

Inverted Metal-Organic Frameworks: Isorecticular 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 isorecticular frameworks. The construction of the frameworks is based on the application of a tetrafunctional organic cyclobutane ligand synthesized in the organic solid state.

Introduction

Metal-organic frameworks (MOFs) comprise one- (1D), two- (2D), or three-dimensional (3D) 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 MOFs³⁻⁵ for separation,⁶ storage,⁷⁻⁸ detection⁹ and catalysis purposes, to name a few.¹⁰⁻¹¹ While 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 focused upon 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 two-dimensional (2D) ‘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) *rcitt*-tetrakis(4-pyridyl)cyclobutane (**4,4'-tpcb**) - a tetrapyridine obtained from a templated-directed synthesis performed in the organic solid state¹⁴ (**Fig. 1**, inset). 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 2D structure wherein the cyclobutane

ligand serves as a four-connected node within a (4,4)-topology. The grids of the 2D framework are defined by sizable cavities (**Fig. 1**), which stack to produce 1D 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

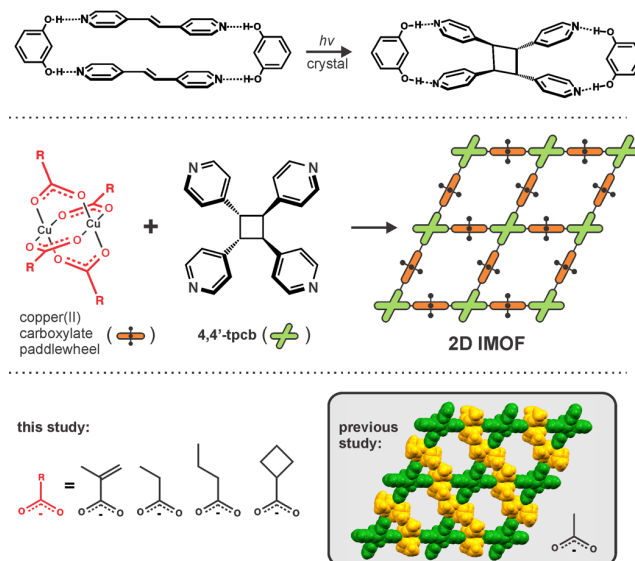


Figure 1. Solid-state synthesis of **4,4'-tpcb** (top) and 2D IMOFs using Cu(II) carboxylate paddlewheels and **4,4'-tpcb** (middle). Inset depicts structure of IMOF-1 based on Cu(II) acetate paddlewheel and **4,4'-tpcb** (bottom).

functionalize the size and shape of the copper(II) paddlewheel; namely, inward-directed methacrylate (**maa**), propionate (**pra**), butyrate (**bu**a) and cyclobutanecarboxylate (**cba**) anions (**Fig. 1**). Our work affords structurally-related, or isorecticular²⁰ 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 2D IMOF in the presence of CH₃OH and C₆H₆, namely [(Cu₂**maa**)₂(**4,4'-tpcb**)(C₆H₆)₈] (IMOF-2) (**Fig. 2**). IMOF-2 crystallises in the monoclinic space group *C2/m*. The framework displays a (4,4)-topology being structurally analogous to IMOF-1. Specifically, each **4,4'-tpcb** unit is surrounded by four paddlewheel

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	2D (flat)	rhombus - sides: 17.2 Å; corner angles: 75°, 105°; diagonals: 20.9 Å, 27.2 Å (channels)	CH ₃ OH/C ₆ H ₆	3 C ₆ H ₆
2	maa	2D (flat)	rhombus - sides: 17.2 Å; corner angles: 86°, 94°; diagonals: 23.5 Å, 25.2 Å (channels)	CH ₃ OH/C ₆ H ₆	8 C ₆ H ₆
3	pra	2D (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 ₃ CN/CHCl ₃	4 CH ₃ CN, 2 CHCl ₃
4	bua	2D (flat)	rhombus - sides: 17.2 Å; corner angles: 70°, 110°; diagonals: 19.7 Å and 28.3 Å (isolated compartments)	CH ₃ CN/C ₆ H ₆ /DMF	2 CH ₃ CN, 2 C ₆ H ₆
5	cba	2D (flat)	rhombus - sides: 17.2 Å; corner angles: 79°, 101°; diagonals: 21.9 Å, 26.6 Å (isolated compartments)	C ₄ H ₈ O/C ₃ H ₇ NO	2 C ₄ H ₈ O, 2 C ₃ H ₇ NO

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 2D 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) (**Fig. 2a**). 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 (**A**₁ and **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 (**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 **A**₁ of adjacent frameworks (**Fig. 2b**). The IMOFs are stacked in an offset fashion along the crystallographic (201) plane. Compartments **A**₁ and **A**₂ of the stacked IMOFs overlay to give rise to 1D channels that run along the crystallographic *c*-axis. The channels account for 28% of the unit cell volume (*i.e.* nearly 1100 Å³) and are occupied by C₆H₆ molecules (eight C₆H₆ guest molecules per **4,4'-tpcb** ligand, **Fig. 2c**).

