



# Two isorecticular pillared-layer frameworks as stationary phases for gas chromatographic applications – Unusual peak broadening in size exclusion chromatography, determination of thermodynamic and kinetic data

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## ABSTRACT

Short GC capillary columns were coated with micro particles of the two isorecticular pillared-layer frameworks (PLFs)  $[\text{Cu}_2(\text{cam})_2(\text{dabco})]$  and  $[\text{Cu}_2(\text{cam})_2(\text{bipy})]$  ( $\text{cam}^{2-} = (+)\text{-camphoric acid}$ ,  $\text{dabco} = 1,4\text{-diazabicyclo}[2.2.2]\text{octane}$ ,  $\text{bipy} = 4,4'\text{-bipyridine}$ ) by the technique of the so called “Controlled SBU Approach”. It is demonstrated that the small pore openings of  $[\text{Cu}_2(\text{cam})_2(\text{dabco})]$  enable size dependent gas chromatographic separations which were not observed on  $[\text{Cu}_2(\text{cam})_2(\text{bipy})]$ . In some cases the interaction with the smaller pore system lead to unusual peak broadening. Both compounds offer excellent properties for the high resolution separation of light hydrocarbons including isomers. Chromatographic parameters, including resolution factors and selectivities, as well as thermodynamic data characterizing the interaction between the stationary phase and the analytes were determined from the temperature-dependent retentions times. Furthermore, isothermal measurements were used for the calculation of diffusion constants of selected analytes in the mobile phase and in the  $[\text{Cu}_2(\text{cam})_2(\text{dabco})]$  and  $[\text{Cu}_2(\text{cam})_2(\text{bipy})]$  structures.

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## 1. Introduction

Because of the specific properties of metal-organic frameworks such as exactly adjustable pore sizes by isorecticular expansion, the possibility to intentionally adjust their organic backbone structure to specific needs while keeping a sharp pore size distribution, and the general flexibility in their design by the means of organic chemistry [1–8], the exploration of MOF utilization for separation purposes was very actively pursued during the last decade. Although the focus was primarily on applications connected to large scale industrial separation aspects (such as pressure swing adsorption [9–13], separation by membranes [14–17], as well as the detection [18] and removal of harmful gases [19,20]), some investigations addressing analytical separations were also conducted. One of the applications of MOFs in this respect is their utilization as stationary phases in gas [21–35] and liquid [36–43] chromatography. Over the course of the last few years as part of

the German national research program on MOFs (DFG priority program 1362), our group set out to investigate in which way features that are typical for MOFs, such as tunable pore size, presence of open metal sites, chirality of the backbone, or a breathing lattice structure can be utilized in capillary gas chromatography or influence the results in such investigations. In this respect the presented article is intended as one of a series of papers addressing all of these features [27,28,35,44,45].

As MOF coated capillary columns belong to the type of PLOT (porous layer open tubular) columns which are mainly used for the separation of permanent gases and volatile organic compounds, the first MOF coated capillary columns were demonstrated to be efficient in the separation of hydrocarbons [25,27]. But beyond these first applications, the possibility to create exactly tailored pores may offer new separation possibilities, especially in gas-adsorption chromatography where only few porous materials such as molecular sieves, porous polymers, carbon, and aluminum oxide are available as stationary phases so far. MOFs have already proven to be suitable materials for the favored adsorption of molecules with a smaller diameter and the exclusion of larger molecules from the adsorptions which is known as molecular sieving. However, there

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are only few studies on size exclusion effects for MOFs as stationary phases in chromatography. A first example was given by Ahmad *et al.* demonstrating size dependent separations of 1,3,5-triphenylbenzene on HKUST-1 and 1,3,5-tris(4-bromophenyl)benzene on MOF-5 by HPLC columns [42].

At first sight, the concept of molecular sieving seems to be simple, since all molecules being larger than the pore apertures should be excluded from entering the pores and thus a sharp cut-off should be observed. In this context the most appropriate measure of molecular size is the critical molecular diameter which is defined as the diameter of the smallest cylinder that can just circumscribe the molecule in its equilibrium conformation [17]. Investigations on ZIF-8 [46] (ZIF = zeolitic imidazolate framework) as a zeolite-type structure revealed that there was no sharp size cut-off at the estimated crystallographic pore aperture of 3.4 Å. Experiments with ZIF-8 coated membranes proved the permeation of *n*-hexane (4.3 Å) and benzene (5.45.9 Å) having kinetic diameters far beyond the estimated pore apertures, while only much bigger molecules such as mesitylene (6.8 Å) were not able to enter the pores. The key to understand this effect is the dynamics of the linker molecules within the framework structure, which causes flexible and thus varying pore apertures [17,47].

Since shape and size selective properties of porous media in general do have importance for various technical areas, even on industrial scale (classical examples are zeolites as shape selective catalysts for isomerization reactions (UOP ISOMAR process), xylene separation also with zeolites (UOP PAREX process), and olefin separations (UOP OLEX process)), the chromatographic investigation may serve as a tool for the qualitative (screening) and quantitative (analyte-MOF interaction) investigation of new MOF materials for similar applications. The potential of MOFs in this respect with their much more versatile ways of becoming modified by means of organic chemistry used for the design of MOF linkers is still largely unexplored.

