

In Situ Synthesis of an Imidazolate-4-amide-5-imidate Ligand and Formation of a Microporous Zinc–Organic Framework with H₂- and CO₂-Storage Ability**

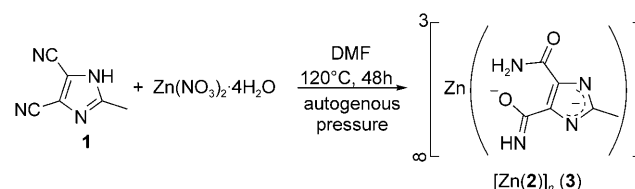
Franziska Debatin, Arne Thomas, Alexandra Kelling, Niklas Hedin, Zoltan Bacsik, Irena Senkovska, Stefan Kaskel, Matthias Junginger, Holger Müller, Uwe Schilde, Christian Jäger, Alwin Friedrich, and Hans-Jürgen Holdt*

Metal–organic frameworks (MOFs) are an emerging class of materials with various potential applications in gas adsorption and separation,^[1] catalysis,^[2] ion exchange,^[3] sensors,^[4] photo-voltaics,^[5] and drug release.^[6] Besides a distinct porosity, many of these applications demand a MOF with high chemical and thermal stability, as well as organic linkers with designated chemical or physical functionalities.^[7]

A recent advance has been the development of a class of MOFs known as zeolitic imidazole frameworks (ZIFs),^[8] in which tetrahedral coordinated metal atoms, such as zinc, are linked through N atoms by ditopic imidazolate linkers to form neutral frameworks. These compounds have high chemical and thermal stabilities. Yaghi and co-workers used functionalized imidazolate linkers for synthesizing ZIFs with varying pore diameters and surface polarities. Gas-sorption experiments with the ZIFs revealed high capacities for selective CO₂ uptake; this capacity is influenced primarily by the polar functionalities (NO₂, CN, Br, Cl).^[8b,h] Recently, ZIFs were used as microporous metal–organic frameworks (MMOFs) for the kinetic separation of propane and propene.^[8a]

Imidazolate-4,5-dicarboxylate (IDC^{3−}) is a rigid planar ligand containing, besides the two imidazolate donor N atoms, two carboxylate groups as coordination sites. IDC^{3−} is beneficial, for example, for the construction of anionic zeolite-like metal–organic frameworks (ZMOFs).^[9] IDC^{3−}, as well as its mono- and diprotonated forms HIDC^{2−} and H₂IDC[−], respectively, can coordinate multiple metal ions to form a series of MOFs with different structures and interesting topologies and properties.^[10]

In situ ligand synthesis is of growing interest as a new approach for the synthesis of coordination polymers.^[11] Herein, we present the synthesis of the first zinc–imidazolate-4-amide-5-imidate framework. The new imidazolate chelate ligand, 2-methylimidazolate-4-amide-5-imidate (**2**), was generated in situ by partial hydrolysis of 4,5-dicyano-2-methylimidazole (**1**)^[12] under solvothermal conditions in *N,N*-dimethylformamide (DMF) in the presence of Zn(NO₃)₂·4H₂O (Scheme 1). Ligands **2** link with Zn²⁺ ions and form the neutral microporous imidazolate metal–organic framework (IMOF) [Zn(**2**)]_n (**3**) with 1D hexagonal channels.



Scheme 1. Synthesis of the IMOF [Zn(**2**)]_n (**3**).

The chelate ligand **2** shows a strong structure-directing effect: the combination of amide/imidate and imidazolate groups causes a strong tendency for coordination and generates a permanent porosity in the coordination polymer **3**. The rigidity and stability of **2** also impart excellent thermal and chemical stability to the IMOF. Moreover, the imidazolate–amide–imidate linker and its hydrogen bonds polarize the walls of the microporous channels. The microporous and polarized channels have significant capacity for the capture of H₂ and CO₂.

