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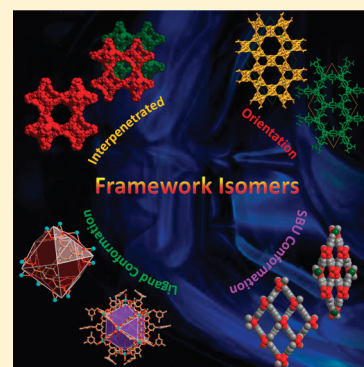
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# Isomerism in Metal–Organic Frameworks: “Framework Isomers”

Trevor A. Makal, Andrey A. Yakovenko, and Hong-Cai Zhou\*

Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, Texas 77842, United States

**ABSTRACT:** Metal–organic frameworks (MOFs) are very important in the development of new technologies and study of gas storage and separation. MOFs are based on the complexation of metal clusters with organic ligands. Occasionally, the same building components combine in multiple different ways to produce different structures. These different structures are what we would call “framework isomers.” This type of isomerism is unique to the field of MOFs. In this Perspective, we classify the different types of framework isomers and provide examples of each type. Additionally, we provide an analysis of the structure/property relationship. In addition, possible methods for future control over the synthesis of a particular framework isomer and characterization techniques have also been discussed.



The first decade of the new millennium has seen rapid progress in the field of metal–organic frameworks (MOFs).<sup>1–8</sup> These materials have generally been synthesized by combining different metal salts with various organic ligands under a variety of reaction conditions. Usually, for each “metal–ligand combination” only one framework is produced. However, in some cases such a combination forms two, three, or more frameworks with different structures and properties. The potential diversity of such isomerization and distinct characteristics of each framework isomer necessitate the study, organization, and development of nomenclature to fully define and understand their unique behaviors.

Previous researchers have studied and attempted to define such phenomena. However, no term has been presented in the literature that appropriately describes these systems with general acceptance by the scientific community.<sup>9,10</sup>

The most closely related term currently available to describe such framework isomers is “polymorphs.” However, polymorphs are defined as compounds that are identical in composition, but with different crystal packing, often reflected by different space groups and unit cell parameters. By contrast, MOFs very often contain pores that are filled with solvent. Sometimes these guest molecules can be different, or the number of molecules associated with the framework may be different. Hence, we cannot describe them as polymorphs. The most accurate term for describing these types of materials would be solutes. However, in most cases, the solvate residing in the pores is quite disordered, preventing the accurate determination of position or number of its molecules in each case. Thus, researchers “squeeze” those solvent molecules from the structure and primarily discuss the topology of the framework itself. In this case, it is much more logical to refer to these materials as “framework isomers”.

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The term “framework isomers” has previously been used “to describe structurally similar but conformationally distinguished... frameworks... which arise from different anions and solvent molecules.”<sup>11</sup> However, a number of interpenetrated and non-interpenetrated frameworks have been reported.<sup>12–14</sup> The nets that make up these frameworks are structurally and conformationally the same but differ by the level of interpenetration within the structures. Therefore, in our mind, we must also call them “framework isomers”.

To clarify, we provide the following definition of framework isomers: MOFs constructed from the same ligand and metal species that display different network structures (Figure 1). This implies that the construction of networks from isomers of building units (such as R and S isomers of an organic ligand) do

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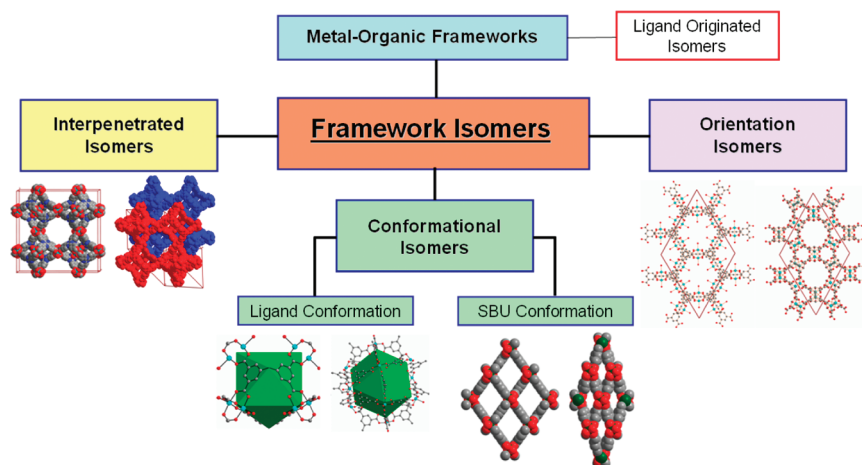


Figure 1. Schematic representation of the classification of framework isomers.

not form framework isomers. We would, instead, refer to them as ligand-originated isomers.

