

# Guest Uptake and Exchange in One-Dimensional Channels of Metal-Organic-Framework Films

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Supporting Information  
available online

*Dedicated to Prof. Dr. rer. nat. Jörg Kärger on the occasion of his 80th birthday*

The mass transfer in a film of metal-organic framework with one-dimensional pores, oriented perpendicular to the substrate surface, was gravimetrically explored. The diffusion coefficients of the probe molecules cyclohexane and *p*-xylene were determined from the transient uptake curves. When exchanging cyclohexane by *p*-xylene in the MOF pores, the mass transfer was significantly slower than the plain, single-component uptakes. However, a single-file-diffusion situation, where mutual passage is hindered, tremendously slowing down the mass transfer, was not found.

**Keywords:** Diffusion, Metal-organic frameworks, One-dimensional nanopores, Thin films

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## 1 Introduction

Diffusion of molecules is a fundamental process in nature [1–5]. It is the primary mechanism for the mass transport of molecules in nanoporous materials [6]. Such materials are highly attractive for various applications due to their enormous surface areas [7–11]. For a single fluid diffusing in the pores, the mass transport can be generally described by Fick's laws [12, 13]. For more insights in the diffusion and mass transport in nanoporous crystalline materials, we like to refer to the work of Jörg Kärger and other experts in the field [6, 14–17].

In the last two decades, metal-organic frameworks (MOFs) became a valuable model system for diffusion studies. MOFs are a class of nanoporous crystalline materials, made of metal nodes connected by organic linker molecules, forming a three-dimensional scaffold [10, 18]. MOFs possess many unique properties, like high porosities, high specific surface areas as well as very diverse structures and functionalities. In pioneering works by the group of Jörg Kärger, the diffusion of light hydrocarbons in MOFs was explored [19–21]. By using infrared and interference microscopy to explore the uptake and release of the guest molecules by/from single crystals, unique insights in the diffusion in nanopores were obtained [19, 20, 22, 23]. A special focus was on the verification and analysis of transport resistances at the external MOF surface, termed surface barriers [19, 22, 24–27]. The experimental work showed that, not only many zeolites [28–32], but also many MOF

materials possess such a transport resistance at the surface [19, 22–26]. This finding was verified by other groups [17, 33, 34]. For a few examples, which are MOFs of type Zn(tbip) [26, 35], Co-MOF-74 [36] and HKUST-1 [37, 38], the surface barriers were characterized as a thin layer of destructed MOF at the external surface which is widely nonporous and thus impermeable. There, the molecules can enter the intracrystalline pore space only via a few remaining openings that are not destructed [26]. More details of the structure of surface barriers and whether these findings can be generalized to further members of the large class of MOFs remain a future task.

Inspired and motivated by the diffusion studies in single crystals, well-defined MOF films prepared and stored under controlled conditions were employed to further explore the surface barrier phenomenon [37–39]. To date, infrared and interference microscopy were not yet applied to visualize the transient concentration profiles and to gain deeper insights in the uptake and release kinetics in thin films. Instead, a quartz crystal microbalance (QCM) [40] was employed to gravimetrically quantify the transient uptake of the guest

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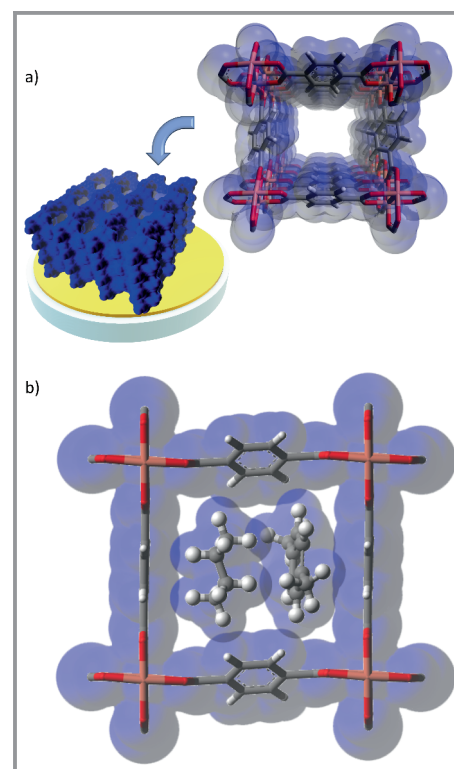
molecules by the MOF film grown on the QCM sensor. So far, the diffusion studies using MOF films have been focused on MOF materials with three-dimensional pore systems. In this communication, we like to introduce thin films of metal-organic frameworks with one-dimensional channels as defined model system for diffusion studies.

