Chiral Metal-Organic Frameworks: Synthesis, Characterization and Catalytic Activity

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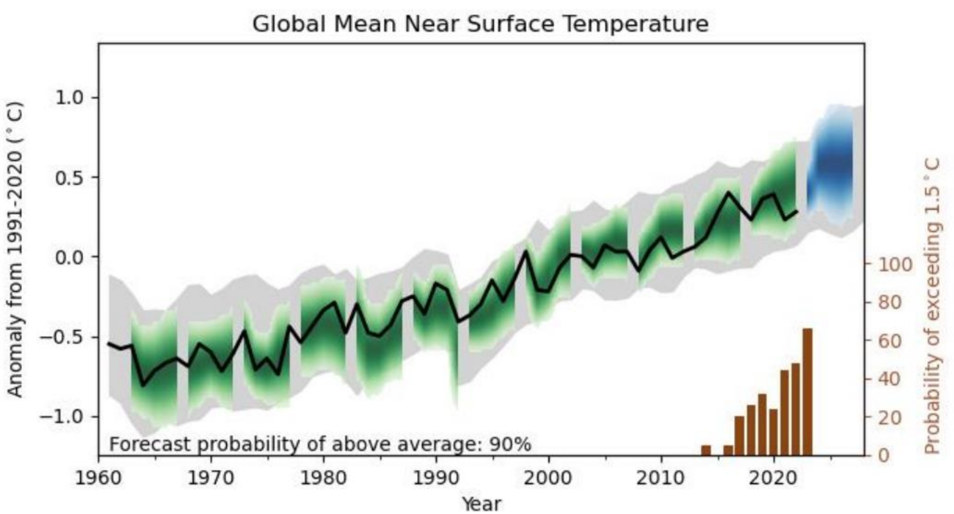
OUR #1 PROBLEM (?)

How I Learned to Stop Worrying and Love the Heat

Monday July 3 was the hottest day on record on Earth

July 4th was the hottest day on Earth in recorded history, scientists calculate

Earth sees third straight hottest day on record, though it's unofficial: "Brutally hot"

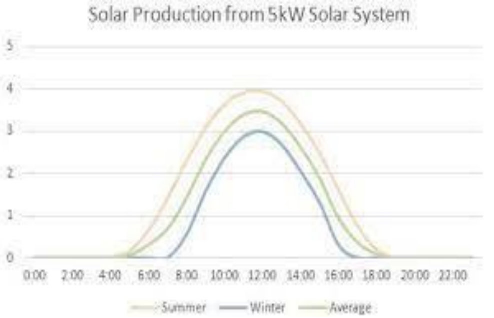


Earth saw hottest day yet Thursday, the fourth straight global record

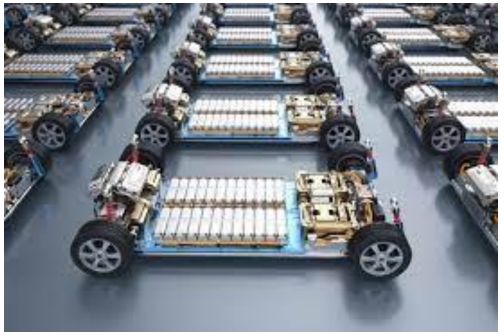
RENEWABLE ENERGY

A solution with its own problems

We need to **scale up** quickly the installed power of **renewable energy sources**, mainly solar and wind, and to fully electrify the economy.



In this scenario, we need a way to overcome one of the main issues with renewables: their fluctuating energy production depending on the time of day and weather conditions
→ **storage necessities**.



Storage technologies - **Batteries**: lithium, flow batteries (electrochemical), **Hydrogen** (chemical), **Hydro-pumped** (physical) → different long term storage capability.

A DROP IN THE OCEAN

Hydrogen can and will play a role

Let's be real: H_2 is **NOT** going to fuel our cars or houses as some people say (or at least, it shouldn't…).

BUT we have to replace the «brown» H_2 from steam reforming (produced using fossil fuels) with «green» H_2 (produced through renewables). Today H_2 production accounts for around 3% of global greenhouse emissions.

AND H_2 can play other roles, for example as energy storage in some specific applications (industrial sites), or fuel for some particular vehicles (ships). It can be transported (pipelines).

