ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

INORGANIC CHEMISTRY AREA
CURRENT RESEARCH TOPICS

Dipartimento di Chimica Industriale
"Toso Montanari"

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ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

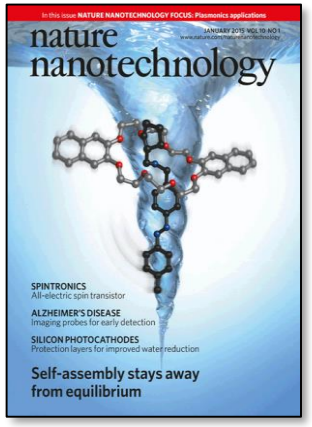
SUPRAMOLECULAR CHEMISTRY, PHOTOCHEMISTRY AND NANOSCIENCE

DESIGNING, MAKING AND OPERATING NANOSCALE DEVICES, MACHINES AND MATERIALS

Area di Chimica Inorganica

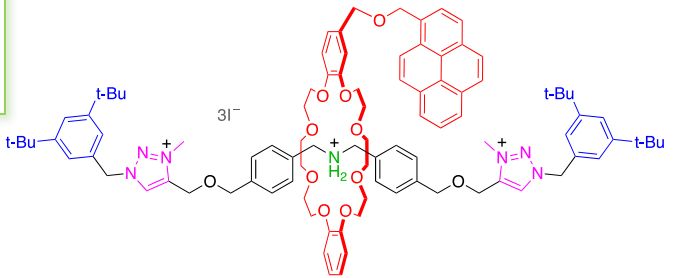
Dipartimento di Chimica Industriale "Toso Montanari"

1. Artificial molecular machines and motors



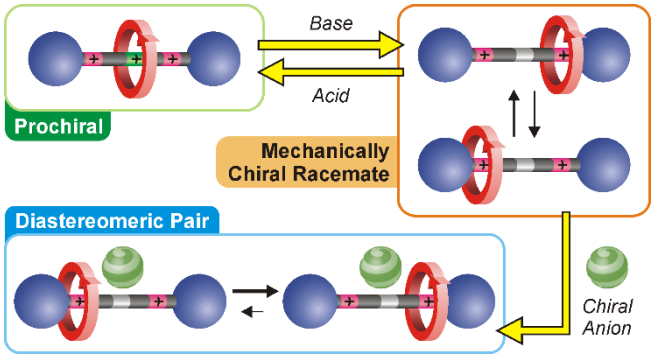
CONTEXT

The realization of mechanical machines and motors of nanoscale size is a stimulating scientific challenge and a primary objective of nanotechnology, as demonstrated by the award of the Nobel Prize in Chemistry in 2016.



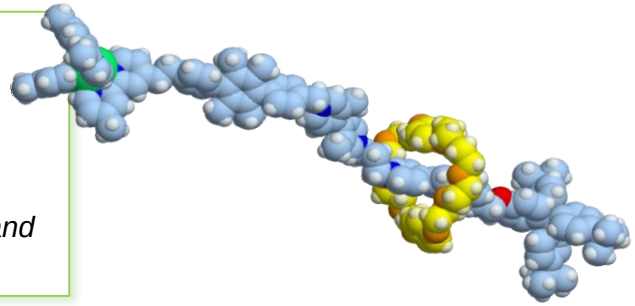
ACTIVITIES

Construction and investigation of **supramolecular complexes** and topologically nontrivial molecules (**rotaxanes**, **catenanes** and related species) that can perform controlled movements in response to light stimulation or other types of chemical or physical signals. Problems include the design of directed motion, its use to carry out tasks, autonomous operation away from equilibrium, and incorporation in complex matrices such as vesicles and polymers.



OBJECTIVES

Realization of innovative systems and intelligent materials for *catalysis, robotics, medicine, information technology and solar enery conversion.*



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Nature Nanotech. **2015**, *10*, 70

Proc. Natl. Acad. Sci. USA **2018**, *115*, 9385

J. Am. Chem. Soc. **2019**, *141*, 9129

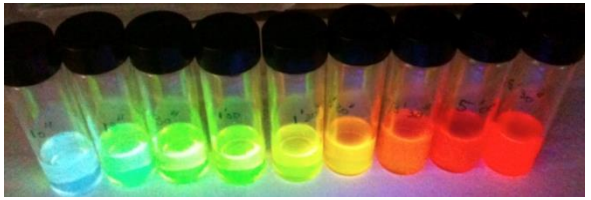
Angew. Chem. Int. Ed. **2019**, *58*, 14341

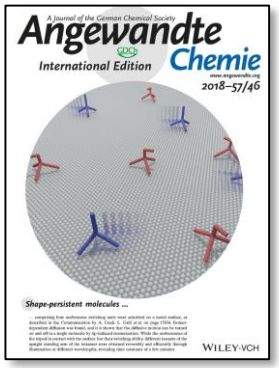
Chem. Rev. **2020**, *120*, 200

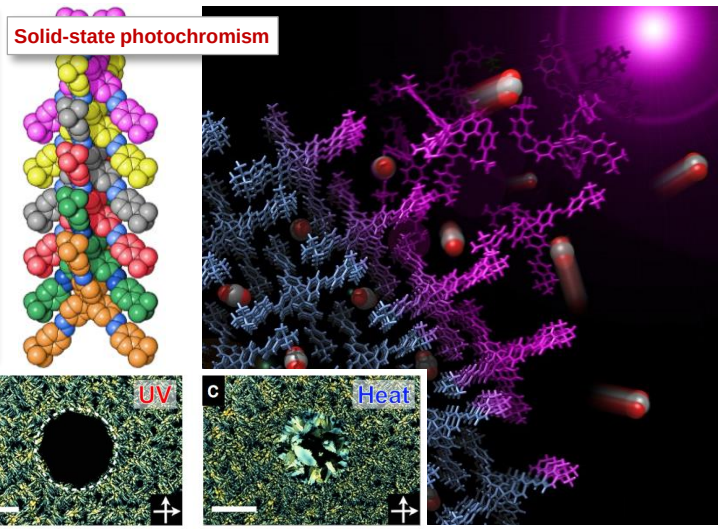
2. Photoactive molecules, nanoparticles and materials

CONTEXT

Molecular and supramolecular-based systems and materials that can perform predetermined functions in response to light stimulation are highly interesting for the inherent scientific value related to a bottom-up approach to functional nanostructures, and for the prospective applications in diverse fields of technology and medicine.







ACTIVITIES

Synthesis and characterization of **luminescent** and/or **photoreactive** species and related phenomena, including: molecular photoswitches, photochromism in solution and in the solid state, luminescent molecules and nanocrystal quantum dots, solid-state emission.

OBJECTIVES

Development of molecules and nanostructured materials suitable for applications in *analytical sciences, bioimaging, mechanical actuation, photopharmacology, gas adsorption, modification of surfaces, photocatalysis and solar energy conversion*.

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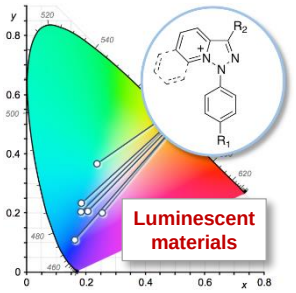
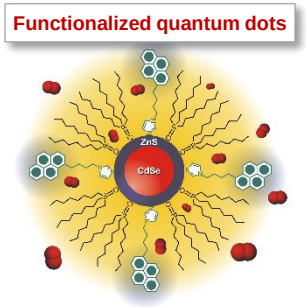
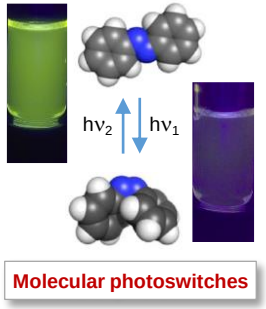
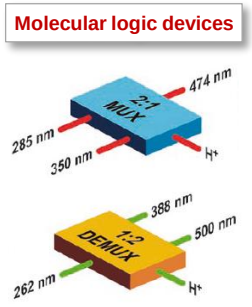
Angew. Chem. Int. Ed. **2018**, *57*, 3104
Angew. Chem. Int. Ed. **2018**, *57*, 15034
Chem. Sci. **2019**, *10*, 5104









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The research team, laboratories and equipment

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Prof Serena Silvi Dipartimento di Chimica “G. Ciamician”

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Post-doc | Stefano Corrà | Massimiliano Curcio | Jessica Groppi | Ozlem Seven | Marina Tranfic-Bakic | **PhD students** | Leonardo Andreoni | Martina Canton | Federico Nicoli | Erica Paltrinieri | Chiara Taticchi

Collaborations | Ivan Aprahamian Dartmouth College-USA | Arturo Arduini, Andrea Secchi Università di Parma | Luigi Cavallo KAUST-Saudi Arabia | Angiolina Comotti Università di Milano-Bicocca | Antonella Fontana Università di Chieti | Ettore Fois Università dell’Insubria Diego Frezzato Università di Padova | Leonhard Grill University of Graz-Austria | Steve Loeb University of Windsor-Canada | Marco Lucarini Università di Bologna | Nathan McClenaghan University of Bordeaux-France | Maurizio Prato Università di Trieste

CLAN CENTER FOR LIGHT ACTIVATED NANOSTRUCTURES

All activities are carried out in the Center for Light Activated Nanostructures (Clan), a joint laboratory between the University of Bologna and Cnr, located in the Bologna campus of Cnr – just across the street to the new ChimInd building. The laboratory has cutting-edge skills and equipment, and is funded by European and national grants.






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CHINANOR
Nanomaterials Group

PLANNING, SYNTHESIS AND CHARACTERIZATION OF NEW NANOSTRUCTURED MATERIALS FOR CATALYTIC, ENVIRONMENTAL, AND ENERGETIC APPLICATIONS

Gruppo Multidisciplinare – Aree di Chimica Inorganica/Analitica/Organica

Dipartimento di Chimica Industriale
"Toso Montanari"

CHINANOR Nanomaterials Group

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«only a 360 degrees knowledge of materials allows to take full advantages from their properties»

CHINANOR Nanomaterials is a multidisciplinary team made by three researchers with consolidate skills in **CH**emistry, in particular in the field of **IN**organic, **AN**alytical and **OR**ganic chemistry.

Topics:
planning, synthesis and characterization of new nanostructured materials for catalytic, environmental and energetic applications.

