Scientific report

[2.2]Paracyclophane linkers for Metal-Organic Frameworks,

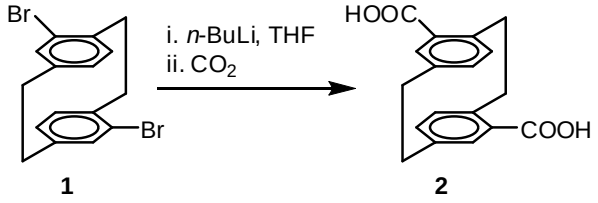
stage 2 – 2020

Stage 2 summary- The synthesis of [2.2]paracyclophane carboxylic linkers and their use in MOF design

During this stage, the desired carboxylic linkers were obtained. *Pg*, *po*, *pm* and *pp*-biscarboxy[2.2]PC were obtained according to the methods described by the literature. *Pg*, *po*, *pm* and *pp*-bis(4-carboxyphenyl)[2.2]PC, as well as the two tetracarboxylated derivatives were obtained through Suzuki coupling reactions. The carboxylated linkers were used in conjunction with s-block metals in various attempts to obtain new MOFs.

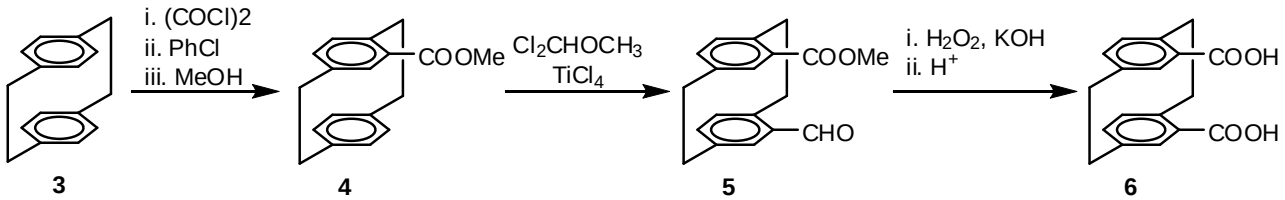
Stage 2 methodology

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



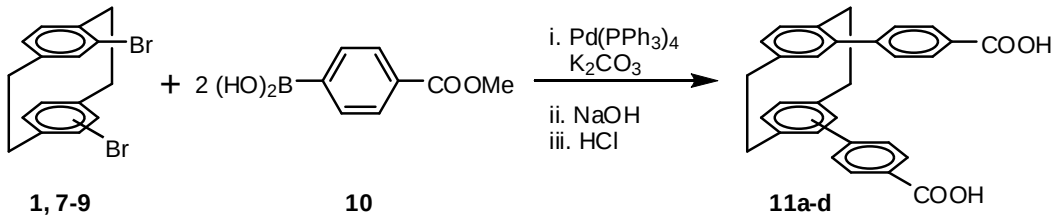
Scheme 1 – The synthesis of *pm*-biscarboxy[2.2]PC.

The *pseudo-gem* derivative was obtained from 4-methoxycarbonyl[2.2]PC by formilation, oxidation and hydrolysis of the ester that forms (Scheme 2).



Scheme 2 – The synthesis of *pg*-biscarboxy[2.2]PC.

Pg, po, pm and pp-bis(4-carboxyphenyl)[2.2]PC were synthesized by coupling the corresponding brominated derivatives with (4-methoxycarbonyl)phenylboronic acid, followed by the hydrolysis of the obtained esters (Scheme 3).



Scheme 3 – 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 singe crystall X-Ray structures of their methylated esters were also recorded. The ^{1}H-NMR spectrum of *pp*-bis(4-carboxyphenyl)[2.2]PC can be found in Figure 1.

