Polymolybdates are a group of compounds where molybdenum atoms (usually at VI oxidation state) surrounded by six oxygen atoms join into more complex units forming polyanionic assemblies. These compounds display a diversity of forms and find applications among other fields in sensor manufacture (e.g. smoke detectors), in materials production as flame retardants as well as reduction-oxidation reactions catalysts.

The aim of the studies described in this project is to develop synthesis methods and obtain a family of crystalline polymolybdate-derived compounds modified with organic compounds. Determination of crystal structures (description of the spacial distribution of atoms in a crystal) based on X-ray diffraction data registered for these materials, as well as characterization of their physicochemical and catalytic properties also lie in the scope of the project.

The subgroup of this type of materials of interest for the project contains organic compounds bonded to the polyoxomolybdenum moieties through carboxylic oxygen atoms, which through binding with the molybdenum centres incorporate the organic molecules into the “polyanion”. These modifications will affect the possible forms/structures as well as the chemical properties of the materials. They will also allow introduction of further modifications through proper choice of organic compounds, that apart from the carboxylic group used for binding, have other groups like: amine, thiol, hydroxyl, or additional carboxyl as substituents.

Application of compounds containing a larger number of carboxylic groups may lead to crosslinking of the formed assemblies that can be considered as creating connections between polymolybdate-derived moieties with polycarboxylic molecules acting as connectors. Successful obtaining of such assemblies will allow tailoring materials with interesting properties through proper selection of organic molecules.

A particularly interesting group of organic compounds that can modify the properties of materials obtained as a result is characterized by containing more than one carboxylic group that are all connected by conjugated unsaturated bonds systems. Such systems have “conductive properties” and upon binding of the carboxylic groups to different molybdenum centres, redox properties of resulting compounds would be greatly modified owing to the increase in electron availability thanks to the option of transfering them from another centre (not taking part in the reaction directly) or stabilizing electrons/holes introduced in oxidation/reduction reactions due to the character of the conjugated bonds. Similar studies with application of materials where polymolybdate assemblies are bonded to conducting polymers can be found in literature. The major difference between those studies and these planned as parts of the project is that we plan to obtain the products as ordered crystalline phases, which would allow for greater control over their properties and would affect any further attempts at application oriented research.

The project will contain many different synthesis approaches like: heating of the substrates, dissolved in a solvent, under reflux; solvothermal technique (reaction under increased pressure proceeding in an overheated solvent, in a closed, high pressure resistant vessel); reaction on the interface of non-miscible solvents containing substrates dissolved in different liquid phases; mechanochemical reaction occuring between solid state reagents being ground/milled together. The heat generated by grinding/milling activates the chemical reactions allowing for performing processes with highly unusual outcomes. Additionally utilizing a microwave reactor is planned since microwave heating can produce results different from conventional heating due to so called non-thermal microwave effect

Characterization of the obtained materials will largely be based on crystal stucture determination using X-ray diffraction data. Typically an in-lab diffractometer will be used in the studies, however in particularly challenging cases applications for beam time at a synchrotron facility will be submitted to register data with highly improved quality. Diffraction measurements performed in a function of temperature (with temperature changing stepwise) will allow a thermal stability determination as well as detection of potential phase transitions. Crystal phase identification of the thermal decomposition products will also be performed. Data on the temperature dependent response of the sample will be supplemented by thermogravimetric and differential scanning calorimetry measurements. The characterization will also include morphology analysis of the crystals based on images collected with the help of a scanning electron microscope. Last step of the studies on the obtained materials will include catalytic test that will be performed in specialized reactors. The quantitative catalytic effect will be determined based on product analysis of redox reactions performed in the presence of the catalyst using the results obtained without the catalyst as reference. Product analysis will require chromatographic separation methods (GC and HPLC).

Initial impulse for the selection of the research topic was the accidental obtaining of a compound of this type while trying to obtain a different one. This new unforeseen material consisted of polyoxomolybdenum strands with acetic acid molecules built into the structure of the strand. Later a similar compound was obtained with molecules of nicotinic acid. These results along with the fact that neither the synthesis of such compounds nor their structures have been previously described in the literature and also that their properties could be very interesting stood behind the decision to pursue this topic