

Final Scientific Report

[2.2]Paracyclophane linkers for Metal-Organic Frameworks

Stages 1-3 (2020-2022)

Project code: *PN-III-P1-1.1-PD-2019-0751*

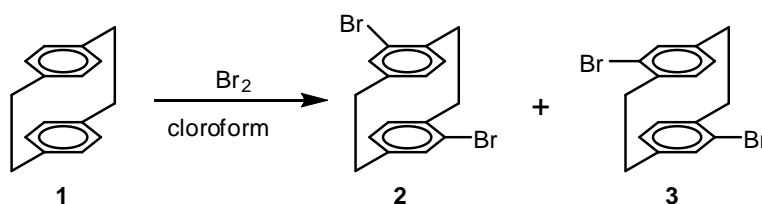
Contract: *PD 8/2020*

Timeframe: *04.08.2020-31.07.2022*

The **objectives** of this project were as follows:

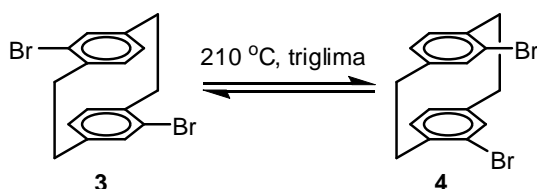
1. The synthesis of the 10 carboxylic linkers with a [2.2]paracyclophane core.
2. The synthesis and characterization of MOFs using the [2.2]PC based linkers and s-block metals.
3. The synthesis and characterization of MOFs using the [2.2]PC based linkers and d-block metals.
4. Result dissemination by publishing at least two papers in ISI ranked journals and participating at one national/international scientific event.

The first step in achieving these **objectives** was the bromination of the parent molecule **1** in chloroform, which yielded the *pseudo-meta* and *pseudo-para* isomers **2** and **3**. Their separation was achieved by taking advantage of their different solubilities in dichloromethane/ethanol. The NMR data recorded for the two isomer is similar to that reported in the literature.



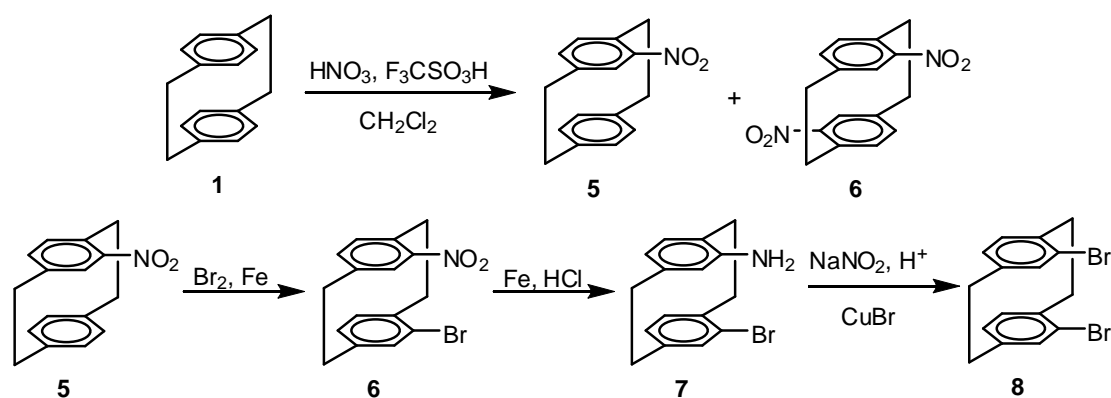
Scheme 1 – *Pseudo-meta* and *pseudo-para* dibromo[2.2]paracyclophane synthesis.

The *pseudo-ortho* isomer **4** was obtained by heating **3** to 210 °C in triglyme, followed by precipitation of the unreacted material using ethanol (Scheme 2).



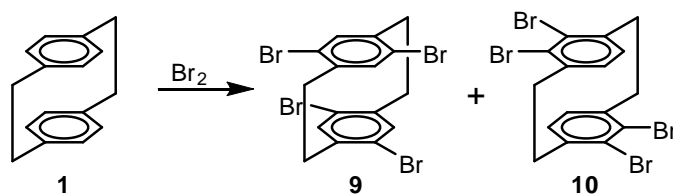
Scheme 2 – Thermal conversion of **3** to the *pseudo-ortho* isomer **4**.

