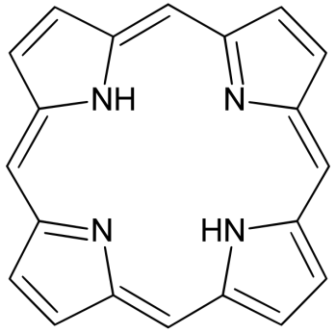


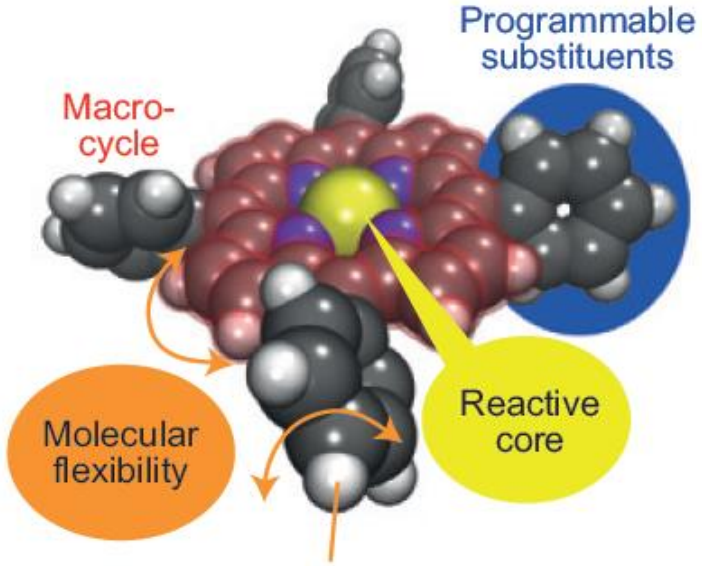
Eperon et al, 2016

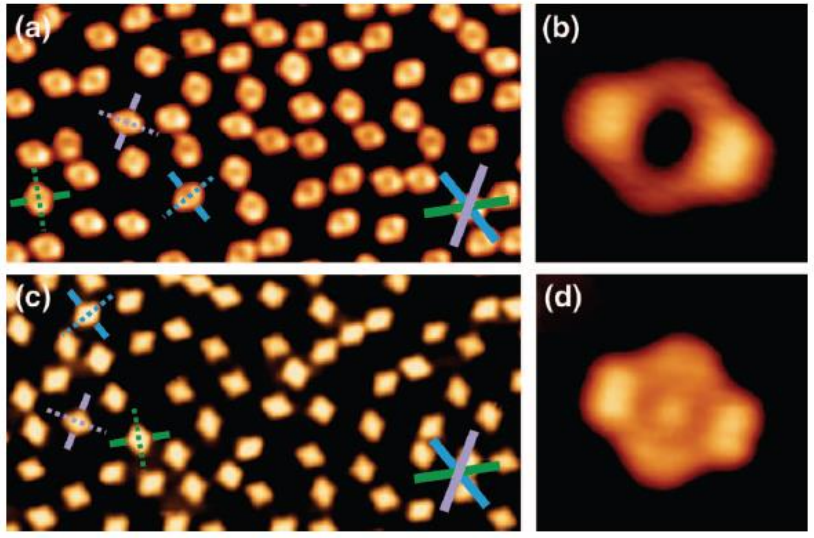
Tetrapyrroles: Porphyrins and Phthalocyanines

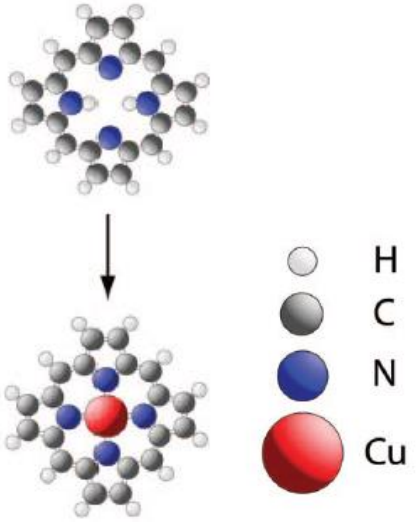
A "nature's choice" molecule that shows:

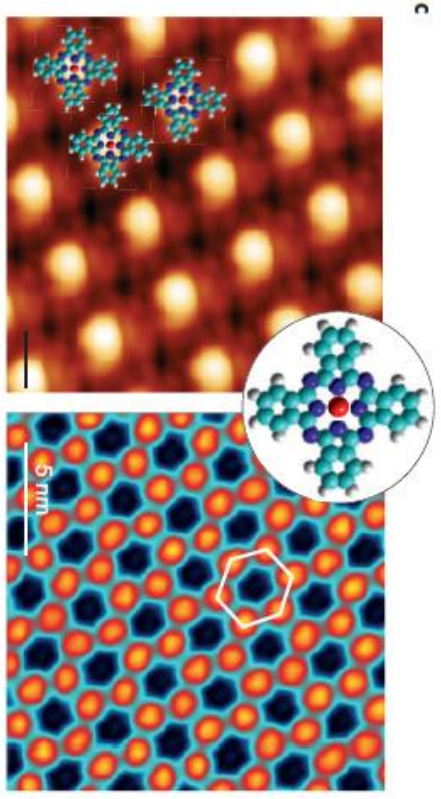
- Intense absorption bands in the visible region;
- Remarkable thermal stability;
- Self-assembly property;
- High functionalization.

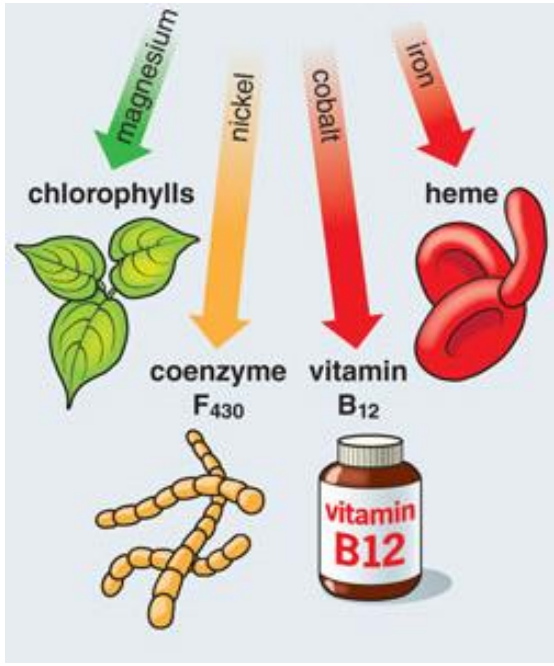












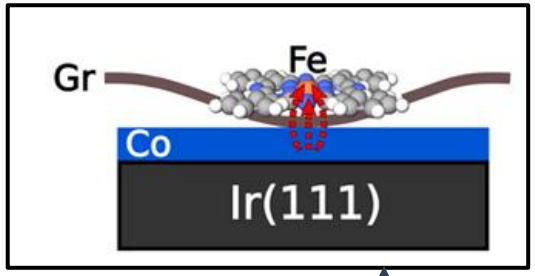
Diller et al, 2013

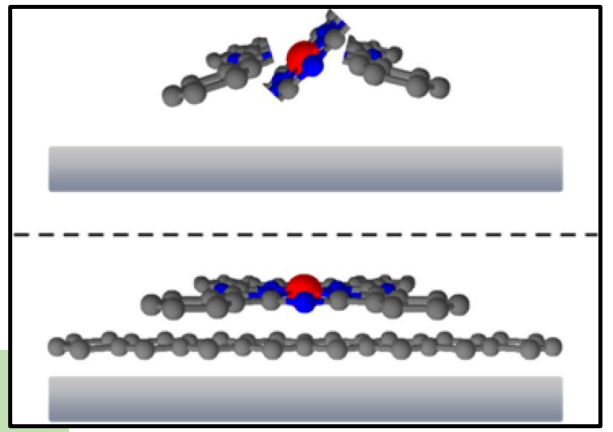
Decoupling Porphyrins: state-of-the-art

Porphyrins have very good features but..

Interaction with the substrate can alter optical and electronic properties (HOMO-LUMO gap)

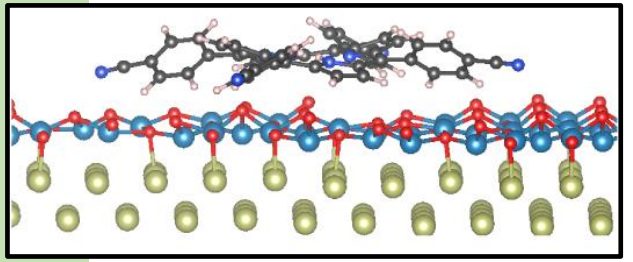
Solutions adopted





Buffer layers:

- M-Pc on Ir(111) with graphene-Co
[Avvisati et al. 2016]
- Fe-Pc on Ni(111) with graphene
[Massimi et al. 2014]
- Fe-Pc on Ni(111) with graphene
[Uihlein et al. 2014]
- DBP on Ni(111) with h-BN
[Schaal et al. 2020]
- Co-TPP on Cu(110) with Cu3N
[Zoldan et al. 2013]
- Co-DPP on Ir(100) with CoO
[Xiang 2020]



Oxydation of the substrate:

- Zn-TPP on Fe(001)-p(1×1)O
[Bussetti et al. 2016]
- Co-TPP on Cu(110)-(2×1)O
[Bussetti et al. 2020]

