

Incorporation of an intact dimeric Zr_{12} oxo cluster from a molecular precursor in a new zirconium metal-organic framework

 Andrey A. Bezrukov, Karl W. Törnroos, Erwan Le Roux and Pascal D. C. Dietzel*^a

 Received 00th January 20xx,
 Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

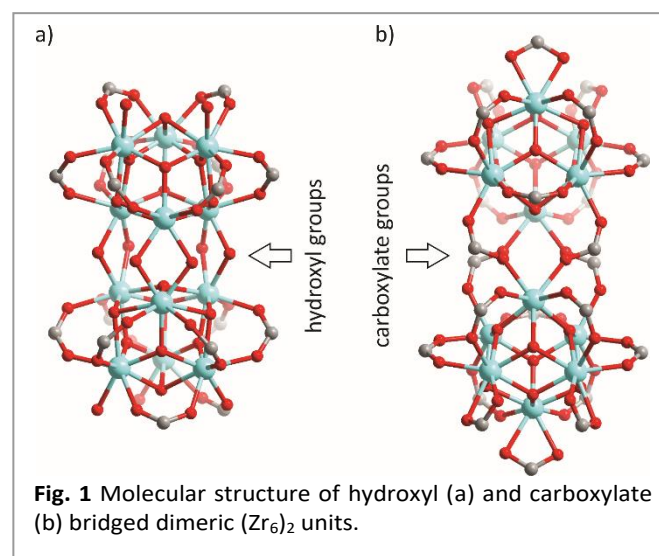
Two zirconium-organic frameworks were synthesized by exchanging the acetate ligands in $[Zr_{12}O_8(OH)_8(CH_3COO)_{24}]$ with polydentate linkers. Partial substitution of acetate groups by a phosphine based linker yielded a new porous framework with this unique dimeric Zr_{12} cluster unit as molecular building block. More exhaustive substitution of acetate resulted in cleavage of the Zr_{12} unit and formation of UiO-67.

Metal-organic frameworks based on Zr inorganic clusters (Zr-MOFs) are characterised by variety of structures, ease of tailoring of the functionality, and outstanding thermal and chemical stability.¹ Most Zr-based MOFs contain metal oxide clusters as inorganic secondary building units (SBUs), in particular $[Zr_6O_4(OH)_4]^{12+}$ clusters found in the structure of UiO-66 and related materials. In UiO-66, the clusters are connected into the framework by 12 carboxylate groups of the organic linker molecules which are positioned along the edges of the octahedral Zr_6 unit.² Other MOFs contain the same cluster based on the octahedral Zr_6 unit, but have only six,³ eight⁴ and ten⁵ carboxylate groups coordinated to the inorganic cluster. In addition, there are a few Zr-MOFs based on different inorganic SBUs such as a $[Zr_8O_6]^{20+}$ cluster,⁶ discrete Zr(IV) atoms⁷ and infinite chains.⁸

In comparison to the few zirconium oxo cluster units that have been found in MOFs to date, many more structurally diverse Zr oxo-clusters have been isolated in the form of discrete molecular compounds, e.g. based on distorted butterfly Zr_4 , square pyramidal Zr_5 and Zr_{10} units⁹. Recently, an isorecticular series was reported in which two Zr_6 oxo-clusters are connected through common hydroxyl groups (Fig. 1a),¹⁰ as can form in a condensation reaction involving two Zr_6 based clusters with terminating water or hydroxyl ligands instead of carboxylate ligands. For clusters carrying terminal carboxylate

units, these carboxylates have to be substituted first by water or hydroxide. Alternatively, a non-coordinating oxygen of a carboxylate group from one cluster can replace a terminal ligand on another cluster unit, thus becoming a bridging ligand. Such dimeric $(Zr_6)_2$ units have been obtained with a number of monocarboxylate organic ligands (e.g. acetate, acrylate, propionate, methacrylate etc.) (Fig. 1b).^{11, 12} These clusters were used for incorporation into inorganic-organic hybrid copolymers¹³ and as catalysts,¹⁴ but to the best of our knowledge there is as yet no report of MOF structures based on such carboxylate-bridged dimers.