In this contribution we exploit the option to generate structurally related MOFs by changing only one type of linker in a multi-linker MOF structure. This isoreticular expansion bears the advantage that a large portion of the pore structure remains unaltered and offers the same physical and chemical functionalities to the analytes and thus allows to attribute changes in the MOF performance to the pore size effects more justifiably. The isoreticular systems chosen in this work belong to the so called pillared-layer frameworks (PLF) [2,48–51], i.e. [Cu<sub>2</sub>(cam)<sub>2</sub>(dabco)] [52] (PLF-1) and [Cu<sub>2</sub>(cam)<sub>2</sub>(bipy)] [52] (PLF-2), with which short capillary columns were coated and a portfolio of analytes with similar molecule sizes was investigated.

## 2. Experimental section

### 2.1. Capillary coating

Fused silica capillary columns ( $L = 11 \text{ m} \times ID = 0.53 \text{ mm}$ , CS-Chromatographie Service GmbH, Germany) were modified with a CO<sub>2</sub>H-terminated SAM according to the procedure previously published by Böhle *et al.* [35].

[Cu<sub>2</sub>(cam)<sub>2</sub>(dabco)] and [Cu<sub>2</sub>(cam)<sub>2</sub>(bipy)] were deposited in the pre-treated capillary columns in a cyclic deposition mode. For one cycle, solutions of Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O (0.02 M in EtOH), (+) camphoric acid (0.02 M in EtOH/DMF  $v:v = 1:1$ ), and the appropriate pillar linker (DABCO or BIPY, 0.01 M in EtOH) were alternately flushed through the capillary with a speed of 5 cm s<sup>-1</sup>. The excess solutions were removed by flushing the capillary with air between every coating step. The lack of a solvent rinsing step leaves a liquid film of the reaction solutions remaining on the wall of the capillary, a phenomenon that is an essential part of the preparation

method. After a total number of 25 subsequently conducted cycles a blue-green layer of the material deposited in the column was visible. The wall-bonding of the PLF-particles is conducted via the COOH-terminated SAMs and leads to a fixation of the MOF material by the formation of chemical bonds. To activate the column, it was rinsed with EtOH and Et<sub>2</sub>O for 5 min each, dried in a stream of air, connected to a gas chromatograph, and conditioned at 160 °C for 20 h. As a control experiment, solutions leaving the capillaries were transmitted over similarly pre-treated fused silica surfaces (4 mm × 4 mm) and collected in flasks. The materials precipitated were investigated via powder X-ray powder diffraction (XRPD). A nitrogen adsorption isotherm of the precipitate was recorded to demonstrate its microporosity.

### 2.2. Methods and instruments

X-ray powder diffractograms were measured on a Siemens D5000 diffractometer using a CuK $\alpha$  radiation ( $\lambda = 1.541 \text{ \AA}$ , 40 kV, 30 mA) source. The nitrogen adsorption isotherms of [Cu<sub>2</sub>(cam)<sub>2</sub>(dabco)] and [Cu<sub>2</sub>(cam)<sub>2</sub>(bipy)], degassed under vacuum at 363 K for 12 h, were obtained at 77 K with a self-constructed Sieverts apparatus. Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDX) scans were taken using a JEOL JSM 7001F scanning electron microscope with an EDX-detector made by Bruker. The GC experiments were performed using an HP 5890 series II gas chromatograph equipped with a flame-ionization detector (FID). Helium was used as carrier gas in all cases. The data evaluation was conducted with the EZChrome software.

### 2.3. Analytes

Chromatographic experiments with the gaseous hydrocarbons methane, ethane, propane, isobutene, and *n*-butane were performed using a mixture ( $v:v = 1:1$ ) of natural gas (from the grid of Freiberg, Saxony, Germany, November 2011) and butane gas (TYCOON PREMIUM BUTANE GAS, Curly & Smooth Handels GmbH). For all other measurements either the pure hydrocarbons or mixtures (binary  $v:v = 1:1$  or ternary  $v:v:v = 1:1:1$ ) of different light hydrocarbons were used. To avoid overloading effects, for each measurement the initially conducted injection of liquid analyte samples was replaced by the injection of gas samples of 2  $\mu\text{L}$  taken from the vapor phase in the analyte containers. In addition a split ratio of 1:25 was chosen. Methane was used as mobile substance to measure the mobile time simultaneously since there was no measurable retention of methane on the coated columns at the temperatures used for the investigations.

## 3. Results and discussion

The two metal-organic frameworks [Cu<sub>2</sub>(cam)<sub>2</sub>(dabco)] (PLF-1) and [Cu<sub>2</sub>(cam)<sub>2</sub>(bipy)] (PLF-2) chosen for our studies belong to the isoreticular series of the so called pillared-layer frameworks (PLFs) having the general formula [M<sub>2</sub>L<sub>2</sub>P] ( $L =$  dicarboxylate linker,  $P =$  diamine pillar linker). This MOF-type has shown to be suitable for the dip deposition on various surfaces. Typically, for such a procedure, the PLF particles are grown in 2050 cycles by alternately dipping the pretreated surfaces into solutions of the SBU-precursor and the linker molecules while rinsing them with ethanol between each step [53,54]. As this dip-deposition is not suitable for the coating of a capillary column, a procedure previously published by Münch *et al.* [27] was modified to enable the deposition of the two desired PLFs in a cyclic mode. Therefore, short fused silica capillary column ( $L = 11 \text{ m} \times ID = 0.53 \text{ mm}$ ) being coated with a COOH-terminated SAM (self-assembled monolayer) were alternately

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