Exp. 1 - Decoupling Porphyrins

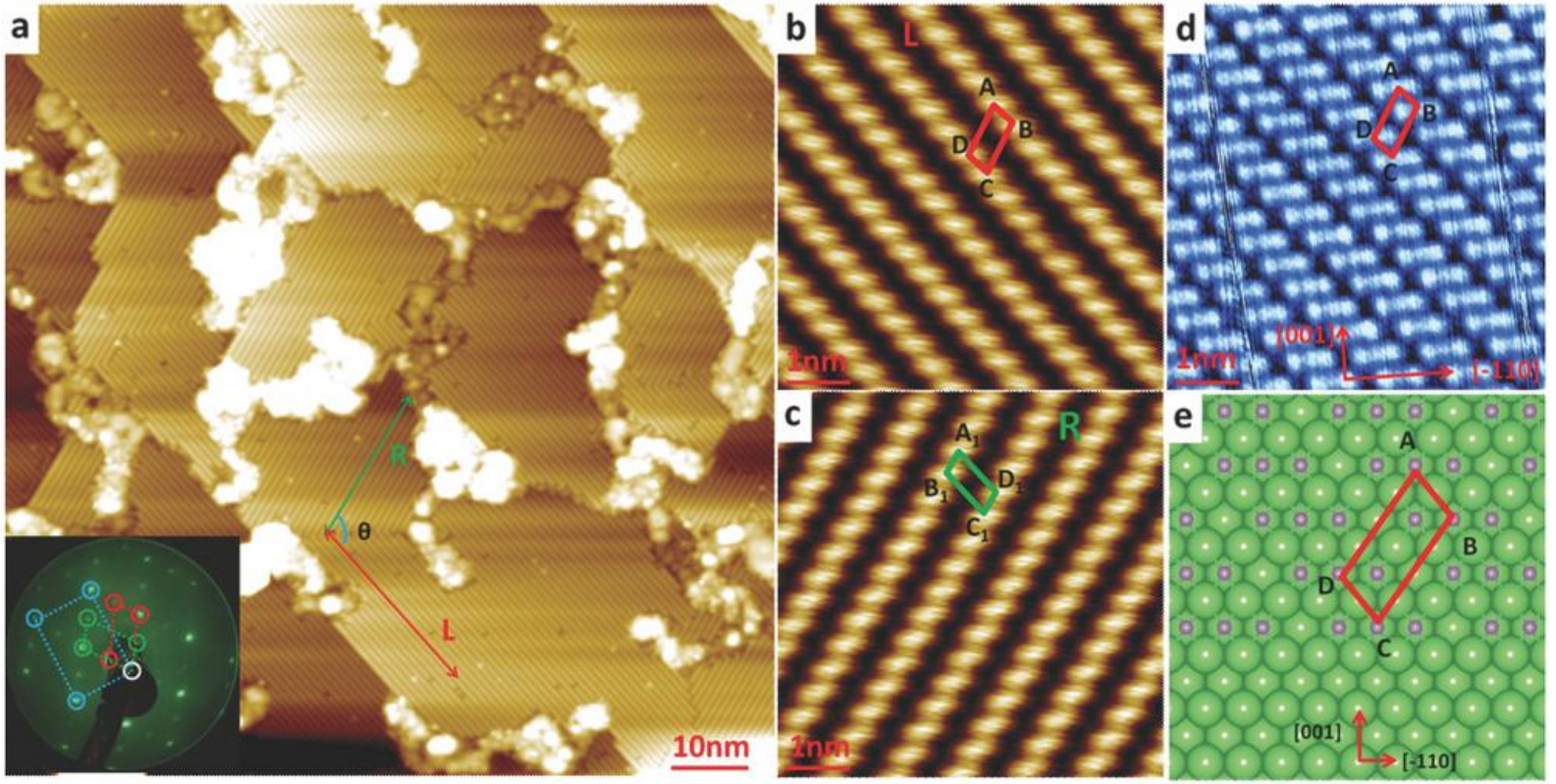
Decoupling Porphyrins: Phosphorus on Cu(110)

Phosphorus grown on top of a Copper (110) surface

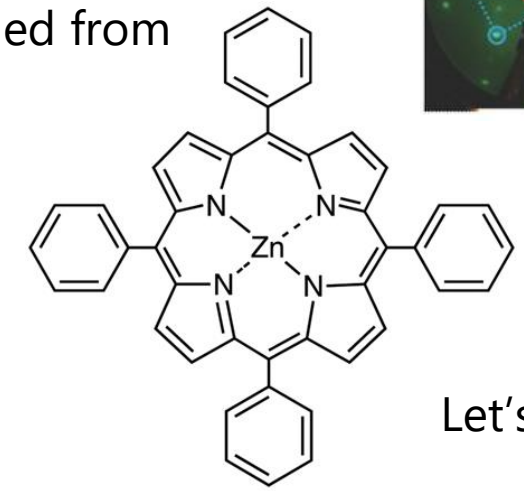
- Ordered nanostripes of P
- Two domains at 109°

→ interaction with the substrate

Can we use Phosphorus as a buffer layer to grow molecules as decoupled from the substrate?



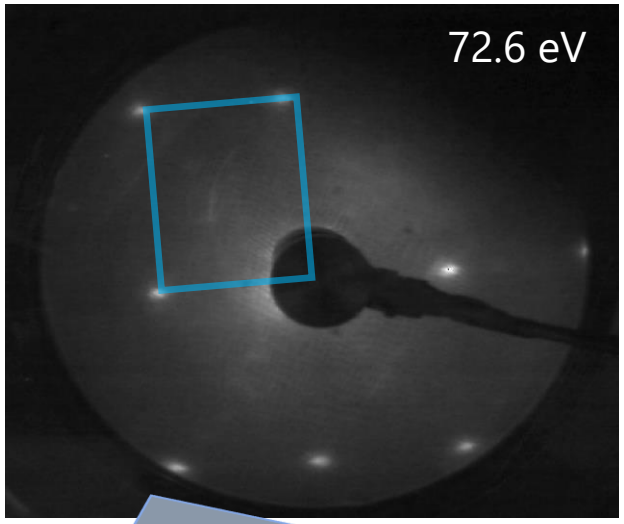
J.L. Zhang (2017)



Let's try with Zn-TetraPhenylPorphyrin (TPP)

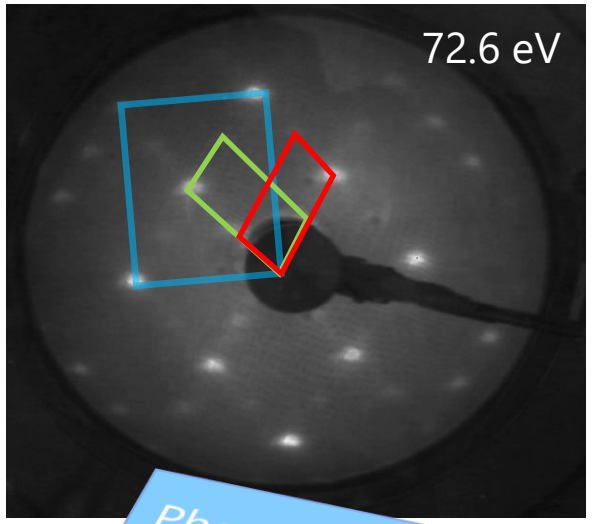
Decoupling Porphyrins: preliminary work

LEED (Low Energy Electron Diffraction)



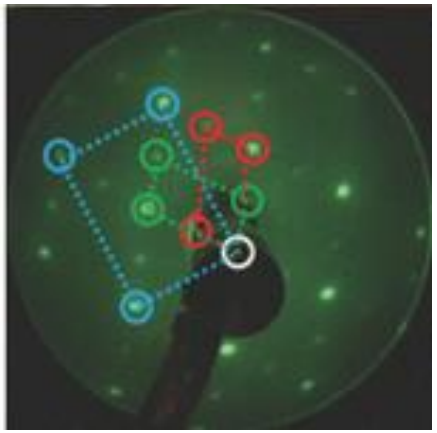
Cu(110)

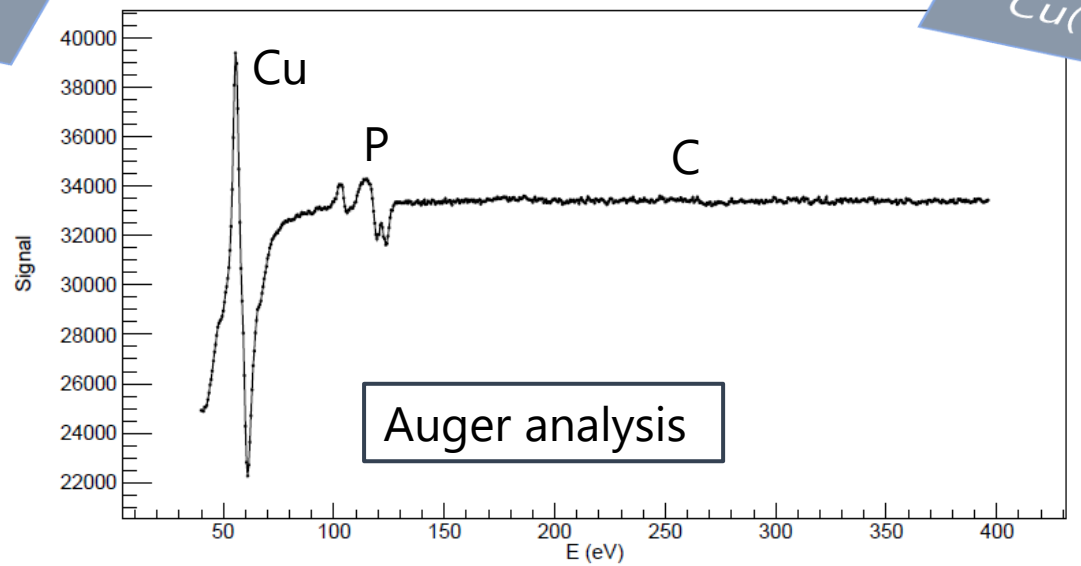
Phosphorus deposition
(sample kept at 300°C and annealing for 10 min at 450°C)



