



UNIMORE

UNIVERSITÀ DEGLI STUDI DI
MODENA E REGGIO EMILIA

Metal-Organic Frameworks (MOF) CHIRALI: Sintesi, Caratterizzazione e attività Catalitica per l'elettrolisi dell'acqua (*Water Splitting*) e la produzione di H₂ *green*

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OUR #1 PROBLEM (?)

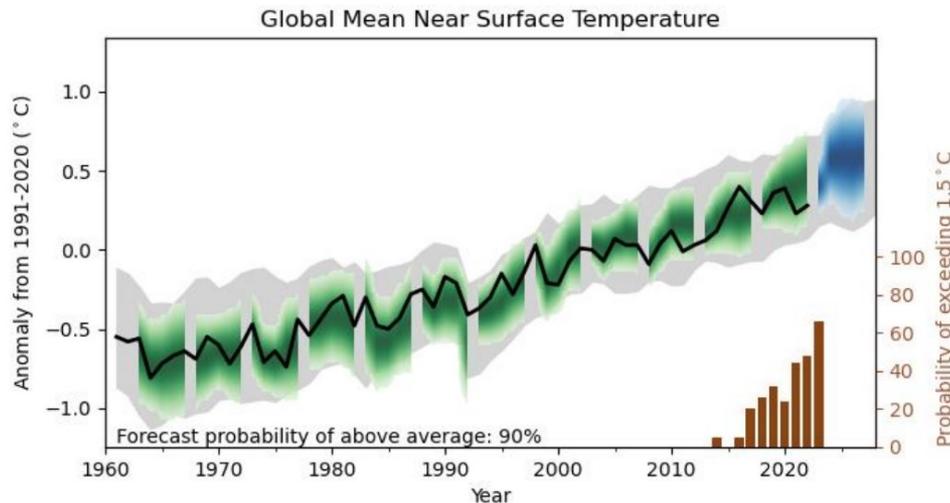
How I Learned to Stop Worrying and Love the Heat

Monday July 3 was the hottest day on record on Earth

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

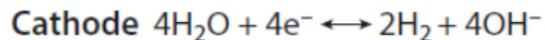
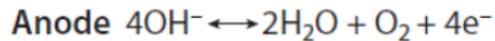
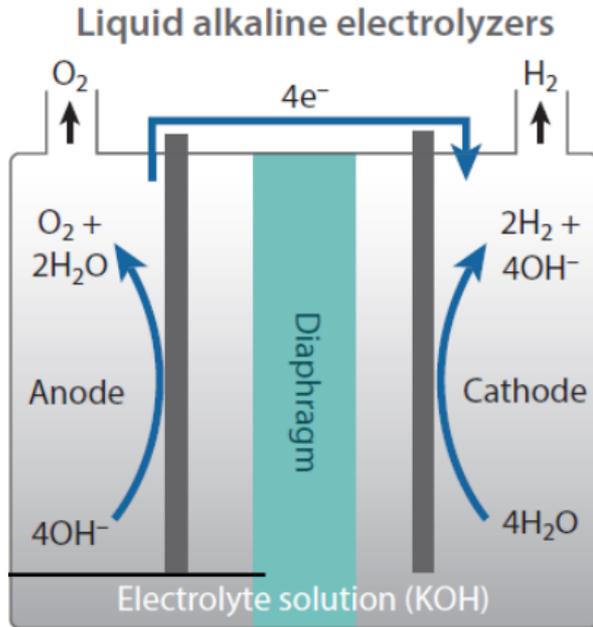
Earth sees third straight hottest day on record, though it's unofficial: "Brutally hot"

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

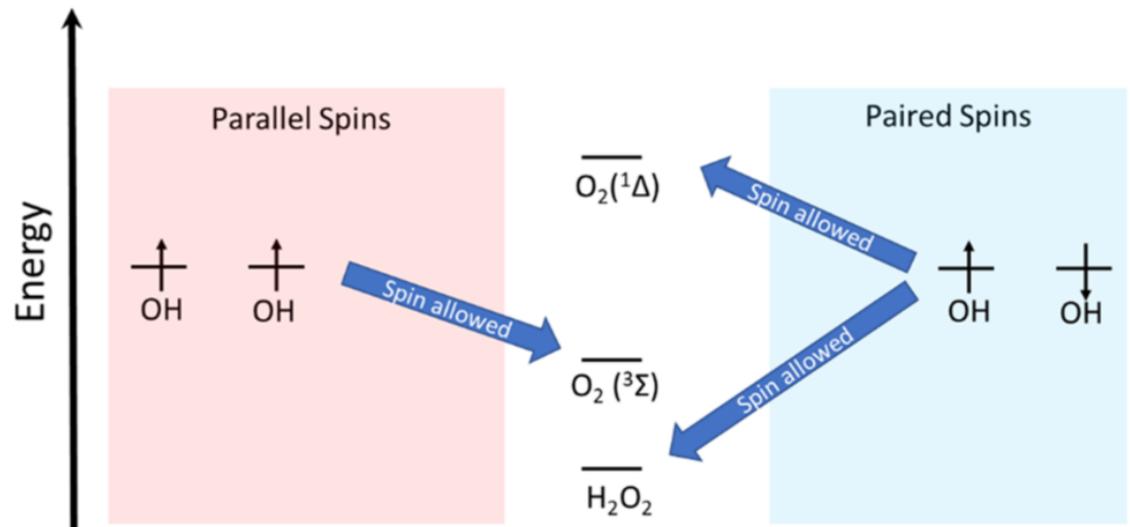


ENERGIE RINNOVABILI: H₂ verde!