Nitration of the parent molecule led to 4-nitro[2.2]paracyclophane, which was then brominated using bromine and iron filings. The resulting intermediary was then reduced and the newly formed amino group was converted to a bromo substituent by means of a diasotisation reaction (Scheme 3).



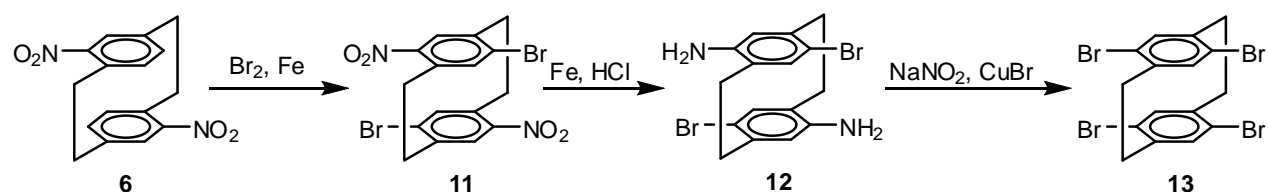
Scheme 3 – The synthesis of *pseudo-gem* dibromo[2.2]paracyclophane **8**.

4,7,12,15-Tetrabromo[2.2]paracyclophane **9** was obtained along 4,5,12,13-tetrabromo[2.2]paracyclophane **10** using molecular bromine, in the absence of light. The two isomers were separated based on their different solubilities in dichloromethane/ethanol.



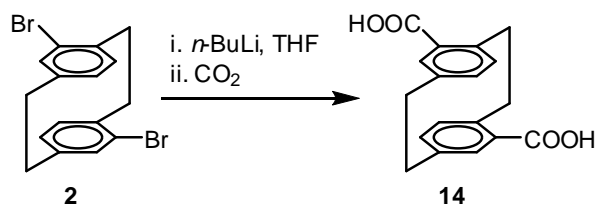
Scheme 4 – The synthesis of 4,7,12,15-tetrabromo[2.2]paracyclophane **9**.

Pseudo-para dinitro[2.2]paracyclophane **6**, synthesized by means of [2.2]paracyclophane nitration, was brominated using bromine and iron fillings. The nitro groups were then reduced and converted to bromo substituents using diazotisation reactions, yielding 4,7,11,14-tetrabromo[2.2]paracyclophane **13** (Scheme 5).



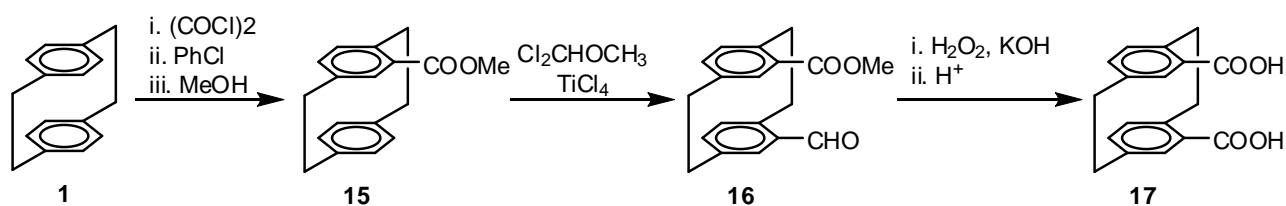
Scheme 5 – 4,7,11,14-Tetrabromo[2.2]paracyclophane **13** synthesis.

Pseudo-ortho, meta and para biscarboxy[2.2]PC (Objective 1) were obtained by means of lithiation of the corresponding brominated derivatives, followed by treatment with dry ice (Scheme 6).



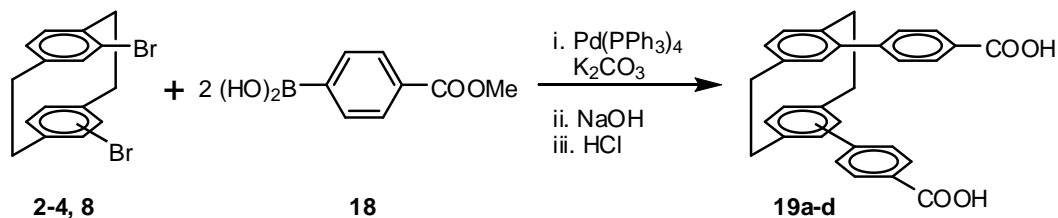
Scheme 6 – The synthesis of *pm*-biscarboxy[2.2]PC.

