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Inverted metal–organic frameworks: isoreticular decoration with organic anions using principles of supramolecular chemistry

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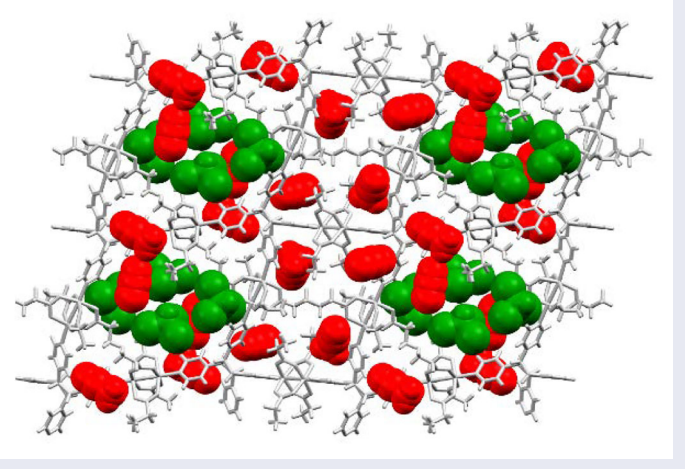
ABSTRACT

A structural study of two-dimensional inverted metal–organic frameworks demonstrates that the interior cavities of the framework structures can be systematically modified by changing the organic anion of a Cu(II)-paddlewheel unit. Changing the anion allows modifications to the shapes and sizes of the cavities in a series of isoreticular frameworks. The construction of the frameworks is based on the application of a tetrafunctional organic cyclobutane ligand synthesized in the organic solid state.



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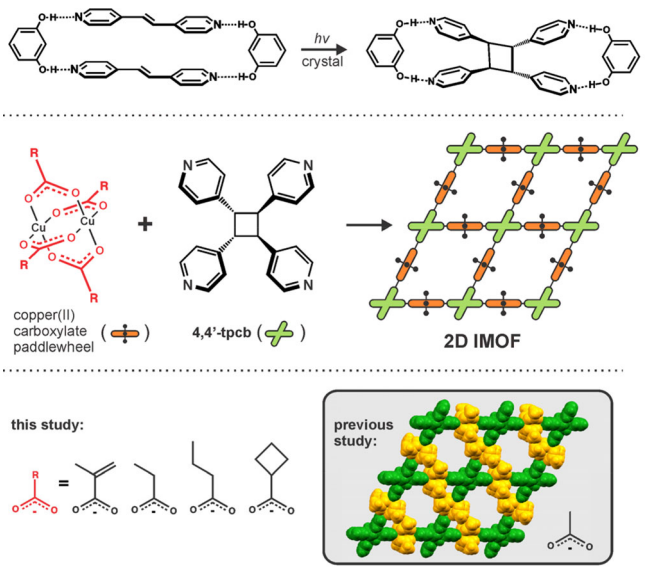

Figure 1. Solid-state synthesis of **4,4′-tpcb** (top) and 2-D IMOFs using Cu(II) carboxylate paddlewheels and **4,4′-tpcb** (middle). Inset depicts structure of IMOF-1 based on Cu(II) acetate paddlewheel and **4,4′-tpcb** (bottom).

Introduction

Metal–organic frameworks (MOFs) comprise one- (1-D), two- (2-D) or three-dimensional (3-D) networks composed of metal ions (and/or metal ion clusters) and organic bridging ligands held together by coordination forces [1, 2]. Much work has been accomplished to develop a wide range of such functional coordination compounds, with attention focused on the design of porous MOFs [3–5] for separation [6], storage [7, 8], detection [9] and catalysis purposes, to name a few [10, 11]. Although important strides have been made to design and develop MOFs that exhibit tailorable properties and function, there is a continued need to understand the impact of organic functionalization on the interiors of MOFs (e.g. host–guest chemistry). Whereas much attention has been focused on post-synthetic covalent modifications of MOFs, comparatively less attention has been directed to the decoration of MOF interiors (namely cavities and channels) in a pre-selection manner using principles of supramolecular chemistry.