From careful analysis of the literature, we have identified three distinct groups of framework isomers. The first group has been well-studied and reported, and is termed “interpenetration” or “catenation isomers”. Materials in this group are defined by the parameters mentioned above. The second group is termed “conformational isomers”. These isomers contain the same secondary building unit (SBU) and ligand, but differ based upon the conformation of one or more of these building units (different twists or bends of bonds). The third, and seemingly most rare, group is termed “orientation isomers”. These isomers are composed of ligand and SBU which, taken as independent entities, are indistinguishable based upon atomic makeup, connectivity, symmetry, or any other factors. The isomers are generated by the different orientations of the ligands and/or SBUs within the crystal structures.

In this Perspective, we aim to exemplify each of these classifications of isomers with examples from the literature. Both similarities and differences in structure and properties of each group have been discussed. Synthetic conditions for controlled synthesis of individual isomers have been identified, with an attempt to elucidate the process by which one isomer is formed over the other.

We will first examine a few examples of interpenetration/catenaion isomers. One of the representative sets of catenation isomers was introduced with the isorecticular metal–organic framework (IRMOF) series.<sup>12</sup>

The IRMOF series first published in 2002 in *Science* by Yaghi and co-workers systematically explored the isorecticular synthesis of MOFs.<sup>12</sup> Additionally, they synthesized four pairs of catenation isomers: IRMOF-9/10, IRMOF-11/12, IRMOF-13/14, and IRMOF-15/16. Following reaction conditions similar to that of MOF-5 (IRMOF-1), they obtained doubly interpenetrated MOFs IRMOF-9, -11, -13, and -15 by extending the linear ditopic ligand from 1,4-benzene-dicarboxylate for IRMOF-1 to [1,1'-biphenyl]-4,4'-dicarboxylate (BPDC), 4,5,9,10-tetrahydropyrene-2,7-dicarboxylate (HPDC), pyrene-2,7-dicarboxylate (PDC), and [1,1':4',1''-terphenyl]-4,4''-dicarboxylate (TPDC), respectively. While this led to the discovery of new isomers, the original goal was to synthesize an isorecticular series. Through the use of more dilute reaction solutions, the noninterpenetrated counterparts IRMOF-10, -12, -14, and -16 were obtained, thereby completing their isorecticular series.

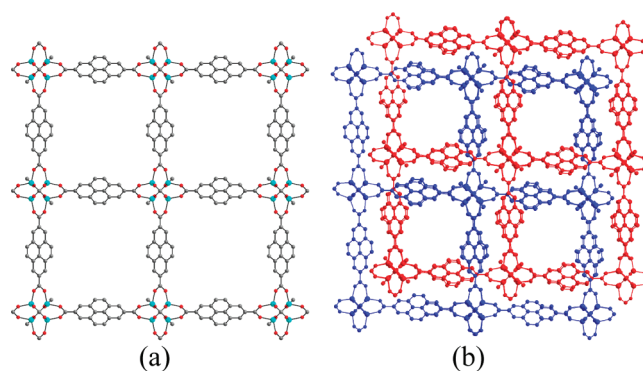


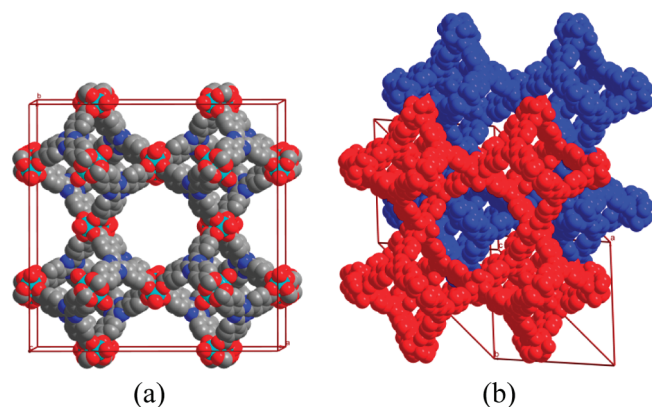
Figure 2. Structures of noninterpenetrated IRMOF-14 (a) and interpenetrated IRMOF-13 (b) viewed from the  $[4 -4 7]$  direction.

While each set of catenation isomers mentioned above exemplifies the theme of this Perspective, we choose to elaborate on IRMOF-13 and -14.

The cubic IRMOF-14 (Figure 2a) crystallizes in the space group  $Fm\bar{3}m$  from the reaction of  $H_2PDC$  and  $Zn(NO_3)_2 \cdot 4H_2O$  in *N,N*-diethylformamide (DEF) under solvothermal conditions. Six carboxylates bind on the edges of the well-known  $Zn_4O$  tetrahedral metal cluster to form the octahedral SBU. The combination of an octahedral SBU with linear organic ligand leads to the formation of a three-dimensional cubic net.

The doubly interpenetrated IRMOF-13 crystallizes in the rhombohedral space group  $R\bar{3}m$ . The two independent cubic nets that form IRMOF-13 have been highlighted in Figure 2b. Since the two nets do not occupy exactly the center of the open space of the other, a reduction in the symmetry of the framework occurs.