The *pseudo-gem* derivative was obtained from 4-methoxycarbonyl[2.2]PC by formylation, oxidation and hydrolysis of the ester that forms (Scheme 7).



Scheme 7 – The synthesis of *pg*-biscarboxy[2.2]PC.

Pg, po, pm and pp-bis(4-carboxyphenyl)[2.2]PC (Objective 1) were synthesized by coupling the corresponding brominated derivatives with (4-methoxycarbonyl)phenylboronic acid, followed by the hydrolysis of the obtained esters (Scheme 8).



Scheme 8 – The synthesis of *pg, po, pm* and *pp*-bis(4-carboxyphenyl)[2.2]PC.

The four new linkers were characterized using NMR, IR and mass spectrometry. The single crystall X-Ray structures of their methylated esters were also recorded. The $^1\text{H-NMR}$ spectrum of *pp*-bis(4-carboxyphenyl)[2.2]PC can be found in Figure 1.

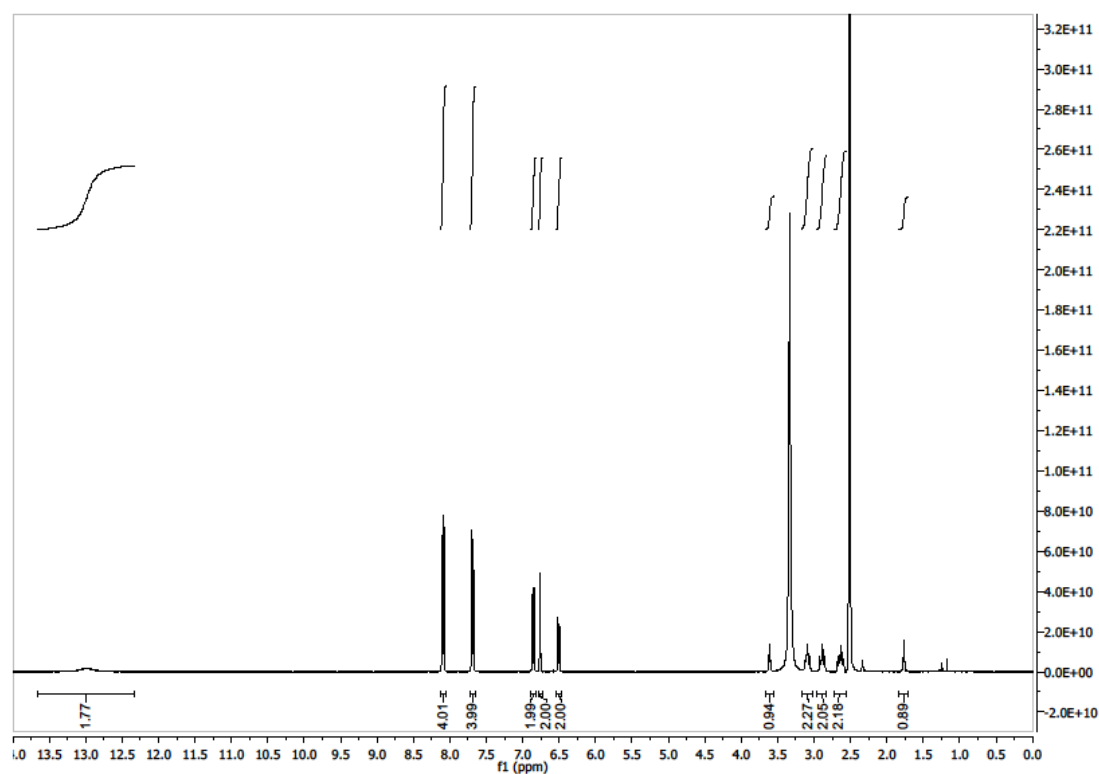
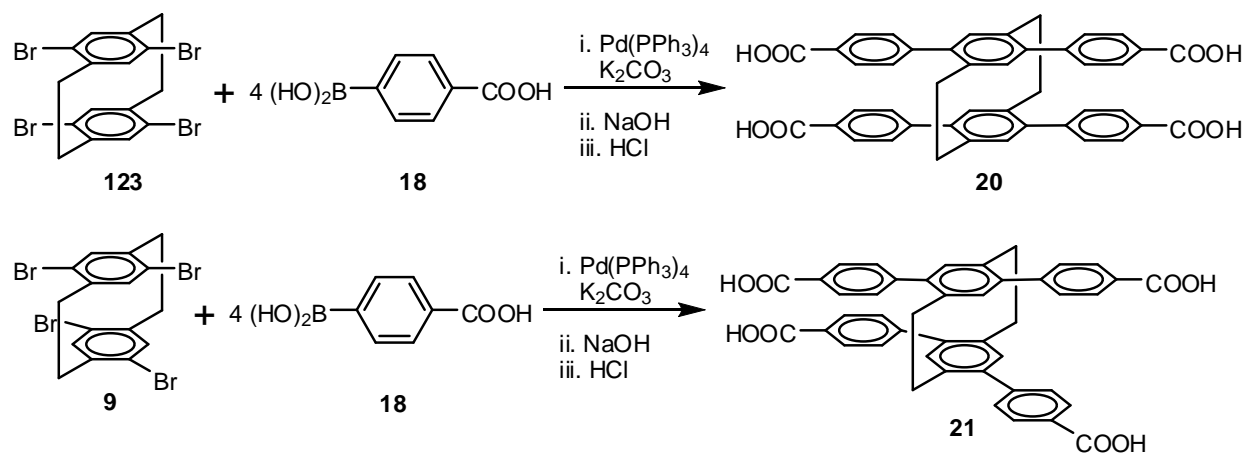


