This article can be cited before page numbers have been issued, to do this please use: A. Schneemann, R. Rudolf, S. Henke, Y. Takahashi, H. Banh, I. Hante, C. Schneider, S. Noro and R. A. A. Fischer, *Dalton Trans.*, 2017, DOI: 10.1039/C7DT01195D.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [author guidelines](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the ethical guidelines, outlined in our [author and reviewer resource centre](#), still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Linker Functionalisation Triggers an Alternative 3D-Topology for Zn-Isophthalate-4,4′-Bipyridine Frameworks

Andreas Schneemann,a,b Robin Rudolf,c Sebastian Henke,c Yukiko Takahashi,d Hung Banh,a,b Inke Hante,a Christian Schneider,a Shin-ichiro Noro,a and Roland A. Fischer*a

A series of four Zn2+ metal-organic frameworks containing functionalised isophthalate linkers and 4,4′-bipyridine pillars has been prepared and characterised. The isophthalates which contain −O(=C)(CH2)nO− (with n = 1, 2 or 3) form frameworks with a 3D pillared-layer topology instead of the typical 2D layer topology of the renowned coordination polymers with an interdigitated structure (CIDs), which is found for shorter −O(=C)(CH2)3 side chains. The gas adsorption properties of the materials were analysed using N2, CO2 and O2 adsorption measurements at low temperatures.

Introduction

Metal-organic frameworks (MOFs) are porous materials, which are constructed from a metal-containing building block connected by organic linkers.1–3 These materials show many outstanding properties, e.g. ultrahigh surface areas,4–5 unprecedented capabilities for designing pore space in a molecular fashion6–10 and previously unseen structural responsivity.11–14 The properties can be influenced by different approaches, e.g. by the judicious choice of material composition1 or morphology.15 Furthermore, controlling the framework topology is a crucial aspect during the preparation of MOFs, since the topology significantly influences the material properties. An interesting example would be the structural isomers MIL-88B15 and MIL-101.16 Both frameworks are built from the same metal-clusters and organic linkers, however, they differ in the connectivity of these building blocks, which leads to strikingly contrasting materials properties. MIL-88B shows a massive swelling/shrinking of the cell volume depending on the presence of guest molecules. Contrary, MIL-101 is a very rigid and highly stable framework that features open metal-sites suitable for catalytic reactions under harsh conditions.17 There are different methods to influence the formation of a certain framework topology. The most straight forward and obvious is the change of reaction conditions. For example, by using a suitable solvent mixture, it is possible to crystallize the Zn2(bdc)2(dabco) (bdc = 1,4-benzenedicarboxylate; dabco = diazabicyclo[2.2.2]octane) framework in a kagome lattice pillared-layered structure22 instead of the commonly observed square-grid structure.23 Linker functionalisation can also be a tool to control the formation of certain topologies. It has been shown that employing fu-bdc (2,5-functionalized-1,4-benzenedicarboxylate) linkers leads to the formation of a new honeycomb-like topology,24,25 contrary to the non-functionalized analogue Zn2(bdc)2(bpy) (bpy = 4,4′-bipyridine) which features an interpenetrated square-grid pillared-layered structure.26

Within this work we want to present new frameworks of the type Zn(fu-ip)(bpy) (fu-ip = 5-functionalized-isophthalate). Frameworks of the composition Zn(ip)(bpy) have been reported by Kitagawa and coworkers and coined coordination polymers with an interdigitated structure (CIDs).27,28 In these frameworks, Zn(ip) 1D chains are interconnected by bpy, forming a 2D sheet with protrusions. The sheets are arranged in an interdigitated fashion to form a 3D structure of layered sheets. Similar compounds have also been reported with other angular linkers (e.g. containing functional groups),29–32 elongated pillars33 and with other metals (i.e. Mn, Fe...).34–35 In our approach, we prepared four functionalised linker molecules, namely 5-ethoxyisophthalic acid (H2E-ip), 5-propoxyisophthalic acid (H2P- ip), 5-allyloxyisophthalic acid (H2A- ip) and 5-propynoxyisophthalic acid (H2PPy- ip) which only differ in the chain length and degree of saturation of the side chain (Figure 1). These four linker molecules were used to prepare the frameworks Zn[E- ip](bpy) (1), Zn[P- ip](bpy) (2), Zn[A- ip](bpy) (3) and...
Experimental