IMOF **3** is best prepared by treating **1** with an equal amount of Zn(NO₃)₂·4H₂O at 120°C for 48 h under autogenous pressure (Scheme 1). Under these reaction conditions, the cyano groups of **1** are partially hydrolyzed to an amide and an imidate (–C(O[−])=NH) group to form the chelating linker **2**.

[*] F. Debatin, A. Kelling, M. Junginger, H. Müller, Prof. Dr. U. Schilde, Dr. A. Friedrich, Prof. Dr. H.-J. Holdt
Institut für Chemie, Anorganische Chemie, Universität Potsdam
Karl-Liebknecht-Strasse 24–25, 14476 Golm (Germany)
Fax: (+49) 331-977-5055
E-mail: holdt@chem.uni-potsdam.de

Prof. Dr. A. Thomas
Institut für Chemie, Fakultät II, Technische Universität Berlin
10623 Berlin (Germany)

Dr. N. Hedin, Dr. Z. Bacsik
Department of Physical, Inorganic and Structural Chemistry
Arrhenius Laboratory, Stockholm University
10691 Stockholm (Sweden)

Dr. I. Senkovska, Prof. Dr. S. Kaskel
Anorganische Chemie, Chemie und Lebensmittelchemie
Technische Universität Dresden, 01062 Dresden (Germany)

Prof. Dr. C. Jäger
BAM, Federal Institute for Materials Research and Testing
Division I.3, 12489 Berlin (Germany)

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The hydrolysis of **1** is conducted in situ and is directly affected by the acidity of the solution in DMF. At intermediate pH values (when the reaction is carried out with an initial pH value of 6.1), the coordination polymer **3** with the amide–imide–imidazolate ligand **2** is formed. In more acidic solutions (when HCl is added to establish an initial pH value of 3.5), 2-methylimidazole-4,5-diamide is formed.

The in situ hydrolysis of the CN groups of the reactant **1** to amide and imide moieties can be observed by IR spectroscopy. Thus, the IR spectrum of **3** shows no CN bands. Instead, the typical absorption bands for an amide are observed between 3350 and 3100 cm^{-1} and at 1664 and 1562 cm^{-1} (see Figure S1 in the Supporting Information). X-ray crystallography^[13] of **3** revealed that the compound crystallizes in the high symmetrical trigonal space group $R\bar{3}$. The asymmetric unit of **3** contains one Zn^{2+} ion and the bridging ligand **2** divided into three parts (see Figure S4 in the Supporting Information). The coordination environment of the Zn^{2+} ion and the bridging mode of **2** are shown in Figure 1. The Zn^{2+} ion is pentacoordinated by donor atoms of three ligands **2** to form a distorted environment with a trigonal-bipyramidal character (Figure 1). In this arrangement, the two imidazolate N atoms (N1 and N2) occupy the axial positions, and the imide N and O and amide O atoms reside in the equatorial positions (for selected geometric parameters, see Table S2 in the Supporting Information). Such an arrangement is a precondition for the Zn atom to be a triconnected node, as described below. The ligand **2** functions as a pentadentate linker that coordinates three Zn^{2+} ions (Figure 1).

The amide and imide groups, formed by the in situ hydrolysis of cyano groups, enable each ligand **2** to participate

in the formation of two five-membered chelate rings. One ring is formed by the coordination of a Zn^{2+} ion to the N2 (imidazolate) atom and the O1 (amide) atom. The second chelate ring is generated by the coordination of the N1 (imidazolate) atom and the N4 (imide) atom to a second Zn^{2+} ion. The negatively charged O2 (imide) atom is coordinated to a third Zn^{2+} ion. Moreover, the structure of **3** is additionally stabilized by three hydrogen bonds, one “inner ligand” between an amide NH group and an imide O atom ($\text{H3A}\cdots\text{O2}^{\text{I}}$) and “intermolecular” hydrogen bonds between an amide NH group and an amide O atom ($\text{H3B}\cdots\text{O1}^{\text{II}}$) as well as between an imide NH group and an imidazolate N atom ($\text{H4}\cdots\text{N1}^{\text{III}}$).