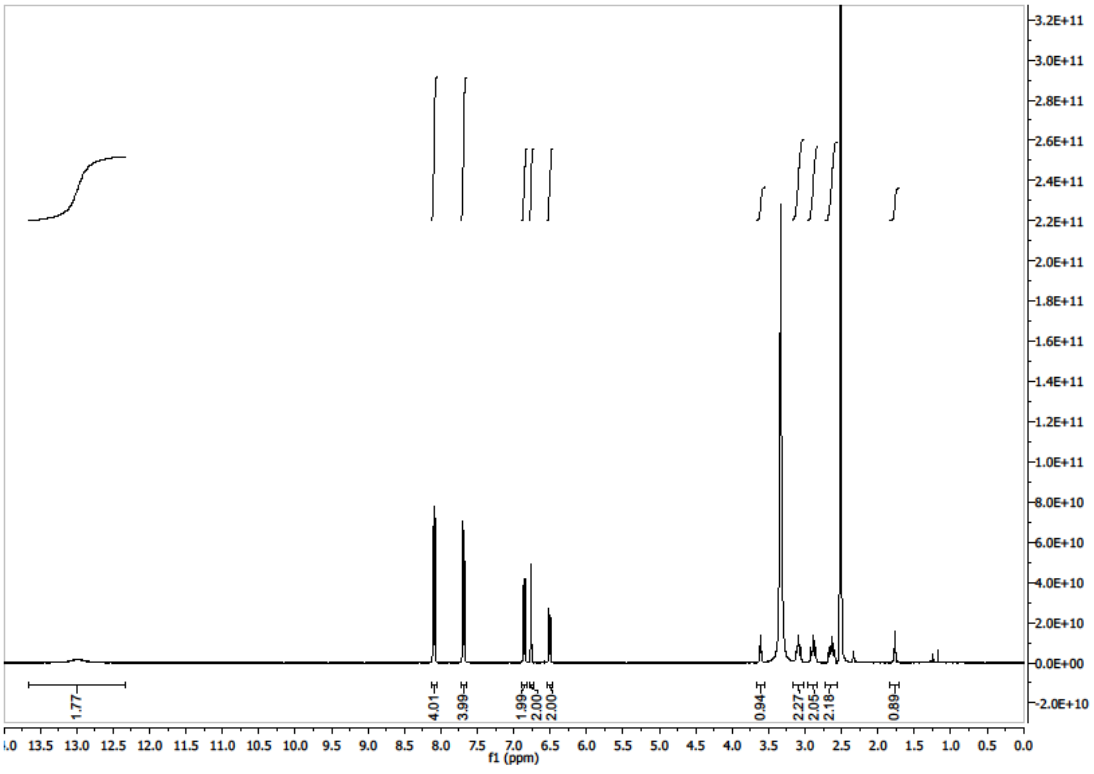
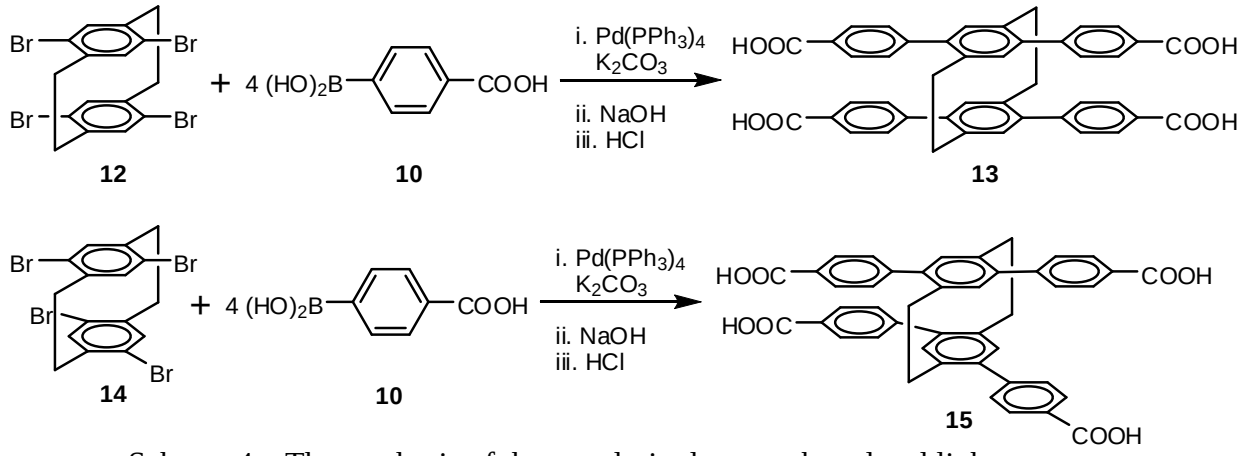


Figure 1 – The ^{1}H-NMR spectrum of *pp*-bis(4-carboxyphenyl)[2.2]PC, recorded in DMSO-*d6*.

The desired tetracarboxylic derivatives were also synthesized through Suzuki coupling reactions, as presented in Scheme 4.



Scheme 4 – The synthesis of the two desired tetracarboxylated linkers.