These structural differences between catenation isomers lead to significant differences in pore aperture size, accessible pore volume, crystal density, and surface area. In general, interpenetration leads to a decrease in the first two values and an increase in crystal density. The surface area, on the other hand, should generally decrease with interpenetration in principle. While this may initially appear as a disadvantage for interpenetrated networks, the changing of pore size very close to that of the target guest and the improved stability of the porous framework have been shown to impose dramatic effects on both the guest selectivity of the



**Figure 3.** (a) Structure of noninterpenetrated PCN-6' and (b) doubly interpenetrated PCN-6.

material as well as the overall gas loading. On the other hand, the formation of large, noninterpenetrated networks with pores in the mesoporous range (2–50 nm) may lead to the development of materials that can accommodate large molecules, such as pharmaceuticals, proteins, and enzymes.

Several pairs of isomers were synthesized by controlling the concentration of the reaction solutions. A concentrated reaction solution leads to the crystallization of the doubly interpenetrated network, whereas more dilute reaction conditions do not promote interpenetration. The growth of two independent nets within one another would require a large number of reacting species to be in close proximity to each other. When the concentration of reactants is lower, components that come in close contact with an initially forming net will bind to extending sites rather than form a second net. While this is a somewhat straightforward method for developing supramolecular isomers and controlling interpenetration, it is tricky to find the threshold of concentration that will promote or inhibit catenation completely.

It is imperative to learn how to further control interpenetration through other methods such as using a template. One such study has been demonstrated for two pairs of isomers, including the isomer pair PCN-6'<sup>15</sup> and PCN-6'.<sup>13</sup> Both isomers are reaction products of copper(II) salts with 4,4',4''-s-triazine-2,4,6-tris(tribenzoic acid) ( $H_3TATB$ ) except for the reaction conditions: for the noninterpenetrated isomer, oxalate was used as a template. Presumably, the metal salt reacts with oxalate to form a tentative oligomer, which releases metal building units that further react with ligands. The released oxalates would hinder the formation of the second network in close proximity to the first one, practically inhibiting interpenetration.

The structures of doubly interpenetrated PCN-6 and noninterpenetrated PCN-6' isomers, determined by single crystal X-ray diffraction analysis, are shown in Figure 3. The network in PCN-6' has cubic space group symmetry  $Fm\bar{3}m$ , and is isostructural with the HKUST-1 network. In the network, dicopper tetracarboxylate paddlewheel units connect among each other through linkers. Such connection leads to the formation of the framework with cuboctahedral and octahedral cavities. The average size of the void inside the cuboctahedron is about 30 Å, while open square channels are 21.44 Å in size (atom to atom distances).

The structure of PCN-6 is formed by two identical interpenetrated nets shifted one from the other by 3.45 Å. Because of this, the overall symmetry of the interpenetrated isomer lowers from

$Fm\bar{3}m$  to  $R\bar{3}m$ . Figure 3 shows the packing of pores in PCN-6', where the octahedra of the first net are located inside the cuboctahedral cavities of the other. Due to such interpenetration, the channel size in the framework is reduced to 9.2 Å.

Such difference in the size of the openings is reflected by the solvent-accessible volume for the two frameworks. In the case of PCN-6' it is 86%, while for PCN-6 it is 74%. Therefore, we should expect better gas adsorption properties for the noninterpenetrated isomer. However, low-pressure  $N_2$  sorption measurements at 77 K have shown that the Langmuir surface area for PCN-6 (3800 m<sup>2</sup>/g) is 41% larger than for PCN-6' (2700 m<sup>2</sup>/g). This unusual fact can be explained by the formation of new adsorption sites in the interpenetrated framework and increasing of the interaction energy between framework walls and guest molecules. There also exists the strong possibility of framework partial decomposition of the noninterpenetrated framework.

Similar results have been reported in the  $H_2$ <sup>16</sup> and  $CO_2$ <sup>17</sup> adsorption measurements. For example, low-pressure adsorption measurements have shown that PCN-6 at 760 Torr and 77 K adsorbs 1.9 wt % of hydrogen, whereas PCN-6' can adsorb only 1.62 wt %.

The most interesting research for these two isomers involves their controlled synthesis. In fact, two successful methods have been reported for the synthesis of the interpenetrated and noninterpenetrated forms.

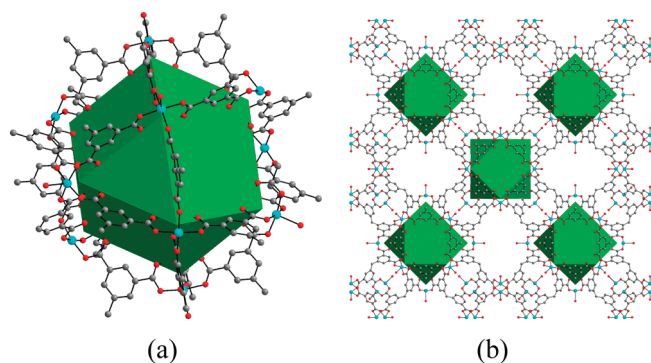
The first method, which has been discussed briefly above, involves the use of the oxalate anion as a template.<sup>16</sup> The reaction between copper(II) salts and  $H_3TATB$  in dimethylamine (DMA), dimethylformamide (DMF), DEF or dimethyl sulfoxide (DMSO), in the presence of oxalic acid, results in the noninterpenetrated PCN-6', while the reaction under the same conditions, but without the addition of oxalic acid, produces the interpenetrated PCN-6.

