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# The structure of a coordination polymer constructed of manganese(II) biphenyl-4,4'-dicarboxylate

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**Abstract:** Manganese(II) biphenyl-4,4'-dicarboxylate, prepared by crystallization of a mixture of biphenyl-4,4'-dicarboxylic acid, manganese(II) chloride, and di(4-pyridyl) acetylene as base in a mixture of dimethylformamide, ethanol and water in a closed vessel at elevated temperatures forms a 3D network of  $\{[\text{Mn}(\text{bpdc})(\text{H}_2\text{O})_2][\text{Mn}(\text{bpdc})(\text{H}_2\text{O})]\}$  containing one five-fold coordinated and one six-fold coordinated Mn metal center (X-ray structure determination). Scanning tunneling microscopic (STM) measurements of manganese biphenyl-4,4'-dicarboxylate adsorbed on highly oriented pyrolytic graphite showed strands, the averaged diameter of which amounts to  $18 \pm 1$  nm, whereas the apparent height is about  $0.5 \pm 0.02$  nm.

**Keywords:** di(4-pyridyl)acetylene; manganese biphenyl-4,4'-dicarboxylate; MOF; STM; X-ray diffraction analysis.

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## 1 Introduction

Metal-organic frameworks (MOFs) are one-, two-, or three dimensional micro-, meso-, or macro-porous coordination polymers which are constructed of metal cations as connectors and organic ligands as linker molecules [1–3]. They possess high surface areas ( $>3000$  m<sup>2</sup> g<sup>-1</sup>) and pores, the sizes of which cover the range from less than 20 Å to larger than 500 Å. Due to the broad applicability of metal-organic frameworks the interest in the development and design of new architectures is very high, and – as a consequence – numerous books and review articles have been published in the last decade. As examples, metal-organic frameworks are applied as hybrid materials for the purification of small gaseous molecules [4], as heterogeneous catalysts [5–7], in photonics [8], and for the design of new materials [9]. They have also been applied as separation membranes [10], for water adsorption [11], in device fabrications [12], in artificial photosynthesis and photocatalysis [13], and methane [14] as well as hydrogen storage [15–18].

Biphenyl-4,4'-dicarboxylate (bpdc) is a well suited organic linker of coordination polymers as well as metal-organic frameworks. Thus it has been applied very recently for the construction of a quaternary Zn<sub>4</sub>O-carboxylate metal-organic framework for carbon dioxide and methane sorption [19], for the preparation of aluminum based coordination polymers possessing polysilane chains with hole-transporting abilities [20], and as building block of the robust Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(bpdc)<sub>6</sub> framework for the incorporation of a photosensitizer and proton reduction catalyst [21]. It was used to prepare the new flexible vanadium-containing metal-organic framework COMOC-2 for adsorption of light hydrocarbons [22] as well as new Ni, Co, and Cu-based coordination polymers for the adsorption of carbon dioxide, methanol, and water [23]. The Li salt of biphenyl-4,4'-dicarboxylate, Li<sub>2</sub>(bpdc), was described as ultra-light metal-organic framework (ULMOF) which consists of alternating antiferrotype type LiO layers connected by bpdc bridging units forming a 3D network [24]. The Zn

and Cd coordination polymers  $\{[\text{Zn}(\text{bpdc})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$  and  $[\text{Cd}(\text{bpdc})(\text{H}_2\text{O})]_n$  have also been described [25].

In continuation of our interest in metal-organic frameworks [26, 27], adsorption of organic substrates on metal surfaces [28], catalysis [29], and heterocycle synthesis from carbenes and polycations [30–32] we report here on the structure of the Mn salt of biphenyl-4,4'-dicarboxylate.

