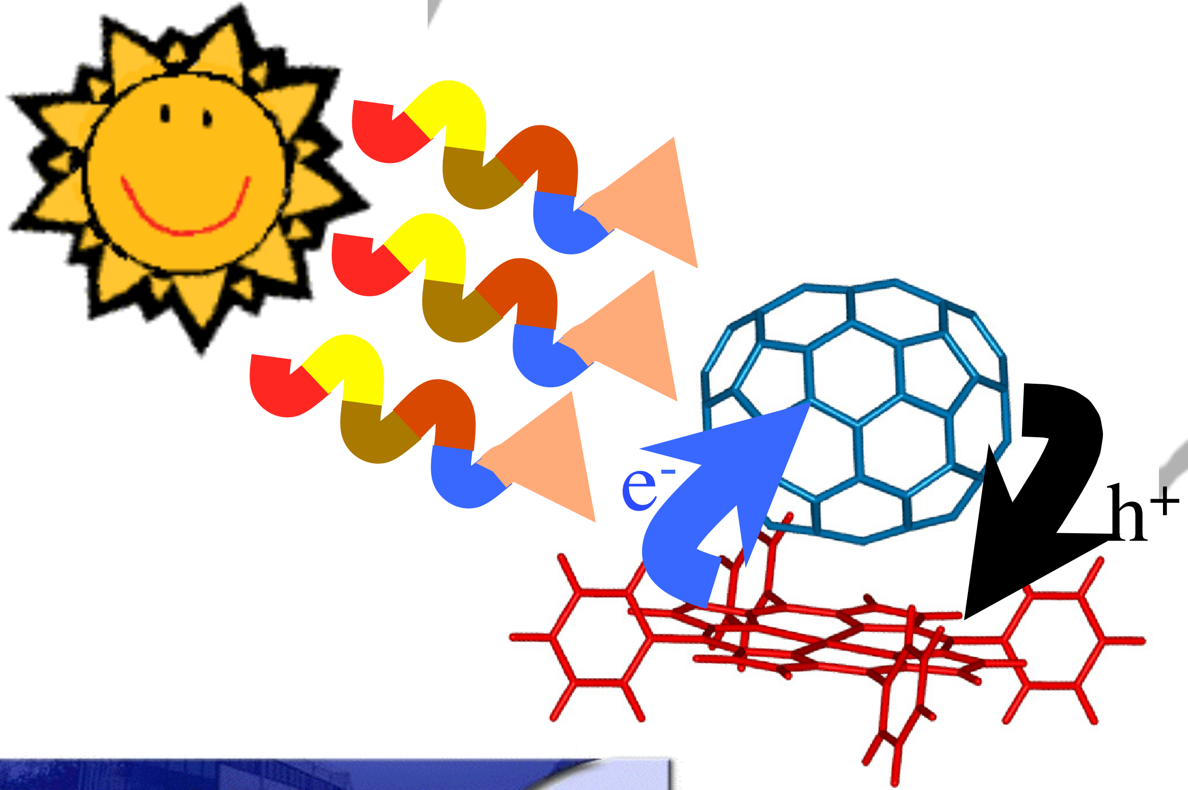
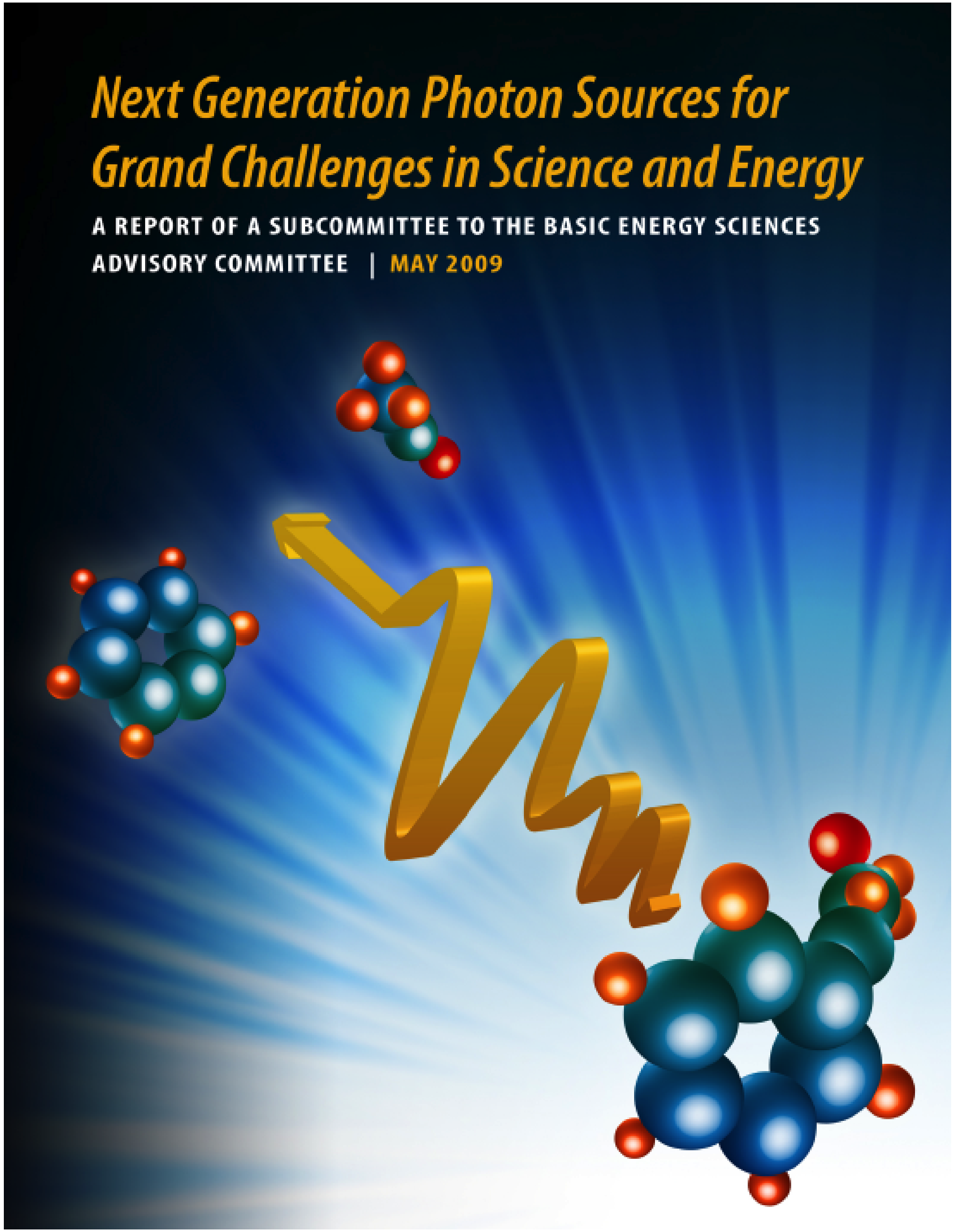
Exploiting Synchrotron Radiation in the Study of Materials for Energy Applications

Andrea Goldoni



Elettra Synchrotron Light Source



Next Generation Photon Sources for Grand Challenges in Science and Energy

A REPORT OF A SUBCOMMITTEE TO THE BASIC ENERGY SCIENCES ADVISORY COMMITTEE | MAY 2009

Report of the Workshop on

Solving Science and Energy Grand Challenges with Next-Generation Photon Sources

October 27-28, 2008
Rockville, Maryland

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A Report of the
Basic Energy Sciences Advisory Committee
Submitted to DOE

The next generation of sustainable energy technologies will revolve around new materials and chemical processes that convert energy efficiently among photons, electrons, and chemical bonds. New materials that tap sunlight, store electricity, or make fuel from splitting water or recycling carbon dioxide will need to be much smarter and more functional than today’s commodity-based energy materials. To control and catalyze chemical reactions or to convert a solar photon to an electron requires coordination of multiple steps, each carried out by customized materials and interfaces with designed nanoscale structures. Such advanced materials fabricated using principles revealed by basic science are not found in nature the way we find fossil fuels; they must be designed. Success in this endeavor requires probing, and ultimately controlling, the interactions among photons, electrons, and chemical bonds on their natural length and time scales.

Nanostructures
Interfaces

Bottom-up
approach

Systems for the sustainable production, storage, and utilization of energy, such as solid-state lighting, photovoltaics, batteries, and fuel cells, depend critically on the development of new materials. Key challenges include observing the formation mechanisms of desired material and molecular phases, determining the nanoscale structure of nucleation sites, and following the dynamics of structural and electronic changes on attosecond to second time scales. Developing a capability to observe in situ the atomistic mechanisms of materials synthesis is essential if we are to achieve the fundamental understanding that will enable transformation of empirical trial-and-error efforts at synthesis into science-based materials and process design. A second area of emphasis is the need for understanding the effect of specific defects on the performance of a material or device. The ability to observe the evolution of defects and the nanostructural changes they induce in a material during device operation will enable the understanding and control of such features in real devices. Moreover, electronic properties crucially determine the device performance. Generation, transport, transfer and trapping of charges are key parameters that need to be observed in real time and with sufficient spatial and temporal resolution to characterize their behavior at interfaces, grain boundaries, and nanostructures controlling the macroscopic performance.

This report identifies two aspects of energy science in which synchrotron light sources have the deepest and broadest impact:

- The temporal evolution of electrons, spins, atoms, and chemical reactions, down to the femtosecond time scale.

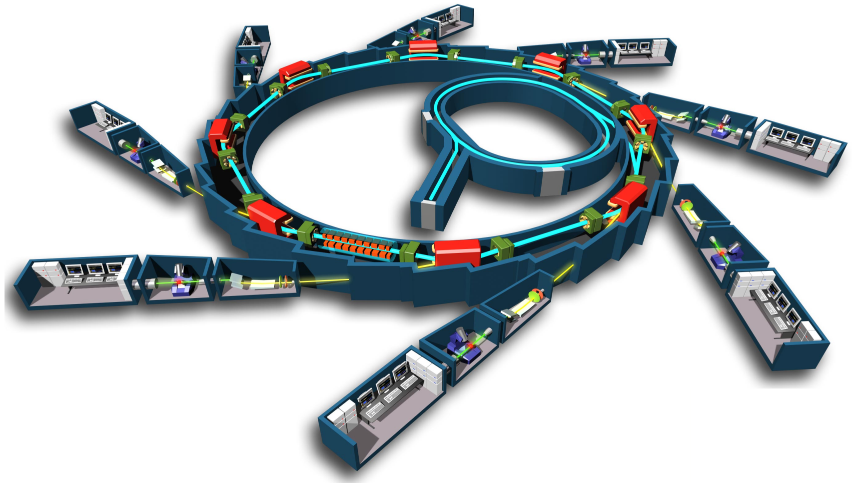
- Spectroscopic and structural imaging of nano-objects with nanometer spatial resolution and ultimate spectral resolution.

Instrumentation and recent implementations

For many decades, X-ray tubes were at the leading edge of materials research. The application of X-rays in the study of materials had not only revolutionized our knowledge of matter on the fundamental level of atoms, electrons, and spins but also redefined entire fields of physics, chemistry, biology, and medicine.

The transformations enabled by laboratory-scale sources were profound and inspired the development of larger-scale user facilities (synchrotron). There have now been three generations of synchrotron-based ultraviolet and X-ray light sources. With each light source generation, new performance parameters have emerged. Typically, the performance of these light sources has improved by about four orders of magnitude from one generation to the next, leading to qualitatively new capabilities and to an enormous growth in the user community.

The third generation conditioned the electron beam with magnetic insertion devices to produce unprecedented spectral brilliance, which allowed spectroscopy with high energy resolution and microscopy and crystallography with high spatial resolution.



Laboratory sources:

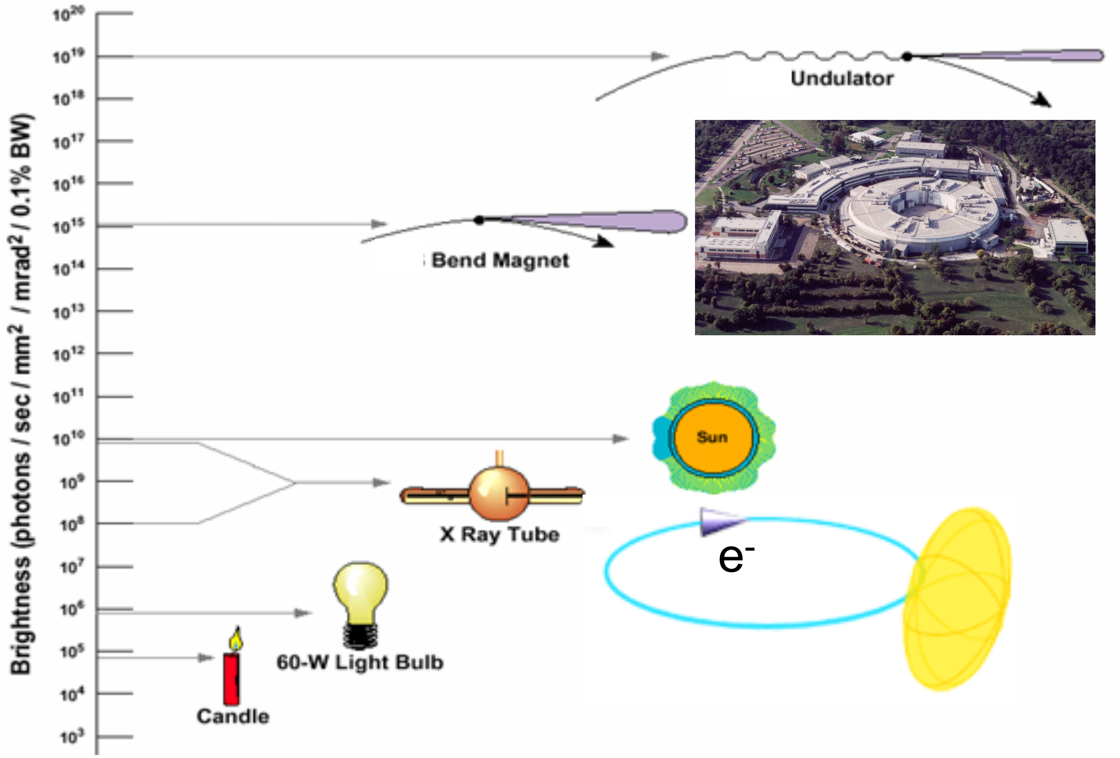
- rare gas discharge lamps
- x-ray tubes

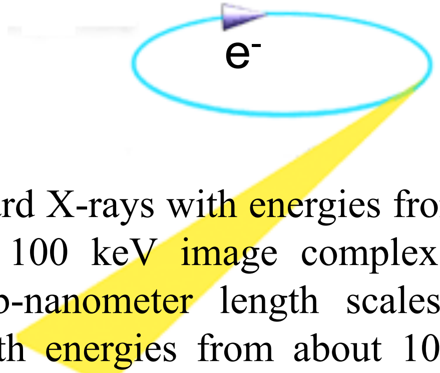
Synchrotron radiation:

- tunable, $h\nu$ = 10 eV…10 keV
- polarized (linear and circular)
- brilliant
- temporal structure

More properties on the Synchrotron Light

1. **Intensity** – many orders of magnitude higher than a conventional lab. source: fast experiments allowed on small sample



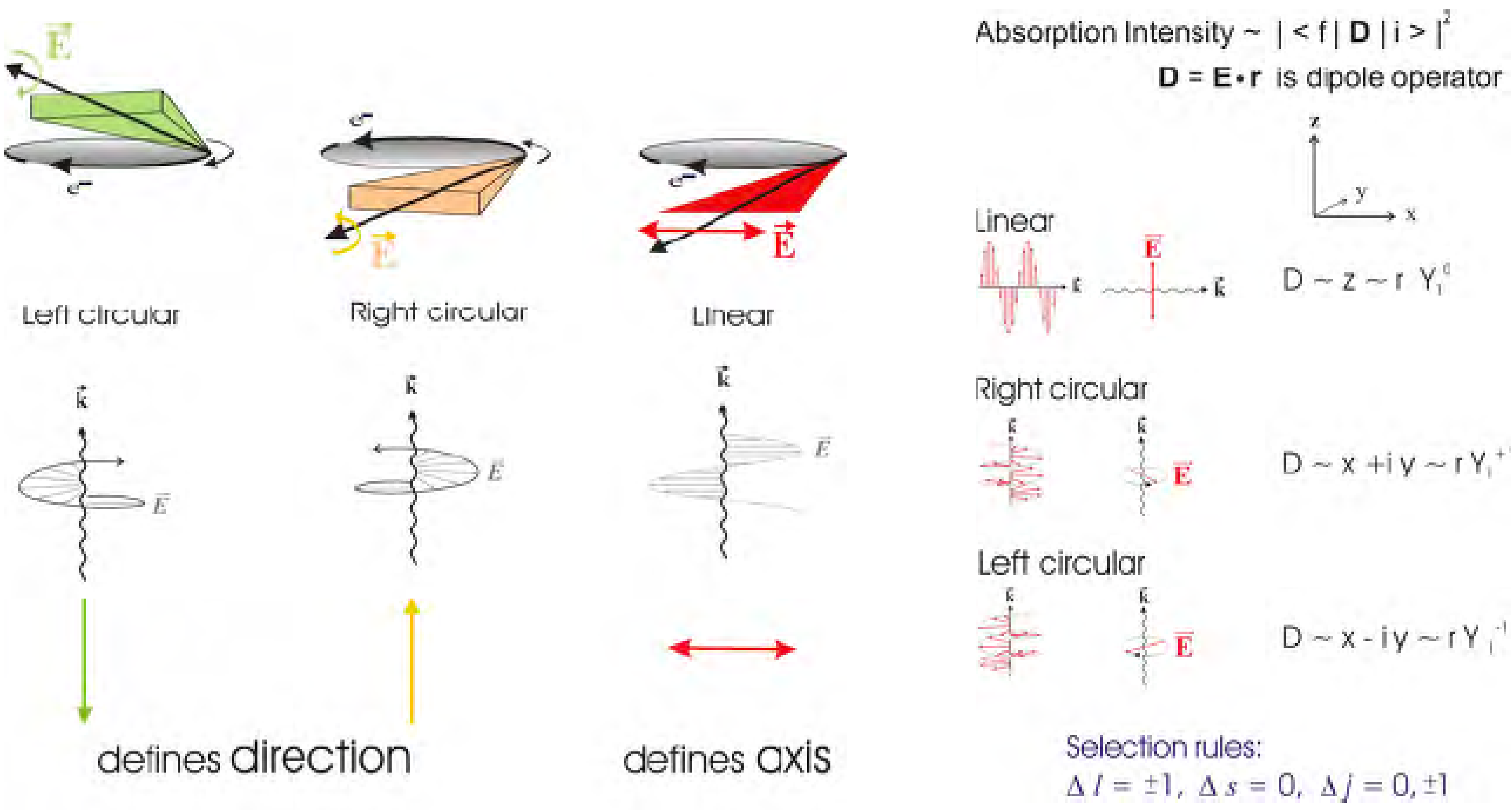


Hard X-rays with energies from about 3 keV to 100 keV image complex structures on sub-nanometer length scales. Soft X-rays with energies from about 10 eV to 3 keV probe the electronic structure of matter using near-edge X-ray absorption fine structure (NEXAFS), X-ray emission spectroscopy (XES), and photoemission spectroscopy (PES).

2. **Brightness and tunability** – Allow to focalize the beam up to nanometers
3. **Polarization** – all kinds of polarizations
4. **Pulsed time structure** – The light is produced by electron packets: the distance between the packets is the time scale

We are presently on the brink of a fourth generation light sources. These sources will bring two new capabilities, femtosecond time resolution and laser-like coherence, along with many orders- of-magnitude increase in peak and average brilliance.

Polarization Change



Absorption Intensity ~ $|\langle f|\mathbf{D}|i\rangle|^2$

$\mathbf{D} = \mathbf{E} \cdot \mathbf{r}$ is dipole operator

Selection rules:

$\Delta l = \pm 1,\ \Delta s = 0,\ \Delta j = 0, \pm 1$

Probing Charge orientations and Spin directions

Techniques

- Photoemission Spectroscopy

Core level (XPS)
Photoelectron diffraction
Valence band (UPS)
Resonant photoemission

- X-ray absorption Spectroscopy

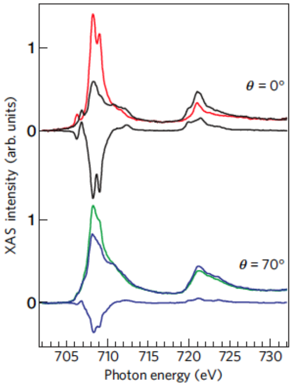
Near edge X-ray absorption Spectroscopy
EXAFS
X-ray Magnetic Circular Dichroism (XMCD)

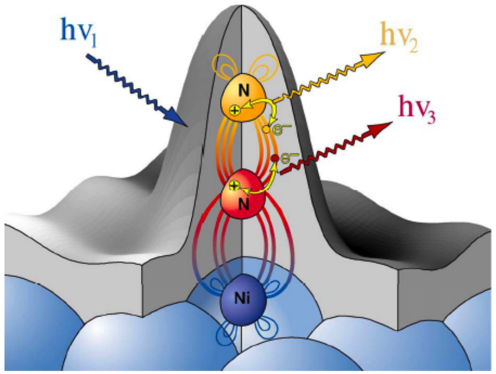
- Auger Spectroscopy

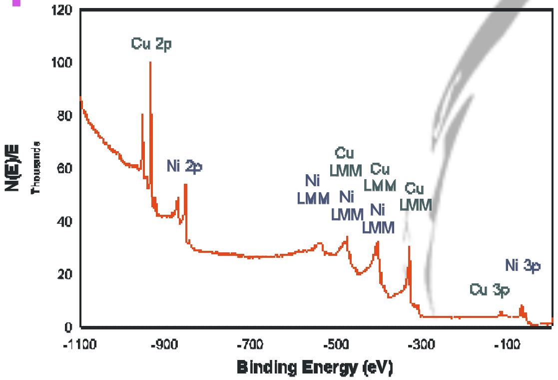
- X-ray emission Spectroscopy

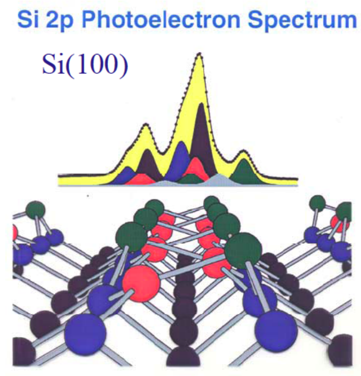
Useful to have information on:

Electronic structure
Elemental (chemical) analysis
Chemical bonding & catalysis
Magnetism
Geometric structure
Dynamics (future!!)



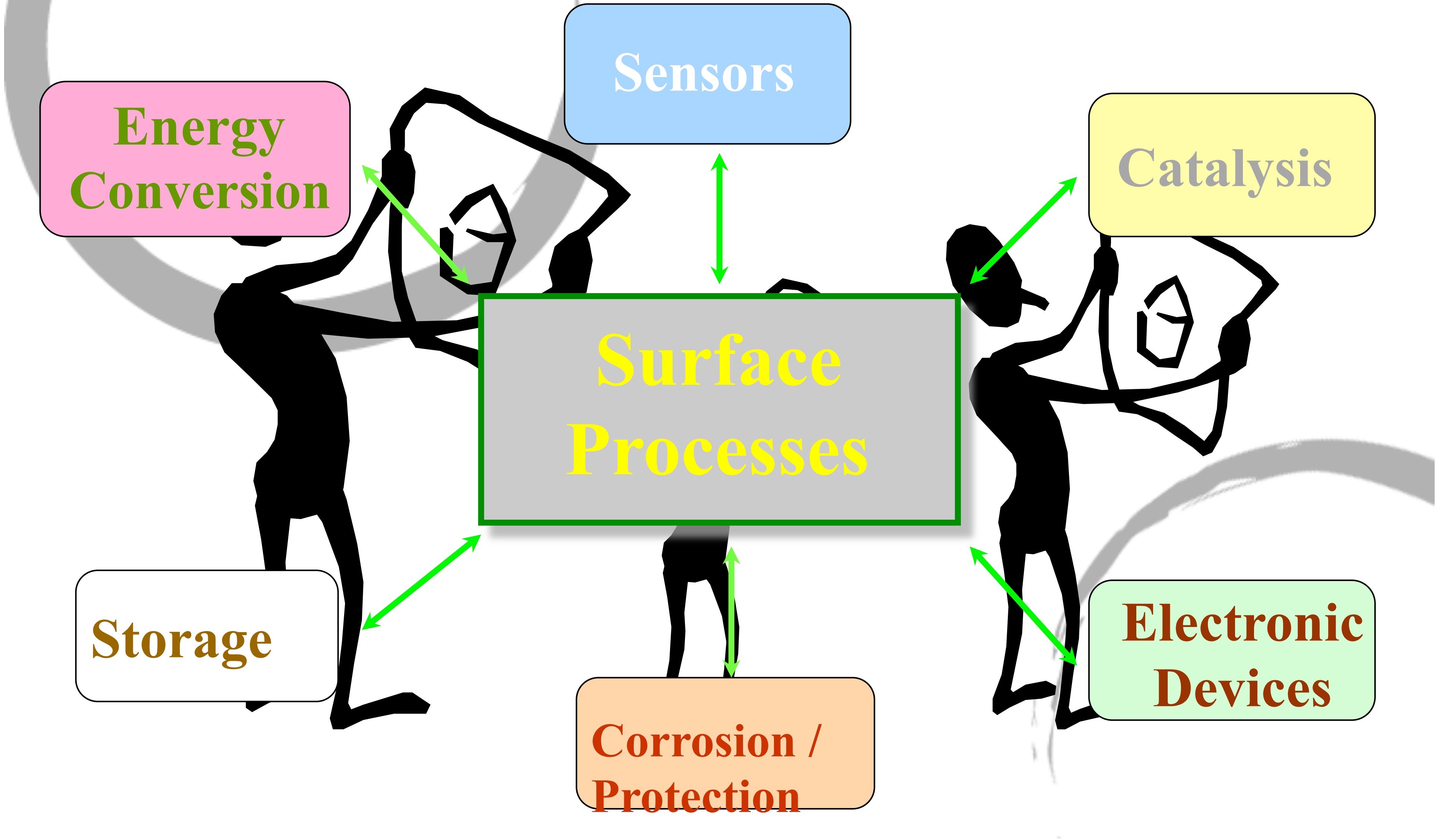






Surface reconstruction

Why are surfaces (interfaces) important?



Energy Conversion

Sensors

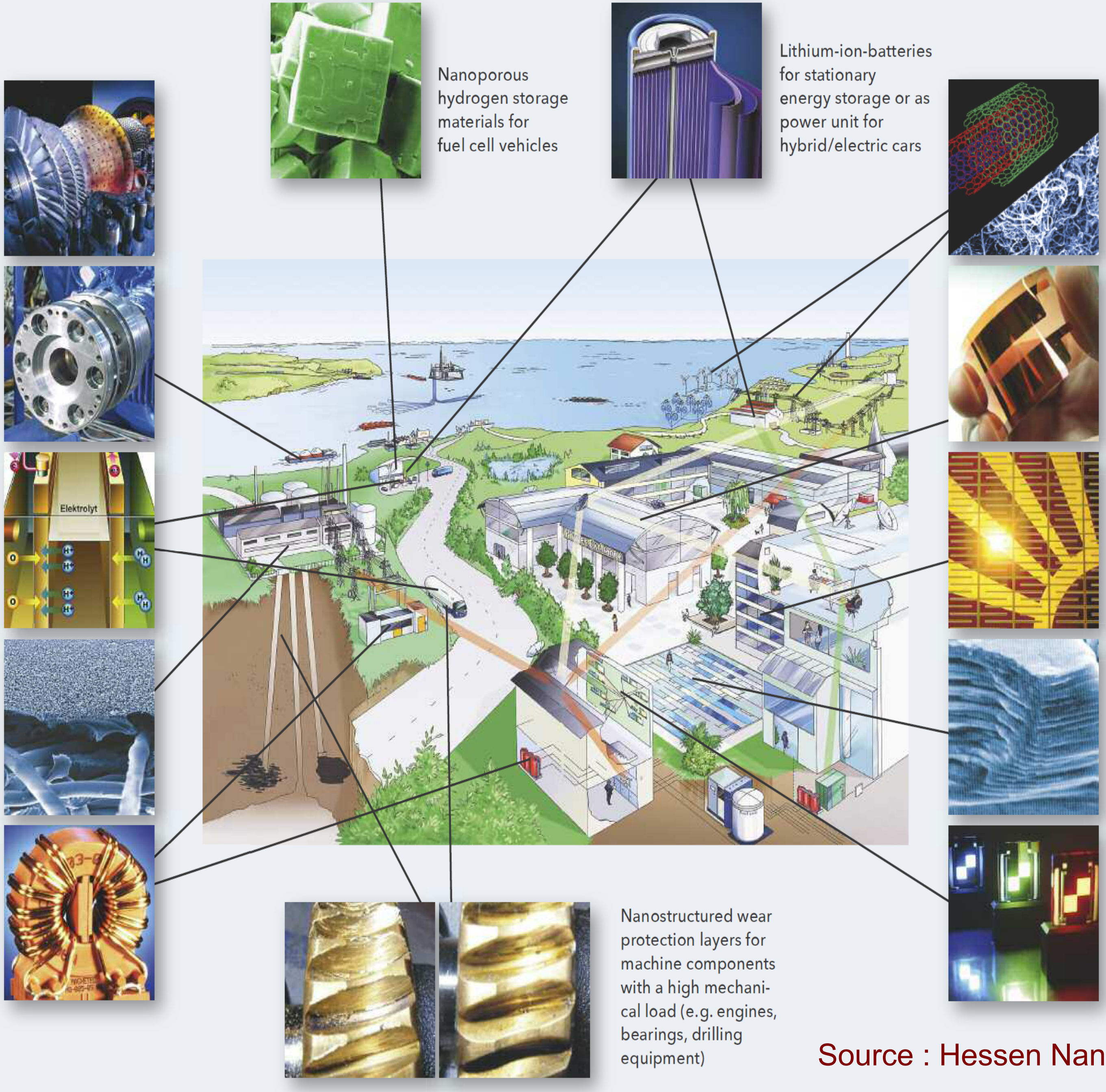
Catalysis

Surface Processes

Storage

Corrosion / Protection

Electronic Devices



Nanostructured heat protection layers for gas turbines

High temperature superconductors for motors and generators in ships

Nano-optimized fuel cells for automobiles and transport vehicles

Nanomembranes for separation of carbon dioxide in CCS (Carbon Capture and Storage) power plants

Nanocrystalline magnetic materials for efficient components in current transformation and supply (e.g. transformers, electric meters etc.)