The second method uses different energy in ultrasonic synthesis of the materials.<sup>17</sup> It was shown that both PCN-6 and PCN-6' can be synthesized in 1 h by ultrasonication of the solution at 20 kHz. By applying different power, researchers found that at low sonication power (150 W) the noninterpenetrated framework was produced, while at high sonication levels (300 W) the production of the interpenetrated product is dominant. It is also interesting that, by using sonication power between 150 and 300 W, mixtures of both isomers are produced. It was also found that when higher power sonication is used, a larger percentage of the interpenetrated framework is synthesized. A similar method has been used for the controlled synthesis of IRMOF-9 and IRMOF-10.

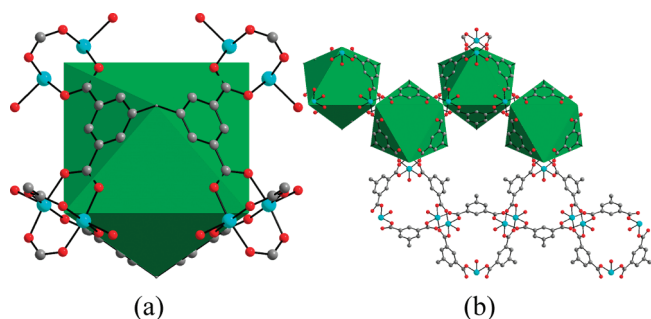
Conformational isomers are typically not as simple as interpenetration isomers. These materials differ by conformation of building units and a number of such isomers have been previously reported in the literature.<sup>18–22</sup> Here we present two examples of conformational framework isomers.

The PCN-12 and -12' set of framework isomers were first published in 2008 by Zhou and co-workers.<sup>23</sup> They documented an interesting case of the symmetry of the organic ligand controlling alignment of coordinatively unsaturated metal centers (UMCs). The two materials are composed of dimetal copper paddlewheels and 5,5'-methylene-di-isophthalate (MDIP) as the building units with water molecules binding the axial coordination sites of the paddlewheels. The combination of isophthalate and the dimetal paddlewheel may lead to the formation of two different types of supramolecular polyhedra: a cuboctahedron and an anticuboctahedron. Furthermore, the addition of a flexible





**Figure 4.** (a) A single cuboctahedron in PCN-12 formed from isophthalate moieties and dicopper paddlewheel SBUs. (b) Packing of cuboctahedra in PCN-12 viewed along the  $c$ -axis.



**Figure 5.** (a) One tricapped trigonal prism in PCN-12' (methylene bridge of MDIP and center of copper paddlewheels taken as vertices). (b) Packing of polyhedra in PCN-12' to form a Kagome pattern, viewed in the  $ab$ -plane.

linkage between two of these isophthalate moieties leads to inherent variations in possible topologies of the extended structure. Namely, the MDIP ligands may be found in one of two extreme conformations: a form with  $C_s$  symmetry, in which the two phenyl rings of MDIP are perpendicular to one another, and a  $C_{2v}$  symmetric form.

The reaction of  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  and  $\text{H}_4\text{MDIP}$  in DMA at 85 °C forms PCN-12,  $[\text{Cu}_6(\text{C}_s\text{-MDIP})_2(\text{C}_{2v}\text{-MDIP})(\text{H}_2\text{O})_6] \cdot 3\text{DMA} \cdot 6\text{H}_2\text{O}$ , which crystallizes in the tetragonal space group  $P4_1/mmm$ . The isophthalate moieties bind the paddlewheel SBUs to form octahedral polyhedra, as expected (Figure 4). These polyhedra are then extended into a porous three-dimensional framework by the methylene bridge connecting another cuboctahedron. Furthermore, the removal of coordinated solvent molecules leads to UMCs that are aligned toward the center of each polyhedral cage.

Using the same reactants in DMSO at 120 °C produces crystals of PCN-12',  $[\text{Cu}_2(\text{C}_{2v}\text{-MDIP})(\text{H}_2\text{O})_2] \cdot 3\text{DMSO}$ . The framework crystallizes in the space group  $P6_3/mmc$  and all MDIP ligands have only  $C_{2v}$  symmetry. Due to the binding pattern of all  $\text{C}_{2v}$ -MDIP to paddlewheels, none of the expected polyhedra, cuboctahedra, and anticuboctahedra were observed, but rather what can be viewed as a tricapped-trigonal-prism, when copper paddlewheels and the methylene bridge of MDIP are considered vertices (Figure 5a). Consequently, unlike PCN-12, after solvent removal, none of the UMCs in PCN-12' are directed toward the center of the polyhedral cages. The extended structure when viewed in the  $ab$ -plane has the symmetry of a Kagome pattern (Figure 5b).