IMOF **3** is a rare example of MOFs in which the Zn^{2+} ion is pentacoordinated.^[10,14] In these systems, imidazolate-4,5-dicarboxylate (IDC^{3-}), its monoprotonated form (HIDC^{2-}), and other ligands are coordinated to the Zn^{2+} ion. However, IMOF **3** is the first example of an MOF in which fivefold coordination to the Zn^{2+} ion by only one ligand type is observed.

To the best of our knowledge, the coordination polymer **3** is the first example of an imide–metal complex. Imidates are usually unstable. The imide group in **3** appears, however, to be stabilized by coordination to two Zn^{2+} ions and by participation in two hydrogen bonds.

In **3**, each zinc ion is connected to three ligands, and through these ligands to six other zinc ions. The underlying net consists of two types of nodes: Zn atoms and imidazolate ligands. This net is inherently uninodal; for example, both Zn and the ligand play the same topological role. It is the three-coordinated etb net ($3/8h1$).^[15] If one considers only Zn atoms and simplifies this net by contracting the ligands, the structure can be described as the six-coordinated smg net ($6/3h16$).^[16] The topological analysis was performed with TOPOS^[17] including the Reticular Chemistry Structure Resource (RCSR) database.^[16] With the program OLEX,^[18] in which all atoms are taken into consideration, IMOF **3** was assigned the long topological vertex symbol $3.4.10.10.12.14.14_2$.

The 3D coordination polymer **3** forms 1D hexagonal channels running along the [001] direction (Figure 2). An open channel of IMOF **3** with a view of the channel wall lying in the bc plane is shown in Figure 3. The wall of the channel in **3** is essentially formed by the rigid and planar pentadentate imidazolate–amide–imide linkers **2**. The Zn^{2+} ions are located almost on the edges of the hexagonal channels. They are bridged by the linkers **2** through coordination with both N atoms of the imidazolate heterocycle. The imide and amide functional groups of the ligand **2** are embedded in the wall of the channel. The imide group bridges two zinc ions of two channel edges through its N and O atoms. The three different types of hydrogen bonds are all confined to the channel wall as well. The localization of the imide and amide groups and the hydrogen bonds in the channel walls of the IMOF **3** polarize and functionalize the coordination space of this material. Hence, guest molecules can be hydrogen bonded by potential donors and acceptors. Moreover, Lewis acids can interact with the nitrogen atom of the amide moiety. The hydrophilic character of the surface of the channel is expected to be decreased by the methyl groups of the ligands

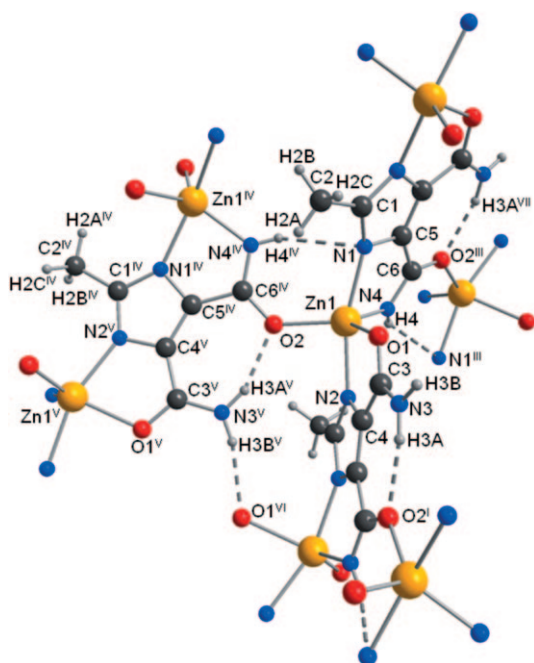


Figure 1. Portion of the crystal structure of $[\text{Zn}(\mathbf{2})]_n$ (**3**) showing the coordination environment of Zn^{II} , the bridging mode of linker **2**, and the hydrogen bonds (dotted lines). For the symmetry codes and for details of the hydrogen bonds, see the Supporting Information.