Linker Synthesis

Dimethyl-5-hydroxyisophthalate

In a 500 mL round-bottom flask 5-hydroxyisophthalic acid (18 g, 87 mmol) and 20 mL BF₃Et₂O were dissolved in 400 mL methanol and refluxed overnight. The solvent was evaporated and the remainder was washed several times with cold water to remove BF₃ residues. The obtained yellow solid was dried in vacuo at 60 °C overnight. Yield: 78% (14.2 g, 67.6 mmol).

Functionalized Isophthalate Linkers

In a schlenk flask dimethyl-5-hydroxyisophthalate (2 g, 9.5 mmol) and 3 eq K₂CO₃ (3.9 g, 28.5 mmol) were suspended in 60 mL of DMF. Under vigorous stirring, 3 eq of a bromohydrocarbon (see Table S1 and Table S2; ESI) were added dropwise via a syringe. The mixture was heated to 85 °C overnight and afterwards the DMF was removed in vacuo. The remainder was suspended in NaOHₐq (800 mg in 80 mL of deionized water) and refluxed for 4 h. After cooling to room temperature, the mixture was acidified with aqueous HCl and the white precipitate was filtered off and dried in vacuo. For yields and NMR data see Table S2 and Section S3 in the ESI.

MOF Synthesis

A 25 mL screw cap bottle was filled with Zn(NO₃)₂·6H₂O (300 mg, 1.01 mmol) and fu-isophthalic acid linker (H₂E-ip 2.38 mg; H₂P-ip 252 mg; H₂A-ip 250 mg; H₂PY-ip 248 mg; each 1 mmol). The reagents were dissolved in 20 mL DMF via sonication at RT. The solutions were carefully overlaid with 2 mL of a 0.08 mg/mL bipy/MeOH·stock solution and heated to 70 °C for 48 hours. After cooling to room temperature, the DMF was decanted and replaced by 20 mL fresh DMF and subsequently replaced by 20 mL CHCl₃ three times. Afterwards the MOFs were filtered, washed three times with approximately 10 mL of CHCl₃ and dried in vacuo. Until further manipulation the samples were stored in a glovebox filled with Argon.

Analytical Methods

Liquid phase NMR spectra were recorded on a Bruker Advance DPX 200 spectrometer (ɪH, 200 MHz) or a Bruker Advanced DPX 250 spectrometer (ɪH, 250 MHz) at 293 K. ɪH NMR spectra of the synthesised linker molecules were recorded in DMSO-d₆ and the spectra of digested MOFs were recorded in 0.5 mL DMSO-d₆ and 0.05 mL of DCI/D₂O (20%). Chemical shifts are given relative to TMS and were referenced to the solvent signals as internal standards. Infrared spectra were recorded on a Bruker Alpha-P FT-IR situated in a glovebox. For all measurements, the ATR-Mode of the spectrometer was used and measurements were performed with 48 scans. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409 PC/PG apparatus. A heating rate of 5 K/min was applied and the samples were placed in a pre-weighted, clean aluminium oxide crucible. All measurements were performed in a stream of N₂ gas with a constant flowrate of 20 mL/min. Powder X-ray diffraction (PXRD) measurements were performed on a PanAlytical X’Pert Pro with Cu Kα Radiation in Bragg-Brentano geometry with an automatic divergence slit and a position sensitive detector while using a continuous scan mode in the range of 20 = 5° – 50°. The samples were measured on zero-background silicon substrates cut along the [510] plane. For measurements of the as-synthesized samples, the MOF powders were taken directly from the synthesis solution and measured while still slightly wet from the solvent. For measurements of the dried samples, the substrate was covered with a thin film of grease and the dried samples were distributed on the grease. The obtained PXRD patterns were fitted by the Pawley Method using TOPAS academic 4.5. Gas adsorption measurements conducted for the samples 2, 3 and 4 were performed at the Research Institute for Electronical Sciences at Hokkaido University in Sapporo, Japan, using a Belsorp Max adsorption instrument. The samples were filled under ambient conditions into pre-weighted sample tubes. Prior to measurements the samples were evacuated and heated to 120 °C on a Belprep sample preparation station, for the first measurement overnight and for every subsequent measurement for at least three hours. Single crystal X-ray diffraction (SCXRD) data were collected on an Agilent Technologies SuperNova diffractometer equipped with an Atlas CCD and multilayer X-ray optics using Cu Kα. The crystals were coated with a perfluoropolyether and picked up with a glass fiber. After mounting, the crystals were slowly cooled from room temperature to the measurement temperature. The obtained data was processed with CrysAlisPro and absorption corrections based on multiple-scanned reflections were carried out with ABSPACK in CrysAlisPro. The crystal structures were solved by direct methods using SHELXS and SUPERFLIP using the OLEX2 interface. After refinement with SHELXL, the residual electron density of disordered solvent molecules present in the framework voids was subtracted from the data using the “Solvent Mask” routine of OLEX2.