We should think of green H_2 production as an energy sink, a place where to store the excess renewable energy production.

WATER SPLITTING: SOME PROBLEMS

Not as straightforward as it sounds

Electrochemical water splitting → 2 reactions → HER and OER

In alkaline conditions: Anode $4OH^- \leftrightarrow 2H_2O + O_2 + 4e^-$

Cathode $4H_2O + 4e^- \leftrightarrow 2H_2 + 4OH^-$

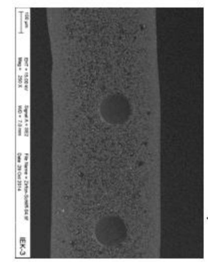
The OER is quite sluggish due to the $4e^-$ needed.

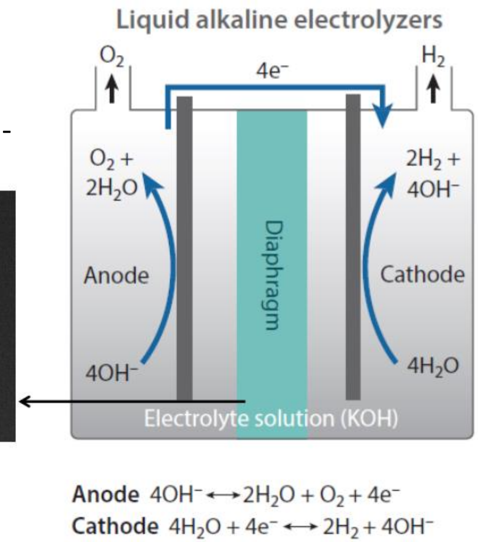
$OH^- \rightarrow OH_{ad} + e^-$

$OH_{ad} + OH^- \rightarrow O_{ad} + H_2O + e^-$

$O_{ad} + OH^- \rightarrow OOH_{ad} + e^-$

$OOH_{ad} + OH^- \rightarrow O_2 + H_2O + e^-$





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The overpotential η needed to drive the reaction is mainly due to the OER.

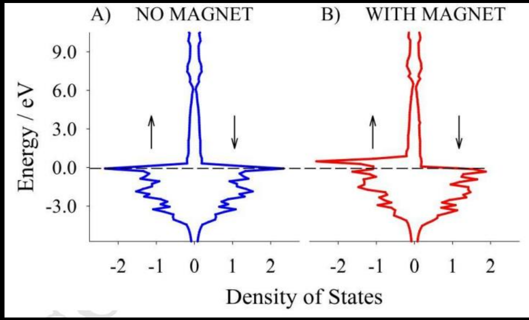
One of the problems: O2 has a triplet ground state while the reagents are singlet state: a spin flip is required.

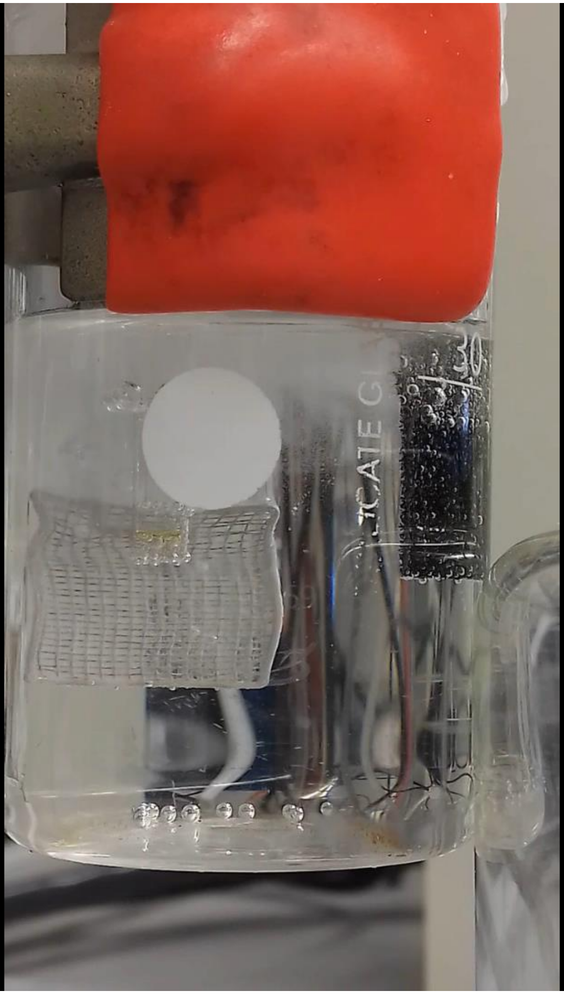
Spin effect on the OER: using a spin-polarized current lowers the needed overpotential.