A solution with its own problems



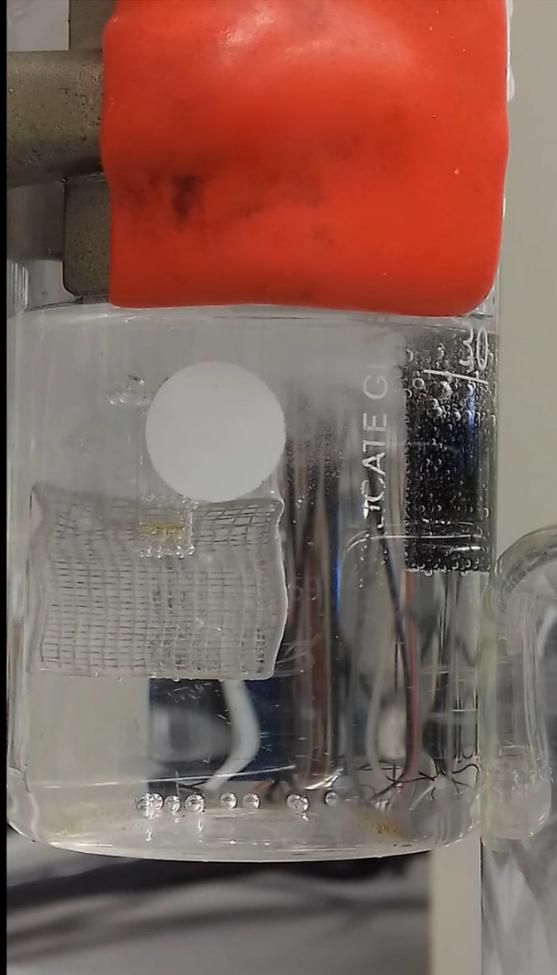
Oxygen Evolution Reaction (OER): il limite della reazione del Water Splitting



SPIN POLARIZED OER

A small trick that goes a long way

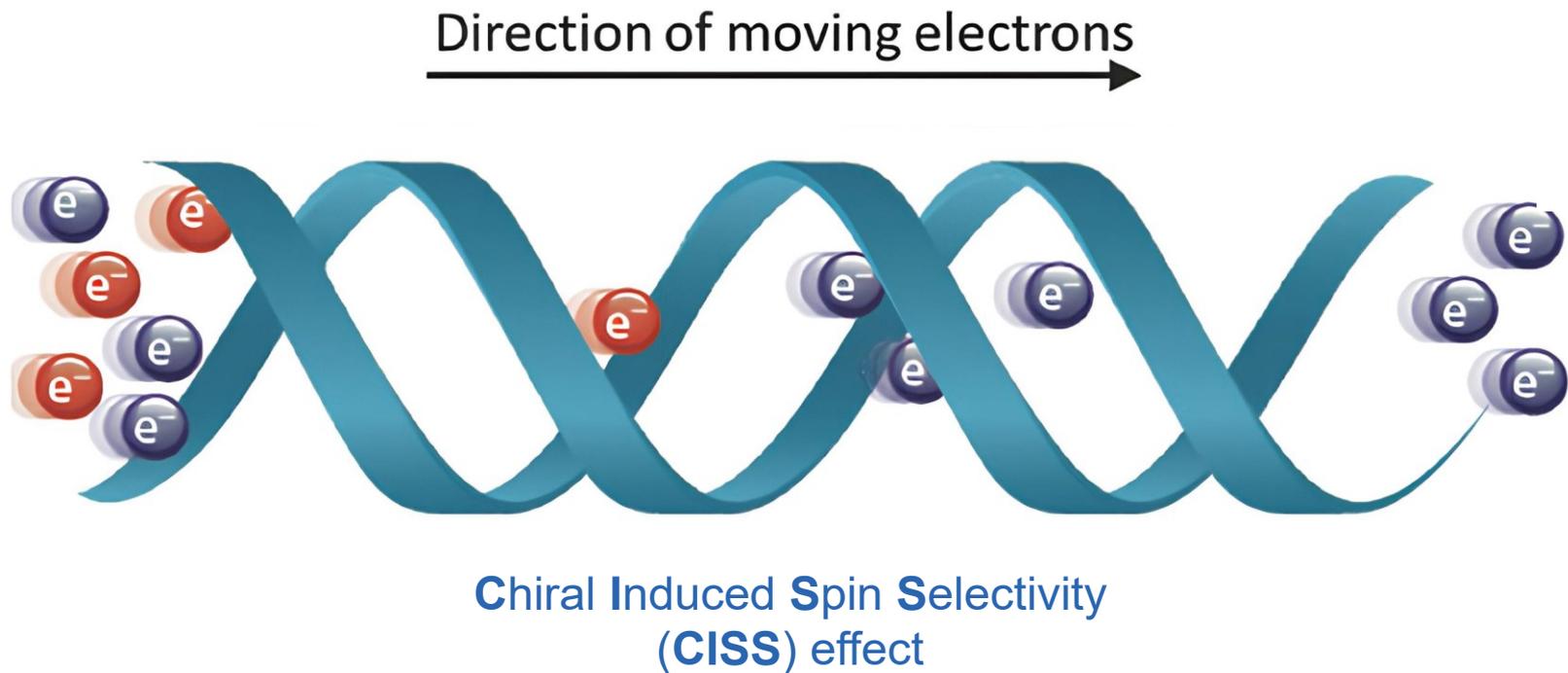
Catalizzatore
ferromagnetico
 $\text{NiZnFe}_4\text{O}_x$



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

E senza campo magnetico??

