FINAL PUBLISHABLE SUMMARY REPORT

Metal-organic frameworks (MOFs) have been an area of intense research over the past two decades and a large number of MOFs have been synthesized and reported since then.[1] These materials deserve special attention due to their potential applications in diverse areas, such as catalysis, gas storage, separation, sensors and drug delivery.[2] Although there is a large pool of reported MOFs, only a very few of them are stable in aqueous medium or in other solvents. This is a major disadvantage that pulls back many interesting MOFs from applications. One of the main concerns for research in this area is to develop stable and processable MOFs which can be used for different applications.

During the first one year of this project, the fellow focused on developing homochiral metal-organic frameworks as proposed in the original proposal. During the first phase, the following four ligands were synthesized.

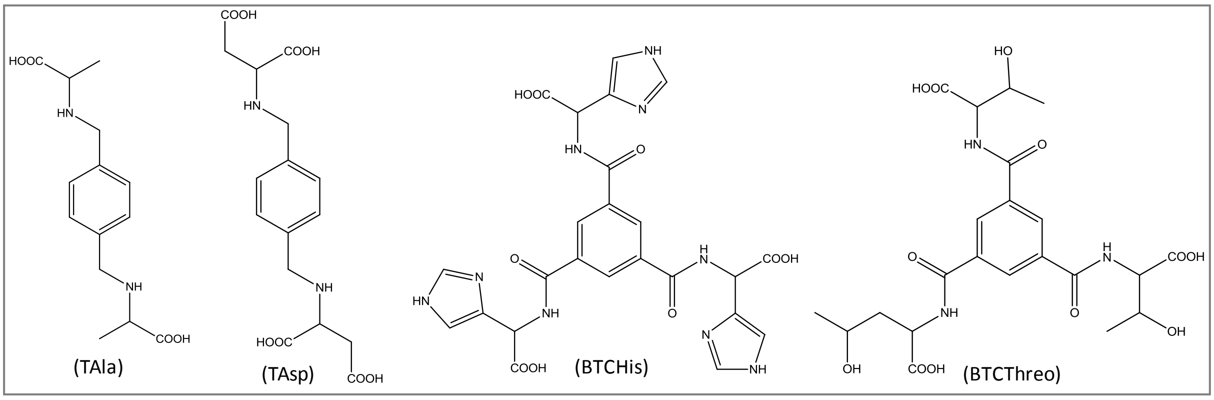


Figure 1. The chiral ligands used in this project for the synthesis of different metal-organic frameworks.

These chiral ligands were then used for synthesis of homochiral metal-organic frameworks (HMOFs). Extensive synthetic work including the use of high-throughput methods resulted into a family of one dimensional coordination polymer with the formula of $[M^{II}(TAla^{2-})(H_2O)_2]$ (where M = Mn, Co, Ni, Cu, Zn) when $M(OAc)_2 \cdot nH_2O$ salts were treated with the ligand TAla.

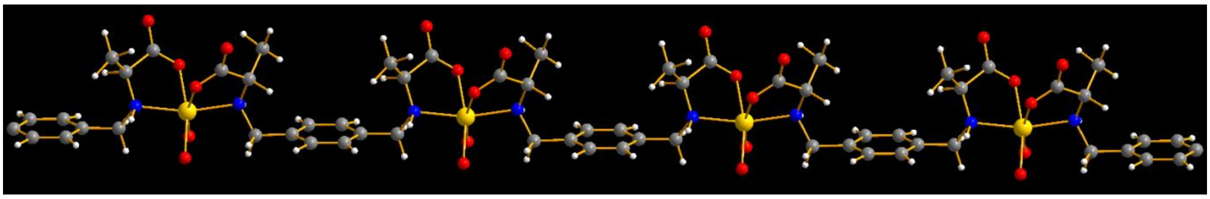


Figure 2. The structural view of one dimensional $[Zn^{II}(TAla^{2-})(H_2O)_2]$ in *ball and stick* model. Colour codes: blue (nitrogen), grey (carbon), red (oxygen), white (hydrogen), and yellow (zinc).

Formation of a crystalline compound was found from high-throughput reactions, and another one dimensional chain compound $[Zn^{II}(TAsp^{2-})(H_2O)_2]$ was isolated with post optimization, from the reaction between $Zn(NO_3)_2 \cdot 6H_2O$ and TAsp from a hydrothermal reaction at 85 °C. Due to exteremely small size of the crystals, single-crystal diffraction measurement was carried out in diamond light source (I19 beamline, Diamond Light Source). The crystallographic structure is shown in Figure 3.