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THE NANOWORLD FOR INDUSTRIAL APPLICATIONS

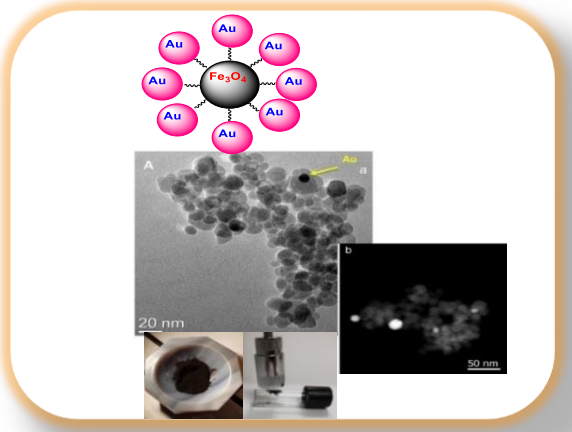
Development of nanostructured systems based on metallic nanoparticles

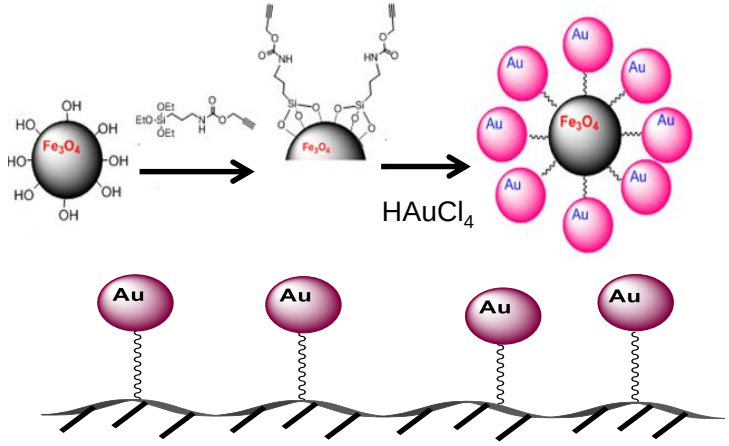
This aspect of research develops synthetic/electrosynthetic procedures to obtain nanostructured systems based on metallic nanoparticles (Au, Ag, Pt etc.) supported on different substrates (silica, allumina, titania, magnetite, hydrotalcite, cellulose, etc.) funzionalized with organic residues.

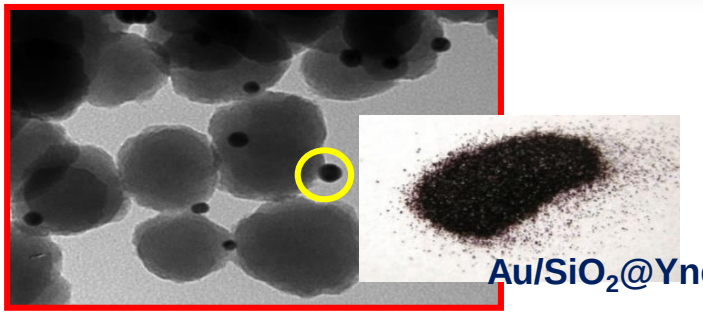
The obtained systems, completely characterized from the chemical-phisical point of view, are used as:

a) catalysts for some organic syntheses;

b) applications in the environmental and cosmetic field.





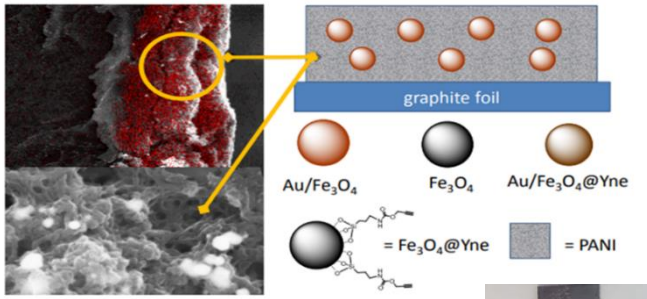


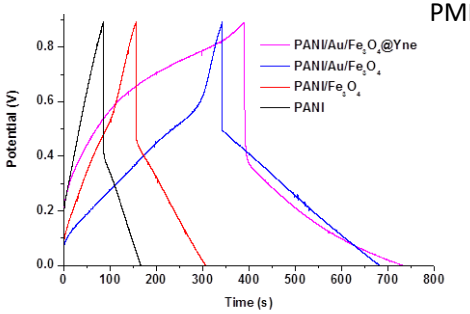
COMPOSITE MATERIALS FOR ENERGY STORAGE AND SENSING APPLICATIONS

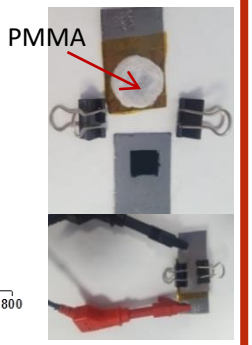
The goal of this kind of research is to find more environmental friendly sistems for future industrial applications. The research can be devided into two main topics:

1. **Energy storage applications**: electrodepositation of thin films based on conductive polymers modified with different kind of nanoparticles like inorganic oxides, and the study of their properties with the aim of making devices able to store energy;

2. **Paper electronics**: modification of bare fibers of cellulose with conductive polymers to create materials with high conductivity and flexibility to make smart and cheap sensors with different applications (touch sensors and gas sensors for example).

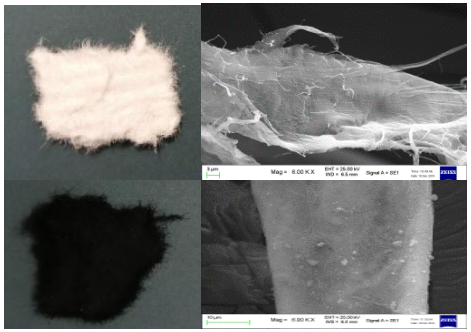


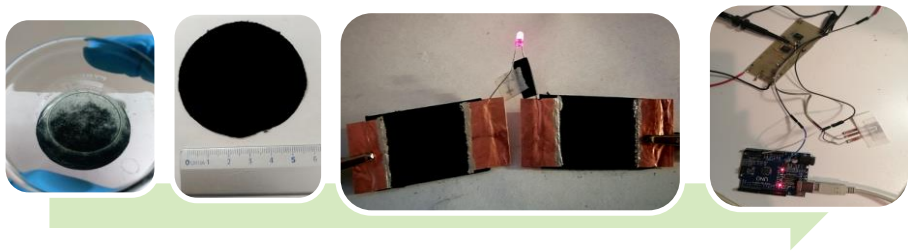




Bare cellulosic fibers

Modified fibers





METAL ORGANIC FRAMEWORKS (MOFs) - SUITABLE POROUS MATERIALS FOR CATALYTIC APPLICATIONS

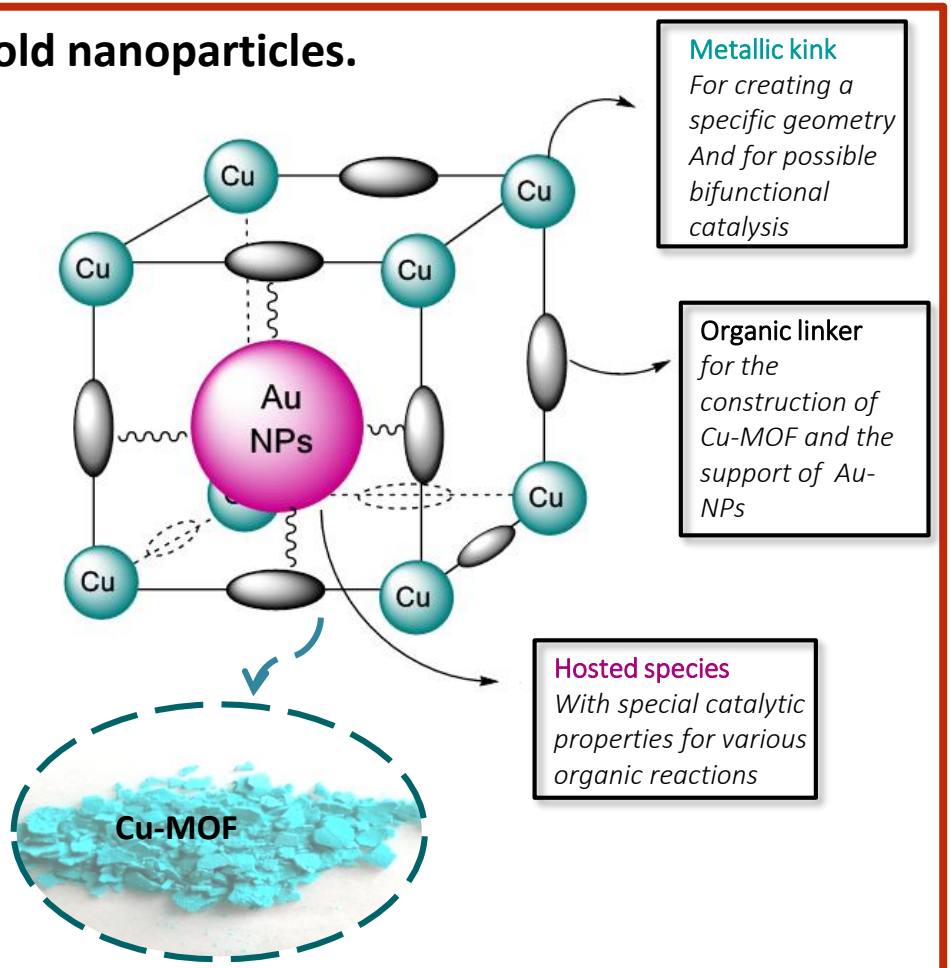
Development of MOFs systems containing gold nanoparticles.

The Aim of this project in three key steps:

- **Synthesis** of a new **organic linker** able to react with **copper ions** leading to the construction of a new, porous, crystalline material **Cu-MOF**.

- **Characterization** of the new material by means of several complementary techniques such as **NMR** spectroscopy, **IR-ATR** spectroscopy, atomic absorption spectroscopy (**AAS**), thermogravimetric analysis (**TGA**), **Raman** analysis.

- **Realization** of a useful platform with high surface area capable of hosting **gold nanoparticles** due to his porosity and his organic funcionality, with promising **catalytic capacities**.