Results and Discussion

Compounds 1-3 yielded crystals suitable for SCXRD measurements (CCDC 1540824-1540826), while the structure of compound 4 could not be solved satisfactorily because of severe twinning of the crystals. However, PXRD clearly demonstrates that 4 is isoreticular to compounds 2 and 3 (see Figure S5, ESI). Interestingly, compounds 2-4 crystallise with a different framework topology than compound 1, which features the renown two-dimensional CID structure. In Figure 2a the comparison of the secondary inorganic building units of both...
Our findings indicate that the influence of reaction time and temperature on the crystallography and interconversion of polymorphous, but differently dense, phases of related pillared-layered MOFs. In fact on one occasion, for Zn(P-iip)(bipy), single crystals exhibiting the CID structure were obtained, however, this result was not reproducible and seems to be a serendipitous result (see ESI for details). Interestingly, the crystal structure of the Zn(P-iip)(bipy) framework in the CID structure reveals a crystallographic density of 1.233 g/cm³ which is substantially higher than the density of the corresponding pillared-layered phase (0.984 g/cm³), the densities represent skeletal densities, neglecting any guest molecule in the pores. It is sensible that the more dense CID phase should preferentially form because of thermodynamic reasons, however, this does not seem to be the case here. We strongly assume that by tuning the synthesis conditions, both phases, the pillared-layered as well as the CID phase, are accessible. In fact, it is likely that the linkers featuring small (or even no) side groups on the isophthalate backbone, previously reported by Kitagawa et al., also can form a pillared-layered network instead of the CID structure.

In order to assess the porosity of compounds 2-4, the synthesis solvent guests were removed by solvent exchange followed by evacuation at elevated temperatures. Complete solvent removal was verified by ¹H NMR spectroscopy and TGA (ESI). Phase purity and structural integrity after activation was confirmed using powder X-ray diffraction (PXRD) of grinded powders of the samples (ESI).

The pore apertures in materials 2-4 are very small and each channel is gated by neighbouring -OC₆H₄ip- chains. In previous studies we were already able to show the striking effect that pendant side chains have on the gas adsorption properties of flexible as well as rigid MOFs. Thus, low temperature adsorption isotherms were performed on compounds 2-4 for N₂, O₂ (all at 77 K) and CO₂.

Figure 2: Depiction of the arrangement of the linkers around the inorganic building unit based on an eight membered ring composed of Zn₆(CO₃)₄ for compound 1 (a) and compounds 2-4 (b). Carbon atoms are depicted in grey, oxygen in red and zinc in dark green. The functional unit attached to the isophthalates is depicted by purple spheres. Bipy pillars and hydrogen atoms are omitted for clarity.