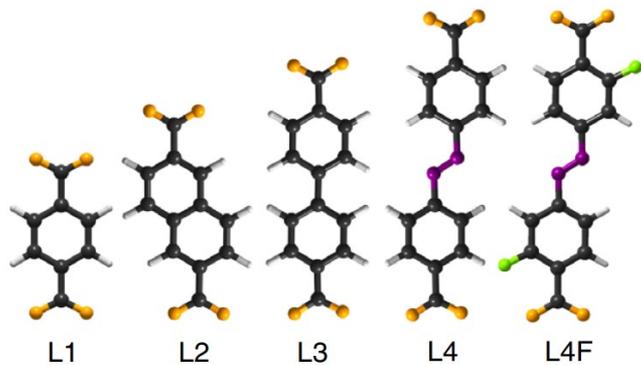
Sfruttamento dell'effetto CISS per creare correnti spin-polarizzate!



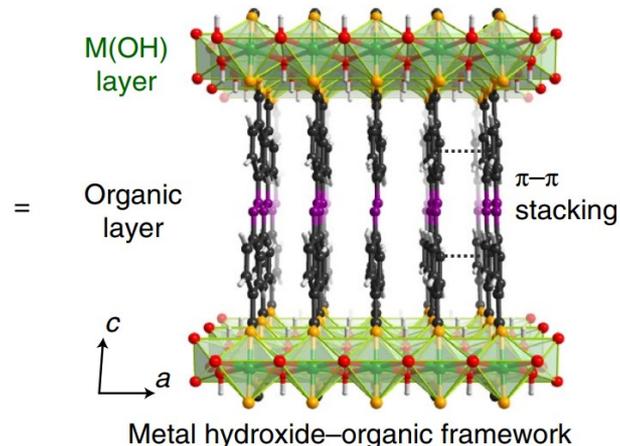
WHAT DO WE WANT TO DO?

Sintesi di nuovi Catalizzatori per OER: Metal-Organic Frameworks (MOF) CHIRALI!

Ni^{2+}
 Co^{2+}
 $\text{Fe}^{2+/3+}$

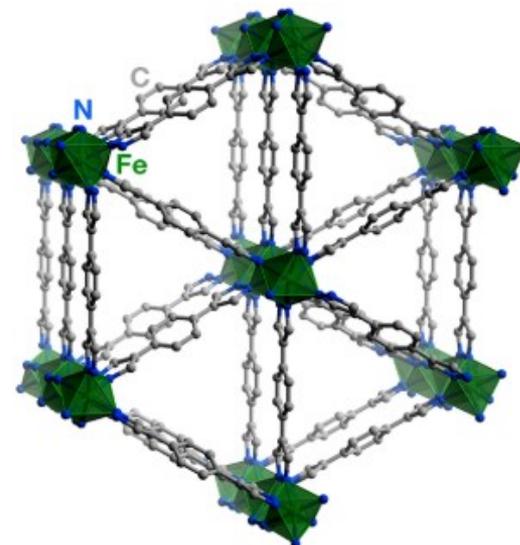


Aromatic organic linkers



Perché Metal-Organic Frameworks?

- Sono basati su metalli della prima serie di transizione
 - Alta area superficiale e porosità
 - Sono un campo inesplorato!
- Le loro proprietà sono modulabili grazie alla strategia del *design chimico*
 - Correlazione struttura-proprietà

