

Scientific report

Metal-organic frameworks based on fluorinated terphenilic ligands for gas storage and separation

Stage 2-2021

The synthesis of coordination polymers with the three fluorinated aromatic ligands and the evaluation of the metal-organic frameworks properties-Part I

Stage 2 summary

In accordance with the project plan, in the second stage the fluorinated aromatic dicarboxylic acids were used for the synthesis of coordination polymers with transitional metal salts. Reproducible and up-scalable synthesis protocols have been identified for the synthesis of MOFs composed of 2',5'-difluoro-[1,1':4',1''-terphenil]-4,4''-dicarboxylic acid H₂F₂ and zirconium and 2',5'-bis(trifluoromethyl)-[1,1':4',1''-terphenil]-4,4''-dicarboxylic acid H₂CF₃ and zinc. The structure of the three-dimensional networks has been identified by single crystal X-ray diffraction, while the phase purity was confirmed by X-ray powder diffraction. The identified reaction protocols were applied to the other two ligands and the iso-structural relationship between the MOFs has been confirmed by X-ray powder diffraction.

In terms of thermal stability, the obtained Zn MOFs are stable up to approx. 400 °C whereas the Zr networks are stable up to 500 °C. Following the evaluation of the gas sorption capacity of the synthesized MOFs, notable results were obtained for the zirconium Zr-F₂ MOF (approx. 1300 m²/g) and zinc (460 m²/g). Various activation methods (thermal or solvent exchange) have been tested.

A part of the obtained results have been disseminated at "Progress in Organic and Macromolecular Compounds 28th Edition" Iasi, Romania, 7 – 9 October 2021 with a poster presentation entitled „TOWARDS ROBUST METAL-ORGANIC FRAMEWORKS BASED ON FLUORINATED LINKERS FOR GAS STORAGE" (<https://icmpp.ro/macroiiasi2021/files/proceedings-POMC.pdf>). During this conference, the poster presentation was awarded the **Best Poster Communication** award.

In this stage the first manuscript entitled „Direct synthetic approach for fluorinated terphenilic ligands with fluorine addends. Structural characterization and molecular modeling." has been prepared and will be sent for publication in the next project stage. The manuscript describes an experimental approach for the synthesis of the three ligands, their extensive characterization and a molecular modeling section. In addition, the Hirschfeld surface calculation is

included, which alongside the molecular modeling study will offer additional information for explaining the MOFs behavior in contact with the stored or separated gas.

In the framework of the project, a research stage has been performed abroad at the Institute for Inorganic Chemistry and Structural Chemistry Heinrich-Heine-University Düsseldorf, Germany, under the supervision of the Mentor Prof. Dr. Christoph Janiak.

The scientific description of stage 1

In this stage, two main objectives have been followed: (i) MOF synthesis with the three aromatic fluorinated ligands and (ii) the characterization and properties evaluation of the obtained MOFs.

1. The synthesis, characterization and properties evaluation of MOFs composed of the aromatic fluorinated ligands and zirconium.

Initially, preliminary reactions were screened in order to facilitate the isolation of UiO-68 type MOFs in crystal form.¹ DMF was used as the reaction solvent and zirconium chloride as the metal salt. The reaction temperature, acid modulator type and quantity were varied. Before heating the reaction vials to the desired temperature, the reaction mixtures were homogenized in an ultrasound bath for 15 minutes. Notable results were obtained from solvothermal reaction (120 °C, 72 h) using acetic (exp 13F2) or trifluoroacetic (exp 15F2) as acidic reaction modulators. The identified reaction conditions afforded the isolation of a coordination polymer composed of the deprotonated ligand 2',5'-difluoro-[1,1':4',1''-terphenil]-4,4''-dicarboxylic acid H₂F₂ and zirconium (Zr-F₂) as crystals which lead to the identification of the structure through single crystal X-Ray diffraction (Figure 1).

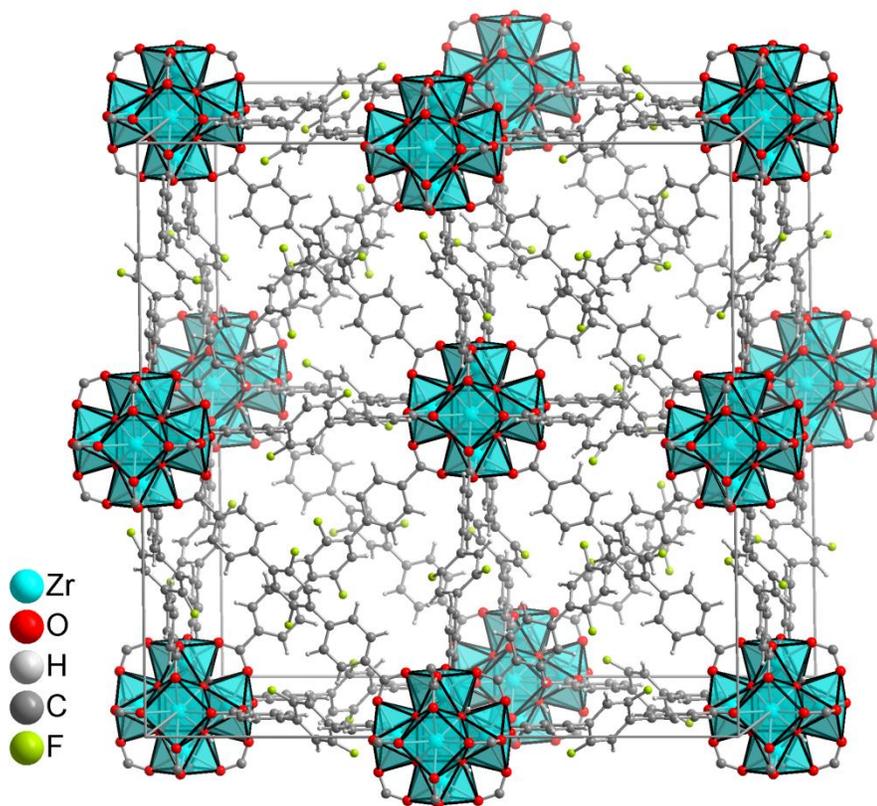


Figure 1. Graphical representations of the 3D structure obtained by single crystal X-ray diffraction of the MOF composed of ligand 2',5'-difluoro-[1,1':4',1''-terphenil]-4,4''-dicarboxylic acid H₂F₂ and zirconium (Zr-F₂).