Structure of IMOF-3. Reaction of Cu(II)-**pra** and **4,4'-tpcb** in acetonitrile and chloroform resulted in the formation of the corrugated 2D IMOF [(Cu₂**pra**)₂(**4,4'-tpcb**)(CH₃CN)₄(CHCl₃)₂] (IMOF-3) with a (4,4)-topology (**Fig. 3a,b**). IMOF-3 crystallizes in the triclinic space group *P*-1. Each **4,4'-tpcb** unit acts as a 4-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.

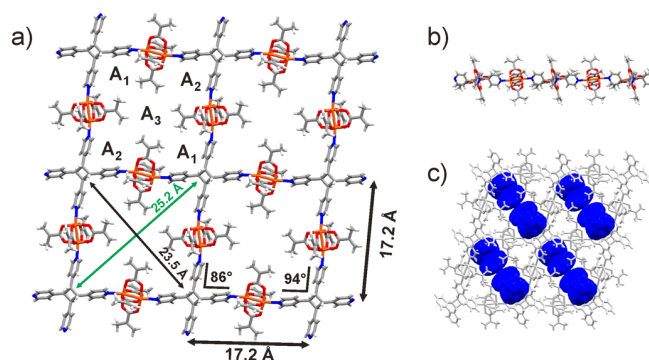


Figure 2. X-ray crystal structure IMOF-2: a,b) 2D structure and c) packing viewed along crystallographic *c*-axis (grey: host framework; blue: C₆H₆).

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**) 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. 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 **B**₁ and **B**₂), while cavity **C** is apportioned into three compartments (type **C**₁ and **C**₂). The IMOFs are stacked along the crystallographic plane (001), with compartments **C**₁ and **C**₂ forming 1D channels that run along the crystallographic *a*-axis. Compartments **B**₁ and **B**₂ host acetonitrile molecules, while

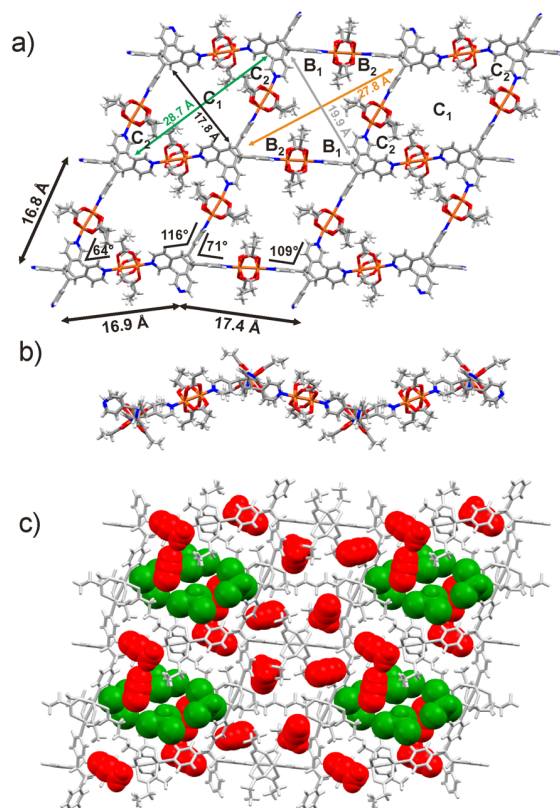


Figure 3. X-ray structure of IMOF-3: a,b) corrugated structure and c) packing along crystallographic *a*-axis (grey: host framework; red: CH₃CN; green: CHCl₃).

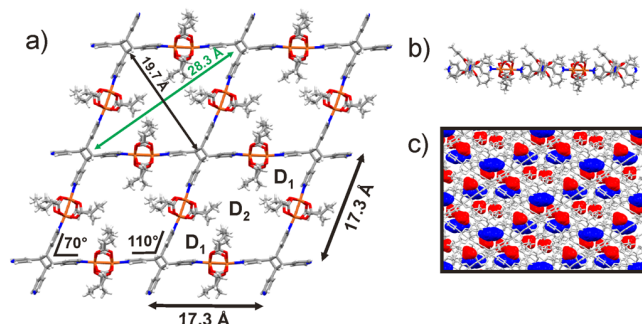


Figure 4. X-ray structure of IMOF-4: a,b) flat 2D structure of 3, and c) crystal packing of 3 viewed along the crystallographic plane (-20-1) (grey: host framework; blue: C₆H₆; red: CH₃CN).