Generally, the size, the shape and the connectivity of the pore space has a severe impact on the molecular mass transport [6, 16]. A particularly interesting case can be found in one-dimensional channel-like pores where the mutual passage of the molecules is excluded. This situation is usually referred to as single-file diffusion [41, 42]. In such single-file-diffusion systems, the mobility of the particles is highly correlated. In particular, the mobility of the particles at large diffusion times (and large pore fillings) is tremendously decreased by the phenomenon of single-file diffusion. In the equilibrium case, the average mean square displacement of the particle scales with the square root of time, rather than with the time, as expected for plain Fickian diffusion. Single-file diffusion in different zeolite structures has been experimentally explored by pulsed field gradient nuclear magnetic resonance and quasi elastic neutron scattering techniques [42–47]. For MOFs, the observation of single-file diffusion has been published only once to date [48]. However, due to the huge versatility and tunability of MOFs, where the pore size and shape can be adjusted, we expect that using this class of material as host for single-file diffusion studies will provide further insights. Besides, the channel length can be controlled by controlling the MOF particle size or the film thickness, in case of diffusion studies with MOF films.

It should be noted, that many different MOF structures with one-dimensional channels have been presented [49–52]. When growing the MOF structures in the form of thin films, the pores are usually oriented parallel to the substrate surface [53, 54]. There, the uptake, which is assumed to occur via defects and domain boundaries, can be explored [55], but a thorough characterization of the mass transfer is difficult. Please note, although the layer-by-layer synthesis of making surface-mounted MOFs (SURMOFs) possesses many advantages for studying the diffusion in the nanopores (such as a small defect density and a controlled thickness) [56], SURMOF films with sub-nm-sized channels perpendicular to the substrate surface have not yet been presented to date. To the best of our knowledge, except of metal-organic-graphene-like MOFs such as CuHHTP with relatively large pores [57, 58], the only report of a homogenous MOF film with one-dimensional channels perpendicular to the substrate surface is a Cu(BDC) MOF film made by chemical vapor deposition [59]. The mass transfer in these pores has not yet been explored.

Here, we present uptake and exchange experiments in MOF films with one-dimensional channels perpendicular to the substrate. Since the pores are perpendicular to the substrate, each pore has one open end, where the molecules can enter and leave the pores, and one end that is blocked

by the substrate. The pore diameter is approximately 0.8 nm. The guest molecules cyclohexane and *p*-xylene are slightly smaller than the pore diameter of the defect-free MOF structure, Figure 1. The transient molecular uptake from the vapor phase was gravimetrically recorded by QCM. From the transient guest uptake, the diffusion coefficients were determined. When exchanging cyclohexane guest molecules in the pores by *p*-xylene, the time constant of the exchange is about 4 times smaller than of the pure guest uptake. This points on a strong interaction of the diffusing guests. However, single-file diffusion, which would cause a tremendous mobility drop, can be excluded.



**Figure 1.** a) Sketch of the MOF film on the QCM sensor. The MOF film (blue) is grown on the gold-coated QCM sensor. The channels are perpendicular to the substrate surface. The channel with the MOF structure (Cu – orange, O – red, C – grey and H – white) and the van-der-Waals surface (transparent blue) are also shown. b) The MOF pore with one cyclohexane (left) and one *p*-xylene (right) guest molecule in the pores. The molecules are next to each other in the pore. The van-der-Waals volume of all atoms (MOF and guest) are shown in semi-transparent blue. Flexibility, vibrations, and defects are not considered here.

## 2 Experimental Section

The MOF films of type Cu(BDC) were prepared via chemical vapor deposition, following published directions [59, 60] (BDC stands for 1,4-benzene dicarboxylic acid, i.e., terephthalic acid). The synthesis was performed in two steps. First, a 100nm-thick copper layer was deposited on the substrate,

which was plain quartz or a gold-coated-QCM sensor, via vapor-phase deposition using a BAL-TEC MED 020 coating system. The metallic copper film was oxidized by thermal treatment at 300 °C in air for 30 min. In the second step, the substrate was placed in a Schlenk flask in an upside-down position, 4 cm above the BDC molecules (about 500 mg). Then, the reaction vessel was evacuated (down to  $2 \cdot 10^{-1}$  mbar), heated to about 200 °C and kept for 18 h. After cooling down, the final sample was obtained.