Herein, we report the use of the $[Zr_{12}O_8(OH)_8(CH_3COO)_{24}]$, in which two Zr_6 based units are bridged by carboxylate groups, as a precursor for the synthesis of porous MOFs. By choosing the appropriate organic linker and tailoring the reaction conditions it was possible to obtain various degrees of substitution of the acetate groups of $[Zr_{12}O_8(OH)_8(CH_3COO)_{24}]$, which led to different inorganic building units in the resulting MOF, including the intact dimeric $\{[Zr_6O_4(OH)_4]_2(CH_3COO)_4\}^{20+}$ unit.



^a Department of Chemistry, University of Bergen, P. O. Box 7803, N-5020 Bergen, Norway. E-mail: pascal.dietzel@uib.no

† Electronic supplementary information (ESI) available. CCDC 1585873 and 1585874. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

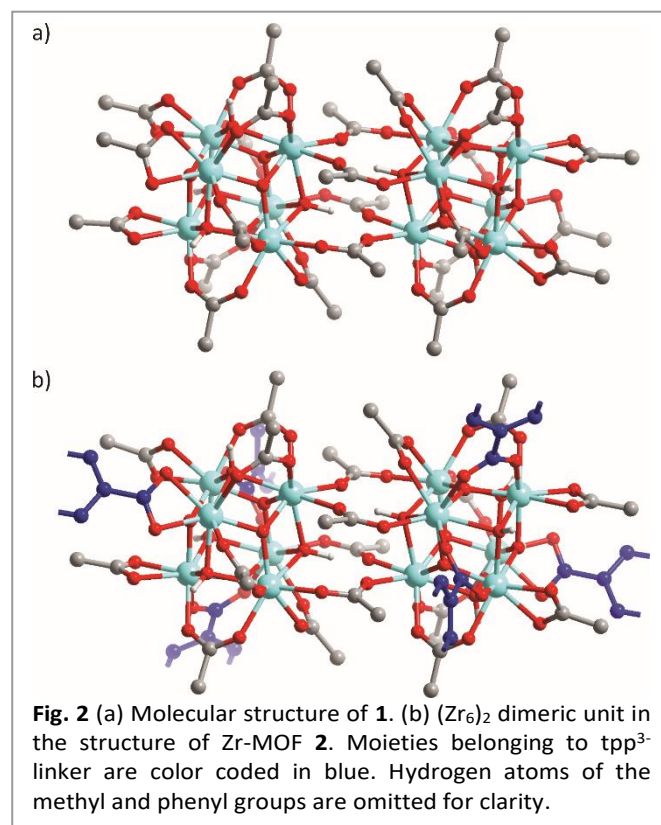
Schubert et al. prepared $[\text{Zr}_{12}\text{O}_8(\text{OH})_8(\text{CH}_3\text{COO})_{24}] \cdot 6\text{CH}_3\text{COOH} \cdot 3.5\text{CH}_2\text{Cl}_2$ which contains isolated molecules composed of dimeric $[\text{Zr}_6\text{O}_4(\text{OH})_4]^{12+}$ clusters which are bridged and terminated exclusively by acetate groups as ligands.¹² We developed an alternative synthetic route by reacting $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ with acetic acid under solvothermal conditions and obtained $[\text{Zr}_{12}\text{O}_8(\text{OH})_8(\text{CH}_3\text{COO})_{24}] \cdot 4\text{CH}_3\text{COOH} \cdot 2\text{HCOOH} \cdot 0.5\text{H}_2\text{O}$ **1**. The advantage of this synthesis procedure is that it does not require inert atmosphere for the reaction and uses readily available, inexpensive and non-toxic $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$,¹⁵ replacing zirconium butoxide from the original procedure, as the zirconium source.

