Andrea Rossin, PhD.
Institute of Chemistry of OrganoMetallic Compounds, ICCOM-CNR
Via Madonna del Piano, 10 – 50019 Sesto Fiorentino (Firenze)
Phone: +39 055 5225248; Fax: +39 055 5225203; email: a.rossin@iccom.cnr.it

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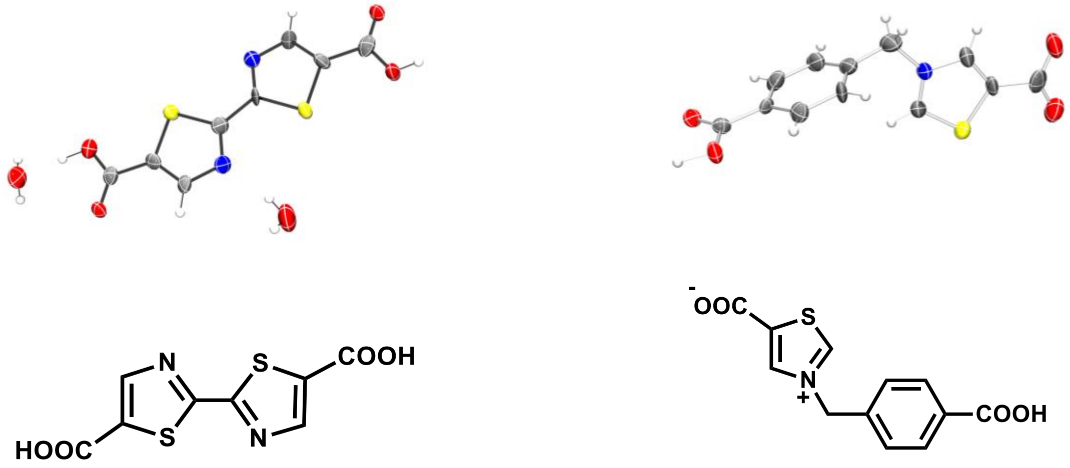
Scientific report on the activity of Dr. ANDREA ROSSIN during his STM at Northwestern University (Evanston, IL United States).

During the two-weeks stay in Evanston, the undersigned Dr. ANDREA ROSSIN has visited the laboratories and staff of Northwestern University Chemistry and Engineering Departments; he has given an introductory seminar to the American colleagues, describing Florence research activity in the Metal-Organic Frameworks (MOFs) field (on October 17th 2016 – see the seminar announcement in the sent documents). In the same period, the basis for a joint work has also been set, focusing on the proposed STM project topics. In particular, thiazole-based organic linkers **1** and **2** prepared at ICCOM-CNR (Figure 1) were brought to Evanston; starting from them, the American colleagues will try to prepare novel MOFs for catalytic and gas sorption applications.



1

2

Figure 1. XRD structures of the thiazole ligands prepared at ICCOM-CNR for the construction of novel MOFs: the bis(thiazole) ligand **1** (left) and the quaternary thiazolium salt **2** (right).

A porous Zirconium MOF containing the bis(thiazole) ligand **1** has already been prepared and characterized: $[Zr_6O_4(OH)_4(\mathbf{1})_6]_\infty$ (Figure 2). It is featured by a microporous structure with a BET surface area of ca. 900 m^2/g. H_2 and CO_2 adsorption experiments have been planned, in order to test it as a hydrogen and carbon dioxide storage material.

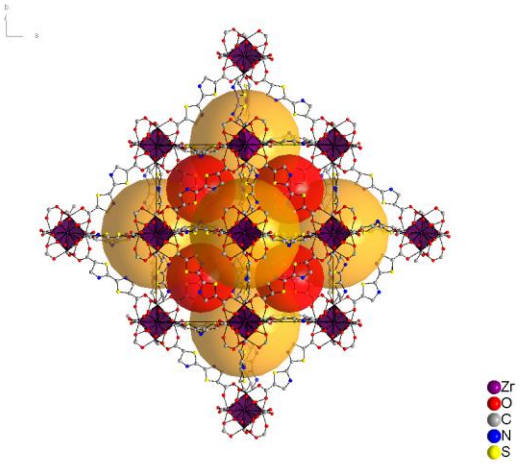


Figure 2. XRD structure of the Zr MOF $[Zr_6O_4(OH)_4(OOC\text{-}Tz\text{-}Tz\text{-}COO)_6]_\infty$.

Further synthetic efforts are planned for the future, in order to get new materials with different application fields. The following approaches have been planned in particular:

1) Synthesis of an Iron-containing MOF with ligand **1** based on the $[Fe_3(\mu_3\text{-}O)(RCOO)_6]$ cluster node (Figure 3). Pre-formed iron clusters described in the literature[1] will be utilized as the source of metal node and multiple reactions will be setup to grow the MOFs containing the Iron node and the bis(thiazole) ligand. Due to the stability of the iron MOF, many applications can be investigated after the synthesis and characterization (gas sorption, electrocatalysis, magnetism).

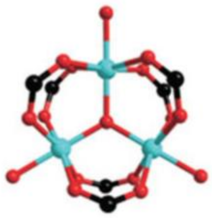
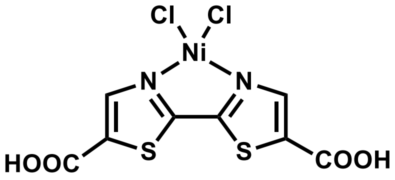


Figure 3. Structure of the Iron-based inorganic SBU $[Fe_3(\mu_3\text{-}O)(RCOO)_6]$.