Nanoporous hydrogen storage materials for fuel cell vehicles

Lithium-ion-batteries for stationary energy storage or as power unit for hybrid/electric cars

Carbon nanotubes as high-tensile construction materials e.g. for rotor blades of wind power stations or as material for low-loss cables/power lines

Polymer solar cells for large-scale applications in buildings or for mobile electronics

Dye solar cells as decorative facade elements in buildings

Nanostructured thermoelectric materials for power supply of mobile electronics

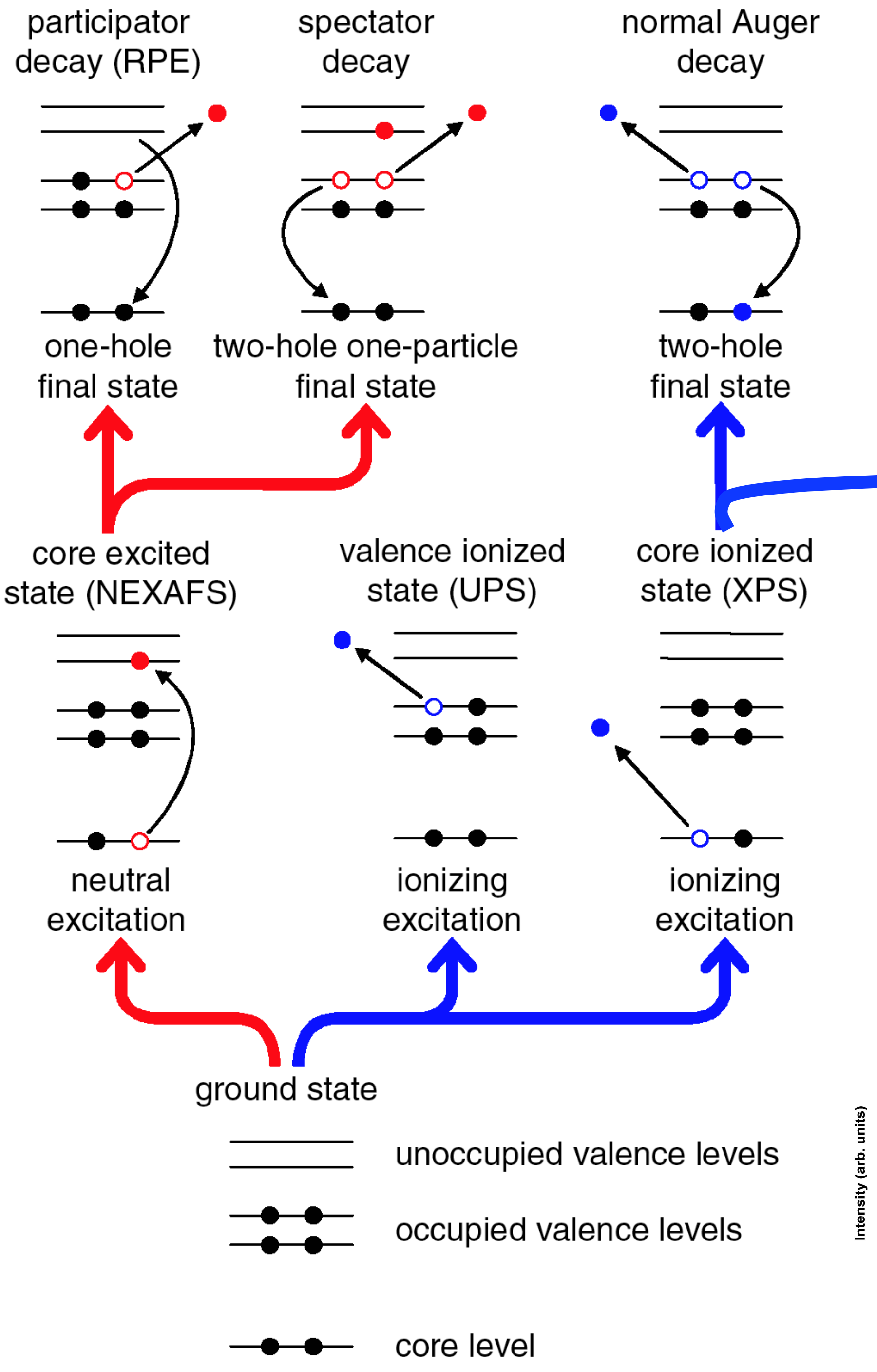
OLED for large-scale displays and lighting devices

Nanostructured wear protection layers for machine components with a high mechanical load (e.g. engines, bearings, drilling equipment)

Source : Hessen Nanotech 2008

The application of knowledge at the frontier of science to control phenomena and create new functionality - realized through the generation of ultraviolet and X-ray photon sources - has the potential to be transformational for sustainable energy. The opportunity is for third- and fourth-generation light sources to extend these insights to the control of dynamic phenomena through ultrafast pump-probe experiments, time-resolved coherent imaging, and high-resolution spectroscopic imaging. Similarly, control of spin and charge degrees of freedom in complex functional materials has the potential not only to reveal the fundamental mechanisms of high-temperature superconductivity, but also to lay the foundation for knowledge in future generation materials.

EXPERIMENTAL EXAMPLES



participator decay (RPE)

spectator decay

normal Auger decay

one-hole final state

two-hole one-particle final state

two-hole final state

core excited state (NEXAFS)

valence ionized state (UPS)

core ionized state (XPS)

neutral excitation

ionizing excitation

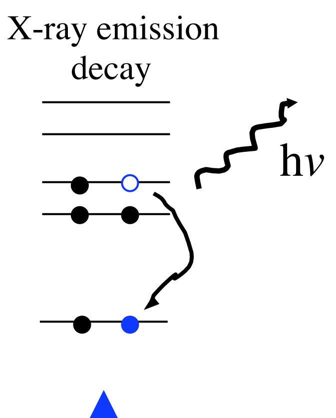
ionizing excitation

ground state

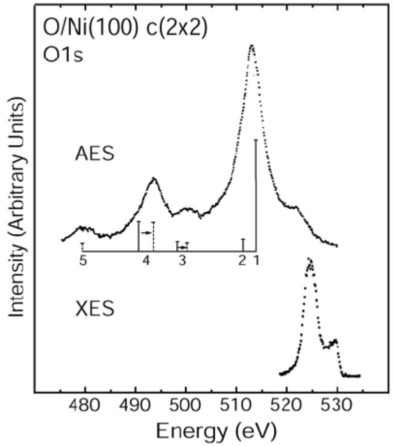
unoccupied valence levels

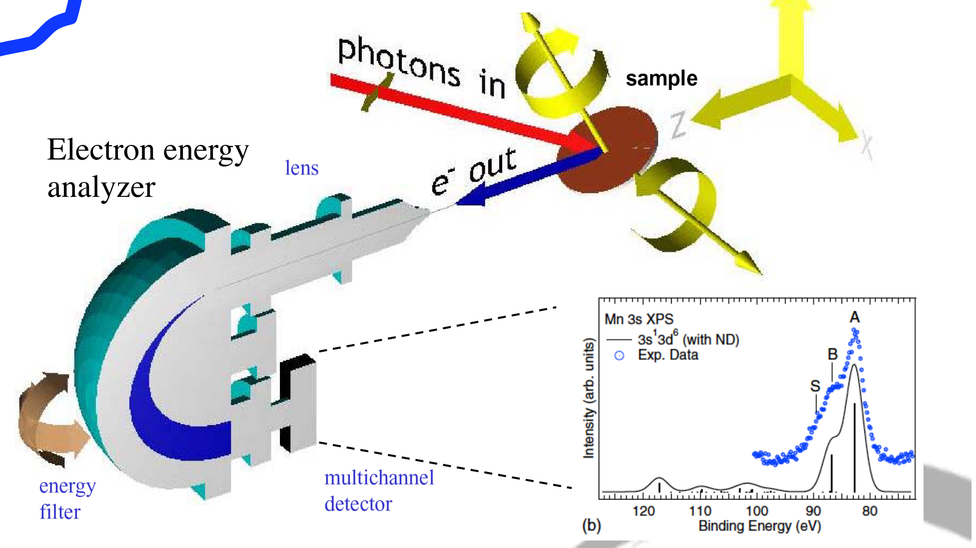
occupied valence levels

core level

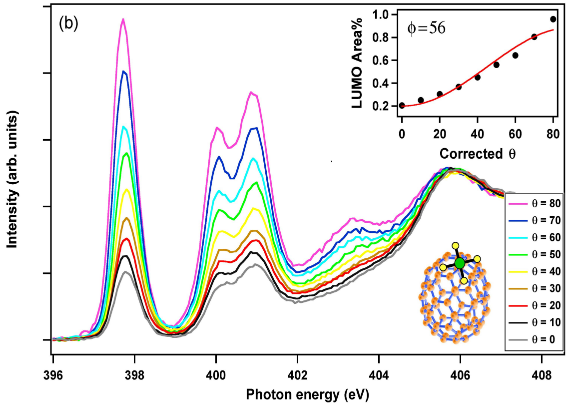


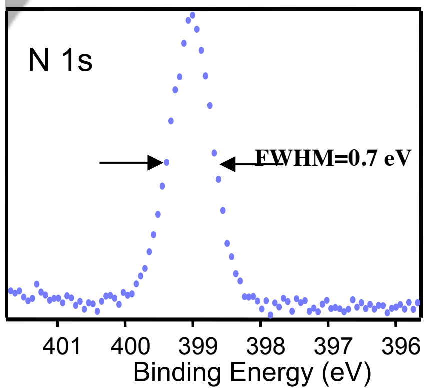
X-ray emission decay



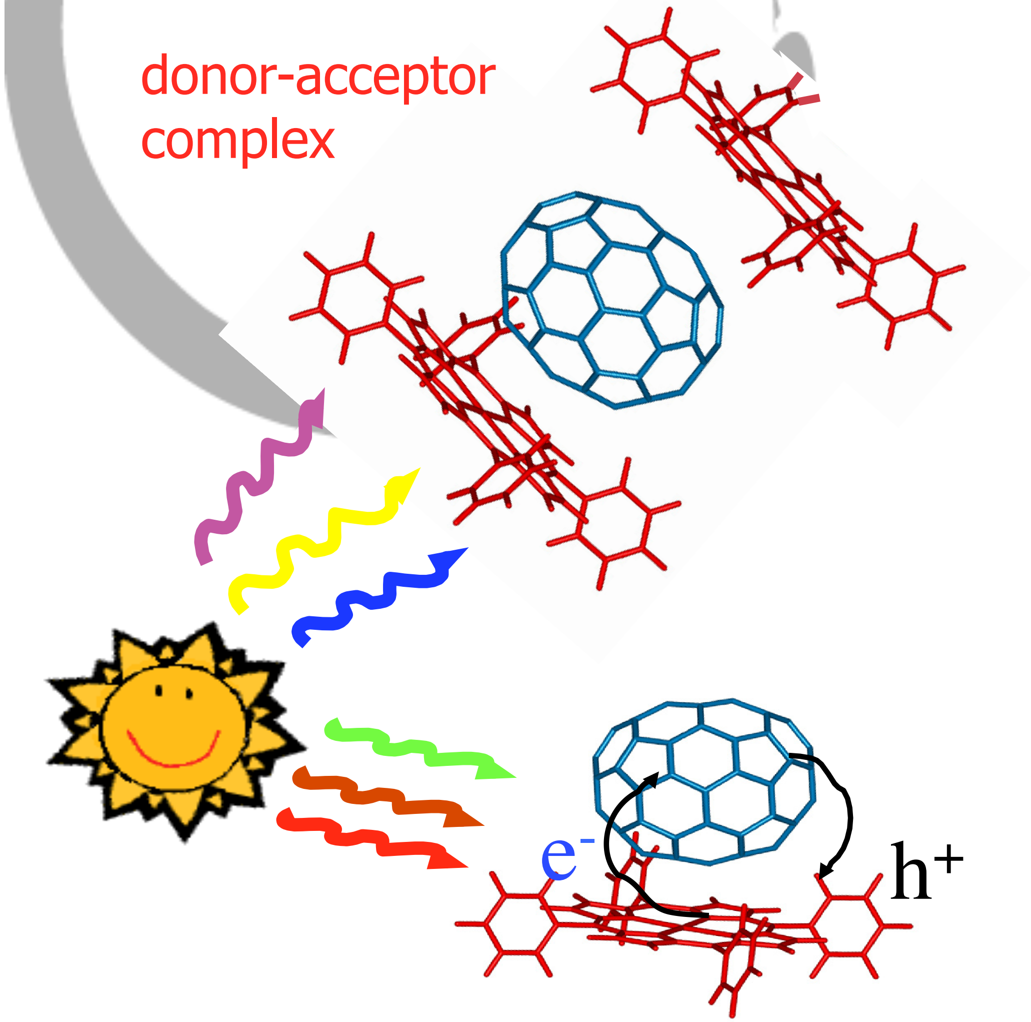


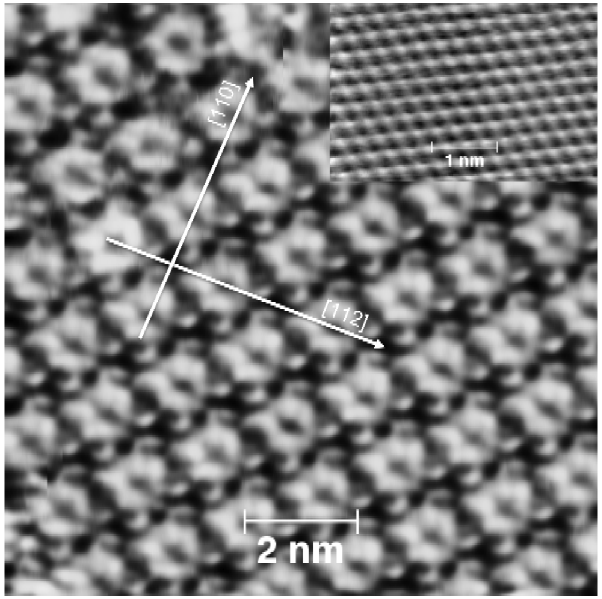
Electron energy analyzer

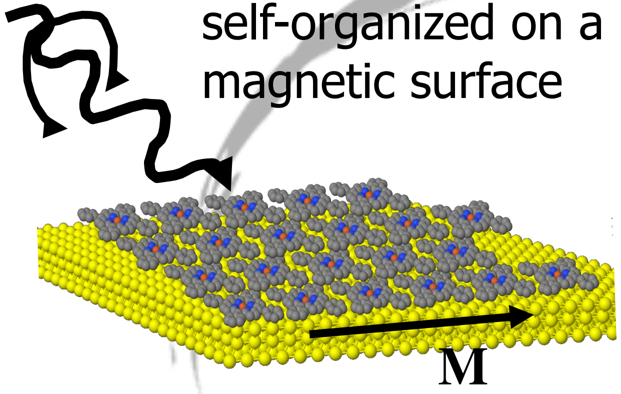




Porphyrins and fullerenes: supramolecular engineering for solar cells and molecular magnets

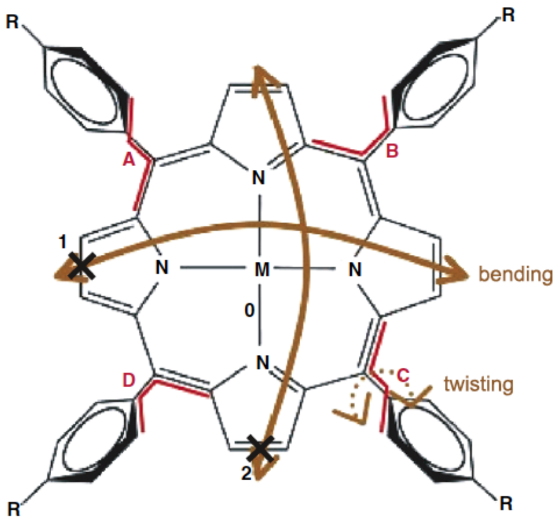

donor-acceptor complex

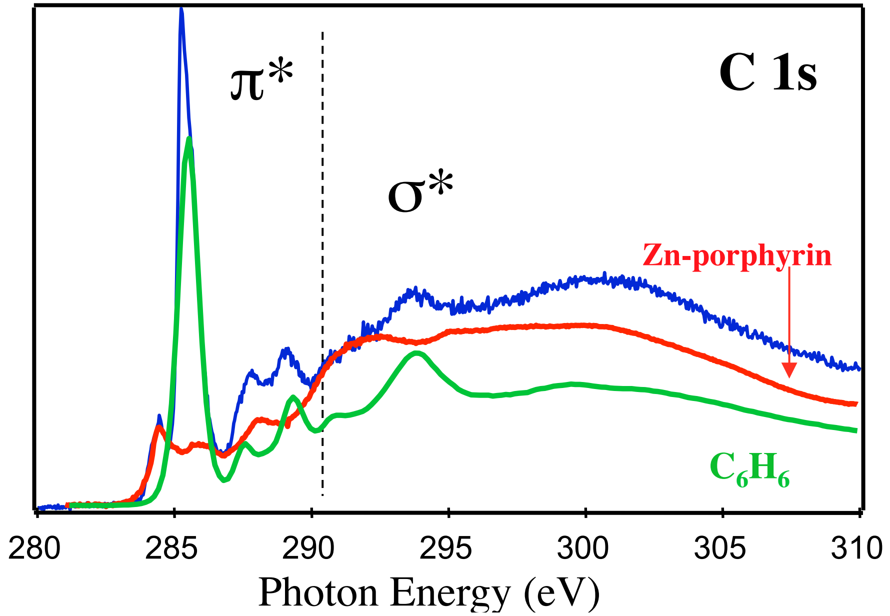


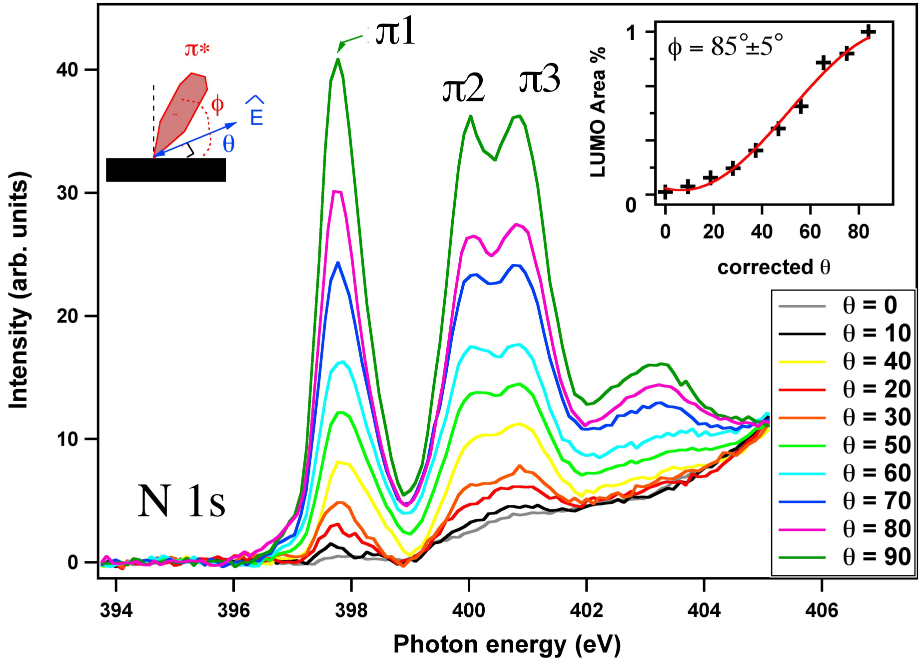

Magnetic molecules self-organized on a magnetic surface

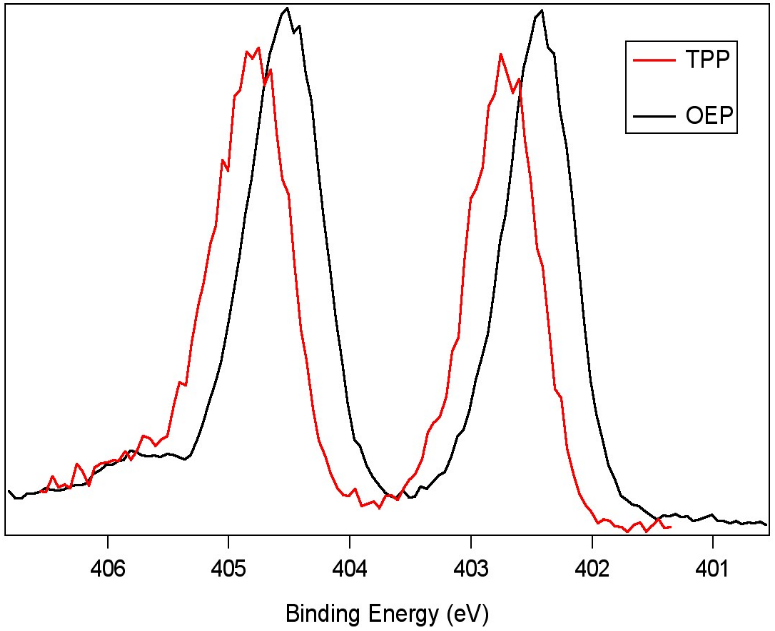
ZnTPP multilayer

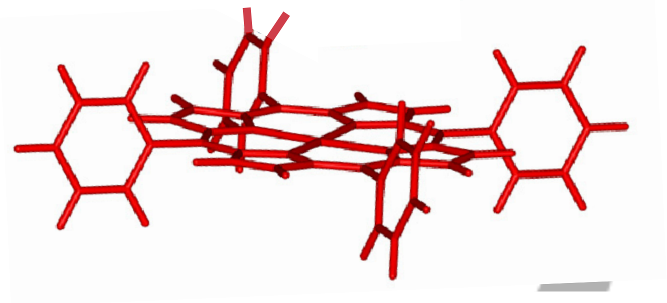
C. Castellarin-Cudia et al., Surf. Sci 600, 4013 (2006)



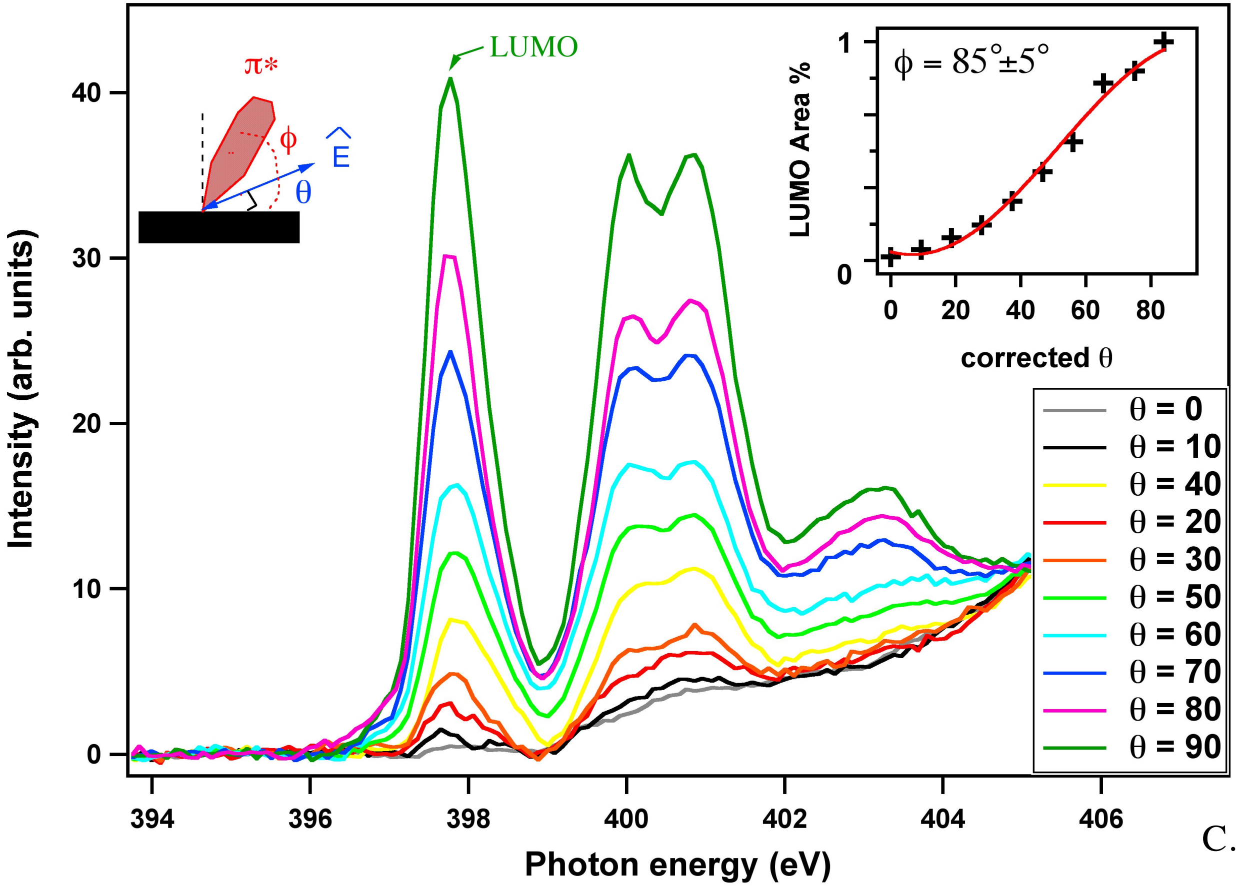








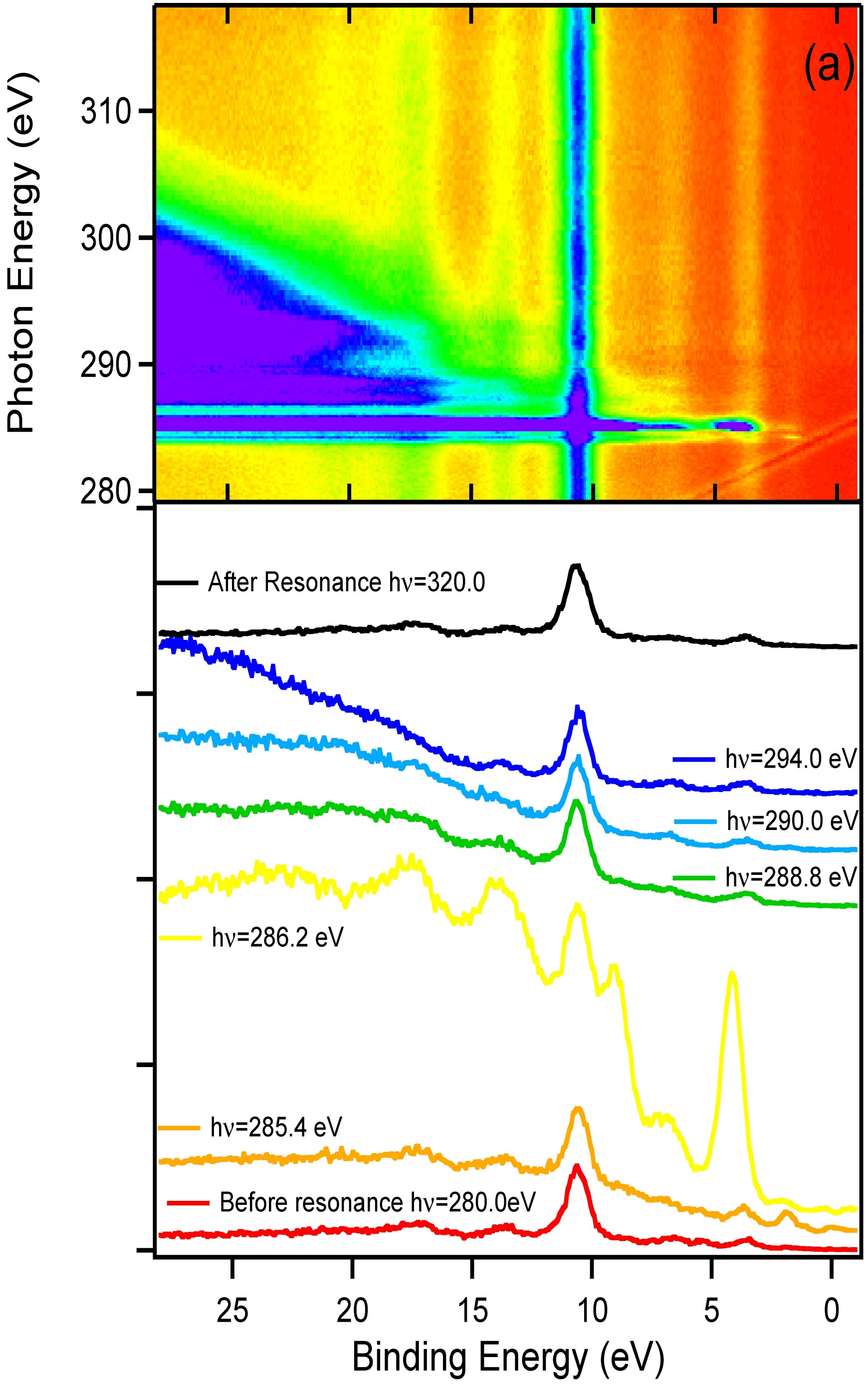
When the polarization is perpendicular to the surface, the π^* are at maximum, while when it is on the surface the π^* are almost zero.