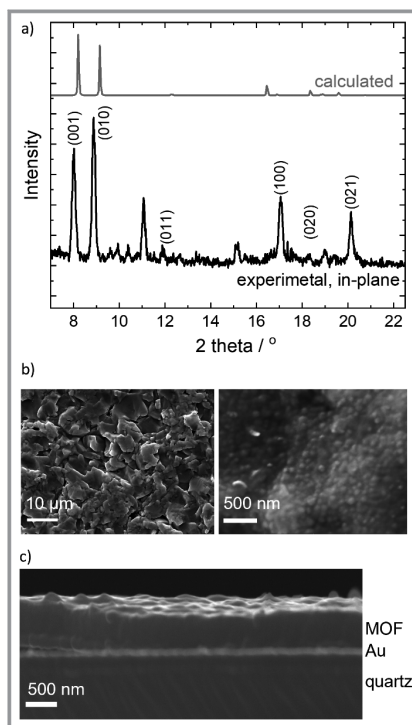
The crystallinity was investigated by in-plane X-ray diffraction (XRD) using a Bruker D8 DISCOVER Plus XRD diffractometer. The resulting diffractogram was compared with the data calculated for the corresponding published crystal structure (ZUBKEO in the Cambridge Crystallographic Data Centre).[59]

The uptake experiments were performed using a quartz crystal microbalance (QCM) with the Cu(BDC) film on the gold-coated QCM sensors. The QCM is a QSense QCM-D E4. The QCM cell was purged by a nitrogen stream with a constant flow rate of 100 SCCM. Before the experiments, the sample was activated in pure nitrogen at 45 °C for 24 h, to ensure that the MOF pores are activated (i.e., empty). In the uptake experiments, the gas flow was instantly switched from pure nitrogen to the nitrogen flow enriched with the guest molecules (*p*-xylene or cyclohexane), which was realized by the nitrogen stream flowing through a wash bottle filled with the liquids. The partial pressure of the vapors is slightly below the saturated vapor pressure at room temperature [61]. The setup was optimized in our previous studies [38, 39, 61, 62]. The experiments were performed at a temperature of 30 °C.

After the uptake experiments, the sample was imaged with scanning electron microscopy (SEM). The SEM measurements were performed with a TESCAN Vega III electron microscope. The secondary electron detector, a beam voltage of 30 kV and a working distance of 8–9 mm were used. Before the SEM imaging, the sample was covered with a thin (~5 nm) layer of platinum.

### 3 Results and Discussion

The MOF film was prepared following the synthesis directions, recently presented by Ameloot et al. [59, 60]. The targeted MOF is made of Cu-nodes which form linear chains. The Cu-chains are connected by terephthalate. The pore cross section of the Cu(BDC)-MOF-channels is approximately square-shaped with an edge length of approximately 0.8 nm. The structure of the thin MOF films was explored by X-ray diffraction, Fig. 2a. There, the diffractogram was recorded in the in-plane-geometry, since the out-of-plane X-ray diffraction of this MOF structure shows only weak diffraction peaks [59]. The in-plane-XRD shows that the film is crystalline and it has the structure of the targeted MOF. Moreover, it shows that the MOF pores are aligned perpendicular to the substrate surface, see [59].



**Figure 2.** a) In-plane X-ray diffractogram of the Cu(BDC) MOF film (black) compared with the calculated structure (grey). The experimentally observed peaks are labelled. b) and c) SEM top view and the cross-section of the broken sample. The quartz sensor and its Au coating as well as the MOF film are labeled.

The sample morphology was imaged by SEM, Fig. 2b and c. The images show that the film covers the substrate homogeneously. The film has a thickness of approximately 500 to 700 nm, in average about 600 nm. A small surface roughness can also be observed.

The film thickness of these sample is somewhat larger than the films in [59], indicating a higher CuO → MOF-conversion, most likely due to the longer synthesis time and a somewhat different synthesis setup. Based on the CuO-thickness of 100 nm and on the CuO → MOF-volume-conversion factor of 13 [59], a maximum MOF-film-thickness of 1.3 μm is expected.