With the help of powder X-ray diffraction, the phase purity of the two samples in comparison with the calculated diffractogram (from the single crystal structure) was confirmed (Figure 2). In addition, the iso-structurality of the MOFs prepared using the two identified reaction protocols was confirmed using the same characterization technique.

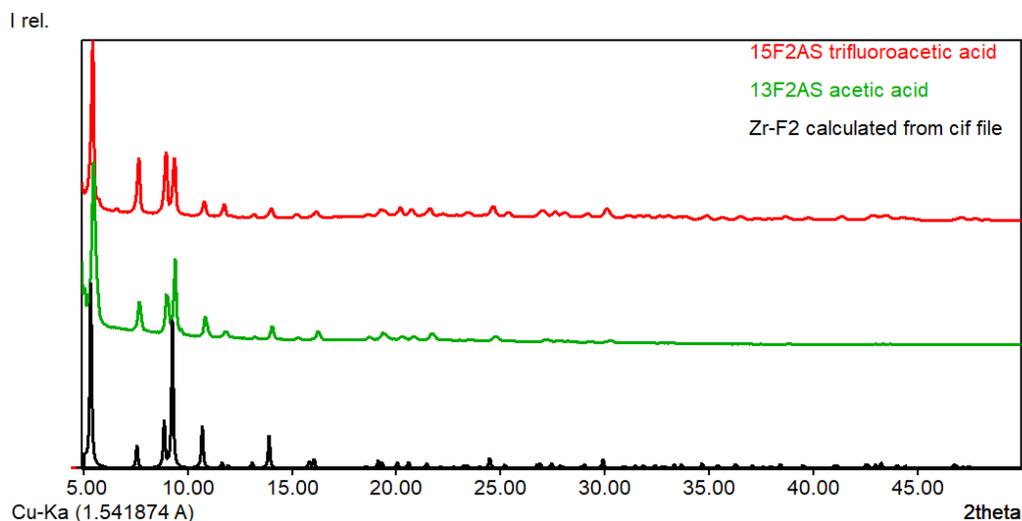


Figure 2. The diffractograms of the Zr-F2 MOFs prepared in the presence of acetic acid (green) and trifluoroacetic acid (red) in comparison with the calculated diffractogram using the single crystal structure (black).

The use of a higher reaction temperature (125 and 130 °C) reduces the reaction time to 48 h but the phase purity decreases due to the formation of an amorphous phase. The experiments were repeated in triplicate using the initial conditions to confirm the reproducibility of the reaction protocols. The results showed that the optimal protocol was the one where acetic acid was the modulator. In addition, the same reaction was up-scaled (x2 and x4) in order to obtain the Zr-F2 MOF in an adequate quantity necessary for the characterization and properties evaluation of the coordination polymer. With the help of pXRD, the reaction protocol was validated by means of reproducibility and up-scalability (Figure 3). The purification of the MOF was accomplished by repeated washing with DMF, centrifugation and removal of the supernatant, followed by a rapid washing with methanol and drying in an oven at 80 °C. The reaction yield in all the repeated experiments at the same scale or up-scaled was between 60-70%.

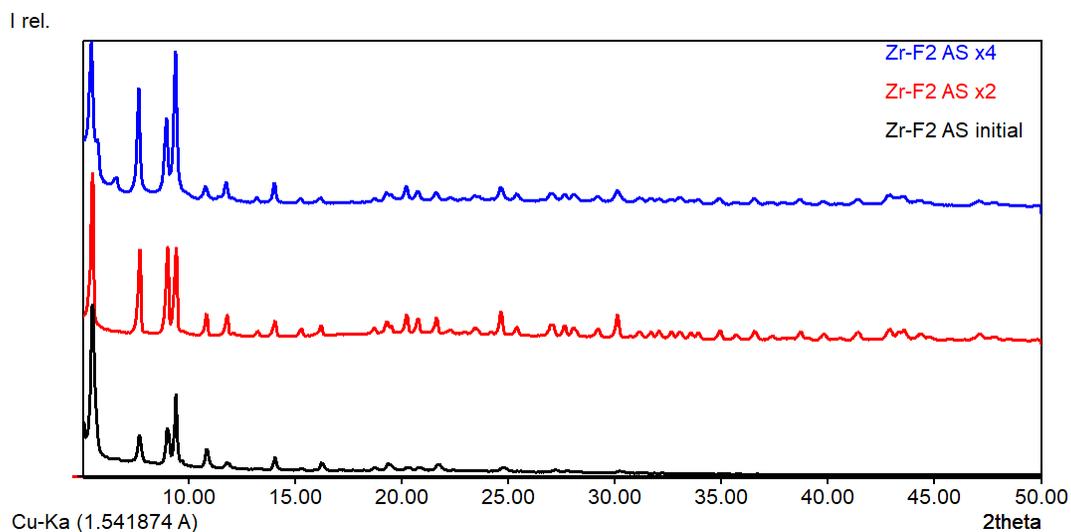


Figure 3. Zr-F2 diffractograms: the initial experiment (black), up-scaled 2x (red) and 4x (blue), synthesized in the presence of acetic acid.