Figure 3: Illustration of the crystal structures of materials 1-4. Representation of two adjacent 1D chains formed in compound 1 (a) and the 2D sheets formed in compounds 2-4 (b). Depiction of the interdigitated layers in compound 1, viewed along the a-axis (c) and the pillared layers in compounds 2-4 viewed along the b axis (d). Carbon atoms are represented in grey, oxygen in red, nitrogen in blue and zinc in dark green. The functionalised side chains are represented by purple spheres. Hydrogen atoms are omitted for the sake of clarity.
Figure 4: Gas adsorption and desorption isotherms for materials 2, 3 and 4 are depicted as black squares, blue diamonds and green triangles respectively. CO\textsubscript{2} sorption isotherms (a) were measured at 195 K, N\textsubscript{2} (a) and O\textsubscript{2} (b) at 77 K. P\textsubscript{0} for O\textsubscript{2} is 16.69 kPa at 77 K. The lines indicate a guide to the eye only.

(at 195 K) (Figure 4). All three materials have a negligible uptake of N\textsubscript{2}, while the CO\textsubscript{2} uptake varies with the utilised side chain pinned to the ip-linker. Material 2 contains a completely saturated propoxy side chain and has the smallest CO\textsubscript{2} uptake at p/p\textsubscript{0} = 1 and 195 K (~26 cm\textsuperscript{3}/g). 3 containing additional unsaturated sites on the appendant side chain takes up considerably larger amounts of CO\textsubscript{2} (~43 cm\textsuperscript{3}/g). The highest CO\textsubscript{2} uptake can be found for 4, which has triple bonds present in the side chain (~81 cm\textsuperscript{3}/g). The amount of CO\textsubscript{2} adsorbed at p/p\textsubscript{0} = 1 depends (nearly linearly) on the degree of saturation of the side chain, whereby the lower the degree of saturation of the side chain, the higher the overall CO\textsubscript{2} uptake. In a previous report on the adsorption of vapours in similarly functionalised copper frameworks,\textsuperscript{35} the flexibility of the side chains (i.e. their probability of occupying different positions due to their rotational degrees of freedom) caused the differences in uptake and the fully saturated framework showed the highest guest adsorption. In contrast, within our study, the framework with the most rigid functionality, namely 4, shows the highest uptake. This leads to the conclusion that the CO\textsubscript{2} adsorption increases with higher dispersive interactions of the unsaturated side chains with the guest molecules. Note that the slight hysteresis in the adsorption isotherm of 4 is due to a kinetically hindered desorption process. The exact opposite trend can be found for the oxygen adsorption. The highest uptake can be found for material 2 containing propoxy chains. The materials containing double and triple bonds on the linker side chains have considerably lower uptakes. This result is not surprising as saturated hydrocarbons also tend to dissolve oxygen better than unsaturated hydrocarbons.\textsuperscript{45} However, it should also be noted that the overall adsorbed amount of oxygen is quite low in all three cases.

Conclusions

We were able to prepare a 3D pillared-layered topology for MOFs of the type Zn(fu-(ip)(bipy) by linker functionalisation. We rationalise the formation of the 3D frameworks instead of the typical 2D layer structure on the basis of the pore space available to host DMF solvent molecules during synthesis. The novel materials feature very narrow 2D-connected channels, which are partially populated by alkoxy side chains. The degree of saturation of these side chains has a profound impact on the sorption properties of these materials. Future studies, which are currently under development, will feature the analysis of these materials towards the adsorption of hydrocarbons and the effect of new side chains on the formed framework topology and adsorption properties.

Acknowledgement

A. S. gratefully acknowledges the Ruhr University Research School PLUS for a travel grant to conduct experiments at the Research Center for Electronic Sciences at Hokkaido University, Japan. Ruhr University Research School PLUS is funded by Germany’s Excellence Initiative [DFG-GSC 98/3]. This work is supported by the Cluster of Excellence RESOLV (EXC 1069, https://ruhr-uni-bochum.de/solvation) funded by the Deutsche Forschungsgemeinschaft (DFG). The authors gratefully acknowledge Dr. Stephen R. Hughes (DST Innovations, Bridgend, United Kingdom) for proof reading the manuscript.

Notes and references
