AMINO-DECORATED ZINC BIPYRAZOLATE MOFS: AN EXAMPLE OF CARBON DIOXIDE CAPTURE AND CONVERSION

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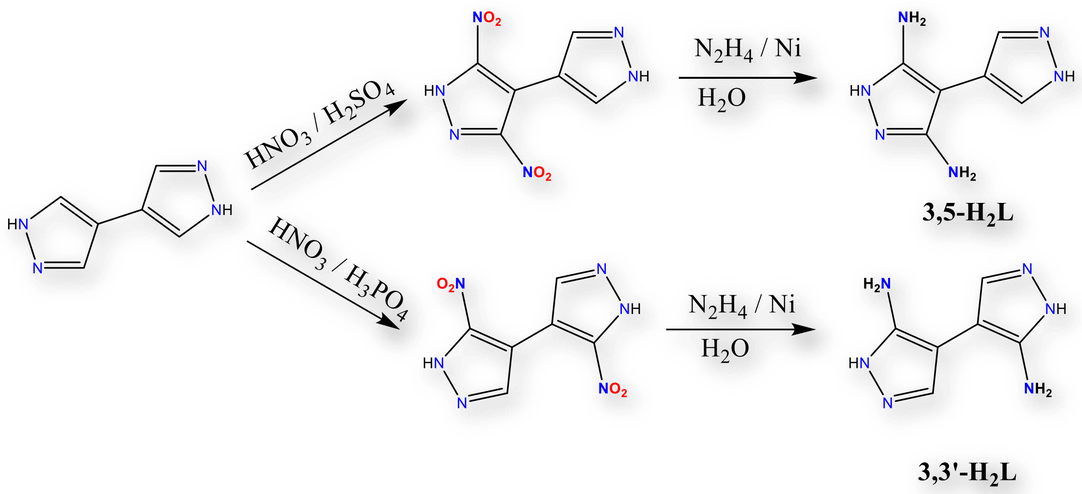
INTRODUCTION

Carbon dioxide emissions in atmosphere have been increasing relevantly due to anthropogenic activities. This gas is considered the main greenhouse gas responsible for global warming; it is involved in the depletion of stratospheric ozone and is causing the acidification of oceans. For this reason, it is necessary to find solutions to face this fast growth. Metal-Organic Frameworks (MOFs) seem to be valid candidates, due to the surprising ability of some MOFs in selective adsorption of CO_2, in its storage and also conversion into other products . In this work, two isomeric forms of diamino-decorated zinc bipyrazolate MOFs **Zn(3,3'-L)** and **Zn(3,5-L) (L = diamino-4,4'-bipyrazolate)** have been synthesized under solvothermal conditions in DMF and characterized by IR, TGA/DTA, EA and XRPD. The structures of these MOFs were solved, showing in both cases 3D (4,4)-connected network structures with 1D squared channels, isostructural with respect to Zinc MOFs based on 3-amino-4,4'-bipyrazole and 4,4'-bipyrazole linkers previously reported. BET surface area, pore size distribution and the ability as CO_2 adsorbents were investigated through N_2 and CO_2 adsorption, together with their potential as heterogeneous catalysts in the solvent-free conversion of epichlorohydrin or epibromohydrin and carbon dioxide into the corresponding cyclic carbonates at 393K and p_{CO2} = 5 bar.

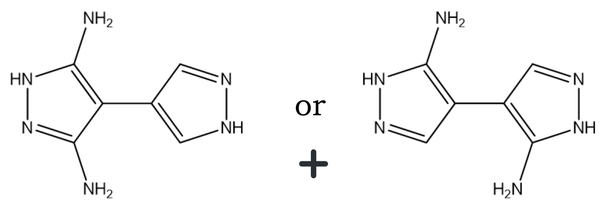
SYNTHESIS OF ORGANIC LINKERS



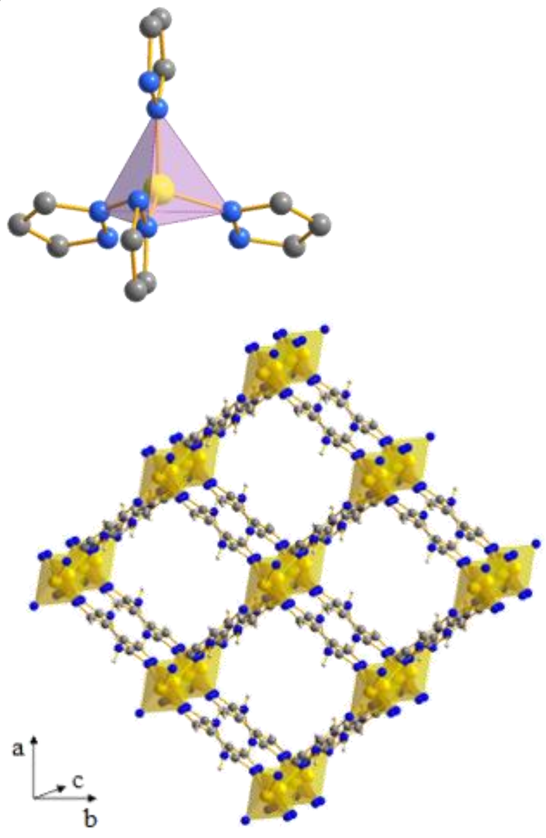
Starting from 4,4'-bipyrazole, **3,3'-H_2L** and **3,5-H_2L** are obtained after **dinitration** and consequent **reduction** with hydrazine and Raney Nickel slurry.