The FT-IR spectra of the Zr-F2 MOF synthesized in the presence of the above mentioned acid modulators are identical (Figure 4) and indicate a complete deprotonation of the ligand as a consequence of its reaction with the zirconium atoms. The evidence for this observation is the shift of the carbonylic absorption band from 1700 cm^{-1} to 1664 cm^{-1} .

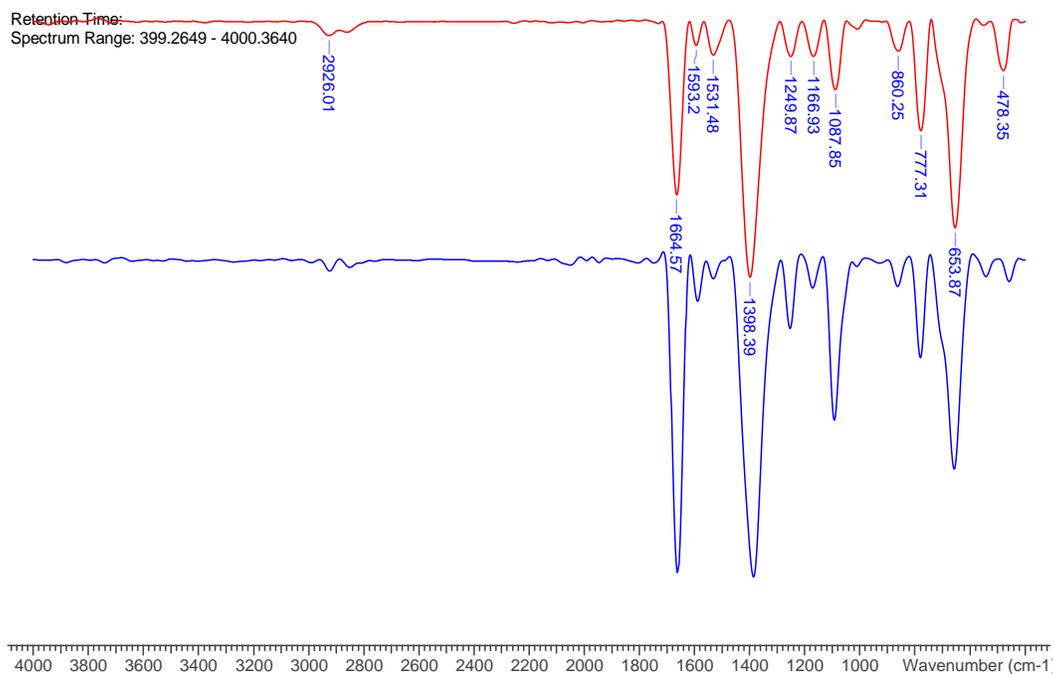


Figure 4. FT-IR spectra of the Zr-F2 MOF synthesized using acetic acid (red) or trifluoroacetic acid (blue).

Evaluation of the Zr-F2 thermal stability (Figure 5) indicated that the 3D network retains a large quantity of solvents due to its porous nature, as evidenced by a 25 % mass loss in the 34-400 °C interval, while the actual decomposition begins after 500 °C.

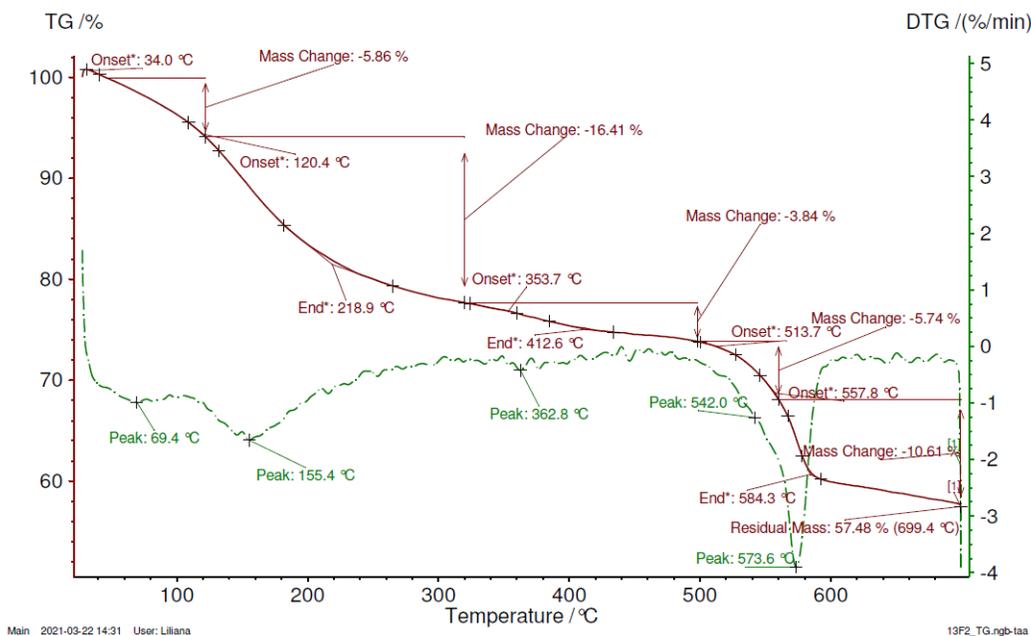


Figure 5. Zr-F2 MOF TGA-DTG curve.

After the thermal decomposition threshold was established, the thermal activation of the network was made at 150 °C, under vacuum (10^{-2} mbar). After the activation, the nitrogen adsorption and desorption isotherms were recorded (Figure 6).