The $[\text{Zr}_{12}\text{O}_8(\text{OH})_8(\text{CH}_3\text{COO})_{24}]$ clusters are packed differently in **1** than in the structure described by Schubert et al., possibly because of the difference in crystal solvent (Fig. S1). They are composed of two octahedral $[\text{Zr}_6\text{O}_4(\text{OH})_4]^{12+}$ units which are connected into their dimeric form by four acetate groups (Fig. 2a). Of the remaining acetate ligands, seven are shared between two Zr atoms in bridging coordination mode along the edge of each Zr_6 octahedron and three acetate ligands are coordinated to a single vertex of each Zr_6 octahedron with both of their O atoms in chelating mode.

Substitution of terminal monocarboxylate ligands in the isolated inorganic precursor by polycarboxylate linkers has been used successfully to synthesize MOFs that contain unchanged inorganic cluster units.¹⁶ For instance UiO-66 and isostructural compounds were synthesized by using isolated methacrylate or benzoate Zr_6 oxo clusters as starting material.¹⁷ In a first attempt to substitute terminal monocarboxylate ligands by bridging polycarboxylate ligands to synthesize a MOF containing the Zr_{12} unit, we reacted **1** with biphenyl-4,4'-dicarboxylic acid (H_2bpdc), a commonly used ditopic linker. Instead of substituting only non-bridging acetate groups in **1** and leaving the Zr_{12} unit intact, the reaction of **1** with H_2bpdc in *N,N*-dimethylformamide (DMF) under solvothermal conditions yielded UiO-67 as product (Table S1, entry 1 and Fig. S4). Apparently, substitution of acetate by bpdc^{2-} broke up the dimeric $\{[\text{Zr}_6\text{O}_4(\text{OH})_4]_2(\text{CH}_3\text{COO})_4\}^{20+}$ cluster and led to the assembly of the UiO-67 network with discrete $[\text{Zr}_6\text{O}_4(\text{OH})_4]^{12+}$ clusters.

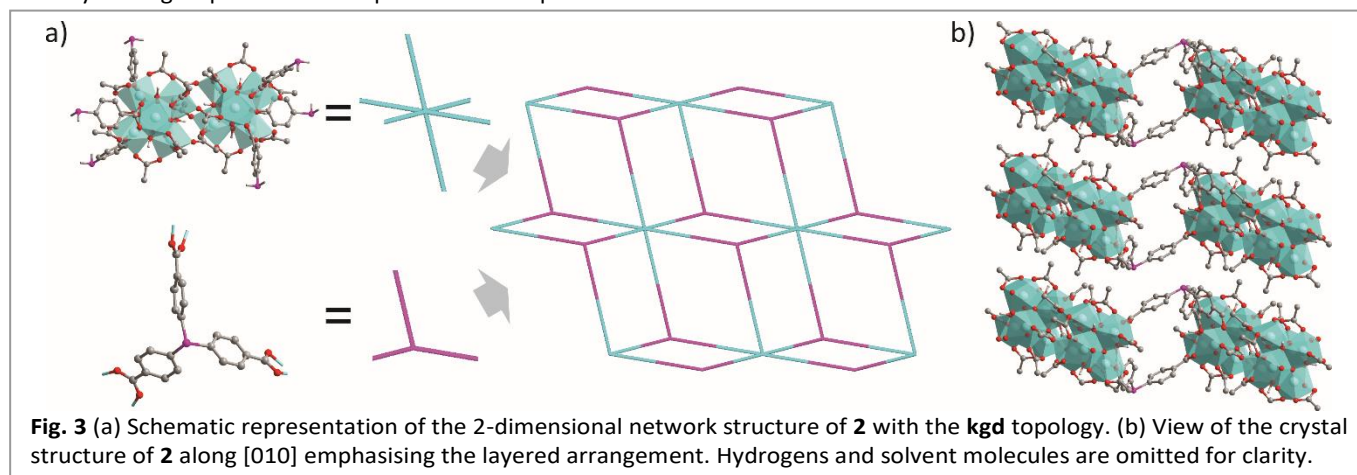
We then used the tritopic linker tris(4-carboxyphenyl)phosphine (H_3tpp)¹⁸ that contains three carboxylate groups in attempts to incorporate the