The transient uptakes of the pure probe molecules, either cyclohexane or *p*-xylene, by the MOF film are shown in Figure 3a and b as well as in Figure S1. The increase of the mass can be described with a mono-exponential decay function with a time constant  $\tau$  of about 1.3 s for cyclohexane and 20 s for xylene. The uptake experiments were repeated several times. An average uptake time constant of  $1.3 \pm 0.2$  s for cyclohexane and  $19 \pm 6$  s for xylene was determined, see Figure S1, supporting information. The average observed cyclohexane uptake amount was  $1.7 \pm 0.1 \mu\text{g cm}^{-2}$  and  $2.2 \pm 0.2 \mu\text{g cm}^{-2}$  for *p*-xylene.

For diffusion-controlled uptake by a thin homogeneous film (or infinite slab) of thickness  $l$ , the time constant  $\tau$  corresponds to  $l^2/3D$ , see ref.<sup>8</sup> (page 278) or ref.<sup>6</sup> (page 445).



Based on the film thickness of 600 nm, we calculate a diffusion coefficient of  $\sim 9.5 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$  for cyclohexane and  $6.2 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$  for *p*-xylene.

The transient uptake data can also be described with the analytical solution of the diffusion equation (i.e., Fick's law) with the respective boundary conditions [6, 62, 63]. By this approach (see Fig. S1 in the Supporting Information, SI) a diffusion coefficient of  $(9.5 \pm 0.7) \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$  was determined for cyclohexane and  $(6.6 \pm 2.7) \cdot 10^{-15} \text{ m}^2 \text{ s}^{-1}$  for *p*-xylene. Both methods result in very similar diffusion coefficients.

The release of the guest molecules was significantly slower. The release-time-constants were approximately one order of magnitude larger than the uptake-time-constants (representative release curves are shown in Fig. S2, SI). We assume that this is caused by a diffusion coefficient which increases strongly with the guest loading, where similar differences in the time constants have been found before [30, 64]. Here, this is not explored in detail.

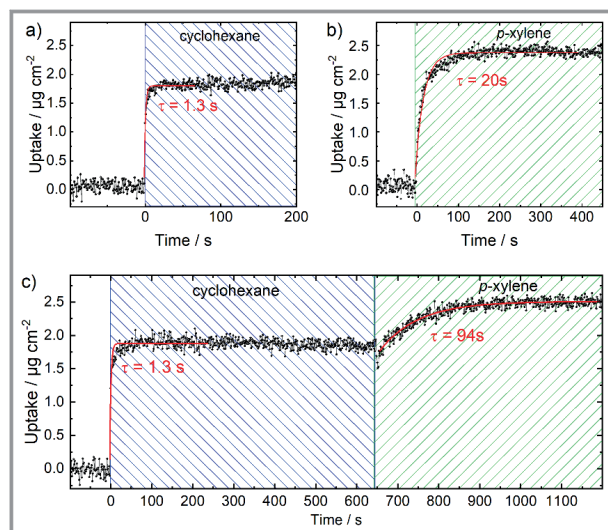
In order to explore the diffusion mechanism, particularly whether the mass transfer is governed by single-file diffusion, guest-exchange experiments were performed. In case of single-file diffusion, a tremendously slowed-down exchanged kinetics would be obtained. To this end, the samples were first loaded with cyclohexane. Then, after the MOF pores are filled with cyclohexane, the cyclohexane vapor in the gas atmosphere was exchanged by the xylene vapor. The change of the recorded mass is shown in Fig. 3c. There, it can be seen that the mass uptake slowly changes

from  $1.8 \mu\text{g cm}^{-2}$  to  $2.5 \mu\text{g cm}^{-2}$ . We interpret this as an exchange of the guest molecules from cyclohexane to xylene. The time constant of the exchange is 94 s, which is about 4 times slower than the uptake of xylene by the initially empty MOF film.

Since the cyclohexane diffusion is one order of magnitude faster than the xylene diffusion, we believe the kinetics of the cyclohexane  $\rightarrow$  xylene exchange is essentially limited by the xylene mobility, not by cyclohexane. (We believe the current communication is a great starting point for a thorough study, which also includes the xylene  $\rightarrow$  cyclohexane exchange, where the kinetics are presumably governed by the slow release of xylene.) Based on the exchange curves, the counter diffusion coefficient of xylene is 4 times smaller than the single-component diffusion coefficient (in the initially empty MOF pores). We believe the reason for the significantly slower counter diffusion, compared to the plain single-component diffusion, is the interaction of the guests, where the mass transport of both components occurs in opposite directions during the exchange. Moreover, the multi-component adsorption equilibrium may also affect the uptake kinetics. The effect of the adsorption amount as well as the shape of the isotherm may also contribute.