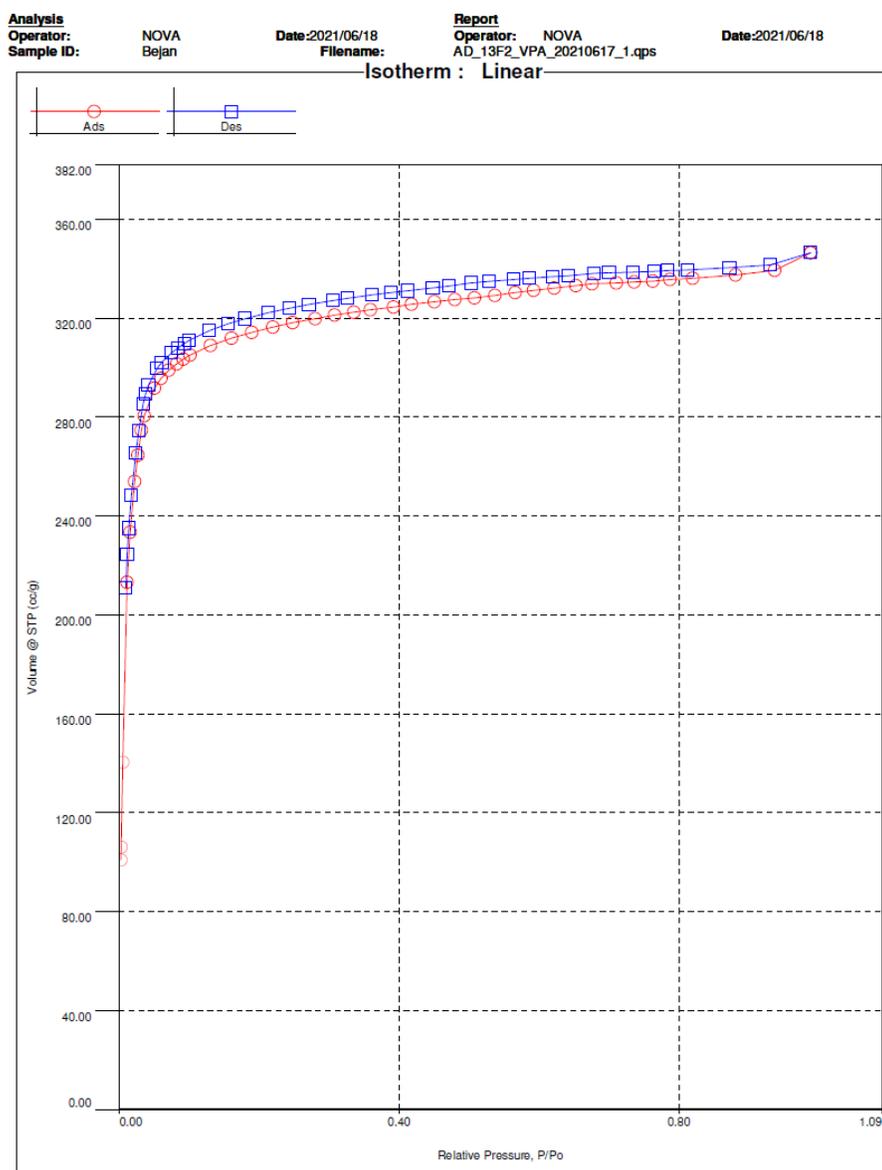


Figure 6. Nitrogen adsorption (red) and desorption (blue) isotherm of Zr-F2 MOF after thermal activation; $S_{\text{BET}} = 1304 \text{ m}^2/\text{g}$. Total pore volume = $5.249\text{e-}01 \text{ cc/g}$ at $P/P_o = 0.93695$.

2. The synthesis, characterization and properties evaluation of MOFs composed of the aromatic fluorinated ligands and zinc.

In the synthesis experiments various solvents were tested, such as DMF, DEF or dimethylacetamide. Initially no modulator was used and as a consequence, the first tests were deployed at $70 \text{ }^\circ\text{C}$. Notable results were obtained from the solvothermal reaction ($70 \text{ }^\circ\text{C}$, 72 h) using the 2',5'-bis(trifluoromethyl)-[1,1': 4',1''-terphenil]-4,4''-dicarboxylic acid H_2CF_3 and zinc nitrate in DMF. The identified reaction conditions afforded the isolation of the zinc MOF as crystals which allowed the identification of the structure of the compound (Figure 7). In the

case of the two other ligands H2F2 and H2F4, all synthesis experiments afforded microcrystalline powders.