Phosphorus
Cu(110)

To compare with





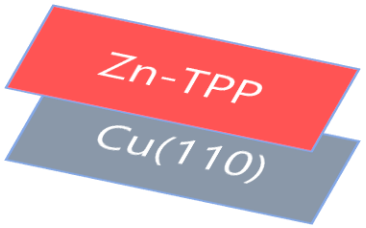
Auger analysis

→ The structure of P atoms over Cu(110) is reproduced

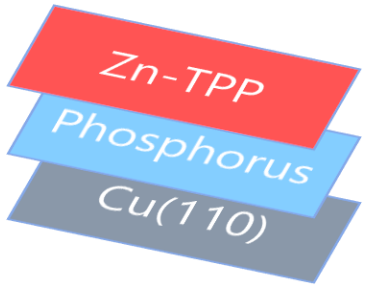
Decoupling Porphyrins: experiment outline

Proposal N.20220280 Accepted
@ Elettra – Aloisa beamline
Beamtime: 01/08/22 → 06/08/22

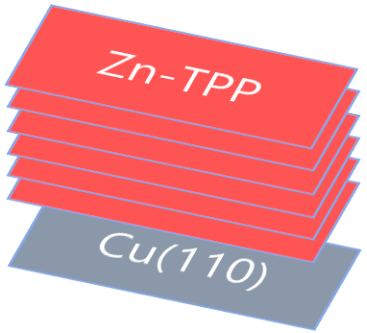
Three systems investigated:



1. Zn-TPP in direct contact with the substrate.



2. Zn-TPP deposited on top of a monolayer of phosphorus.



3. Multilayer of Zn-TPP: reference as non interacting.

Systematically, we performed for each system:

1. Deposition via PVD (Physical Vapor Deposition) of the layers on cleaned Cu(110);
2. Check of the deposition with quarz microbalance and PES;
3. Measurement of PES and NEXAFS spectra.