SPIN POLARIZED OER

A small trick that goes a long way

Catalyst : $NiZnFe_4O_x$
Upon magnetization, current densities increase about **100%**.
The source of the spin-polarized current is due to the FM material, that under external magnetic field gets spin-polarized at the Fermi level.





Measurements by J.R. Galán-Mascarós group *Nature Energy* **2019**, *4* (6), 519–525

SPIN POLARIZED OER

A small trick that goes a long way

We know we can have spin-polarized currents also using chiral systems thanks to the CISS effect. So far different chiral systems have been used to modify the anode to boost the OER.

1) Supramolecular Assemblies
2) Semiconducting Polymers
3) Monolayers
4) Metal Oxides

Some of the chiral systems tried so far…

These systems have been used in proof-of-concept works, and they all show that chiral electrodes/catalysts work better then their achiral counterparts. Some of these also show a very low overpotential. A recent paper from Waldeck group using chiral metal oxides nanoparticles for the OER shows great performances compared to benchmark catalysts such as IrO_2.

Chiral electrocatalysts eclipse water splitting metrics through spin control

Aravind Vadakkayil, Caleb Clever, Karli N. Kunzler, Susheng Tan, Brian P. Bloom & David H. Waldeck

Nature Communications **14**, Article number: 1067 (2023) | Cite this article

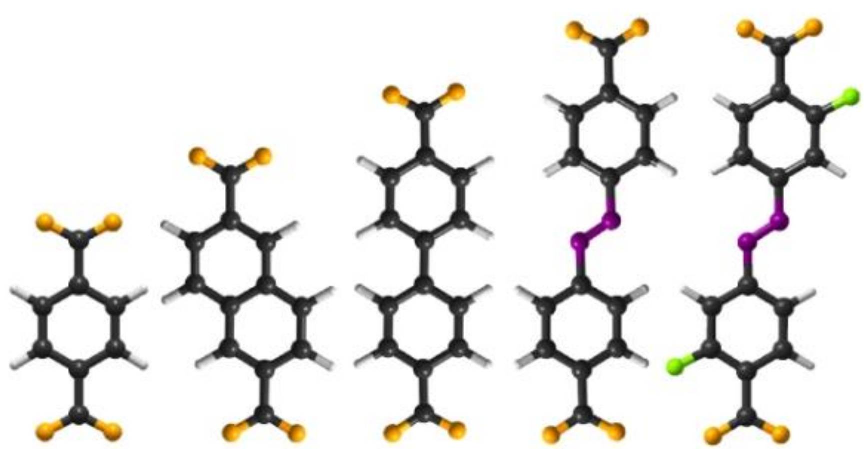
WHAT DO WE WANT TO DO?

We want to be able to have a complete control over the structure of the catalyst so that we can investigate structure/properties relations…

We want to be able to control the parameters that are important for the spin-polarization AND the catalytic activity…

We need to be able to tune the structure by design…

A possibility: Metal Organic Frameworks,
Promising materials for OER catalysis.