In this context, we have reported the construction of 2-D "inverted metal–organic frameworks" (IMOFs) wherein the roles of the metal ions and organic ligand, in terms of connectivity, are reversed as compared to more common MOFs [12, 13]. We employ organic ligands that act as network nodes and metal ions (or clusters) that act as linear linkers. The approach to IMOF design makes use of terminal organic anions of dimetal carboxylates to decorate the interior of MOF cavities. The degree of modularity also implies that the self-assembly process could be more sensitive to the structural and chemical changes of the decorating organic components. With this in mind, we have used the following components as building blocks for an IMOF: (1) copper(II)-acetate (**act**) paddlewheel – a metal cluster with transoid coordination sites and (2) *rctt*-tetrakis(4-pyridyl)cyclobutane (**4,4′-tpcb**) – a tetrapyridine obtained from a templated-directed synthesis performed in the organic solid state [14] (Figure 1, inset).

Table 1. Descriptors of IMOFs **2**–**5** compared to IMOF-1.

IMOF	Anion	Structure	Shape and dimensions of framework openings (shape of solvent accessible voids)	Crystallization medium	Guest molecules per **4,4′-tpcb**
1	**act**	2-D (flat)	Rhombus – sides: 17.2 Å; corner angles: 75°, 105°; diagonals: 20.9 Å, 27.2 Å (channels)	CH_3OH/C_6H_6	3 C_6H_6
2	**maa**	2-D (flat)	Rhombus – sides: 17.2 Å; corner angles: 86°, 94°; diagonals: 23.5 Å, 25.2 Å (channels)	CH_3OH/C_6H_6	8 C_6H_6
3	**pra**	2-D (corrugated)	Parallelogram 1 – sides: 16.8 Å, 17.4 Å; corner angles: 71°, 109°; diagonals: 19.9 Å, 27.8 Å; parallelogram 2 – sides: 16.8 Å, 16.9 Å; corner angles: 64°, 116°; diagonals: 17.8 Å, 28.7 Å (channels)	$CH_3CN/CHCl_3$	4 CH_3CN, 2 $CHCl_3$
4	**bua**	2-D (flat)	Rhombus – sides: 17.2 Å; corner angles: 70°, 110°; diagonals: 19.7 Å and 28.3 Å (isolated compartments)	CH_3CN/C_6H_6/DMF	2 CH_3CN, 2 C_6H_6
5	**cba**	2-D (flat)	Rhombus – sides: 17.2 Å; corner angles: 79°, 101°; diagonals: 21.9 Å, 26.6 Å (isolated compartments)	C_4H_8O/C_3H_7NO	2 C_4H_8O, 2 C_3H_7NO

Cyclobutanes lined with pyridyl groups have emerged as useful building blocks of MOF materials [12, 14–17]. The resulting IMOF was shown to exhibit a 2-D structure wherein the cyclobutane ligand serves as a four-connected node within a (4,4)-topology. The grids of the 2-D framework are defined by sizable cavities (Figure 1), which stack to produce 1-D channels. The channels can release included solvent guests *via* a single-crystal-to-single-crystal (SCSC) process.

In light of recent interest in the design of porous solids and the separation of industrial chemical feedstock (such as petrochemicals) [18], we describe the results of a study aimed to evaluate structural effects of modifying the channels and cavities of our archetypal IMOF using principles of supramolecular chemistry [19]. To chemically alter the IMOF cavities, we used four distinct carboxylate anions to functionalize the size and shape of the copper(II) paddlewheel; namely, inward-directed methacrylate (**maa**), propionate (**pra**), butyrate (**bua**) and cyclobutanecarboxylate (**cba**) anions (Figure 1). Our work affords structurally related, or isoreticular [20] IMOFs decorated with saturated and unsaturated functional groups. We show the uses of carboxylates to affect host–guest properties of the IMOFs.