$\{[\text{Zr}_6\text{O}_4(\text{OH})_4]_2(\text{CH}_3\text{COO})_4\}^{20+}$ dimeric unit into the structure of a MOF. The initial reaction of **1** with the H_3tpp linker in DMF did



not yield a crystalline product (Table S1, entry 3), but we successfully obtained a new crystalline product **2** with formula $[\text{Zr}_{12}\text{O}_8(\text{OH})_8(\text{CH}_3\text{COO})_{18}(\text{tpp})_2] \cdot 4\text{CH}_3\text{COOH} \cdot n\text{solvent}$ using a solvent mixture of acetic acid and DMF (Table S1, entries 4-5). **2** is a rare example of a Zr based coordination polymer that contains a phosphine functional group in the structure.¹⁹

The crystal structure of **2** does indeed contain an inorganic SBU that is derived from the dimeric $(\text{Zr}_6)_2$ units in **1** by substitution of six acetate groups with carboxylate groups of the tpp^{3-} linker (Fig. 2b). Two of these were coordinating vertices with single Zr atoms and four were coordinating two Zr atoms along edges of the Zr_6 octahedron. The bridging acetate ligands that hold the dimer together remained in place under these reaction conditions, thus preserving the $(\text{Zr}_6)_2$ dimeric inorganic



SBU, in a rare example of site-selective substitution of carboxylate ligands in this type of cluster.^{12, 20}

Each inorganic SBU is coordinated to six different tpp^{3-} ions forming an infinite network structure (Fig. 3a). The topology of the network can be represented as **kgd**, with the $(\text{Zr}_6)_2$ dimeric unit as 6-connected node and the tpp^{3-} linker as 3-connected node. Even though the **kgd** topology is rather frequent and there are Zr-MOFs with this topology of the network,²¹ **2** is the first example of a MOF with the $[\text{Zr}_{12}\text{O}_8(\text{OH})_8(\text{CH}_3\text{COO})_4]^{20+}$ inorganic SBU. The layers of the 2D network structure are stacked on top of each other in AA packing (Fig. 3b). In fact, there are voids within the 2D network and between the layers forming a three-dimensional pore system with the main opening along $[1\bar{1}0]$ (Fig. S6). The pores occupy 36% of the unit cell volume and contain acetic acid and disordered solvent molecules.

The phosphine moiety in the organic linker is potentially susceptible to oxidation.²² Thermal analysis in O_2/Ar atmosphere shows that **2** decomposes at temperatures below those usually associated with oxidation of phosphine to phosphine oxide.²³ The thermogravimetric trace shows no well-defined plateau of stability of the structure after evaporation of the pore content (Fig. S9), indicating that decomposition of the framework commences immediately after removal of the solvent or even concomitantly. To obtain more information about the intrinsic stability of the framework structure, **2** was investigated by performing powder X-ray diffraction while heating the material in helium gas flow (Fig. 4). Initially, a

smooth shift of peaks is observed in the diffraction patterns before a discontinuous phase transition occurs in the temperature range from 333 to 355 K. The similarity of the diffraction patterns of the two phases indicate they are structurally very similar; it also allowed indexation of the high temperature phase even though there were only a few well-resolved reflections. The most pronounced change is a contraction of the *b* axis by ~ 1 Å (Fig. S10). The unit cell volume of the high-temperature phase is approximately 9% lower in comparison to unit cell volume of the as-synthesized phase, which means the pore volume is reduced to 30%. **2** loses crystallinity in the range from 384 to 414 K.

Because of the low decomposition temperature of the structure, it appeared unlikely that thermal removal of the relatively high boiling pore content would succeed without affecting the integrity of the framework structure. Instead, the solvent inside the pores of as-synthesized **2** was exchanged with low-boiling CH_2Cl_2 and the material was consequently treated in dynamic vacuum at 298 K. Desolvated **2** is permanently porous as confirmed by uptake of N_2 at 77 K and CO_2 at 278 K (Fig. S11). The nitrogen specific surface area is $505 \text{ m}^2 \text{ g}^{-1}$ and $400 \text{ m}^2 \text{ g}^{-1}$ derived using the Langmuir and BET theory respectively. Preliminary tests indicate that **2** selectively catalyses the coupling of CO_2 and styrene oxide to styrene carbonate in the presence of $[\text{nBu}_4\text{N}]\text{Br}$ as co-catalyst (see ESI).