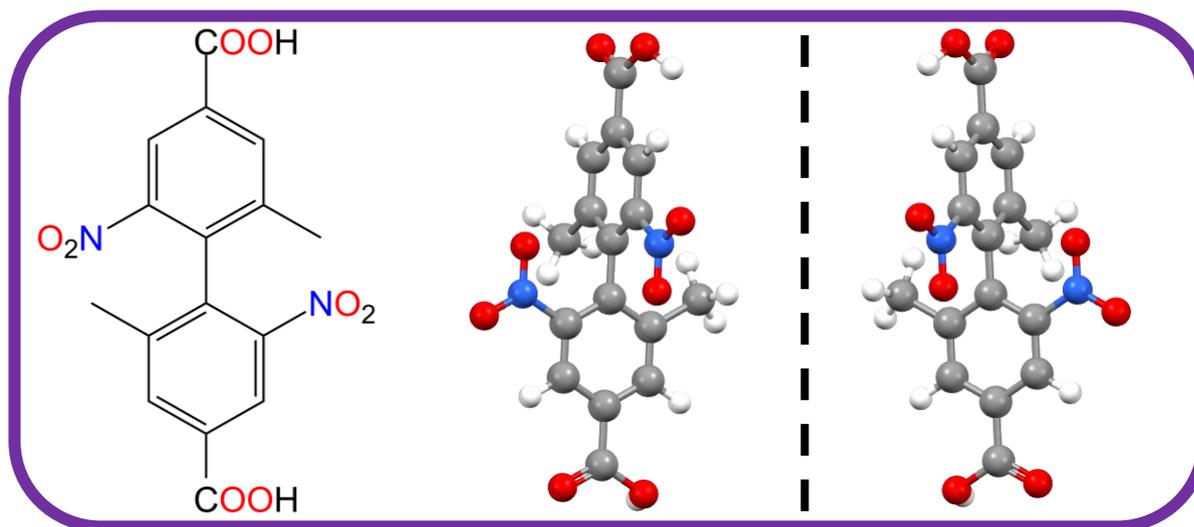


PRIMA proposta di Tesi

Tesi in Sintesi Organica di Leganti Chirali

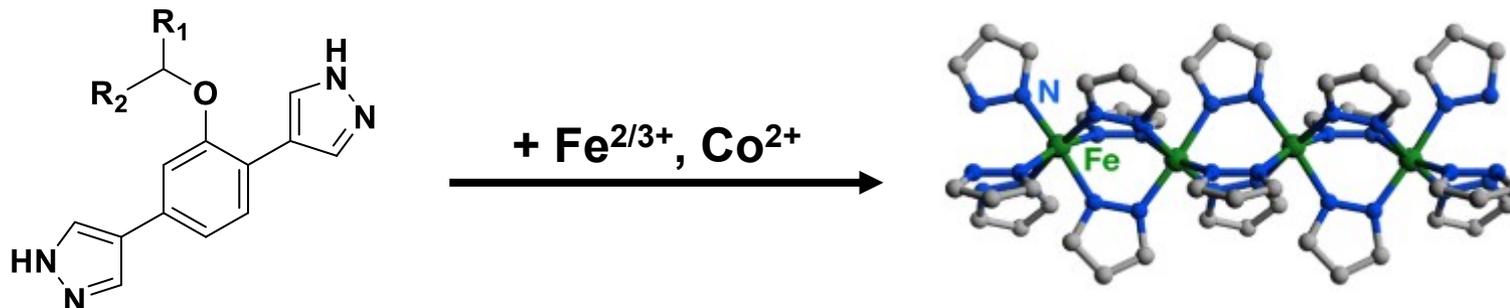
Sintesi di piccole **molecole organiche enantiopure** in grado di collegare i centri metallici del MOF e trasferire la chiralità alla struttura tridimensionale del polimero di coordinazione.

- 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 (^1H , ^{13}C , bidimensionali), Spettroscopia di Massa, HPLC, GC



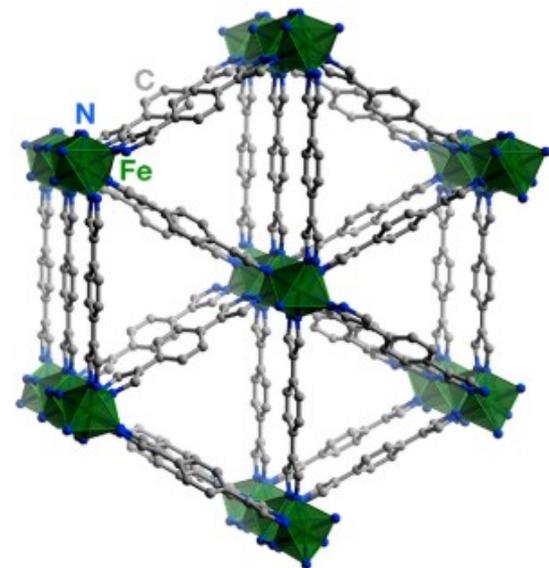
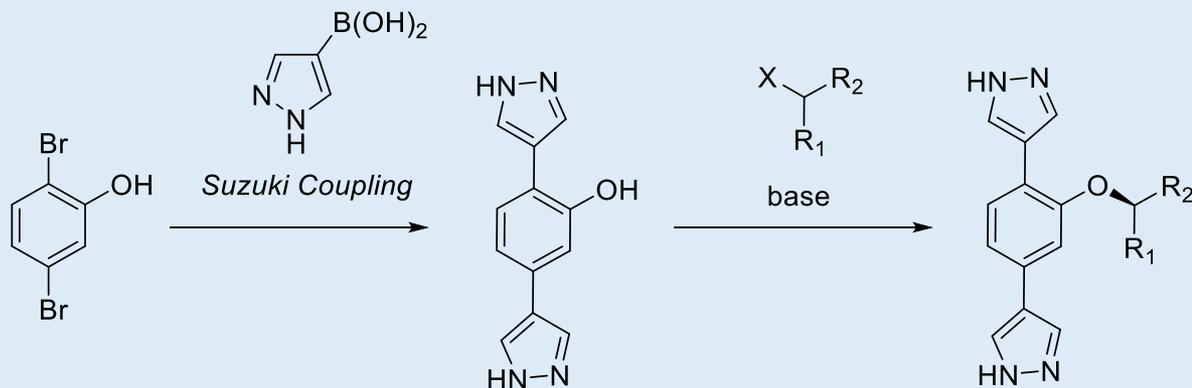
SECONDA proposta di Tesi

Chiral Bipyrazolate/Bitetrazolate Metal-Organic Frameworks



- Leganti bis-pirazolati per MOF conduttivi e porosi
- Aggiunta di un gruppo chirale per ottenere spin-selezione

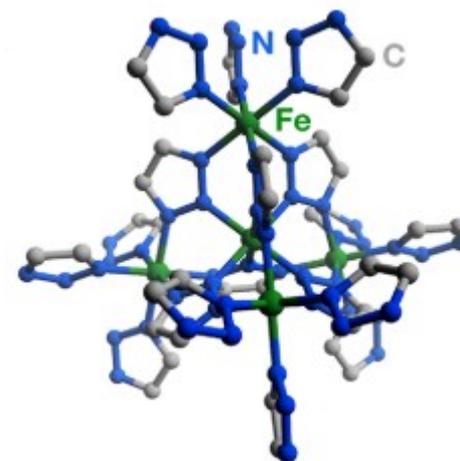
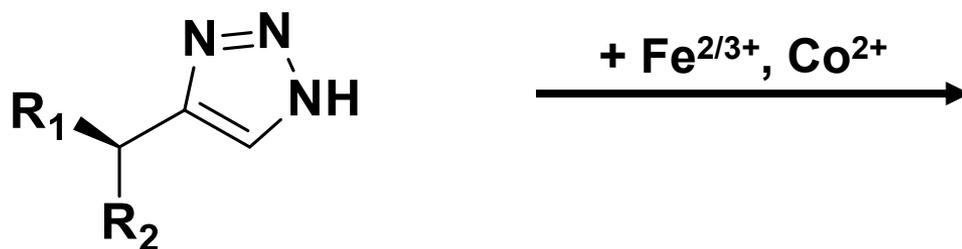
Strategia Sintetica