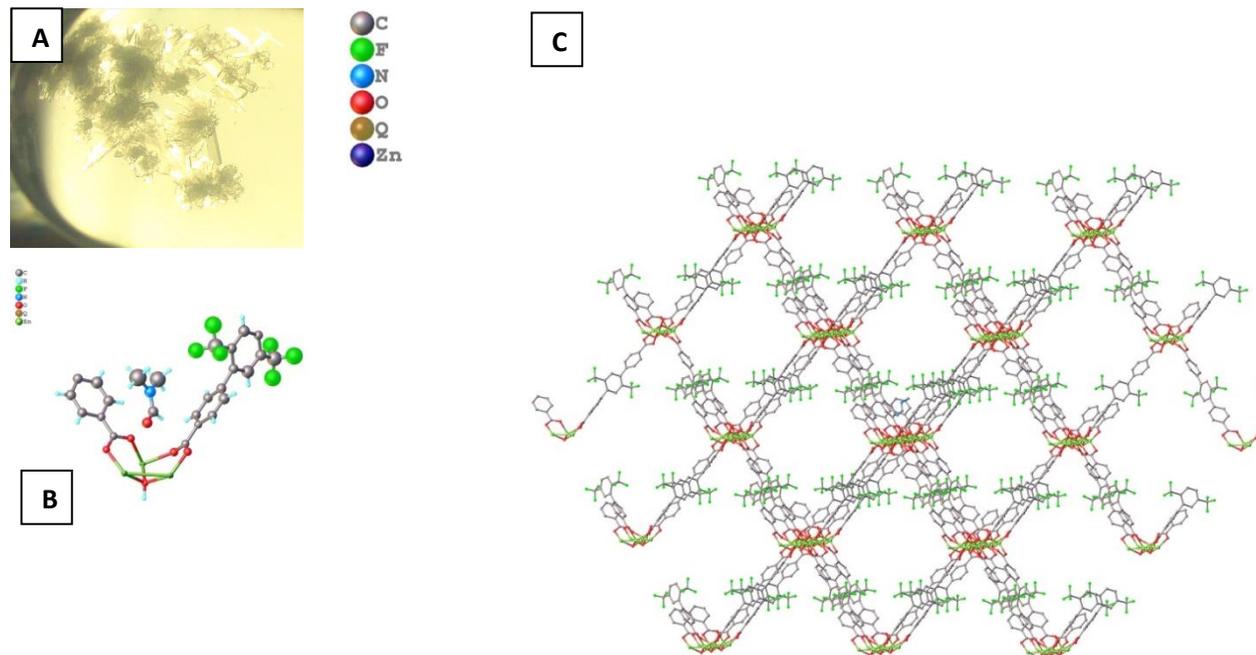


Figure 7. Microscope image of the crystals (A) obtained in the synthesis experiment between the 2',5'-bis(trifluoromethyl)-[1,1': 4',1''-terphenil]-4,4''-dicarboxylic acid H2CF3, zinc nitrate in DMF, the asymmetric unit (B) and the 3D structure of the MOF Zn-CF3.

The phase purity of the Zn-CF3 MOF and the iso-structural relationship with the analogues Zn-F2 and Zn-F4 (obtained as microcrystalline powders) were established by pXRD (Figure 8). The small differences observed between the calculated and measured diffractograms for the Zn-CF3 sample were attributed to the fact that the DMF solvent molecules were not “squeezed” from the single crystal structure.

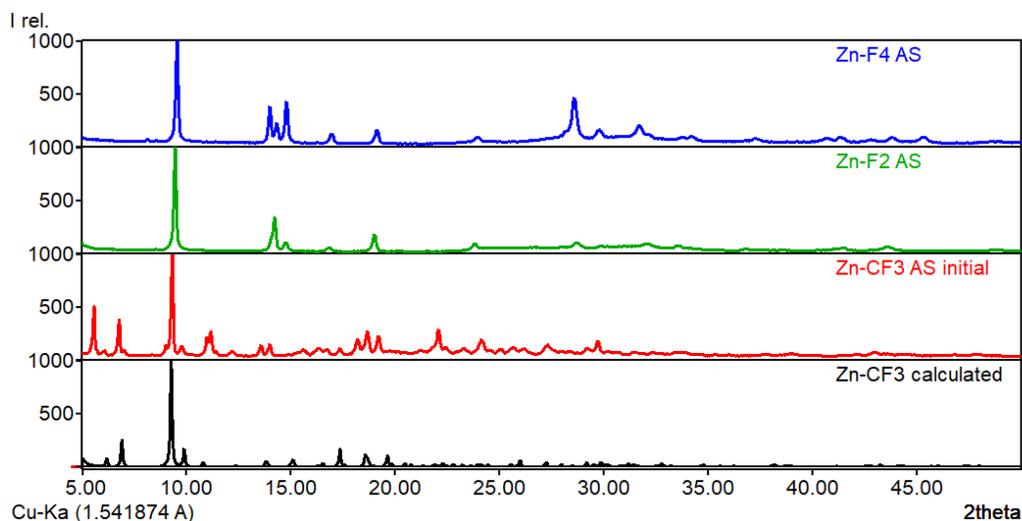


Figure 8. The calculated (black) diffractogram of the Zn-CF3 MOF vs the measured one (red) and that of the analogues Zn-F2 (green) and Zn-F4 (blue).

The influence of temperature on the reaction speed and phase purity was also tested. The results showed that conducting the reaction at 90 °C does not speed the process considerably, but the reaction product is formed as well defined independent crystals. The reaction protocol deployed at 90 °C was validated in triplicate at the same scale and later was up-scaled (2x and 4x). pXRD was used to confirm that the same product was formed and that the phase purity was optimal (Figure 9).

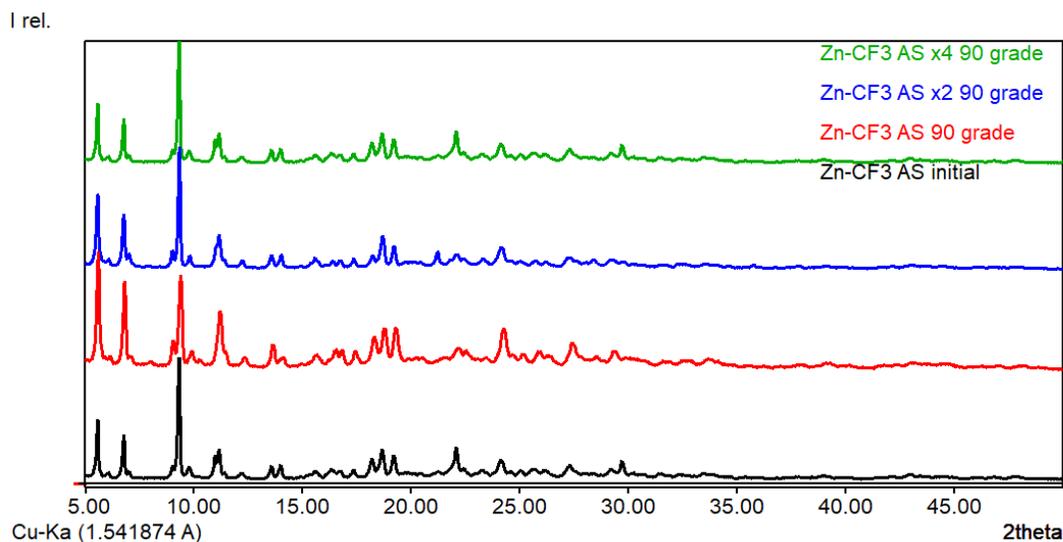


Figure 9. pXRD diffractograms of the initial as-synthesized MOF Zn-CF3 (black), in comparison with the product synthesized at 90 °C at the same scale (red), up-scaled 2x (blue) and 4x (green).