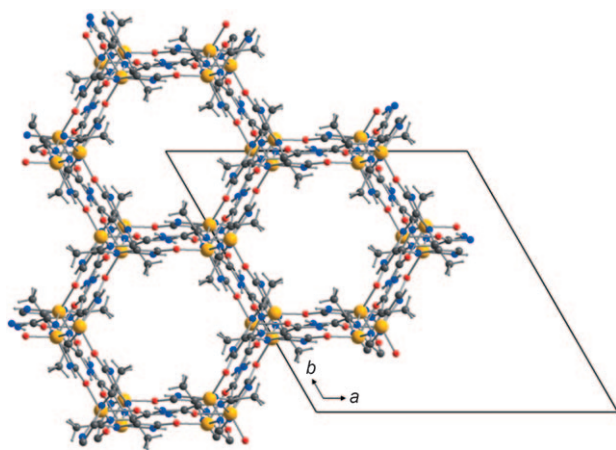


Figure 2. Hexagonal channels in **3**; view along the *c* axis (orange Zn, blue N, red O, dark gray C, light gray H).

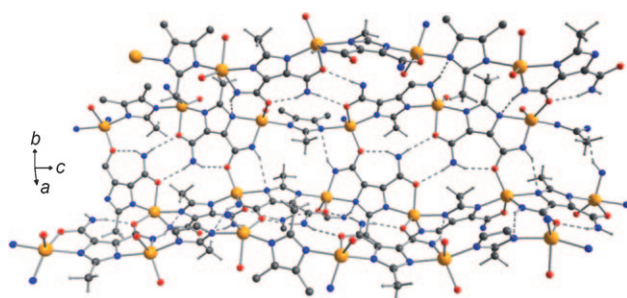


Figure 3. Open channel in IMOF **3**; view of the channel wall lying in the *bc* plane (dotted lines are hydrogen bonds).

2; these methyl groups protrude into the open channels (Figure 2). We assume that the methyl group of **2** has a structure-directing effect for the formation of the channels in the IMOF **3**.

The accessible diameter of the channel in the structure **3** was estimated to be 3.82 Å by considering van der Waals radii.^[19] Calculations with the PLATON toolkit indicated that IMOF **3** contains 41 % void space.^[20]

The channels of the as-synthesized IMOF **3** contain significant amounts of solvent molecules. The presence of water could be concluded from single crystals of **3**. Within the channels, significant residual electron density was found. The solvent-accessible void volume and the number of electrons were calculated by the program PLATON,^[20] which revealed a content of two or three H₂O molecules per formula unit (for details, see the Supporting Information). Solid-state NMR spectroscopy and thermogravimetric analysis (TGA)/differential thermal analysis (DTA)/mass spectrometry of the as-synthesized material also provided evidence for the presence of water molecules as well as some DMF.

Solid-state magic-angle-spinning (MAS) ¹³C and ¹H NMR spectra of as-synthesized and activated **3** (see Figure S2 in the Supporting Information) showed the ¹H and ¹³C MAS NMR signals of the ligand **2** coordinated in **3** by three Zn²⁺ ions. Moreover, the ¹H MAS NMR spectrum of the as-synthesized material showed a water signal at $\delta = 3.8$ ppm, and the ¹H and ¹³C MAS NMR spectra of as-synthesized **3** exhibited typical

signals for DMF. By monitoring the ¹H and ¹³C MAS NMR spectra we found that IMOF **3** is solvent-free after an activation procedure involving heating at 250 °C and 10^{−3} mbar for 2 days.

TGA/DTA/MS measurements of as-synthesized **3** indicated a loss of water and DMF up to 300 °C on the basis of a weight loss of 17–18 % (see Figure S3 in the Supporting Information). After the loss of the water and DMF molecules, no further weight loss was observed until 380 °C. X-ray powder diffraction (PXRD; see Figure S10 in the Supporting Information) demonstrated that the framework structure of the IMOF **3** is maintained upon the removal of solvent molecules and is stable up to 380 °C.