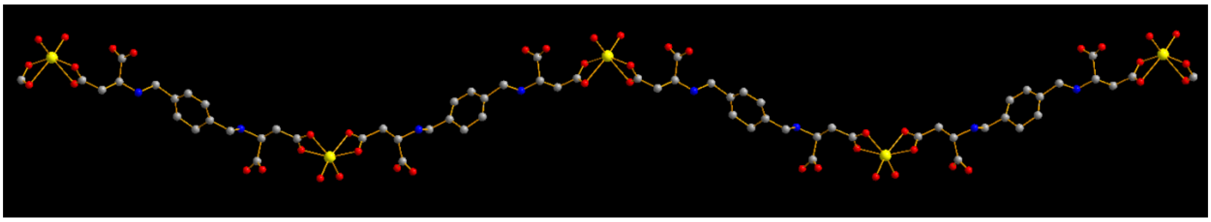
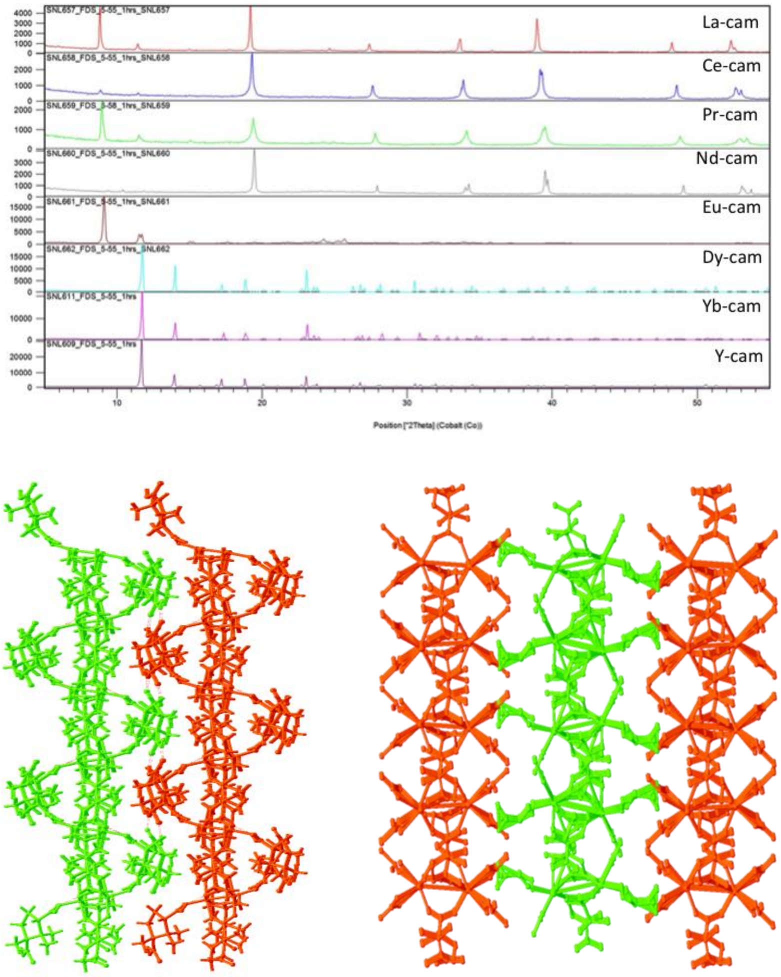


Figure 3. The structural view of one dimensional $[Zn^{II}(TAsp^{2-})(H_2O)_2]$ in *ball and stick* model. Colour codes: blue (nitrogen), grey (carbon), red (oxygen), and yellow (zinc). Hydrogen atoms are omitted for clarity.

Most of the targeted synthesis based on the initially studied ligands resulted in amorphous or one-dimensional or two-dimensional coordination polymers with very low surface area/porosity. A change in the approach was made in order to refocus on more relevant problem in this area of research, namely, to construct stable porous metal-organic frameworks based on extended linkers.

To address the synthesis of chiral porous network for catalysis purpose, some changes in the strategy were adopted. Chirally pure camphoric acid (cam) was used to synthesize lanthanide based MOFs. Two different types of structures with the same formula, $[Ln_2(cam)_2(O)(H_2O)_2]$ (Ln = different lanthanides) were identified from the pxrd and structurally characterized from single crystal x-ray diffraction studies as shown in Figure 4.



(A)

(B)

Figure 4. Top: The pxrd patterns for the materials resulted from camphoric acid and different lanthanides are shown. Bottom: Two different kinds of 2-D networks with the same formula, $[Ln_2(cam)_2(O)(H_2O)_2]$ resulted from different lanthanides. Different types of layered structures are shown in A and B for (La, Ce, Pr, Nd, Eu) and (Dy, Yb, and Y) based MOFs, respectively. Green and red colours are used to distinguish different layers.