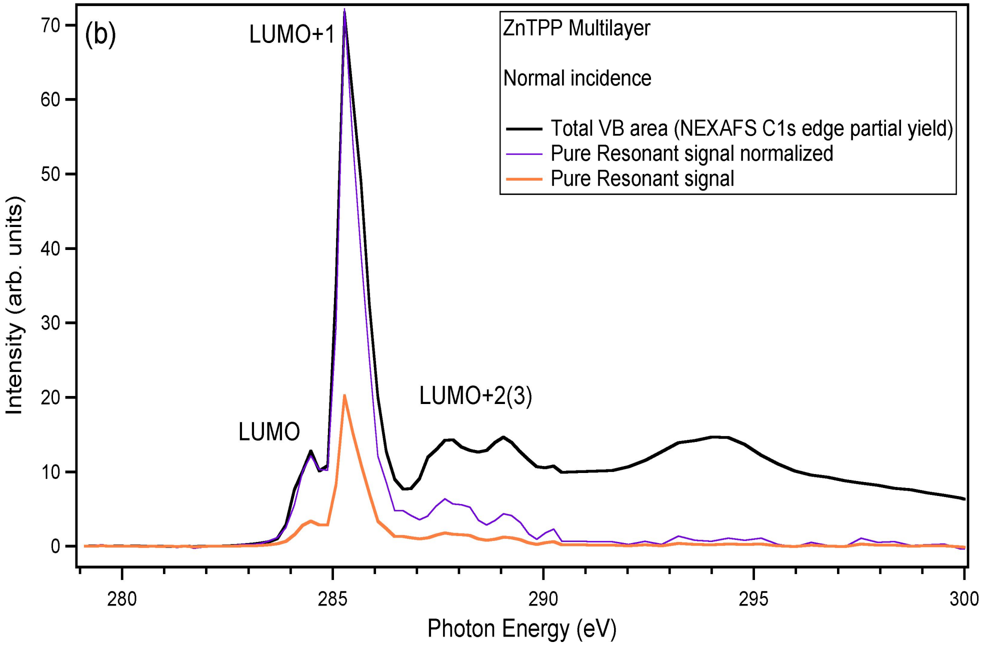


The Zn-TPP in the multilayer adsorbs with the macrocycle parallel to the surface

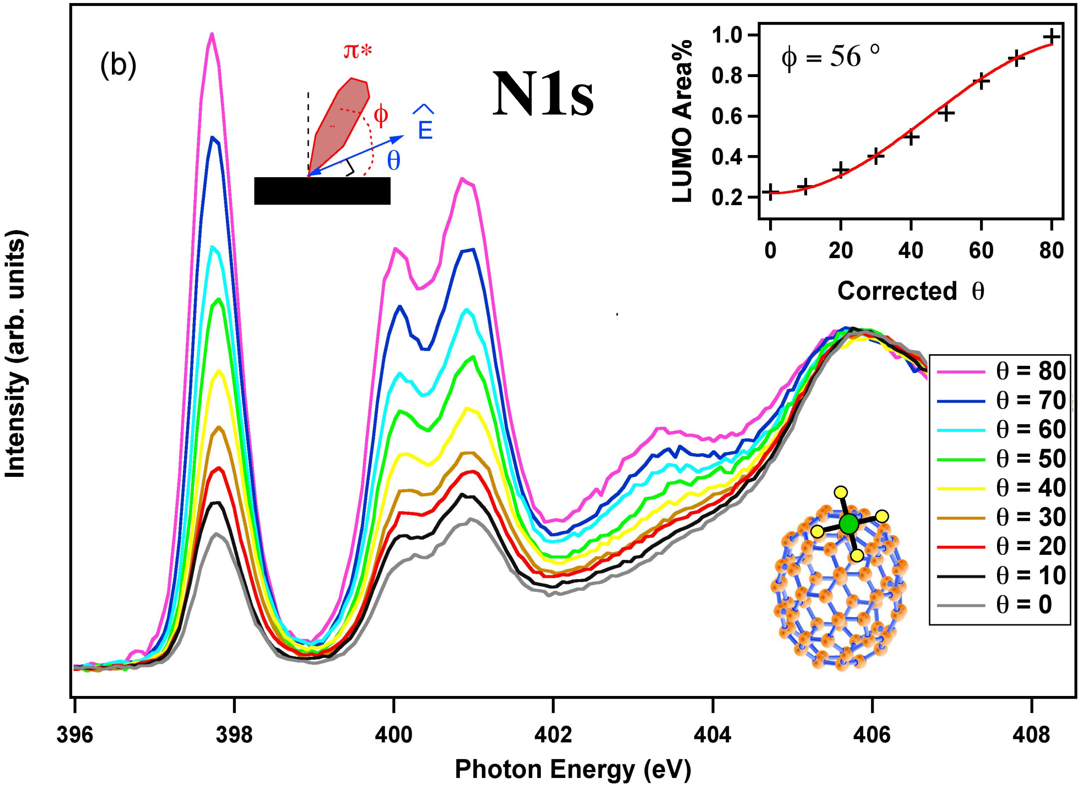
C. Castellarin-Cudia et al, Surf. Sci. (2006)

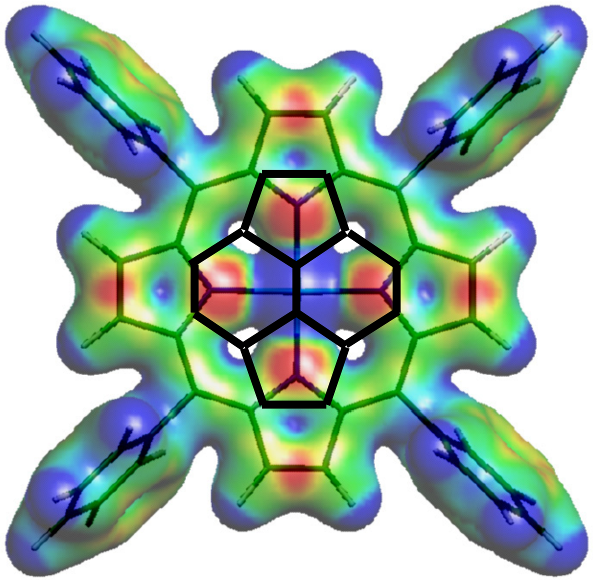
Resonant photoemission across the C1s threshold





LUMO+2(3) feature is reduced. This indicates that when the electron is excited into the LUMO+2(3) states it remains localized on the molecule for a time bigger but comparable (competing) to the core-hole lifetime (~ 5 fs for the C 1s) and therefore this excited states contribute only partly to the core-hole decay as spectator state. On the contrary, in the LUMO and LUMO+1 states the electron remains localized for a time much bigger than the core-hole lifetime.





Y.-B. Wang & Z. Lin, JACS 125, 6072 (2003)

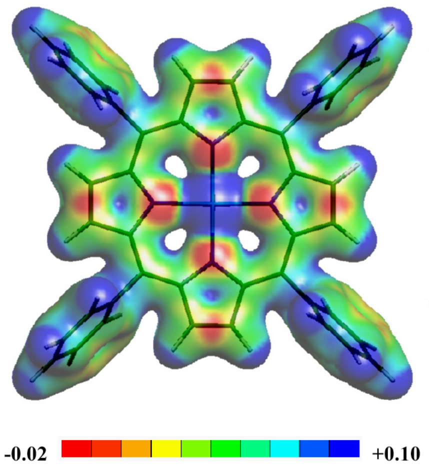


Figure S4. Molecular electrostatic potentials of 5,10,15,20-tetraphenylporphyrinato-zinc, mapped from -0.02 to +0.10 $e/4\pi e_0 a_0$, onto 0.02 e $Å^{-3}$m isosurface of the electron density at the PBE/6-31G(d,p) level

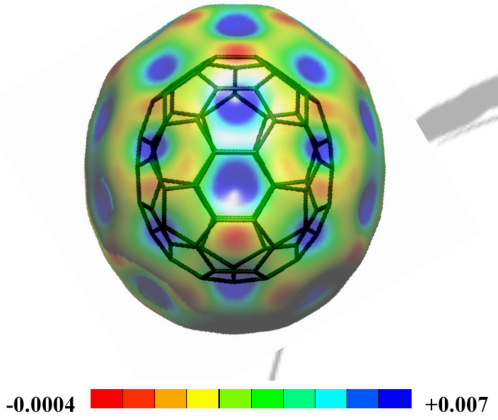
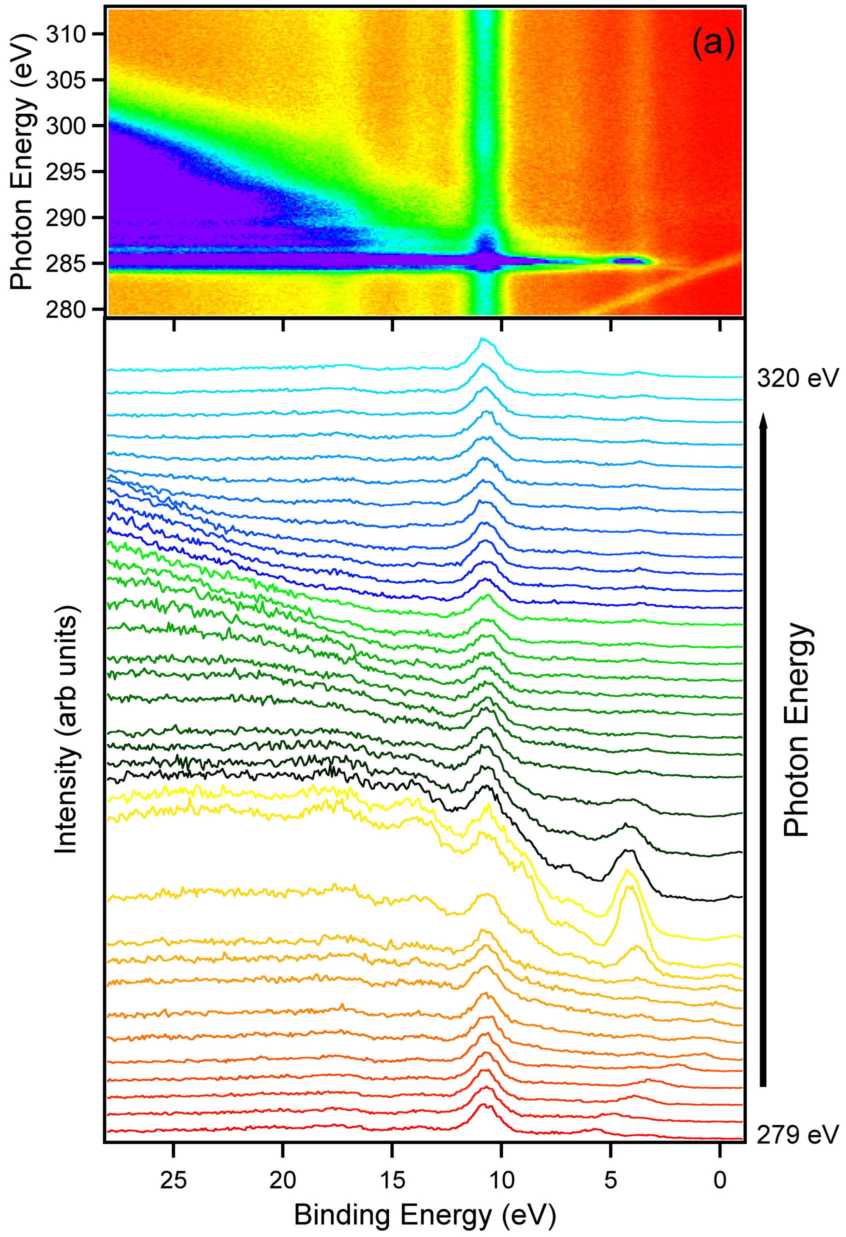


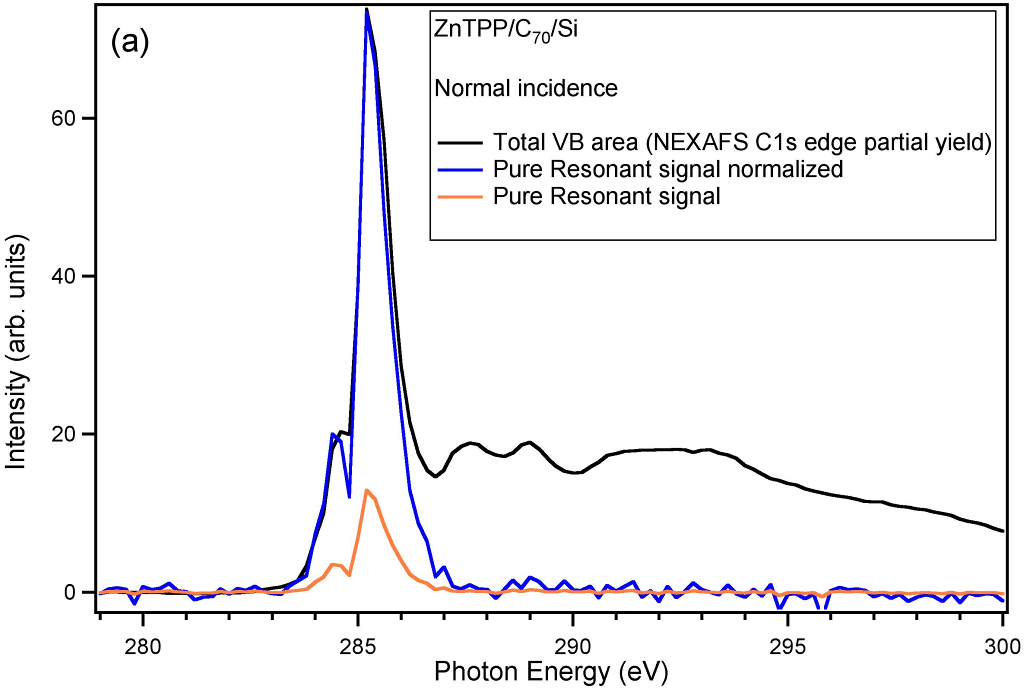
Figure S2. Molecular electrostatic potentials of C_{70} from difference perspective projections, mapped from -0.0004 to +0.007 $e/4\pi e_0 a_0$, onto 0.001 e $Å^{-3}$m isosurface of the electron density at the PBE/6-31G(d,p) level

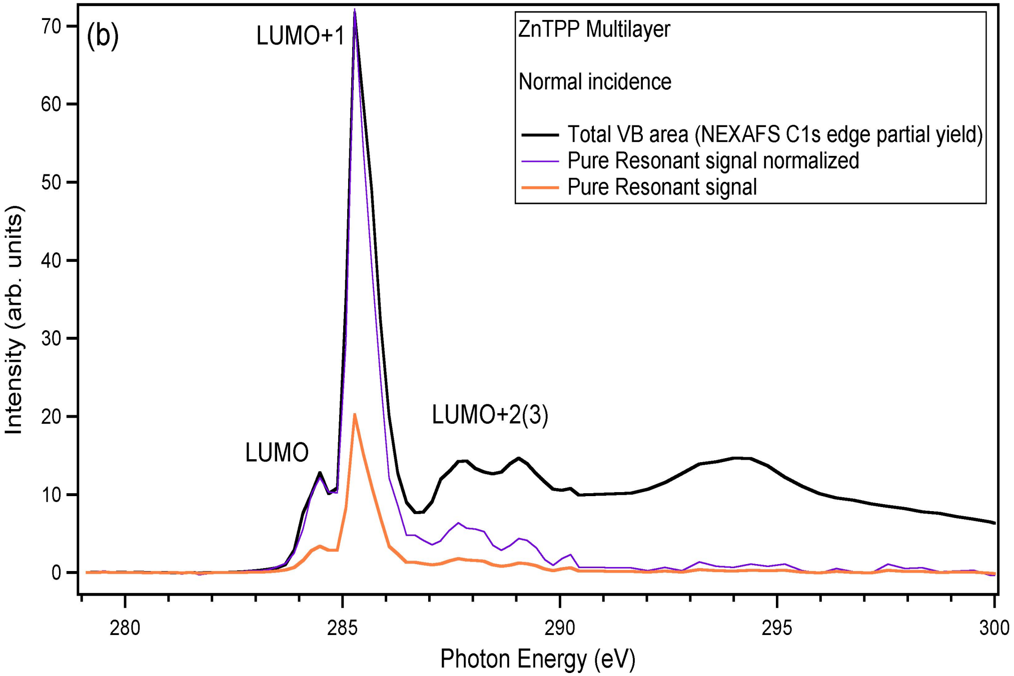
Resonant Photoemission



Already from a first sight in comparison with the ZnTPP multilayer there is a general reduction of the intensity enhancement at resonance (a factor of 1.5).

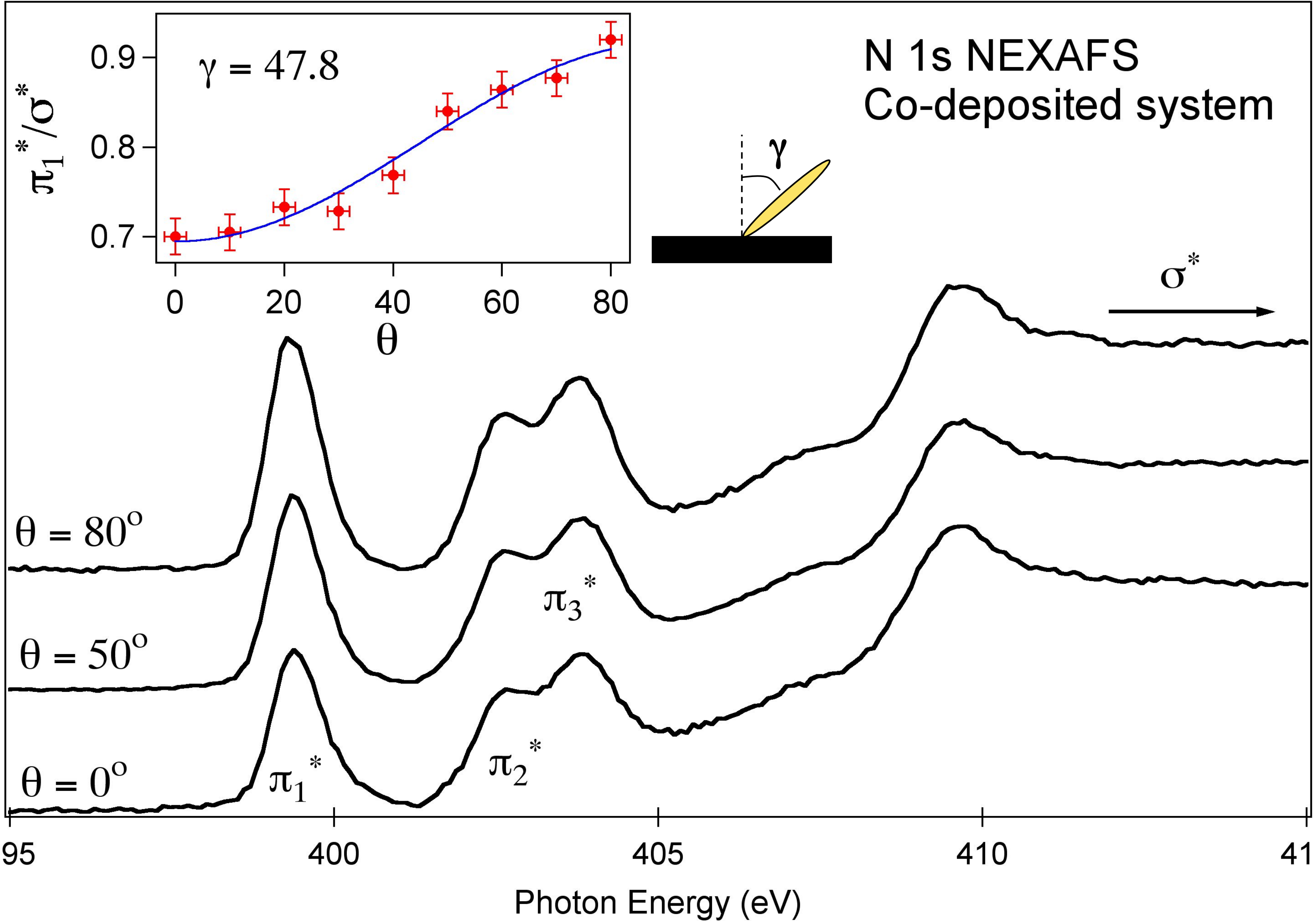
This global reduction of the resonant intensity indicates that in the ZnTPP/C_{70} double layer system the electron excited on a ZnTPP molecule is transferred away on a time scale of ~ 7 fs.

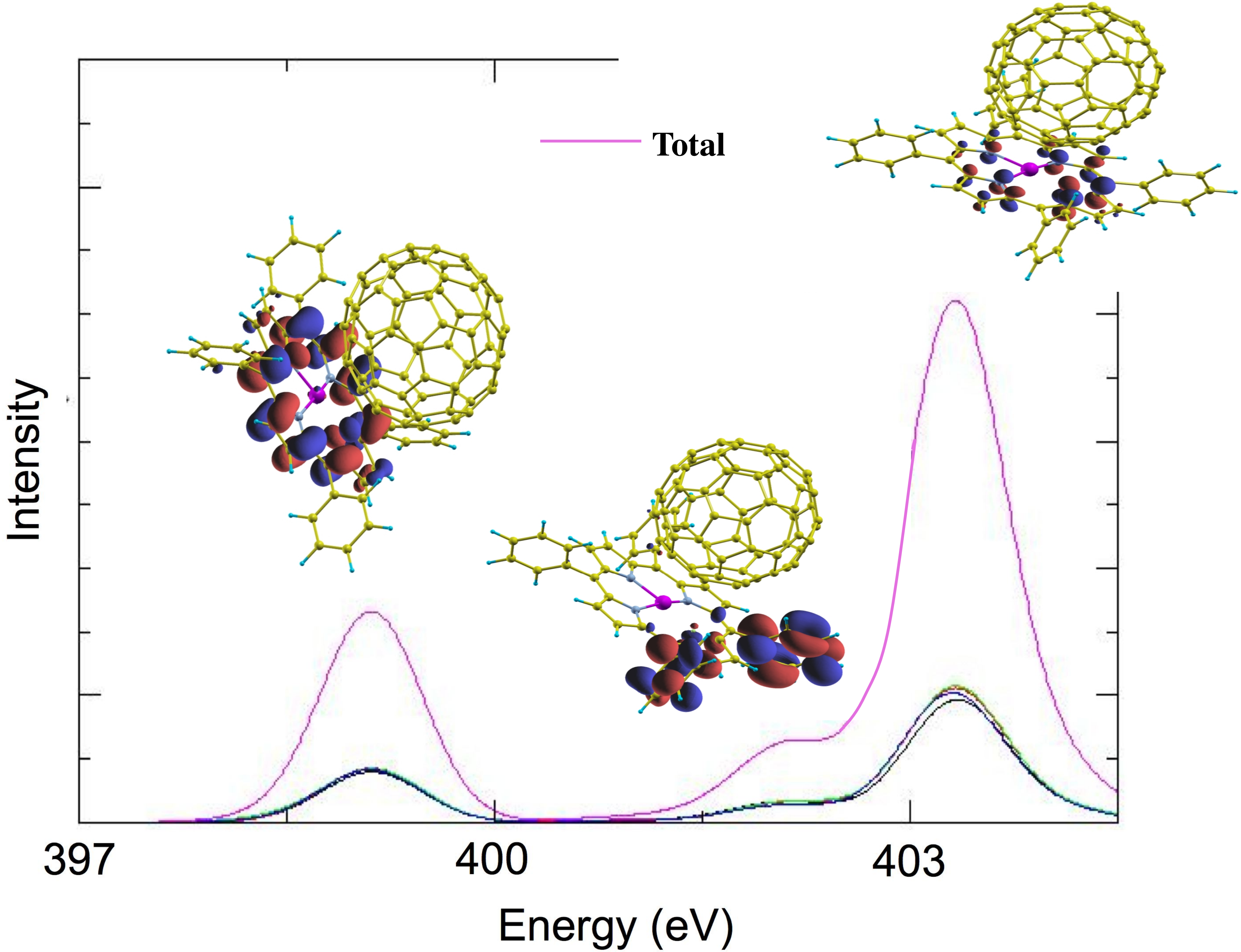




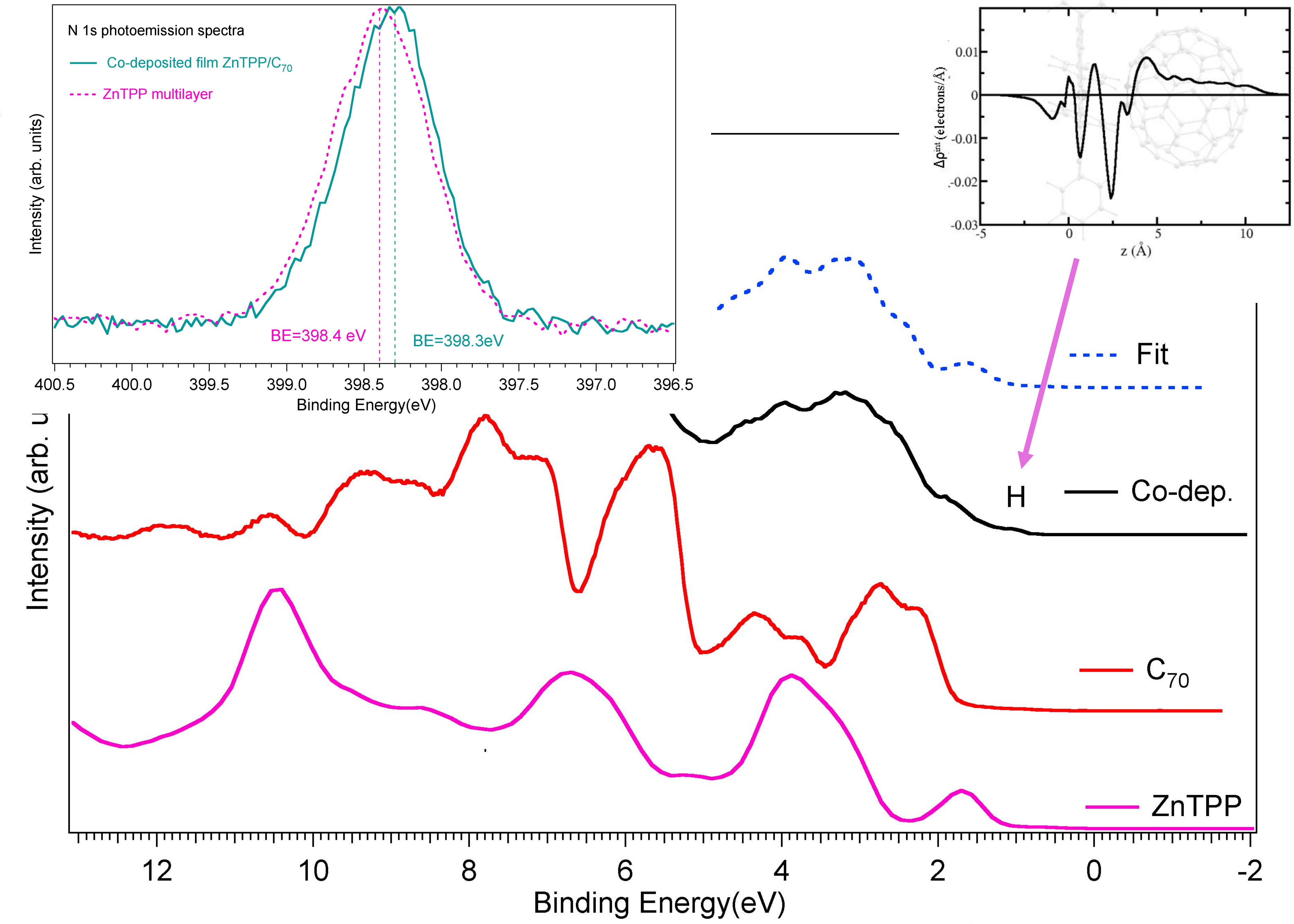
The transition to the LUMO +2(3) is completely quenched: the charge transfer from these states is much faster than the core-hole lifetime (5 fs)

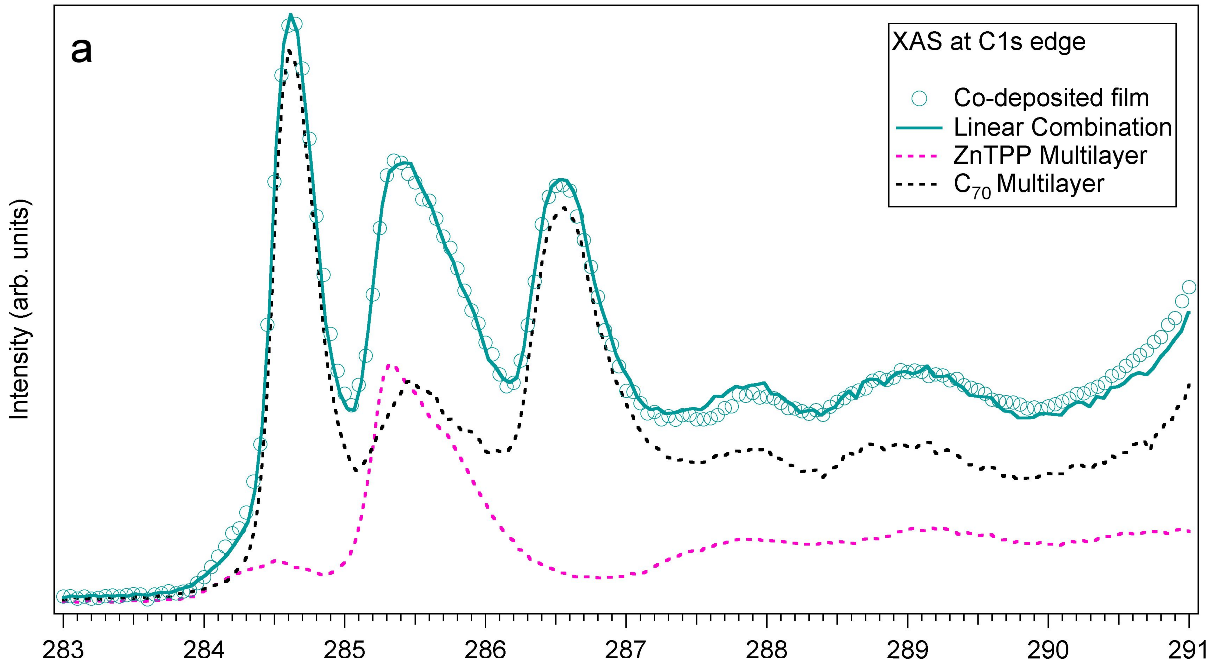
Co-deposited ZnTPP and C_{70}: orientation and charge transfer

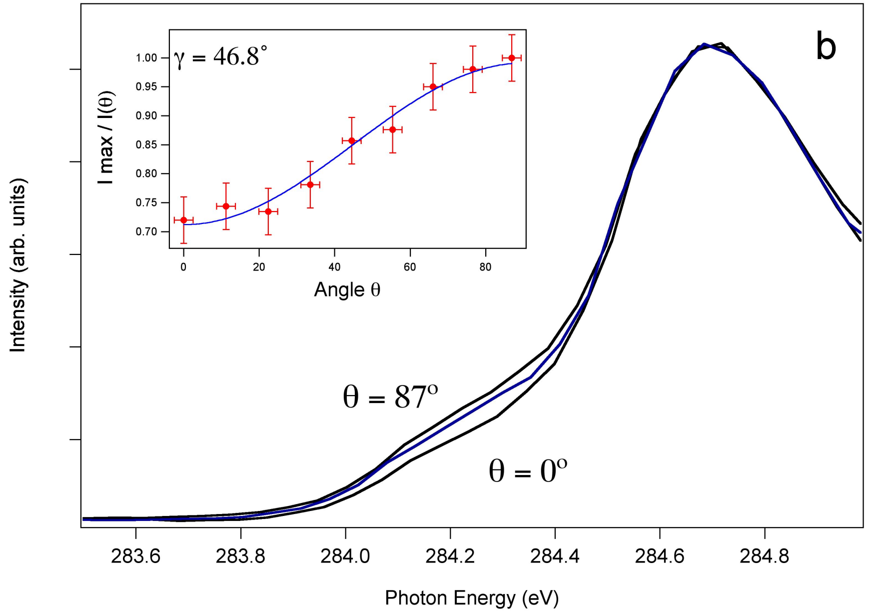



Total
Intensity
397
400
403
Energy (eV)