Along with its thermal stability, **3** showed remarkable chemical stability in boiling water or methanol for 7 days. The PXRD patterns recorded for **3** after such extensive treatment were unchanged (see Figures S7–S9 in the Supporting Information).

The N₂ isotherm of **3** was measured at 77 K (Figure 4). We obtained an apparent surface area (Brunauer–Emmett–Teller (BET) model) of 802 m² g^{−1} by using the data points on the adsorption branch of the N₂ isotherm in the pressure region $p/p_0 = 0.02$ –0.1 and calculated a micropore volume of 0.34 cm³ g^{−1}.

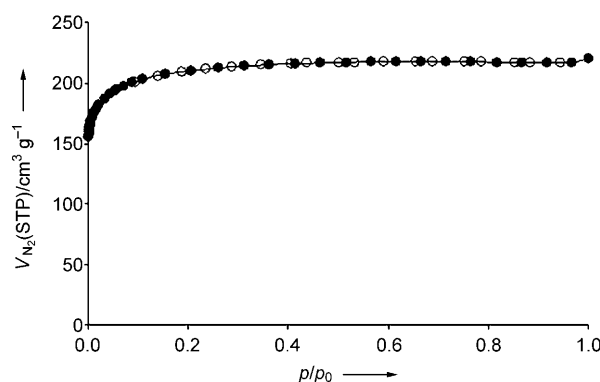


Figure 4. Nitrogen gas sorption isotherm of **3** at 77 K. STP = standard temperature and pressure.

IMOF **3** reversibly adsorbs 1.5 wt % H₂ at 77 K and 1 bar (Figure 5). This capacity is typical for MOFs, which show capacities in the range of 0.57–2.59 wt %, ^[21] however, the H₂ capacity is slightly higher than that of ZIFs (ZIF 8, 1.29 wt %, ^[8k] ZIF 11, 1.37 wt %, ^[8k] ZIF 20, 1.1 wt % ^[8i]). ZIF 8, ZIF 11, and ZIF 20 consist of cages with diameters of 11.6–15.4 Å that are interconnected by small windows (with apertures of 2.8–3.4 Å). The IMOF **3**, on the other hand, has no cages. Its pore structure consists of microporous channels only. The absence of large pores in **3** enhances the interaction potential with H₂ in comparison with that in the ZIFs. Such an enhancement of the interaction with H₂ has been observed for MOFs.^[22] We presume that the narrow channels in the IMOF cause the enhanced uptake of H₂, as compared with that of the ZIFs. In the narrow channels, the interaction potential with H₂ is enhanced because of the overlap of the potential fields of the pore walls.^[22]

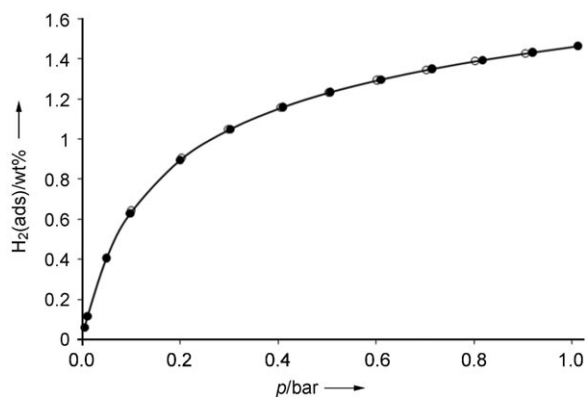


Figure 5. Hydrogen gas sorption isotherm of **3** at 77 K.

