



## A series of amide functionalized isoreticular metal organic frameworks



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### ABSTRACT

2,2-Diamido-1,1'-biphenyl-4,4'-dicarboxylic acids were synthesized with amido functions of different chain lengths and used as starting materials for isoreticular metal organic frameworks (IRMOFs). The IRMOFs were characterized by means of different methods such as single crystal X-ray diffraction, X-ray absorption spectroscopy, powder X-ray diffraction, solid state NMR and IR spectroscopy, powder X-ray diffraction (PXRD), FT-IR and solid state NMR spectroscopy, N<sub>2</sub> physisorption measurements and thermogravimetric analyses (TGA). We here present a detailed study on how systematic variations of the length of the alkylamide side chains influence certain features of the material such as structure, specific surface and gas adsorption properties. In general, this series of MOF materials exhibit high capacities for the storage of gases such as short alkanes and alkenes as well as CO<sub>2</sub>.

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### 1. Introduction

Metal Organic Frameworks (MOFs) are a unique group of organic–inorganic hybrid materials in which coordination of metal centers by organic molecules possessing two or more binding sites results in the generation of three dimensional crystalline and often porous networks. These materials entered the focus of science after the synthesis of MOF-5 (also named as IRMOF-1) by Yaghi et al. [1]. MOF-5 was built up by formally linking [Zn<sub>4</sub>O]<sup>6+</sup> clusters, possessing six octahedrally arranged free coordination sites for μ<sup>2</sup>-bridging carboxylate units, with 1,4-benzenedicarboxylic acid as the organic linker leading to a cubic framework structure.

After this important discovery, a series of such materials having the same topology as MOF-5 were synthesized by employing bifunctional rigid linkers with different lengths and functionalities. According to their structural similarity these systems were named Isoreticular Metal Organic Frameworks (IRMOFs) [2]. They build a basis of adjusting and designing frameworks, in other words reticular chemistry [3], which results in materials differing in pore properties (size and volume), surface area and chemical features. Their special properties made them highly interesting candidates for a plethora of applications such as gas adsorption [4–8], separation [9,10], catalysis [11,12], or drug delivery [13–15]. Among all possible applications of IRMOFs, gas adsorption has attracted most

of the interests. Especially the capturing and adsorption of CO<sub>2</sub> with MOFs has developed into an interesting alternative to other techniques [16–19]. Functionalization of the linker according to the desired application is the most common method to achieve specific MOF materials and different topologies [20–23]. However, Fischer et al. showed that functionalization of the linker can also result in unpredictable network formations involving functional groups [24].

We here report a study, wherein we investigated how small changes in the molecular structures of the linker molecules affect the properties of the derived MOFs. For this purpose we synthesized a series of large-pore IRMOF materials using *ortho*-carbamoylated 4,4'-biphenyldicarboxylic acids differing in the alkyl chain length of their amide groups. The gas adsorption properties of these new materials were investigated for alkanes, alkenes and CO<sub>2</sub>.