Dinitration pathway strongly depends on the acidity of the reaction medium

SYNTHESIS OF Zn-MOFs

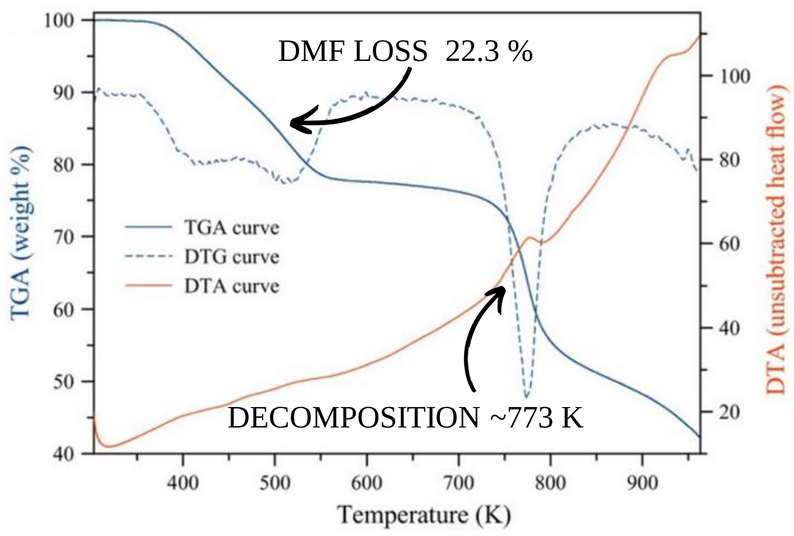


- ZnN_4 tetrahedral nodes
- 3D (4,4)-connected network (**sra** network topology) with 1D square channels running along the c-axis