Small charge transfer from porphyrin to C_{70} ~ 0.013 el/molecule



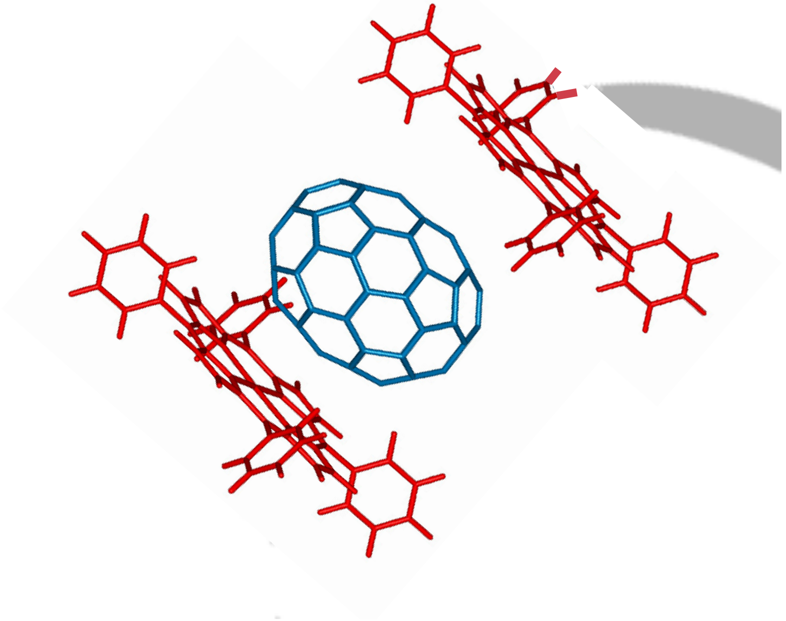


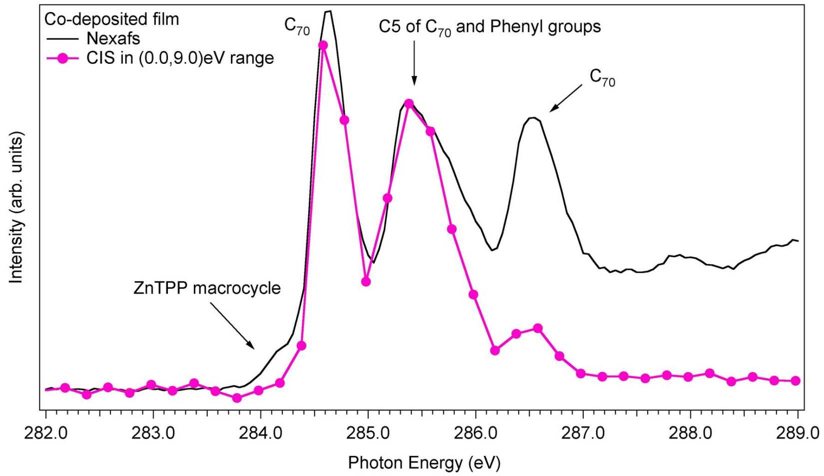


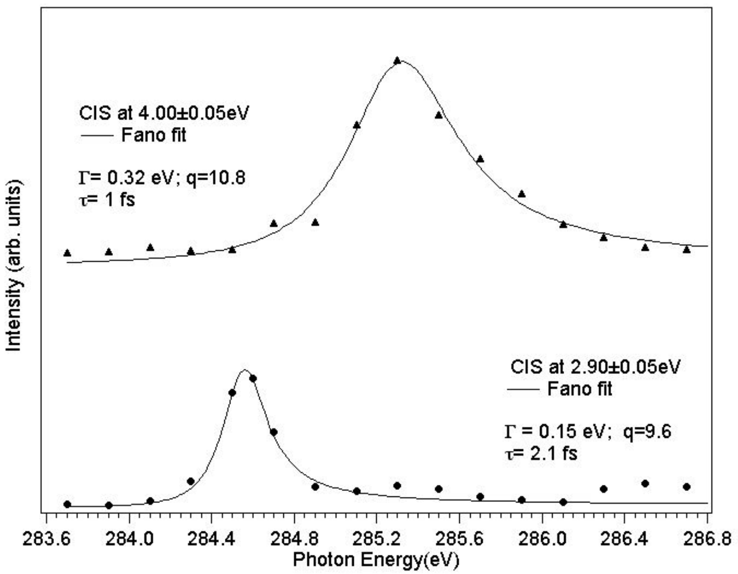
Substantial disorder, but tendency of the π* of porphyrins to stay at ~ 47°

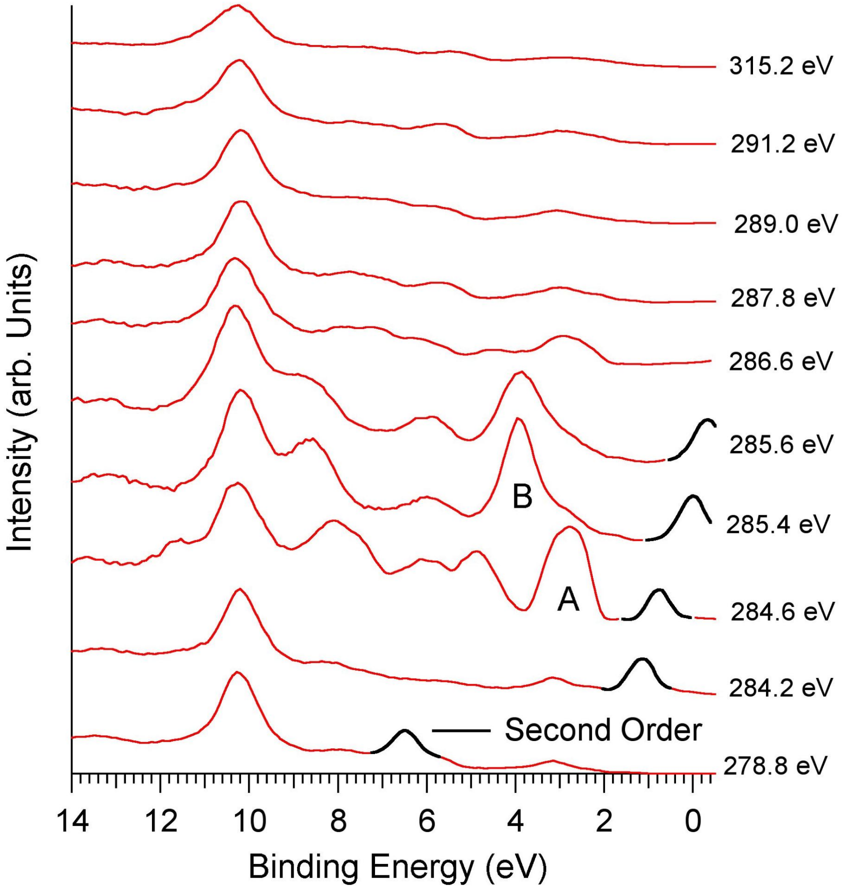
It turns out that C_{70} long axis is almost parallel to the ZnTPP macrocycle.

Maximization of the electrostatic interactions

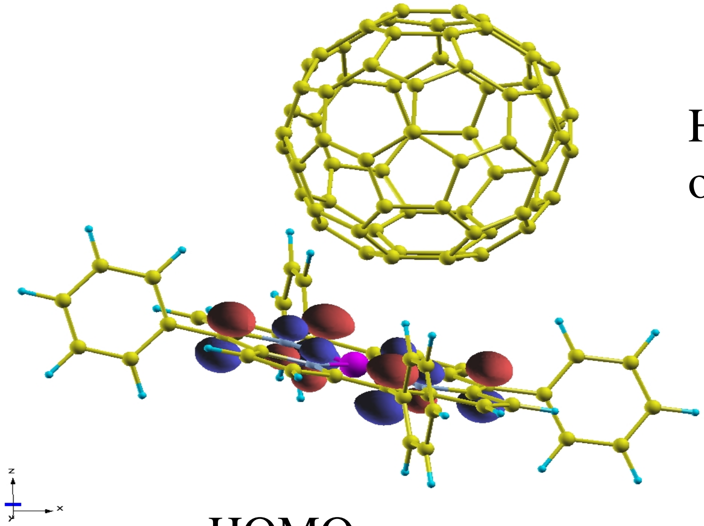






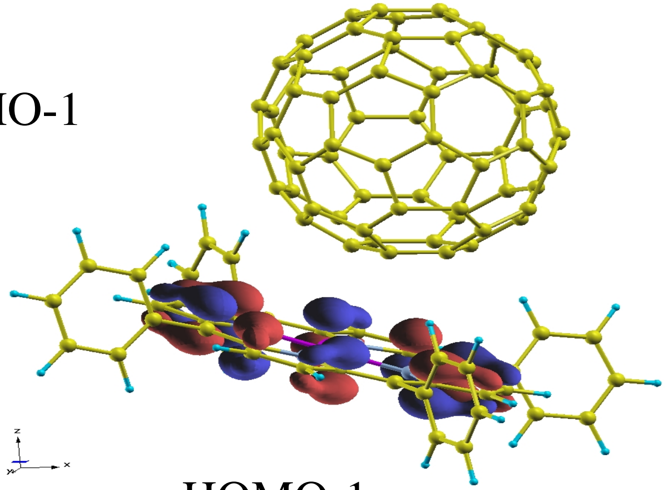


Excited state interactions are present in the contiguous chromophores and this system acts as a *donor/acceptor* junction where the excited charges at the porphyrin macrocycle can fast delocalize to the fullerene. The time scale of the ultra-fast charge transfer is smaller than 1-2 *fs*.

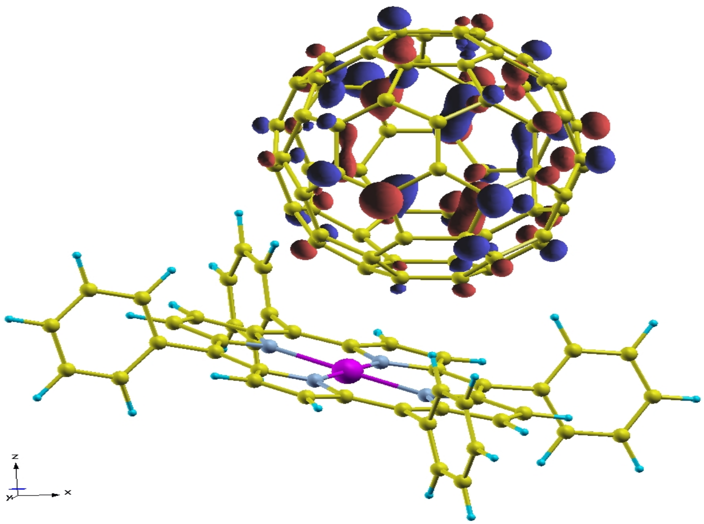


HOMO

HOMO and HOMO-1 on the porphyrin

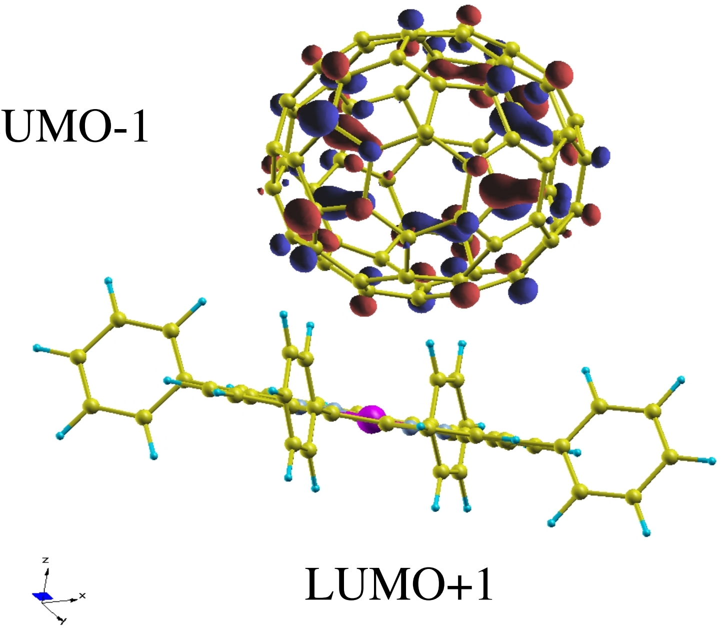


HOMO-1



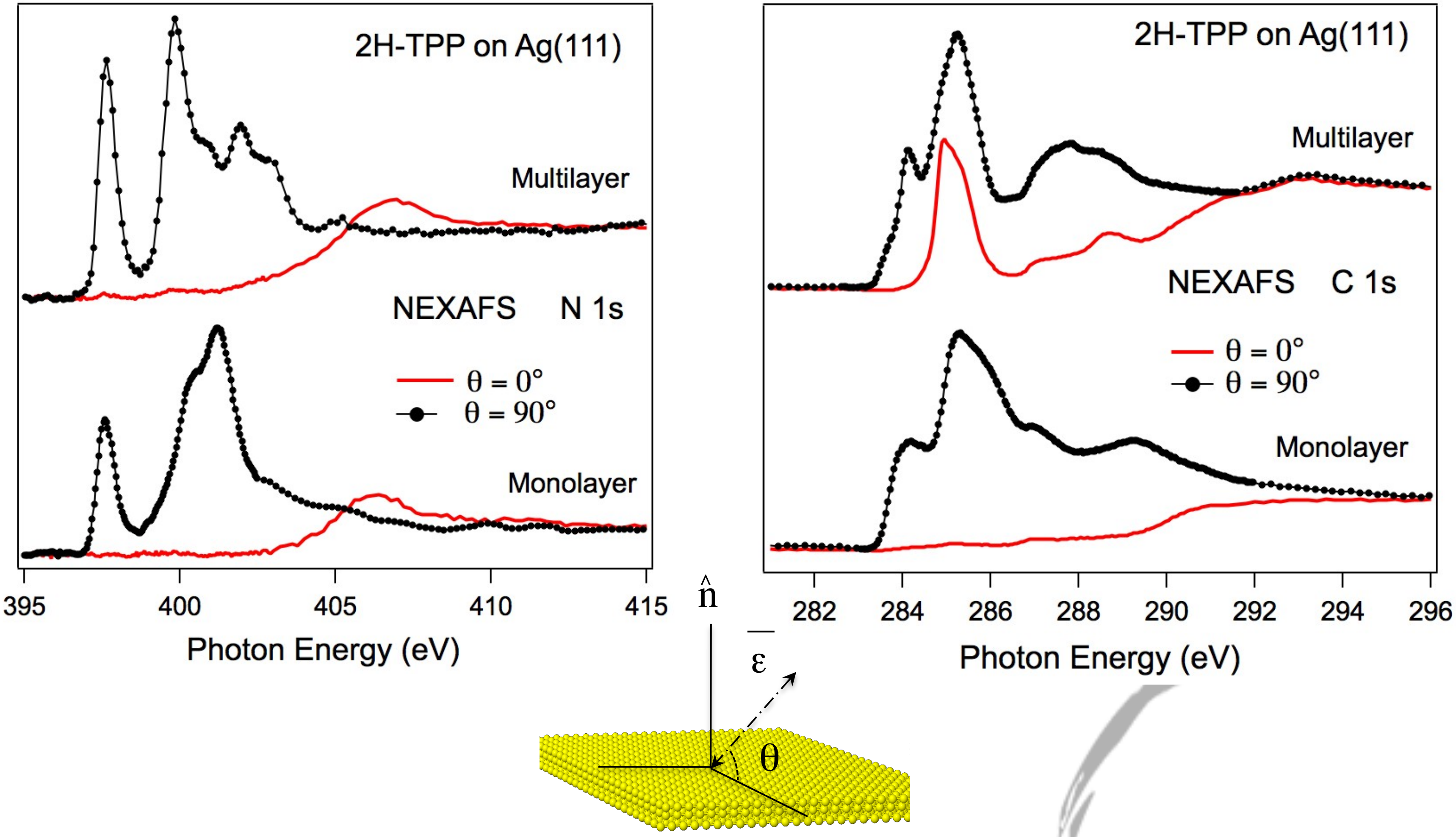
LUMO

LUMO and LUMO-1 on the C_{70}



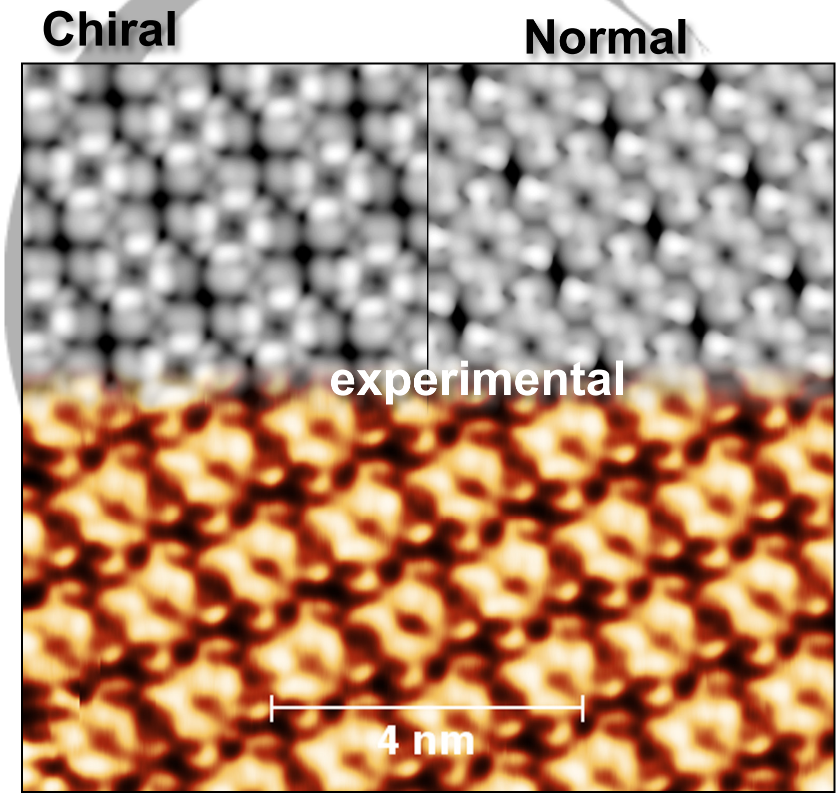
LUMO+1

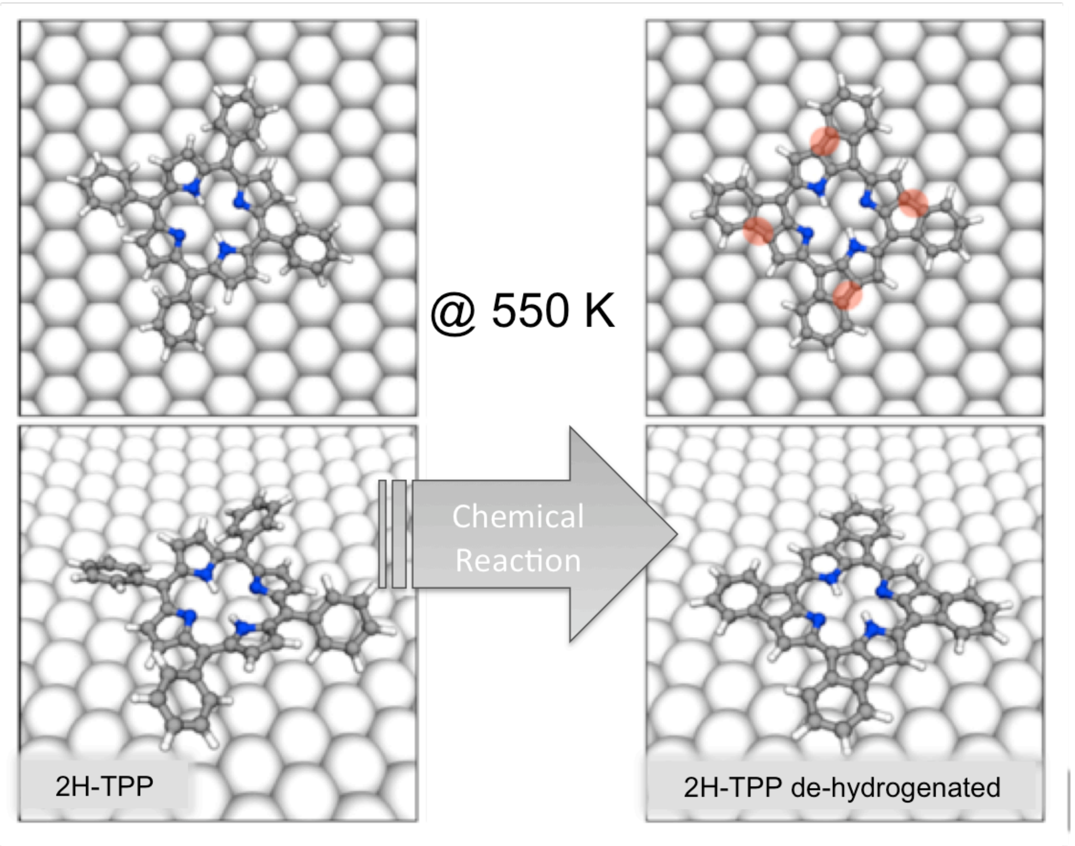
NEXAFS: 2H-TPP/Ag(111)

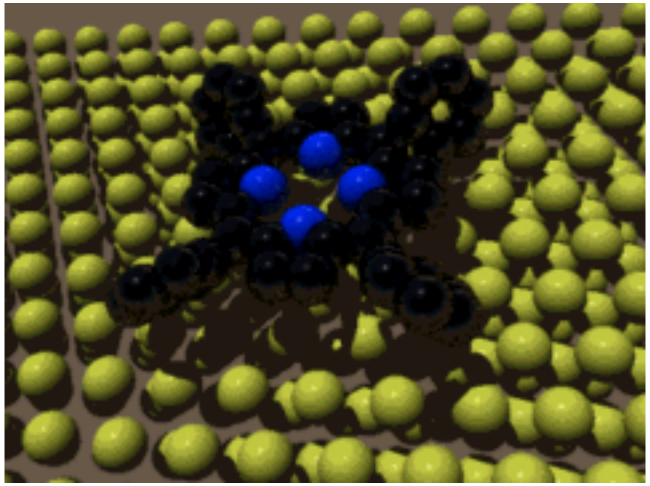


H_2-TPP molecules in monolayer and multilayer have the macrocycle parallel to the Ag(111) surface. The phenyl rings are disordered (approx. as in gas phase) in the multilayer, flat as the macrocycle in the monolayer.

STM & Simulations



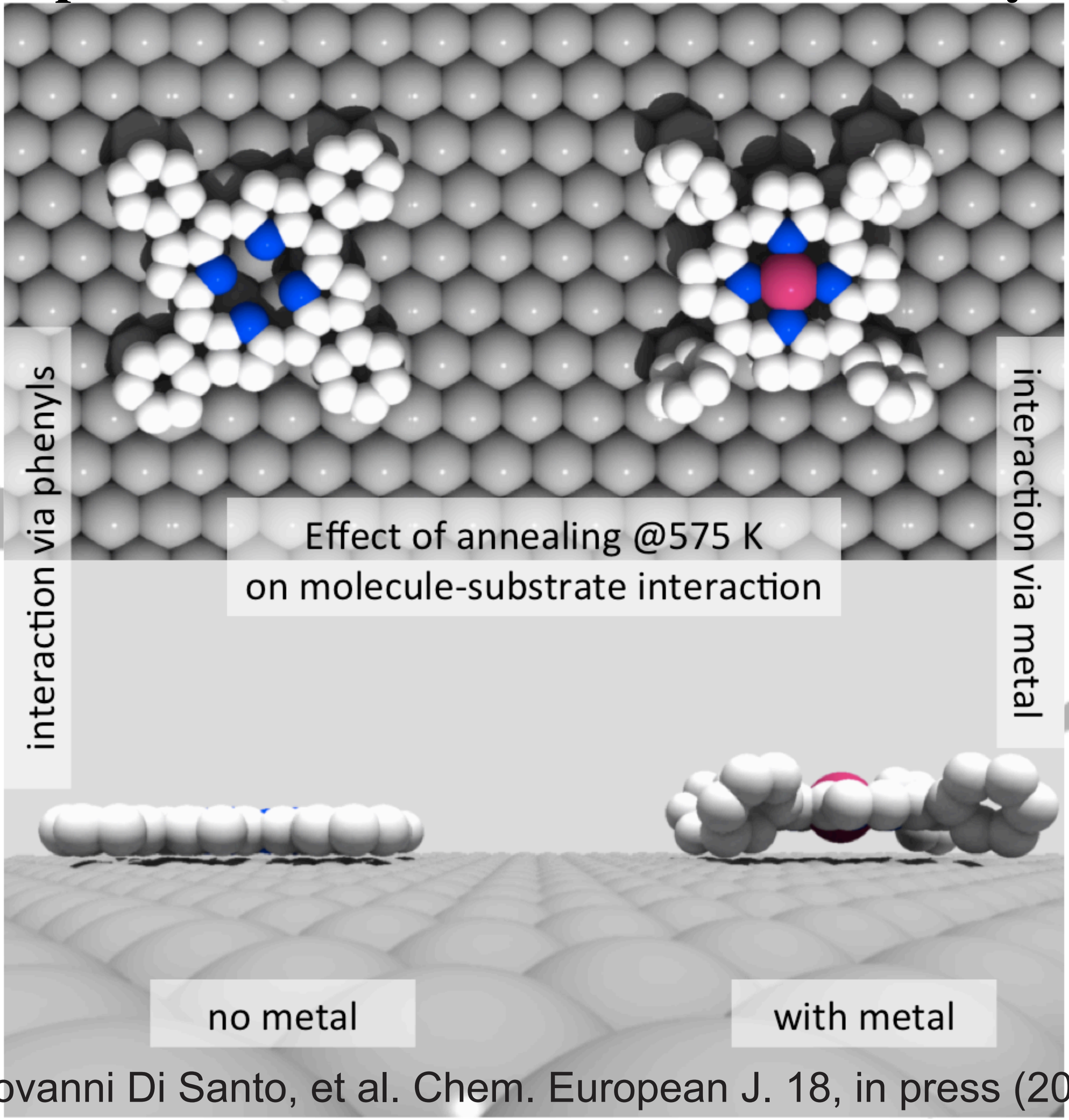




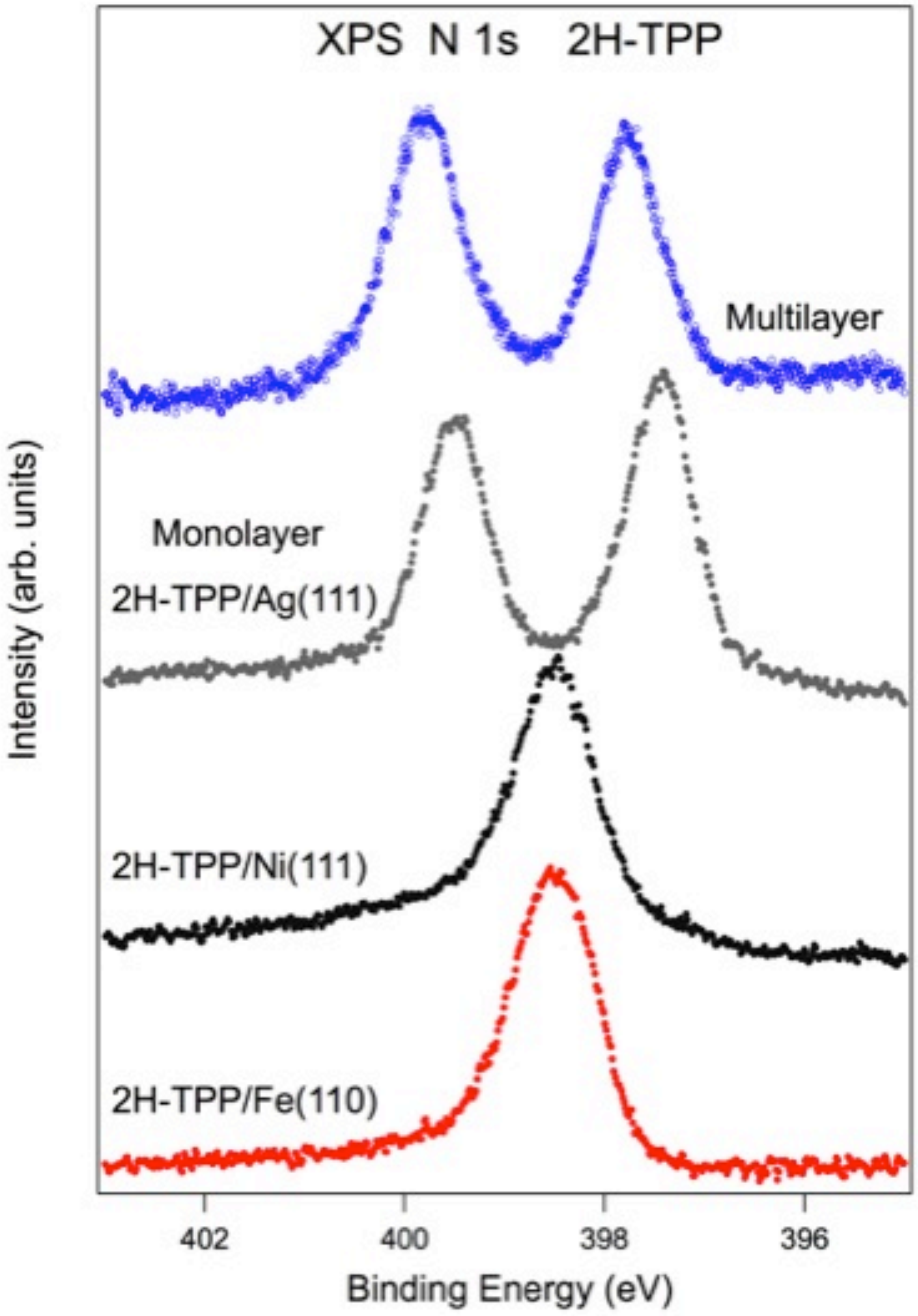
The chiral configuration (left) seems to fit well the experimental data than the RT adsorbed monolayer (right)

Giovanni Di Santo, et al. Chem. European J. 17, 14354 (2011)

The interaction and molecular conformation depend on the presence or not of a metal in the macrocycle

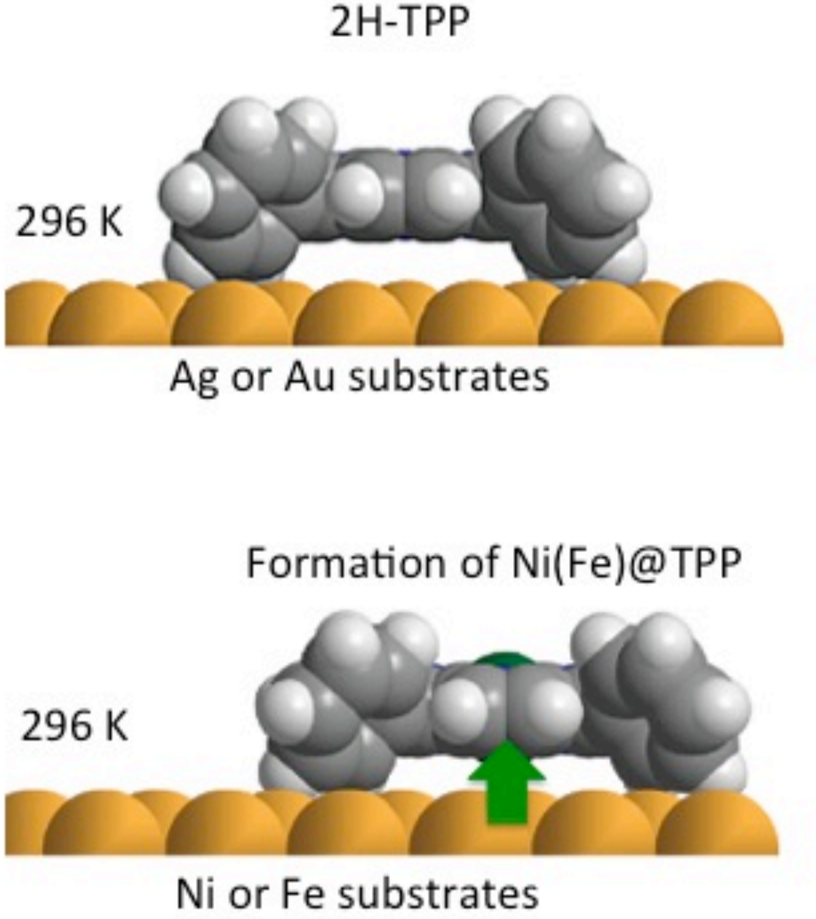


Giovanni Di Santo, et al. Chem. European J. 18, in press (2012)