In summary, a new compound **1** with the isolated $[\text{Zr}_{12}\text{O}_8(\text{OH})_8(\text{CH}_3\text{COO})_{24}]$ cluster was synthesized from $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and acetic acid using an easy to perform solvothermal synthesis in ambient atmosphere. We demonstrated that compound **1** can be used as Zr source and precursor in the syntheses of MOFs. In the reaction of **1** with H_2bpdcc in DMF, substitution of the acetate groups in the precursor with carboxylate groups of H_2bpdcc resulted in cleavage of the dimeric $(\text{Zr}_6)_2$ oxo-cluster and formation of UiO-67. In the reaction of **1** with H_3tpp in acidic conditions, six acetate groups were substituted with carboxylate groups of H_3tpp in the $(\text{Zr}_6)_2$ oxo-cluster. Because the bridging acetate groups remained unaffected, a new MOF, $[\text{Zr}_{12}\text{O}_8(\text{OH})_8(\text{CH}_3\text{COO})_{18}(\text{tpp})_2] \cdot 4\text{CH}_3\text{COOH} \cdot n\text{solvent}$ **2**, was obtained that incorporated the dimeric $(\text{Zr}_6)_2$ oxo-cluster in the structure. **2** contains solvent filled pores in the structure and desolvated **2** adsorbs N_2 and CO_2 . The cycloaddition reaction of CO_2 to styrene oxide is catalysed by **2**.

The authors acknowledge the support of the Research Council of Norway through grants ISP-KJEMI 209339 and SYNKNOYT 247734, and Bergenshalvøens Kommunale Kraftselskap through the BKK-UiB 2015 agreement no. 810596. We thank Dr. I. Dovgaliuk for assistance with measurements at the Swiss-Norwegian Beamlines at the ESRF.

Conflicts of interest

There are no conflicts to declare.

Notes and references

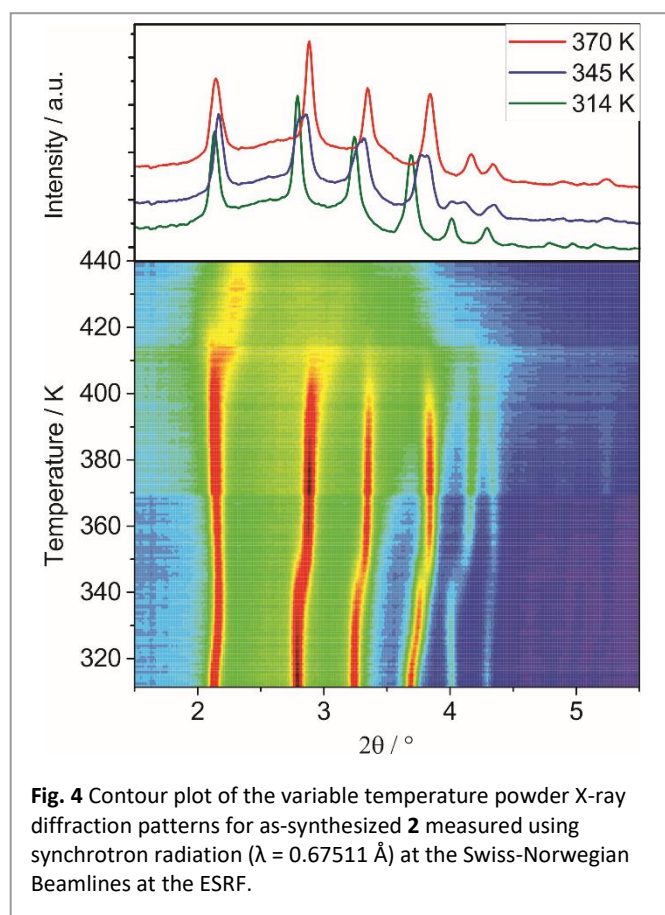


Fig. 4 Contour plot of the variable temperature powder X-ray diffraction patterns for as-synthesized **2** measured using synchrotron radiation ($\lambda = 0.67511$ Å) at the Swiss-Norwegian Beamlines at the ESRF.