Upon solvent removal, PCN-12 and -12' have the same formula as well as the same atom-to-atom connectivity. In terms of per-

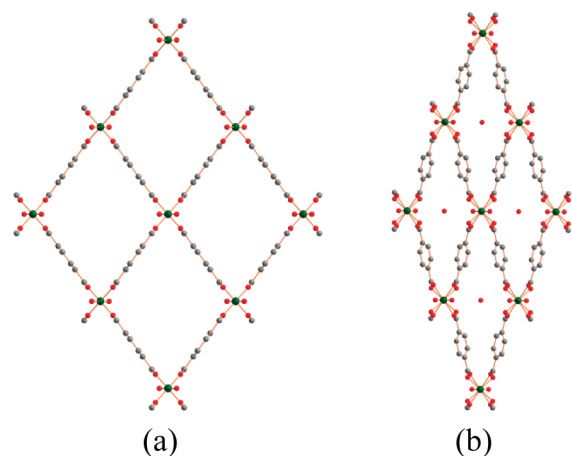
formance, however, PCN-12 takes up 27% more dihydrogen (gravimetric uptake) than PCN-12'. This increase in performance is attributed to the proper alignment of UMCs in the framework toward the center of each pore. The alignment of UMCs maximizes  $\text{M}-\text{H}_2$  interactions and increases accessibility without imposing unnecessary steric constraints upon adsorption. The reasoning behind the formation of isomeric frameworks lies in the symmetry of the MDIP ligand and can be explained by kinetic and thermodynamic favored products. In PCN-12, the  $\text{C}_{2v}$ -MDIP forms an angle between phenyl rings at the methylene C atom,  $\theta$ , and dihedral angle ( $110.6^\circ$  and  $110.3^\circ$ , respectively) very near ideal ( $109.5^\circ$ ). However, the  $\text{C}_s$ -MDIP has a dihedral angle of  $89.6^\circ$  and  $\theta = 116.2^\circ$  due to repulsions generated from the close proximity of two phenyl rings. It seems intuitive that higher temperatures may convert  $\text{C}_s$ -MDIP to the higher symmetry  $\text{C}_{2v}$  form, which is exactly what is observed in PCN-12'. While solvent may often play a role in the formation of different frameworks, in this case the solvent appears to be a secondary factor, whereas the temperature of the solvothermal reaction appears to be the primary reason for different structures.

In many cases, stability of the system after solvent removal proves to be a difficult hurdle to overcome, and generation of a kinetically rather than thermodynamically favored framework may seem like a step in the opposite direction. However, due to the presence of dicopper paddlewheel SBUs and the limited flexibility of the MDIP linkers, PCN-12, as well as PCN-12', retains crystallinity even upon solvent removal. This example describes the realization of isomeric porous frameworks by controlling the symmetry of organic ligands through fine-tuning of reaction temperatures. This technique may be applied in future studies to produce a variety of target frameworks and numerous supramolecular isomers.

Another interesting example of conformational framework isomers, which appear due to the change in the parameters of the metal center coordination geometry, was reported by Férey's group. It has been found that some MOFs formed by reaction of terephthalic acid with trivalent metal ions such as  $\text{Fe}^{3+}$ ,<sup>24</sup>  $\text{Al}^{3+}$ ,<sup>25</sup> and  $\text{Cr}^{3+26}$  can reversibly change the shape of their pores or channels. This structural change was termed a "breathing effect" and was found during the hydration–dehydration process of the frameworks. Here we will present results for the compound MIL-53(Cr),<sup>26</sup> which shows the highest breathing effect in this series.

MIL-53as (as = as synthesized) has been synthesized by the reaction of  $\text{Cr}(\text{NO}_3)_3$  with terephthalic acid ( $\text{H}_2\text{BDC}$ ) in water in the presence of hydrofluoric acid (HF). The synthesized compound appeared as a light purple powder. It was heated at 300 °C to obtain its calcinated form, MIL-53ht (ht = high temperature). All attempts to alter the conditions to obtain suitable single crystals failed; therefore the structure of the material was determined from X-ray powder diffraction studies.

It was found that both as-synthesized and calcinated materials crystallized in orthorhombic space groups with very similar unit cell parameters. They also had analogous three-dimensional framework structures, built from chromium-(III) octahedral SBU and BDC ions (Figure 6). This framework has a one-dimensional pore system with square-like channels. The main difference between the two materials is the presence of two molecules of unreacted  $\text{H}_2\text{BDC}$  in the channels of MIL-53as, while the cavities of MIL-53ht are empty. The channel size of MIL-53ht ( $16.73 \times 13.04 \text{ \AA}^2$ ) is almost the same as those for MIL-53as ( $17.34 \times 12.18 \text{ \AA}^2$ ).



**Figure 6.** (a) Structure of MIL-53ht (structure of MIL-53as is the same, except that it contains two molecules of  $\text{H}_2\text{BDC}$  in the pores) and (b) MIL-53lt.