PES Technique

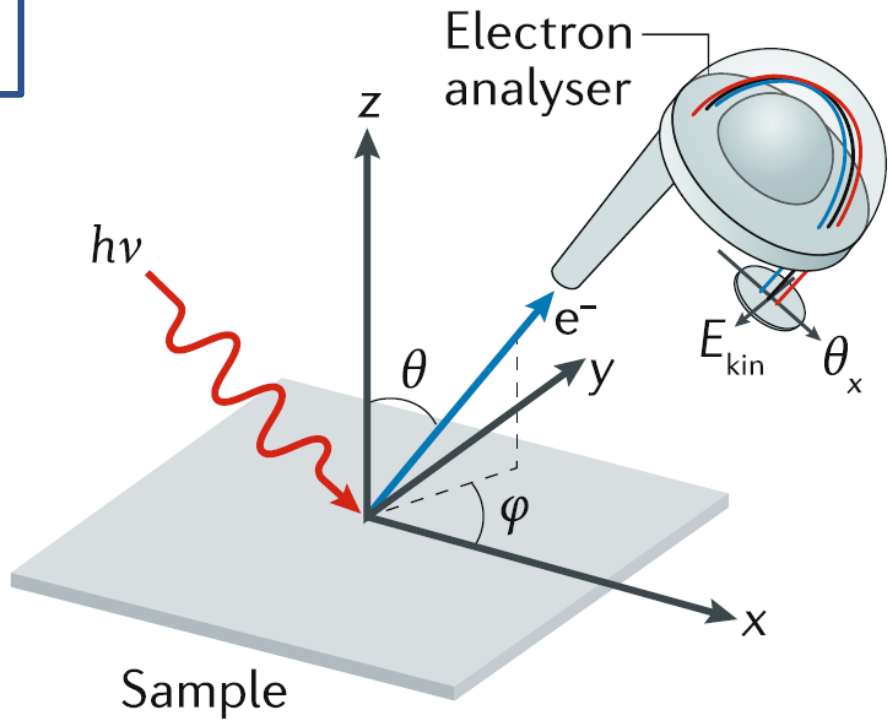
PhotoEmission Spectroscopy

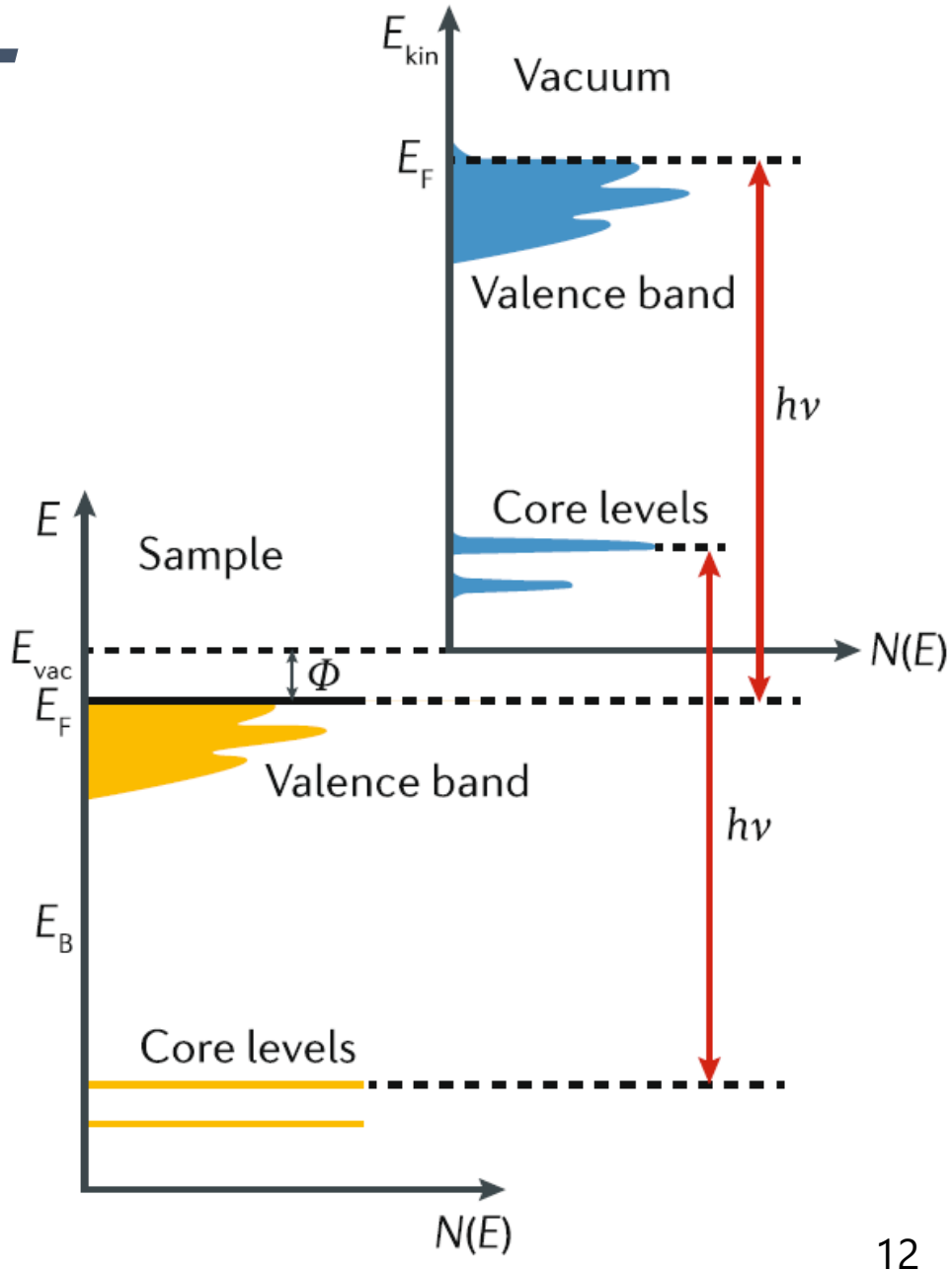
$$E_{kin} = h\nu - \Phi - E_B$$

Photon Energy

Work function

Binding Energy





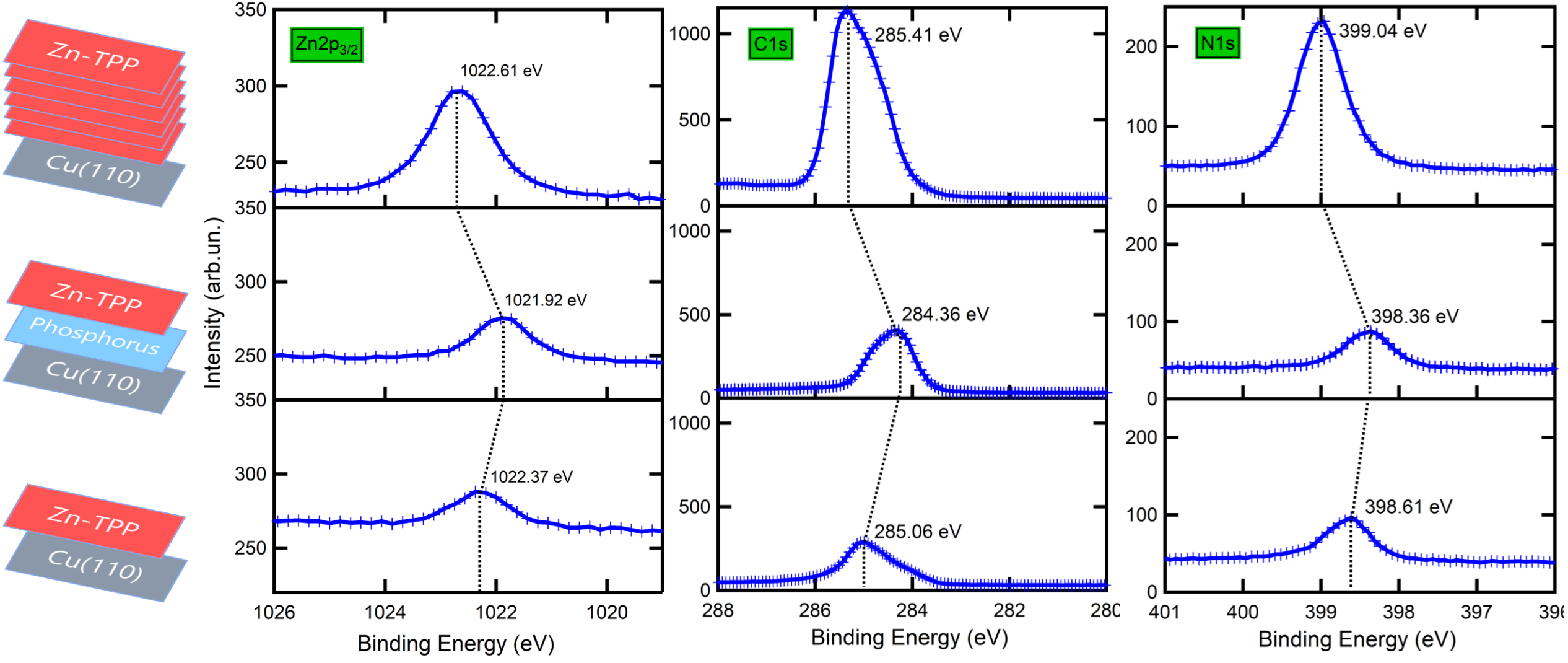
Not to forget:

- Relaxation effects
- Hole limited time life
- Shake up and shake off
- Plasmons and other effects..

What is used for?

- Chemical state
- Electronic state

Decoupling Porphyrins: PES spectra

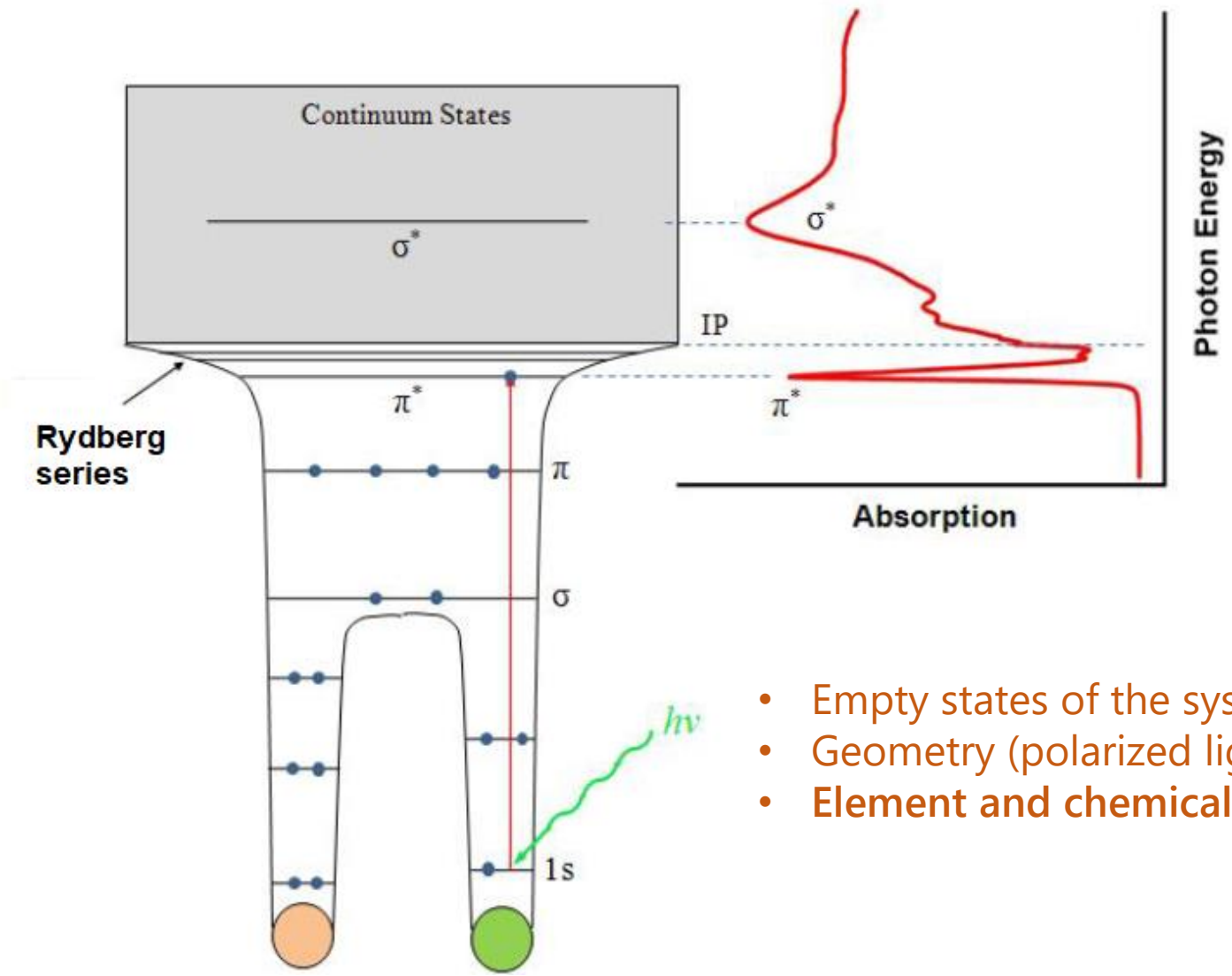


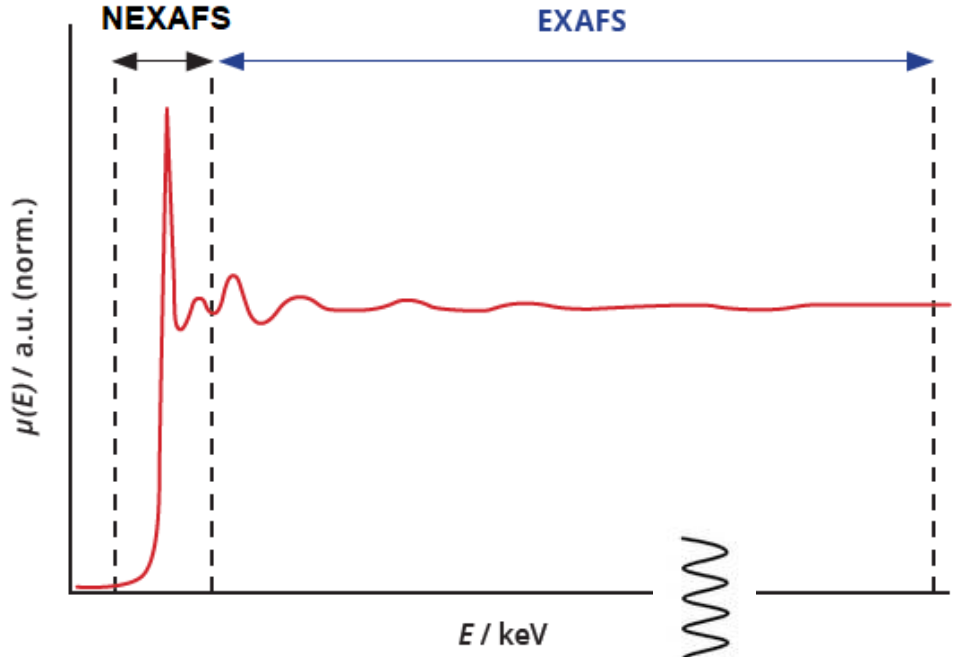
→ Presence of a buffer layer has a consequence on the chemical state

→ Models and analysis needed to have a better understanding..

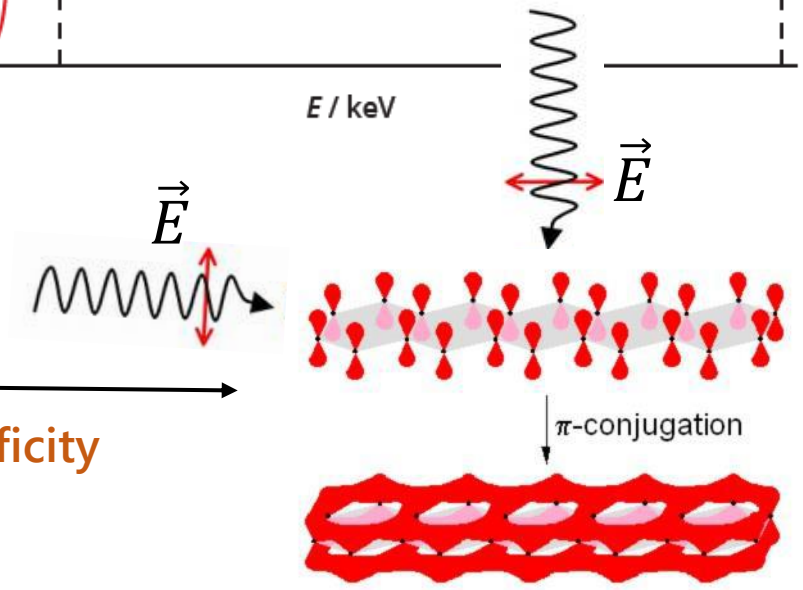
NEXAFS Technique

Near-Edge X-ray Absorption Fine Structure

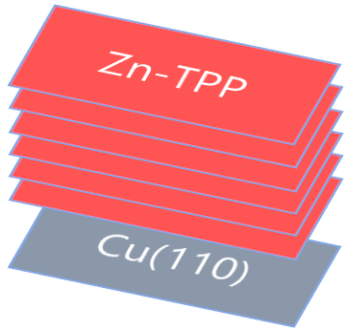


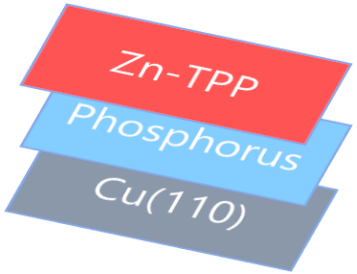


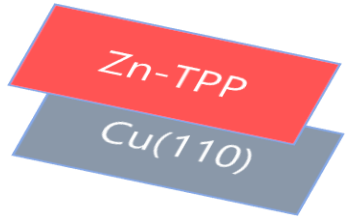
- Empty states of the system
- Geometry (polarized light)
- **Element and chemical state specificity**