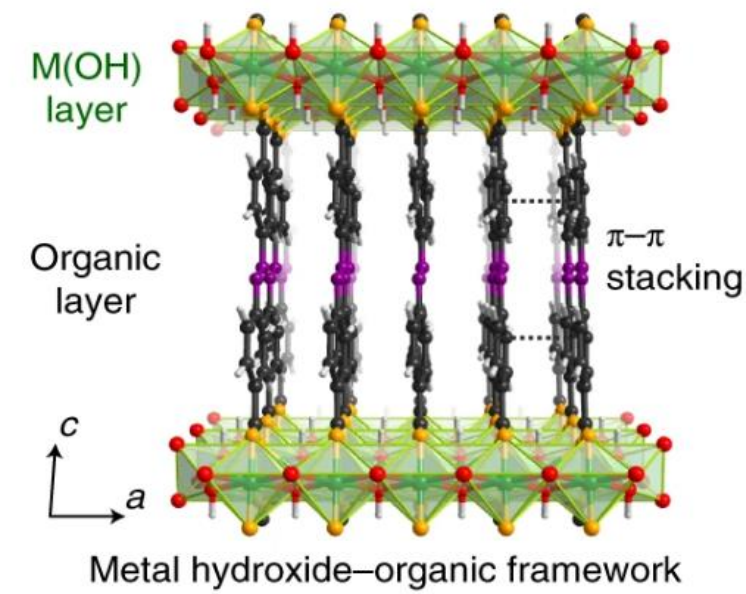


Article | Published: 24 February 2022

Tunable metal hydroxide–organic frameworks for catalysing oxygen evolution

Shuai Yuan, Jiayu Peng, Bin Cai, Zhehao Huang, Angel T. Garcia-Esparza, Dimosthenis Sokaras, Yirui Zhang, Livia Giordano, Karthik Akkiraju, Yun Guang Zhu, René Hübner, Xiaodong Zou, Yuriy Román-Leshkov & Yang Shao-Horn

Nature Materials **21**, 673–680 (2022) | Cite this article

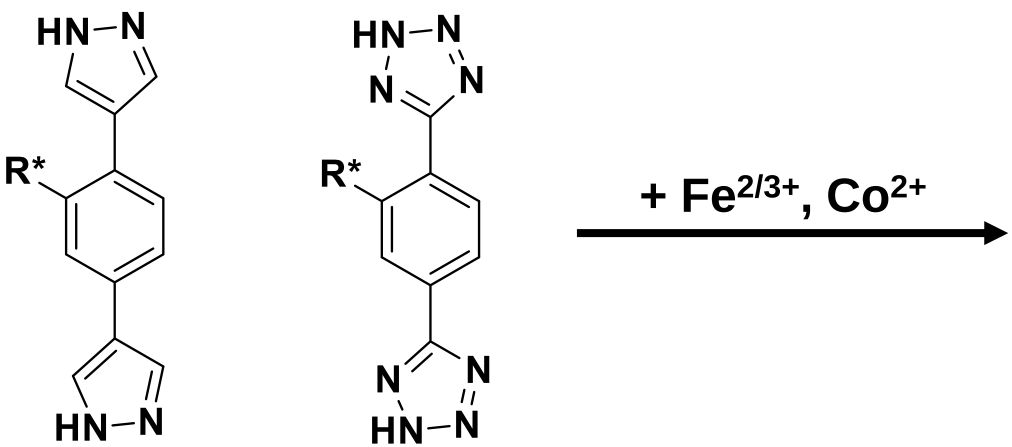


<u>Tesi in Sintesi Organica di Leganti Chirali</u>

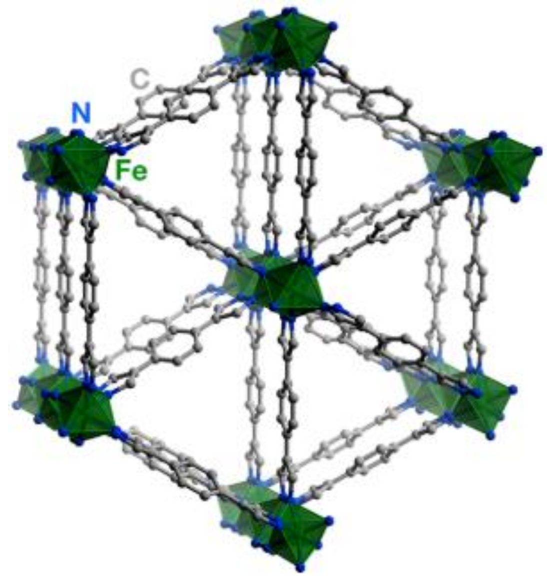
Sintesi di piccole **molecole organiche enantiopure** in grado di collegare i centri metallici del MOF e trasferire la chiralità alla struttura tridimensionale del polimero di coordinazione.