- ‡ $[\text{Zr}_{12}\text{O}_8(\text{OH})_8(\text{CH}_3\text{COO})_{24}]\cdot 4\text{CH}_3\text{COOH}\cdot 2\text{HCOOH}\cdot 0.5\text{H}_2\text{O}$ (**1**), $M = 3116.73$, Monoclinic space group $P2_1/c$, $a = 20.287(3)$ Å, $b = 12.5914(18)$ Å, $c = 20.241(3)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 100.188(2)^\circ$, $V = 5088.9(13)$ Å³, $Z = 2$, $\lambda = 0.71073$ Å, $T = 103(2)$ K, $R_1[F^2 > 2\sigma(F^2)] = 0.0369$, $wR(F^2) = 0.0369$, $S = 1.048$.
- $[\text{Zr}_{12}\text{O}_8(\text{OH})_8(\text{CH}_3\text{COO})_{18}(\text{tpp})_2]\cdot 4\text{CH}_3\text{COOH}\cdot n\text{solvent}$ (**2**), $M = 3444.25$, Triclinic space group $P\bar{1}$, $a = 12.2903(16)$ Å, $b = 16.666(2)$ Å, $c = 19.138(2)$ Å, $\alpha = 72.790(2)^\circ$, $\beta = 80.540(2)^\circ$, $\gamma = 74.886(2)^\circ$, $V = 3598.9(8)$ Å³, $Z = 1$, $\lambda = 0.71073$ Å, $T = 103(2)$ K, $R_1[F^2 > 2\sigma(F^2)] = 0.0470$, $wR(F^2) = 0.1389$, $S = 1.059$.
- M. Kim and S. M. Cohen, *CrystEngComm*, 2012, **14**, 4096; T. Devic and C. Serre, *Chem. Soc. Rev.*, 2014, **43**, 6097; Y. Bai, Y. Dou, L.-H. Xie, W. Rutledge, J.-R. Li and H.-C. Zhou, *Chem. Soc. Rev.*, 2016, **45**, 2327.
 - J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, **130**, 13850.
 - D. Feng, W.-C. Chung, Z. Wei, Z.-Y. Gu, H.-L. Jiang, Y.-P. Chen, D. J. Darensbourg and H.-C. Zhou, *J. Am. Chem. Soc.*, 2013, **135**, 17105; V. Bon, I. Senkovska, M. S. Weiss and S. Kaskel, *CrystEngComm*, 2013, **15**, 9572.
 - S. Yuan, W. Lu, Y.-P. Chen, Q. Zhang, T.-F. Liu, D. Feng, X. Wang, J. Qin and H.-C. Zhou, *J. Am. Chem. Soc.*, 2015, **137**, 3177; H. Reinsch, I. Stassen, B. Bueken, A. Lieb, R. Ameloot and D. De Vos, *CrystEngComm*, 2015, **17**, 331; V. Bon, V. Senkovskyy, I. Senkovska and S. Kaskel, *Chem. Commun.*, 2012, **48**, 8407.
 - H. Furukawa, F. Gándara, Y.-B. Zhang, J. Jiang, W. L. Queen, M. R. Hudson and O. M. Yaghi, *J. Am. Chem. Soc.*, 2014, **136**, 4369; V. Bon, I. Senkovska, I. A. Baburin and S. Kaskel, *Cryst. Growth Des.*, 2013, **13**, 1231.
 - D. Feng, H.-L. Jiang, Y.-P. Chen, Z.-Y. Gu, Z. Wei and H.-C. Zhou, *Inorg. Chem.*, 2013, **52**, 12661.
 - M. Taddei, F. Costantino and R. Vivani, *Inorg. Chem.*, 2010, **49**, 9664; M. Maercz, D. S. Wragg, P. D. C. Dietzel and H. Fjellvåg, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2013, **69**, m152; M. Maercz, D. S. Wragg, P. D. C. Dietzel and H. Fjellvåg, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2013, **69**, m153; M. Taddei, F. Costantino, F. Marmottini, A. Comotti, P. Sozzani and R. Vivani, *Chem. Commun.*, 2014, **50**, 14831; M. Taddei, F. Costantino, R. Vivani, S. Sabatini, S.-H. Lim and S. M. Cohen, *Chem. Commun.*, 2014, **50**, 5737.