Figure 1 – The $^1\text{H-NMR}$ spectrum of *pp*-bis(4-carboxyphenyl)[2.2]PC, recorded in $\text{DMSO-}d_6$.

The desired tetracarboxylic derivatives (**Objective 1**) were also synthesized through Suzuki coupling reactions, as presented in Scheme 9.



Scheme 9 – The synthesis of the two desired tetracarboxylated linkers.

Figure 2 displays the $^1\text{H-NMR}$ spectrum of the methylated ester of **15**.

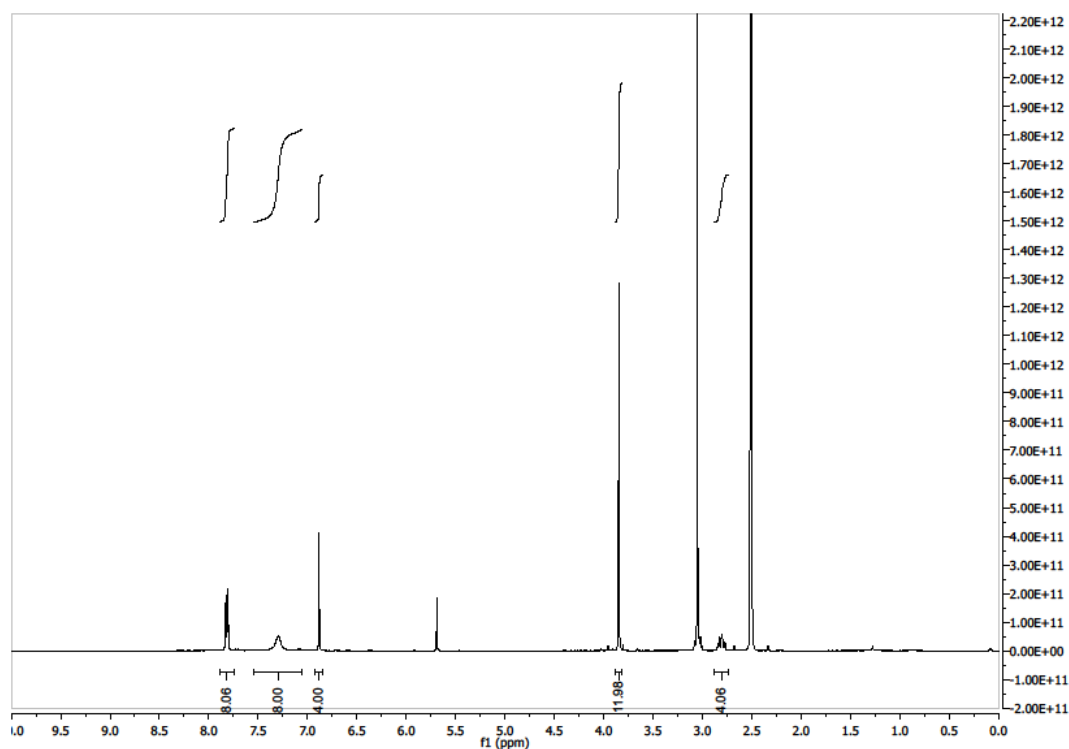


Figure 2 - The ^1H -NMR spectrum of the methylated ester of **15**, recorded in $\text{DMSO-}d_6$ at 80 $^\circ\text{C}$.