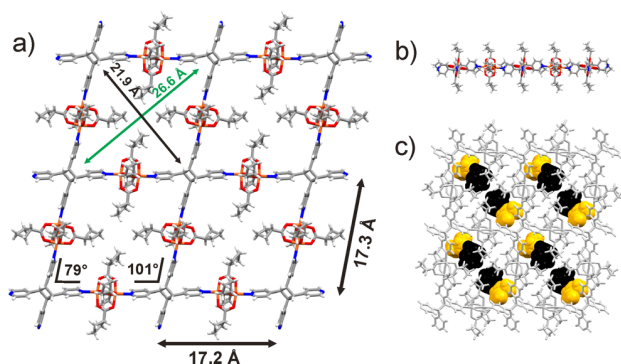


Figure 5. X-ray structure of IMOF-5: a,b) 2D structure and c) packing along crystallographic *a*-axis (grey: host framework; orange: C₄H₄O; black: C₃H₇NO).

compartments **C**₁ and **C**₂ host acetonitrile and chloroform molecules. The channels and compartments account for 30.4% of the unit cell volume (*i.e.* 1113.9 Å³) and accommodate four acetonitrile and two chloroform guest molecules per **4,4'-tpcb** ligand) (Fig. 3c).

Structure of IMOF-4. Crystallisation of Cu(II)-**bu**a with **4,4'-tpcb** from a solution of benzene, acetonitrile, and DMF afforded [(Cu₂**bu**a₄)₂(**4,4'-tpcb**)(C₆H₆)₂(CH₃CN)₂] (IMOF-4). The 2D IMOF crystallises in the monoclinic space group *C2/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 (Fig. 4). The **4,4'-tpcb** ligand lies on a proper 2-fold rotation axes, while the paddlewheel moieties are on an improper 2-fold-rotation axis. IMOF-4 displays large framework cavities of edge lengths (17.3 Å) (denoted as cavity **D**, Fig. 4a), 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 **D**₁) and one larger compartment (type **D**₂). The **D**₁ compartments are located at rhombus corners that display an obtuse angle, while the large compartment **D**₂ occupies the center of the rhombic cavity. The other two **bu**a anions point above and below the plane of the 2D IMOF and are accommodated by compartments **D**₂ of adjacent IMOFs. The IMOFs stack offset along the crystallographic (-201) plane. Compartments **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 Å³) 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)-**cb**a paddlewheel and **4,4'-tpcb** in tetrahydrofuran and dimethylformamide generated [(Cu₂**cb**a₄)₂(**4,4'-tpcb**)(C₄H₈O)₂(C₃H₇NO)₂] (IMOF-5), which crystallises in the triclinic space group *P*-1. The components assemble to form a planar 2D 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**, Fig 5). As in IMOF-1, two of the four **cb**a paddlewheel anions point into the interior of the cavities and divide the cavities into five smaller

compartments. The two compartments (type **E**₁) located at corners that display an obtuse angle are larger in size than the compartments (type **E**₂) located at corners of the rhombus featuring acute angles. The fifth compartment, located in the center of the rhombic cavity, is significantly smaller in size than **E**₁ and **E**₂ and cannot accommodate guest molecules. The further two **cba** anions are directed perpendicularly above and below the plane of the 2D IMOF and point into the compartments **E**₁ belonging to adjacent IMOFs. The IMOFs are stacked in an offset fashion along the crystallographic (-11-1) plane. Compartments **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 Å³) and are fully occupied by C₄H₈O and C₃H₇NO molecules (two C₄H₈O and two C₃H₇NO 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 2D structures to be preserved to generate isorecticular 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 re-shaping of the rhombic openings into more pronounced parallelogram-like openings.

The 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 1D channels (IMOFs-**2** and **3**) while 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. While both factors can be attributed to the changes in the size and shape of the utilized paddlewheel anion, the packing modes of the IMOFs are likely influenced by crystallisation 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 2). 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 a Cu paddlewheel complex. The decoration leads to isorecticular 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.

ASSOCIATED CONTENT

Supporting Information. Crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>. CCDC 2047781-2047784 for **2-5**.

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