- Sviluppo di nuove vie sintetiche attraverso reazioni stereospecifiche/stereoselettive
- Uso di metodologie di sintesi moderne (es. cross-coupling, attivazione C-H, click chemistry)
- Tecniche di caratterizzazione di molecole organiche: NMR (^{1}H, ^{13}C, bidimensionali), Spettroscopia di Massa, HPLC, GC

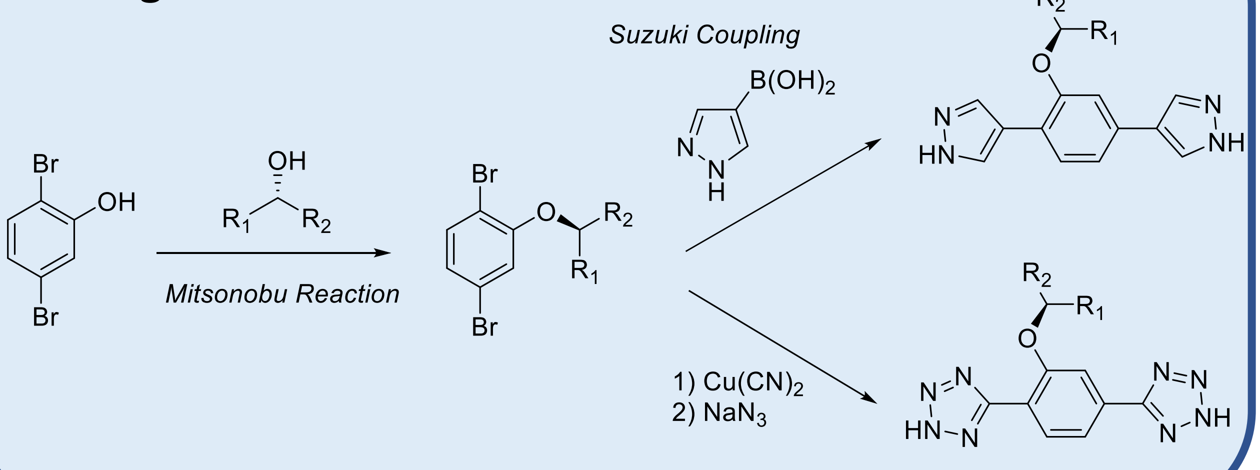
Chiral Bipyrazolate/Bitetrazolate Metal-Organic Frameworks