The purification of the zinc MOFs was accomplished by repeated washing with DMF, centrifugation and removal of the supernatant, followed by a rapid washing with methanol and drying in an oven at 80 °C. The reaction yield in all the repeated experiments at the same scale or up-scaled was between 50-60%.

Evaluation of the thermal stability by TGA (Figure 10) indicated that the 3D network begins the decomposition process after 450 °C. Due to its porous nature, the MOF retains a large quantity of solvents in its pores as evidenced by a 25 % mass loss in the 50-225 °C interval.

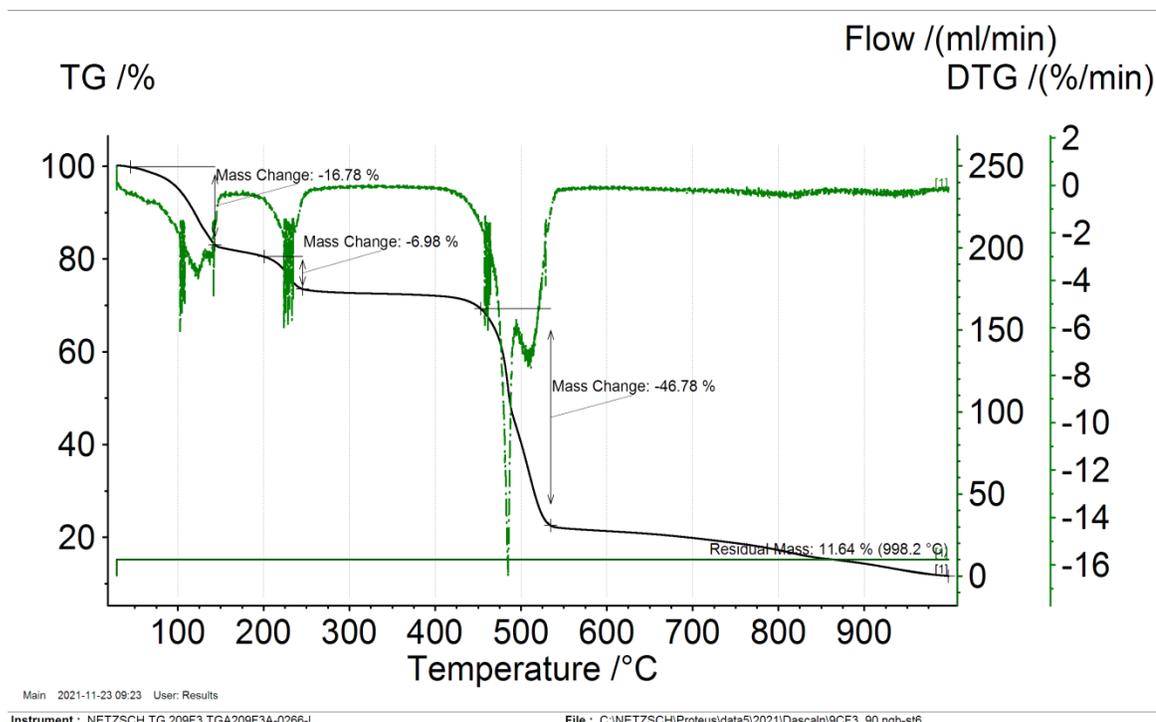


Figure 10. Zn-CF3 MOF TGA-DTG curve.

The direct thermal activation of the zinc MOFs at 120 °C for 16 h proved to be insufficient, as evidenced by the small S_{BET} values obtained from the nitrogen sorption measurements (below 50m²/g).

In this context, with the help of the Mentor, the activation of the metal-organic frameworks by solvent exchange (replacing the adsorbed/coordinated high boiling points solvents with lower boiling point analogues)² was accomplished. Two solvent exchange methods were evaluated, whilst screening for structural modifications by pXRD.

The first approach was made by replacing the retained and coordinated DMF molecules with ethanol. To this purpose, the Zn-CF3 MOF was lightly dispersed in absolute ethanol (25 mL). After approx. 6 h, the dispersion was centrifuged, the supernatant discarded and fresh ethanol was

added. The process was repeated four more times. In the final step the product was dried in an oven for 18 h at 80 °C. The sample was then activated at 150 °C for 18 h under vacuum (1.8×10^{-2} mbar). Nitrogen sorption measurements revealed a slight increase up to $141 \text{ m}^2/\text{g}$ (Figure 11).

