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A structural comparison between Co II and Cu II anilato-based ultramicroporous 3DMOFs

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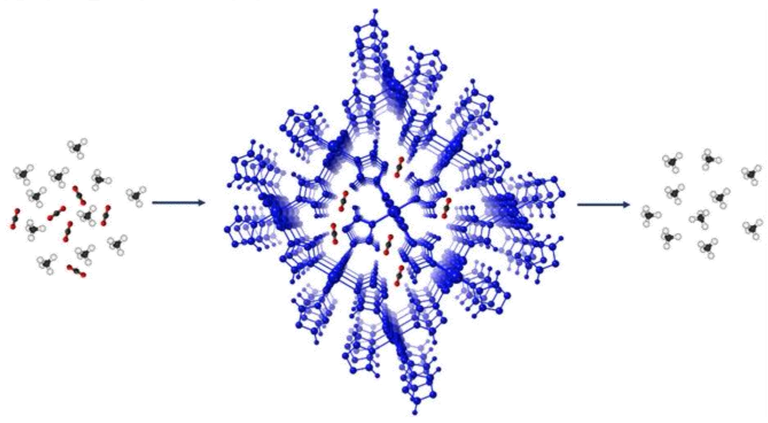
INTRODUCTION & AIM

Metal-Organic Frameworks (MOFs), crystalline porous materials self-assembled by metal ions (nodes) and organic ligands (linkers), are attracting ever-growing interest in material chemistry. Their high porosity, tunable pore size and large surface area make MOFs promising candidates to uptake and separate CO_2 from gaseous mixtures. In particular, the ultramicroporosity (pore size < 0,7 nm) and the presence of nitrogen atoms are crucial requirements in the design of MOFs for CO_2 uptake. On these bases, by combining, 3,6-N-ditriazolyl-2,5-dihydroxy-1,4-benzoquinone (trz $_2$ An), as organic linker, with Co^{II} or Cu^{II} two new ultramicroporous MOFs, formulated as [Co(trz 2 An)]n·3H $_2$ O [1] (**1**) and [Cu(trz $_2$ An)]·(H $_2$ O) 2.5 (**2**) have been obtained.



METHOD

1 and **2** have been synthesized optimizing the synthetic procedure reported in literature. [1] A solution of $CoCl_2 \cdot 6H_2O$ (11.9 mg, 0.05 mmol), or CuCl $_2$ ·2H_2O (8.5 mg, 0.05 mmol), are slowly added to a mixture of trz $_2$ An (13.7 mg, 0.05 mmol), NaOH (4 mg, 0.1 mmol) and water (5 mL) and heated in a autoclave at 130 °C for 48 hours. The rectangular crystals, suitable for single X-ray diffraction study, were washed three times by using an acid aqueous solution (pH=5) in order to solubilize and remove $Co(OH)_2$ and $Cu(OH)_2$ obtained during the reaction.

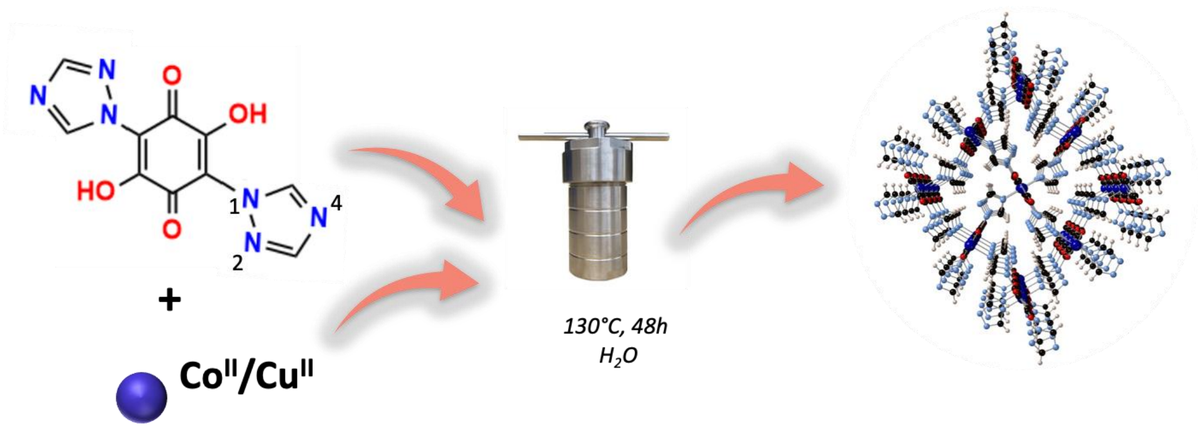


Figure **1.** Schematic representation of MOF_S Synthesis

FUTURE WORK / REFERENCES

[1] Mercuri M.L. *et al.* A Thermally/Chemically Robust and Easily Regenerable Anilato-Based Ultramicroporous 3D MOF for CO_2 Uptake and Separation. *J. Mater. Chem. A* **2021**, **9**, 25189-251

RESULTS & DISCUSSION

In **1**, Co^{II} ions are equatorially coordinated to four oxygen atoms of two bis(bidentate) trz_2An ligands. The distorted octahedral coordination sphere of Co^{II} ions is completed with two nitrogen atoms from the N4 atoms of the 1,2,4-triazole substituted pendant rings of trz $_2$ An ligands. Two voids of 90.4 Å ^{3} were found in the unit cell of the crystals, giving a void volume of 23.5%. **2** is characterized by cubic cavities whit a volume void of 28 %, due to the coordination to the N atom at the 4-position of the triazole ring, which induces an alternated orientation of Cu-anilate chains.