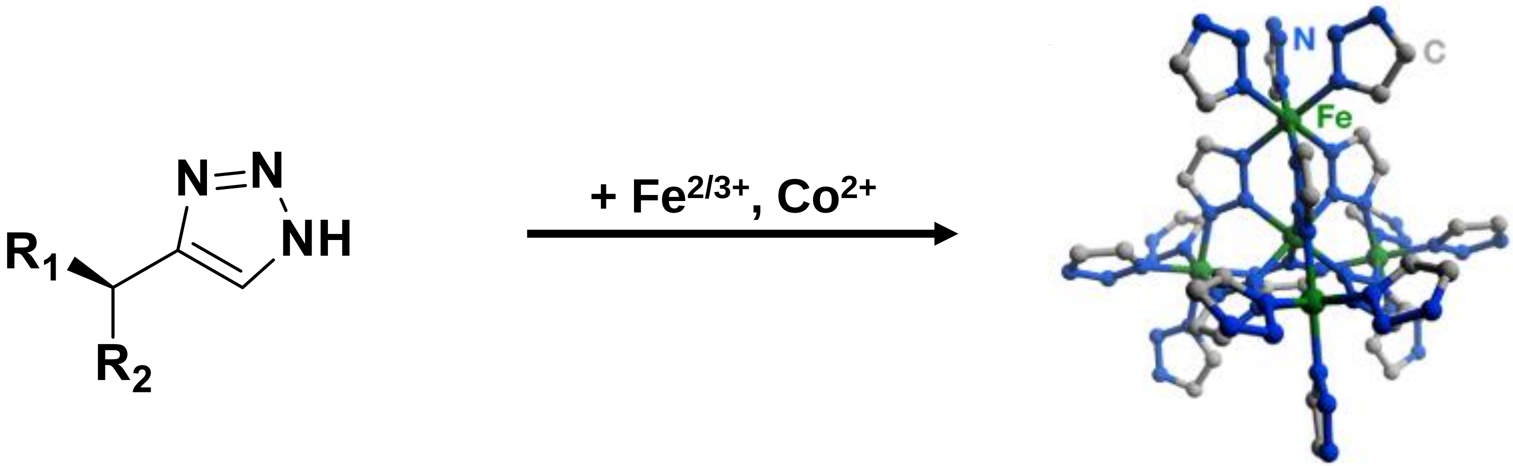
R* = gruppo chirale

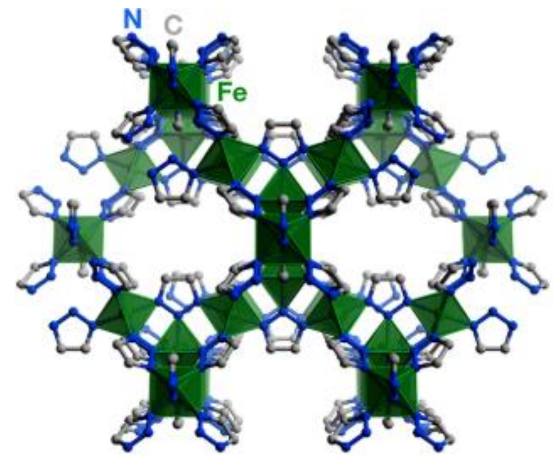


Strategia Sintetica



Chiral Triazolate Metal-Organic Frameworks





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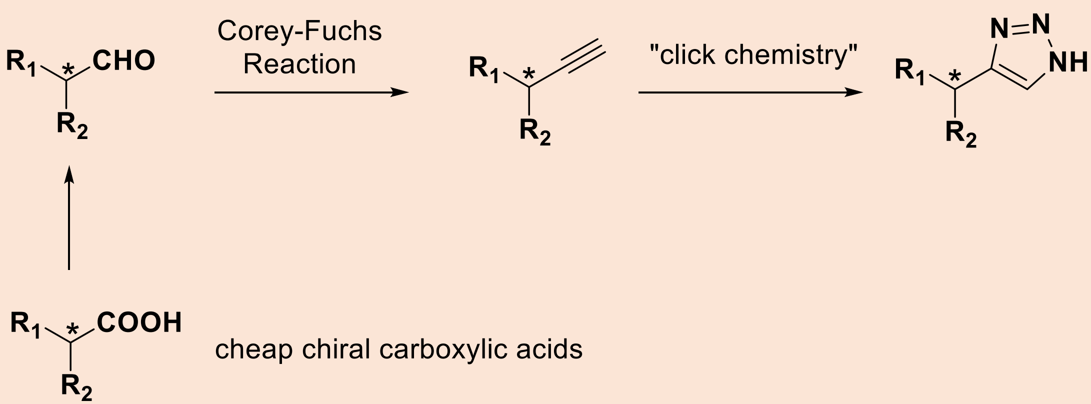
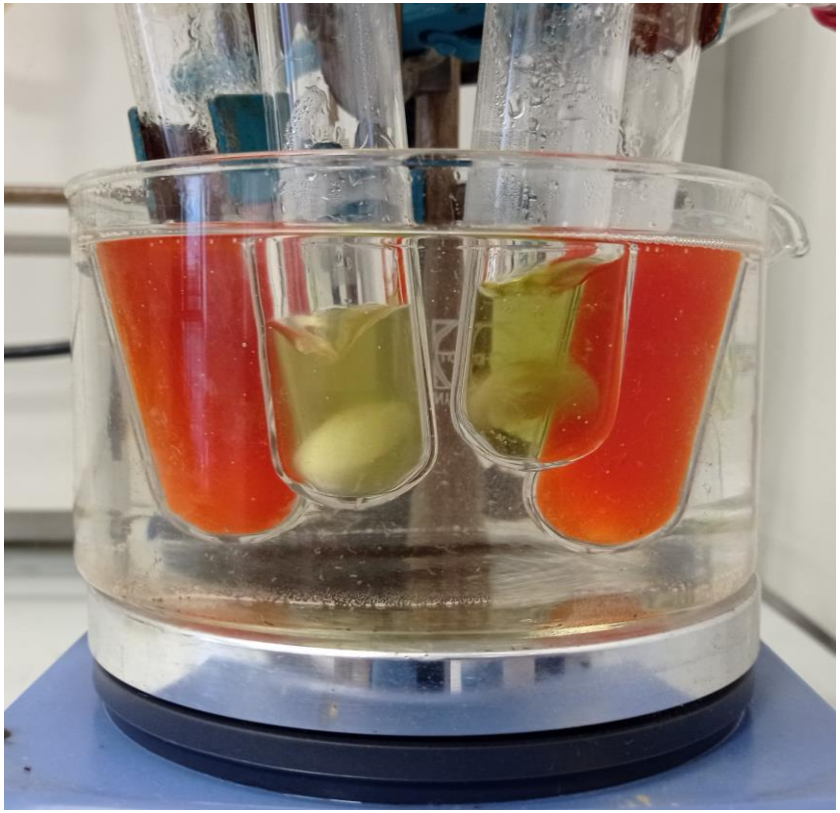