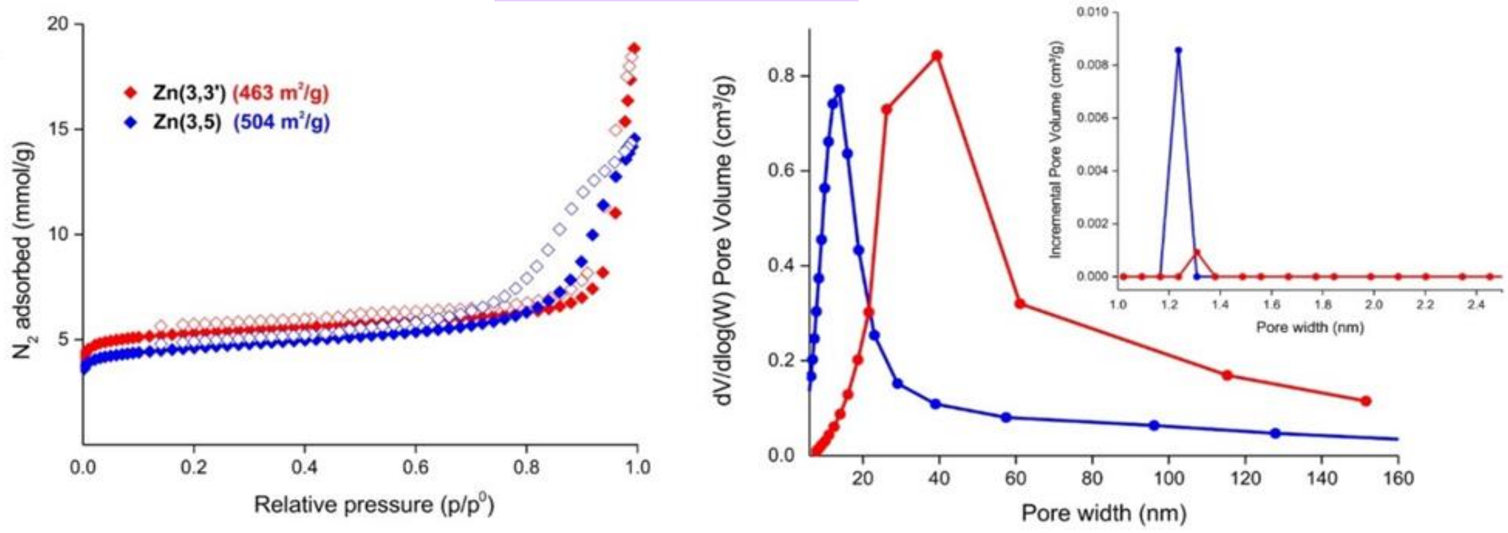


CHARACTERIZATION OF Zn-MOFs

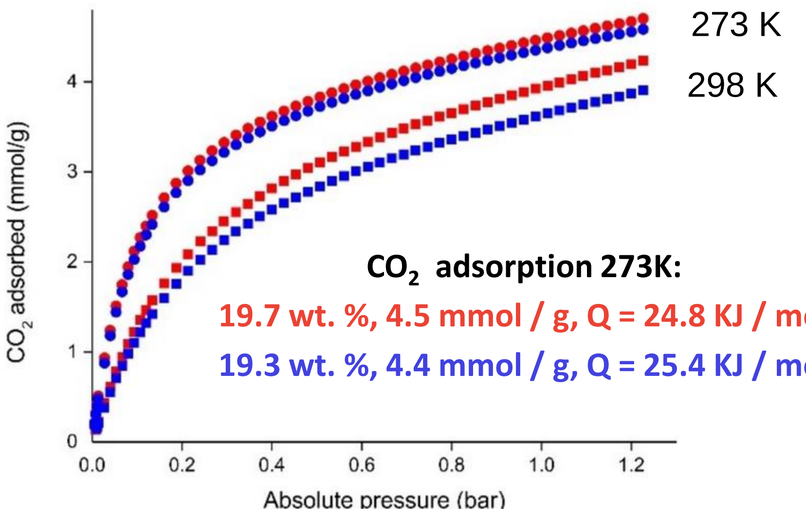
TGA/DTA/DTG Zn(3-3'L)



BET isotherms



CO_2 Adsorption

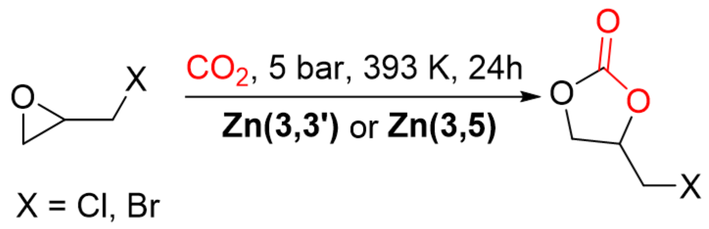


CO_2 adsorption 273K:

19.7 wt. %, 4.5 mmol / g, Q = 24.8 KJ / mol

19.3 wt. %, 4.4 mmol / g, Q = 25.4 KJ / mol

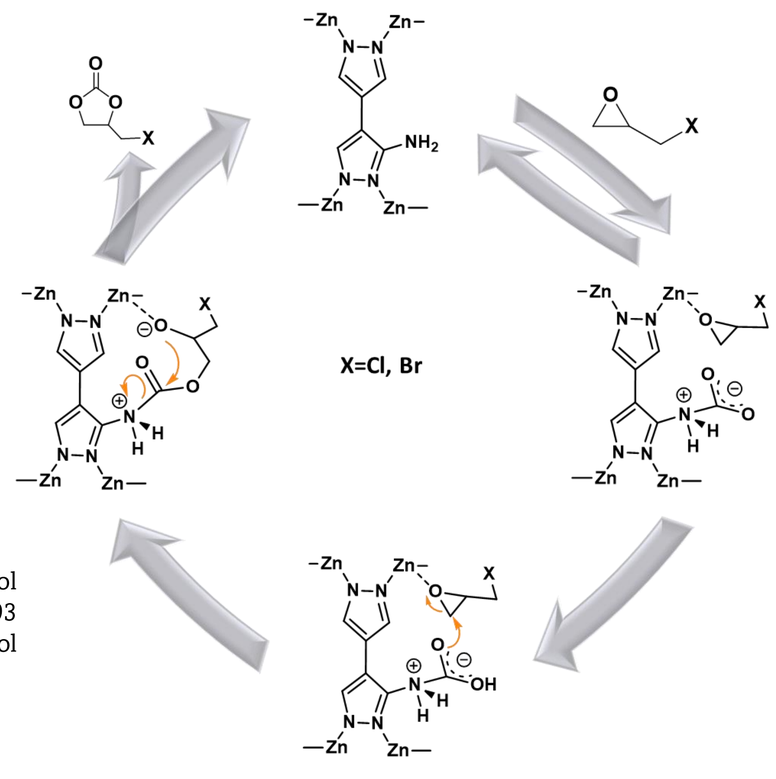
Cycloaddition reaction of epoxide with CO_2



Catalyst	X	Yield (%)	TOF[a]
Zn(3,3')	Cl	49	4.0
Zn(3,5)	Cl	64	5.3
Zn(3,3')	Br	41	3.4
Zn(3,5)	Br	49	4.0

Reaction conditions: mmol catalyst = 0.05; mmol epichlorohydrin or epibromohydrin = 10; P_{CO2} = 5 bar; T = 393 K; reaction time = 24 h. [a] Calculated as (mmol carbonate)·(mmol Zn)$^{-1}$ h^{-1}

PROPOSED MECHANISM



FUTURE PERSPECTIVES

Evaluation of catalytic activity of similar Zinc-based bipyrazolate MOFs decorated with other functional groups

Computational simulation of MOF whole cavity to better understand catalytic mechanism

R. Vismara, G. Tuci, N. Mosca, K.V. Domasevitch, C. Di Nicola, C. Pettinari, G. Giambastiani, S. Galli, A. Rossin, Inorg. Chem. Front., 2019, 6, 533–545