2) Synthesis of a Zirconium MOF bearing the $NiCl_2$-functionalized ligand **1**:



The introduction of a functional group on **1** opens application perspectives in single-site heterogeneous catalysis for alkenes polymerization. The ligand topology is different from that of **1**, where the two carboxylic groups are in a "transoid" conformation. In here, the conformation is "cisoid", and the linker is more similar to the bent dithieno-thiophene-2,6-dicarboxylate (DTTDC) reported in the literature by Kaskel and co-workers,[2] where a 8-connected Zr-MOF with **reo** topology has been obtained (instead of the more common **pcu** motif, also observed in the Zr-MOF built with **1**, see Figure 2 above). The carboxylic groups of this molecule are spaced at a distance of 9.16 Å and with an angle of 148.61°. We plan to use the same synthetic methodology followed in reference [2], replacing the DTTDC ligand with the $NiCl_2$-functionalized **1**.

3) Use of the quaternary thiazolium salt **2** to prepare novel MOFs. Mixed-ligand MOFs will be the target. Given the "bent" and "flexible" nature of **2**, our synthesis will follow that of the mixed-MOF PCN-133 {$Zr_6O_4[OH]_4[BTB]_2[DCDPS]_3$; BTB = benzene tribenzoate; DCDPS = 4,4′-dicarboxydiphenylsulfone}, recently reported in the literature by Zhou and colleagues.[3] PCN-133 bears a flexible DCDPS spacer similar to **2**. We expect the same kind of outcome under the same synthetic conditions, to get a material with general formula $Zr_6O_4[OH]_4[BTB]_2[\mathbf{2}]_3$. Alternatively, linker **2** can also be introduced into a *defective* structure of an already existing MOF *via Sequential Linker Installation* (SLI). This strategy utilizes a stable Zr-MOF with inherent coordinatively unsaturated sites as a matrix, and postsynthetically installs linkers with different functionalities and lengths sequentially through kinetic control. The terminal $–OH^-/H_2O$ ligands capped on the coordinatively unsaturated sites of the Zr_6 cluster can be substituted by dicarboxylate linkers via an acid-base reaction. This approach has been proven to be an efficient method to prepare mixed-ligand species. The starting MOF can be the same PCN-133, with a known amount of defective sites, where some of the pillaring sulfone ligands between adjacent hexagonal Zr_6-BTB layers are missing.

At the same time, in collaboration with the computational team led by Prof. Snurr, a general *ab initio* screening of the most stable structures that can be built from these organic linkers has been started, with the aim at better directing the synthetic work towards specific applications. The adopted "top-down" (also called "reverse topological") approach starting from the network topology is the same as that recently reported by this group,[4] where ligands and metal nodes are seen as "Tinkertoy" components to be matched by the computational algorithm that thus generates several hypothetical structures that can be formed with the chosen building blocks (Figure 4). After their optimization, it is possible to select a limited number of them that is particularly well-performing in a specific practical context (*i.e.* H_2 storage, CO_2 storage, CH_4 storage, etc…) that can be subsequently synthesized and tested for that application. At the time being, 16 different structures containing the linker **1** and various metal nodes (based on Zr, Cu, Zn, Co, Cr) have been found by the algorithm, belonging to different network topologies (from the more common **pcu** to other less common motifs like **she** or **reo**). Optimization of these structures is in progress. This will be followed by Monte-Carlo Molecular Dynamics simulations of the H_2 and CO_2 adsorption isotherms on selected examples, to understand which combinations are the best-performing as gas storage materials. In a second stage, selected samples from this group will be synthesized and the experimental isotherms recorded, to validate the computational prediction. The same approach will also be adopted with linker **2**.

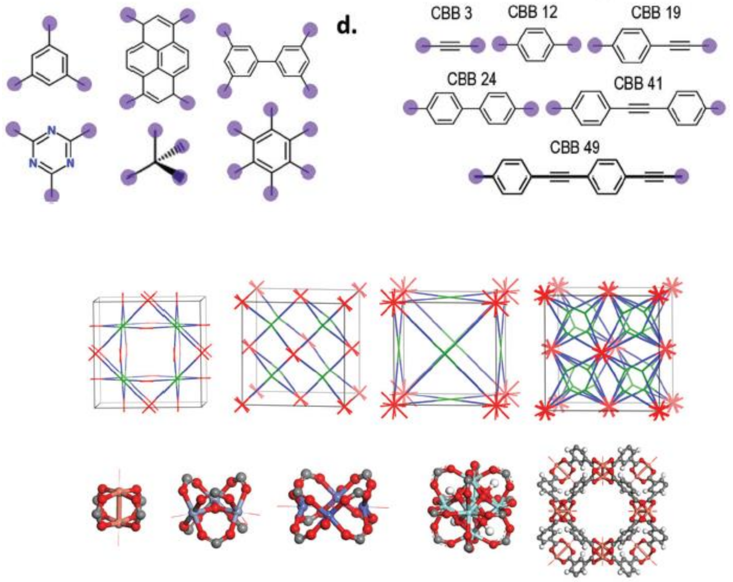


Figure 4. Schematic representation of the “top-down” approach used to generate new MOF structures from a known topology through combination of metallic SBUs and organic linkers. Taken from reference 4b.

Sesto Fiorentino, November 7th 2016.

Andrea Rossin

References

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[1] (a) *J. Chem. Soc. Dalton Trans.* **1985**, 2509-2520. (b) *Nat. Commun.* **2014**, *5*, N°5723.

[2] *Chem. Commun.* **2012**, *48*, 8407-8409.

[3] *J. Am. Chem. Soc.* **2016**, *138*, 6636-6642.

[4] (a) *Chem. Soc. Rev.* **2014**, *43*, 5735-5749. (b) *Energy Environ. Sci.* **2016**, *9*, 3279-3289. (c) *Nat. Chem.* **2012**, *4*, N°83.