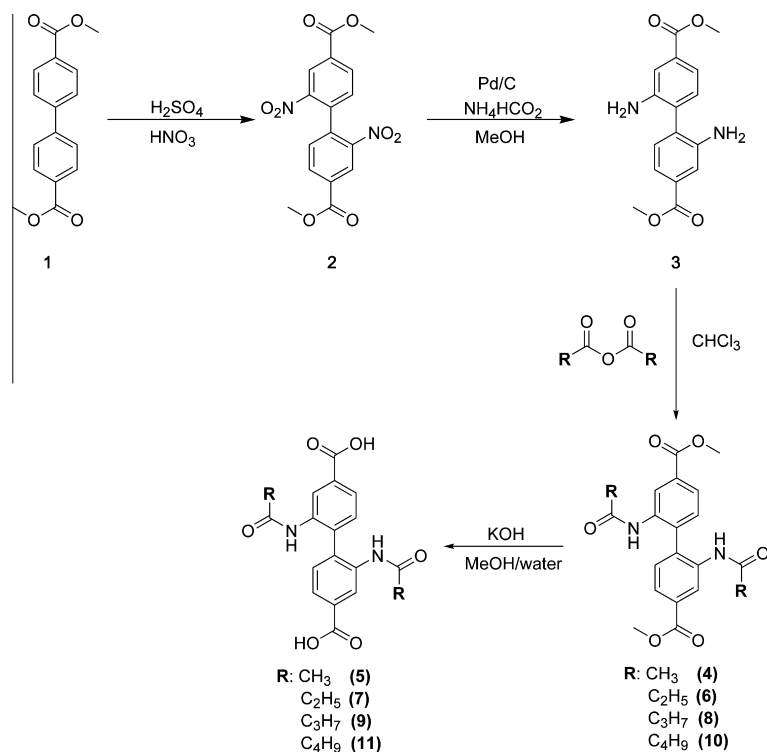
### 2. Experimental section

#### 2.1. General

All chemicals applied in the syntheses were purchased from Sigma Aldrich Ltd., Merck, Fluka or Acros Organics and used without further purification. Powder X-ray diffraction data of the as-synthesized samples and the samples that were activated with supercritical carbon dioxide were collected on a STADI P diffractometer with Cu-K<sub>α1</sub> radiation (λ = 1.5405 Å). Diffraction data obtained from

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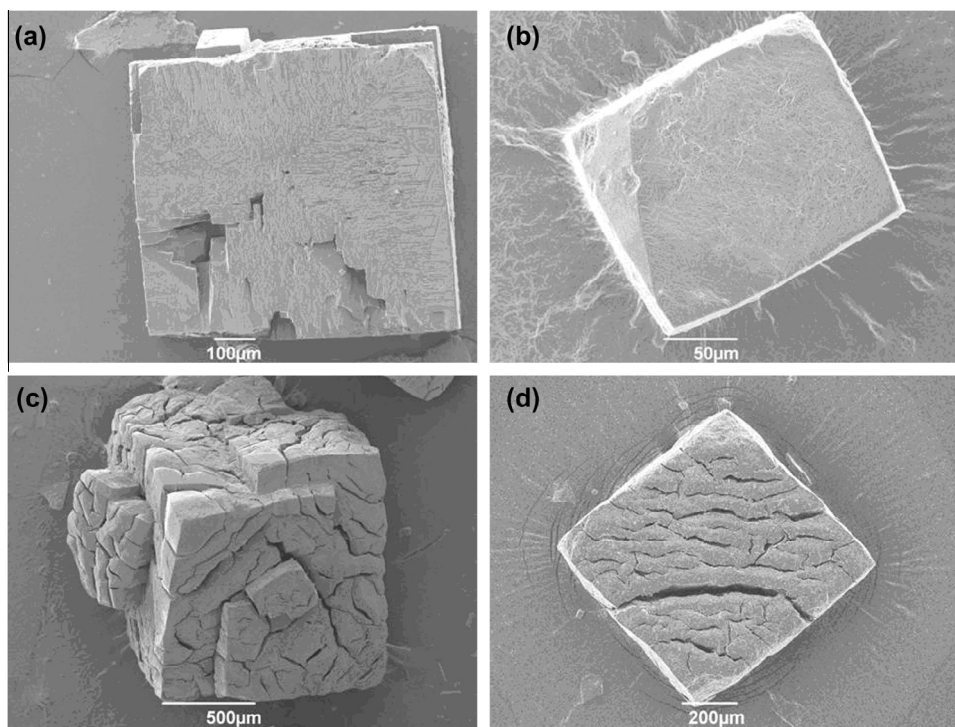
E-mail address: [thiel@chemie.uni-kl.de](mailto:thiel@chemie.uni-kl.de) (W.R. Thiel).



**Scheme 1.** Synthesis of the linkers **5**, **7**, **9** and **11**.

acetone exchanged samples were collected on a Siemens D5005 diffractometer with  $\text{CuK}\alpha$  radiation ( $\lambda = 0.15418$  nm). Nitrogen adsorption/desorption measurements were performed on a Quantachrome Autosorb-1 at a temperature of 77 K. Thermogravimetric analyses were performed on a Setaram Setsys 16/18 analyzer at a heating range of 5 K/min. Crystallinity and morphology of the

synthesized samples were examined on a JEOL JSM-6490LA scanning electron microscope with a tungsten cathode at accelerating voltages of 5–25 kV and a working distance of 10 mm. Solid state NMR measurements were performed on a 500 MHz Bruker Avance III widebore NMR spectrometer. The infrared spectra were recorded with a resolution of  $\pm 4$   $\text{cm}^{-1}$  using a Perkin Elmer FT-ATR IR 1000



**Fig. 1.** SEM images of the MOFs, **ZnAcBPDC** (a), **ZnPrBPDC** (b), **ZnBuBPDC** (c) and **ZnPeBPDC** (d).

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