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

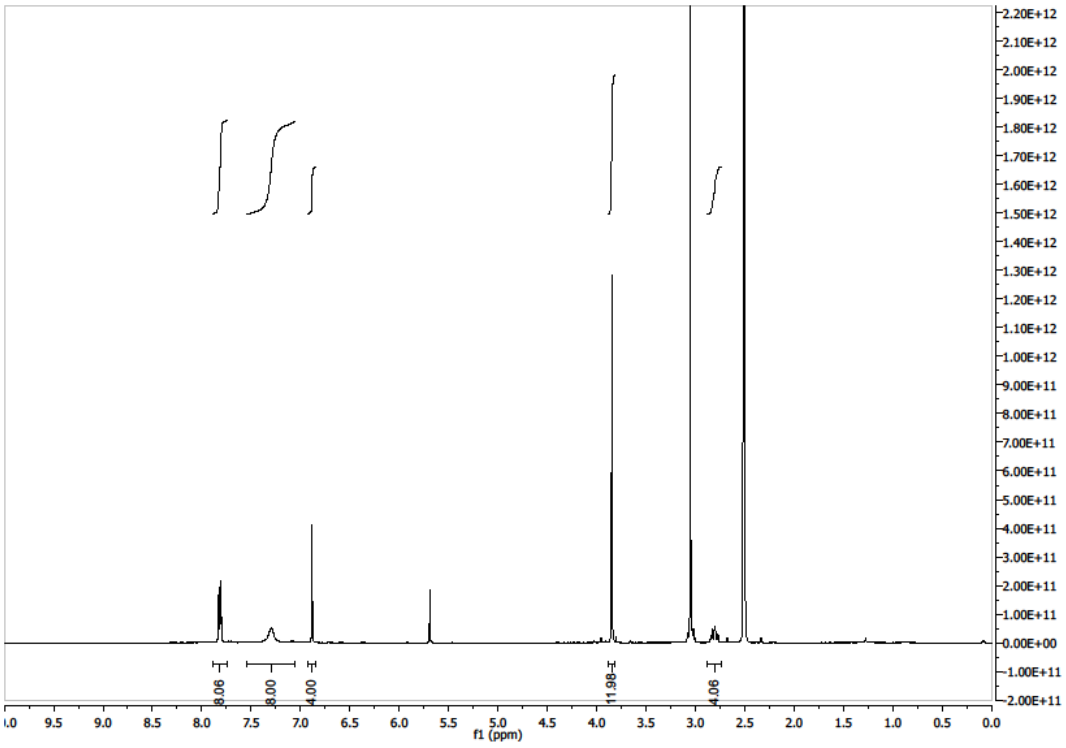


Figura 2 - The ^{1}H-NMR spectrum of the methylated ester of **15**, recorded in DMSO-*d6* at 80 °C.

Synthesis of metal-organic frameworks

The previously described linkers were reacted in various conditions with s-block (Na, Mg, Ca) metals. Generally, the solvents used were mixtures of DMF and water and nitrates were used as metal sources. Reactions were run at 80 °C for 24-72 hours.

In several cases, small sized needle-like crystals were obtained. Three such examples can be found in Figure 3.

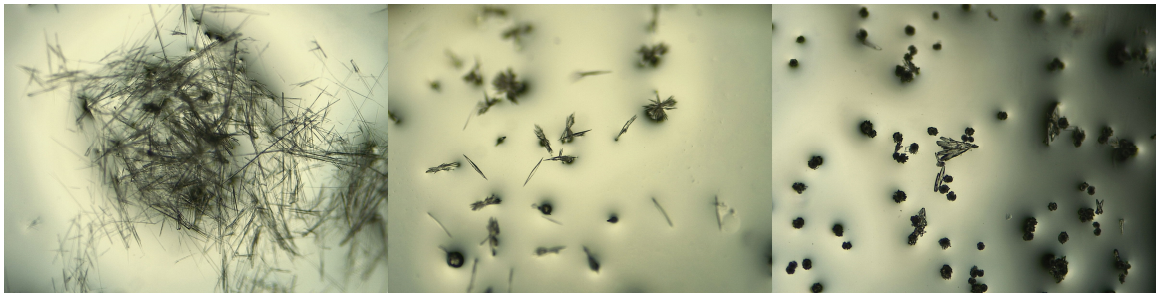


Figure 3 – Cristals obtained by reacting [2.2]PC carboxylated linkers with Mg and Ca nitrates.

These reactions are still under optimization, with one of the goals being single crystall X-Ray structures.

Dissemination

A part of the results obtained during this stage were published in the journal *Molecules*, **2021**, *26*, 5952. Moreover, a poster titled "[2.2]PARACYCLOPHANE-BASED LINKERS FOR MOF SYNTHESIS" was presented at the 13th Edition of the National Chemistry Symposium in Craiova, Romania.

Project director,

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