On the other hand, for single-file diffusion in channels with a length  $L$  of 600 nm, the effective diffusion coefficient  $D_{\text{eff}}$  would drop and the time constant would increase by many orders of magnitude, depending on the pore filling [65]. The effective diffusion coefficient for (tracer) exchange in single-file-diffusion systems can be calculated by  $D_{\text{eff}} = D \frac{1-\theta}{\theta} \frac{\lambda}{L}$  [65]. As a rough estimation, assuming a pore filling (occupancy  $\theta$ ) of 50% and a diffusion step length ( $\lambda$ ) of 1 nm, the effective diffusion coefficient is 600-times smaller than the diffusion coefficient. This means the time constant of the exchange would be 600-times larger than of the uptake. Such a larger difference between the uptake and exchange processes is not observed, thus, we exclude (pure) single-file diffusion in our system.

The gas kinetic diameter of cyclohexane is 0.60 nm and 0.67 nm for *p*-xylene [66, 67]. Thus, if both molecules would be rigid spheres of that diameters, their passage would be excluded in the (defect-free) MOF pores with a diameter of about 0.8 nm. However, *p*-xylene has a planar shape and cyclohexane is also more flat than spherical, so that both molecules can pack next to each other in the pores, see Fig. 1c. This means, mutual passage is possible, and the exchange process is not hindered by single-file diffusion. Moreover, the flexibility of the MOF and of the guest might also contribute. In addition, defects in the MOF structure, where the pore shape deviates from the straight channel form, may also allow the guest passage.



**Figure 3.** Transient guest uptake and exchange recorded by QCM. a,b) Uptake of cyclohexane and *p*-xylene. The exposure to the vapor is indicated by the blue and green area, respectively. The description of the data with monoexponential decay functions as well as its time constants are shown in red. Zoomed-in views of the uptakes are shown in Fig. S1, Supporting Information. c) Exchange of cyclohexane by xylene. Upon the sample was exposed to the cyclohexane vapor for about 10 min, the cyclohexane vapor was exchanged by the xylene vapor, see labels.

## 4 Conclusion

An uptake and diffusion study with MOF films of type Cu(BDC) with one-dimensional channels and cyclohexane and *p*-xylene as probe molecules is presented. From the transient uptake curves, the diffusion coefficients were determined to be  $(9.5 \pm 0.7) \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$  for cyclohexane and  $(6.6 \pm 2.7) \cdot 10^{-15} \text{ m}^2 \text{ s}^{-1}$  for *p*-xylene. When the cyclohexane molecules in the MOF pores are exchanged by xylene, the exchange mass transport is four times slower than the single-component uptake of xylene. We interpret this as slow counter diffusion. A situation where the passage of the molecules is fully excluded, causing single-file diffusion (with tremendously decreased exchange rates), is not present. We speculate that larger, more spherical guest molecules will not be able to pass each other in the pores, so their mass transport might follow the single-file-diffusion mechanism.

The study intends to suggest and to highlight MOF films as model system for diffusion study. Since the thickness of the MOF film and, thus, the channel length as well as the pore diameter can be tuned [59], many critical parameter can be modified. At the moment, the study suffers from the fact that QCM is only sensitive to the mass changes, and not to the type of molecules. Thus, it is insensitive to the guest exchange. In future studies, the QCM data should be combined with vibrational spectroscopy. Moreover, we believe the combination with theoretical data by molecular-dynamics simulations will help to gain deeper and more profound insights.

## Supporting Information

Supporting Information for this article can be found under DOI: <https://doi.org/10.1002/cite.202300045>.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request. The data are also available on Radar4Chem (<https://radar4chem.radar-service.eu>).

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## Abbreviations

BDC	1,4-benzene dicarboxylic acid / 1,4-benzene dicarboxylate
MOFs	metal-organic frameworks
QCM	quartz crystal microbalance
SEM	scanning electron microscopy
XRD	X-ray diffraction

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## Guest Uptake and Exchange in One-Dimensional Channels of Metal-Organic-Framework Films

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**Short Communication:** The mass transfer in a film of metal-organic framework with one-dimensional pores, oriented perpendicular to the substrate surface, was explored. The diffusion coefficients of the probe molecules, cyclohexane and *p*-xylene were determined from the transient uptake and exchange curves. ....



Supporting Information  
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