# A method for production of nanoMOF and prelimiary characterization by selected analytical techniques

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**Abstract.** Metal-organic frameworks (MOFs) are a class of porous hybrid materials comprising metal ion-based vertices and multitopic organic ligands (linkers). The possibility of combining a wide range of metals with similarly large number of available ligands opens ways to design the structures meeting specific purposes. At present, many potential applications of MOFs may require them to be constructed at the nanometer length scale (nanoMOFs). The possibility of filling the track-etched membrane pores with MOF HKUST-1 has been demonstrated in this work.

**Key words:** HKUST-1 • metal-organic frameworks (MOFs) • solvothermal method • template synthesis

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## Introduction

Metal-organic frameworks (MOFs) are a class of porous hybrid materials comprising metal ion-based vertices and multitopic organic ligands (linkers) which serve to connect the vertices into three-dimensional periodic structures. The possibility of combining a wide range of metals with similarly large number of available ligands opens ways to design the structures meeting specific purposes. In particular, the shape and dimensions of pores, preferred adsorption sites for gas molecules and binding energy for adsorbed molecules are the primary factors when considering specific application.

From the beginning, interest for these materials has been driven by a possible use for greenhouse gases removal by physisorption, hydrogen storage for future clean energy technologies and for highly selective separation of gaseous mixtures [3–7]. At present, many potential applications of MOFs may require them to be constructed at the nanometer length scale (nanoMOFs) [2] because nanoscopic dimensions are essential to:
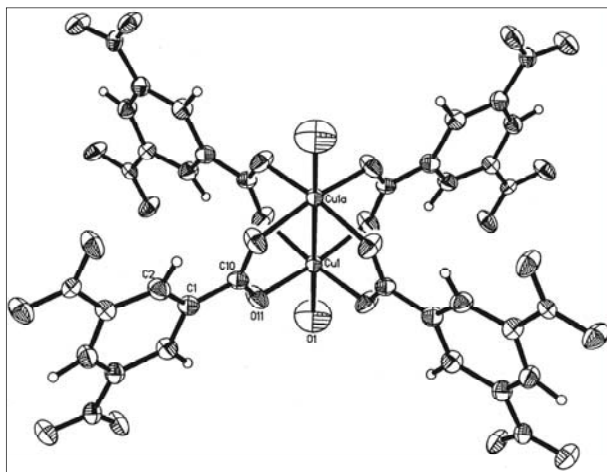- provide MOFs with higher surface areas than do their macroscopic counterparts, opening up novel avenues for tuning their catalytic, ion exchange, separation, sensing and sorption properties;
- provide MOFs that can be integrated on surfaces or directly incorporated into the polymer matrix, to create thin MOF membranes;
- provide materials of sufficiently small and uniform sizes, dispersible and bio-compatible for their use as delivery vehicles (e.g. drugs, vaccines, etc.) and diagnostic agents for biomedical applications.
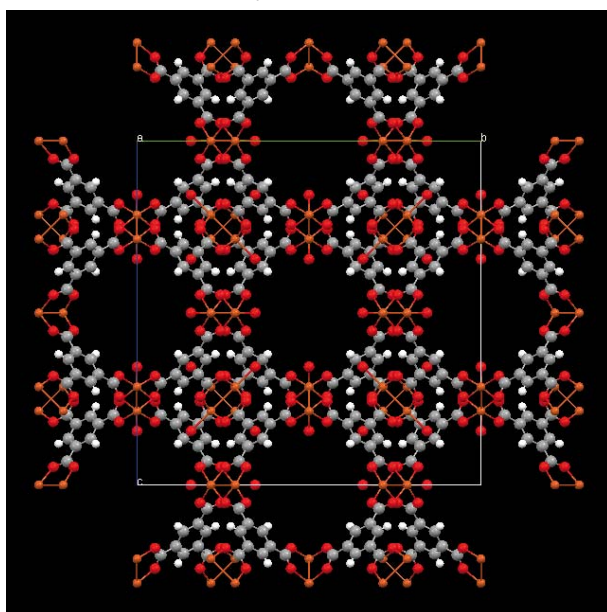
**Fig. 1.** Dicopper(II) tetracarboxylate building block for HKUST-1.