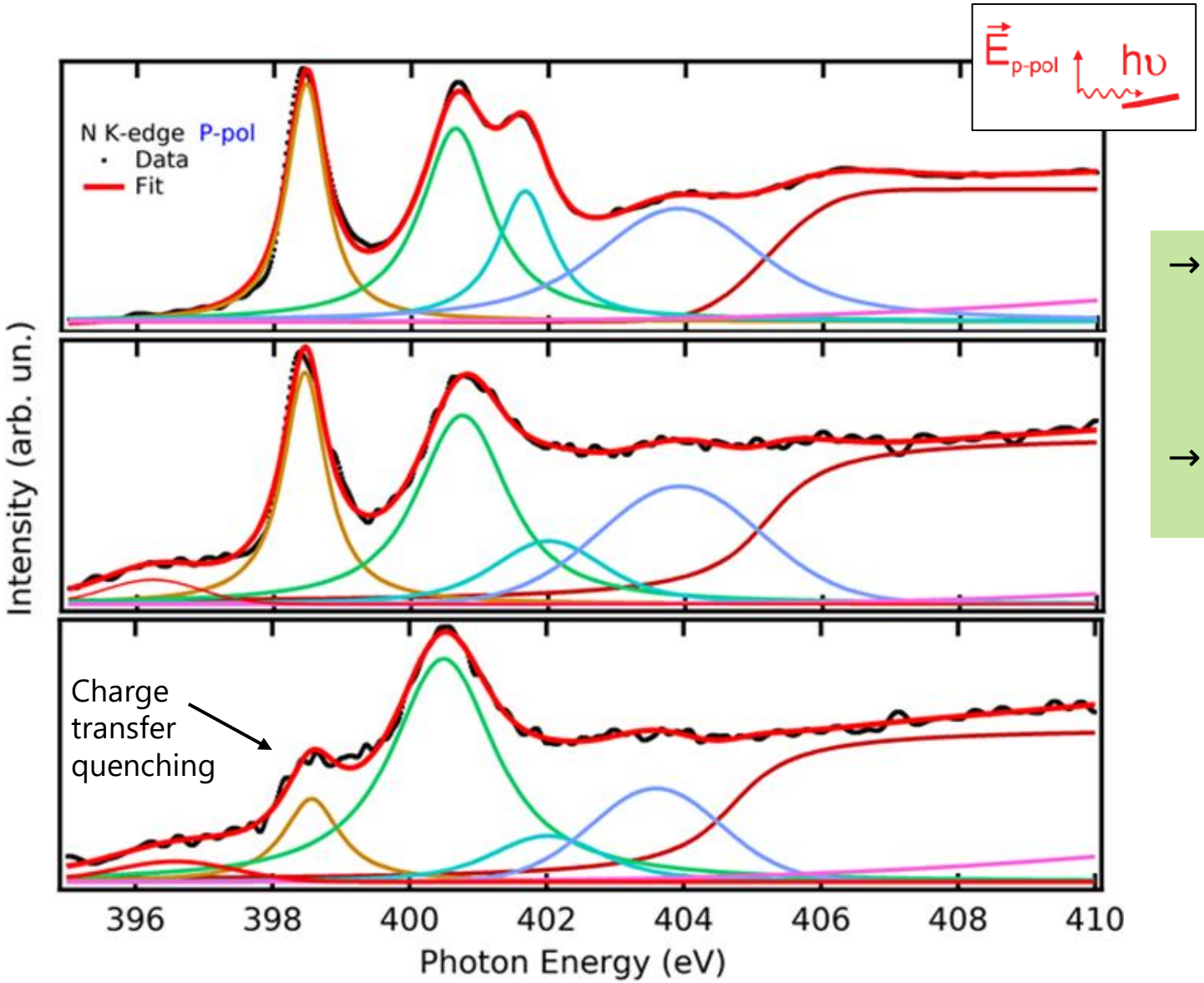


Decoupling Porphyrins: NEXAFS spectra (1)





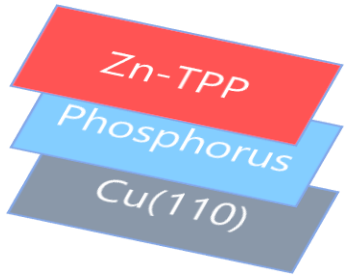


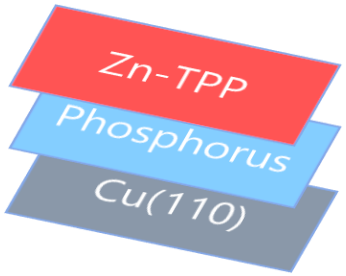


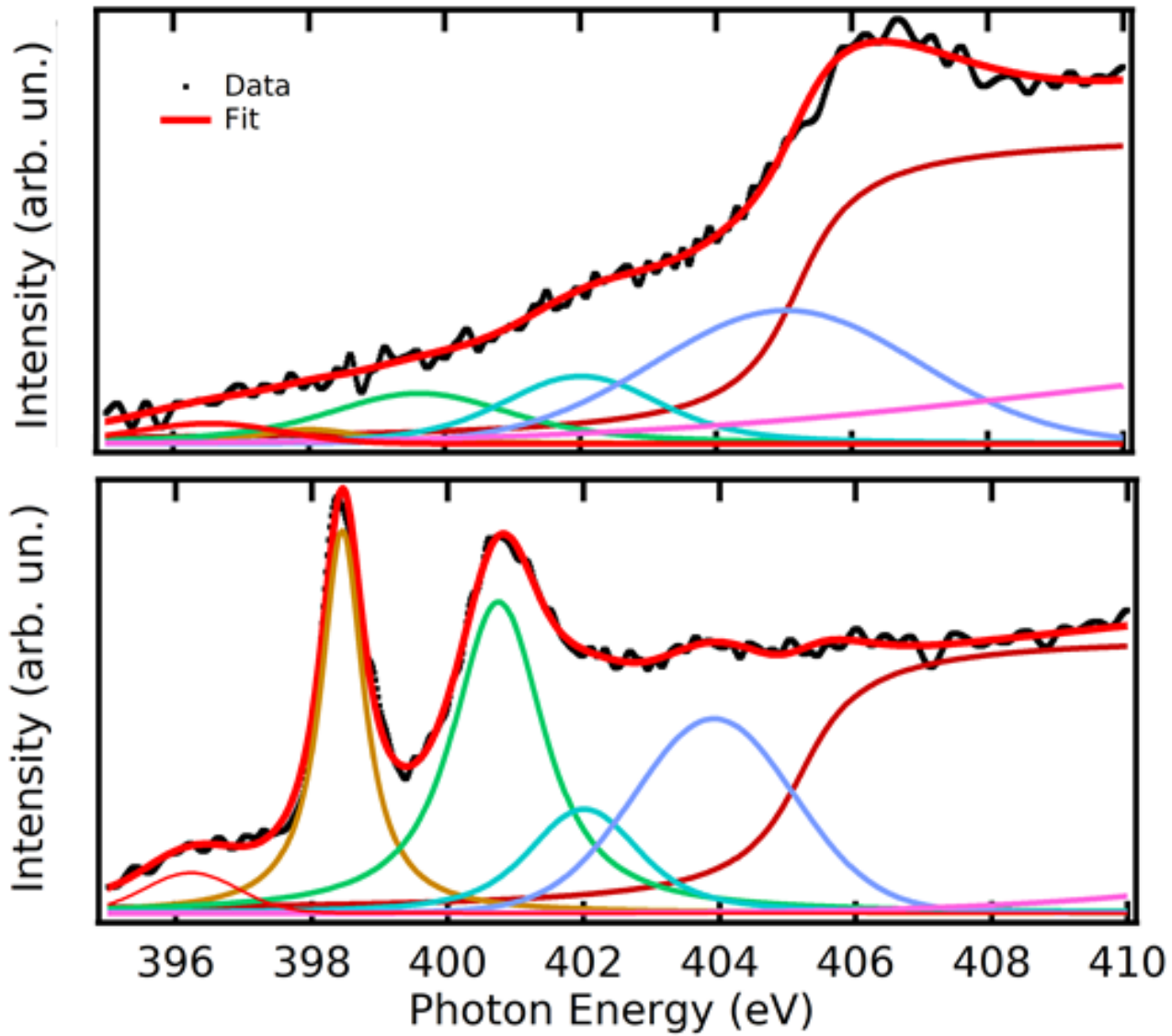
→ Charge transfer with substrate almost suppressed with phosphorus

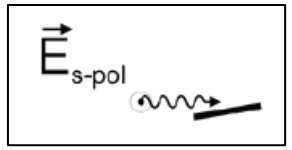
→ Molecules remain anchored to the substrate