## 2 Results and discussion

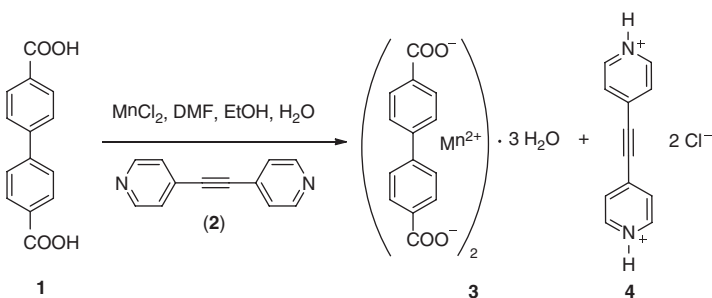
The manganese salt of biphenyl-4,4'-dicarboxylate **3** was obtained by slow crystallization of a mixture of biphenyl-4,4'-dicarboxylic acid **1**, di(4-pyridyl)acetylene **2**, and manganese(II) chloride in a mixture of dimethylformamide, ethanol and water in a closed vessel which was heated at 110 °C for three days (Scheme 1). After cooling to room temperature the product **3** was formed as complex  $\{[\text{Mn}(\text{bpdc})(\text{H}_2\text{O})_2][\text{Mn}(\text{bpdc})(\text{H}_2\text{O})]\}$  which crystallized as long yellow needles. Di(4-pyridyl)acetylene **2** played the role of a base under these conditions and remained in solution as salt **4**. It has been found earlier that the coordination polymer consisting of cobalt(II) biphenyl-4,4'-dicarboxylate did neither react with pure water nor with pure pyridine, but it dissolved in pyridine-water mixtures and formed one-dimensional chains of  $^1\infty[\text{Co}(\text{bpdc})(\text{py})_2(\text{H}_2\text{O})_3] \cdot 2 \text{py}$  or 2D networks of  $^2\infty[\text{Co}(\text{bpdc})(\text{py})_2] \cdot \text{H}_2\text{O}$  [33]. In our case no crystallization or MOF formation under participation of the bipyridine present was observed. A thermogravimetric analysis of **3** under a nitrogen atmosphere showed the loss of three molecules of water (−8.66%) between 150 °C and 190 °C. At approximately 400 °C decomposition of the material begins.

The results of a single crystal X-ray analysis are given in Table 1 and are shown in Figs. 1, 2, and 3. Selected bond lengths and bond angles are presented in Table 2. The obtained species crystallized in the monoclinic space group  $C2/c$  with  $Z = 4$ .

**Table 1:** Crystal structure data for **3**.

<b>3</b>	
Formula	$\text{C}_{28}\text{H}_{22}\text{Mn}_2\text{O}_{11}$ $[\text{Mn}_2(\text{C}_{14}\text{H}_8\text{O}_4)_2(\text{H}_2\text{O})_3]$
$M_r$	644.34
Cryst. size, mm <sup>3</sup>	$0.36 \times 0.06 \times 0.06$
Crystal system	monoclinic
Space group	$C2/c$
$a$ , Å	53.097(8)
$b$ , Å	6.495(1)
$c$ , Å	7.352(1)
$\beta$ , deg	90.01(2)
$V$ , Å <sup>3</sup>	2535.4(6)
$Z$	4
$D_{\text{calcd}}$ , g cm <sup>−3</sup>	1688
$\mu(\text{MoK}\alpha)$ , mm <sup>−1</sup>	1.062
$F(000)$ , e	1312
$hkl$ range	$\pm 68, \pm 8, \pm 9$
$2\theta_{\text{max}}$ , deg	55
Refl. total/unique/ $R_{\text{int}}$	20836/2911/0.059
Param. refined/restraints	198/5
$R1$ (for 2755 with $I > 2\sigma(I)$ )	0.026
$wR2$ (all reflexions)	0.061
GoF ( $F^2$ )	1.10
$\Delta\rho_{\text{fin}}$ (max/min), e Å <sup>−3</sup>	0.32/−0.41