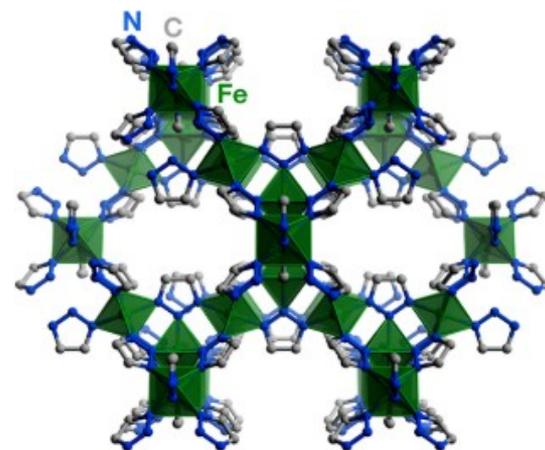
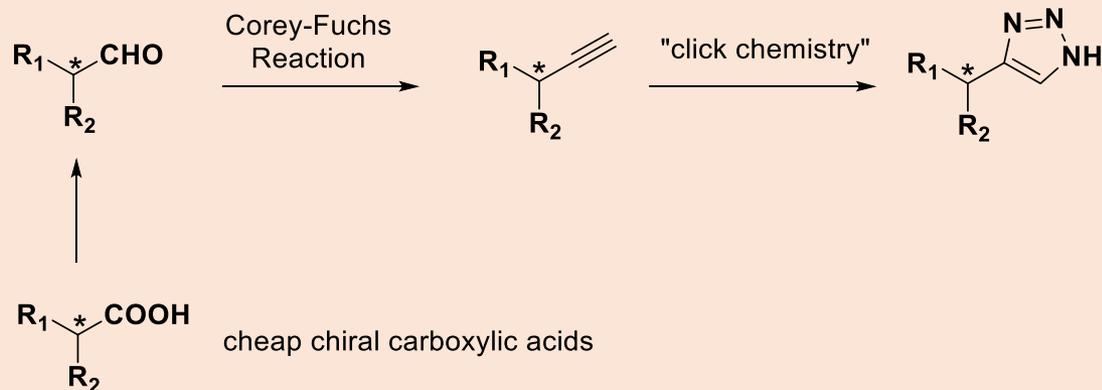
Creare una libreria di nuovi leganti chirali attraverso utilizzo di diversi alogenuri alchilici

SECONDA proposta di Tesi

Chiral Triazolate Metal-Organic Frameworks

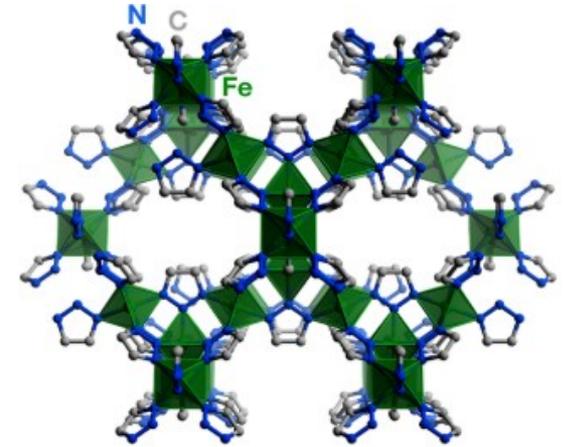
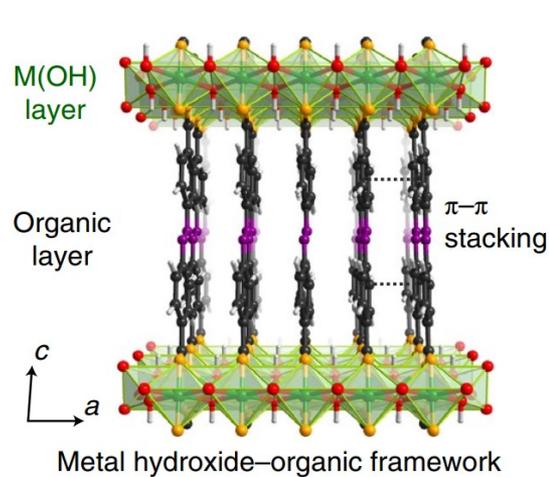
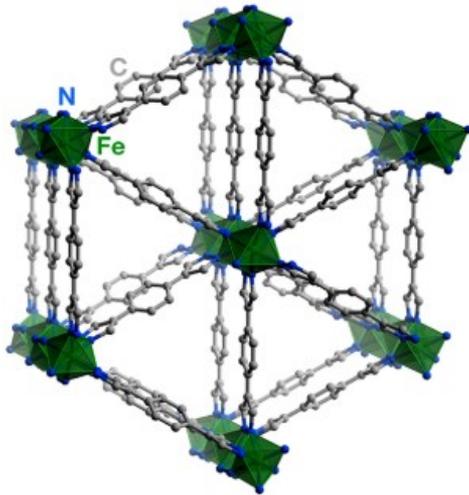