Collaborations

- **Prof. Carla Boga**, Dipartimento di Chimica Industriale «Toso Montanari»: Preparation of new magnetic nanoparticles coated with (R)-9-Acetoxystearic Acid for Biomedical Applications.

- **Università Politecnica delle Marche**: preparation of inorganic/organic scintillators.

- **Dipartimento di Chimica "Giacomo Ciamician", Università di Bologna**: XRD, TGA, TEM.

- **Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Ferrara**: Flow Chemistry.

- **Dipartimento di Scienze Chimiche, Università di Padova**: XPS, FE-SEM.

- **Consiglio Nazionale delle Ricerche di Bologna e Faenza.**

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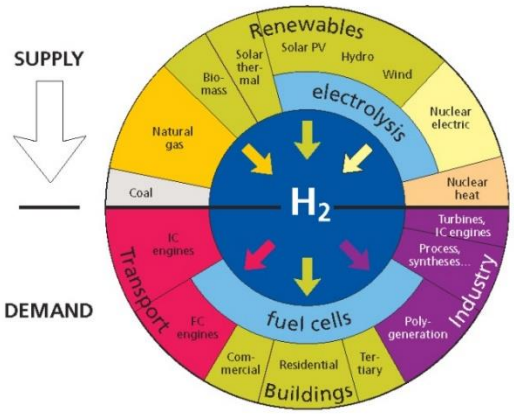
Laboratory of organometallic chemistry

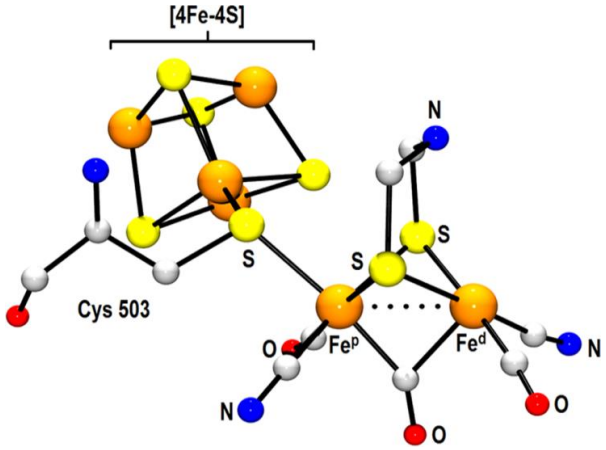
Prof.: Valerio Zanotti, Silvia Bordoni, Stefano Stagni, Rita Mazzoni.

Dipartimento di Chimica Industriale «Toso Montanari»

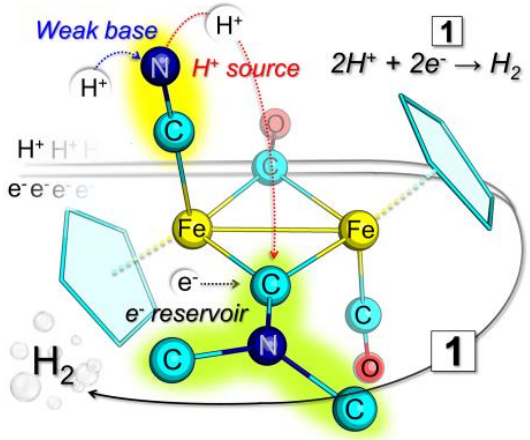
Valerio Zanotti Dipartimento di Chimica Industriale «Toso Montanari»



Hydrogen economy: H_2 will have a major role as energy vector in the transition from fossil fuels to renewables, but there are some challenging issues to be addressed: one is the development of efficient catalysts for H_2 generation from water splitting, based on sustainable metals, such as Fe, in the place of Pt and other noble metals.



Learning from the nature: Enzymes hydrogenases, which are the most efficient catalysts for the conversion of protons and electrons into hydrogen, contain Fe. In particular, the active site of the [FeFe]-hydrogenase consists of a diiron organometallic complex which had inspired a multitude of works aimed to obtain new diiron catalysts for H_2 production.



Beside complexes which mimic [FeFe]-hydrogenase, other **diiron organometallic complexes** might act as electrocatalysts for H_2 production, providing new mechanisms and catalytic routes. In particular diiron complexes with bridging aminocarbyne ligands have shown interesting catalytic activity and are under investigation in our group.

Ref: Arrigoni, F.; Bertini, B.; De Gioia, L.; Zampella, G.; Cingolani, A.; Mazzoni. R.; Zanotti, V. *Inorg. Chem*. **2017**, *56*, 1352.

Rita Mazzoni Dipartimento di Chimica Industriale «Toso Montanari»

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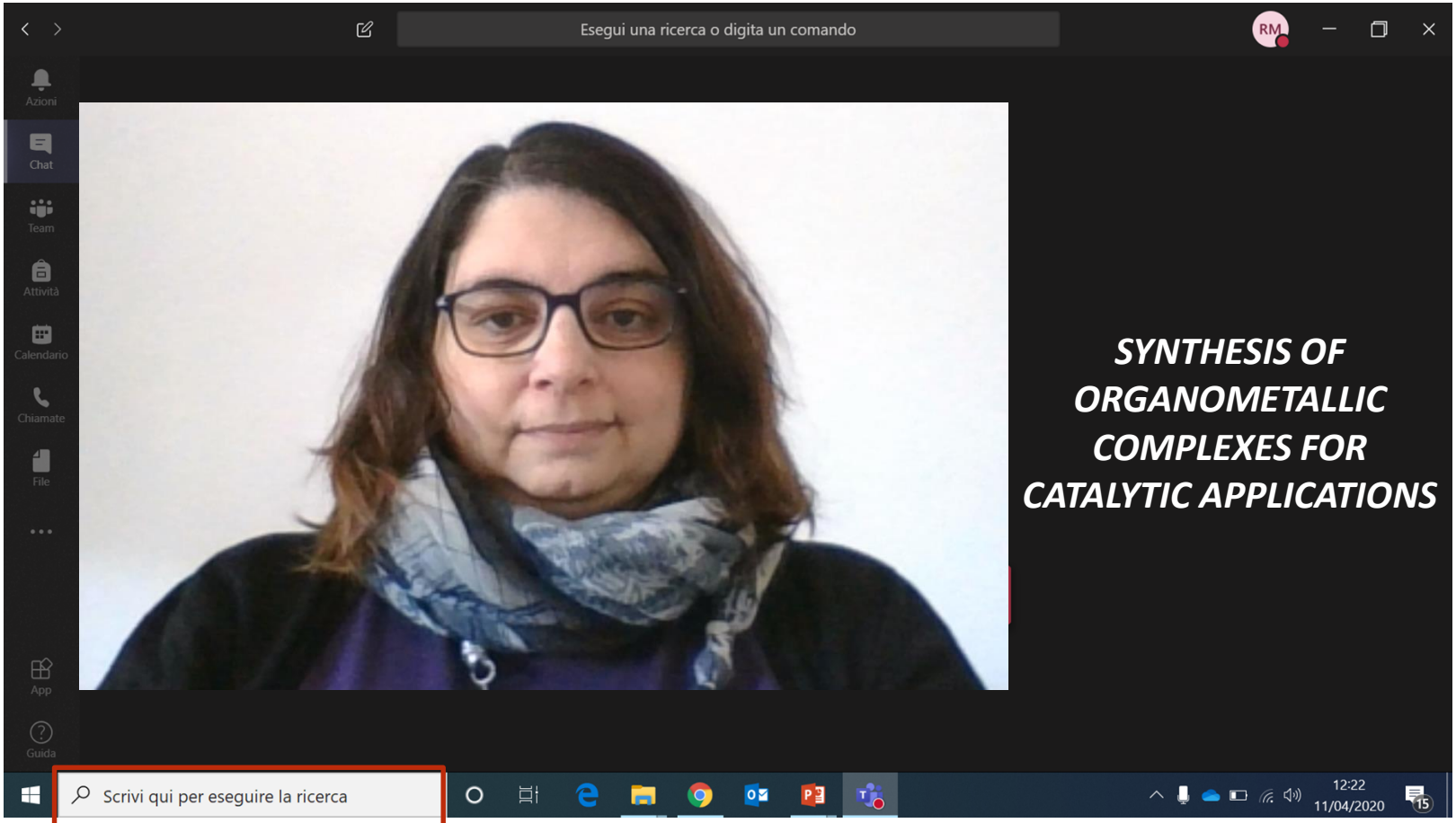
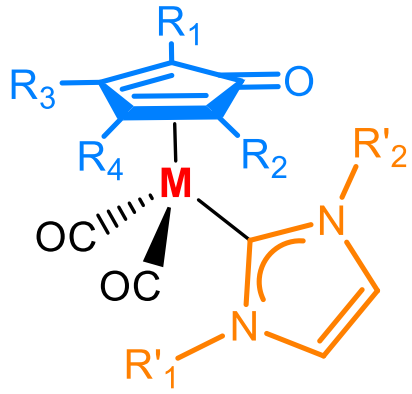


WHAT WE DO?

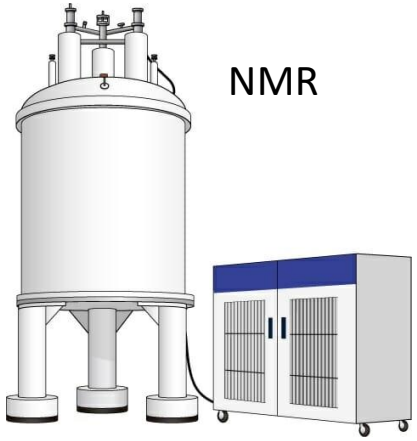
WHAT YOU ARE SUPPOSED TO DO DURING THE THESIS?