The crystal structure of **3** is a 3D network containing Mn atoms in two different symmetry environments. The manganese atom Mn1 (occupation 0.5) is located in a  $2(C_2)$  symmetric environment with 5-fold coordination. Four bonds are formed to carboxylate groups ( $2 \times \text{O1}$ ,  $2 \times \text{O2}$ ) and one bond is formed to a water molecule (O3). Mn1 and the oxygen atom of the water molecule (O3) reside on the crystallographic twofold axis. The Mn2 atom (occupation 0.5) is located in a crystallographic  $\bar{1}(C_i)$  symmetric environment and is six-fold coordinated. Here, four carboxylate groups ( $2 \times \text{O4}$ ,  $2 \times \text{O5}$ ) and two water molecules ( $2 \times \text{O6}$ ) form an octahedron. Each Mn cation is bonded to the four biphenyl-4,4'-dicarboxylate anions via



**Scheme 1:** Manganese salt formation from biphenyl-4,4'-dicarboxylate **1** and manganese(II) chloride in the presence of di(4-pyridyl)acetylene **2** as base.

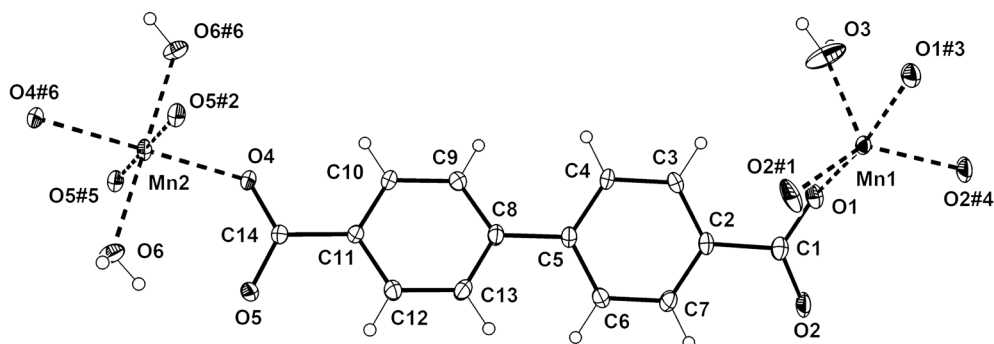


Fig. 1: Biphenyl-4,4'-dicarboxylate, manganese(II) and coordinated water molecules in the crystal structure of **3** (displacement parameters are drawn at the 50 % probability level, H atoms as spheres with arbitrary radii; crystallographic numbering; for symmetry operations used see footnote at Table 2).