Strategia Sintetica



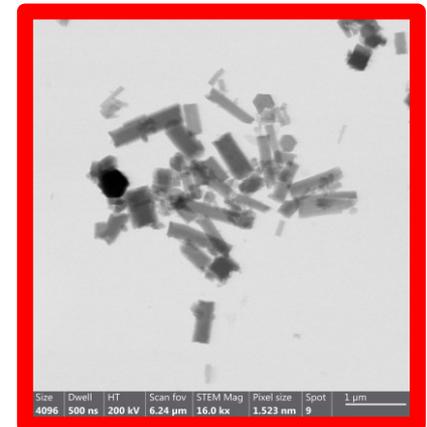
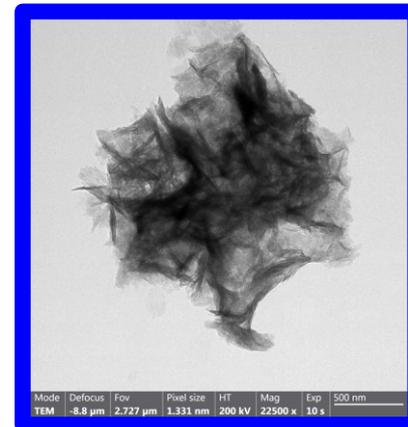
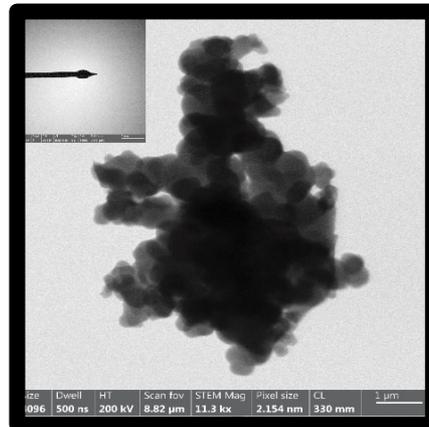
TERZA proposta di Tesi

Sintesi di nuovi Catalizzatori per OER: Metal-Organic Frameworks (MOF) CHIRALI!



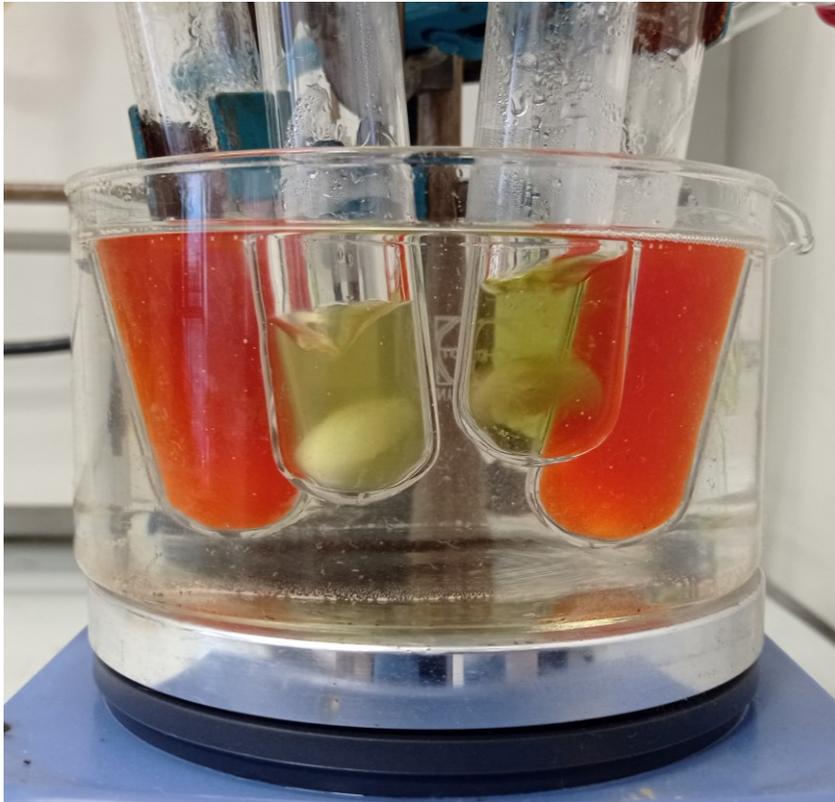
Caratterizzazione strutturale

- AE
- FT-IR, UV-Vis-NIR
- BET
- SEM, TEM, etc...