EXPERIMENTAL TECHNIQUES

Sintesi organica, sintesi inorganica, chimica di coordinazione



EXPERIMENTAL TECHNIQUES

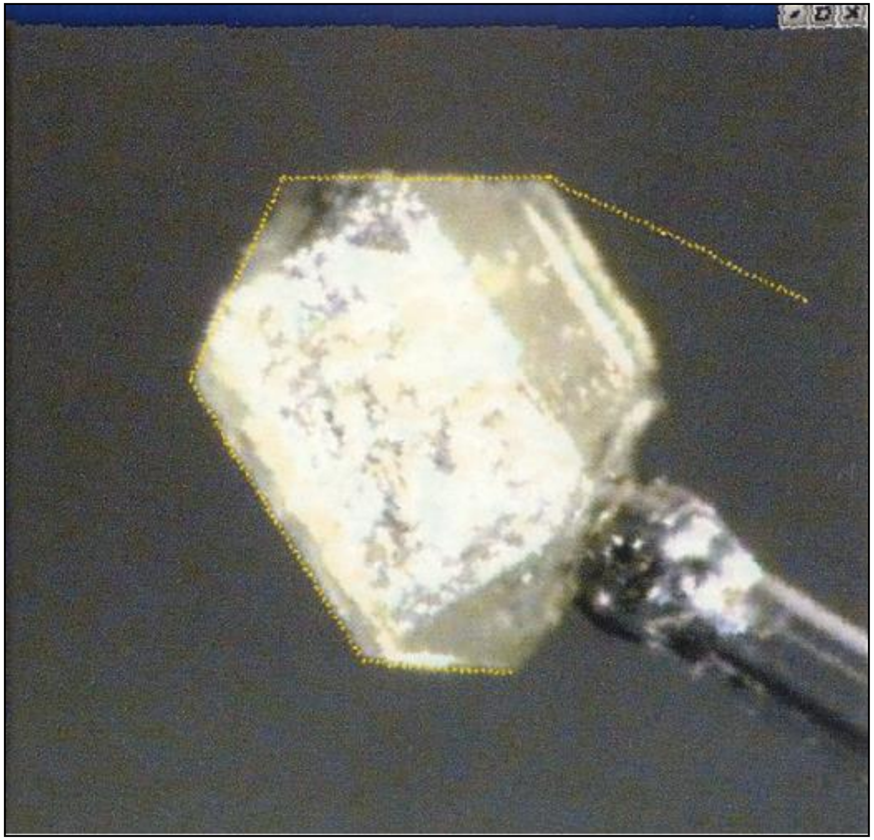
Sintesi organica, sintesi inorganica, chimica di coordinazione (eventualmente composti sensibili ad O_2 ed H_2O, reazioni in atmosfera controllata, glove-box)