All the evolved networks from this system were two dimensional with negligible porosity. Therefore, further changes in the linkers were introduced.

It is well-evidenced that the incorporation of extended aromatic linkers increases the porosity and surface area of MOFs.[2a, 3] Based on this, the following two new linkers, namely 4,4',4'',4'''-([1,1'-biphenyl]-3,3',5,5'-tetrayltetrakis(ethyne-2,1-diyl))tetrabenzoic acid (H_4bptba) and 4,4',4'',4'''-((3a1,5-dihydropyrene-1,3,6,8-tetrayl)tetrakis(ethyne-2,1-diyl))tetrabenzoic acid (H_4ptba) were designed and synthesized (Fig 5). Extensive research was carried out to synthesize porous MOFs with accessible channels using these two new ligands.

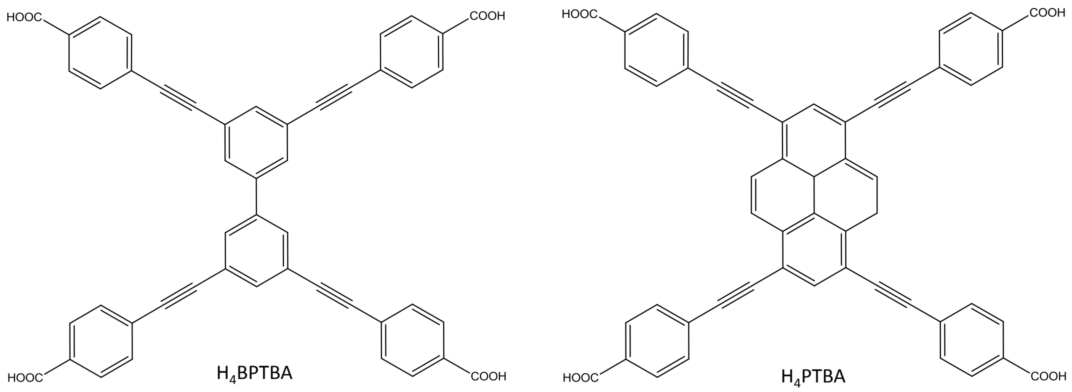


Figure 5. Two new ligands H_4BPTBA and H_4PTBA designed to synthesize stable extended porous MOFs.

A number of compounds have been synthesized during the project using these two ligands. For example, a zinc based MOF, $[Zn_5(BPTBA)_2(OH)_2(H_2O)_4]$ resulted when H_4BPTBA was treated with zinc nitrate in solvothermal condition in dmf at 120 °C for 48 hours. The structural characterization was performed by x-ray single crystal diffraction using synchrotron radiation (Diamond Light Source, Oxford, UK). The structure is shown in Figure 6. The three dimensional network consists of $[Zn_5]$ units which are interconnected by eight BPTBA linkers. The structure is triply interpenetrated as shown in Figure 5. Even with this high degree of interpenetration, calculation shows that the structure is porous to some extent. For example, theoretical calculations (using *calcvoid* feature of