Results

All structures are described in succession, with main structural features summarized in Table 1.

Structure of IMOF-2

4,4′-tpcb and Cu(II)-**maa** paddlewheel components self-assemble to form a flat porous 2-D IMOF in the presence of CH_3OH and C_6H_6, namely [$(Cu_2$**maa**$_4)_2$(**4,4′-tpcb**)$(C_6H_6)_8$] (IMOF-**2**) (Figure 2). IMOF-**2** crystallizes in the monoclinic space group *C*2/*m*. The

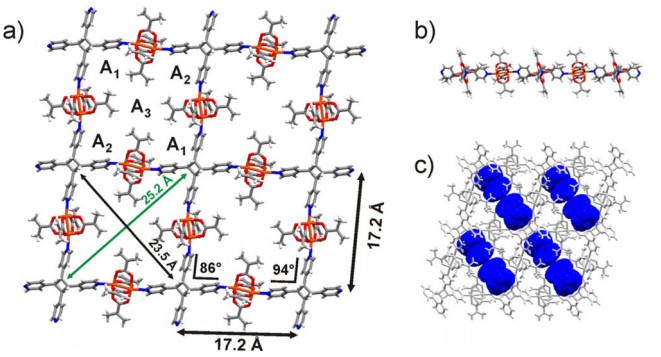

Figure 2. X-ray crystal structure IMOF-**2**: (a,b) 2-D structure and (c) packing viewed along crystallographic *c*-axis (gray: host framework; blue: C_6H_6).

framework displays a (4,4)-topology being structurally analogs to IMOF-**1**. Specifically, each **4,4′-tpcb** unit is surrounded by four paddlewheel complexes, each of which sits around a crystallographic center of inversion, such that **4,4′-tpcb** acts as a 4-connected vertex. The **4,4′-tpcb** nodes are statistically disordered (occupancies: 0.30:0.70). The 2-D IMOF displays sizable cavities (**A**) of edge lengths (17.2 Å) that are rhomboid in shape (corner angles 86° and 94°, diagonals 23.5 Å and 25.2 Å) (Figure 2(a)). Two of the four **maa** anions that belong to the paddlewheel unit converge on the interior of the cavities, dividing the cavities into five smaller compartments. Four compartments are similar in size and shape ($\mathbf{A_1}$ and $\mathbf{A_2}$) are located next to the paddlewheels being located at the corners of the rhombic cavity. The compartments are similar in size and shape. The fifth compartment ($\mathbf{A_3}$) is located in the center of the cavity. The two remaining **maa** anions are directed perpendicularly above and below the plane of the IMOF and point into the compartments $\mathbf{A_1}$ of adjacent frameworks (Figure 2(b)). The IMOFs are stacked in an offset fashion along the crystallographic (201) plane. Compartments $\mathbf{A_1}$ and $\mathbf{A_2}$ of the stacked IMOFs overlay to give rise to 1-D channels that run along the crystallographic *c*-axis. The channels account for 28% of the unit cell volume (i.e. nearly 1100 Å^3) and are occupied by C_6H_6 molecules (eight C_6H_6 guest molecules per **4,4′-tpcb** ligand, Figure 2(c)).

Structure of IMOF-3

Reaction of Cu(II)-**pra** and **4,4′-tpcb** in acetonitrile and chloroform resulted in the formation of the corrugated 2-D IMOF $[(Cu_2\mathbf{pra}_4)_2(\mathbf{4,4'\text{-}tpcb})(CH_3CN)_4(CHCl_3)_2]$ (IMOF-**3**) with a (4,4)-topology (Figure 3(a,b)). IMOF-3 crystallizes in the triclinic space group *P-1*. Each **4,4′-tpcb** unit acts as a four-connected vertex and is surrounded by four paddlewheel complexes, with each sitting on a center of inversion. The **4,4′-tpcb** nodes are statistically disordered (occupancies: 0.92:0.08). The IMOF exhibits two distinct parallelogram-shaped cavities.