EXPERIMENTAL TECHNIQUES

Sintesi organica, sintesi inorganica, chimica di coordinazione



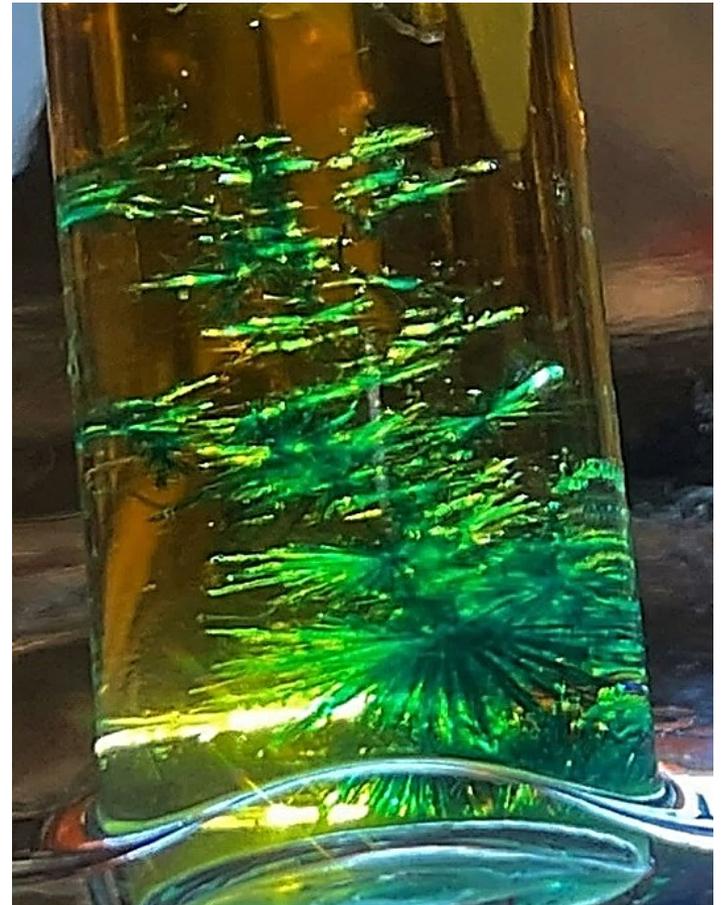
EXPERIMENTAL TECHNIQUES

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



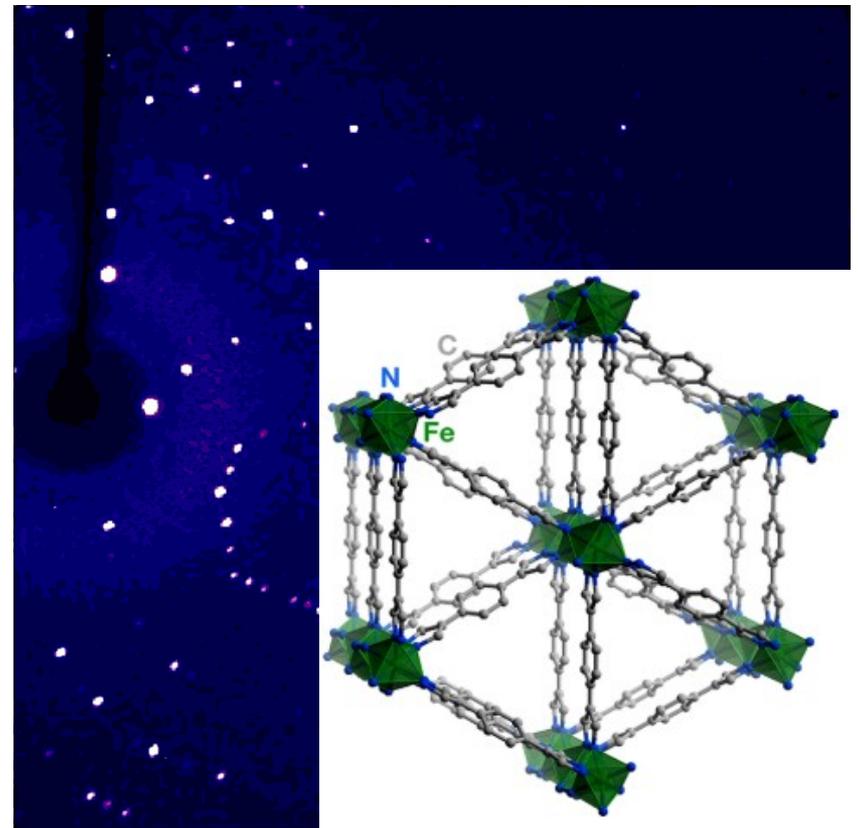
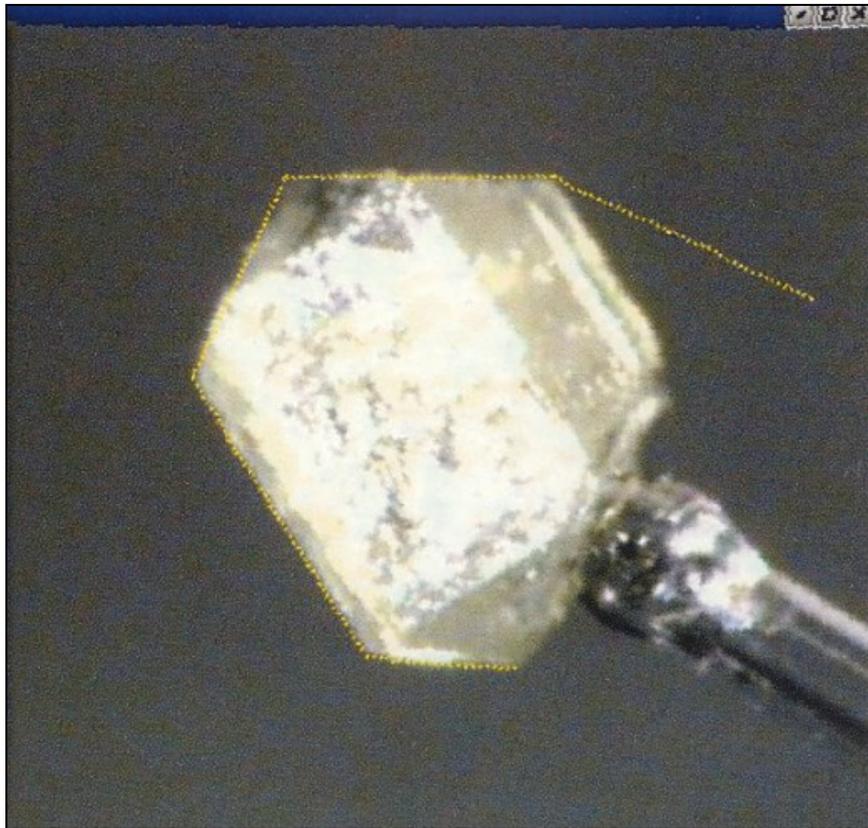
EXPERIMENTAL TECHNIQUES

