

[1] a) Wang, B. et al., *Nature*, **2008**, 453, 207. b) Horcajada, P. et al., *J. Am. Chem. Soc.*, **2008**, 130, 6774. [2] a) Monge, A. et al., *Chem. Commun.*, **2005**, 1291. b) Gándara, F. et al., *Chem. Mater.*, **2008**, 20, 72. c) Gándara, F. et al., *Cryst. Growth Des.*, **2008**, 8, 378. [3] a) Dinca, M. et al., *J. Am. Chem. Soc.*, **2005**, 127, 9376. b) Rossin, A. et al., *Cryst. Growth Des.*, **2008**, 8(9), 3302.

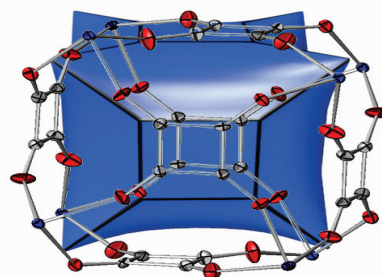
**Keywords:** organic inorganic hybrid materials; hydrothermal synthesis; materials science

#### FA4-MS08-P06

**A New Sc MOF Built up from Octadecasil Zeolitic Cages as Heterogeneous Catalyst.** Felipe Gándara<sup>a</sup>, Berta Gómez-Lor<sup>a</sup>, Marta Iglesias<sup>a</sup>, Natalia Snejko<sup>a</sup>, Enrique Gutiérrez-Puebla<sup>a</sup>, Angeles Monge<sup>a</sup>. <sup>a</sup>*Department of Synthesis and Structure of Oxides, Instituto de Ciencia de Materiales de Madrid-CSIC.*  
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Metal-organic Frameworks (MOFs) continue receiving a great attention since they are a very attractive type of materials due to their potential applications in several fields<sup>[1]</sup>. Specific organic and inorganic units, with predefined geometric characteristics, are employed to obtain predesigned secondary building blocks, with the aim of obtaining networks with preferred features, and therefore, desired properties. We have selected an organic ligand with a well defined geometry, like is the squarate dianion and scandium, a trivalent cation that is usually found in octahedral environment. The combination of these two well geometrically defined building elements has led to the formation of a new Metal-organic framework with a zeolite related structure, and with interesting properties as heterogeneous catalyst. The new framework is constructed with presence of zeolitic cages of the AST type, formed by six 4MR and twelve 6MR. Each scandium atom belongs to two adjacent cages since they are coordinated to six O atoms from six different squarate anions: The result is a new binodal net, 3 and 6 connected net with point symbol

(4.6<sup>2</sup>)<sub>6</sub>(6<sup>6</sup>.12<sup>9</sup>). The new material is stable above 400 °C and it has been tested as an acid heterogeneous catalyst in cyanosilylation and acetalization of carbonyl compounds. A high degree of conversion is achieved with the new Sc-MOF as catalyst, which can also be easily recovered and reused in several cycles of reaction.



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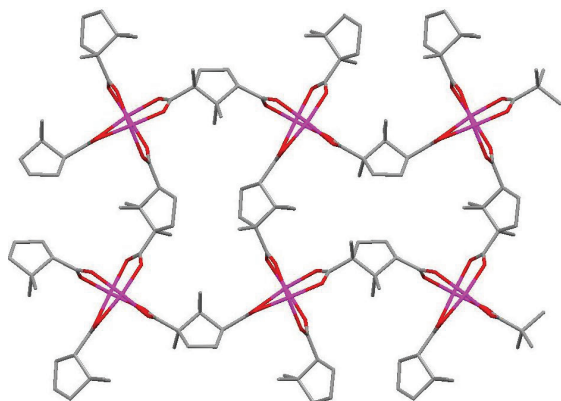
**Keywords:** metallorganic compounds; crystal structure topology; heterogeneous catalysis

#### FA4-MS08-P07

**Axial Ligand Removal and Subsequent Pillaring of a Layered Zinc Dicarboxylate MOF.** P. Smart<sup>a</sup>, C. Mason<sup>a</sup>, A. J. Florence<sup>b</sup>, L. Brammer<sup>a</sup>. <sup>a</sup>*Department of Chemistry, University of Sheffield, UK,* <sup>b</sup>*Department of Pharmaceutical Sciences, University of Strathclyde, Glasgow, UK.*

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Vapour diffusion of pyridine into an ethanolic solution of zinc nitrate and (+)-camphoric acid produces a MOF comprising of Zn<sub>2</sub> paddlewheel units bridged by camphorate to form a 2D layered structure. The axial sites of the paddlewheel are occupied by coordinated pyridine and the remaining inter-layer space is occupied by ethanol. Heating this framework removes the trapped ethanol and the coordinated pyridine in a two step process. The alcohol-free framework remains crystalline and several other alcohols can then be taken up into the framework including the chiral alcohol 1,2-propanediol. Heating the framework removes the coordinated pyridine ligands to produce a semi-crystalline material of the formula [Zn<sub>2</sub>(Camphorate)<sub>2</sub>]. This semi-crystalline 2D material can then be used as a starting material to produce frameworks with various ligands coordinated in the axial position of the Zn<sub>2</sub> paddlewheel. Reaction with solutions of ditopic diimine pillaring molecules such as pyrazine and 4,4'-bipyridine result in 3D MOFs with large pores. Reaction with substituted pyridines produces frameworks which have proved difficult to make by other methods. X-ray powder diffraction using both lab and synchrotron radiation was used to follow the ligand uptake reactions and to structurally characterise the pillared MOFs.



