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Reticular control of interpenetration in a heterogeneity metal-organic framework

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Metal-organic frameworks (MOFs) are a new generation of crystalline porous materials covering the broad spectrum of research fields due to its high porosity and feasible modification of structure. Owing to large void space, MOF structures tend to be more stable during the growth of crystals leading to interpenetrated frameworks. Control of interpenetrated frameworks in MOFs is not only useful for various kinds of practical application but also provides insight towards understanding the reaction process and catenated behavior in the MOF chemistry. In this research, we sought to investigate and successfully achieve how to reticularly control the interpenetration of PCN-280, a complex MOFs with 2-folds interpenetrated framework containing heterogeneity building blocks, two kinds of polytopic organic linking unit-based carboxylate, to form a new isoreticular single-frame MOF, termed MOF-908 and isoreticular MOF-909. The crystal structure and underlying network of MOF-908 and MOF-909 are proven by X-ray diffraction analysis as well as other related characterizations. Indeed, the mechanism of reticular control of the interpenetration of PCN-280 is studied in detail under the light of density functional theory (DFT) calculation.

Reticular chemistry at its best leads to open the window towards the blue sky of metal-organic frameworks (MOFs) chemistry, a highly-crystalline ordered material owning the permanent porosity and designable properties potentially applied for gas/vapor uptake, catalysis, energy conversion and chemical sensing. Interpenetration behavior widely comes from the huge void fraction of a large unit cell of MOF where the next-multi frameworks could grow to occupy the vacancy reckoning to stabilize the resulting structures. Given the fact that control the process of reaction in MOF synthesis, in which the interpenetration happens when increasing the lengths of organic likers, to obtain the host single frame is one of the most interesting studies for paving the way into understanding the mechanism of MOF’s growth, usually in connection with lack of full exploration in MOFs research.

Scheme 1 Synthetic strategy to produce hetetogeniety MOFs based on mixed linker system. From top to bottom: linking units containing the 3-topic (3-c), 2-topic (2-c) organic likers to react with 6-c Fe-based cluster to form complex MOFs including MOF-907,17 PCN-280,17 PCN-285,17 MOF-908, and MOF-909 whose topological networks are correspondingly presented.

It is noted that the interpenetration reportedly belongs to the MOFs material generated through the reaction of single carboxylate-based link–which, in some cases, could be the mixture of carboxylate and bipyridine linking units–and metal-oxo cluster.17 In order to entirely control the structures of interpenetrated frameworks,17 i) synthetic conditions were

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varied, for example the bulky molecules can be introduced into the reaction which unpredictably produces the host single frame or another different structure,\textsuperscript{14} ii) organic templates were utilized and somehow the interpenetrated control looks like trial and error;\textsuperscript{15} iii) the organic linker was functionalized to modify the geometrical direction of point of extension and carboxylate moiety;\textsuperscript{13} the coordinated/uncoordinated solvents removal was additionally carried out after the structure formation.\textsuperscript{15} Here, we report a strategy utilizing the power of reticular chemistry in control the structure of a tertiary MOF, we terminology this methodology “reticular control”, which is independently 2-folds interpenetrated framework formed by triangular 4,4',4''-benzene-1,3,5-triyl-tris(benzoic acid) (H$_2$BTB) and linear biphenyldicarboxylic acid (H$_2$BPDC) linkers and trigonal prism Fe$_3$O$_2$(CO$_3$)$_6$ cluster, a heterogeneity MOF reported by Zhou and co-workers termed PCN-280.\textsuperscript{17} Two complex MOFs, namely MOF-908 and MOF-909 (Scheme 1), the isoreticular single net of PCN-280, are successfully produced by reticular control of the rational input linkers using the mixture of H$_2$BPDC and 3,3'-azoBDC (azobenzene-3,3'-dicarboxylic acid). This is the first time the structure of a tertiary interpenetrated MOF is designedly controlled to achieve the non-interpenetrated framework. Indeed, the “deinterpenetration”, the process to remove the interpenetrated frameworks to obtain a single-frame structure, was not successfully either using the reported methods, varied synthetic conditions, using template, and bulky organic solvents or in the absence of 3,3'-azoBDC. The role of 3,3'-azoBDC in that reticular control is subsequently demonstrated by adopting density functional theory (DFT) calculations to explore the process of reaction. Both 3,3'-azoBDC$^{2-}$ and BPDC$^{2-}$ are competitive in the first reaction stage, but BPDC$^{2-}$ is more favorable to substitute 3,3'-azoBDC$^{2-}$ in a subsequent process, which leads to the formation of MOF-908. In terms of mechanical stability, we also verify that MOF-908 is much more stable than MOF-909. Not only has our finding provides the way to open the new insight of interpenetrated control in MOFs by reticular synthesis, but contributes to understanding of reaction process and mechanism in MOFs chemistry.