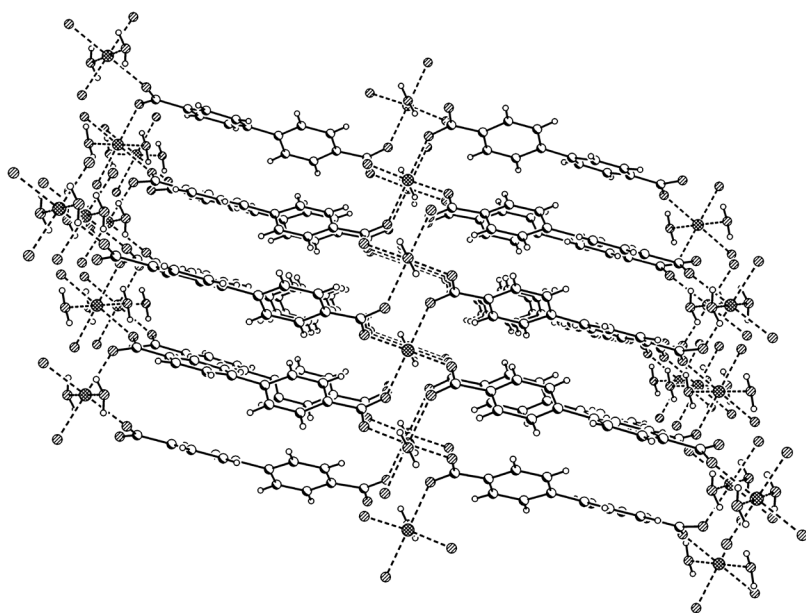


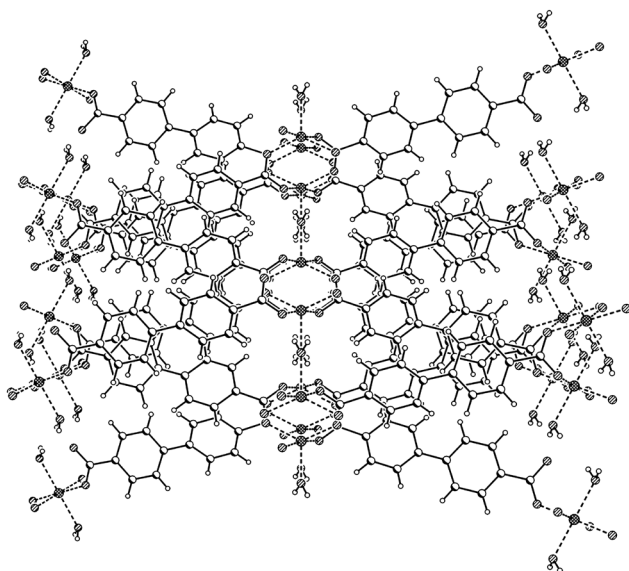
Fig. 2: Crystal structure of **3** as projected down the crystallographic *b* axis.

monodentate carboxylic oxygen and the aforementioned molecules of water. The C–O bond lengths of the carboxylate groups of bpdc are slightly different. Thus, the distance C1–O1 was determined to be 1.269(2) Å, whereas the bond length C1–O2 amounts to 1.251(3) Å. The corresponding bond lengths of O1 and O2 to manganese cations are 2.1558(16) Å and 2.0653(14) Å. The C–O bond lengths of the second carboxylate group were found to be 1.248(2) and 1.278(2) Å. Their bond lengths to manganese cations are 2.1795(14) and 2.1642(15) Å. The bond lengths of the manganese cations to oxygen atoms of the water molecules are 2.100(2) Å and 2.1761(14) Å. The two phenyl rings of the biphenyl-4,4'-dicarboxylate of the asymmetric unit are slightly tilted against each other as is exemplified by the

dihedral (torsion) angle C4–C5–C8–C9 = 28.9(3)°. One of the carboxylate planes is virtually in plane with the phenyl ring to which it is attached as is evident from the dihedral angle C3–C2–C1–O1 = 0.3(3)°. The second carboxylate group is slightly more tilted with respect to the other phenyl ring (dihedral angle C10–C11–C14–O4 = –13.8(3)°). For further dihedral angles see Table 2.

## 2.1 STM Results

To get real space images of the new compound, scanning tunneling microscopy (STM) measurements of thin films of **3** adsorbed on highly oriented pyrolytic graphite (HOPG)



**Fig. 3:** Crystal structure of **3** in projection down the crystallographic *c* axis.

**Table 2:** Selected bond lengths (Å), angles (deg), and dihedral angles (deg) for **3** with estimated standard deviations in parentheses<sup>a</sup>.

Distances	
Mn1–O1	2.1558(16)
Mn1–O2#1	2.0653(14)
Mn1–O3	2.100(3)
Mn2–O4	2.1795(14)
Mn2–O5#2	2.1642(15)
Mn2–O6	2.1761(14)
Angles	
O1–Mn1–O3	85.94(4)
O1–Mn1–O1#3	171.88(8)
O2#1–Mn2–O2#4	131.38(10)
O4–Mn2–O5#2	94.01(5)
O4–Mn2–O5#5	85.99(5)
O4–Mn2–O6	95.70(5)
O4–Mn2–O6#6	84.30(5)
Dihedral Angles	
C4–C5–C8–C9	28.9(3)
C6–C5–C8–C13	30.4(3)
O1–C1–C2–C3	0.3(3)
O2–C1–C2–C7	3.2(3)
O4–C14–C11–C10	–13.8(3)
O5–C14–C11–C12	–13.5(3)

<sup>a</sup>Symmetry transformations used to generate equivalent atoms: #1  $x, -y+2, z+1/2$ ; #2  $x, -y+1, z+1/2$ ; #3  $-x, y, -z+1/2$ ; #4  $-x, -y+2, -z$ ; #5  $-x+1/2, y-1/2, -z+1/2$ ; #6  $-x+1/2, -y+1/2, -z+1$ .