SYNTHESIS OF ORGANIC LIGANDS AND TRANSITION METAL ORGANOMETALLIC COMPLEXES



M = e.g. (Fe, Ru)

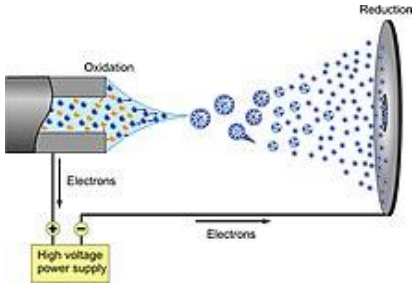
CHARACTERIZATION OF THE NEW ORGANOMETALLIC COMPLEXES



NMR

IR

ESI-MS



X-RAY DIFFRACTION

APPLICATION OF THE SYNTHESIZED COMPLEXES IN THE ONGOING PROJECT

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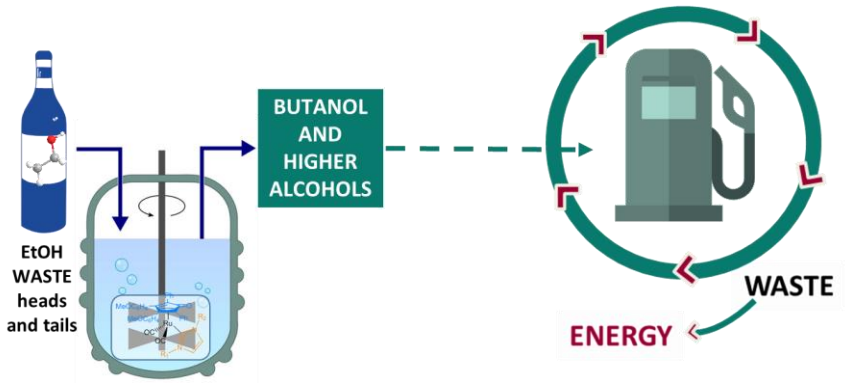
WHERE DO WE GO? … *the ongoing projects*

HOMOGENEOUS CATALYSIS APPLIED TO SUSTAINABILITY

- ***Valorization of biomass derivatives***;
  in collaboration with the group of *Prof. Cavani*;



- ***Electrocatalytic water oxidation;*** in collaboration with *Prof. Scavetta* and *Dr. Gualandi*;
- ***«Hydrogen storage»****: de-hydrogenation of amino-borane*;
- ***In situ (FT-IR) for mechanisms studies****;* in collaboration with *Prof. Lucarelli and Basile*.

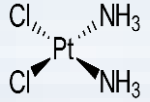
MATERIALS

- **Synthesis of organometallic co-polymers** for variable applications**;**
  in collaboration with *Dr. Mazzocchetti and Benelli*.
- ***Design and synthesis of chiral enantioselective catalysts***
  in collaboration with *Prof. Mazzanti*.

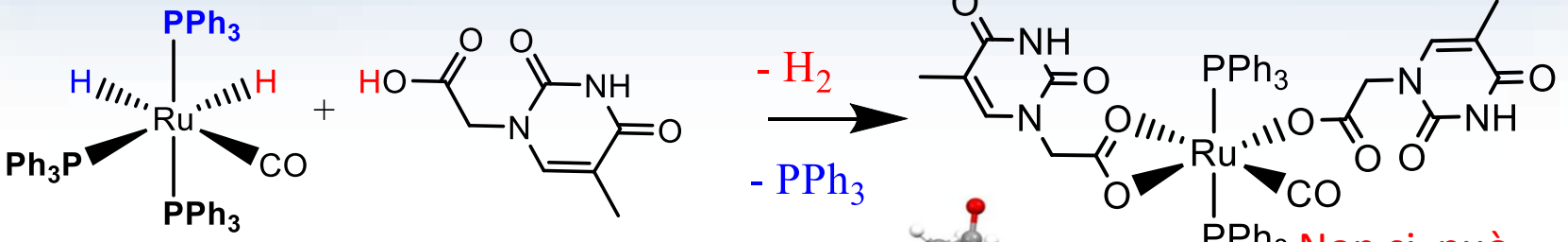
Interazione Nucleobasi-Metalli: Timina/Ru (II)

Silvia Bordoni Dipartimento di Chimica Industriale «Toso Montanari»

in collaborazione con: Magda Monari RX, Riccardo Tarroni DFT, Gabriele Micheletti e Carla Boga sintesi HSA e leganti organici

Coordinare nucleobasi (monomeri costituenti il DNA) al Ru(II) e' una strategia sintetica di nuovi potenziali farmaci anticancerogeni per **ridurre** gli effetti tossici e bioresistenza di  dopo prolungato trattamento.

Lippert, 2009; Correa, 2018



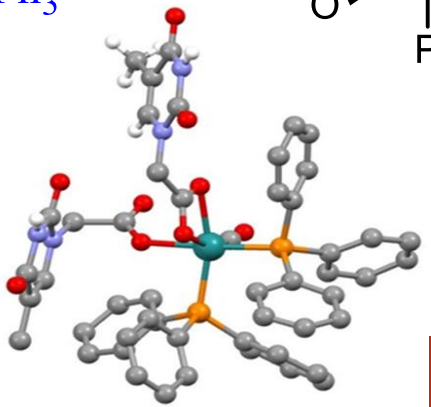
THAc

Timina acetato

legante biocompatibile

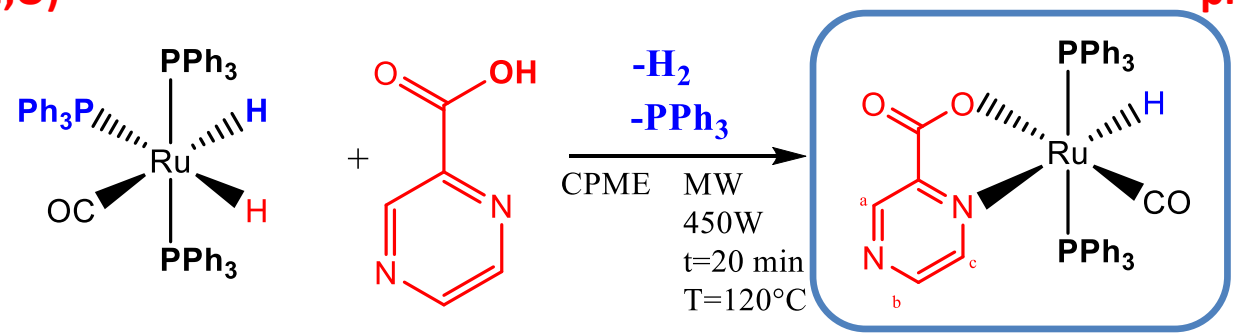
induce stabilità

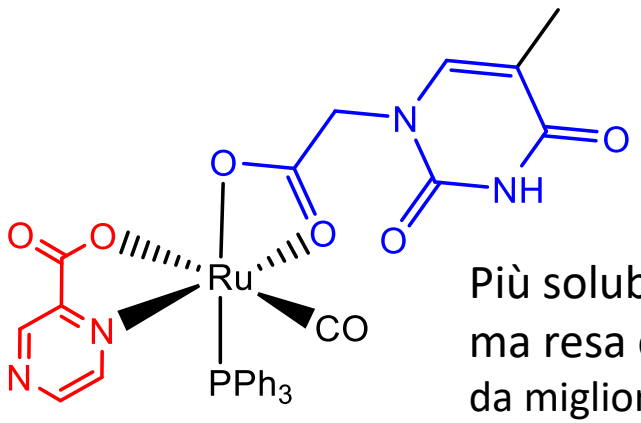
$(k^1\text{-}O)(k^2\text{-}O,O)[Ru(CO)(PPh_3)_2THAc_2]$



Non si può studiare in vitro per la sua scarsa solubilità

E per migliorare la solubilità e stabilità ➡ sostituzione di PR_3 con leganti chelanti k^2-(N,O) **più donatori**

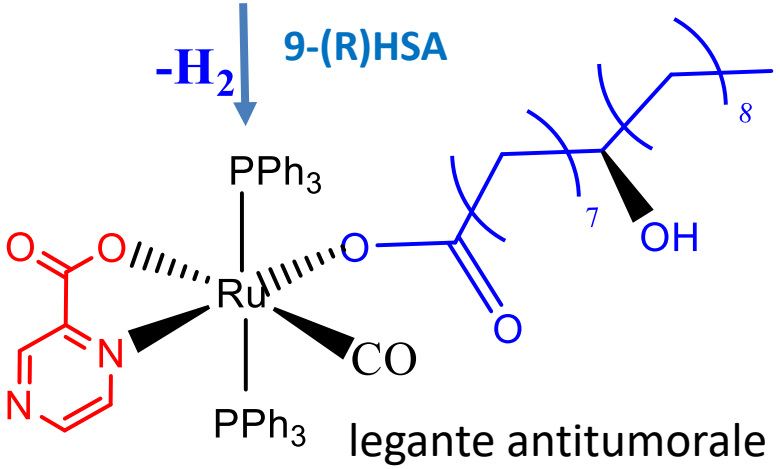




THAcH
$-H_2$
$-PPh_3$

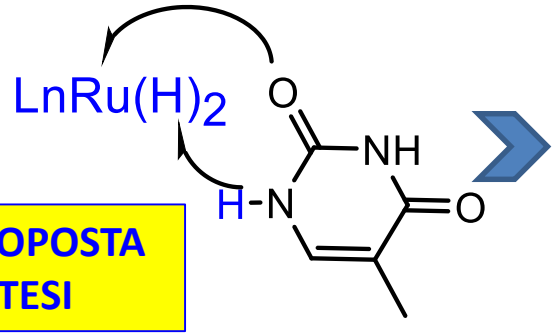
Più solubili ….
ma resa e stabilità
da migliorare

$-H_2$ 9-(R)HSA



legante antitumorale

LA TIMINA PUO' ESSERE DIRETTAMENTE COORDINATA come CHELANTE SUL Ru diidruro per sintetizzare nuovi potenziali ANTICANCEROGENI?



PROPOSTA DI TESI

Possiamo rendere la sintesi green utilizzando H_2O come solvente?