In response to verify the role of the geometrical requirement of both organic linkers in a heterogeneity MOF,\textsuperscript{18} we previously reported the concept of “perfect fit” of the ratio lengths of the tritopic H$_2$BTB linker over various ditopic linkers and the number of links surrounding the triangular Fe-based cluster which is more convenient for noninterpenetrated structure formation.\textsuperscript{19} When increasing the length of linear ditopic linker in the mixed linker system, the complex MOFs had a tendency to become interpenetrated structures; in particular, those listed below are a series of MIL-142 (MIL-142A to E),\textsuperscript{14} PCN-280—a complex MOF structure comprising of two kinds of link, BTB$^{3-}$ and BPDC$^{2-}$, and trigonal prism Fe$_3$O$_2$(CO$_3$)$_6$ cluster (Scheme 1).\textsuperscript{17} However, by replacing BPDC$^{2-}$ in PCN-280 structure by azobenzene-4,4'-dicarboxylate (4,4'-azoBDC$^{2-}$), an isoreticular structure with single net was formed that is termed PCN-285.\textsuperscript{17} This observation is still ambiguous and not either received any explanation proposed by experimental or calculation methodology.

Before controlling the interpenetration behavior of PCN-280, we start synthesizing the isoreticular structure of PCN-280 and PCN-285 in which 3,3'-azoBDC linker whose length is longer than H$_2$BPDC and shorter than 4,4'-azoBDC is used and the single frame MOF is expected to be obtained. MOF-909 microcrystalline powder was isoretically produced with the synthetic condition different from that using for PCN-280 and PCN-285 preparation in line with our speculation. The powder X-ray diffraction (XRD) patterns of as-synthesized and activated samples are coincident with the pattern calculated from structural modeling (Supporting Information, SI, Section 3). Single crystal of PCN-280 was then prepared by the same synthetic method utilized for MOF-909 manufacturing. The single-frame structure of PCN-280, MOF-908, cannot be obtained after exhausted efforts following the reported
methodologies including synthetic modification, bulky organic solvent changing, and templates. We hypothesize that there exists an energy barrier of the reaction when the mixed linker system, H₂BTB and H₂BPDC, interacts with the triangular Fe-oxo cluster preventing the final structure from the single network of MOF-909- or PCN-285-type topology which is unseen in MOFs chemistry and was not acknowledged in the original publication. In order to prove that postulation, we then move forward to rational investigation of the reaction in which H₂BTB linker was an independent reagent and was constrained to be unchanged in molar while the mixture of 3,3'-azoBDC over H₂BPDC was proportionally controlled from 0:100 mol% to 100:0 mol%. As depicted in Figure 1, after 24 h of reaction, the highly crystalline products were observed for all of the samples. The PXRD patterns clearly show that PCN-280 is only formed when the molar percentage of 3,3'-azoBDC over H₂BPDC is 90:10 mol%. Interestingly, increasing the rational molar of 3,3'-azoBDC over H₂BPDC to 60:40 mol% leads to achieve noninterpenetrated structure of PCN-280, MOF-908 (The zoom-in of Figure 1 at low angle was found in SI, Section 4).