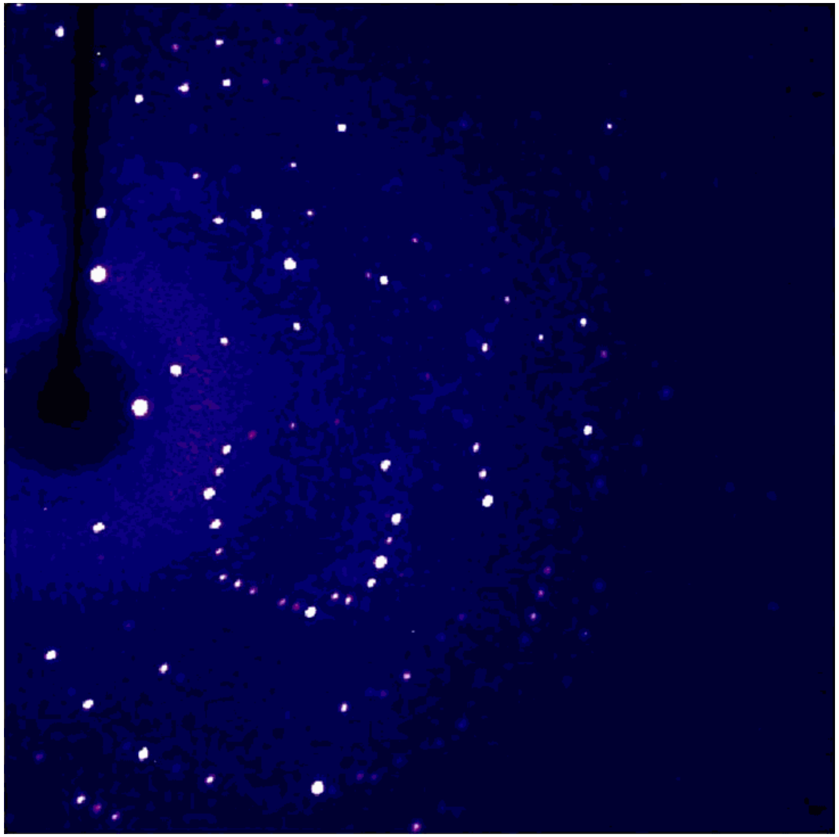
EXPERIMENTAL TECHNIQUES

Tecniche di cristallizzazione

EXPERIMENTAL TECHNIQUES

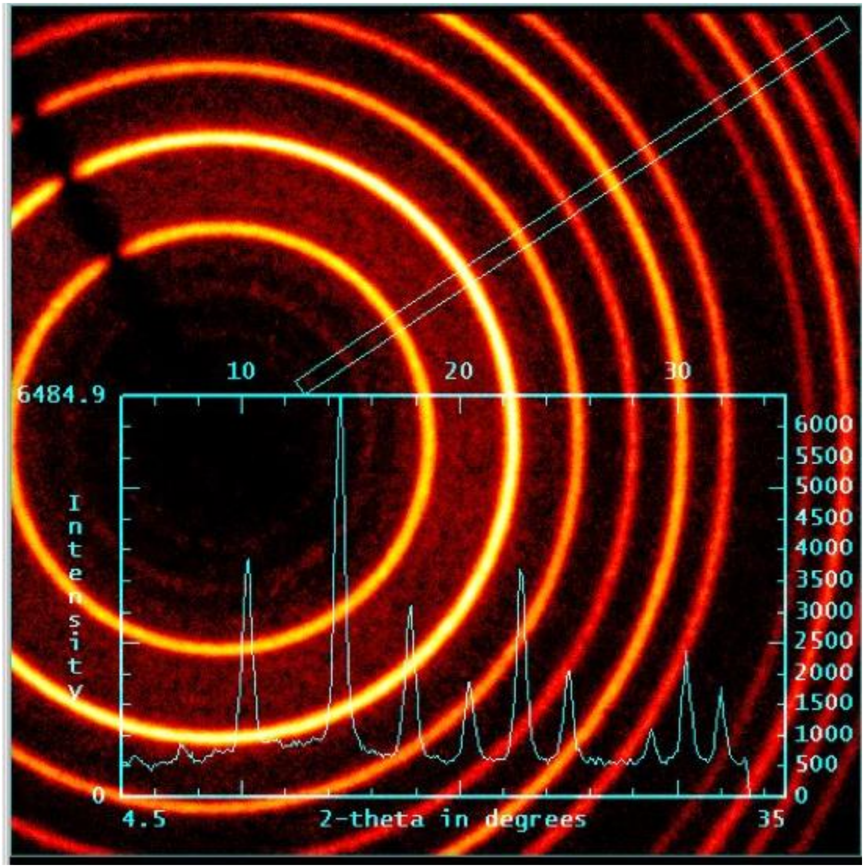
Diffrazione di raggi-X su cristallo singolo (da RT a 100 K)





EXPERIMENTAL TECHNIQUES

Diffrazione di raggi-X su polveri



EXPERIMENTAL TECHNIQUES

- **IR, analisi superficiale BET, microscopia TEM, etc. etc…**