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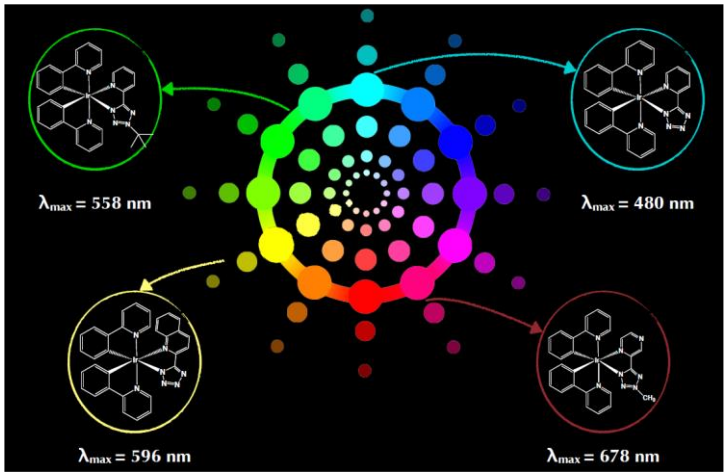
UNIVERSITÀ DI BOLOGNA

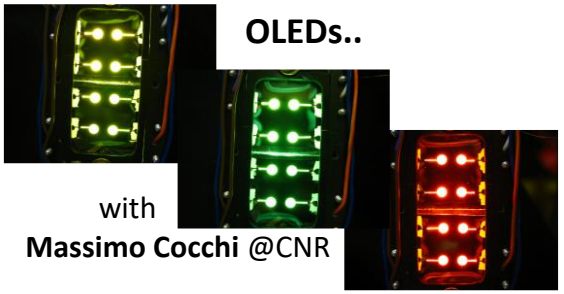
Stefano Stagni Dip. Chimica Industriale Toso Montanari
stefano.stagni@unibo.it



Photoactive Metal Complexes for Materials Science

Organic molecules are combined with **transition metal ions** such as **Ir(III)**, **Re(I)**, **Ru(II)**, **Cu(I)**, **Pt(II)**, to prepare **coordination/organometallic complexes** that can efficiently **absorb visible light**, can display **bright luminescence,** are able to **transfer electrons** or, possibly, can do **all these things together**.

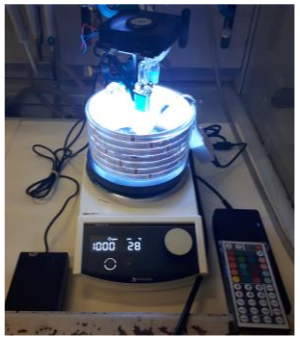
Luminescent Metal Complexes are designed for obtaining **a full-coloured palette** of emissive molecules to be used in **photocatalysis**, **light emitting devices** (OLEDs, LEECs), **luminescent solar concentrators**, **white light** emitters.



OLEDs..

with
Massimo Cocchi @CNR

LSC
Luminescent Solar Concentrators
with Proffs **Andrea Pucci** @UniPI
and **Loris Giorgini** @UniBO



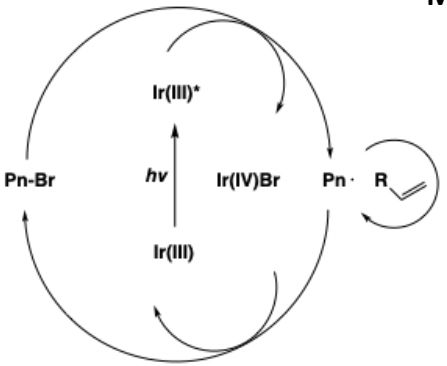
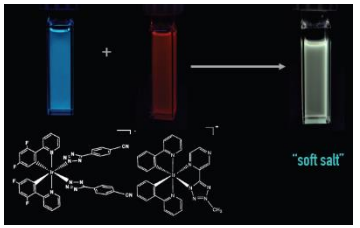


Photo-ATRP
Atom Transfer Radical Polymerization
with Prof. **Loris Giorgini** @UniBO

White Light emission



Crew:
Valentina Fiorini PostDoc
Nicola Monti PhD
Giulia Vigarani PhD
(co supervised with Prof . Giorgini)

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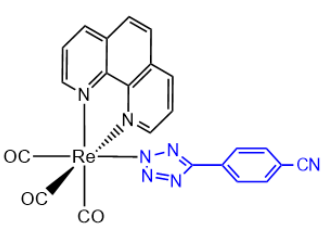
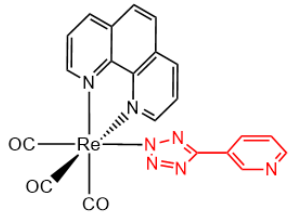
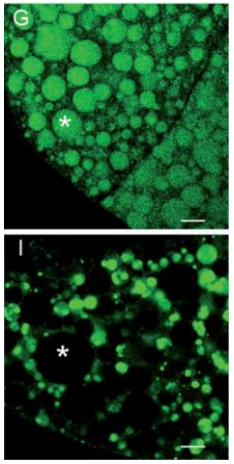
Photoactive Metal Complexes for Life Science

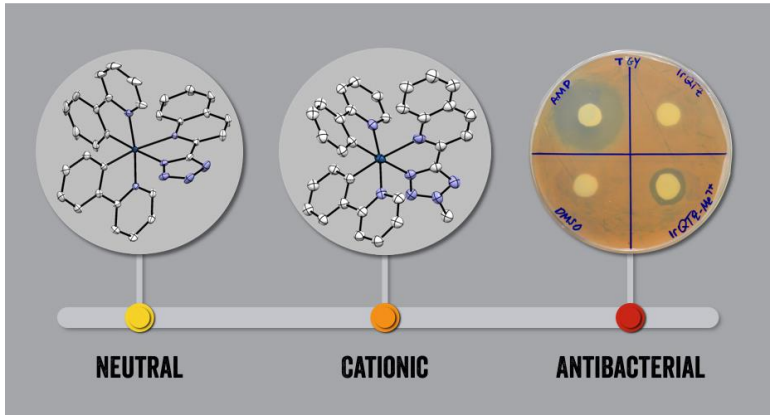
Luminescent metal complexes of Ir(III), **Re(I)**, and **Ru(II)**, are designed and synthesized for obtaining new **optical markers for live cells**, new classes of **selective antibacterials** and new **luminescent dyes for protein staining**.





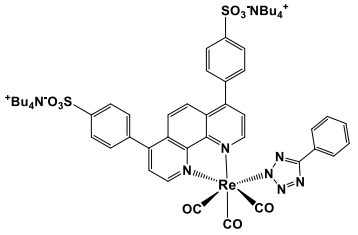


Luminescent Imaging
of Live Eukaryotic Cells and Live Bacteria
with Prof. **Max Massi** @Curtin Uni. **Australia**



Metal complexes as new ANTIBACTERIALS
with Dr. **Alessandra Stefan** @UniBO
alessandra.stefan@unibo.it

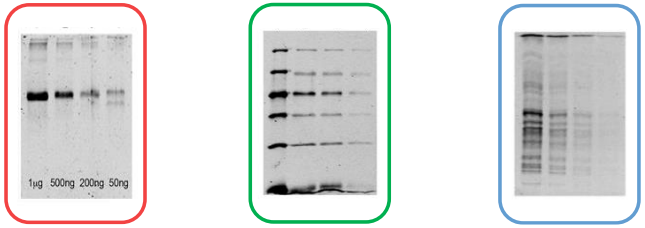
Luminescent Staining of Proteins
with Dr. **Alessandra Stefan** @UniBO



Bovine Serum Albumine

Protein molecular weight marker

E. coli protein extract



Crew:
Valentina Fiorini (Post Doc), **Nicola Monti** (PhD),
Giulia Vigarani (PhD with Prof Giorgini)

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HOMOGENEOUS CATALYSIS
With Transition Metal Complexes

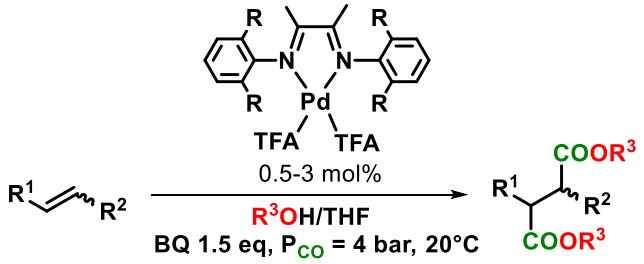
Carbonylation Reactions of unsaturated compounds.
CO/alkenes copolymerizations.
DFT calculations for the study of the mechanisms involved in the catalytic cycles.

GROUP MEMBERS:
Prof. Carla Carfagna, Inorganic Chemistry
Prof. Riccardo Tarroni, Physical Chemistry
Dr. Diego Olivieri, postdoctoral researcher

The research will be carried out at the Rimini Campus in collaboration with the University of Urbino

For information contact:
Prof. Carla Carfagna
https://www.unibo.it/sitoweb/carla.carfagna
E-mail: carla.carfagna@unibo.it

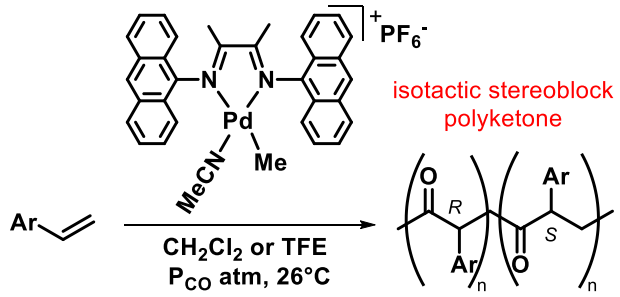
What do we do?