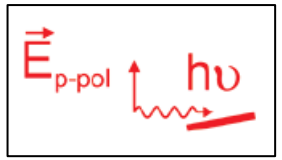
Decoupling Porphyrins: NEXAFS spectra (2)











→ **Strong dichroism**: Molecules lie almost flat on the substrate (~30°)

Decoupling Porphyrins: next

→ **Change the metal:**
Porphyrin metaled with Co (Co-TPP) ⟶ Proposal submitted to Elettra

→ **Change the substrate:**
Using also Cu(111) and Cu(100) ⟶ In-house experiments

FINAL GOAL is to find a general method for decoupling organic molecules from metal substrates

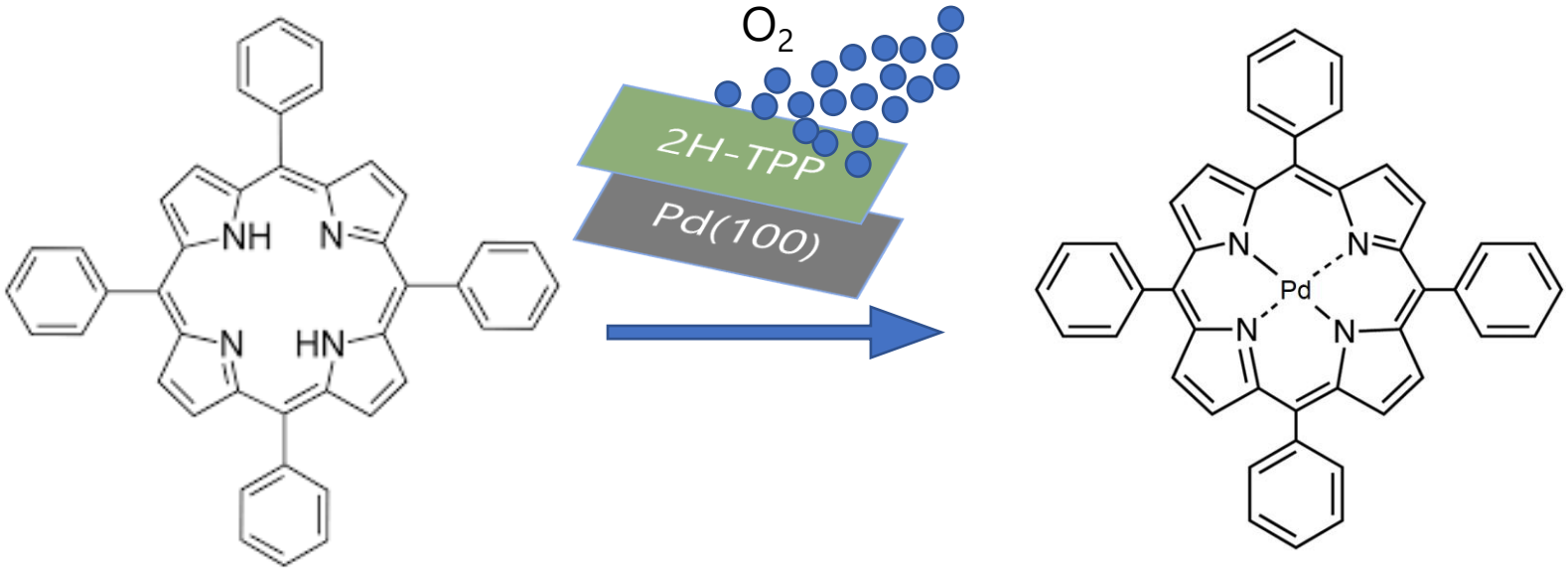
Exp. 2 – Tetrapyrroles metalation

Porphyrin metalation: recap

Armilotta et al, 2021

Self-metalation process:

Molecules pick up metal atoms from the substrate



2H-TetraPhenylPorphyrin

Pd-TetraPhenylPorphyrin

You need:

- Geometry (molecule – substrate distance)
- Activation Energy

Temperature ~300 K (damage)

Oxygen exposure

→ Metalation doesn't take place with temperature only

→ With oxygen, metalation occurs at room temperature

Phthalocyanines metalation: results

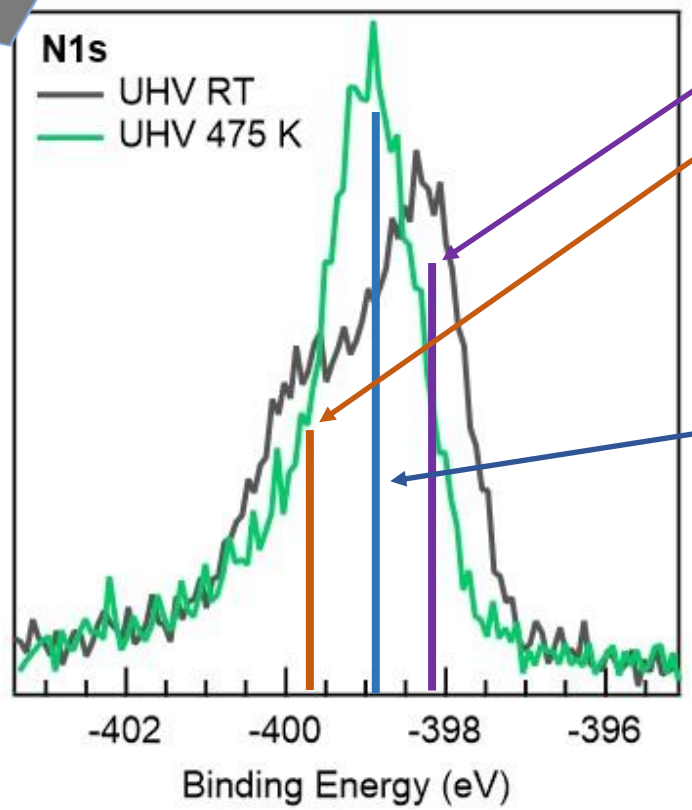
@ Elettra – Aloisa beamline
Beamtime: 30/05/22 → 01/06/22

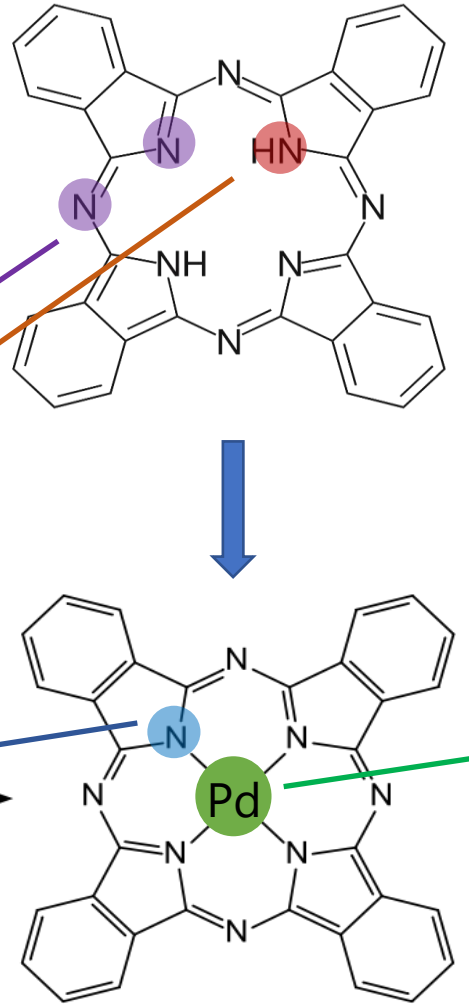
In collaboration with group of prof Vesselli (UniTS)

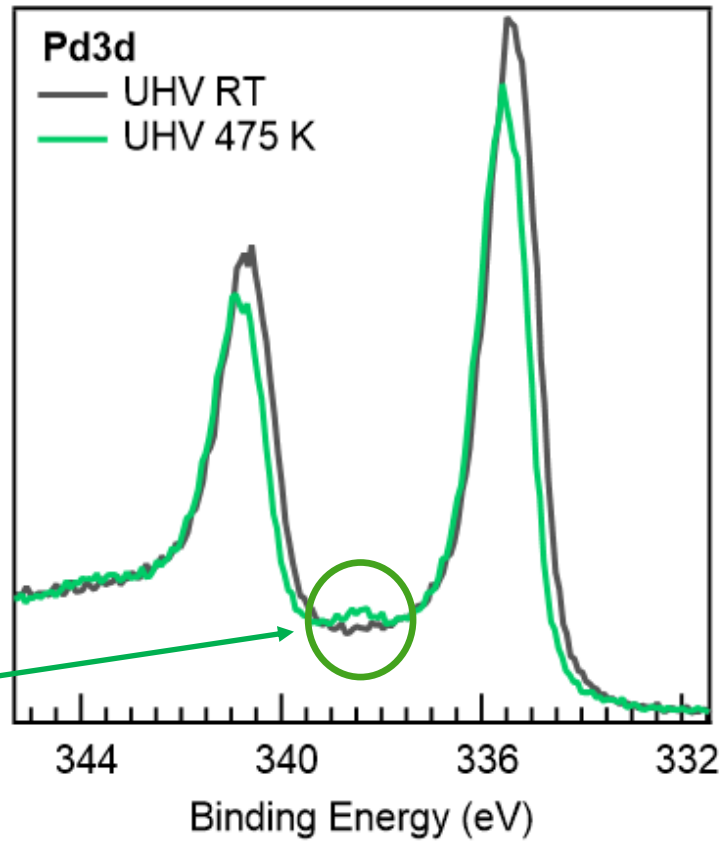
Now with phthalocyanines on Pd(100)

Metalation takes place with temperature!