Promising properties of MOF's coupled with the ease by which their structures can be modified makes MOFs one of the most exciting, diverse, and rapidly growing areas of modern materials chemistry research. Our group activities in this field are concerned mainly with nanoscale MOFs synthesis by a template synthesis method. Development of hybrid track-etched membrane having the pores filled with MOF material is also of primary interest. Such composite membranes can find application in sensing and removal of harmful gases, particularly gaseous radioactive species released during nuclear fuel reprocessing or in the case of nuclear accidents.

## Experimental

The well known copper(II) benzene-1,3,5-tricarboxylate MOF (HKUST-1) has been selected for deposition inside the pores of track-etched membranes. It forms a face centred cubic crystalline framework that is com-
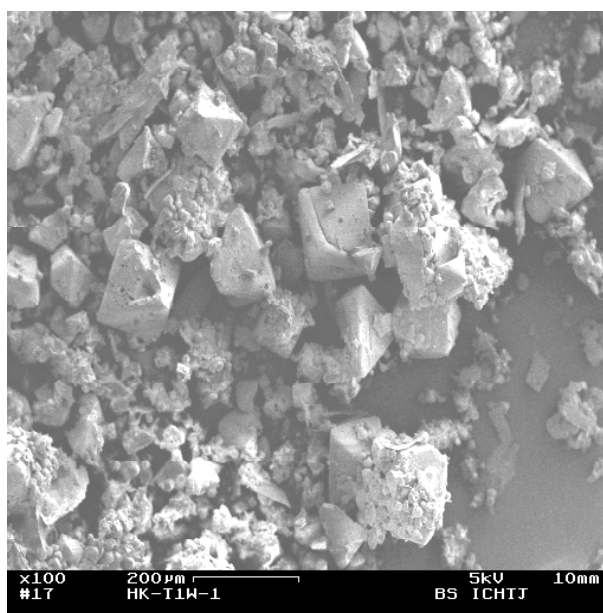
posed of dimeric cupric tetracarboxylate units shown in Fig. 1. They give an intersecting 3D-channel system with a micropore diameter of 0.7–0.8 nm shown in Fig. 2. Synthesis of HKUST-1 has been performed by a solvothermal method. Benzene-1,3,5-tricarboxylic acid (1.9664 g, 0.009 mol) was dissolved in ethanol (20 ml) with stirring. Cupric nitrate trihydrate (4.48 g, 0.018 mol) was dissolved in distilled water (10 ml) in another flask. The two solutions were then mixed and stirred at room temperature for 16 h. The resulting viscous mixture was transferred into a Teflon lined stainless steel autoclave. The autoclave was heated inside a hot air oven at 413 K for 48 h. The reaction vessel was then left to cool to room temperature.
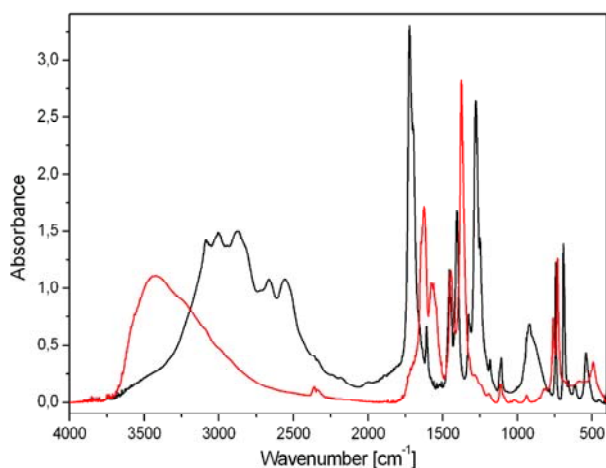
Small octahedral in shape, blue coloured single crystal has been selected from reaction product for structure determination by single crystal X-ray diffraction with an Xcalibur-R single crystal diffractometer. The measurements confirmed the presence of face centred cubic structure of $Cu_3(BTC)_2(H_2O)_3$, (BTC – benzene-1,3,5-tricarboxylate), with lattice parameter of 26.346 Å.