R^1 = aryl, alkyl, EWG
R^2 = alkyl, H
R^3 = Me, *i*-Pr, Bn, *t*-Bu

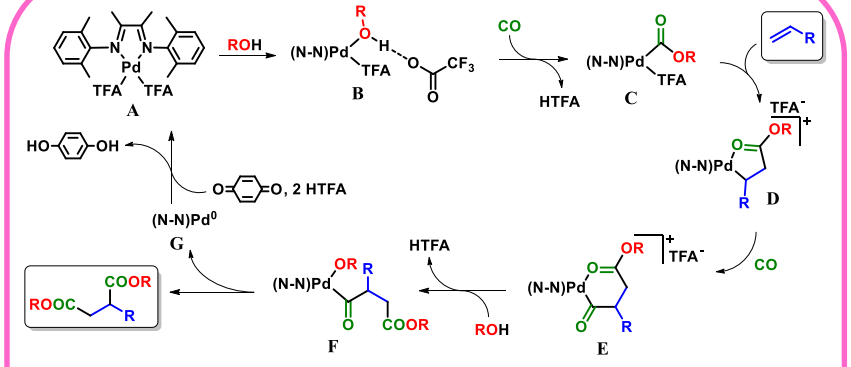
Oxidative bis-alkoxycarbonylation reactions of variously substituted olefins, including unsaturated fatty acids, for the synthesis of succinic ester derivatives

Carfagna Group

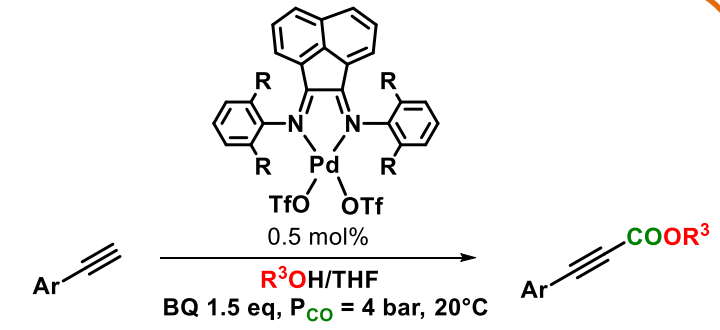


Productivity: up to 500 g_{CP}/g_{Pd}
Isotacticity: 73% *II* triads, $n_I = 7$

Synthesis of CO/olefin copolymers with isotactic, syndiotactic, atactic or isotactic stereoblock structure depending on the utilized catalyst



Mechanistic studies and DFT calculations to investigate the catalytic cycle

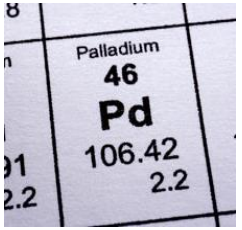


Oxidative mono- and bis-alkoxycarbonylation reactions of alkynes for the synthesis of propiolic esters and maleic diesters

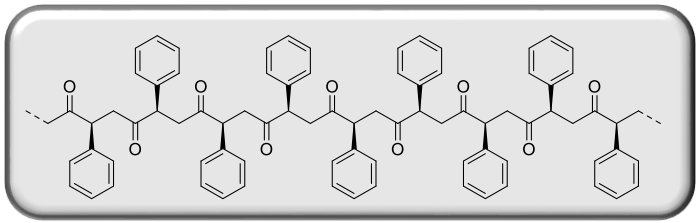
Applications: **pharmaceutical chemistry, material science, cosmetics, agrochemistry**

Group skills

- **Design and Synthesis of Palladium (Pd), Platinum (Pt) and Nickel (Ni) based catalysts for the realization of C-C and CO-unsaturated substrates couplings**

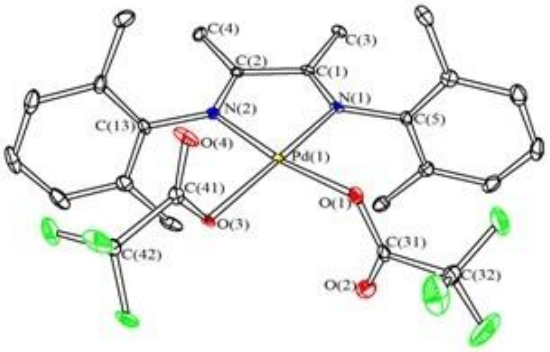


▪ Carbonylation reactions of unsaturated molecules (i.e. olefins and alkynes) for the synthesis of target products with high added value;

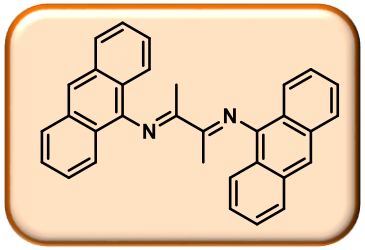


▪ Stereoselective CO/olefin copolymerization reactions for the synthesis of polymers;

▪ Isolation of reaction intermediates to identify the mechanisms involved in the processes;



▪ Study of the proposed catalytic cycles through DFT calculations in order to improve the efficiency and selectivity of the reactions;



▪ Synthesis of new (symmetric, asymmetric and optically active) bidentate nitrogen ligands.

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TRANSITION METAL CARBONYL CLUSTER COMPOUNDS

DESIGN, SYNTHESIS AND CHARACTERIZATION OF METAL CARBONYL CLUSTERS AS MOLECULAR METAL NANOPARTICLES

Area di Chimica Inorganica

Dipartimento di Chimica Industriale "Toso Montanari"

RESEARCH GROUP

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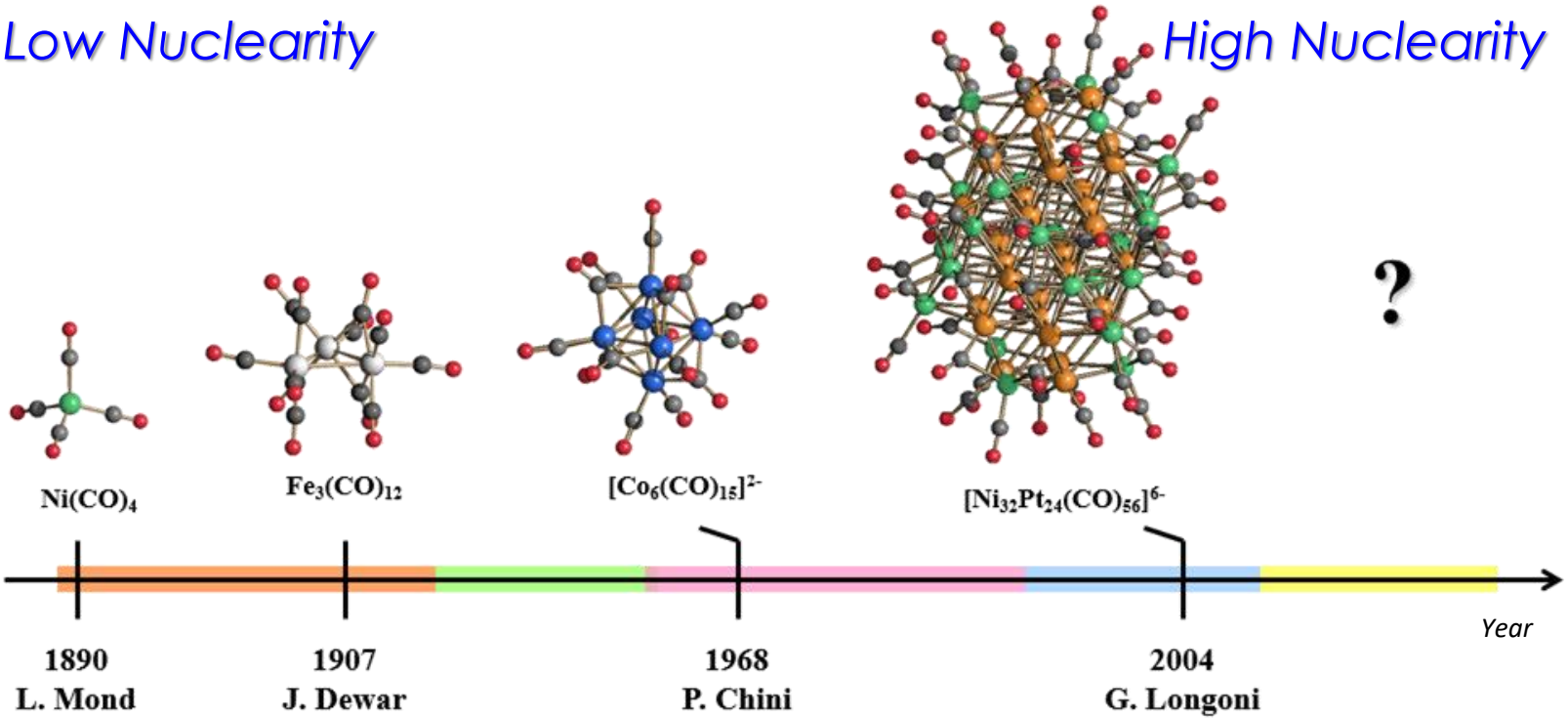
What is a Metal Cluster?

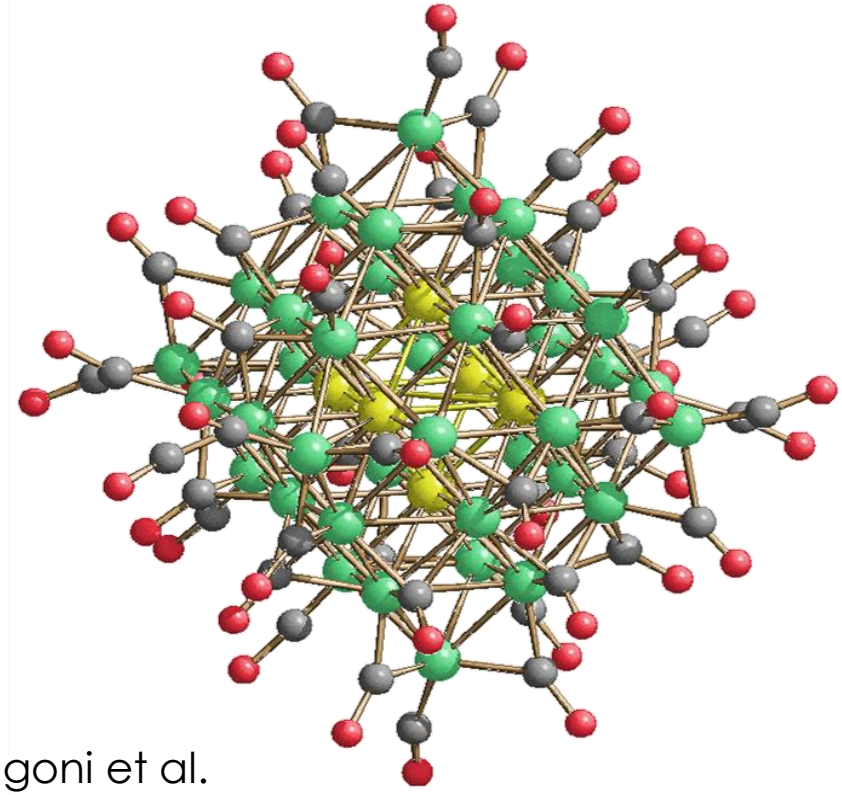
F. A. Cotton (1966): a metal cluster is a molecular species consisting of "…*a finite group of metal atoms held together mainly, or at least to a significant extent, by* ***metal-metal bonds.***"



Coord. Chem. Rev., **2006**, *250*, 1580; *Eur. J. Inorg. Chem.*, **2011**, 4125; *J. Clust. Sci.*, **2014**, *25*, 115; *Coord. Chem. Rev.*, **2018**, *335*, 27; *Eur. J. Inorg. Chem.*, **2018**, 3285, *Acc. Chem. Res.*, **2018**, *51*, 2748