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**Keywords:** metal-organic framework; crystal engineering; X-ray powder diffraction

#### FA4-MS08-P08

**Structure Influence on Sorption Properties in a Dynamic Metal-Organic Framework Based on Calcium.** Víctor A. de la Peña-O'Shea<sup>a</sup>, Ana E. Platero-Prats<sup>b</sup>, Natalia Snejko<sup>b</sup>, Ángeles Monge<sup>b</sup>, Enrique Gutiérrez-Puebla<sup>b</sup>. <sup>a</sup>*Instituto Madrileño de Estudios Avanzados en Energía (IMDEA Energía)*. <sup>b</sup>*Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC)*. E-mail: [victor.delapenya@imdea.org](mailto:victor.delapenya@imdea.org)

The design of new porous 3D polymeric structures is becoming increasingly important, due to their applications as catalysts and molecular sieves. Over the last years, metal-organic frameworks (MOFs) have emerged as an important new class of nanoporous materials with potential applications as gas storage and separation, catalysis, and chemical sensing. Nowadays, there is growing interest in metal-organic frameworks (MOFs) with flexible and dynamic frameworks, in particular, those that reversibly change their structures and properties in response to external stimuli as they may be used as sensors [1]. However, porous materials which have both high framework stability and framework flexibility are rare [2].

To date, MOFs have been proved to be promising materials for gases adsorption and separation (e. g. H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub> [3]. Moreover, recently the use of a flexible MOF for hydrocarbon adsorption in vapor phase was reported [4]. Understand the influence of flexibility on liquids sorption in MOFs would be of great interest in order to determine to what extent liquid adsorption can lead reversible structural changes.

Herein, we report a novel MOF based on calcium which shows an unusual guest-dependent dynamic behavior. This study relates the sorption of both liquids and vapors of different common solvents and gases in terms of adsorption capability and sorbate/sorbent interactions which cause reversible phase transition. In particular, the connection

between structure changes and guest molecules was carefully investigated.

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**Keywords:** organic inorganic hybrid materials; adsorption; structural properties

#### FA4-MS08-P09

**Controlled Growth of Metal-Organic Frameworks (MOFs) on Functionalized Organic Surfaces.** F. Wieland<sup>a</sup>, O. Shekhah<sup>b</sup>, M. Paulus<sup>a</sup>, C. Sterneman<sup>a</sup>, M. Tolan<sup>a</sup>, C. Wöll<sup>b</sup>. <sup>a</sup>*Fakultät Physik/DELTA, Technische Universität Dortmund, Germany*. <sup>b</sup>*Physikalische Chemie, Ruhr-Universität Bochum, Germany*. E-mail: [florian.wieland@uni-dortmund.de](mailto:florian.wieland@uni-dortmund.de)

Metal-organic frameworks (MOFs) are a new class of advanced materials which may be used for various applications. In contrast to the usual synthesis protocol a new approach for the synthesis of MOFs was developed in order to investigate the dynamics and the process of the structural formation [1]. Thin films of the MOF [Cu<sub>2</sub>BTC<sub>3</sub>(H<sub>2</sub>O)<sub>n</sub>] (HKUST-1) are grown by layer-by-layer deposition on top of functionalized organic surfaces which serve as a two dimensional nucleation site [2]. The samples were investigated by x-ray diffraction at the beamline BL9 [3] of the synchrotron light source DELTA. Two dimensional scattering patterns were obtained giving information about the structural order of the films. Comparing x-ray diffraction data of the corresponding bulk material with our data we find that layers of HKUST-1 grow in different preferred directions depending on the functional group of the self assembled monolayer. Also the structural behavior under temperature load was investigated up to a temperature of 320°C. The data shows that the network maintains its structure up to 300°C.

By replacing the the organic ligand by benzenedicarboxylic acid a new MOF can be fabricated. X-ray diffraction patterns show that this MOF exhibits a yet unknown structure that is highly oriented on the substrate. Scanning electron microscopy images reveal small crystallites with uniform distribution on the surface. By investigating the structural stability under temperature load two changes in the properties of the MOF layer could be observed. At temperatures of 160°C and 300°C a change in the orientation of the crystallites could be detected. But more interestingly a reversible change of the lattice constant could be observed which can be attributed to a change of guest molecules in the MOF network.

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**Keywords:** MOF; Thin-films; X-ray diffraction