were performed. For thin film preparation highly diluted solutions ( $2 \times 10^{-9}$  mol L<sup>-1</sup>, methanol) of manganese(II) chloride and the ligand were mixed and subsequently

dropped onto the HOPG substrate which was used due to its inertness and its flat surface geometry. STM was carried out after the methanol was evaporated. Fig. 4 shows two STM images recorded at room temperature of **3** prepared on the HOPG surface. It becomes apparent that **3** forms molecular strands under these conditions. According to the measured line profile seen in Fig. 5, the averaged diameter of the strand amounts to  $18 \pm 1$  nm. The apparent height is about  $0.5 \pm 0.02$  nm. Considering the dimensions of the unit cell of **3** as measured by X-ray crystallography, the STM images suggest that the strands are built up by several agglomerated unit cells.

### 3 Experimental section

Chemicals used were obtained from commercial suppliers and used without further purification. Solvents were distilled before use.

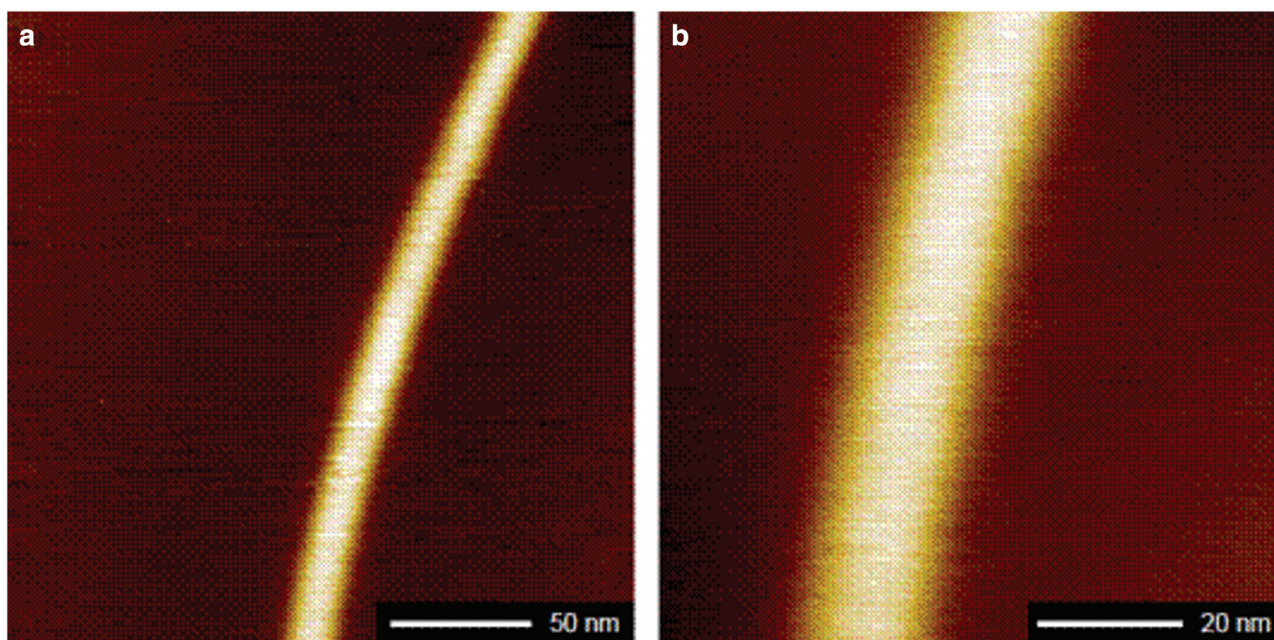
#### 3.1 Manganese biphenyl-4,4'-dicarboxylate

Manganese(II) chloride (0.075 mmol, 10 mg), dipyrildiacetylene (0.075 mmol, 14 mg) and biphenyl-4,4'-dicarboxylic acid (0.075 mmol, 18 mg) were suspended in a mixture of dimethylformamide (8 mL), water (1 mL) and ethanol (1 mL) in a glass autoclave. The closed vessel was then heated at 110 °C over a period of 3 days. Then, the mixture was allowed to cool to rt in a rate of 5 °C h<sup>-1</sup>, whereupon long needles formed which were filtered off and subjected to single crystal X-ray diffraction.