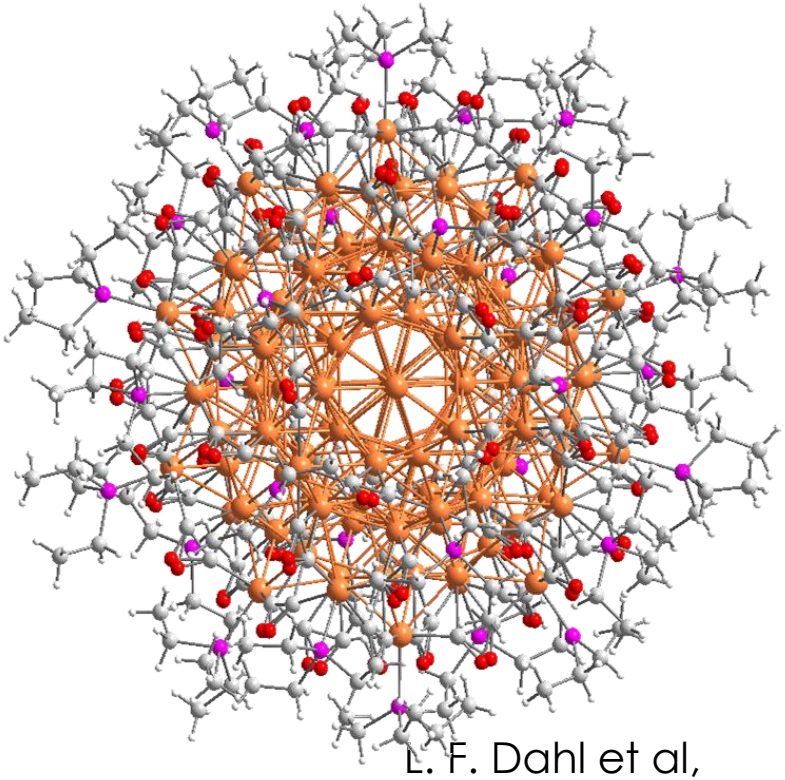
Metal clusters are nanoparticles with "molecular purity" protected by ligands (CO, Phosphines, etc.)

$[HNi_{38}Pt_6(CO)_{48}]^{5-}$
Diameter: 1.9 nm



Longoni et al.
Angew. Chem. Int. Ed. **1985**, *24*, 696

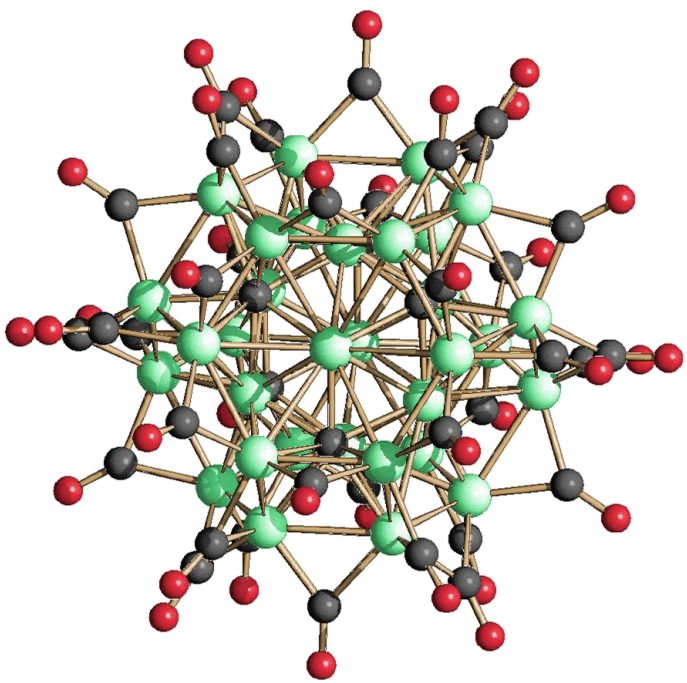
$Pd_{145}(PR_3)_{30}(CO)_{60}$
Diameter: 3.0 nm

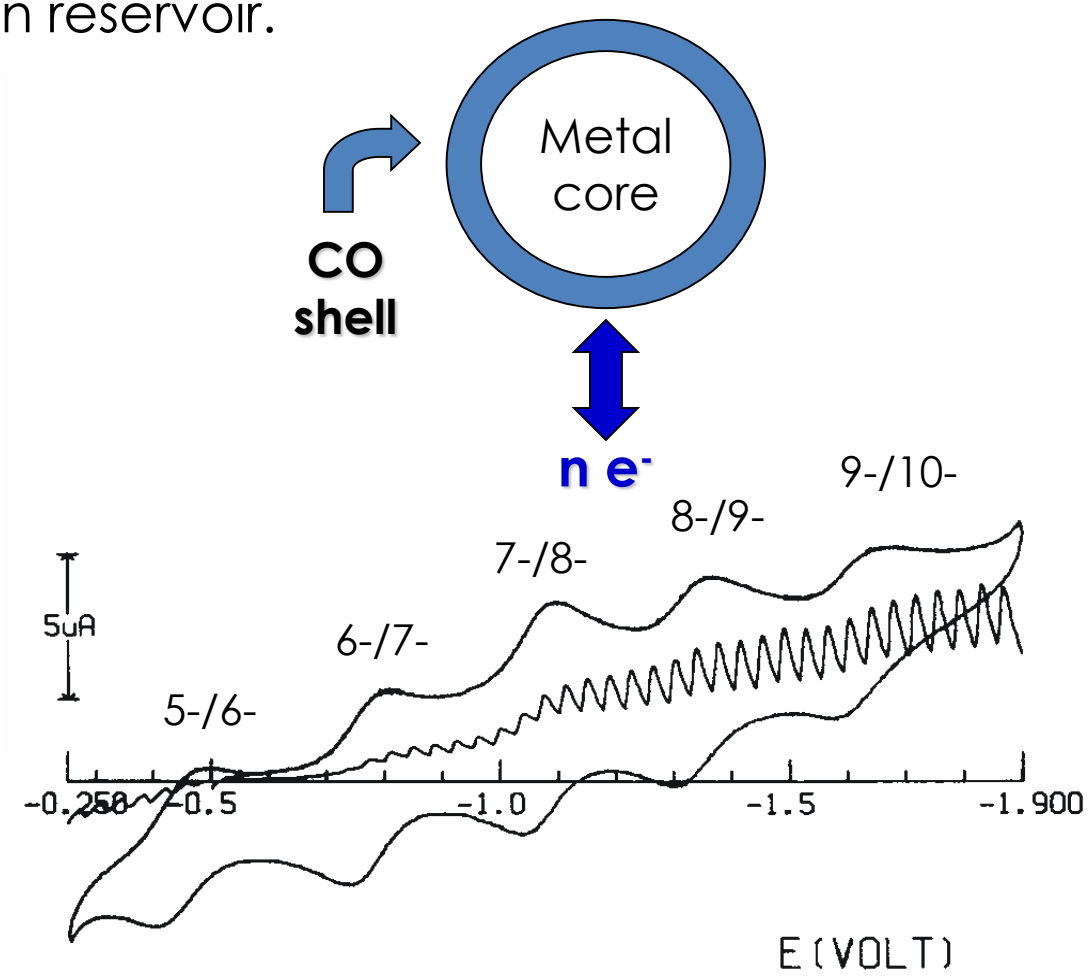


L. F. Dahl et al,
Angew. Chem. Int. Ed, **2000**, *112*, 4287

Some Properties: Possible Molecular Nanocapacitors

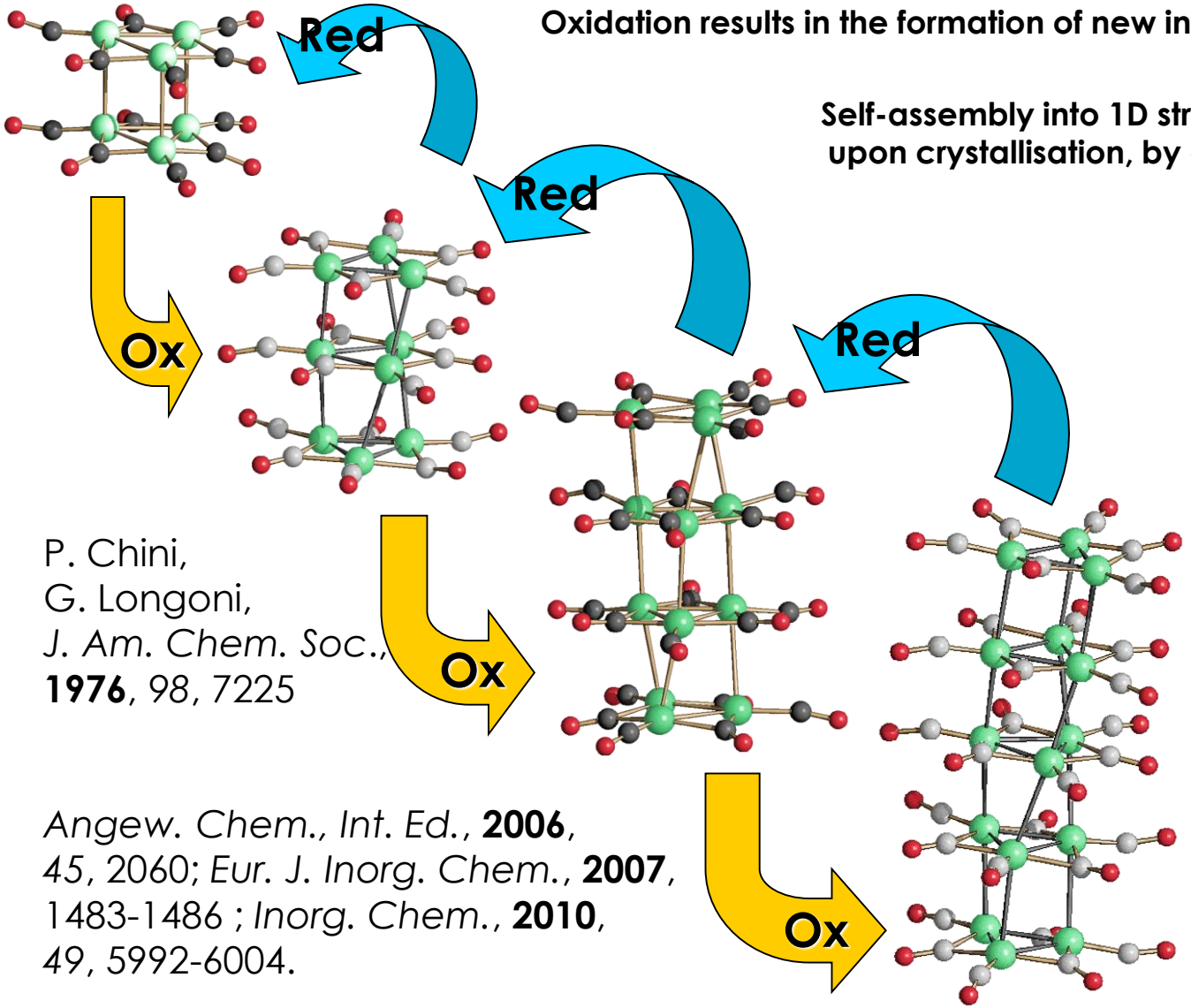
The cluster $[Ni_{32}C_6(CO)_{36}]^{6-}$ is able to accept and release electrons, functioning as an electron reservoir.