 - S. Waitschat, H. Reinsch and N. Stock, *Chem. Commun.*, 2016, **52**, 12698; G. Mouchaham, L. Cooper, N. Guillou, C. Martineau, E. Elkaïm, S. Bourrelly, P. L. Llewellyn, C. Allain, G. Clavier, C. Serre and T. Devic, *Angew. Chem., Int. Ed.*, 2015, **54**, 13297; V. Guillerm, F. Ragon, M. Dan-Hardi, T. Devic, M. Vishnuvarthan, B. Campo, A. Vimont, G. Clet, Q. Yang, G. Maurin, G. Férey, A. Vittadini, S. Gross and C. Serre, *Angew. Chem., Int. Ed.*, 2012, **51**, 9267.
 - G. Kickelbick and U. Schubert, *Chem. Ber.*, 1997, **130**, 473; G. Kickelbick and U. Schubert, *J. Chem. Soc., Dalton Trans.*, 1999, **0**, 1301; G. Kickelbick, D. Holzinger, C. Brick, G. Trimmel and E. Moons, *Chem. Mater.*, 2002, **14**, 4382.
 - P. Ji, K. Manna, Z. Lin, X. Feng, A. Urban, Y. Song and W. Lin, *J. Am. Chem. Soc.*, 2017, **139**, 7004; R. Dai, F. Peng, P. Ji, K. Lu, C. Wang, J. Sun and W. Lin, *Inorg. Chem.*, 2017, **56**, 8128.
 - S. Petit, S. Morlens, Z. Yu, D. Luneau, G. Pilet, J.-L. Soubeyroux and P. Odier, *Solid State Sci.*, 2011, **13**, 665; R. B. Mos, M. Nasui, T. Petrisor, M. S. Gabor, R. A. Varga and L. Ciontea, *J. Anal. Appl. Pyrolysis*, 2012, **97**, 137; G. Kickelbick, P. Wiede and U. Schubert, *Inorg. Chim. Acta*, 1999, **284**, 1.
 - M. Puchberger, F. R. Kogler, M. Jupa, S. Gross, H. Fric, G. Kickelbick and U. Schubert, *Eur. J. Inorg. Chem.*, 2006, **2006**, 3283.
 - F. Graziola, F. Girardi, R. Di Maggio, E. Callone, E. Miorin, M. Negri, K. Müller and S. Gross, *Prog. Org. Coat.*, 2012, **74**, 479; F. R. Kogler and U. Schubert, *Polymer*, 2007, **48**, 4990; M. Sangermano, S. Gross, A. Priola, G. Rizza and C. Sada, *Macromol. Chem. Phys.*, 2007, **208**, 2560; S. Maggini, E. Cappelletto and R. D. Maggio, *J. Appl. Polym. Sci.*, 2013, **127**, 2435; R. Di Maggio, E. Callone, F. Girardi and S. Dirè, *J. Appl. Polym. Sci.*, 2012, **125**, 1713; S. Maggini, E. Feci, E. Cappelletto, F. Girardi, S. Palanti and R. Di Maggio, *ACS Appl. Mater. Interfaces*, 2012, **4**, 4871.
 - A. Corma, L. M. Orozco and M. Renz, *New J. Chem.*, 2013, **37**, 3496; F. Faccioli, M. Bauer, D. Pedron, A. Sorarù, M. Carraro and S. Gross, *Eur. J. Inorg. Chem.*, 2015, **2015**, 210.
 - D. Azarifar and D. Sheikh, *Synth. Commun.*, 2013, **43**, 2517.