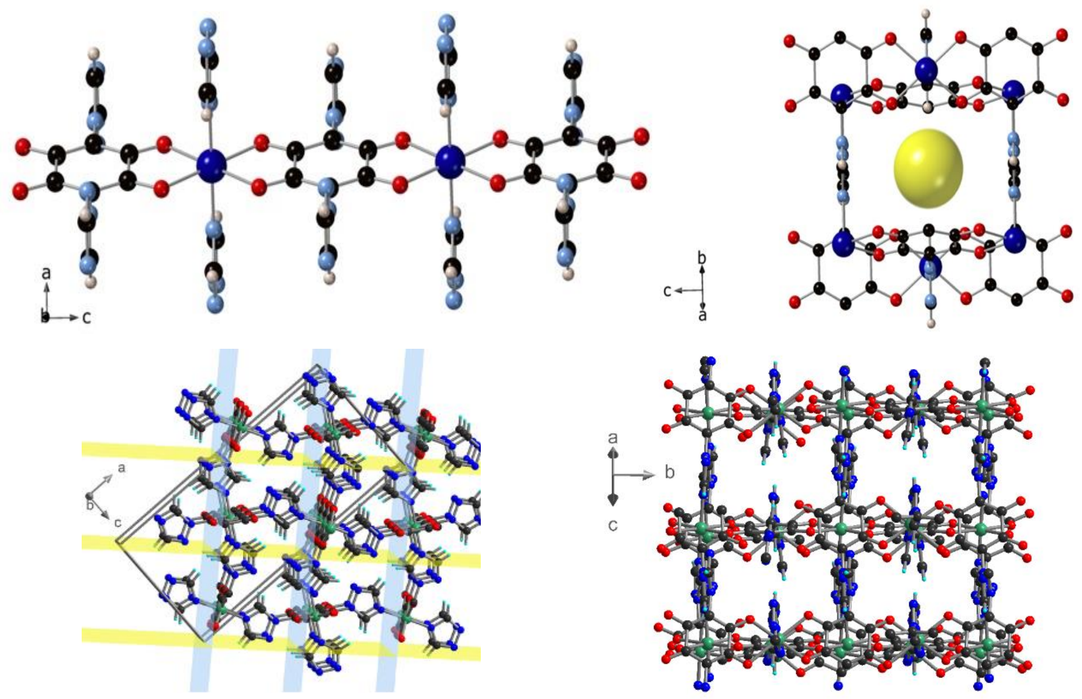


Figure **2.** Structural Characterization of **1** (top) and **2** (down**)**

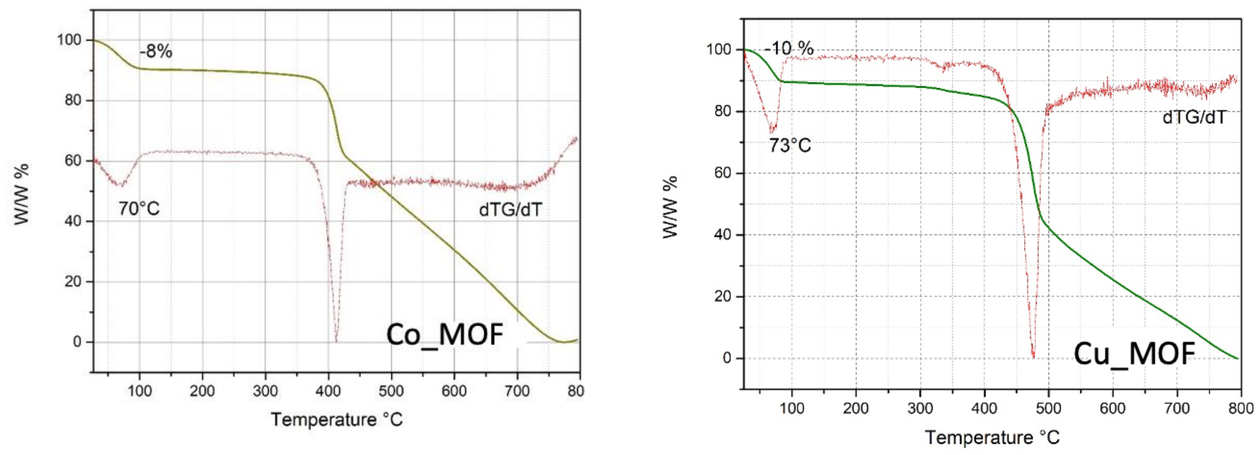


Figure **3.** Thermal Gravimetric Characteriz**ation of 1** and **2**

CONCLUSION

The same trz_2 An linker has been employed to obtain, in combination with Co^{II} and Cu ^{II} , two robust, thermically stable, isomorphous and ultramicroporous MOFs, suitable for CO_2 uptake and separation.