

## In Situ Imidazolate-4-amide-5-imidate Ligand Synthesis Leading to New Microporous Zinc-Organic Frameworks –Tuning of the Pore Size

Debatin, F., Potsdam/D, Behrens, K., Potsdam/D, Thomas, A., Berlin/D, Seifert, G., Dresden/D, Leoni, S., Dresden/D Kelling, A., Potsdam/D, Kaskel, S., Dresden/D, Friedrich, A., Potsdam/D, Holdt, H.-J., Potsdam/D

Franziska Debatin, Universität Potsdam, Karl-Liebknechtstraße 24-25, 14476 Potsdam

Among different metal-organic framework (MOF) classes<sup>[1]</sup> metal-organic frameworks based on metal imidazolates hold a great promise as porous materials for a variety of applications because of their exceptional thermal and chemical stability.<sup>[2]</sup>

We developed an in situ synthesis of functionalized imidazolate MOFs (IFPs = Imidazolate Framework Potsdam) by partial hydrolysis of cyano groups of several linker precursors (4,5-dicyanoimidazoles), which have different substituents in 2-position (**IFP 1**<sup>[3]</sup> = CH<sub>3</sub>, **IFP 2**<sup>[4]</sup> = Br, **IFP 3** = Cl). These in situ hydrolyses occurred under solvothermal reaction conditions in DMF in the presence of Zn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O to form not-yet-synthesized functional microporous networks with the new linker molecules 2-methyl-imidazolate-4-amide-5-imidate (**IFP 1**), 2-bromo-imidazolate-4-amide-5-imidate (**IFP 2**) and 2-chloro-imidazolate-4-amide-5-imidate (**IFP 3**).

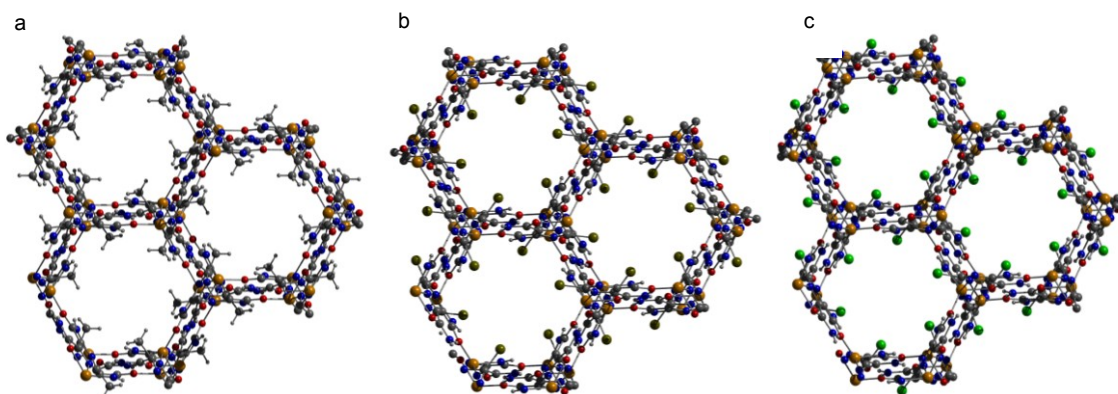


Figure 1. Hexagonal channels in a) **IFP 1**, b) **IFP 2** and c) **IFP 3** view along the c-axis.

To the best of our knowledge these **IFPs** are the first examples of imidate metal complexes. They form 1D hexagonal channels running along the [0 0 1] direction with effective channel diameters of 3.8 Å (**IFP 1**), 3.1 Å (**IFP 2**) and 3.7 Å (**IFP 3**) depended on the linker substituent in 2-position (Figure 1a, b, c). Therefore the **IFPs** are tuned in their pore size. With regard to this aspect, gas sorption properties were determined.

[1] a) G. Férey, *Chem. Soc. Rev.* **2008**, 37, 191; b) D. Tanaka et al., *Chem. Mater.* **2008**, 20, 922.

[2] a) K. S. Park et al., *Proc. Nat. Acad. Sci.* **2006**, 103, 10186; b) H. Hayashi et al., *Nature Materials* **2007**, 6, 501.

[3] F. Debatin et al., *Angew. Chem. Int. Ed.* **2010**, 49, 1258.

[4] K. Behrens et al., publication in preparation.