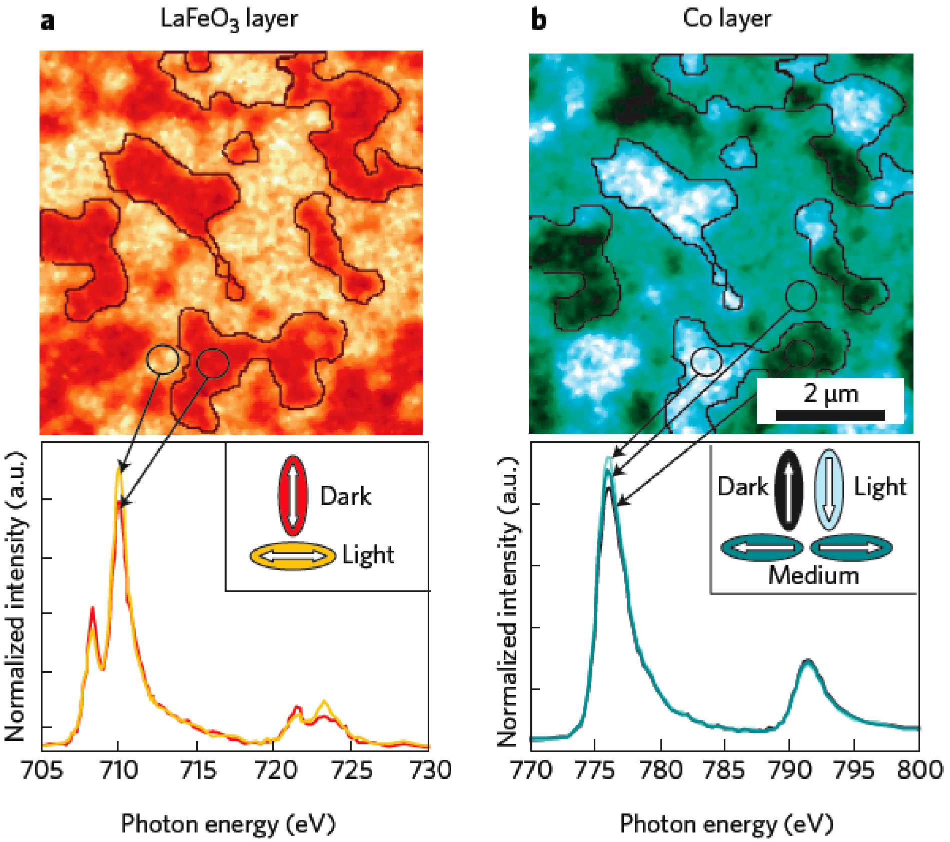
Monolayer on Fe and Ni

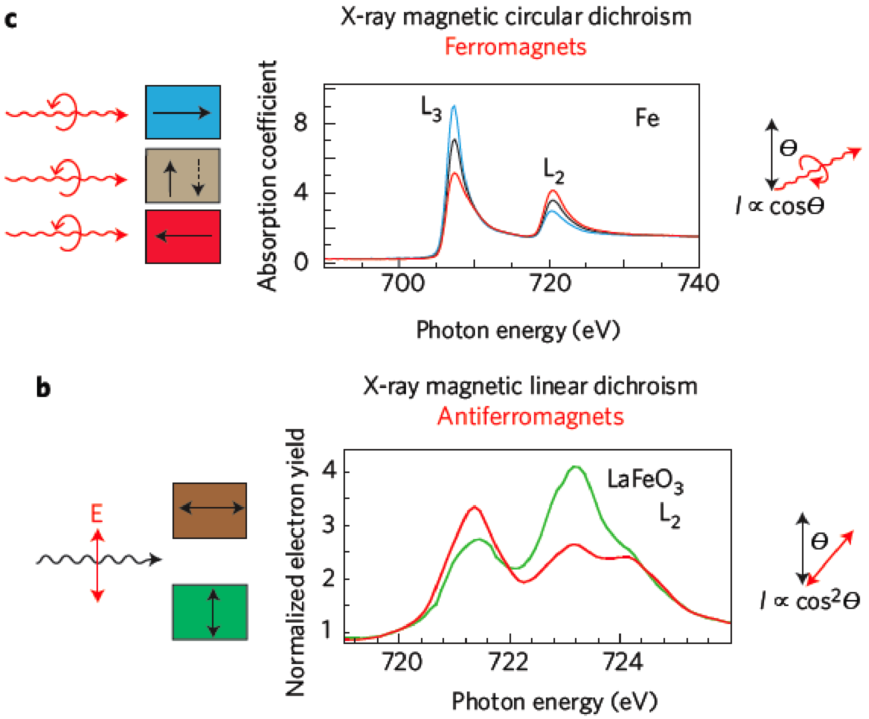
Different with respect to Ag(111) substrate, the H_2-TPP molecules in the monolayer regime on Ni and Fe substrates immediately pick-up a surface atom and metalate.



Study and Manipulation of Spin and Magnetic Properties

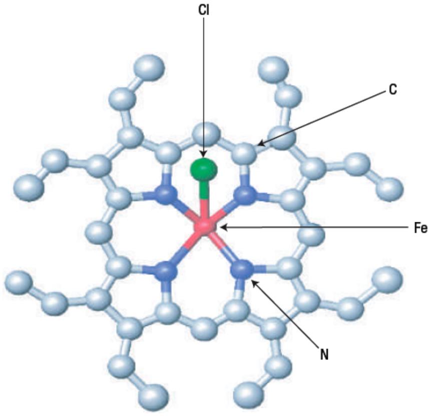
Spin and charge are the basic ingredients for storing and processing information.
Circular magnetic X-ray dichroism allow mapping of the spatially resolved changes in the spin and orbital momentum. This reveals new details about the transfer of spin momentum in the storage materials with the highest data density known, quantum dots or metallo-organic layers, which enables the change in magnetization. Needed: high intensity synchrotron X-ray circularly polarized source with a photon energy tuned to individual absorption edges of magnetic metals.



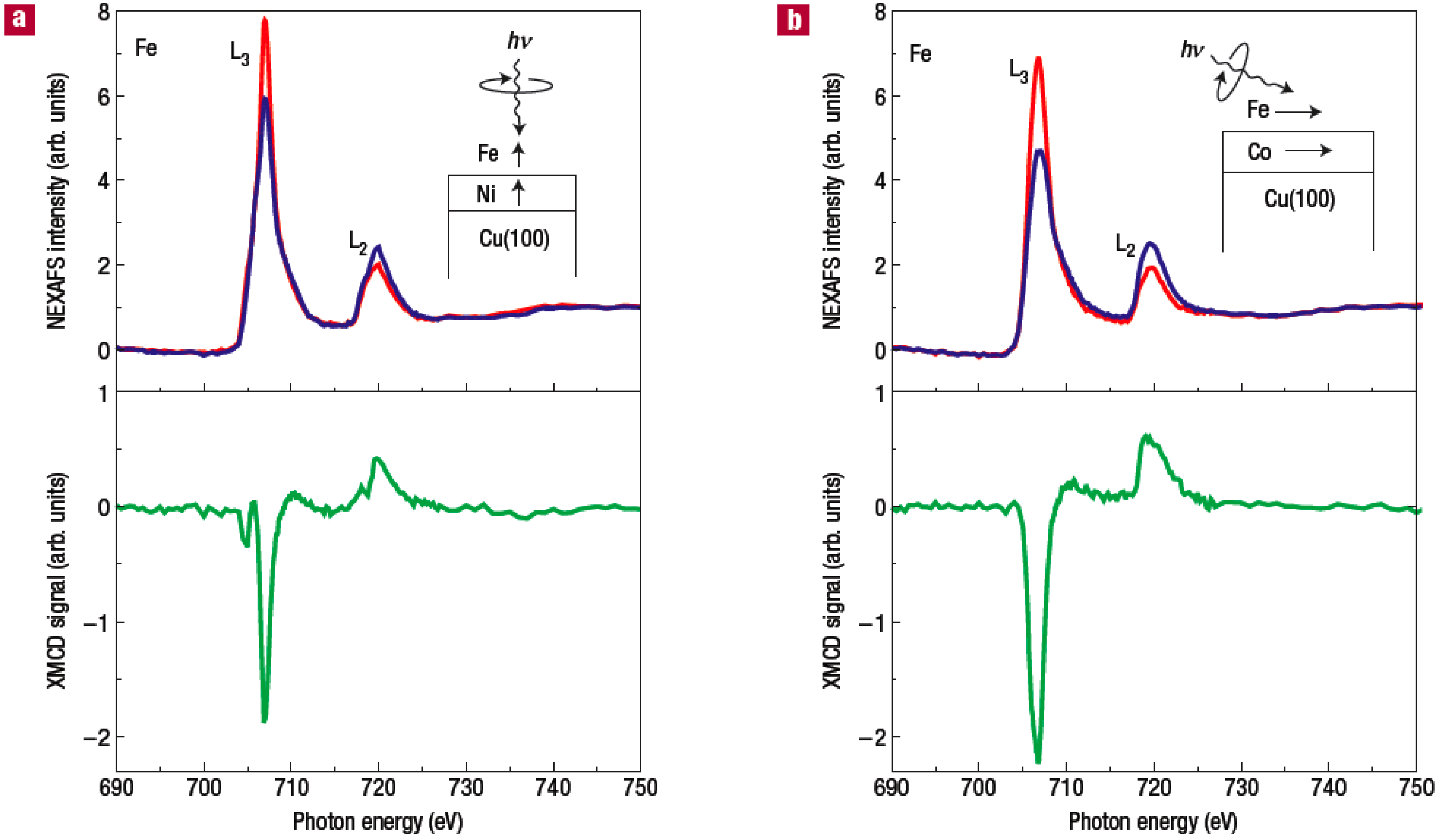


Linear dichroism at Fe L edge images AFM domains (left). Circular dichroism at Co L edge images FM domains (right). Comparison of images shows that the Co domains align with the AFM domains (light and dark regions inside outlined areas).

-XMCD (x-ray magnetic circular dichroism)
-Element specific
-Spin and orbital moments



The magnetism of 3d transition metals and 4f rare earths is key to the operation of many magnetic materials, catalysts, and metallo-proteins. Their magnetic states are probed by photoexcitation of core electrons in the 500–1500 eV energy range, such as the Fe 2p level shown



Polarization of a molecular magnet over a magnetic material

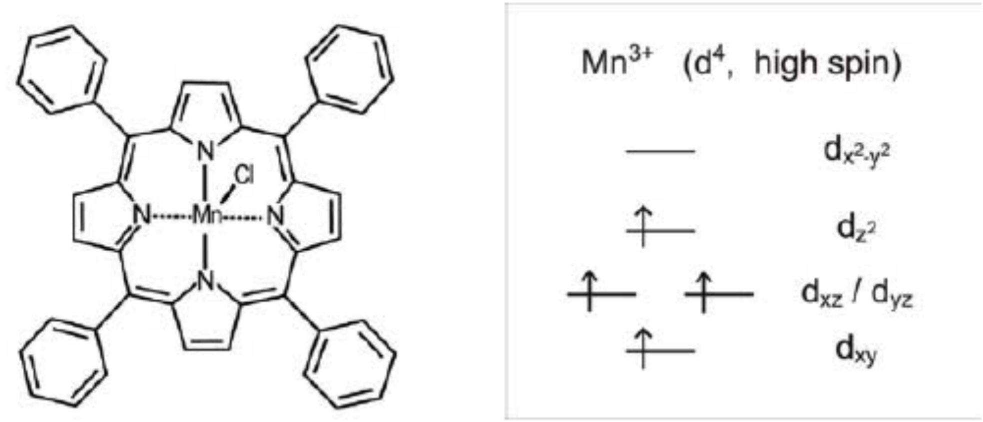
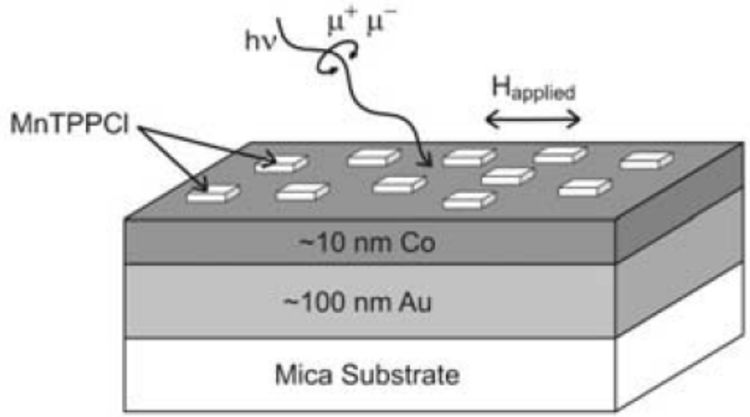
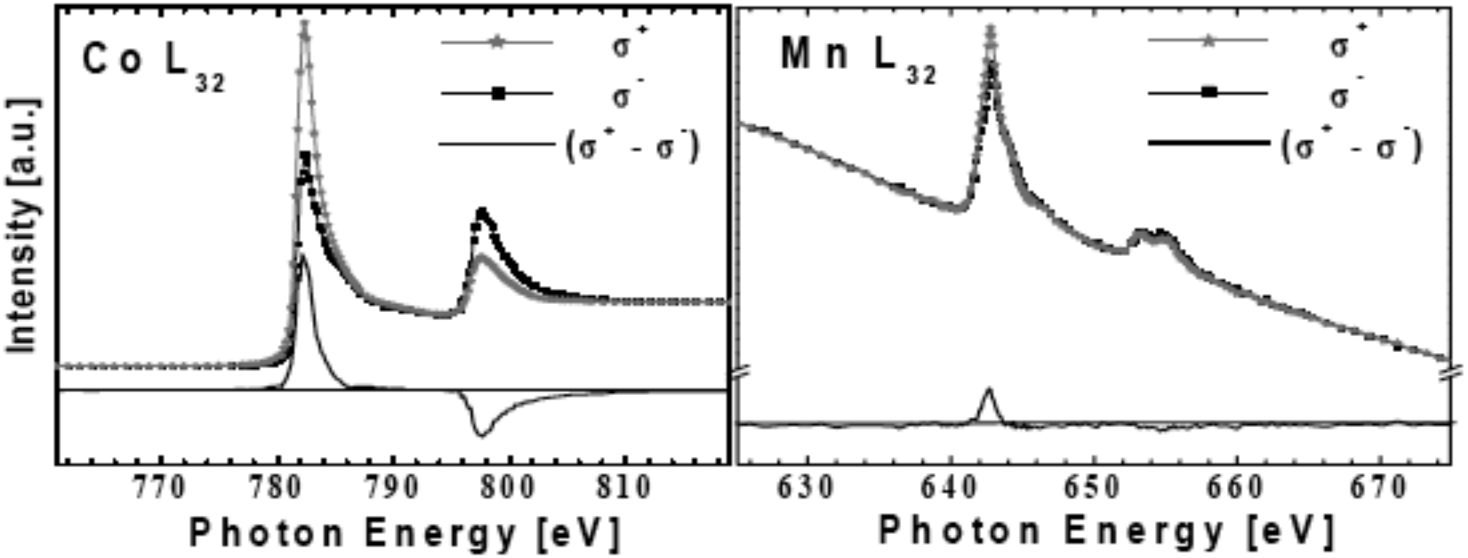
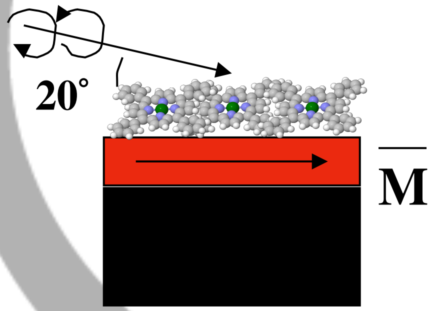


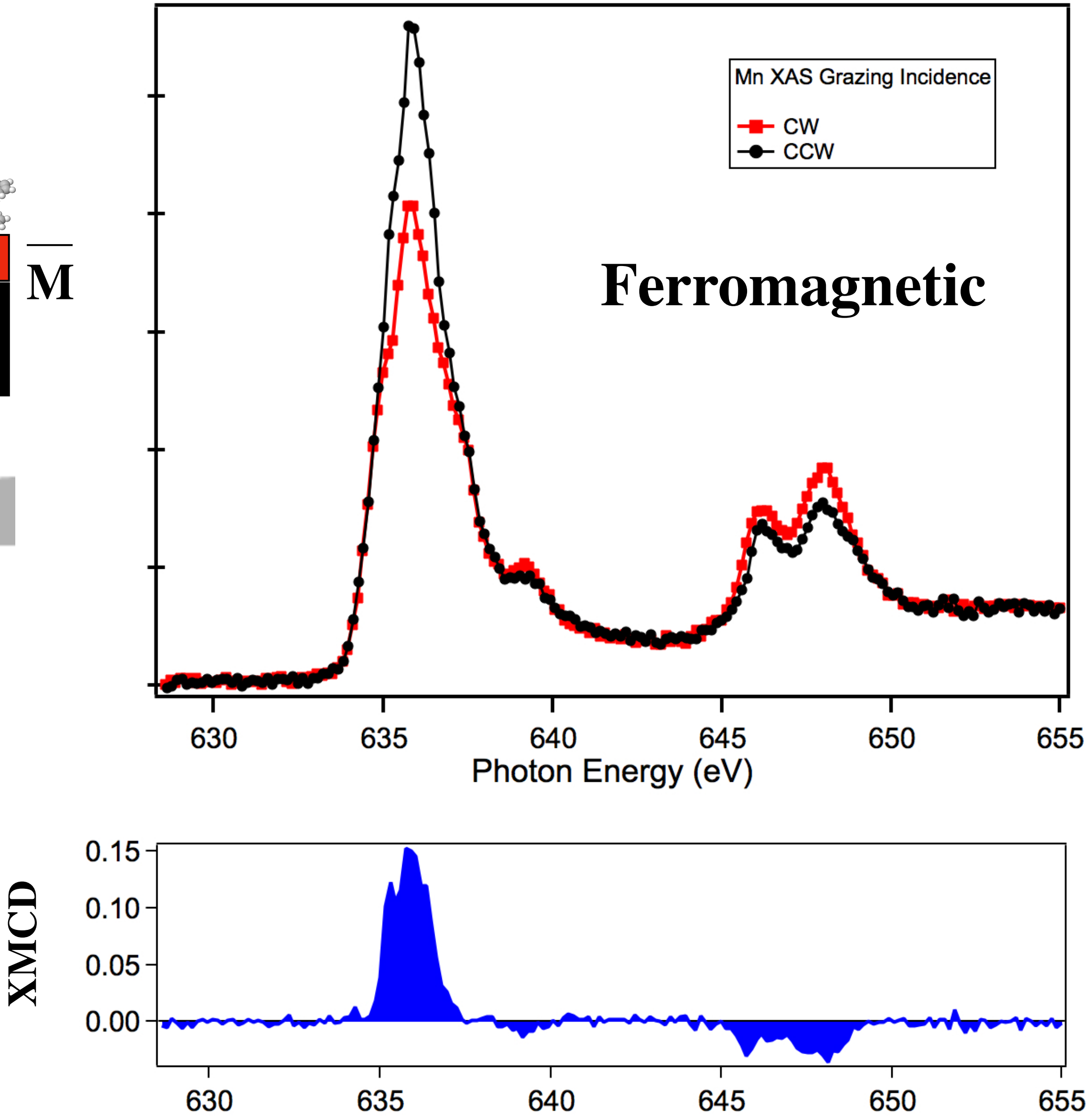
Fig. 1: Structure of the MnTPPCl molecule (left) and scheme of the electron configuration of the Mn^{3+} ion in MnTPPCl (right)



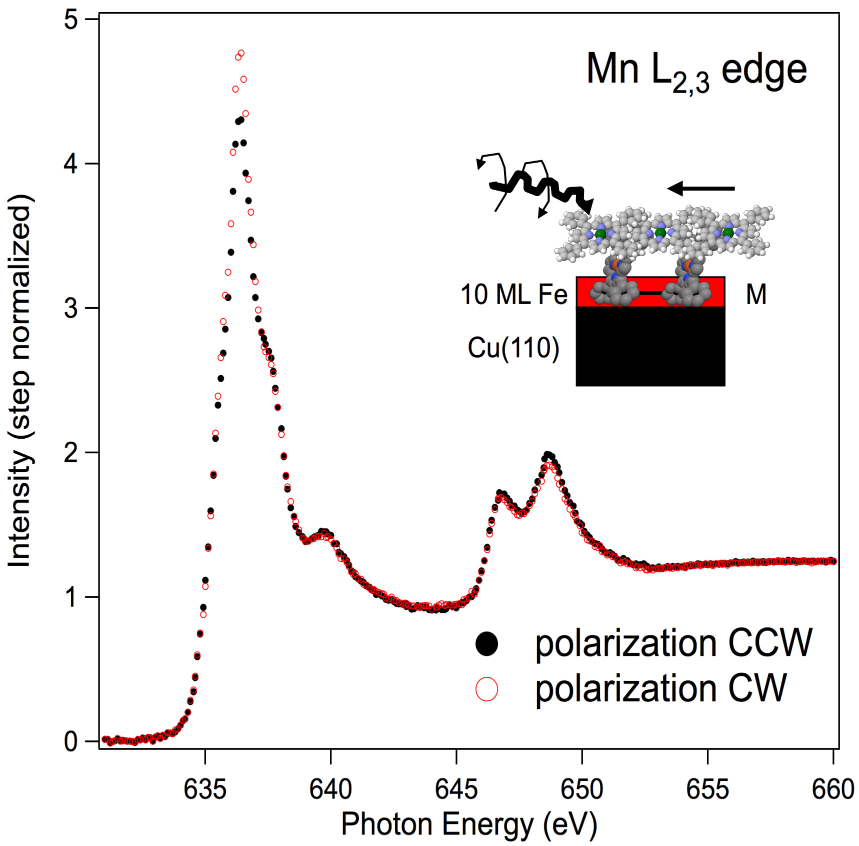


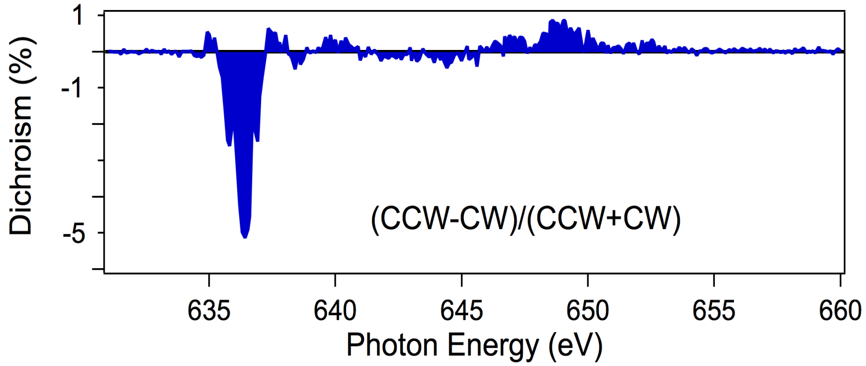
1 ML of Cl-Mn-TPP on Fe substrate at RT

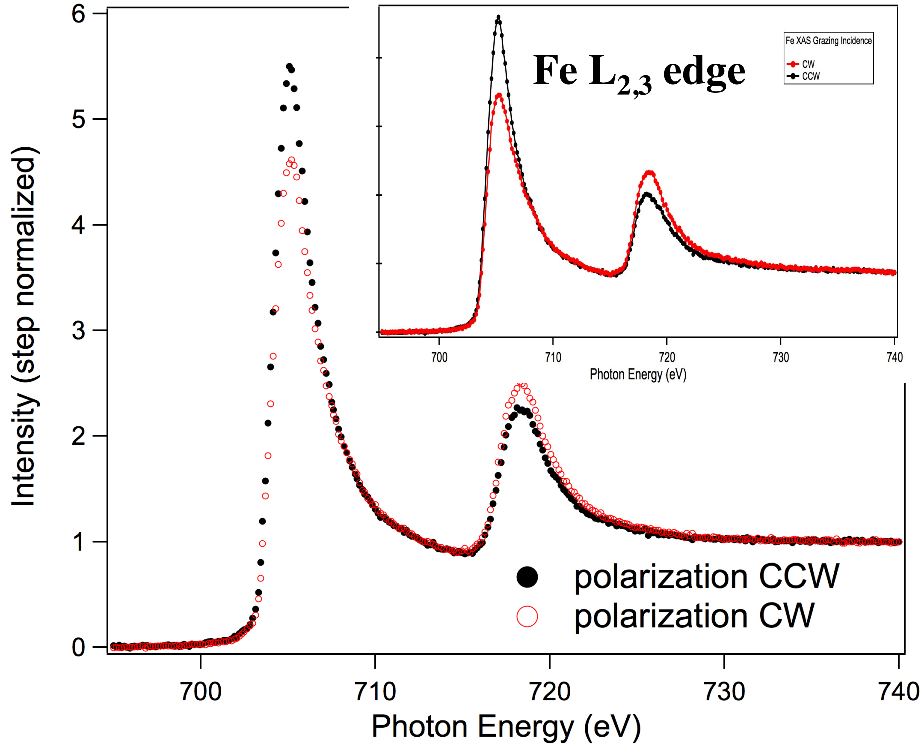


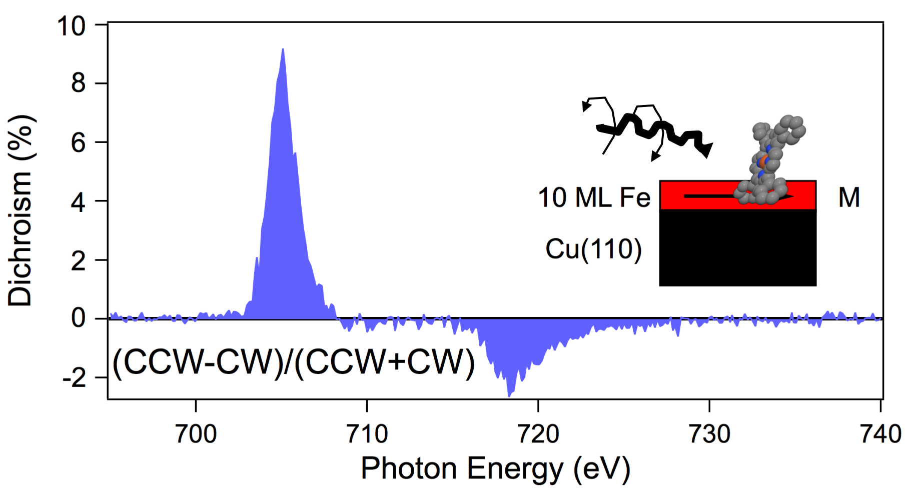


Ferromagnetic









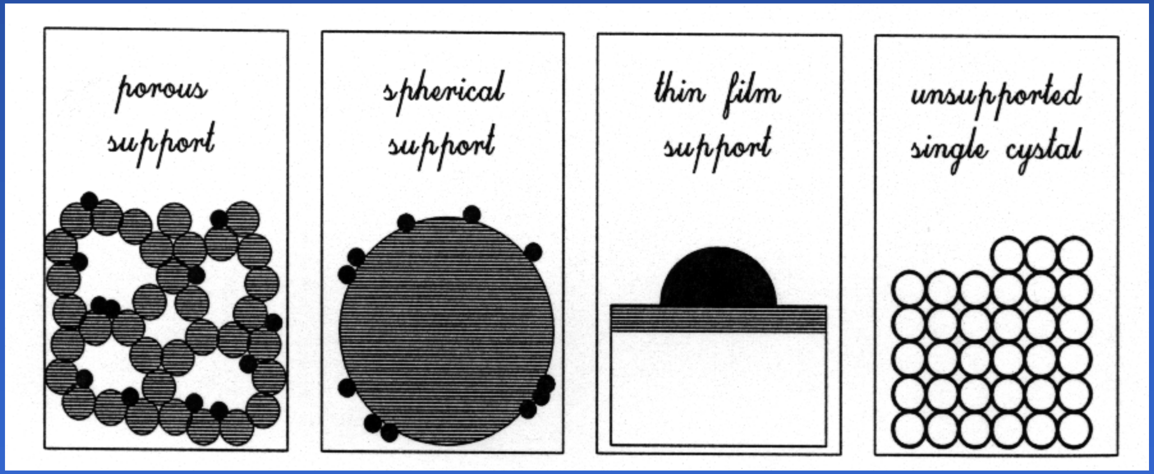
Highly dilute solutions of important metallo-proteins, such as the Fe-containing heme or the Mn-containing photosystem II, provide small spectroscopic signals. New, ultrafast, tunable X-ray sources are required to directly probe the excitation of 3d and 4f levels with suitable sensitivity. Transition metals are important not only for magnetism, but also for catalysis.

CATALYSIS AND THE ENERGY CHALLENGE: STUDYING AND CONTROLLING CHEMICAL REACTIONS

Catalysis—the essential technology for accelerating and directing chemical transformation—is the key to realizing environmentally friendly, economical processes to supply sustainable chemical fuels for our growing energy needs. Producing such fuels as hydrogen from solar water splitting, alcohols from the cellulose of plants, and hydrocarbons from recycled carbon dioxide requires the design and optimization of a diversity of novel catalytic processes.

Third generation photon sources provide the possibility of obtaining a complete picture of chemical reaction dynamics, thereby enabling the rational design of chemical transformations. The electronic and geometric structures of catalytic materials under reaction conditions determine their efficiency, selectivity, and lifetime. Catalyst structure and morphology typically change under reaction conditions and over time. Even extended solid surfaces, traditionally thought to be static, may undergo thermal fluctuations and rearrangement, in addition to undergoing substantial changes in morphology as the catalyst makes and breaks bonds with the reactants and products. Because the geometric and electronic structures of catalysts are inextricably linked, a comprehensive knowledge of both is central to controlling catalytic efficiency and selectivity.