The first cavity (**B**) is defined by distinct edge lengths (16.8 Å and 17.4 Å) and corner angles (71° and 109°) and diagonals (19.9 Å and 27.8 Å) that also define rhomboid cavities. The second cavity (**C**) has more comparable edge lengths (16.8 Å and 16.9 Å) with corner angles (64° and 116°) and diagonals (17.8 Å and 28.7 Å) of a rhomboid.

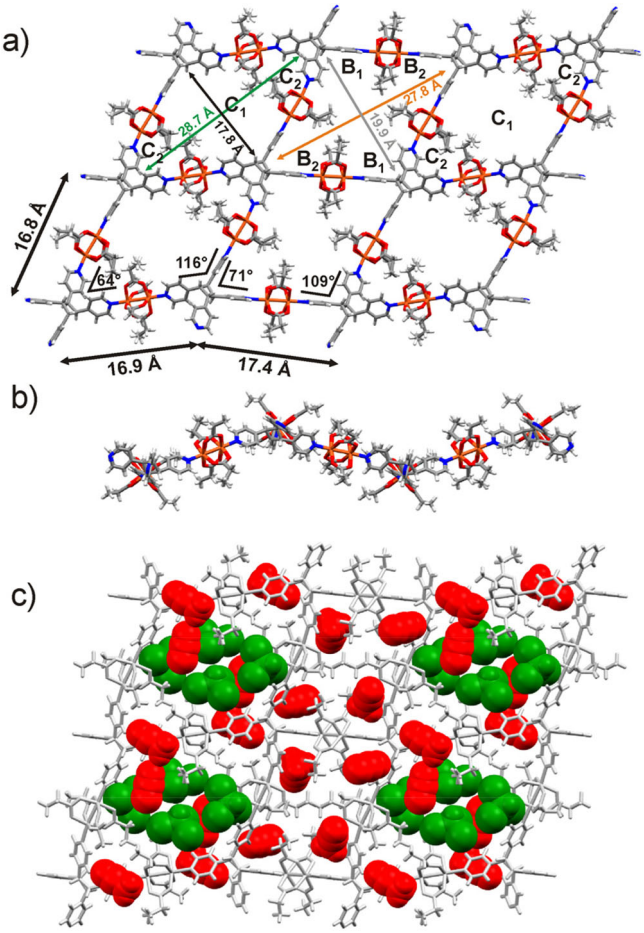

Figure 3. X-ray structure of IMOF-**3**: (a,b) corrugated structure and (c) packing along crystallographic *a*-axis (gray: host framework; red: CH_3CN; green: $CHCl_3$).

The four **pra** anions of each paddlewheel point away from the surface of the IMOF. By doing so, the **pra** anions divide cavity **B** into four compartments (type $\mathbf{B_1}$ and $\mathbf{B_2}$), whereas cavity **C** is apportioned into three compartments (type $\mathbf{C_1}$ and $\mathbf{C_2}$). The IMOFs are stacked along the crystallographic plane (001), with compartments $\mathbf{C_1}$ and $\mathbf{C_2}$ forming 1-D channels that run along the crystallographic *a*-axis. Compartments $\mathbf{B_1}$ and $\mathbf{B_2}$ host acetonitrile molecules, whereas compartments $\mathbf{C_1}$ and $\mathbf{C_2}$ host acetonitrile and chloroform molecules. The channels and compartments account for 30.4% of the unit cell volume (i.e. 1113.9 $Å^3$) and accommodate four acetonitrile and two chloroform guest molecules per **4,4′-tpcb** ligand) (Figure 3(c)).