Reaction product after drying has been analysed by scanning electron microscopy and infrared spectroscopy. The scanning electron microscopy photograph shown in Fig. 3 reveals a mixture of crystalline material having broad range of dimensions.

Infrared absorption spectra of the 1,3,5-tribenzenocarboxylic acid and its copper(II) complex shown in Fig. 4 were recorded at room temperature in the range 400–4000 cm$^{-1}$ using KBr pellets with a Bruker Equinox 55 FTIR spectrometer. All functional groups of 1,3,5-tribenzenocarboxylic acid (hydroxyl and carbonyl) form bonds with copper(II) ions in the obtained complex. This is confirmed by the lack of very broad band in the range 3200–2500 originating from the stretching vibrations of the OH groups in uncoordinated ligand. In addition, the partial loss of the C=O double bond character after complexation of this carboxylic acid to the copper(II) ions is shown by the shift of the ν(C=O) bands to lower wavelengths, from 1723 cm$^{-1}$ in free



**Fig. 2.** $[Cu_3(BTC)_2(H_2O)_3]_n$ polymer framework viewed down the [100] direction, showing nanochannels with fourfold symmetry.



**Fig. 3.** SEM photograph for HKUST-1 showing crystallites with different dimensions.

**Fig. 4.** Infrared spectra of HKUST-1 complex (red) and BTC ligand (black).
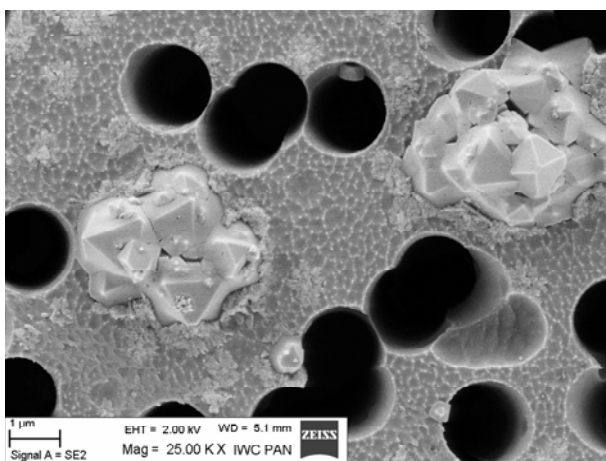


**Fig. 5.** SEM photograph of the PET membrane surface with octahedral in shape, nanoscale crystals.

ligand to 1625 cm$^{-1}$ in complex. Moreover the broad band around 3420 cm$^{-1}$ for copper(II) complex gives evidence for the presence of water molecules in this compound. It is in agreement with single crystal X-ray diffraction measurements for studied complex. Crystal structure investigations show that all copper(II) ions are coordinated additionally by one water molecule.

For deposition of nanoMOF on sensitive material like PET polymer foil, much smaller temperature conditions would be preferable. We adopted the method developed in [1] based on crystallization of the Cu BTC complex from dimethylsulphoxide (DMSO) solution of metal salt and BTC ligand. In our case, 1.170 g of cupric nitrate trihydrate and 0.580 g of BTC ligand have been dissolved in 5 g of DMSO. Droplets of this solution were deposited on the surface of plasma activated PET track-etched membrane with a pore diameter of 1 μm. For plasma activation home made dielectric barrier discharge device working in the air was utilized. Thanks to the plasma chemical modification in the discharge, excellent wettability of membrane surface was achieved resulting in spilling of droplets and thin layer coverage of the membrane. The samples were allowed to stay at ambient temperature for few days. SEM photograph shown in Fig. 5 revealed the presence of octahedral in shape, nanoscale crystals with dimensions significantly below 1 μm filling the fraction of the pores.

## Conclusions

The possibility of filling the track-etched membrane pores with MOF HKUST-1 has been demonstrated. Research on finding the optimal conditions for this process and subsequently to grow thin MOF layer over the membrane surface are in progress.

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