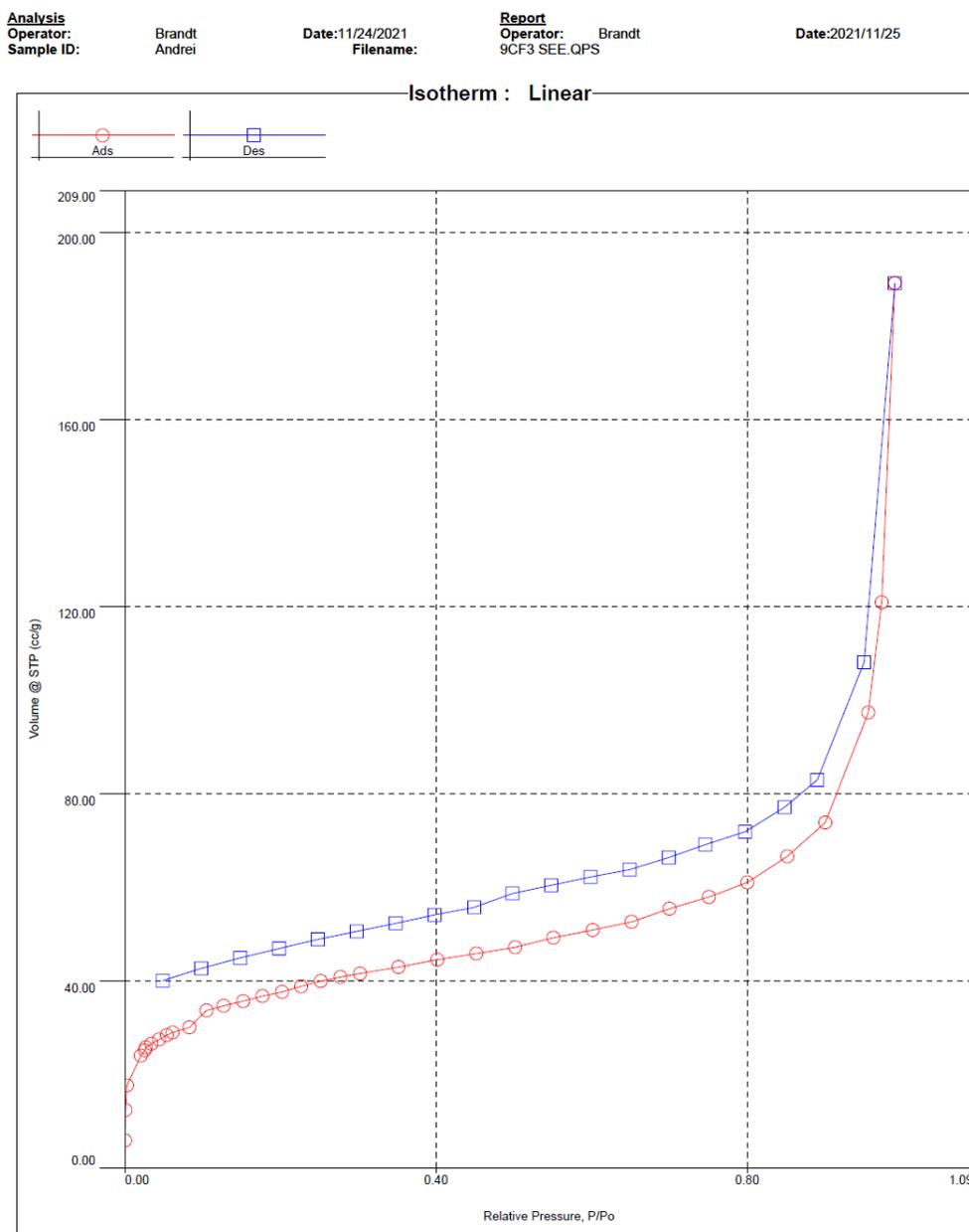


Figure 11. Nitrogen adsorption (red) and desorption (blue) isotherm of Zn-CF₃ MOF after SE with ethanol and thermal activation; $S_{\text{BET}} = 141 \text{ m}^2/\text{g}$.

After each process step (AS-as synthesized, SE-solvent exchange and activated-thermal activation under vacuum) the samples were evaluated by pXRD (Figure 12).

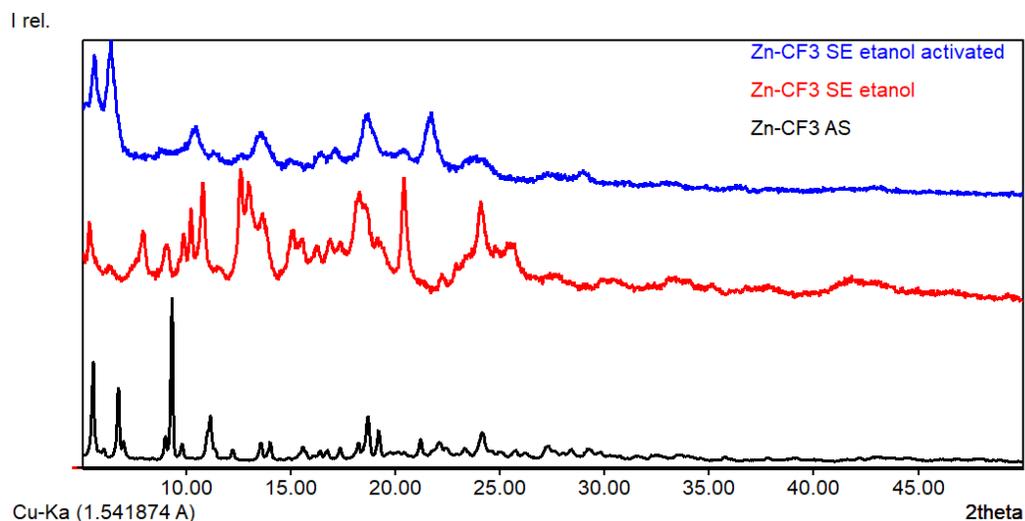


Figure 12. The pXRD diffractogram of the as synthesized coordination polymer Zn-CF3 (black) vs that of the product after solvent exchange with ethanol (red) and that after the thermal activation (blue).

The diffractograms revealed that a partial degradation of the network does take place during the solvent exchange process and after the thermal activation as evidenced by the broadening of the diffraction peaks due to the decrease in crystallite size.

In this context, a different solvent exchange process was tested, using methylene chloride CH_2Cl_2 . To this purpose, the Zn-CF3 MOF was lightly dispersed in CH_2Cl_2 (25 mL). After approx. 6 h, the dispersion was centrifuged, the supernatant discarded and fresh CH_2Cl_2 was added. The process was repeated four more times. In the final step the product was dried in an oven for 18 h at 80 °C. The sample was then activated at 150 °C for 18 h under vacuum (1.8×10^{-2} mbar). Nitrogen sorption measurements revealed an improvement in the S_{BET} value up to 464 m^2/g (Figure 13).