The PXRD pattern of 50:50 mol% as-synthesized sample exhibited 5 characteristic peaks coincident with the simulated pattern which belong to the Miller planes of [101], [003], [21-1-3], and [3-1-1]. It is noted that the [101] Bragg position of the 50:50 mol% sample obviously enhances the intensity after the solvent exchange and activation processes (SI, Section 4), confirming the observation of a single frame structure. Given the fact that PCN-280 appeared to be a single crystal represented by very thin hexagon shape such as contract with the single crystals of MOF-908 appeared in form of the trigonal prism which the crystal growth is priority to be along the c direction (SI, Section 2) resulting in the large unit cell of the crystal structure compared to PCN-280.

To further verify if the purely single phase of MOF-908 was obtained, the activated sample was digested for proton nuclear magnetic resonance spectroscopy (NMR). The post-digestion ¹H-NMR spectrum displaying the presence of only BPDC⁻⁻⁻⁻ linking unit (SI, Section 4) undoubtedly prove that MOF-908 was purely produced by control the rational input of the mixture of organic linkers. The phase transition transferring from MOF-908 to MOF-909 is more distinctly displayed in those samples containing the proportional molar of mixed linker from 70:30 mol% to 100:0 mol% of 3,3'-azoBDC:H₂BPDC (Figure 1).

Due to the small size, large pore volume, and nature of Fe-based MOF, which lead to weakening the resolution (only 1.4 Å of data collection was obtained by Mo X-ray radiation) of single crystal analysis, MOF-908 crystal structure was finally elucidated by Rietveld refinement. This revealed the structural single framework crystallized in trigonal lattice with R3 space group (No 146) and the unit cell parameters of $a = b = 32.9145 Å$, $c = 46.0360 Å$ (SI, Section 3). MOF-909 is an isoreticular network of MOF-908 with the similar unit cell parameters ($a = b = 32.2658 Å$, $c = 45.8488 Å$). The structure of MOF-908 is made up of two kinds of cage. The small primary cage owning the pore size of 12 Å diameter is a distorted octahedra constructed by six trigonal prism Fe-oxo clusters which link together through four BTB⁻⁻⁻⁻ connecting the vertices along opposing equatorial edges, and three BPDC⁻⁻⁻⁻ moieties fill in the remaining equatorial edges composing the triangular window which is found to be 8 Å. The secondary cage is then built up by the connection of eight primary cages concerned as nodes. In particular, those primary cages sharing four vertices when translating a distance equal to the distance of two primary cages (23.2 Å approximately) locate at the vertices of a cube and generate a cubic cage with the diameter of 23 Å. The square channel window of the secondary cage comprised of four sharing vertices of primary cage building units was found to be 15.5 Å (Figure 2b). Possessing the isoreticular structure of MOF-908, MOF-909 with the longer ditopic linking unit gave the larger pores size but the triangular windows size...
is smaller than MOF-908 because of the geometrical arrangement of 3,3′-azoBDC \(^2\). Especially, the diameter of distorted octahedra and cubic cage in MOF-909 is around 12.5 and 24 Å, respectively, while the triangular and square window is calculated to be 7.5 and 16 Å, respectively. It is noted that all of the estimation is based on the model of crystal structure verified by Platon calculation which is also applied to generate the empty of void space of 82% approximately for both MOF-908 and MOF-909.

The topological analysis for MOF-908 representing the underlying net of MOF-909, PCN-280, and PCN-285, which appeared to be isoreticular structures, was performed by Topos Pro package. For the underlying net simplification, the Fe\(_2\)O(CO\(_2\))\(_6\) SBUs and the linkers containing BTB and BPDC\(^2\) were simplified as nodes which are 6 and 3 coordination points corresponding to 6- and 3-c of points of extension of trigonal prismatic Fe-oxo cluster and triangular node of BTB moiety, respectively. The linear 2-c of ditopic linker is reduced and no longer in consideration due to the formation of the 6-c point of extension for the Fe\(_2\)O(CO\(_2\))\(_6\) nodes. It is interesting that the structural deconstruction led to reveal the unseen network, termed nht net, in MOFs chemistry. The transitivity of the nht topology is described by the number of vertices \(p\), the number of edges \(q\), the number of faces \(r\), and the type of tiling \(s\). Indeed, \(pqr\) transitivity of nht is 3553 and the natural tiling of this kind of network is \(3(4.7^2) + 3(4.5^3) + 3.5^7\) (where the symbol \([...m^n]...\) denotes \(n\) faces with \(m\)-membered rings in topological network) (Figure 2c).