Tecniche di cristallizzazione



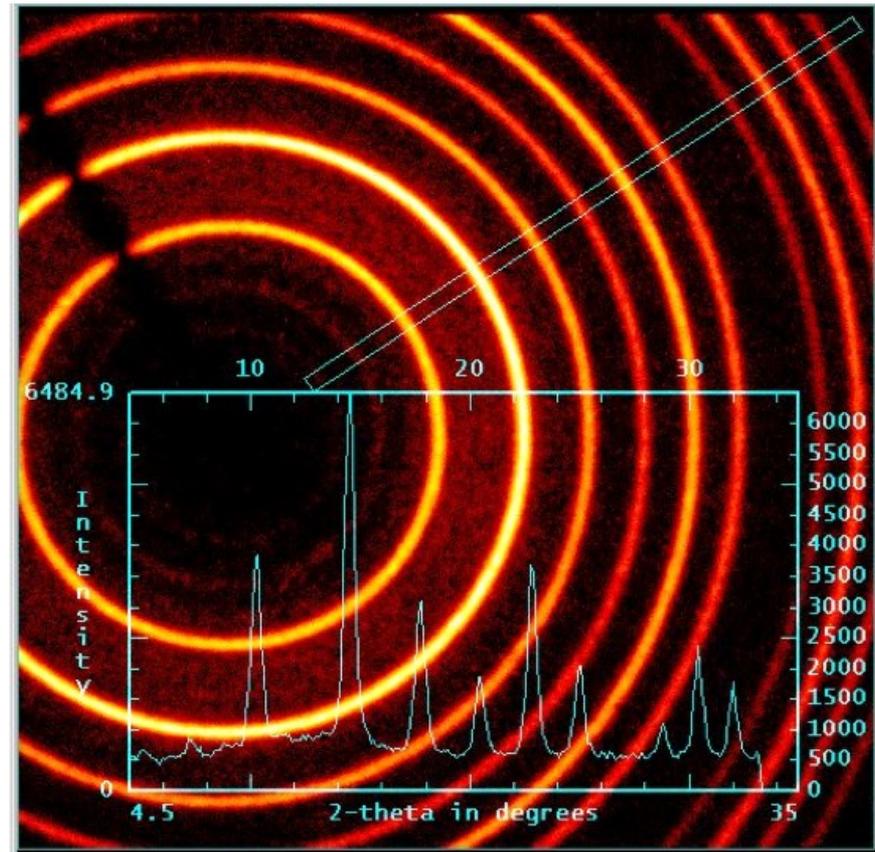
EXPERIMENTAL TECHNIQUES

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

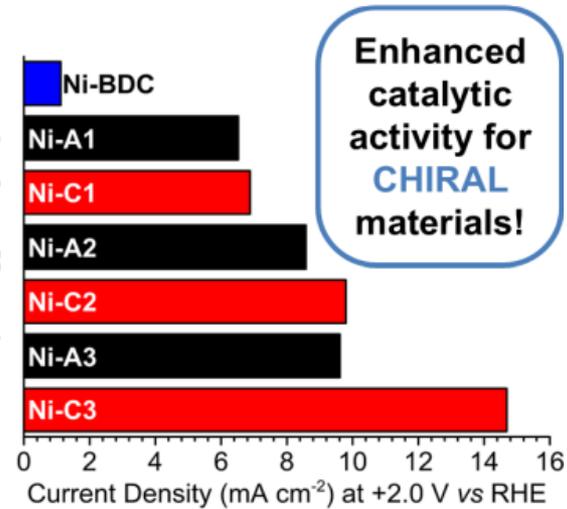
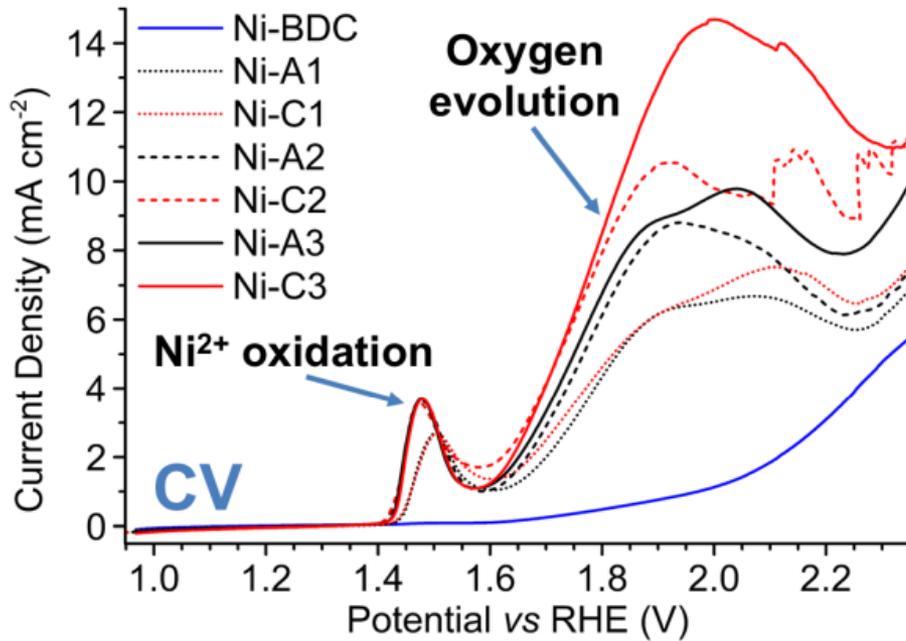


EXPERIMENTAL TECHNIQUES

Diffrazione di raggi-X su polveri



Caratterizzazione Electrochimica



Voltammtria
ciclica