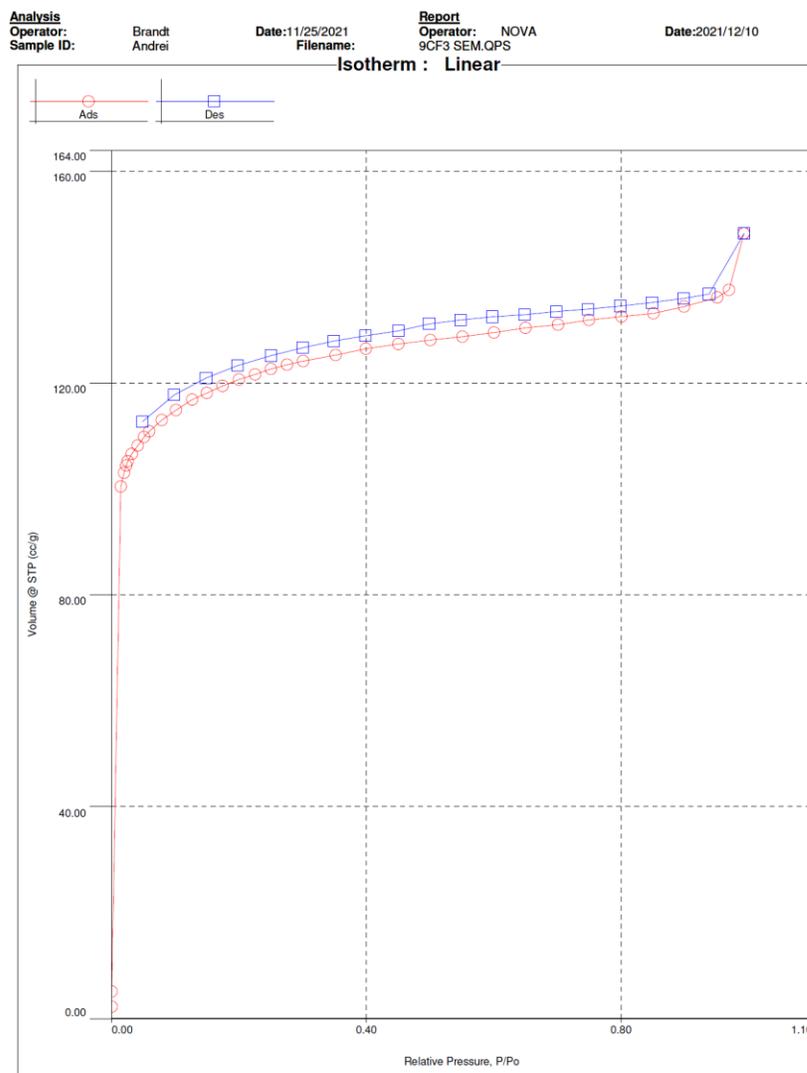


Figure 13. Nitrogen adsorption (red) and desorption (blue) isotherm of Zn-CF₃ MOF after SE with CH₂Cl₂ and thermal activation; $S_{\text{BET}} = 464 \text{ m}^2/\text{g}$.

After each process step (AS-as synthesized, SE-solvent exchange and activated-thermal activation under vacuum) the samples were evaluated by pXRD (Figure 14). The diffractograms revealed that a partial degradation of the network does take place during the solvent exchange process and after the thermal activation as evidenced by the broadening of the diffraction peaks due to the decrease in crystallite size. Although some degradation does occur, it is less pronounced when comparing the diffractograms with those measured after the solvent exchange with ethanol.

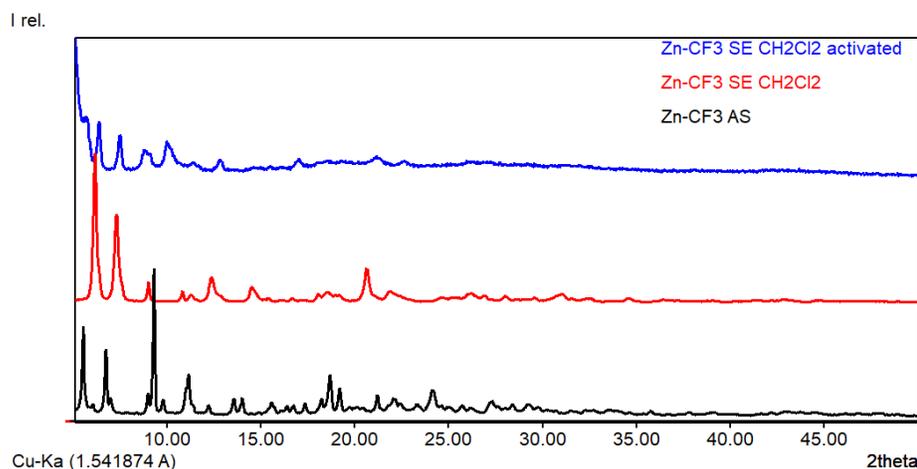


Figure 14. The pXRD diffractogram of the as synthesized coordination polymer Zn-CF3 (black) vs that of the product after solvent exchange with CH₂Cl₂ (red) and that after the thermal activation (blue).

3. Result dissemination

A part of the obtained results have been disseminated at “Progress in Organic and Macromolecular Compounds 28th Edition” Iasi, Romania, 7 – 9 October 2021 with a poster presentation entitled „TOWARDS ROBUST METAL-ORGANIC FRAMEWORKS BASED ON FLUORINATED LINKERS FOR GAS STORAGE” (<https://icmpp.ro/macroiasi2021/files/proceedings-POMC.pdf>). During this conference, the poster presentation was awarded the **Best Poster Communication** award.

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Project Director,

Dr. Ioan-Andrei Dascalu

¹ *Inorg. Chem.* 2017, 56, 21, 13241–13248.

² *Chem. Soc. Rev.*, 2020, 49, 2751-2798.