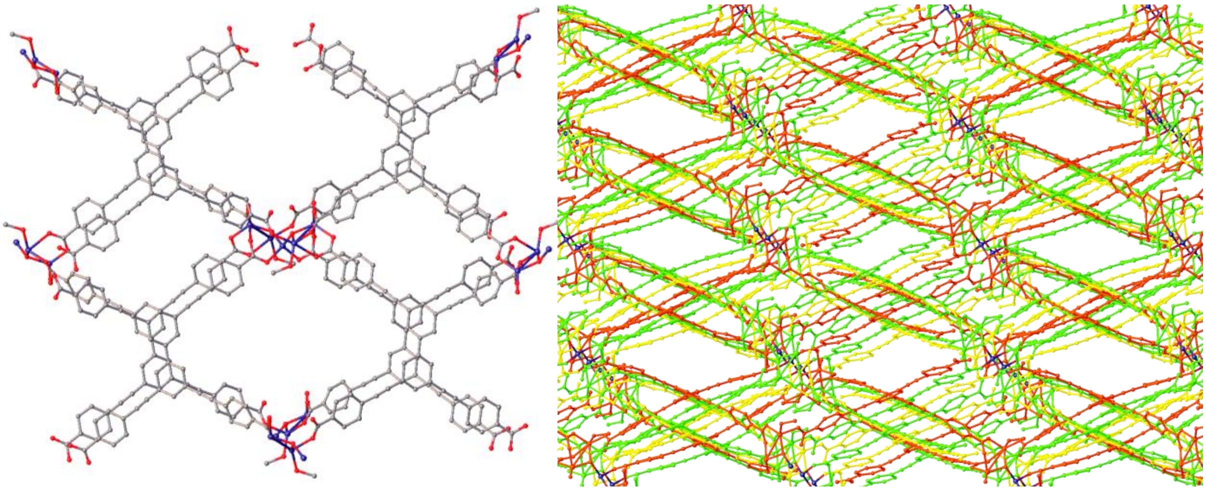


Figure 6. Left: Crystallographic structure of $[Zn_5(BPTBA)_2(OH)_2(H_2O)_4]$ is shown using a single component network (left) and including all three interpenetrated components (right). Three different colors (red, green, yellow) have been used to indicate different components.

OLEX program suit)[4] shows that the crystallographic *a* direction can be penetrated by a sphere of 1.00 Å radius, *b* direction can be penetrated by a sphere of 1.80 Å radius, and *c* direction can be penetrated by a sphere of 1.20 Å radius. The radius of the largest spherical void is 2.60 Å.

Another compound, a zinc-based MOF, $[Zn_6(ptba)_3(H_2O)_4]$(solvents) resulted when $Zn(NO_3)_2{\cdot}6H_2O$ was treated with H_4ptba solvothermally at 90 °C for 48 hours. The deep red crystals were characterized using single-crystal x-ray diffraction, PXRD, TGA, elemental analysis, and infrared analysis. The crystal structure indicates that the structure is packed densely due to strong π-π interactions as shown in Figure 7. The compound is thermally stable until 400 °C and has exceptional stability for a Zn^{2+}-based MOF as demonstrated using the pxrd pattern after treatment at different conditions (Figure 6, right). These two systems are selected as examples from a broad family of new MOF produced from the new ligands designed in this project. This family is currently under study for its gas storage properties, with a focus on methane storage and key separations such as those involving CO_2.

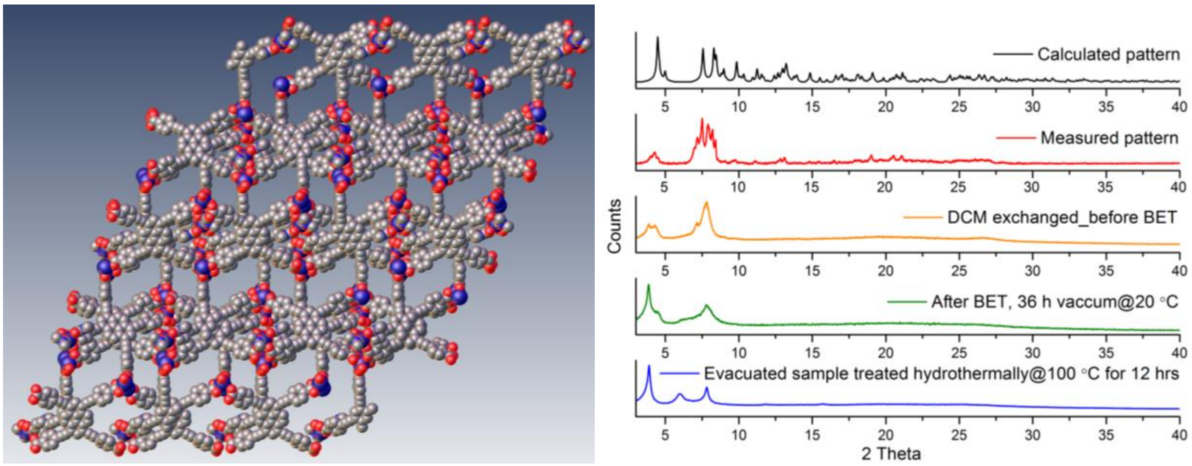


Figure 7. Left: Packing diagram of $[Zn_6(ptba)_3(H_2O)_4]$(solvents); Right: PXRD of $[Zn_6(ptba)_3(H_2O)_4]$(solvents) after treatment under different conditions.

In summary, a number of different amino acid based ligands have been synthesized and has been used to synthesize metal-organic frameworks. However, only one-dimensional coordination polymers resulted from this study – this validates the linker selection to make MOF, but indicates that their detailed chemistry is unsuited for applications. The synthetic approach was revised, and a change was made at the later part of the project with use of different kinds of rigid extended carboxylic acid based linkers. This resulted in a new family of MOFs with high porosity and large solvent accessible volume. The project results will contribute positively towards developing stable porous materials for applications in different areas, like gas storage, separation, and catalysis. At present the results from this project are being assimilated in manuscripts and will be submitted for publication in peer reviewed journals shortly.

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