2H-Pc
Pd(100)







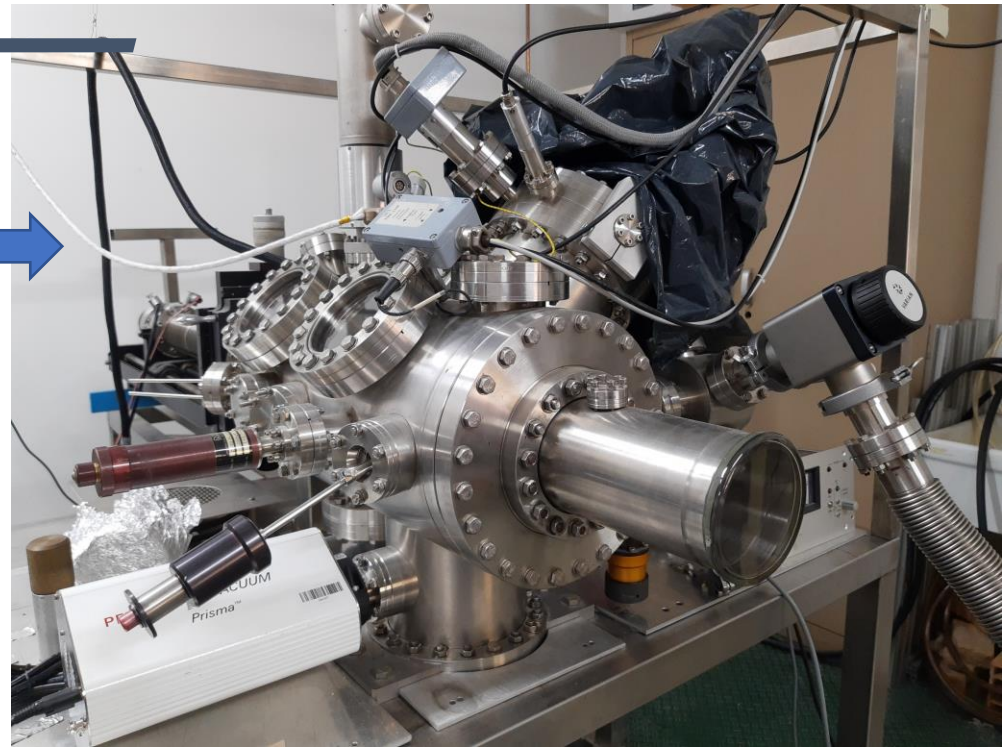
Data analysis still in progress..

Future outlook

→ UPS technique upgrade

Electron analyzer

ACROSS chamber



→ Next experiments:

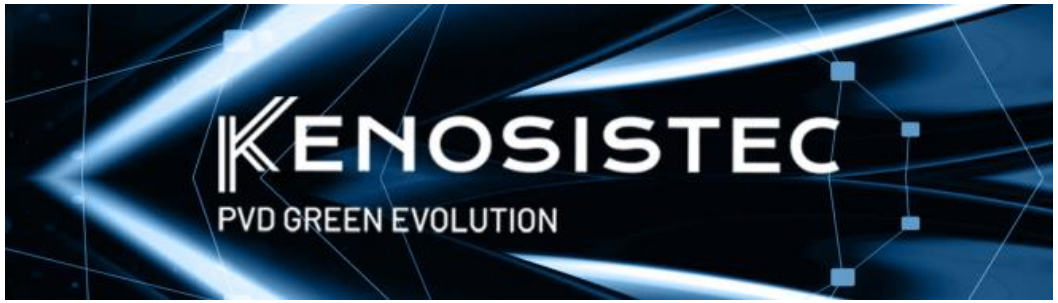
- Decoupling porphyrins:

Using other molecules and substrate

- Phthalocyanine metalation:

Near-ambient-pressure measurements @ Max IV synchrotron

→ Company stage



→ Paper in progress:

- About buffer layers for decoupling

Training activities

→ Courses attended:

= exam held

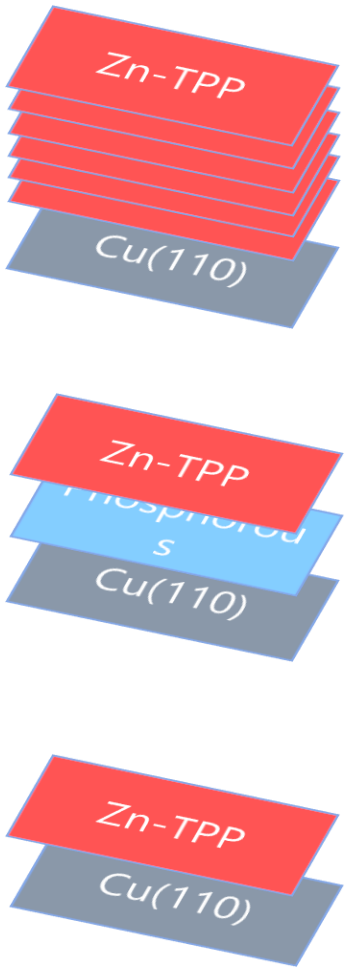
- Uncertainty and Probability
- Effective Field Theory
  - Theory (Buttazzo)
  - Spintronics (Tatara)
- Nanosystems
  - Molecular nanomagnets for quantum computation (Chiesa/Garlatti)
  - Raman spectroscopy (Ripanti)
  - Spectroscopy characterization of nanostructured materials (Pedio)
- Multimessanger
  - Gamma Rays (Tosti)
  - Neutrinos (Germani)
  - Gravitational waves (Punturo)
- Physics at collider (Gallinaro)
- Introduction to space physics (Tomassetti)
- Teaching and learning physics (Organtini)

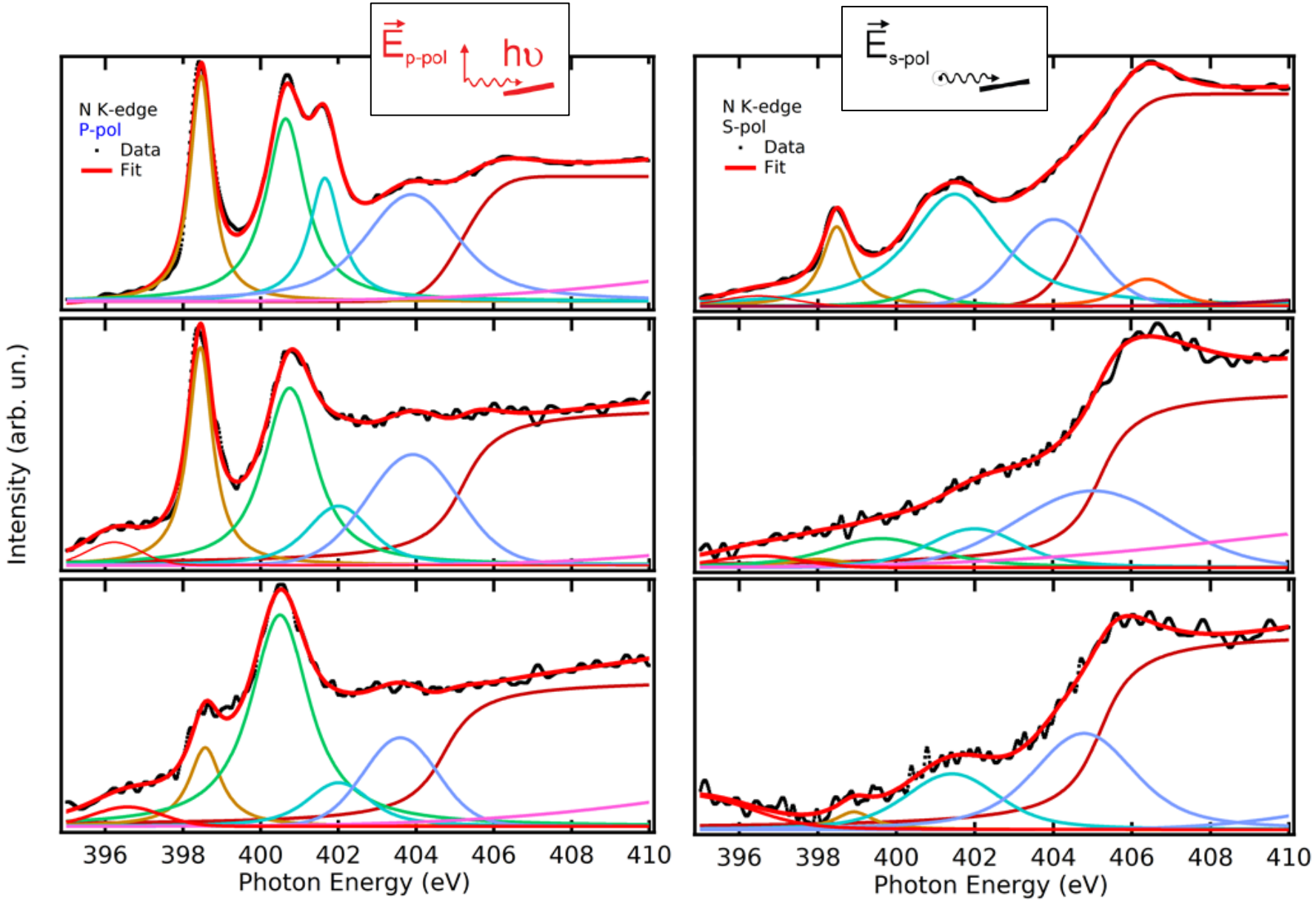
→ School:

XVI School on Synchrotron Radiation
"Gilberto Vlaic":
Fundamentals, Methods and Applications
Muggia (Trieste), Italy / 19-30 September 2022

Thank you!

Decoupling Porphyrins: NEXAFS spectra (2)





→ **Strong dichroism**: Molecules lies almost flat on the substrate

Decoupling Porphyrins: ALOISA beamline

Why Synchrotron?