Structure of IMOF-4

Crystallization of Cu(II)-**bua** with **4,4′-tpcb** from a solution of benzene, acetronitrile and DMF afforded $[(Cu_2\mathbf{bua}_4)_2(\mathbf{4,4'\text{-}tpcb})(C_6H_6)_2(CH_3CN)_2]$ (IMOF-**4**). The 2-D IMOF

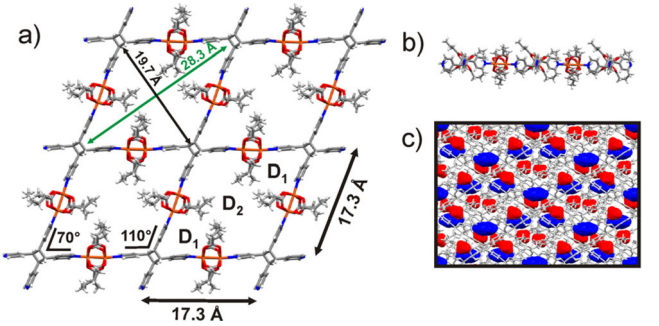

Figure 4. X-ray structure of IMOF-**4**: (a,b) flat 2-D structure of **3**, and (c) crystal packing of **3** viewed along the crystallographic plane (20–1) (gray: host framework; blue: C_6H_6; red: CH_3CN).

crystallizes in the monoclinic space group *C*2/*c* and features a (4,4)-topology wherein each of the disordered **4,4′-tpcb** ligands (occupancies: 0.64:0.32) is surrounded by four paddlewheel complexes (Figure 4). The **4,4′-tpcb** ligand lies on a proper twofold rotation axes, whereas the paddlewheel moieties are on an improper twofold-rotation axis. IMOF-**4** displays large framework cavities of edge lengths (17.3 Å) (denoted as cavity **D**, Figure 4(a)), corner angles (70° and 110°) and diagonals 19.7 Å and 28.3 Å) that define rhomboid cavities. Comparable to IMOFs-**1** and **3**, two of the four paddlewheel anions point into the interior of the cavities and divide the cavities into three smaller compartments based on two smaller compartments (type $\mathbf{D_1}$) and one larger compartment (type $\mathbf{D_2}$). The $\mathbf{D_1}$ compartments are located at rhombus corners that display an obtuse angle, whereas the large compartment $\mathbf{D_2}$ occupies the center of the rhombic cavity. The other two **bua** anions point above and below the plane of the 2-D IMOF and are accommodated by compartments $\mathbf{D_2}$ of adjacent IMOFs. The IMOFs stack offset along the crystallographic (–201) plane. Compartments $\mathbf{D_2}$ of the stacked IMOFs overlay give isolated elongated chambers oriented along the crystallographic plane (–20–1). The chambers account for 11.5% of the unit cell volume (i.e. 797.7 $Å^3$) and are fully occupied by two benzene and two acetonitrile molecules (two acetonitrile and two benzene guest molecule per **4,4′-tpcb** ligand).

Structure of IMOF-*5*

Reaction of Cu(II)-**cba** paddlewheel and **4,4′-tpcb** in tetrahydrofuran and dimethylformamide generated $[(Cu_2\mathbf{cba}_4)_2(\mathbf{4,4'\text{-}tpcb})(C_4H_8O)_2(C_3H_7NO)_2]$ (IMOF-**5**), which crystallizes in the triclinic space group *P-1*. The components assemble to form a planar 2-D framework wherein the **4,4′-tpcb** unit is disordered (occupancies: 0.30:0.70) and surrounded by four paddlewheel complexes. Both **4,4′-tpcb** and paddlewheel moieties units lie on a crystallographic center of inversion. IMOF-**5** exhibits large cavities of edge lengths (17.2 Å), corner angles (79° and 101°) and diagonals (21.9 Å and 26.6 Å) that define rhomboid cavities (denoted as cavity **E**, Figure 5). As in IMOF-**1**, two of the four **cba** paddlewheel anions point into the interior of the cavities and divide the cavities into five smaller compartments. The two compartments (type $\mathbf{E_1}$) located at corners that display an obtuse angle are larger in size than the compartments (type $\mathbf{E_2}$) located at corners of the rhombus featuring acute angles. The fifth compartment,