The solvent-exchange was carried out using anhydrous acetone solvent and the full activation procedure was subsequently followed by heating the material under low pressure at 100 °C for 24 h. The chemical formula of MOF-908 is Fe\(_2\)O(OH)(BTB)\(_{4/3}\)(BPDC) in which the mixed linker ratio of BTB:BPDC was found to be 4/3:1 as proven by \(^{1}H\)-NMR post-digestion (SI, Section 4). Thermal gravimetric analysis (TGA) measurements (SI; Section 4) further supported that formula because the observed residual mass (21.7%) perfectly matched with the expected mass of Fe\(_2\)O\(_3\) (22.8%) after fully decomposing the structural framework at 600 °C. The elemental microanalysis (EA) continuously confirmed the formulation of MOF-908 due to the consistence of the CHN percentage between the experimental and theoretical model (SI; Section 2). Finally, the porosity of MOF-908 was proven by \(N_2\) adsorption isotherms at 77 K exhibiting the permanent surface area based on Brunauer-Emmett-Teller (Langmuir) method of 1,850 (2,315) m\(^2\) g\(^{-1}\) (SI; Section 4) which is in line with the geometrical surface area calculated from the model structure. This exceeds the BET value of 1,500 m\(^2\) g\(^{-1}\) for PCN-280 and lower than that of 1,945 m\(^2\) g\(^{-1}\) for MOF-909 (SI; Section 4) which were conducted with solvent-free under the coincident activated condition. The pore size distribution of PCN-280 and MOF-908 was performed by DFT calculation based on the \(N_2\) adsorption isotherms showing the difference, in which pore size of MOF-908 (~22 Å) is larger than PCN-280 (~12 Å) (SI, Section 4).

We subsequently carried out first-principles density functional theory\(^{22,23}\) (DFT) calculations to unveil the mechanism of interpenetration control of PCN-280 to formulate MOF-908. We proposed to look at two different theoretical aspects, which are believed to be helpful in explaining the overall scenario. First, the reaction mechanisms between Fe\(_2\)O(OH)(CO\(_2\))\(_6\) and H\(_2\)BPDC/3,3′-azoBDC were explored to clarify the energetic favorability of the two cluster-linker combinations. Second, by estimating elastic tensors of the abbreviated MOF-908 and MOF-909 structures, we were able to make conclusion on their relative stability in the condensed phase.

![Diagram](image_url)

**Fig. 3** (a) The initial reactant, in which one O from RCOOH (linker) attached to one Fe site, while the –OH group moved forward to donate the proton toward the pink O atom from CH\(_2\)COOH. The pink O atom would soon depart from Fe, and give RCOOH the chance to establish bonding to the second Fe site. (b) Relaxed scans of the Fe-O(acetate) bond, in which the Fe-O bond was broken with the same energy barrier (0.76 eV). This indicates the competitiveness between H\(_2\)BPDC or 3,3′-azoBDC in the first process of the substitution. The energy difference between two curves came from the difference in binding energies of RCOOH-cluster (~0.8 eV).