F. Calderoni, F. Demartin, F. Fabrizi de Biani, C. Femoni, M. C. Iapalucci, G. Longoni, P. Zanello, *Eur. J. Inorg. Chem.*, **1999**, 663

Molecular Conductive Platinum Nanowires

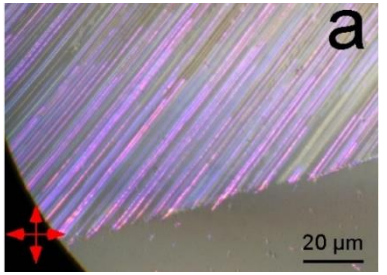


Oxidation results in the formation of new inter-triangular Pt-Pt bonds

Self-assembly into 1D structures can be obtained upon crystallisation, by controlling the size of the cluster and the cation

P. Chini,
G. Longoni,
J. Am. Chem. Soc.,
1976, *98*, 7225

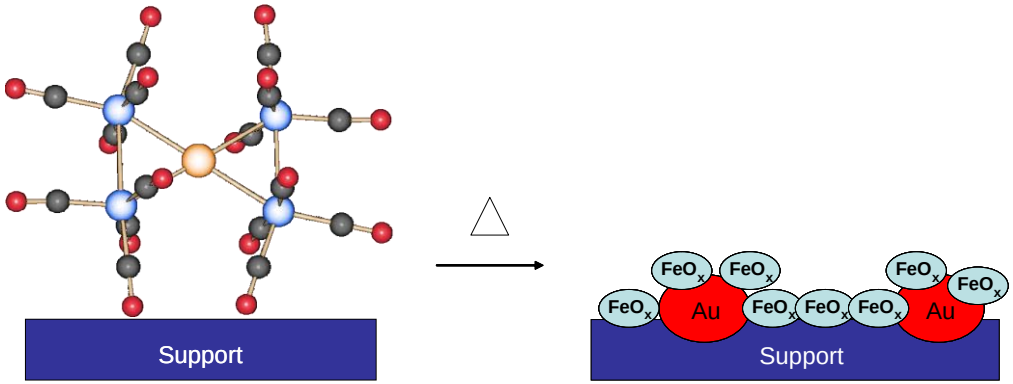
Angew. Chem., Int. Ed., **2006**, *45*, 2060; *Eur. J. Inorg. Chem.*, **2007**, 1483-1486 ; *Inorg. Chem.*, **2010**, *49*, 5992-6004.

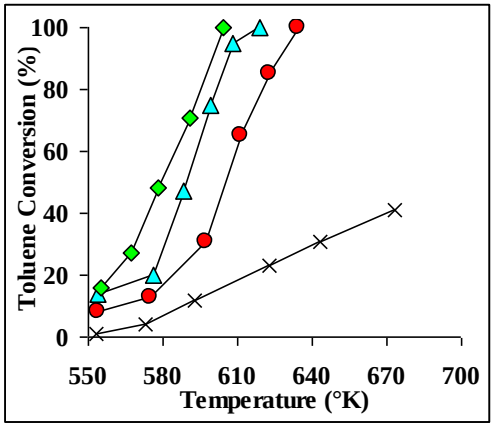


Infinite Pt wires

Au/Fe clusters as precursor for TiO_2-supported Catalysts

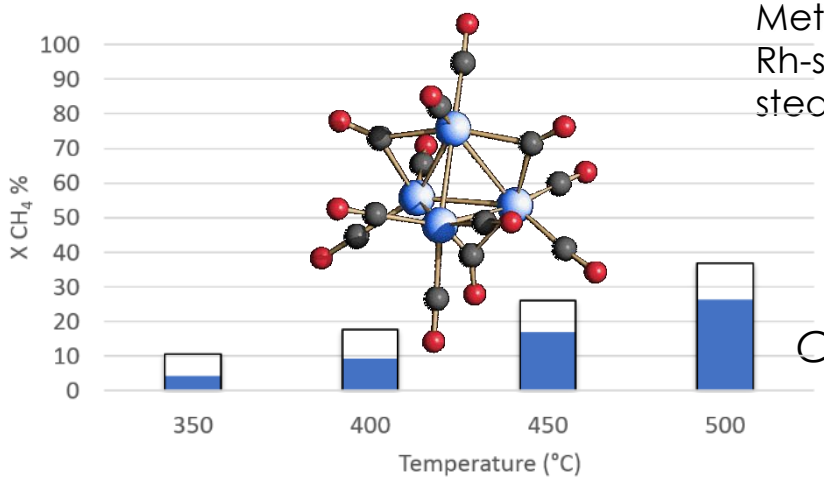
Rh_4 cluster as precursor for $CeZrO_2$-supported Catalyst





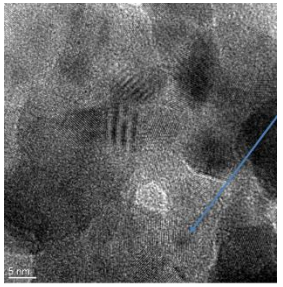
TiO_2 (×), $Fe_{0.6}Au_2$-Ti-N_2 (●), $Fe_{1.2}Au_4$-Ti-N_2 (▲), $Fe_{1.8}Au_6$-Ti-N_2 (◆)

Catalysts, **2012**, *2*, 1; *Appl. Catal. A*, **2011**, *400*, 54, *Appl. Catal. A*, **2010**, *372*, 138.



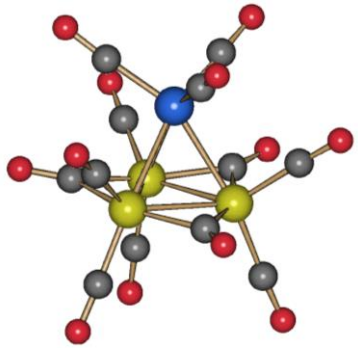
Methane conversion with Rh-supported catalyst in steam reforming of CH_4

Rh-CeZr-oxide catalyst characterization via TEM



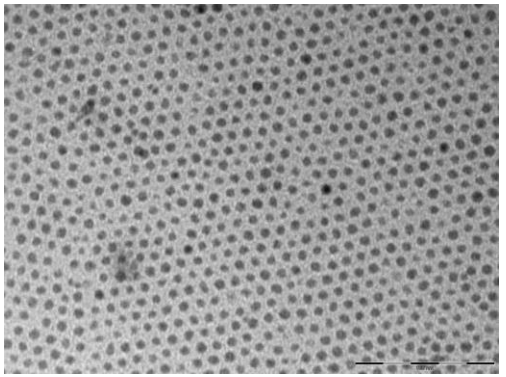
Catalysts, **2019**, 9, 800

Magnetic Nanoalloys from Fe-Co Bimetallic Carbonyl Clusters



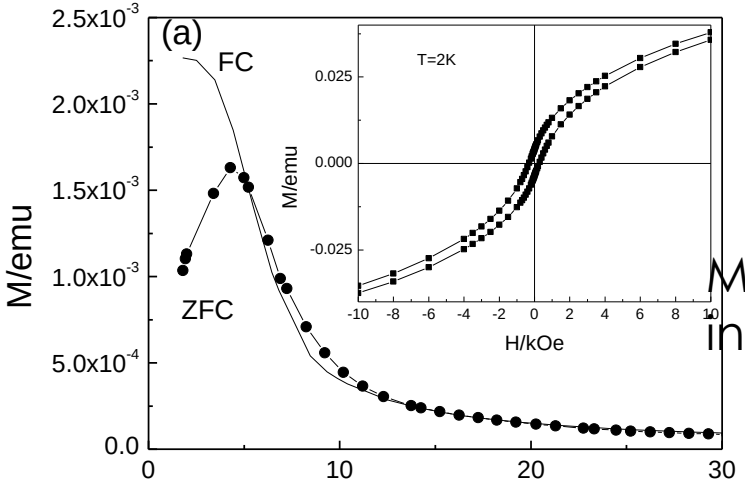
Single bimetallic precursor

Thermal decomposition



Alloy magnetic nanoparticles

The chemical composition of the nanoparticles is the same as the original cluster they were prepared from.



Magnetization curves of $FeCo_3$ alloy NPs. The inset shows the hysteresis curve at 2 K.

I. Robinson, S. Zacchini, L. D. Tung, S. Maenosono, N. T. K. Thanh, *Chem. Mater.*, **2009**

In conclusion, what do we do?

- Synthesis of inorganic compounds under an inert atmosphere (Schlenk technique)
- Spectroscopic characterization (IR, multinuclear NMR)
- Structural characterization through x-ray diffraction on single crystal
- Electrochemical and spectrochemical studies (Prof. Tiziana Funaioli, Università di Pisa)
- Determination of the magnetic properties of molecular nanocluster through SQUID (Prof. Mauro Riccò, Università di Parma)
- Computational studies and DFT calculations (Prof. Marco Bortoluzzi, Università di Venezia)
- Use of molecular nanocluster as anti-cancer agents (Prof. Paul J. Dyson, Ecole Polytechnique Fédérale de Lausanne)
- Use of molecular cluster as precursors of nanostructured catalytic materials (Proff. S. Albonetti and F. Basile, Università di Bologna)