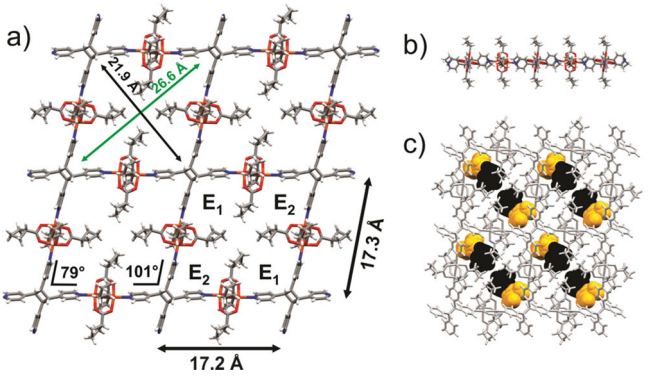

Figure 5. X-ray structure of IMOF-**5**: (a,b) 2-D structure and (c) packing along crystallographic *a*-axis (gray: host framework; orange: C_4H_4O; black: C_3H_7NO).

located in the center of the rhombic cavity, is significantly smaller in size than $\mathbf{E_1}$ and $\mathbf{E_2}$ and cannot accommodate guest molecules. The further two **cba** anions are directed perpendicularly above and below the plane of the 2-D IMOF and point into the compartments $\mathbf{E_1}$ belonging to adjacent IMOFs. The IMOFs are stacked in an offset fashion along the crystallographic (–11–1) plane. Compartments $\mathbf{E_2}$ of the stacked IMOFs form an array of isolated solvent-accessible compartments that run along the crystallographic plane (–1–10). The compartments account for 9.7% of the unit cell volume (i.e. 201.1 $Å^3$) and are fully occupied by C_4H_8O and C_3H_7NO molecules (two C_4H_8O and two C_3H_7NO guest molecule per **4,4′-tpcb** ligand).

Discussion

Structural analyses of IMOFs **2–5** demonstrate supramolecular decoration of the frameworks by changing the organic counterion in the Cu(II) paddlewheel unit. Changing the anion allows a series of 2-D structures to be preserved to generate isoreticular extended solids. Specifically, we show that changing the acetate anion as in our original report is achieved using **maa**, **bua** and **cba**. The organic anions have a significant effect on modifying the sizes and shapes of the rhombic framework cavities (Table 1). Notably, the utilization of **pra** as anion in IMOF-**3** results in an effective reshaping of the rhombic openings into more pronounced parallelogram-like openings.

Decoration of the IMOFs using the different anions also alters host–guest interactions. Specifically, in two (out of four) reported IMOFs, the guests are accommodated in 1-D channels (IMOFs-**2** and **3**), whereas in the two remaining IMOFs (IMOFs-**4** and **5**) the guest solvent molecules are present in isolated compartments (Table 1). Host–guest interactions for IMOFs **2–5** are attributed to: (1) distinct shapes and sizes of the framework openings and/or (2) slightly altered packing modes of the frameworks in respective crystal lattices. Although both factors can be attributed to changes in the size and shape of the utilized paddlewheel anion, the packing modes of the IMOFs are likely influenced by crystallization conditions (i.e. solvent mixtures) to prepare each framework solid. Changing the anion can also affect guest uptake as

demonstrated by IMOFs-**1** and **2** (Table 1). Both IMOFs were obtained from identical crystallization conditions and exhibit different amounts of benzene uptake.