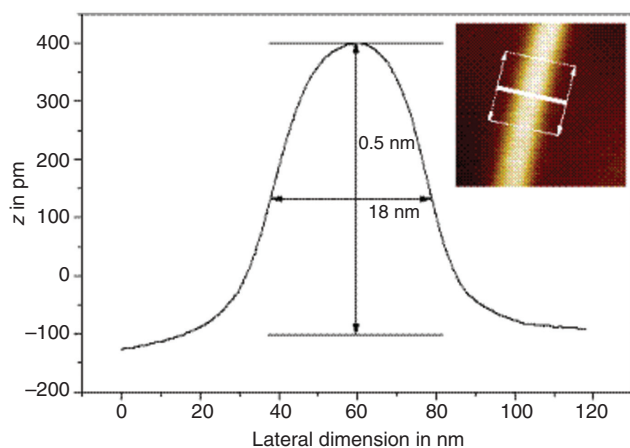
#### 3.2 Crystal structure determination of **3**

Data were collected on a Bruker–Nonius Kappa-CCD diffractometer using graphite-monochromatized MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) at  $T = -100$  °C. The structure was solved by Direct Methods and refined by full-matrix least-squares on  $F^2$  [34]. A semi-empirical absorption correction was applied. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located from  $\Delta F$  maps and refined at idealized positions using a riding model; water hydrogen positions were refined freely). The crystal is a pseudo-merohedral twin with two domains (twin law 1 0 0, 0  $\bar{1}$  0, 0 0  $\bar{1}$  BASF 0.319(1)).

CCDC 1410114 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



**Fig. 4:** STM images of coordination polymer **3** prepared on HOPG surfaces. The images show a molecular strand adsorbed on the HOPG surface. (a)  $217 \times 217 \text{ nm}^2$ ,  $I_t = 0.8 \text{ nA}$ ,  $U_t = 0.5 \text{ V}$ . (b)  $87 \times 87 \text{ nm}^2$ ,  $I_t = 8 \text{ nA}$ ,  $U_t = 0.5 \text{ V}$ .



**Fig. 5:** Averaged line profile of the molecular strand seen in Fig. 4 (see also inset). The averaged diameter amounts to  $18 \pm 1 \text{ nm}$ . The height of the strand is about  $0.5 \pm 0.02 \text{ nm}$ .

### 3.3 Scanning tunneling microscopy

The STM measurements were performed in an Ultra High Vacuum apparatus (OMICRON Multiprobe System) with a base pressure of  $5 \times 10^{-11}$  mbar using a variable temperature STM/AFM (VT-STM/AFM, Omicron). All STM images were recorded in constant current mode with an etched PtIr tip. The HOPG crystal was cleaned *ex-situ* using adhesive tape.