Synthesis of metal-organic frameworks

The previously described linkers were reacted in various conditions with s-block (Na, Mg, Ca) metals (**Objective 2**). Generally, the solvents used were mixtures of DMF, ethanol and water and nitrates, as well as chlorides were used as metal sources. Reactions were run between 80-120 $^\circ\text{C}$ for periods of 24-72 hours.

In several cases, small sized needle-like crystals were obtained. One such example, where Mg was used as a metal source, can be found in Figure 3.

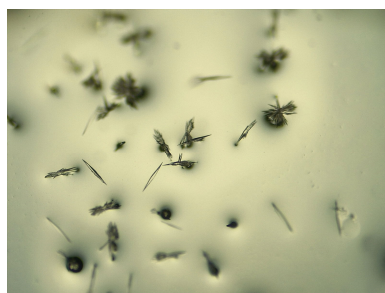


Figure 3 – Crystals obtained by reacting *pp*-bis(4-carboxyphenyl)[2.2]PC with Mg nitrate.

The products that were obtained using s-block metals were screened for gas storage capabilities, but no notable results were obtained in this regard.

The [2.2]PC aroxylated linker were also reacted with d-block metals, such as Cu, Zn, Zr and Cd (**Objective 3**).

Amongst the results obtained, it is worth mentioning the coordination polymer that formed between *pm*-bis(4-carboxyphenyl)[2.2]PC and Cu^{2+} ions. The metal ions form paddlewheel structures with 4 carboxyl groups from 4 different linker molecules, resulting in a chain which extends in one direction, as can be seen in Figure 4.

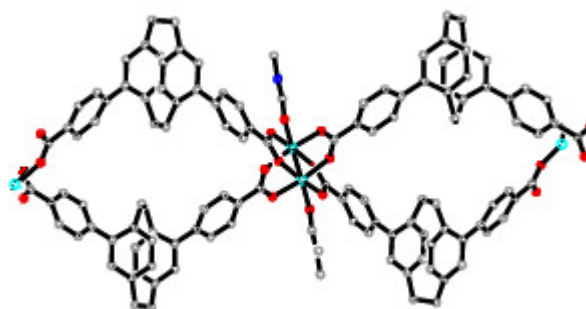


Figure 4 – The structure of the coordination polymer that formed between *pm*-bis(4-carboxyphenyl)[2.2]PC and Cu^{2+} ions.

Also worth mentioning is the 2D network obtained between *pp*-bis(4-carboxyphenyl)[2.2]PC and zinc nitrate. Similarly to the previously presented copper structure, in this case the metal ions form paddlewheel structures with 4 carboxyl groups from 4 different molecules, as depicted in Figure 5.

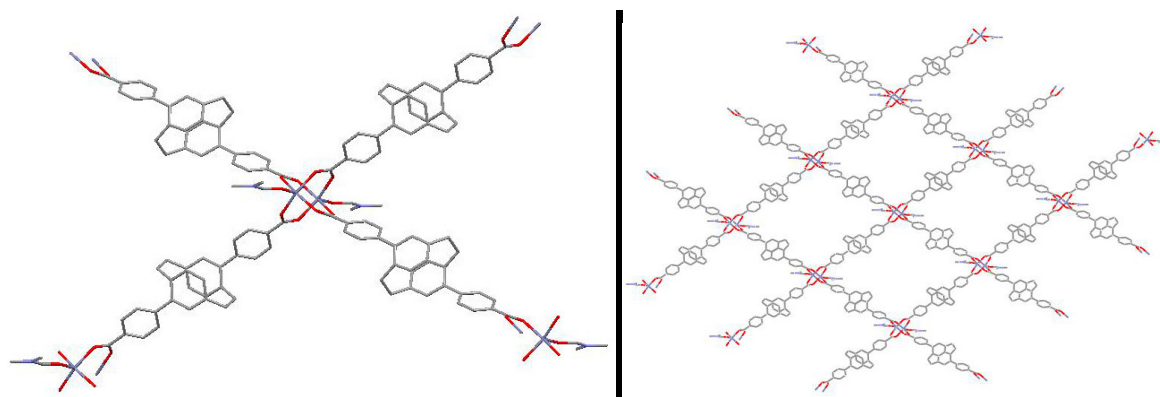
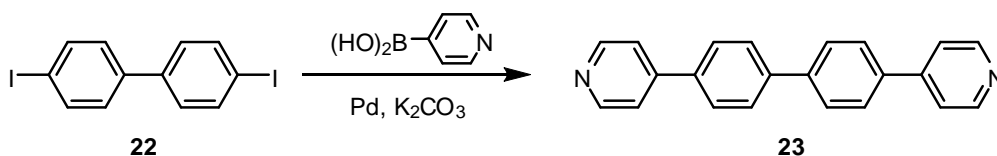