Designing a model catalyst system



Complexing

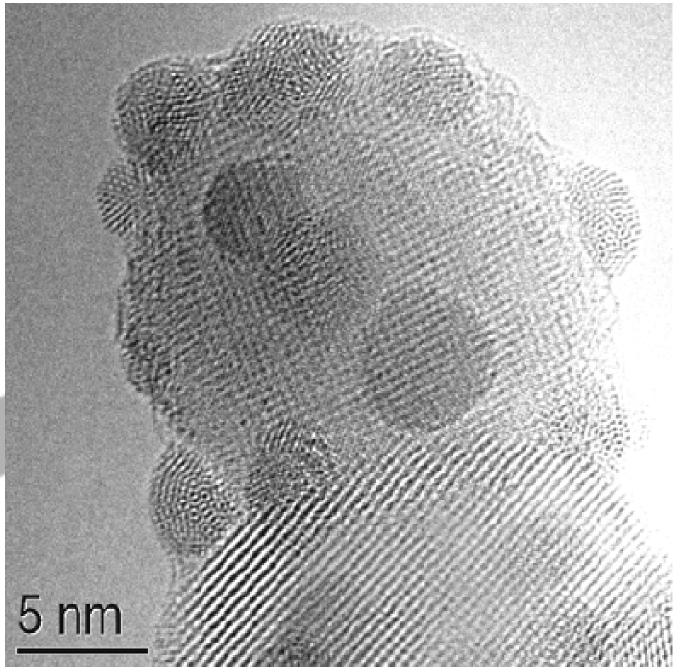
←

Approach - Simplify the problem without losing relevance

G.A. Somorjai et. Al. , "Surface Science Approach to Modeling Supported Catalysts" Catal. Rev. Sci. Eng. 39, 77-168, 1997.

J.W. Niemantsverdriet et. al. , Eds. Modeling Supported Catalysts in Surface Science, Top. Catal. Vol. 13

Knowledge of the reaction mechanism is central to understanding catalytic reactions. The atomic structure, energies, and electronic structure of the initial reactant state, the final product state, and the activated complex transition state must be characterized for each elementary step.

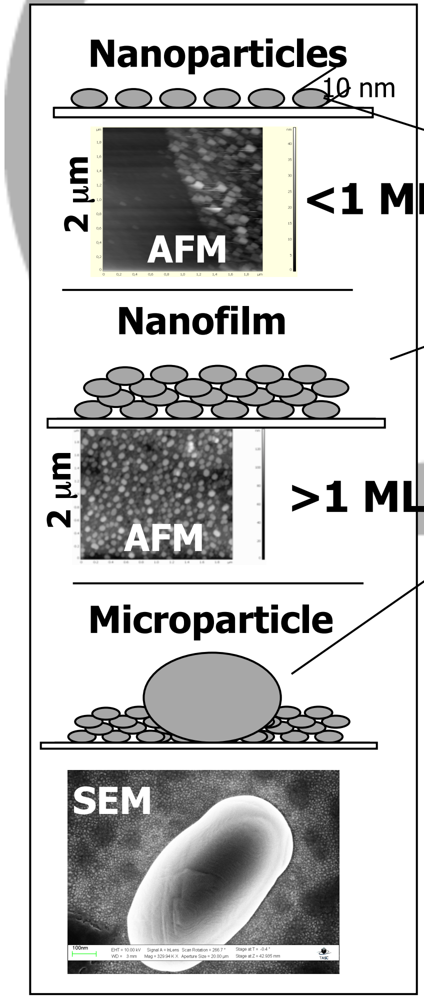


The design of improved catalysts and photocatalysts requires:

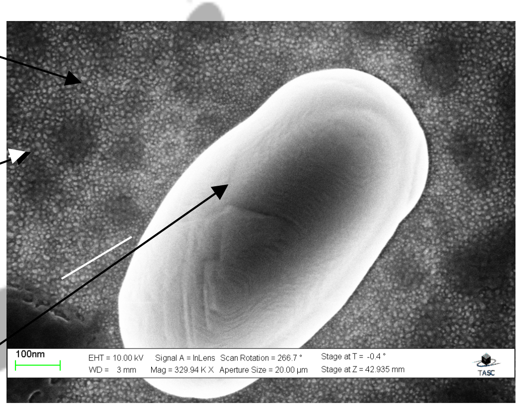
- Temporal measurements on time scales ranging from 10^{-4} - 10^{-18} s for electronic excitations and atomic rearrangements, to 10^{4}s for macroscopic morphological changes.
- Nanometer spatial resolution, since catalysts are by design inhomogeneous materials.

Photoemission microscopy will provide a key approach to this challenge, requiring the highest possible average brilliance of the source in the soft X-ray range.

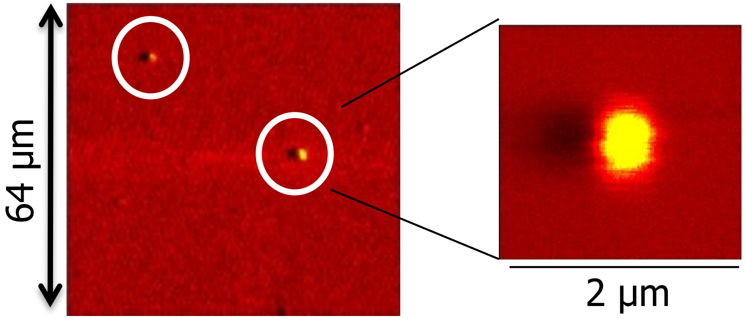
IMAGING STRUCTURE AND REACTIVITY OF INDIVIDUAL NANOPARTICLES



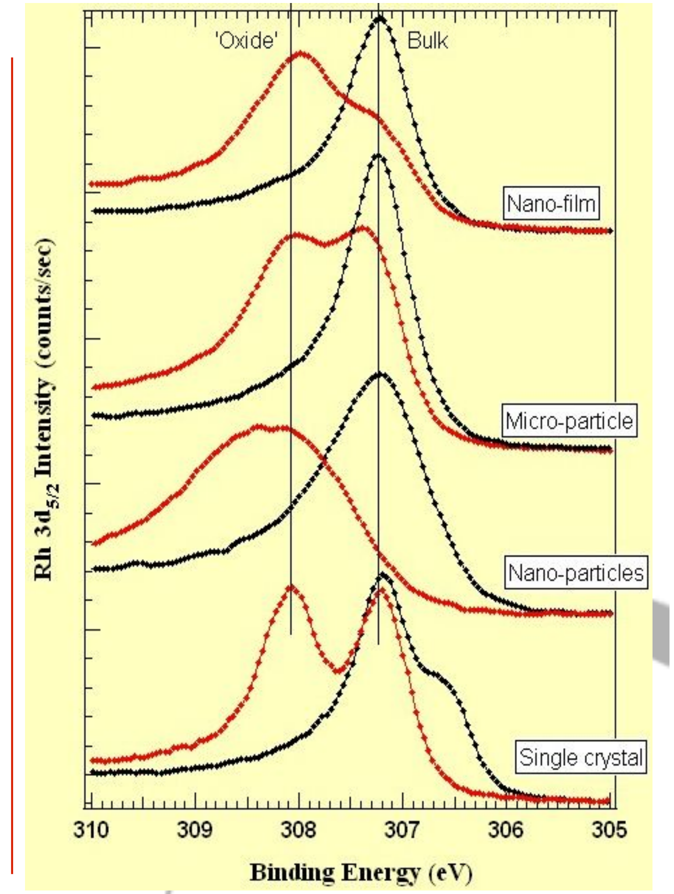
Rh on MgO/W(110) species are highly-defected due to non-thermic evaporation



SPEM Rh3d maps

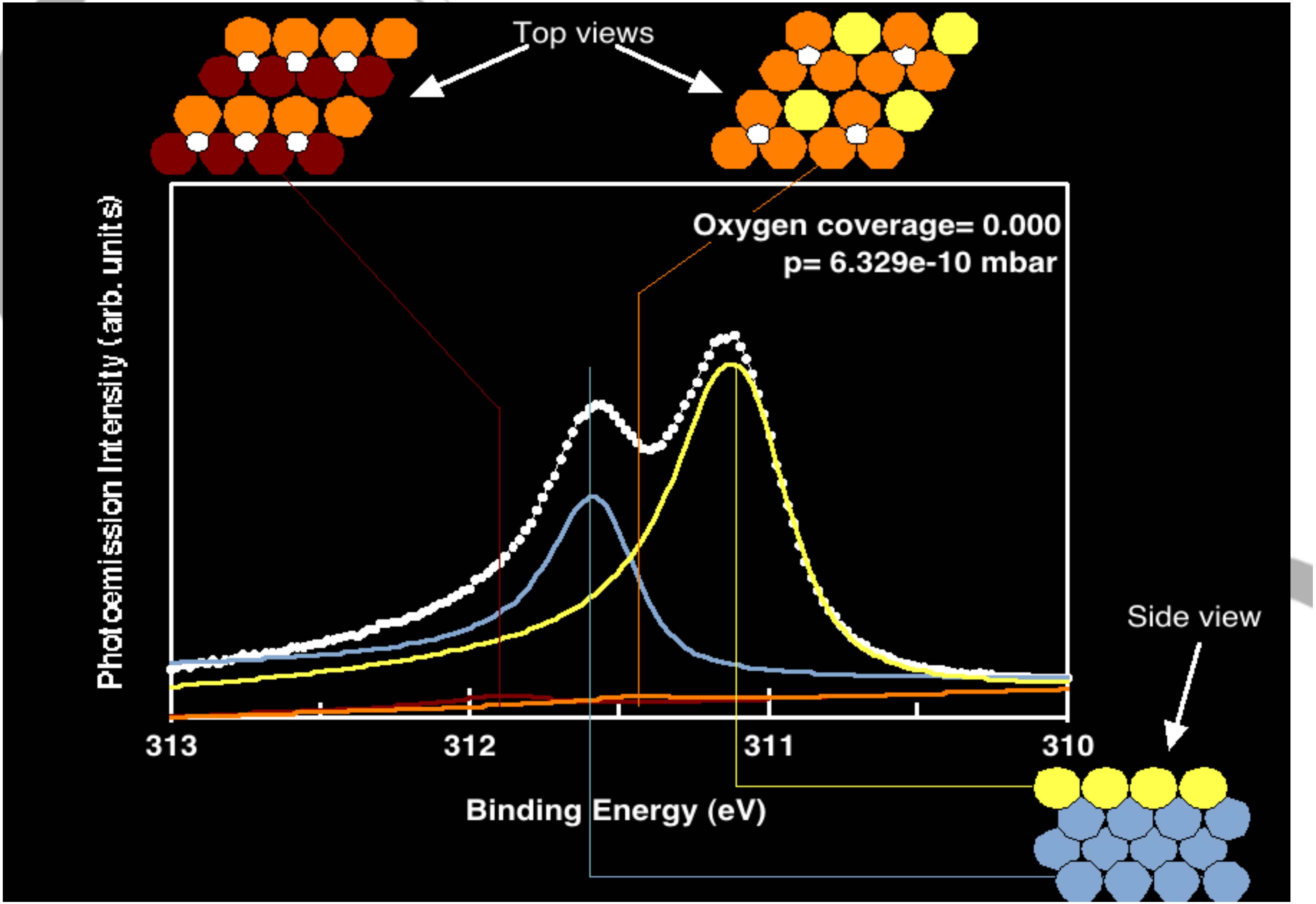


Oxidation/reduction reactions



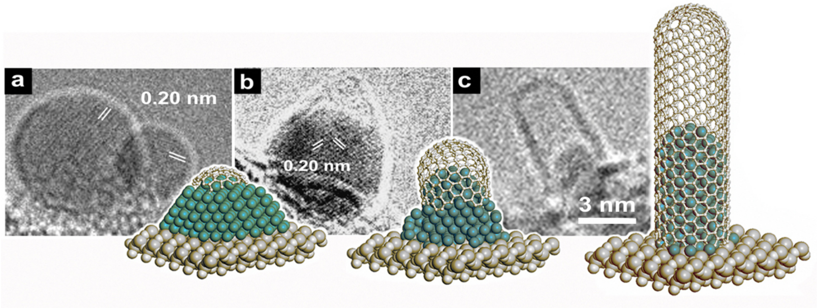
- The nanoparticles/nanofilm possess different oxidation/reduction ability than the micro particle
- Reducing rate: Micro-part.> Nano-crystalline film > Nano-particles
- Micro-particles of similar sizes show variation in the reactive properties: different structure, local environ.

Rh(111): evolution of Rh $3d_{5/2}$ during O_2 dosing



Movies of a Chemical Reaction: Capturing and Controlling Transition States

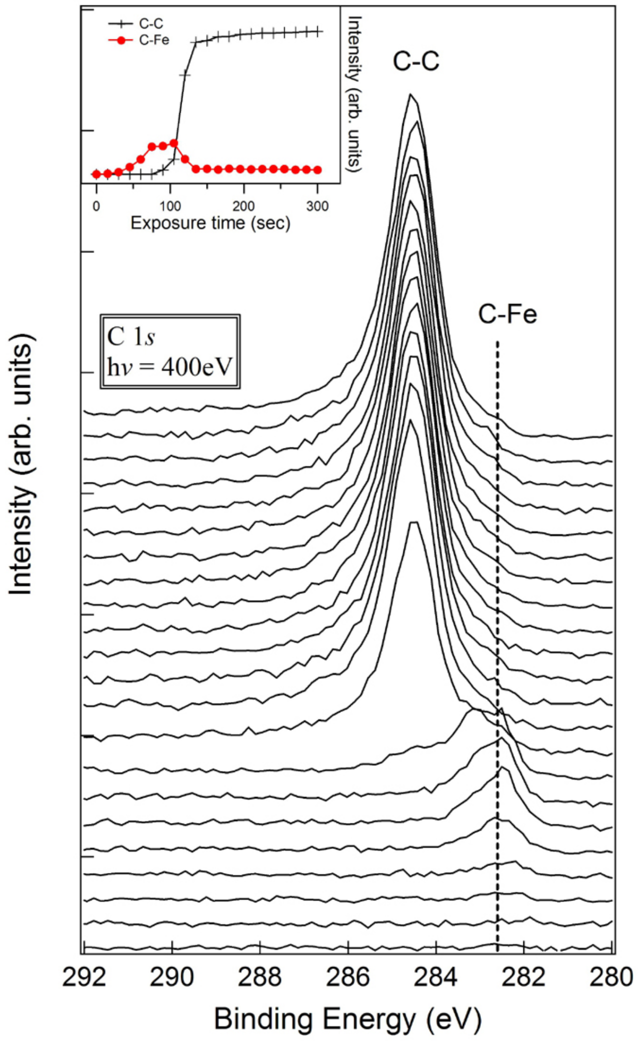
Catalyst dynamics during surface-bound carbon nanotube nucleation



For SWNT we observe crystalline phase contrast from the transition metal catalyst nano-particles. The 0.20 nm reflection observed is expected for metallic fcc Ni(111), but also for Ni_2O_3(200) and Ni_3C (113).

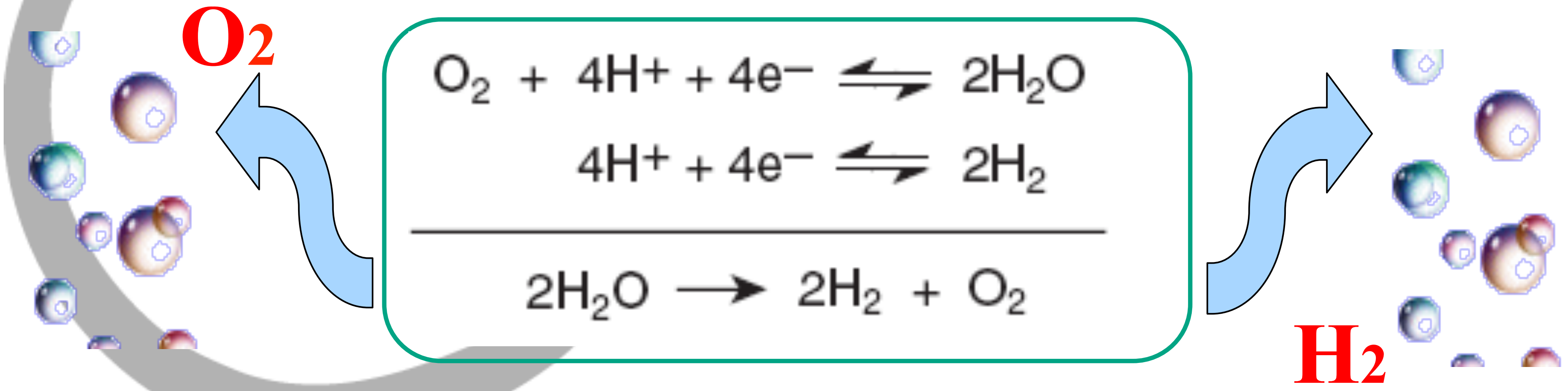
We have highlighted some of the progress made towards an atomistic CNT growth model by combining in-situ TEM and XPS. Selective acetylene chemisorption and the formation of a carbon-rich surface layer were observed on otherwise crystalline transition metal nano-particles. Structural selectivity is determined by the dynamic interplay between carbon network formation and catalyst particle deformation.

The catalyst is active in its metallic state; Fe and Ni films that were deliberately oxidised before annealing showed a lower/no nanotube yield on C_2H_2 exposure.



Splitting of water into **Hydrogen** and **Oxygen**

Thermodinamic and Kinetic challenges



$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$$

$$4H^+ + 4e^- \rightleftharpoons 2H_2$$

$$2H_2O \longrightarrow 2H_2 + O_2$$

- Thermal splitting of water requires temperatures above 2500°C

-Electrochemical splitting of water (ΔE= 1.23 V/e-)

the catalytic $2H_2O/O_2$ half reaction means

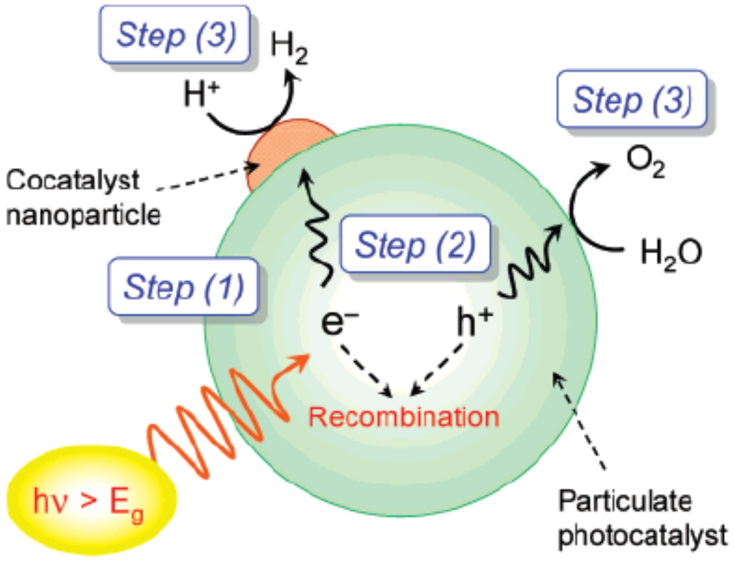
- ✓ **the removal of 4-electrons from 2 H_2O molecules**
- ✓ **the removal and translocation of 4 protons**
- ✓ **the formation of a new oxygen-oxygen bond.**

Water would be the ideal and most sustainable source for H_2 and this H_2 generation concept dates back two centuries. The power for water electrolysis could come from a virtually inexhaustible and freely available energy source like solar energy.

One-step catalysis process

$2\,H_2O \rightarrow 2H_2 + O_2 \quad \Delta V = 1.23V,\ \Delta G = 238kJ/mol$

- Step 1: Photon with energy above 1.23eV ($\lambda <$ 1000 nm) is absorbed.
- Step 2: Photoexcited electrons and holes separate and migrate to surface.
- Step 3: Adsorbed species (water) is reduced and oxidized by the electrons and holes.

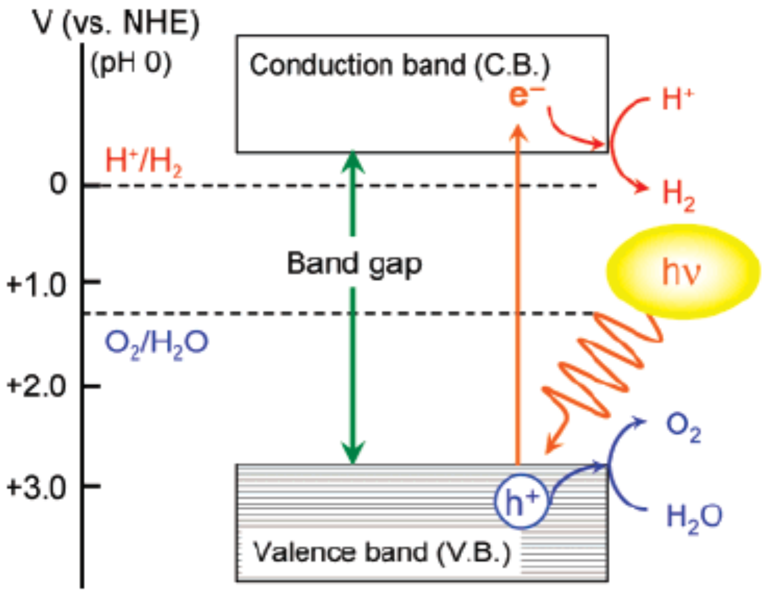


Photocatalyst material requirements

- **Band gap**: Band gap>1.23eV but sufficiently small to make efficient use of solar spectrum (<3.5 eV). Band levels suitable for water splitting.

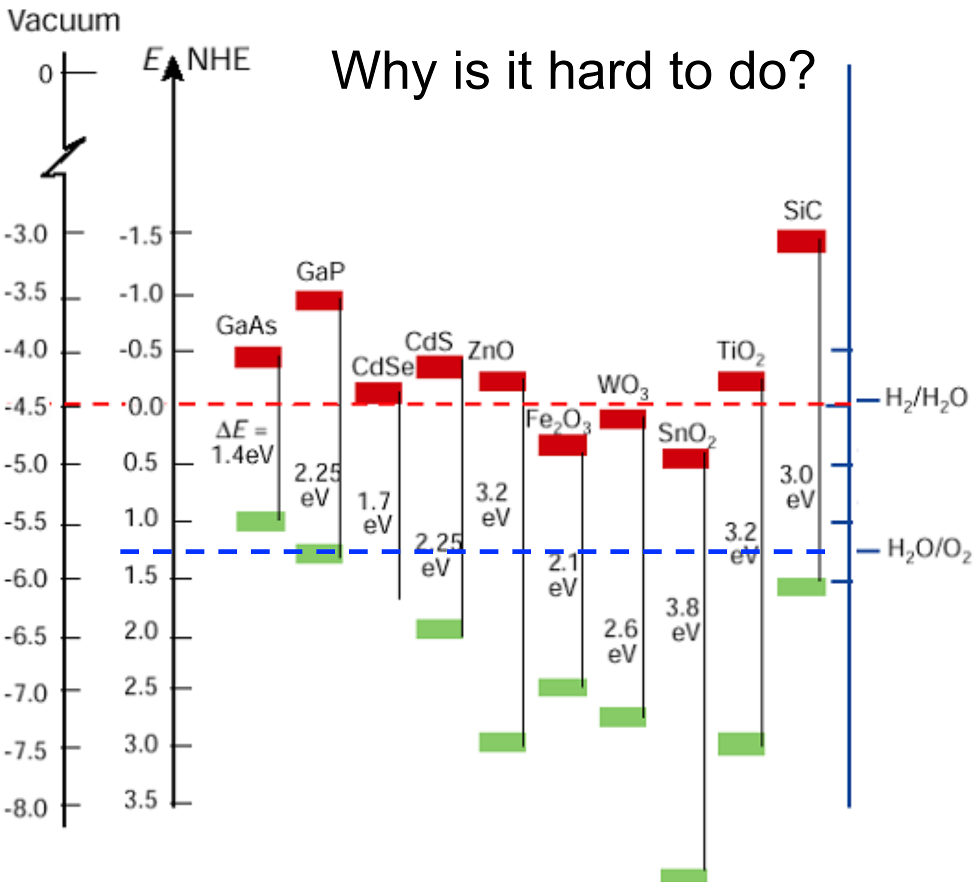
- **High Crystallinity**: Defects can act as recombination sites.

- **Long term stability**: Charge transfer used for water splitting and not corrosion.

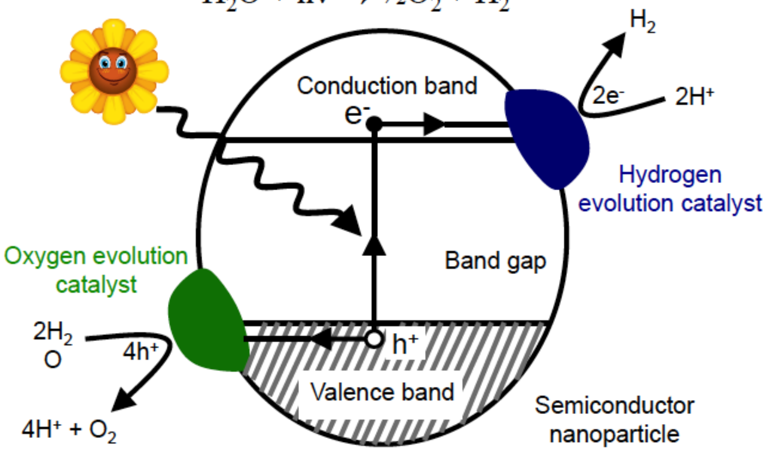


Why is it hard to do?

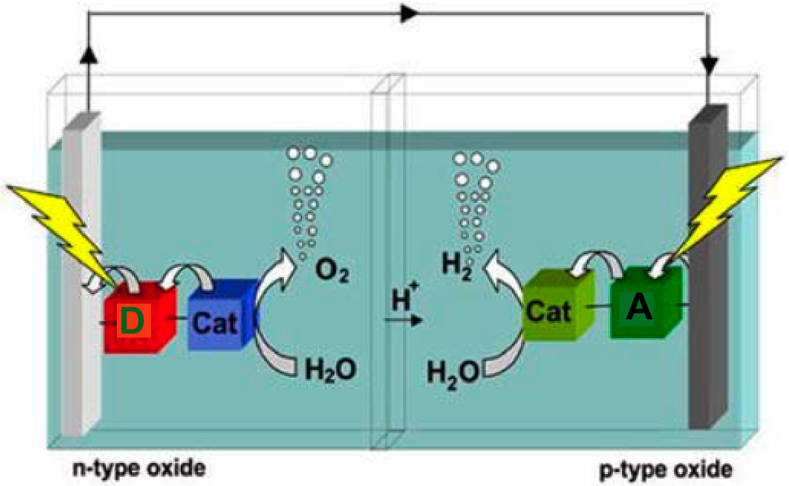
- Oxides
  - Stable but efficiency is low (large gap)
- III-Vs
  - Efficiency is good but surfaces corrode
- Approaches
  - Dye sensitization (lifetime issues): Porphyrins, phtalocyanins, ferrocenes, etc..
  - Surface catalysis

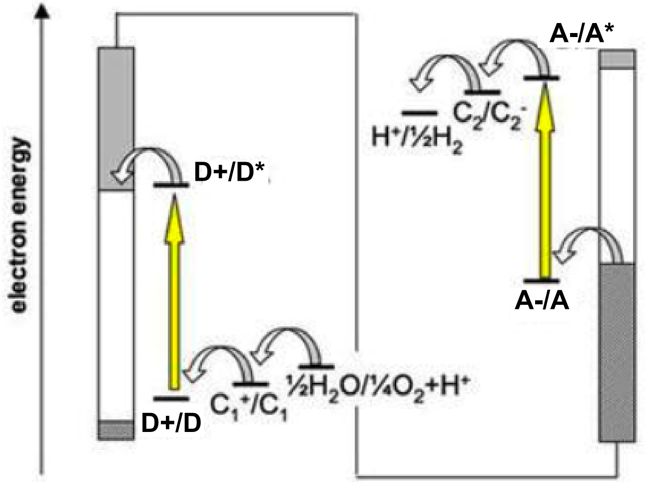


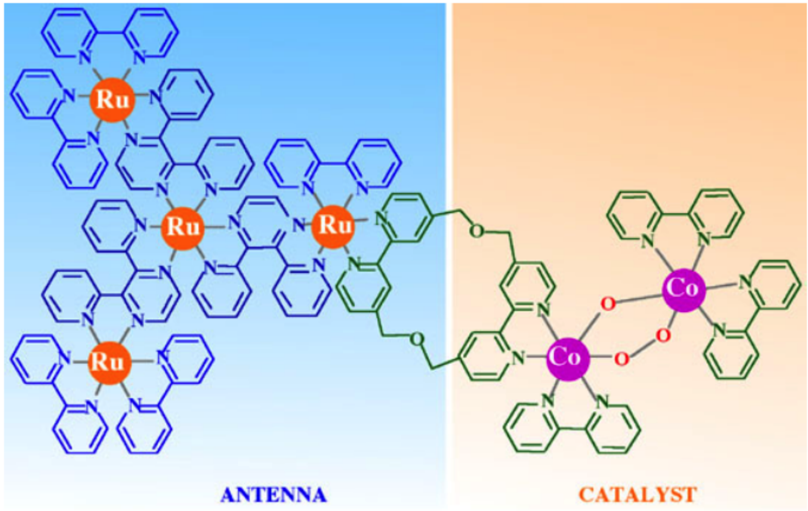
$H_2O + h\nu \rightarrow ½O_2 + H_2$

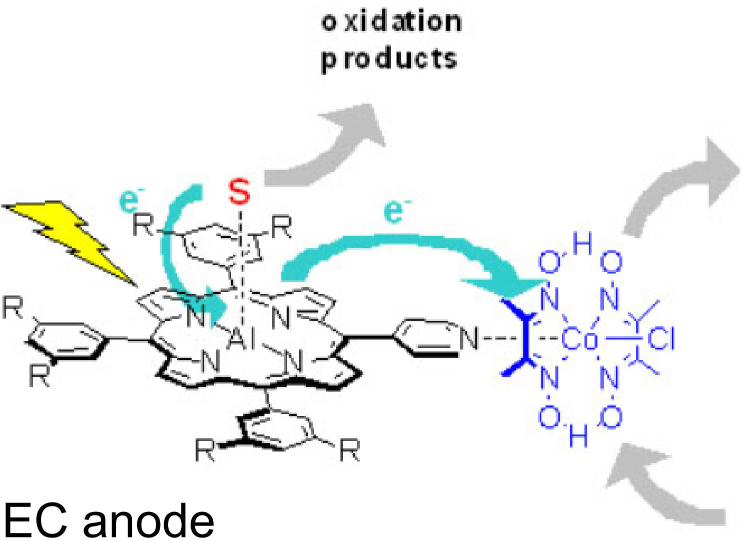


Linsebigler, Lu, Yates, Chem. Rev. **95**, 735 (1995), Grätzel, Lewis, Domen, Li ….