Conclusion

We have demonstrated that supramolecular decoration of IMOFs by changing the nature of the organic anion in a Cu paddlewheel complex. The decoration leads to isoreticular IMOFs with subtle differences in cavity structure and host–guest behaviors. We are investigating the use of chiral anions to prepare IMOFs to develop chiral hosts, as well as the use of paddlewheel components composed of distinct anions to further fine-tune host–guest interactions.

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References

[1] S. Kitagawa, R. Kitaura, S.-I. Noro. *Angew. Chem. Int. Ed. Engl.*, **43**, 2334 (2004).
[2] H. Furukawa, K.E. Cordova, M. O'Keeffe, O.M. Yaghi. *Science*, **341**, 1230444 (2013).
[3] D.J. Tranchemontagne, J.L. Mendoza-Cortes, M. O'Keeffe, O.M. Yaghi. *Chem. Soc. Rev.*, **38**, 1257 (2009).
[4] J.J. Perry Iv, J.A. Perman, M.J. Zaworotko. *Chem. Soc. Rev.*, **38**, 1400 (2009).
[5] M. O'Keeffe, O.M. Yaghi. *Chem. Rev.*, **112**, 675 (2012).
[6] J.-R. Li, J. Sculley, H.-C. Zhou. *Chem. Rev.*, **112**, 869 (2012).
[7] L.J. Murray, M. Dincă, J.R. Long. *Chem. Soc. Rev.*, **38**, 1294 (2009).
[8] K. Sumida, D.L. Rogow, J.A. Mason, T.M. McDonald, E.D. Bloch, Z.R. Herm, T.-H. Bae, J.R. Long. *Chem. Rev.*, **112**, 724 (2012).
[9] L.E. Kreno, K. Leong, O.K. Farha, M. Allendorf, R.P. Van Duyne, J.T. Hupp. *Chem. Rev.*, **112**, 1105 (2012).
[10] M. Yoon, R. Srirambalaji, K. Kim. *Chem. Rev.*, **112**, 1196 (2012). 1231
[11] L. Ma, C. Abney, W. Lin. *Chem. Soc. Rev.*, **38**, 1248 (2009). 1256
[12] D.-K. Bučar, G.S. Papaefstathiou, T.D. Hamilton, Q.L. Chu, I.G. Georgiev, L.R. MacGillivray. *Eur. J. Inorg. Chem.*, **2007**, 4559 (2007).

[13] G.S. Papaefstathiou, L.R. MacGillivray. *Angew. Chem.*, **114**, 2070 (2002).
[14] L.R. MacGillivray, G.S. Papaefstathiou, T. Friščić, T.D. Hamilton, D.-K. Bučar, Q. Chu, D.B. Varshney, I.G. Georgiev. *Acc. Chem. Res.*, **41**, 280 (2008).
[15] T.D. Hamilton, D.-K. Bučar, L.R. MacGillivray. *New J. Chem.*, **34**, 2400 (2010).
[16] D.-K. Bučar, G.S. Papaefstathiou, T.D. Hamilton, L.R. MacGillivray. *New J. Chem.*, **32**, 797 (2008).
[17] Q. Chu, A.J.E. Duncan, G.S. Papaefstathiou, T.D. Hamilton, M.B.J. Atkinson, S.V.S. Mariappan, L.R. MacGillivray. *J. Am. Chem. Soc.*, **140**, 4940 (2018).
[18] J.M. Holcroft, K.J. Hartlieb, P.Z. Moghadam, J.G. Bell, G. Barin, D.P. Ferris, E.D. Bloch, M.M. Algaradah, M.S. Nassar, Y.Y. Botros, K.M. Thomas, J.R. Long, R.Q. Snurr, J.F. Stoddart. *J. Am. Chem. Soc.*, **137**, 5706 (2015).
[19] T.D. Hamilton, G.S. Papaefstathiou, T. Friščić, D.-K. Bučar, L.R. MacGillivray. *J. Am. Chem. Soc.*, **130**, 14366 (2008).
[20] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O.M. Yaghi. *Science*, **295**, 469 (2002).