Figure 5 – The structure of the paddlewheel units (left); the 2D network, obtained by reacting *pp*-bis(4-carboxyphenyl)[2.2]PC and Zn nitrate (right).

In an attempt to extend the 2D structure in 3 dimensions, nitrogen-containing pillar ligands, such as DABCO, 4,4'-bipyridyl or 4,4'-azopyridine were used. Unfortunately, none of these pillar ligands yielded the desired result. As such, a longer pillar ligand, bis(4-pyridyl)-4,4'-biphenyl was synthesized (Scheme 10).



Scheme 10 – The synthesis of bis(4-pyridyl)-4,4'-biphenyl.

After a series of attempts using this linker together with *pp*-bis(4-carboxyphenyl)[2.2]PC and Zn^{2+} , a colorless crystallin material was obtained. Upon activation, it was found that it displayed a BET value of 146 m^2/g . Figure 6 presents the nitrogen isotherm of this material.

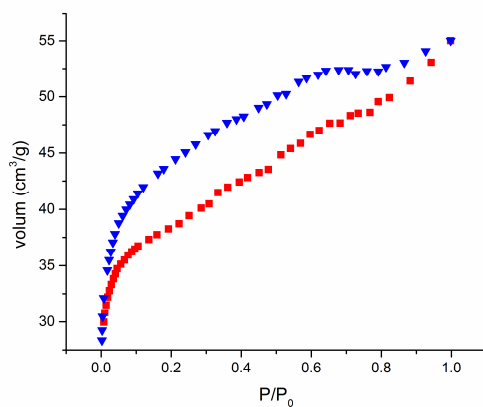


Figura 6 – The nitrogen adsorption/desorption isotherm, measured at 77K; red-adsorption, blue-desorption.

The modest BET value is likely a result of framework degradation upon activation and/or interpenetration.

Some of these results were presented as a poster at 13th Edition of the National Chemistry Symposium in Craiova, Romania (**Objective 4**).

Also three papers were published (**Objective 4**) based on the results obtained during this project:

- Bahrin, L. G.; Hopf, H.; Jones, P. G.; Birsa, M. L.; Sarbu, L. G. An Approach to Paracyclophane-Based Tetrathiafulvalenes: Synthesis and Characterization of a Pseudo-Geminal [2.2]Paracyclophane 1,3-Dithia-2-Thione, *Molecules*, **2020**, *25*, 5262.
- Bahrin, L. G.; Nicolescu, A.; Shova, S.; Marangoci, N. L.; Birsa, M. L.; Sarbu, L. G. Nitrogen-Based Linkers with a Mesitylene Core: Synthesis and Characterization, *Molecules*, **2021**, *26*, 5952.
- Bejan, D.; Dascalu, I. A.; Shova, S.; Trandabat, A. F.; Bahrin, L. G. Mesitylene Tribenzoic Acid as a Linker for Novel Zn/Cd Metal-Organic Frameworks, *Materials*, **2022**, *15*, 4247.

Last but not least, a fourth paper is currently underway and it is estimated that it will be published by the end of 2022.

Concerning the **impact of these results**, it is worth mentioning that the [2.2]paracyclophane molecule presents 8 aromatic positions, as well as 8 aliphatic positions that can be substituted. This can potentially lead to a wide variety of new linkers for MOF design. **The successful implementation** of this project means that this family of linkers was expanded with **6 new structures**, 5 of which were characterized by single crystal X-Ray diffraction. Moreover, these new linkers opened the way to **new metal-organic structures**, such as the 2D network obtained by reacting *pp*-bis(4-carboxyphenyl)[2.2]PC and zinc nitrate.

Further information concerning this project can be found at

<https://icmpp.ro/projects/l1/about.php?id=20>

Project director,

Bahrin Lucian