 - C. Serre, F. Millange, S. Surblé and G. Férey, *Angew. Chem., Int. Ed.*, 2004, **43**, 6285; S. Surblé, C. Serre, C. Mellot-Draznieks, F. Millange and G. Férey, *Chem. Commun.*, 2006, **0**, 284; S. Hausdorf, F. Baitalow, T. Böhle, D. Rafaja and F. O. R. L. Mertens, *J. Am. Chem. Soc.*, 2010, **132**, 10978; D. Feng, K. Wang, Z. Wei, Y.-P. Chen, C. M. Simon, R. K. Arvapally, R. L. Martin, M. Bosch, T.-F. Liu, S. Fordham, D. Yuan, M. A. Omary, M. Haranczyk, B. Smit and H.-C. Zhou, 2014, **5**, 5723; G. Calvez, F. Le Natur, C. Daiguebonne, K. Bernot, Y. Suffren and O. Guillou, *Coord. Chem. Rev.*, 2017, **340**, 134; A. Sapanik, E. N. Zorina-Tikhonova, M. A. Kiskin, D. G. Samsonenko, K. A. Kovalenko, A. A. Sidorov, I. L. Eremenko, D. N. Dybtsev, A. J. Blake, S. P. Argent, M. Schröder and V. P. Fedin, *Inorg. Chem.*, 2017, **56**, 1599; S. Smolders, A. Struyf, H. Reinsch, B. Bueken, T. Rhauderwiek, L. Mintrop, P. Kurz, N. Stock and D. E. De Vos, *Chem. Commun.*, 2018, **54**, 876.
 - V. Guillerm, S. Gross, C. Serre, T. Devic, M. Bauer and G. Férey, *Chem. Commun.*, 2010, **46**, 767; K. Uzarevic, T. C. Wang, S.-Y. Moon, A. M. Fidelli, J. T. Hupp, O. K. Farha and T. Friscic, *Chem. Commun.*, 2016, **52**, 2133.
 - S. M. Humphrey, P. K. Allan, S. E. Oungoulouian, M. S. Ironside and E. R. Wise, *Dalton Trans.*, 2009, **0**, 2298; A. J. Nunez, L. N. Shear, N. Dahal, I. A. Ibarra, J. Yoon, Y. K. Hwang, J.-S. Chang and S. M. Humphrey, *Chem. Commun.*, 2011, **47**, 11855; A. A. Bezrukov, K. W. Törnroos and P. D. C. Dietzel, *Cryst. Growth Des.*, 2017, **17**, 3257.
 - T. Sawano, Z. Lin, D. Boures, B. An, C. Wang and W. Lin, *J. Am. Chem. Soc.*, 2016, **138**, 9783; J. M. Falkowski, T. Sawano, T. Zhang, G. Tsun, Y. Chen, J. V. Lockard and W. Lin, *J. Am. Chem. Soc.*, 2014, **136**, 5213; J. Václavík, M. Servalli, C. Lothschütz, J. Szlachetko, M. Ranocchiaro and J. A. van Bokhoven, *ChemCatChem*, 2013, **5**, 692.
 - J. Kreutzer, M. Czakler, M. Puchberger, E. Pittenauer and U. Schubert, *Eur. J. Inorg. Chem.*, 2015, **2015**, 2889.
 - S. Yuan, J.-S. Qin, L. Zou, Y.-P. Chen, X. Wang, Q. Zhang and H.-C. Zhou, *J. Am. Chem. Soc.*, 2016, **138**, 6636; R. Wang, Z. Wang, Y. Xu, F. Dai, L. Zhang and D. Sun, *Inorg. Chem.*, 2014, **53**, 7086; J. Ma, A. G. Wong-Foy and A. J. Matzger, *Inorg. Chem.*, 2015, **54**, 4591.
 - S. M. Humphrey, S. E. Oungoulouian, J. W. Yoon, Y. K. Hwang, E. R. Wise and J.-S. Chang, *Chem. Commun.*, 2008, **0**, 2891.
 - A. A. Bezrukov and P. D. C. Dietzel, *Inorg. Chem.*, 2017, **56**, 12830.