Upon cooling MIL-53ht in air, the authors repeated X-ray diffraction measurements and found that the material had changed its crystallographic symmetry from orthorhombic  $Imcm$  to monoclinic  $C2/c$ . They named this new compound MIL-53lt (lt = low temperature). After X-ray structure investigation, it was revealed that in MIL-53lt the framework remained the same (Figure 6); however, the parameters of the channels changed dramatically to  $19.69 \times 7.85 \text{ \AA}^2$ . This was attributed to the presence of water molecules in the channels, which formed hydrogen bonds with  $\eta^2$ -OH groups in the metal cluster. These strong interactions between guest molecules and corners of the channels caused the pores to close. Because of this interaction, the shape of the channels changed from square-like to rhombus-like.

It is worth mentioning that the structural parameters of the BDC ligands in this transition change slightly; the dihedral angle between average planes of two adjacent BDC ligands opens from  $108^\circ$  in MIL-53ht to  $142^\circ$  in MIL-53lt.

It appears that this particular transition is reversible. The opening and closing of the pores can be reproduced using hydration–dehydration cycling. Also during the solvent sorption studies, it was found that only MIL-53ht can adsorb molecules of DMF into the cavities, while MIL-53lt adsorbed no DMF even after 4 days of immersion in the solvent.

We can see that MIL-53 compounds are very interesting examples of conformational framework isomers. The isomerism in this case is due to the change of the coordination parameters of the metal center, and does not depend on the conformation of the ligand. This work also demonstrates the potential for determining MOF structure through methods other than single-crystal diffraction methods. The authors were able to apply powder X-ray diffraction techniques to identify and determine the structures of all framework isomers.

It is necessary at this point to emphasize that the previous cases are straightforward examples of framework isomers. However, in MOF chemistry, the possibility of formation of multiple types of framework isomers must be considered. An example of this has been recently described by Xu.<sup>27</sup> In this report, the authors describe the controlled synthesis of three framework isomers,  $\text{Cd}(\text{abdc})\text{bipy}$  (abdc = 2-amino-1,4-benzenedicarboxylate, bipy = 4,4'-bipyridine). By heating a reaction mixture of  $\text{Cd}(\text{II})$  salt and ligands at  $105^\circ\text{C}$ , they identified a noninterpenetrated pillar-layer structure,  $\text{Cd}(\text{abdc})\text{bipy-1}$

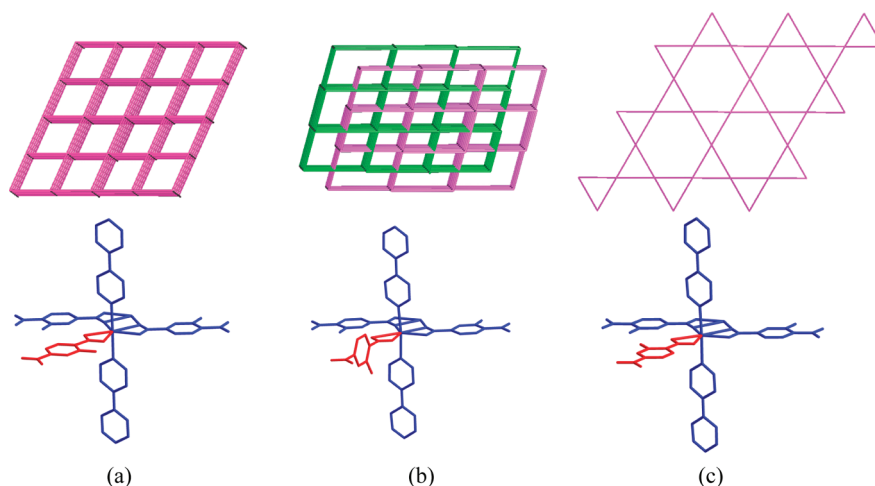
(Figure 7a). By increasing the reaction temperature to  $160^\circ\text{C}$ , a doubly interpenetrated isomer was observed,  $\text{Cd}(\text{abdc})\text{bipy-2}$  (Figure 7b). At the same time, the single nets of  $\text{Cd}(\text{abdc})\text{bipy-1}$  and  $\text{Cd}(\text{abdc})\text{bipy-2}$  are conformational isomers due to a  $\sim 90^\circ$  rotation of one abdc ligand in the asymmetric unit. Furthermore, by decreasing the reaction concentration and reaction time, the authors were able to synthesize  $\text{Cd}(\text{abdc})\text{bipy-3}$ , which may be viewed as a conformational isomer of  $\text{Cd}(\text{abdc})\text{bipy-1}$  (Figure 7c).  $\text{Cd}(\text{abdc})\text{bipy-3}$  exhibits the same structure as  $\text{Cd}(\text{abdc})\text{bipy-1}$  except that a  $180^\circ$  rotation of one abdc ligand in the asymmetric unit leads to an opening of the channel.