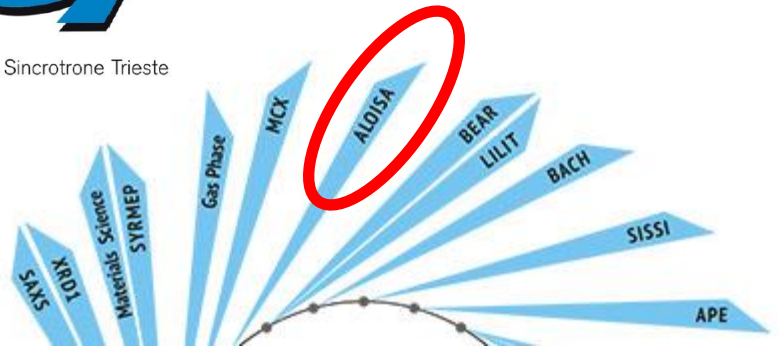
- High Brightness
- Polarized light
- Tunable photon energy

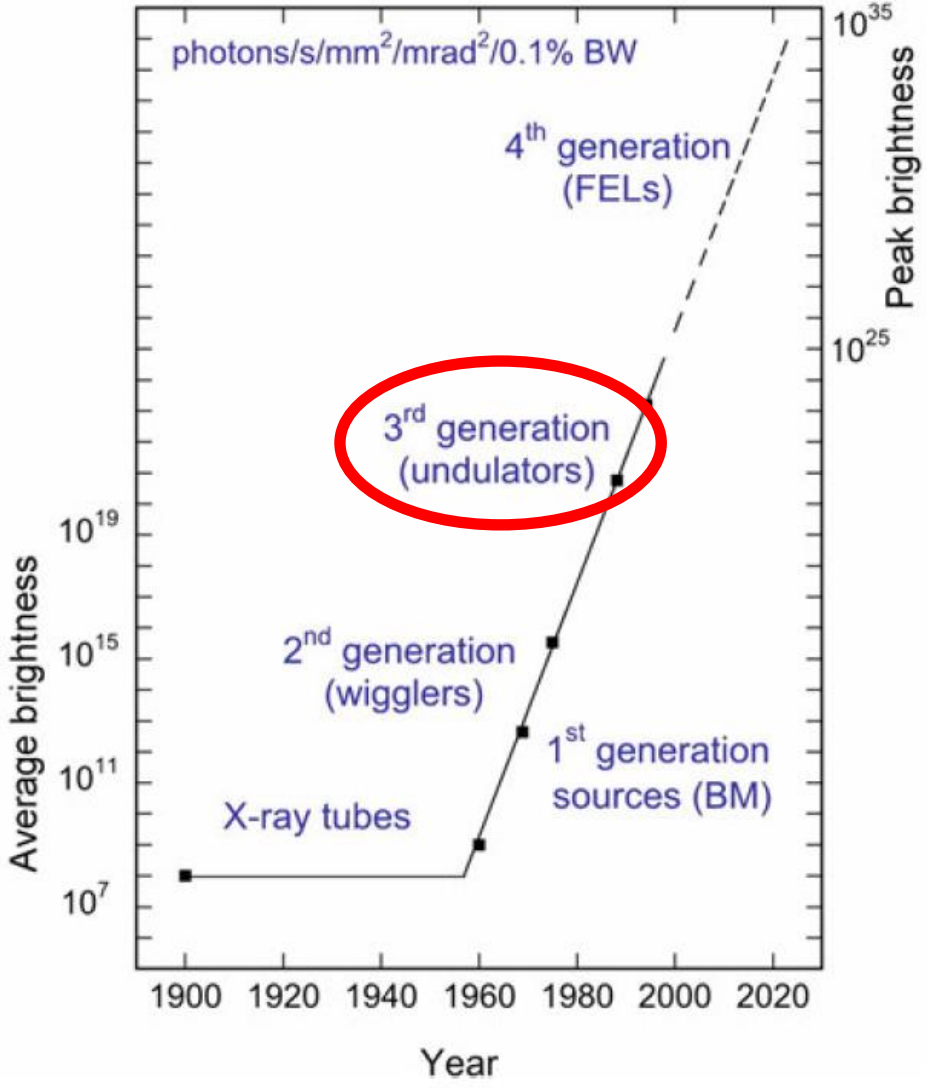
ALOISA beamline:

- Dedicated to surface science
- Ultra-high-vacuum chamber
- Photoemission and Absorbtion spectroscopies

Beamtime: 01/08/22 → 06/08/22

Elettra Sincrotrone Trieste



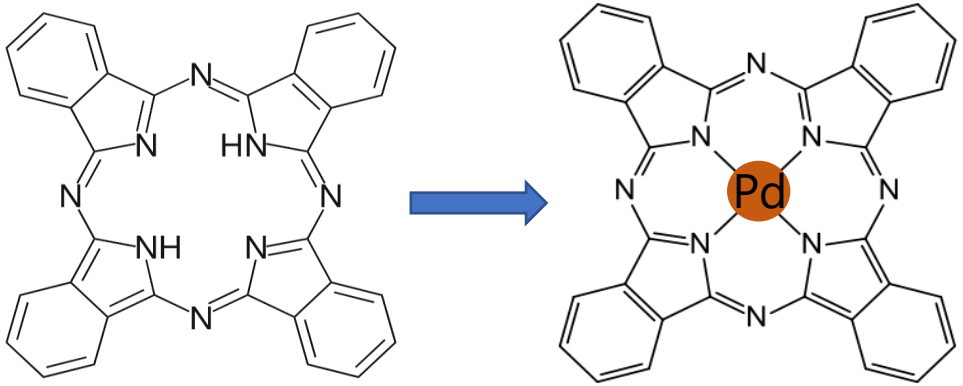


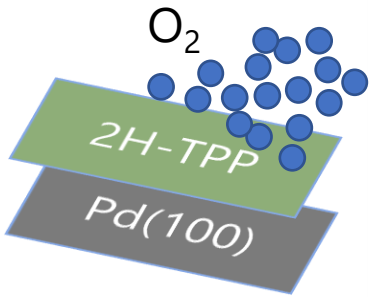
Phthalocyanines metalation: results and next

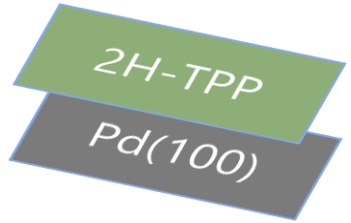
@ Elettra – Aloisa beamline
Beamtime: 30/05/22 → 01/06/22

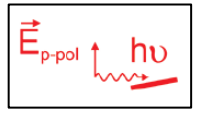
Now with phthalocyanines

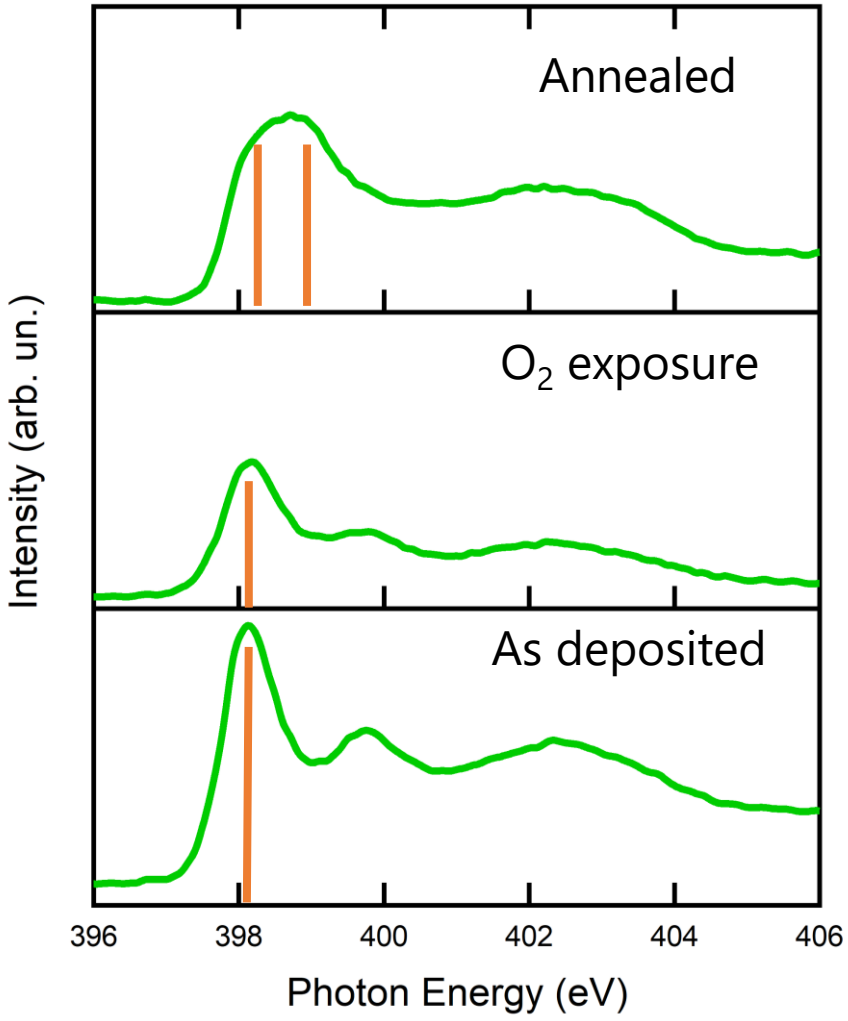
Goals:
- Calculate the activation energy of metalation process
- Repeat it with O_2











In collaboration with prof Vesselli (UniTS).
Analysis still in progress..