IMOF **3** captures CO₂ well. Figure 6 shows the CO₂-adsorption isotherms for **3** at 253, 298, and 343 K. The uptake of CO₂ by **3** at 298 K and 1 bar is about 48 cm³ g⁻¹. A similar high uptake was recently found by Yaghi and co-workers for ZIF 78 and ZIF 82, which were synthesized by using imidazoles containing the functional groups NO₂ and CN.^[8b] We

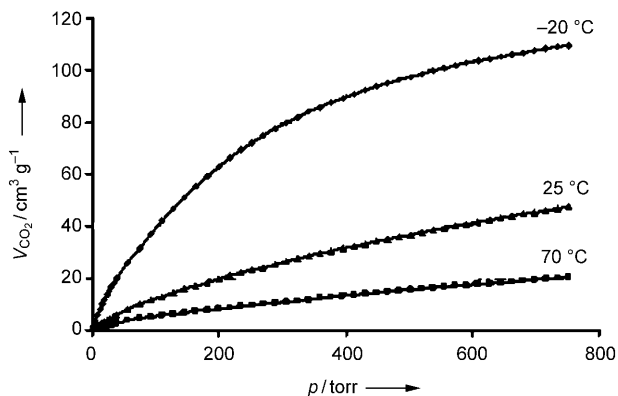


Figure 6. Adsorption isotherms of **3** for carbon dioxide gas at 253, 298, and 343 K.

assume that the high CO₂ uptake of **3** is a result of physisorption. Strong interactions are expected between the polar functional groups (amide and imidate) in IMOF **3** and CO₂, which has a significant quadrupole moment.

In summary, we developed an in situ method for the synthesis of a new imidazolate-4-amide-5-imidate linker generated by the partial hydrolysis of a 4,5-dicyanoimidazole and synthesized the first zinc-organic framework based on an imidazolate-amide-imidate. The resulting IMOF has narrow channels with polar walls. These structural and functional features are responsible for its high capacity for the uptake of H₂ and CO₂. Within microporous materials, the kinetic diameters for carbon monoxide (CO) and methane (CH₄) are 3.76 and 3.80 Å, respectively.^[23] The estimated channel diameter of 3.82 Å suggests that the channels of **3** may be too narrow to enable the (rapid) loading of CO and CH₄. Hence, **3** could potentially be used as a molecular sieve (or a kinetically selective adsorbent) for the separation of H₂/CO, CO₂/CH₄,

and CO₂/CO, which are commercially relevant mixtures. We intend to study these potential applications further.

Experimental Section

4,5-Dicyano-2-methylimidazole (100 mg, 0.76 mmol) and zinc(II) nitrate tetrahydrate (198 mg, 0.76 mmol) were dissolved in DMF (6 mL) in a sealed tube (Ace, type A). The sealed tube was closed, and the mixture was heated at 120 °C for 48 h and then cooled to room temperature. [Zn(**2**)]₂ (**3**; 132 mg, 75 % based on Zn(NO₃)₂·4H₂O) was obtained by filtration as fine pale-yellow crystals and dried in air. It was activated by drying at 250 °C and 10⁻³ mbar. M.p. > 380 °C; elemental analysis: calcd (%) for C₆H₆N₄O₂Zn: C 31.12, H 2.61, N 24.2, Zn 28.24; found: C 30.80, H 2.74, N 23.81, Zn 27.76; IR (KBr pellet): $\tilde{\nu}$ = 3342 (m), 3129 (m), 1664 (s), 1562 (vs), 1462 (m), 1439 (m), 1266 (m), 1115 (m), 813 cm⁻¹ (m).

Full experimental details are presented in the Supporting Information.

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- [13] Crystal data for [Zn(2)]·3H₂O (**3**): C₆H₁₂N₄O₅Zn, *M_r* = 285.57 g mol⁻¹, crystal dimensions: 0.18 × 0.14 × 0.09 mm³, trigonal, space group *R*3̄, *a* = *b* = 17.9244(14), *c* = 18.4454(16) Å, *V* = 5132.2(7) Å³, *Z* = 18, *ρ*_{calcd} = 1.663 g cm⁻³; *μ*(MoKα) = 2.17 mm⁻¹ (*λ* = 0.71073 Å), *T* = 210 K; 2 θ _{max} = 49.98°, 11 122 reflections measured, 2017 unique (*R*_{int} = 0.0594), *R* = 0.0314, *wR* = 0.0825 (*I* > 2 σ (*I*)). For details of data collection and structure solution and refinement, see the Supporting Information. CCDC 732233 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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