Understandably,  $\text{Cd}(\text{abdc})\text{bipy-1}$  and  $\text{Cd}(\text{abdc})\text{bipy-2}$  may not interconvert postsynthesis. However,  $\text{Cd}(\text{abdc})\text{bipy-1}$  and  $\text{Cd}(\text{abdc})\text{bipy-3}$  may undergo conformational changes that interconvert between the two structures. This was observed upon heating  $\text{Cd}(\text{abdc})\text{bipy-1}$  under pressure to generate  $\text{Cd}(\text{abdc})\text{bipy-3}$ , and exposing  $\text{Cd}(\text{abdc})\text{bipy-3}$  to air to reform  $\text{Cd}(\text{abdc})\text{bipy-1}$ . From this example we can clearly observe the complexity and flexibility of framework isomer systems.

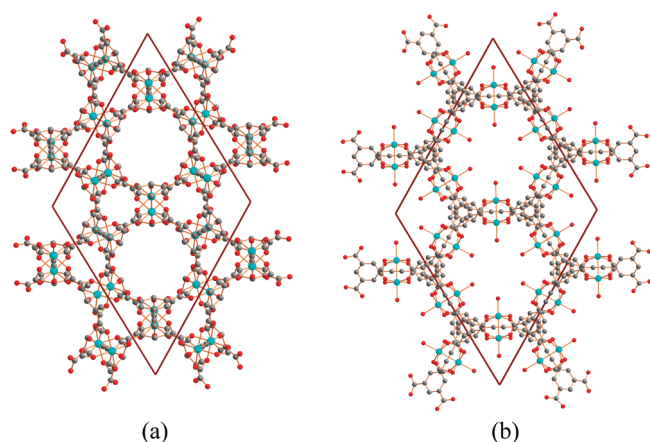
Porous MOFs of NbO topology are numerous in literature.<sup>28–35</sup> The assembly of tetracarboxylate organic ligands with dimetal paddlewheel SBUs often leads to the formation of NbO-type networks, which possess two different types of channels. In 2010, the Zhou<sup>36</sup> and Chen<sup>37</sup> research laboratories independently published the formation of a new NbO-type MOF through combination of rectangular tetracarboxylate organic ligand [5,5'-(1,2-ethyenediyl)bis(1,3-benzenedicarboxylate)] (EBDC) and dicopper paddlewheel SBU. While both papers described the familiar NbO-type structure, the Zhou group noted an extremely rare find: a second NbO-type MOF that is a symmetry-preserving isomer of the framework reported on both accounts. The two different phases were named PCN-16 ( $\alpha$ -phase) and PCN-16' ( $\beta$ -phase). When EBDC is viewed as a discrete molecule, the rectangular ligands when oriented as “portrait” or “landscape” are indistinguishable. However, when crystallized in a framework, this difference in orientation leads to the observation of two distinct phases that possess the same composition, atom-to-atom connectivity, and symmetry ( $R\bar{3}m$ ). Therefore, we can call these isomers orientation isomers. The distinctions between frameworks become obvious when considering the two types of cavities present in each structure. Furthermore, viewing both structures along the  $c$ -axis (Figure 8) quickly provides verification for the formation of two separate phases.

The formation of  $\alpha$ - and  $\beta$ -phase isomers of NbO-type frameworks was realized in a manner similar to that for the isomers PCN-12 and -12'. The reaction of  $\text{H}_4\text{EBDC}$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  under different solvothermal conditions formed the isomeric networks. Upon removal of noncoordinated solvent, both networks are of the formula  $\text{Cu}_2(\text{EBDC})(\text{H}_2\text{O})_2$ .

PCN-16 has been synthesized under two different sets of solvothermal reaction conditions. The first, reported by Chen and co-workers, was in a mixture of DMF, DMSO, and nitric acid at  $65^\circ\text{C}$ . The second, from Zhou and co-workers, was from a solution of DMA with a small amount of  $\text{HBF}_4$  at  $75^\circ\text{C}$ . The additional acid in most MOF synthesis serves to reduce the reaction rate in order to form large, high-quality single crystals for XRD. PCN-16', on the other hand, was synthesized from a solution of DMF and ethanol at  $65^\circ\text{C}$ . The pores of PCN-16' are slightly larger than those of PCN-16, leading to significant differences in physical properties, including gas adsorption.



**Figure 7.** Topological view and rotation of 2-amino-1,4-benzenedicarboxylate ligand in the coordination environment of Cd atoms for three framework isomers: Cd(abdc)bipy-1 (a), Cd(abdc)bipy-2 (b), and Cd(abdc)bipy-3 (c).



**Figure 8.** The structure of the  $\alpha$ -phase (a) and  $\beta$ -phase (b) networks of PCN-16 and PCN-16' viewed along the  $c$ -axis.

The surface areas of both materials were determined from  $N_2$  sorption isotherms recorded at 77 K. PCN-16 has a Brunauer–Emmett–Teller (BET) surface area of  $2273 \text{ m}^2 \text{ g}^{-1}$  ( $2800 \text{ m}^2 \text{ g}^{-1}$ , Langmuir surface area) whereas the BET surface area of PCN-16' is  $1760 \text{ m}^2 \text{ g}^{-1}$  ( $2200 \text{ m}^2 \text{ g}^{-1}$ , Langmuir surface area). Additionally, the hydrogen uptake for PCN-16 is much higher than for PCN-16'. This performance enhancement may be attributed to the smaller pores found in PCN-16. Smaller pores result in an increase in the overlap potential between framework and guest species.