### References

- [1] O. M. Yaghi, H. L. Li, *J. Am. Chem. Soc.* **1995**, *117*, 10401.
- [2] H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276.
- [3] J. L. C. Rowsell, O. M. Yaghi, *Micropor. Mesopor. Mater.* **2004**, *73*, 3.
- [4] B. Seyyedi, S. Bordiga, *Metal-Organic Frameworks: A New Class of Crystalline Porous Materials. Hybrid Materials for Storage and Purification of Small Gaseous Molecules*, Lambert Academic Publishing, Saarbrücken, **2014**.
- [5] F. L. i. Xamena, J. Gascon, *Metal Organic Frameworks as Heterogeneous Catalysts*, Royal Society of Chemistry, Cambridge, **2013**.
- [6] X.-W. Dong, T. Liu, Y.-Z. Hu, X.-Y. Liu, C.-M. Che, *Chem. Commun.* **2013**, *49*, 7681.
- [7] M. I. Gonzalez, E. D. Bloch, J. A. Mason, S. J. Teat, J. R. Long, *Inorg. Chem.* **2015**, *54*, 2995.
- [8] B. Chen, G. Qian, *Metal-Organic Frameworks for Photonics Applications*, Structure and Bonding, Vol. 157, Springer, Berlin, **2014**.
- [9] L. R. MacGillivray, C. M. Lukehart, *Metal-Organic Framework Materials*, John Wiley & Sons, New York, **2014**.
- [10] S. Qiu, M. Xue, G. Zhu, *Chem. Soc. Rev.* **2014**, *43*, 6116.
- [11] J. Canivet, A. Fateeva, Y. Guo, B. Coasne, D. Farrusseng, *Chem. Soc. Rev.* **2014**, *43*, 5594.
- [12] P. Falcaro, R. Ricco, C. M. Doherty, K. Liang, A. J. Hill, M. J. Styles, *Chem. Soc. Rev.* **2014**, *43*, 5513.
- [13] T. Zhang, W. Lin, *Chem. Soc. Rev.* **2014**, *43*, 5982.
- [14] Y. He, W. Zhou, G. Qian, B. Chen, *Chem. Soc. Rev.* **2014**, *43*, 5657.
- [15] N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keefe, O. M. Yaghi, *Science* **2003**, *300*, 1127.

- [16] L. J. Murray, M. Dinca, J. R. Long, *Chem. Soc. Rev.* **2009**, *38*, 1294.
- [17] S. Khoshhal, A. A. Ghoreyshi, M. Jahanshahi, M. Mohammadi, *RSC Advances* **2015**, *5*, 24758.
- [18] Y. Basdogan, S. Keskin, *CrystEngComm*. **2015**, *17*, 261.
- [19] L. Liu, S. G. Telfer, *J. Am. Chem. Soc.* **2015**, *137*, 3901.
- [20] T. Kitao, S. Bracco, A. Comotti, P. Sozzani, M. Naito, S. Seki, T. Uemura, S. Kitagawa, *J. Am. Chem. Soc.* **2015**, *137*, 5231.
- [21] C.-C. Hou, T.-T. Li, S. Cao, Y. Chen, W.-F. Fu, *J. Mater. Chem. A* **2015**, *3*, 10386.
- [22] S. Couck, T. R. C. Van Assche, Y.-Y. Liu, G. V. Baron, P. Van der Voort, J. F. M. Denayer, *Langmuir* **2015**, *31*, 5063.
- [23] Y.-L. Li, J.-A. Hua, Y. Zhao, Y.-S. Kang, W.-Y. Sun, *Micropor. Mesopor. Mat.* **2015**, *214*, 188.
- [24] D. Banerjee, L. A. Borkowski, S. J. Kim, J. B. Parise, *Cryst. Growth Des.* **2009**, *9*, 4922.
- [25] W. Tao, J.-M. Liu, Y.-J. Zheng, C.-Y. Sun, *Chin. J. Inorg. Chem.* **2011**, *27*, 2419.
- [26] M. Albrecht, M. Nieger, A. Schmidt, *Z. Naturforsch.* **2012**, *67b*, 103.
- [27] M. Albrecht, M. Nieger, A. Schmidt, *Z. Naturforsch.* **2011**, *66b*, 209.
- [28] M. Marschewski, C. Otto, L. Wegewitz, O. Höfft, A. Schmidt, W. Maus-Friedrichs, *Appl. Surface Sci.* **2015**, *339*, 9.
- [29] S. Wiechmann, T. Freese, M. H. H. Drafz, E. G. Hübner, J. C. Namyslo, M. Nieger, A. Schmidt, *Chem. Commun.* **2014**, *50*, 11822.
- [30] A. Schmidt, T. Habeck, *Lett. Org. Chem.* **2005**, *2*, 37.
- [31] M. Liu, M. Nieger, A. Schmidt, *Chem. Commun.* **2015**, *51*, 477.
- [32] A. Schmidt, T. Mordhorst, *Synthesis* **2005**, 781.
- [33] L. Pan, N. Ching, X. Huang, J. Li, *Inorg. Chem.* **2000**, *39*, 5333.
- [34] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112.

## Graphical synopsis

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