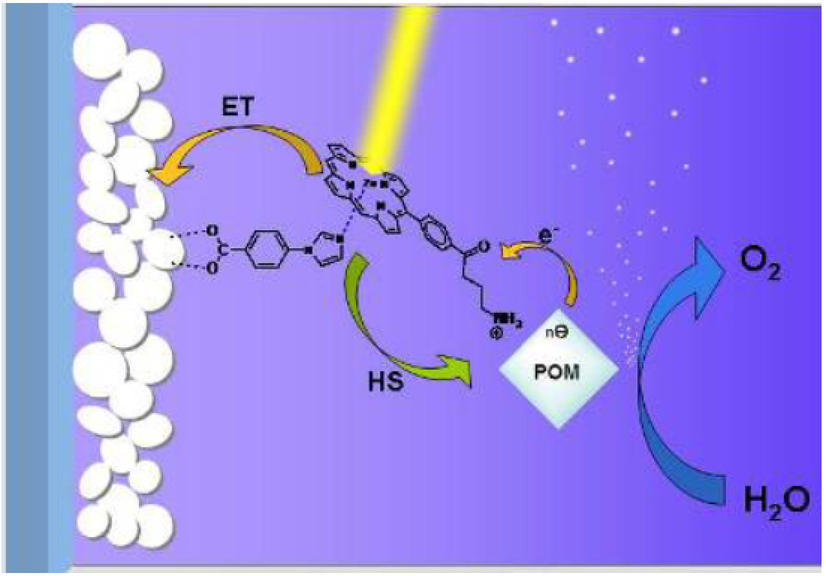


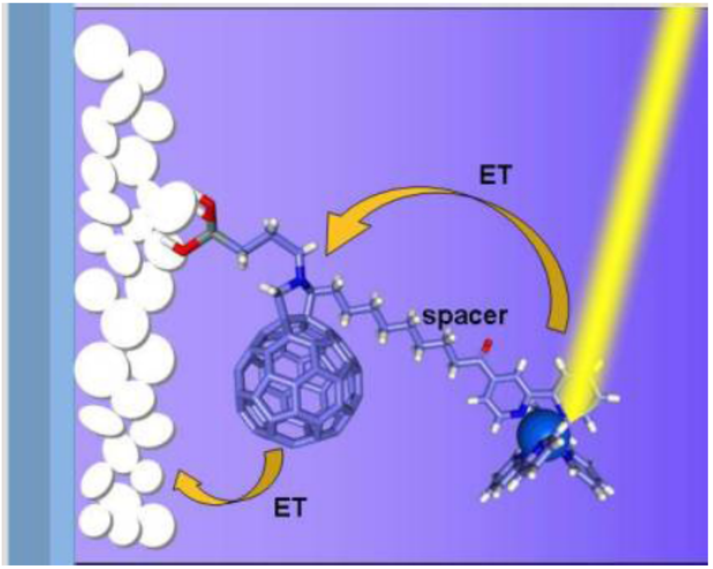






Possible photo-chain structures for the OEC anode



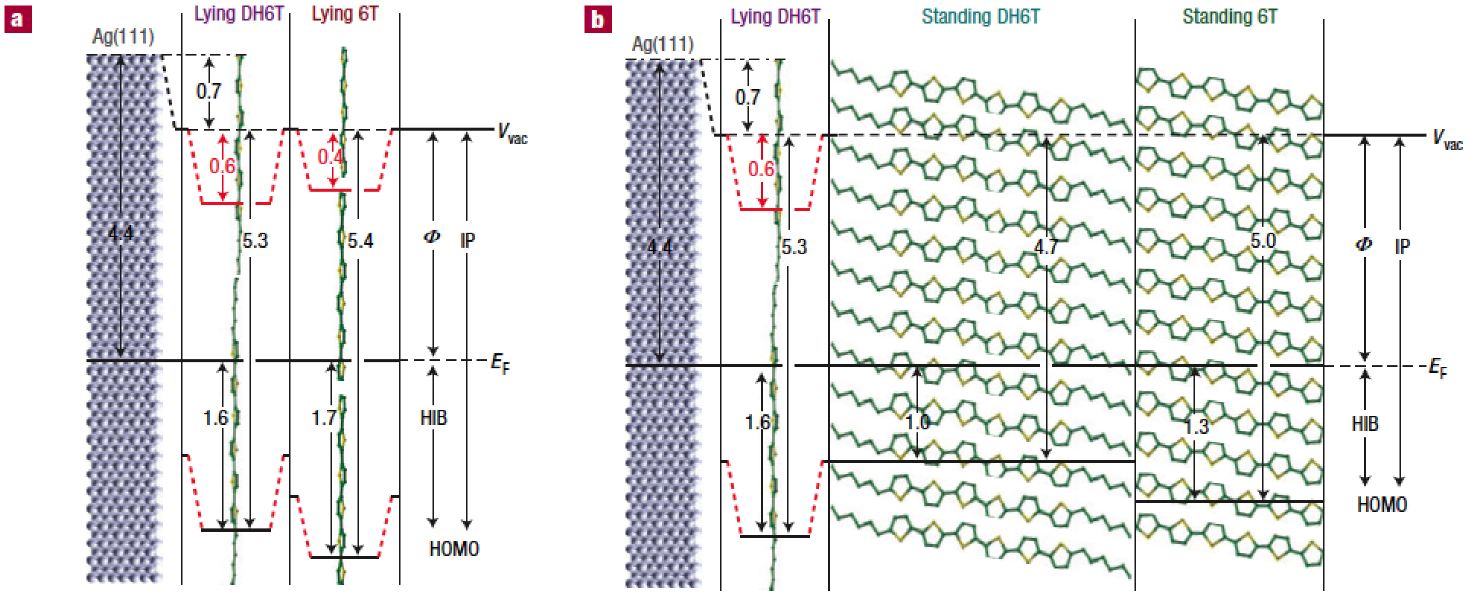


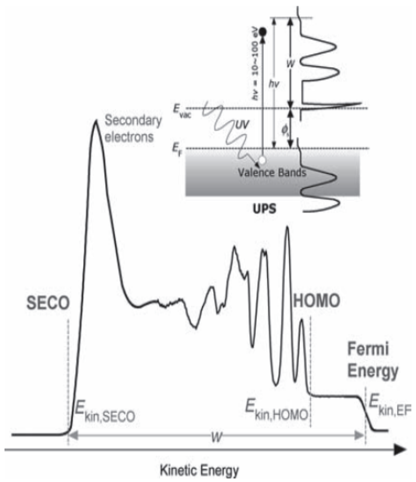
organic/organic and organic/inorganic interfaces. Problems:

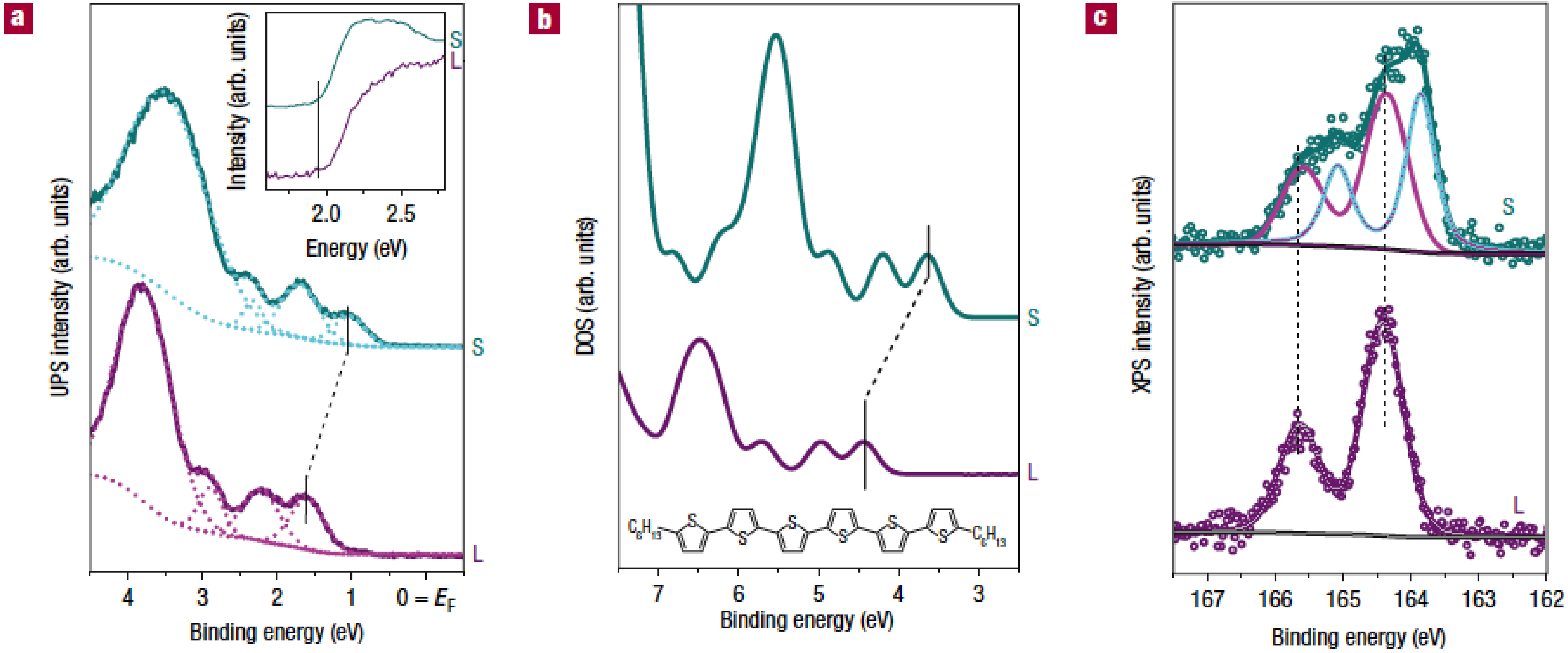
Bands alignment

Adsorption geometry

Photoemission

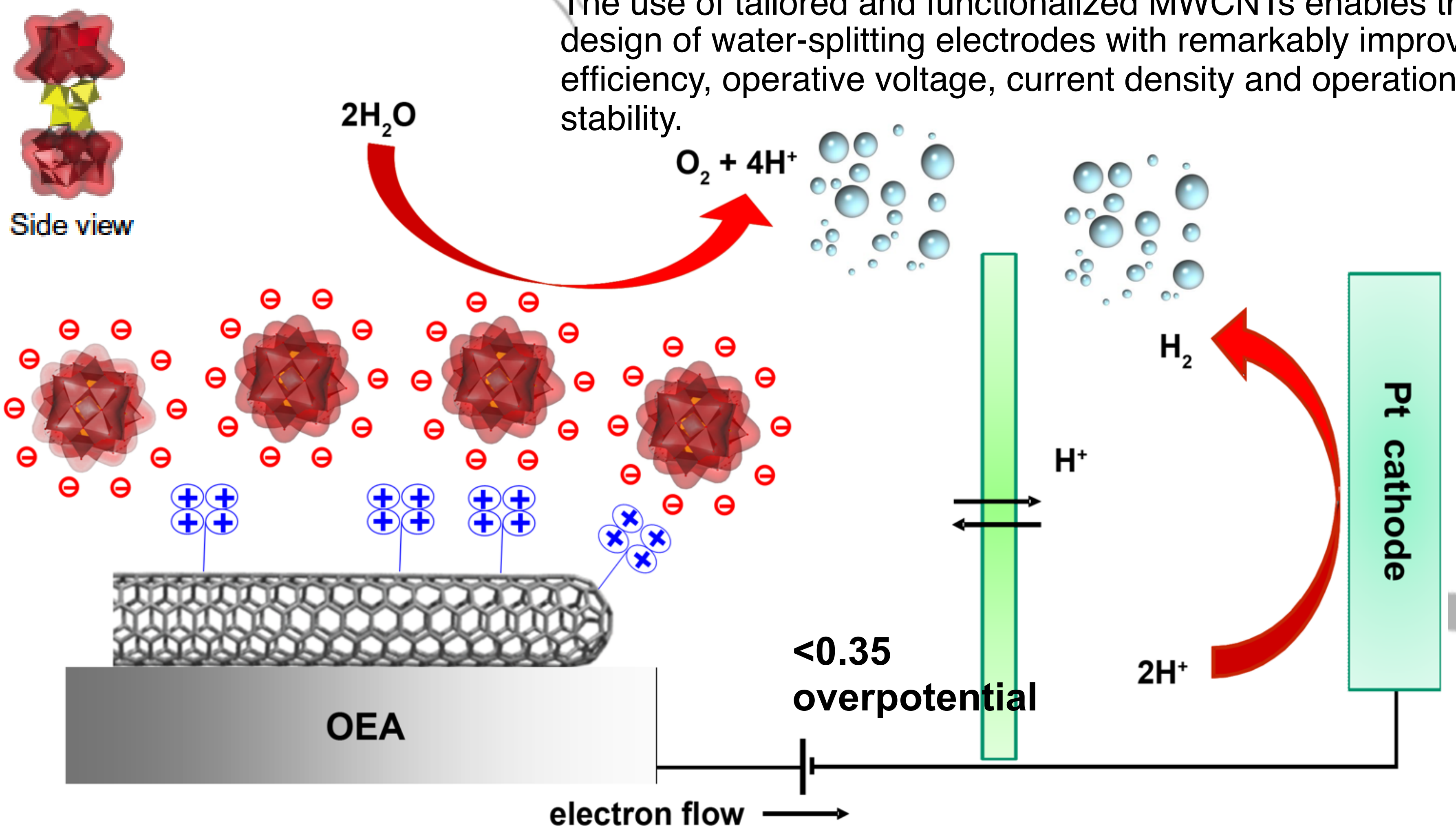






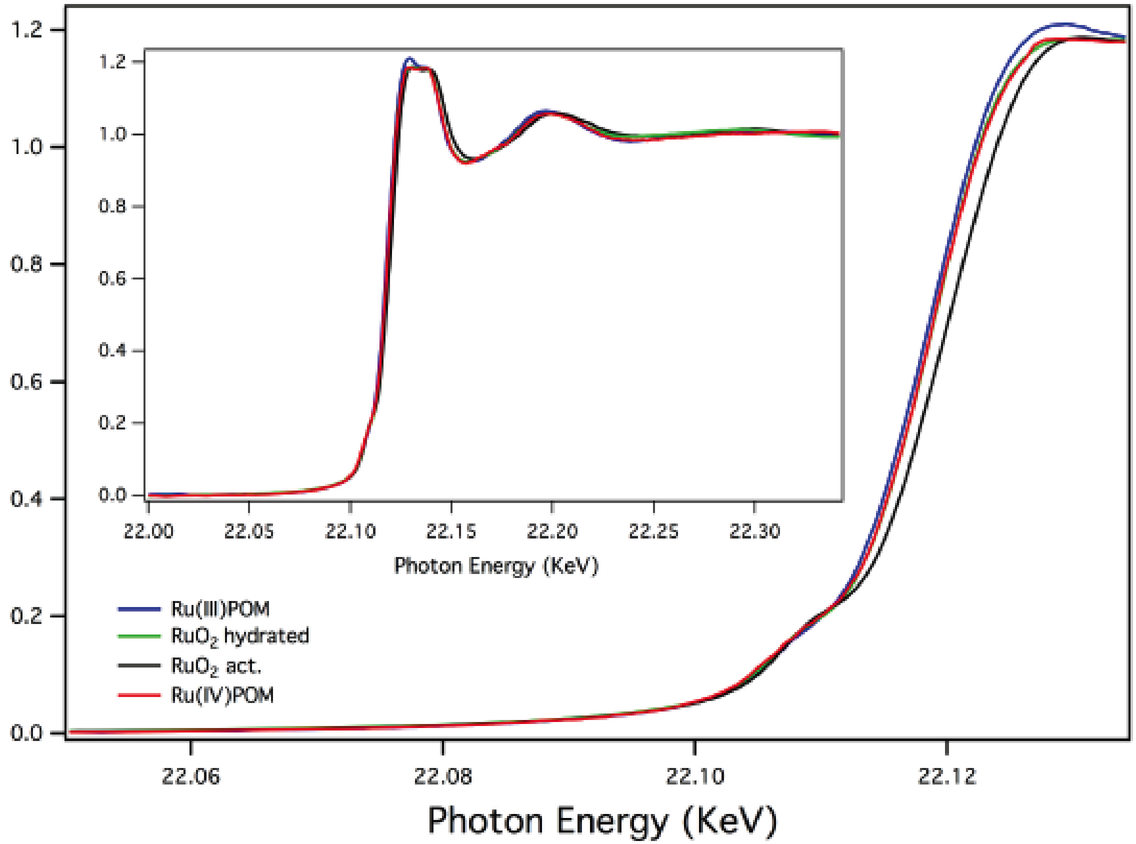
$Ru_4POM@CNTs$: water splitting electrode

The use of tailored and functionalized MWCNTs enables the design of water-splitting electrodes with remarkably improved efficiency, operative voltage, current density and operational stability.



Boosting effect in O_2 evolution with CNTs: TOF (turn over frequency) up to 350 h^{-1}, applied overpotential as low as 0.35V and TON (turn over number) ~ 40

Nature Chem. **2010**, *2*, 82, 831; *Chem Sus Chem* **2011**, Early View



EXAFS spectra demonstrate that the core of Ru4POM behaves exactly as the RuO_2 hydrated: the big advantage is that using the Ru4POM you have very small cluster of RuO_2, i.e. a lot of active surfaces

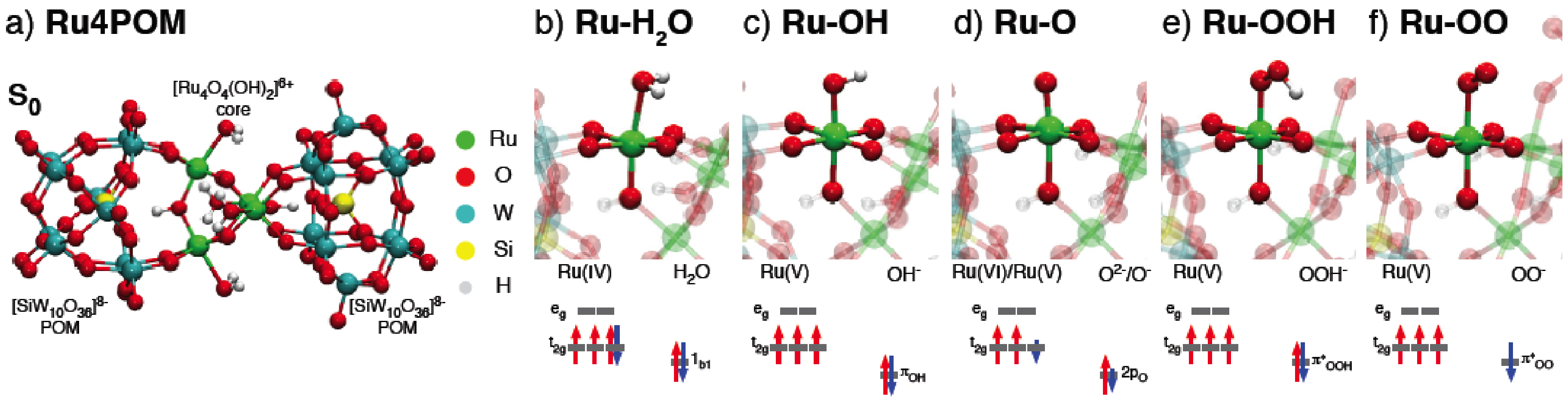


Fig. 1. a) Structure of the Ru4-POM in the resting state S_0. b-f) Octahedral environment around one Ru center of Ru4-POM, ligands involved in water oxidation and schemes of the corresponding electronic structure of the highest occupied molecular orbitals for the Ru-ligand moyeties.

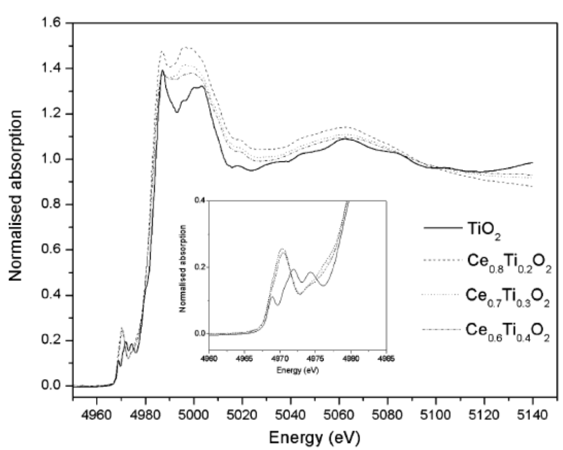
Another use of EXAFS for oxygen storage

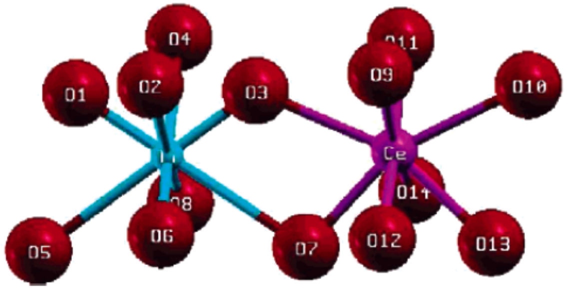
Origin of Enhanced Oxygen Storage Capacity of $Ce_{1-x}Ti_xO_2$ Compared to CeO_2

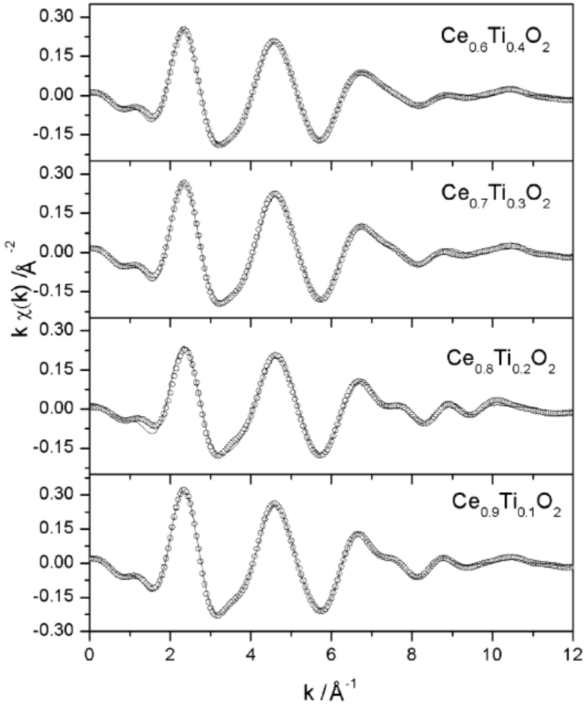
oxygen storage capacity (OSC) = The amount of oxygen that can be released under reducing conditions and can be taken up under oxidizing conditions

Found a chemical origin for the increase in the OSC of CeO_2 upon Ti substitution, $Ce_{1-x}Ti_xO_2$ ($x = 0.0\text{-}0.4$)

EXAFS study of mixed oxides at the Ti K-egde showed that the local coordination of Ti is 4:4, with Ti-O distances of 1.9 and 2.5 Å (strongly and weakly bonded oxygen with different valencies)



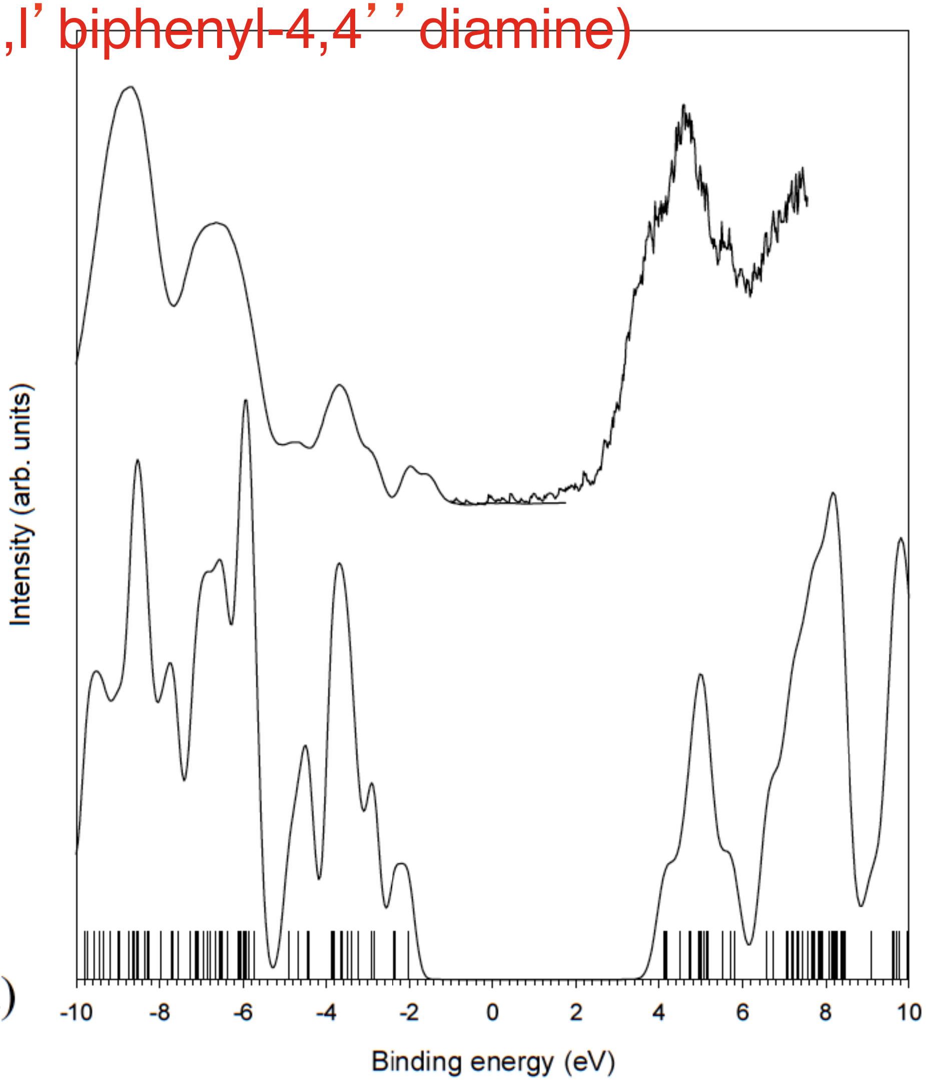




Bond valence analysis of the microscopic structure and energetics determined from first principles is used to evaluate the strength of binding of different oxygen atoms and corresponding vacancies. Weakly bound oxygens in $Ce_{1-x}Ti_xO_2$, have lower valency and are responsible for the higher oxygen storage capacity in the mixed oxides than in pure CeO_2

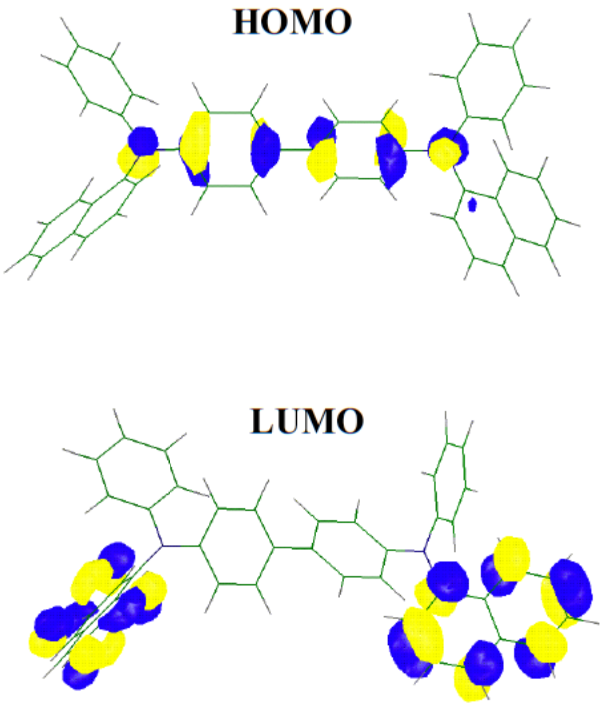
Photoemission from molecules: Small system big problem

α-NPD (N,N’-diphenyl-N,N’-bis(l-naphthyl)-l,l’ biphenyl-4,4’’ diamine)



(a)

DFT calculations are good to find the orbital electron density but not good for the orbital binding energies

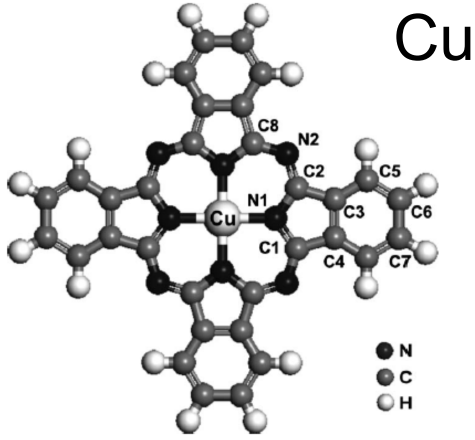


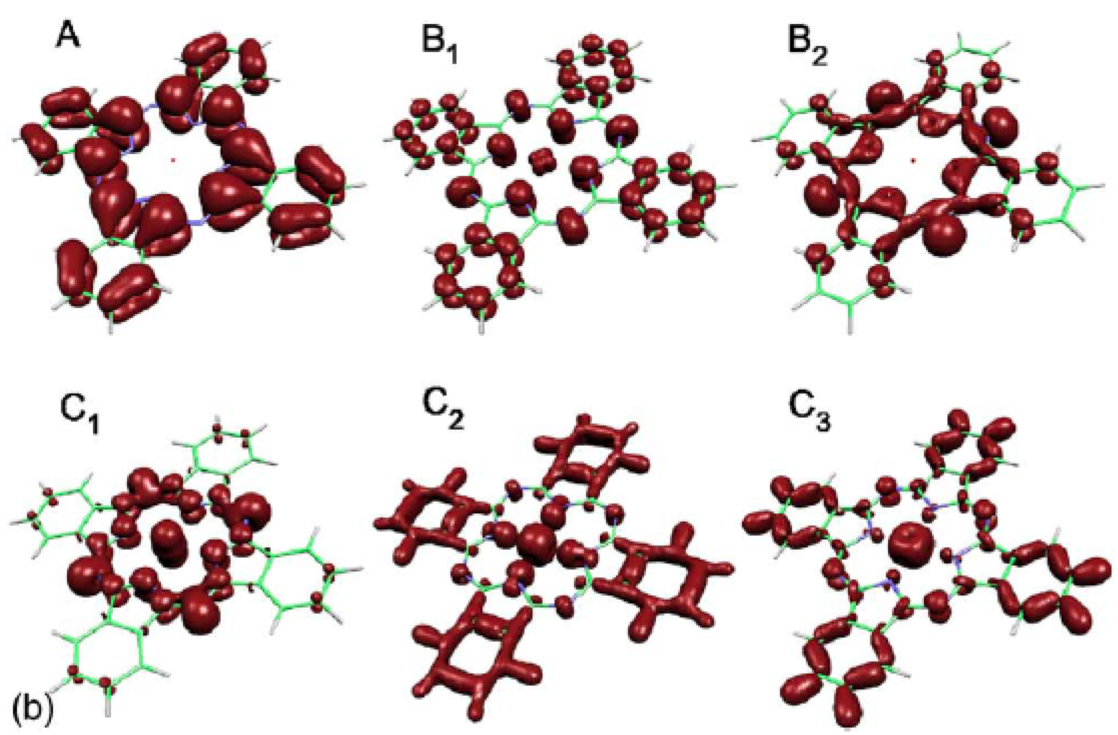
(b)

DFT calculation (energy scale compressed by a factor 1.3)