Theoretically, any NbO-type framework based on rectangular tetracarboxylate linkers and paddlewheel SBUs should exist in both  $\alpha$ - and  $\beta$ -phases, although no other  $\beta$ -phase frameworks have been reported, to date. Additionally, since the two phases are very similar to one another, it is very difficult to predict methods for synthesizing one phase over another. Analyzing the synthetic methods for PCN-16 and -16', there is no one factor that can be easily attributed to the formation of a specific framework. Undoubtedly, a combination of many factors, including solvent, addition of acid or base, and temperature, leads to the differences in framework formation.

In this Perspective we described several types of framework isomers and divided them into three categories: interpenetration,

conformational, and orientation isomers. From the reviewed literature, we have identified that interpenetration isomers are already quite well-known; however, only a few examples of conformational framework isomers have been studied and reported. This can be explained by the fact that combination of a specific SBU and ligand rarely forms multiple distinct frameworks. Additionally, use of alternative synthetic conditions often leads to the formation of new interpenetration isomers or different SBU building blocks to produce nonisomeric materials. Orientation isomers are even more rare, although, as shown through the above example, all NbO-type MOFs fitting the proper criteria are potential candidates for the formation of orientation isomers.

Since the pairs of isomers are structurally inequivalent, it is obvious that they will exhibit different physical properties. This structure/property relationship is fairly predictable for interpenetration isomers, yet somewhat elusive for conformational or orientation isomers. For instance, for interpenetration isomers, the interpenetrated form always possesses smaller pores than its noninterpenetrated counterpart, which often relates to greater stability and gas adsorption properties, due to increased potential overlap. In contrast, few generalizations can be made about structure/property relationships for conformational or orientation isomers due to the unexpected nature of framework construction. For the specific example of NbO-type frameworks, we may generalize that all  $\beta$ -phase isomers will exhibit lower gas uptake and surface area, but other types of orientation isomers have yet to be studied. To fill this void, we propose that additional computational research to study the structural formation of these isomeric frameworks should be performed.

**It is necessary to step outside the bounds of conventional thinking and push the limits of framework design and synthesis with modern, original methods.**



Since few properties of framework isomers change dramatically, there are a limited number of methods available to characterize them. Of course, ultimate structure determination may be obtained from single crystal diffraction analysis. However, this method necessitates the growth of high-quality single crystals, which may be very difficult to obtain for multiple isomeric forms. Also, this method does not determine the purity of the bulk material. We may speculate that since the majority of researchers use this method to characterize MOFs and do not always obtain high-quality single crystals, that many isomers have been overlooked. Researchers will often modify reaction conditions to obtain larger single crystals, yet, as has been noted, modification of reaction conditions may lead to the formation of different frameworks, altogether. Therefore, other forms of characterization should be developed and implemented, which do not necessarily provide atomic positions within a framework, but may differentiate between levels of interpenetration (i.e., 2-fold or 3-fold) and other properties.

While the characterization of these compounds is so difficult, the controlled synthesis of such materials remains even more elusive. Yet, the ultimate goal of designed synthesis of a specific framework isomer requires the attention of all researchers currently working in the MOF field. The discovery of all framework isomers, thus far, has been primarily by luck. Because of this fact, use of simply conservative methods for synthesis will not provide substantial forward progress in the field. It is necessary to step outside the bounds of conventional thinking and push the limits of framework design and synthesis with modern, original methods.

**The ultimate goal of designed synthesis of a specific framework isomer requires the attention of all researchers currently working in the MOF field.**

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: zhou@chem.tamu.edu.

## BIOGRAPHIES

**Trevor A. Makal** obtained his Bachelor's degree from Texas A&M University in 2008. That same year he joined Prof. Hong-Cai Zhou's research group as a Ph.D. student at Texas A&M University. His research interest focuses on the controlled formation, and eventual design, of metal–organic frameworks for application in gas storage for clean energy technologies.

**Andrey A Yakovenko** graduated from the D. Mendeleev University of Chemical Technology, Russia. After that, he completed his M.Sc. in Applied Chemistry at New Mexico Highlands University where he worked on X-ray structure determination of low-melting organic materials and their complexes with mercury-organic compounds. In 2008 he began his Ph.D. studies at Texas A&M University under the guidance of Dr. Zhou, working on new methods development for structural determination of MOF materials.

**Hong-Cai Joe Zhou** (<http://www.chem.tamu.edu/rgroup/zhou/>) obtained his Ph.D. in 2000 from Texas A&M University under the supervision of F. A. Cotton. After a postdoctoral stint at Harvard University with R. H. Holm, he joined the faculty of Miami University, Oxford, in 2002. Since the fall of 2008, he has been a professor of chemistry at Texas A&M University. His research interest focuses on gas storage and separations that are relevant to clean energy technologies.

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