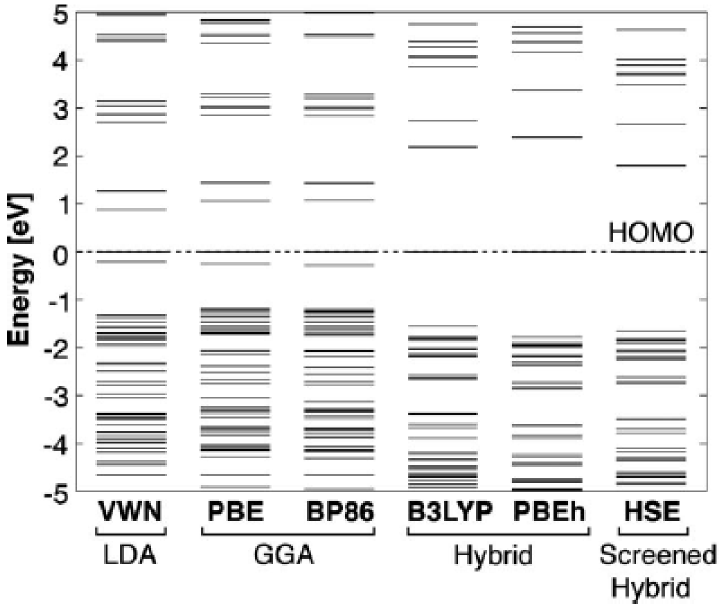
DFT when applied to isolated molecular systems in general gives good results for the description of neutral excitations and for the calculation of optical spectra

CuPc

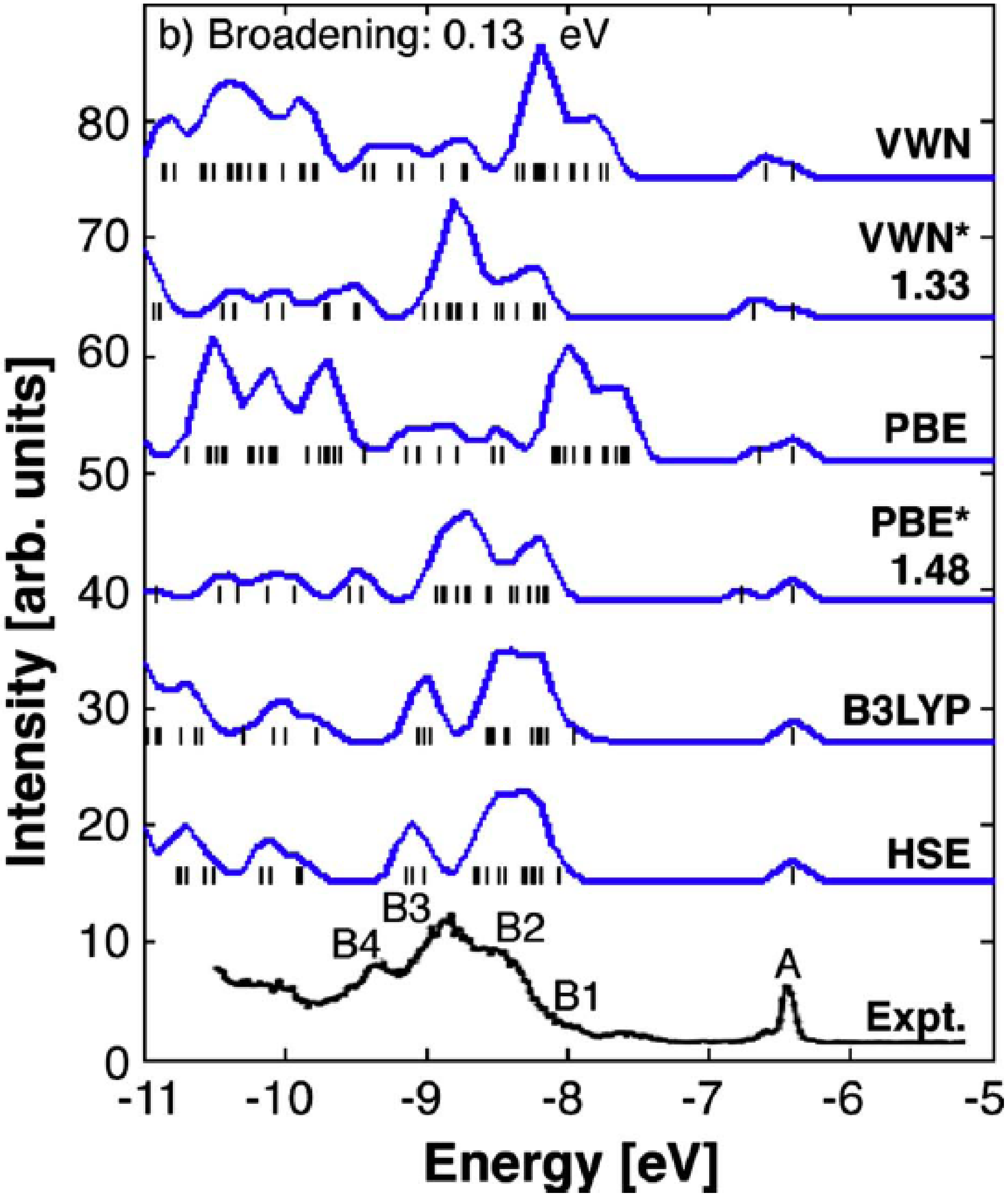


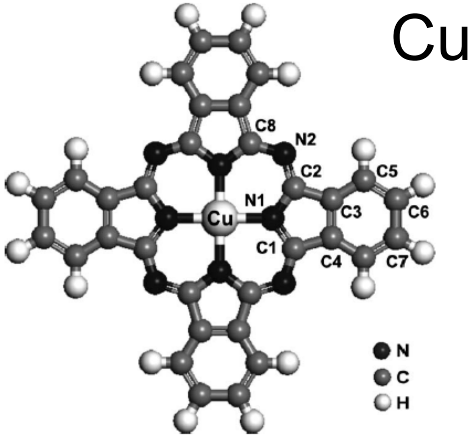


DFT method using different exchange-correlation functionals



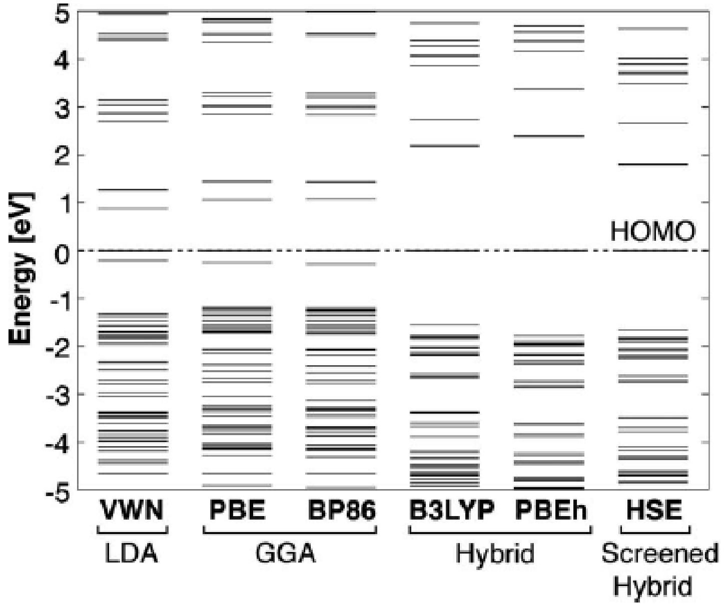
but for photoemission spectra (N-1 excited system)…





CuPc

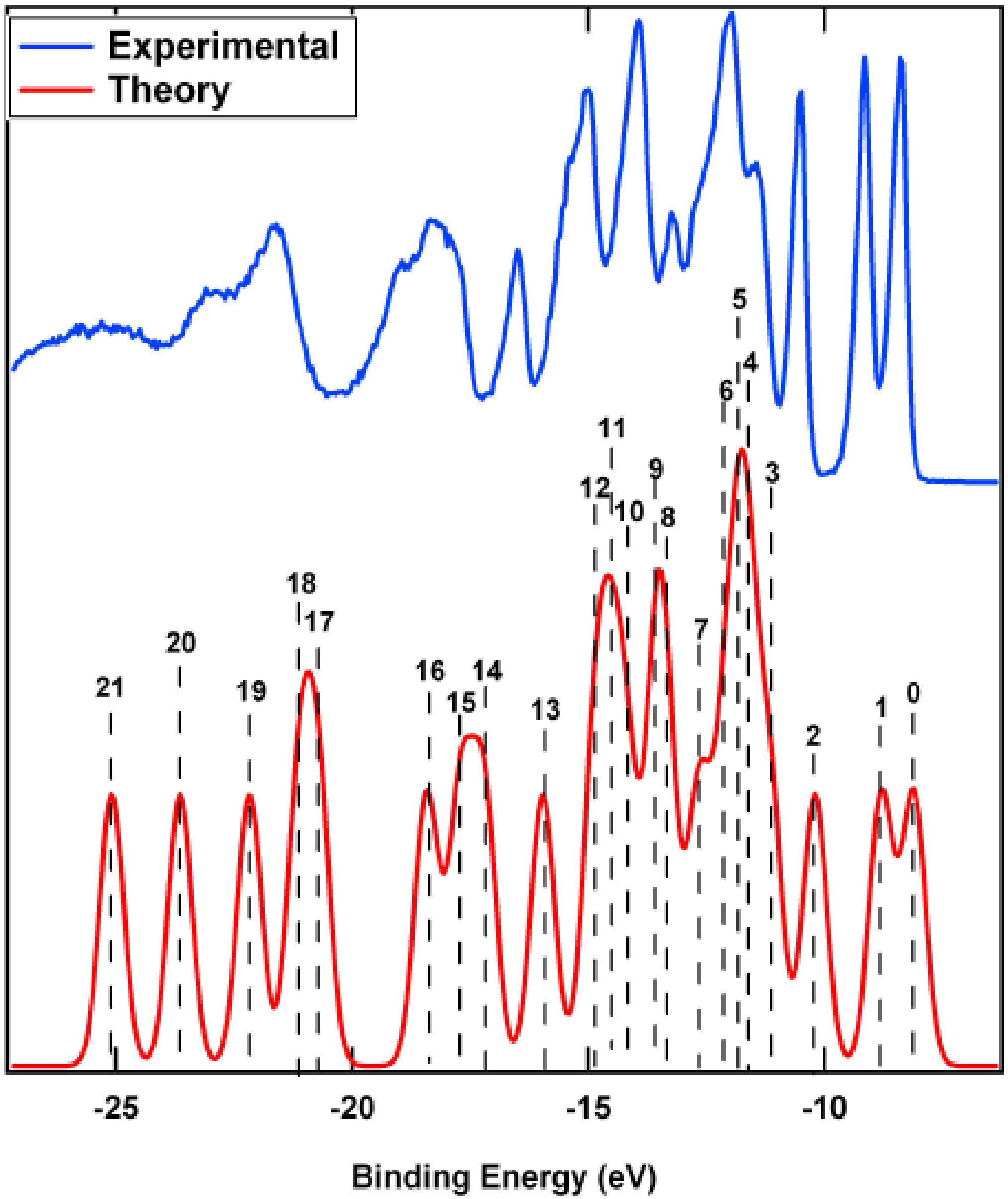
DFT method using different exchange-correlation functionals



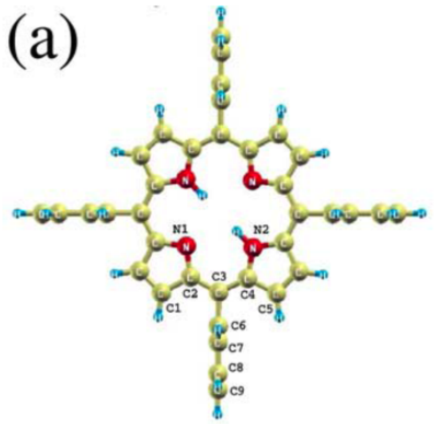
Photoemission on a small molecule

Indene

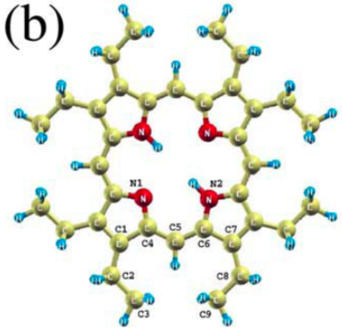
First-principles methods based on many-body perturbation theory, such as those resulting from the so-called GW approximation in which the self-energy operator is expressed as the convolution in frequency of the dynamically screened Coulomb interaction (W) and Green's function (G).



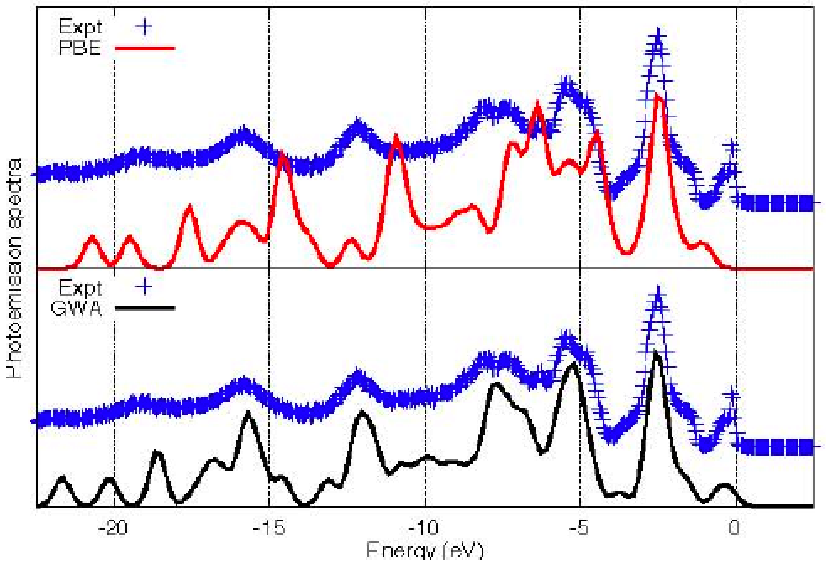
Photoemission on big molecules

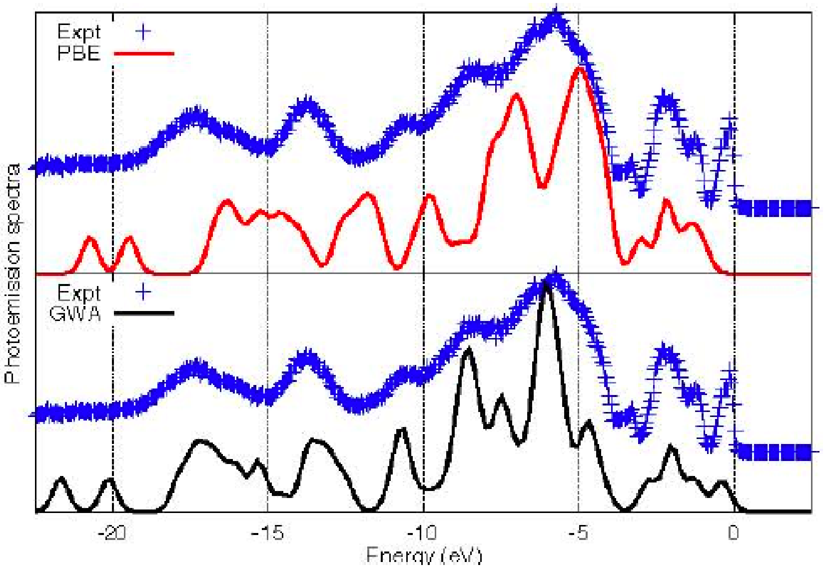


TPP



OEP



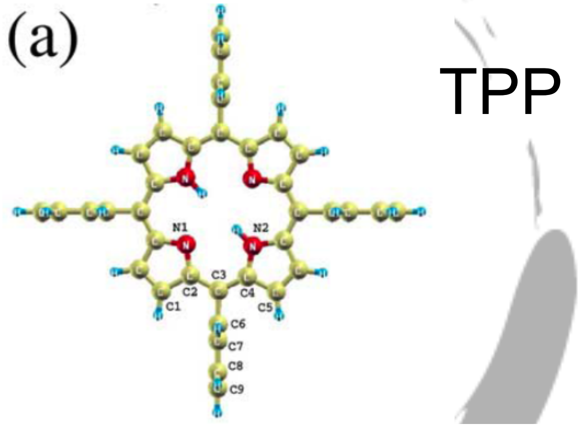


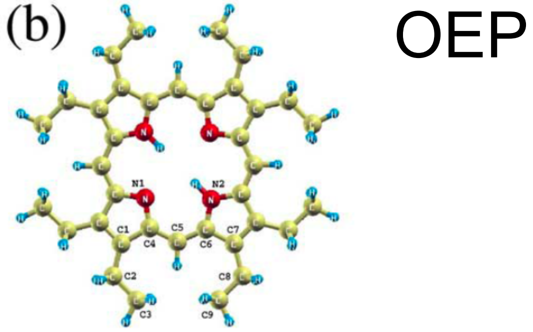
DFT

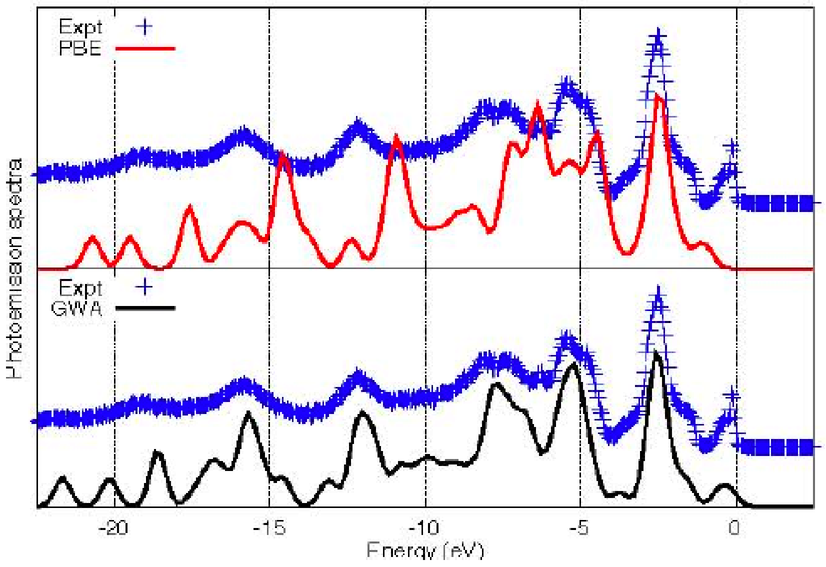
GW

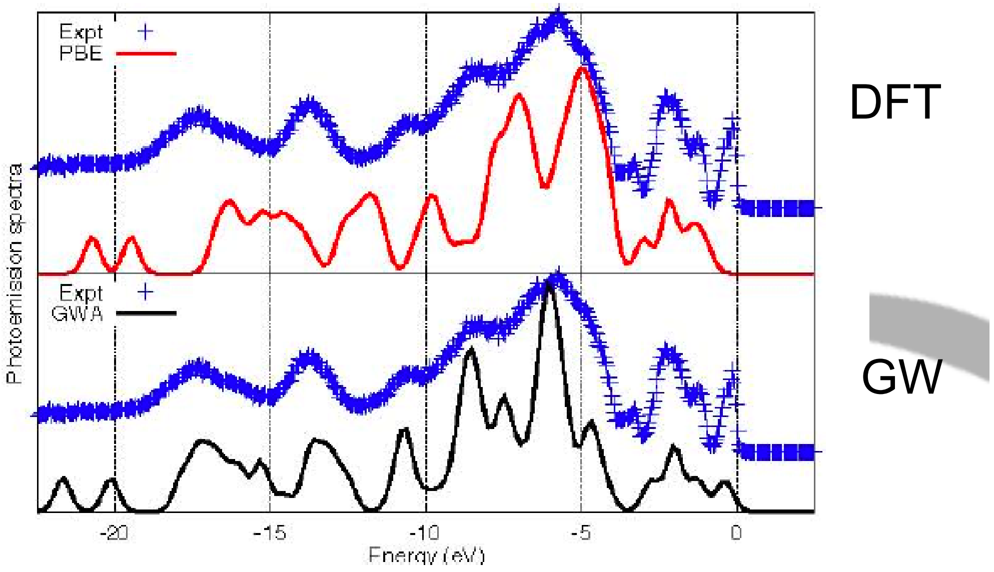
GW ionization potential IP=6.05 eV for TPP and IP=5.7 eV for OEP, Eg=4.4 eV for both
DFT-PBE ionization potential IP =4.8 eV for TPP and IP =4.5 eV for OEP, Eg=1.9 eV
Experimental: IP =6.4 eV for TPP and IP =6.24 eV for OEP

Photoemission on big molecules



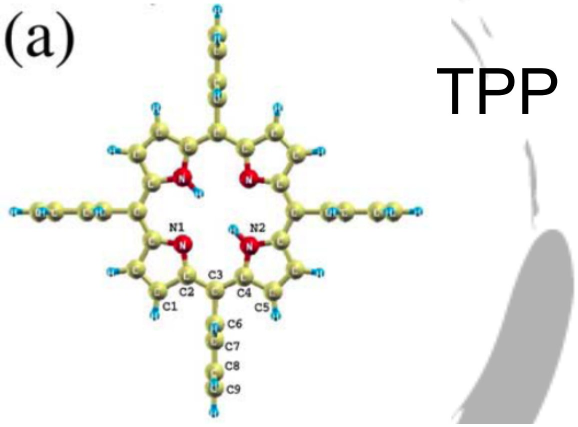


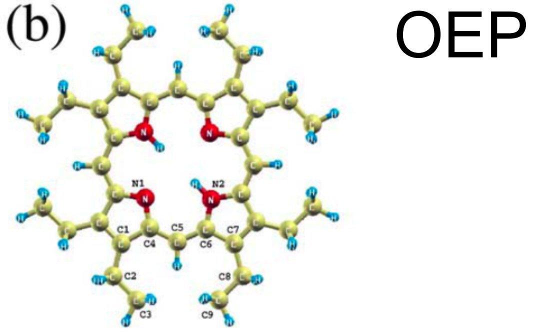


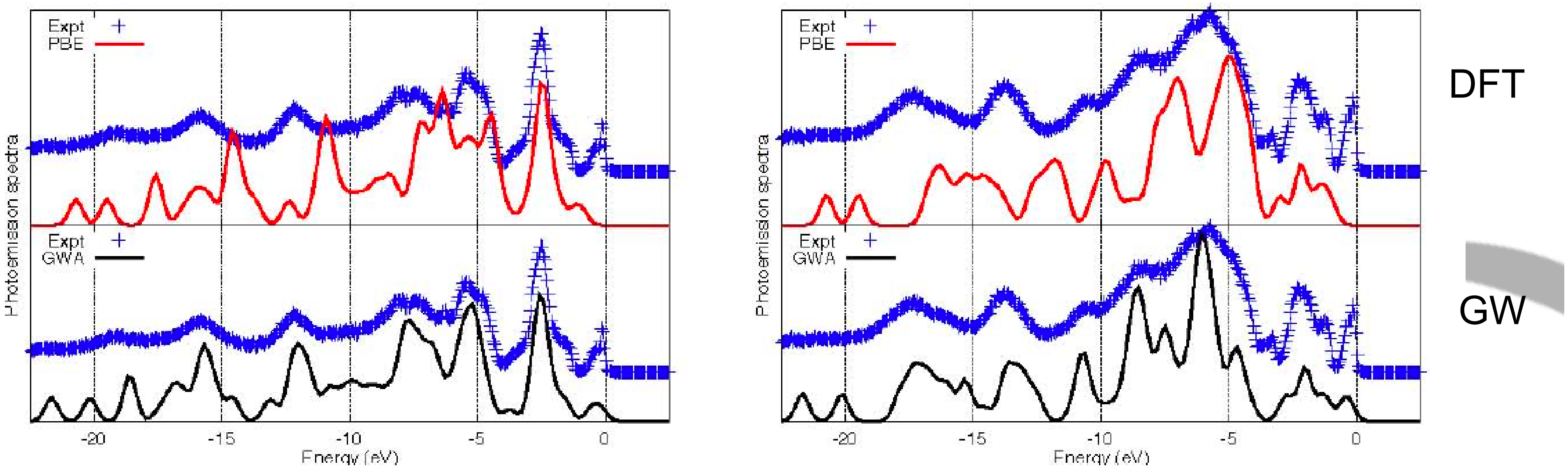


Disagreement between the DFT-PBE valence density of states and the experimental PES: any approximation applying an artificial stretching of the energy axis to the DFT spectra would also fail to reproduce the experimental spectrum.

Photoemission on big molecules







The failure of the DFT-PBE approach to describe even the valence energies in such molecule and the relevance of GW calculations in molecules even not presenting localized d or f states, indicate that electron correlations in the TPP and OEP molecules are important.

CONCLUSIONS

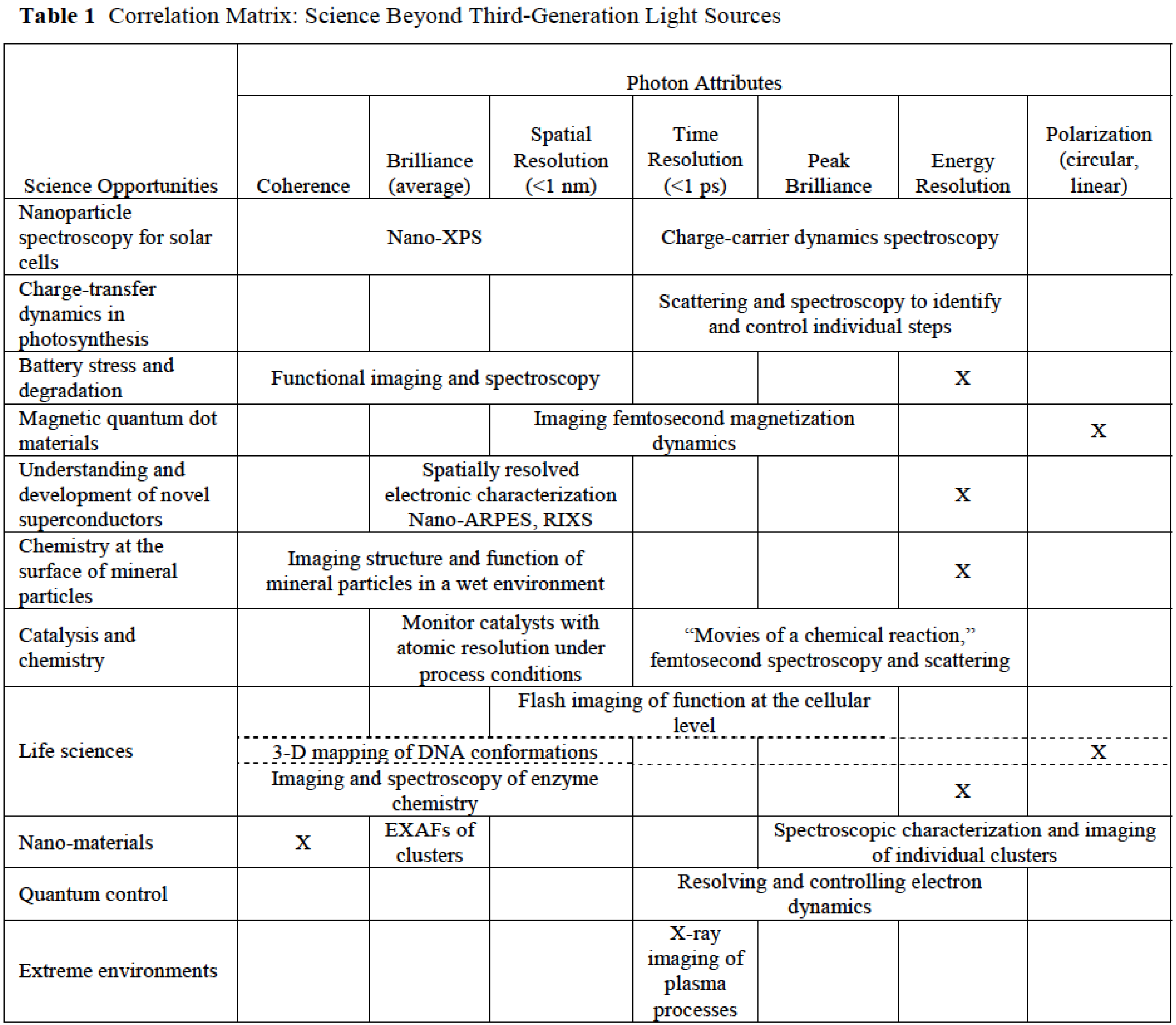


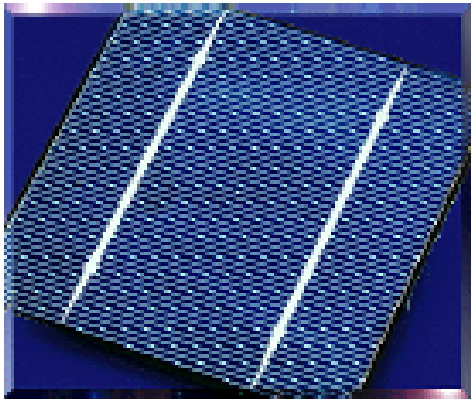
Table 1 Correlation Matrix: Science Beyond Third-Generation Light Sources

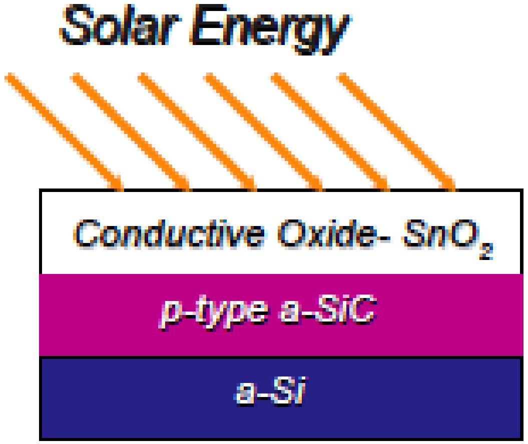
	Photon Attributes						
Science Opportunities	Coherence	Brilliance (average)	Spatial Resolution (<1 nm)	Time Resolution (<1 ps)	Peak Brilliance	Energy Resolution	Polarization (circular, linear)
Nanoparticle spectroscopy for solar cells	Nano-XPS			Charge-carrier dynamics spectroscopy			
Charge-transfer dynamics in photosynthesis				Scattering and spectroscopy to identify and control individual steps			
Battery stress and degradation	Functional imaging and spectroscopy					X	
Magnetic quantum dot materials			Imaging femtosecond magnetization dynamics				X
Understanding and development of novel superconductors		Spatially resolved electronic characterization Nano-ARPES, RIXS				X	
Chemistry at the surface of mineral particles	Imaging structure and function of mineral particles in a wet environment					X	
Catalysis and chemistry		Monitor catalysts with atomic resolution under process conditions		"Movies of a chemical reaction," femtosecond spectroscopy and scattering			
Life sciences			Flash imaging of function at the cellular level				
	3-D mapping of DNA conformations						X
	Imaging and spectroscopy of enzyme chemistry					X	
Nano-materials	X	EXAFs of clusters			Spectroscopic characterization and imaging of individual clusters		
Quantum control				Resolving and controlling electron dynamics			
Extreme environments				X-ray imaging of plasma processes			

Example: analysis of photovoltaic device by XPS depth profiling

The profile indicates a reduction of the SnO_2 occurred at the interface during deposition. Such a reduction would effect the collector's efficiency.

Photo-voltaic Collector





Solar Energy

Conductive Oxide- SnO_2

p-type a-SiC

a-Si