For the reaction mechanism investigation, we employed the localized atomic-orbital-basis calculation method.\(^{24}\) The Perdew-Burke-Ernzerhof (PBE) functional\(^{25}\) was used to execute these calculations as well as the later condensed-phase calculations. The 6-31g\(^*\) basis set\(^{26,27}\) was employed to construct the electronic wave-functions for C, H, O, N, while the LANL2dz basis set\(^{28,29}\) was utilized to describe the effective core potential for Fe. In both gas-phase and condensed-phase calculations, we introduced D3 correction to account for long-range van der Waals interactions.\(^{30}\) The quartet electronic spin state of Fe\(_2\)O(OH)(CO\(_2\))\(_6\) cluster was revealed to be the most energetically-favored spin state; in other words, each Fe\(^{3+}\) site preferred to establish one unpaired electron. For the following investigation of reaction mechanisms, we carried out all localized atomic-orbital-basis calculations at the quartet spin state.
As a linker (H₂BPDC or 3,3'-azoBDC) attempted to substitute an acetate (CH₃COO⁻) residue, one atom from the linker approached closely and made a coordination bond to one Fe cation in the cluster. Because of this connection, the Mulliken charge of the involving Fe⁺⁺ site decreased to 0.57, which was less positive than that of the other two Fe site (0.74) in the cluster. The binding energy of (H₂BPDC)-cluster was 0.67 eV, while the binding energy of (3,3'-azoBDC)-cluster was 0.59 eV, which showed the slight favorability of H₂BPDC connection to the cluster. Such [Fe₃O(OH)(-CO₂)₆]-linker complexes were regarded as initial reactants. The proton (H⁺) still remained linking with the linker molecule while attempted to make a weak bond with an O atom from acetate (Figure 3a). To accomplish the cluster-linker connection, the system had to undergo two transformation stages: (i) O from acetate first departed from Fe (a coordination bond was broken), and (ii) the O atom (from –OH of the linker) approached and made connection with the other Fe cation linked to the same acetate residue. In the first process, H₂BPDC or 3,3'-azoBDC actually played a role as a catalyst to loosen the Fe-acetate linkage. Actually, we performed a relaxed scan of Fe-O(acetate) dissociation in each case, and conceived a barrier of 0.76 eV (17.5 kcal/mol) for both cases, as illustrated in Figure 3b. Hence, there was a competition between H₂BPDC and 3,3'-azoBDC in the first binding process to the Fe₂O cluster and weakening the Fe-acetate bond.

 Soon after the disruption of Fe-O bond in the first step, the linker was more motivated to attack the second Fe site. In the second process, we located the transition states when H₂BPDC/3,3'-azoBDC attempted to replace acetate. In those transition states, the Fe-O(H₂BPDC) distance was observed as 3.21 Å, while the Fe-O(3,3'-azoBDC) was almost similar (3.23 Å). However, the H₂BPDC transition state was found to be 0.43 eV (9.9 kcal/mol) above the initial reactant, while the 3,3'-azoBDC transition state was 0.76 eV (17.5 kcal/mol) above the initial reactant. The energetic scheme (Figure 4) showed that 3,3'-azoBDC was less competitive in forming the framework. Besides, we also took into account a circumstance that 3,3'-azoBDC successfully established connection to the cluster, and verified how H₂BPDC could come in and replace the 3,3'-azoBDC linker. We believe that the substitution should be identical to the mechanism described above when H₂BPDC (or 3,3'-azoBDC) substituted CH₃COO⁻. As a matter of fact, the transition state of H₂BPDC replacing 3,3'-azoBDC was 0.78 eV (18.0 kcal/mol) above the initial state, in which 3,3'-azoBDC was connected to the cluster. The final state, in which H₂BPDC made connection to the cluster and eliminated 3,3'-azoBDC, was found to be more stable than the initial state by 0.24 eV (5.5 kcal/mol). At this stage, by conducting localized atomic-orbital-basis calculations, we found that H₂BPDC and 3,3'-azoBDC were competitive to each other in the first stage of establishing bonding with one Fe cation. This first stage is very important, because the participation of 3,3'-azoBDC involved in the formulation of the single framework and avoided interpenetration. The second stage took place rapidly after the first process, where H₂BPDC was shown to be preferable in bonding with the iron cluster.

### Table 1. Elastic tensors C_{ij}, shear (G), bulk (K), and Young’s (E) moduli of the abbreviated MOF-908 and MOF-909 structures (in kbar).

<table>
<thead>
<tr>
<th>MOFs</th>
<th>C₁₁</th>
<th>C₁₂</th>
<th>C₁₃</th>
<th>C₂₂</th>
<th>C₂₃</th>
<th>C₃₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOF-908</td>
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<td>400</td>
<td>387</td>
<td>1263</td>
<td>510</td>
<td>530</td>
</tr>
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<td>65</td>
<td>193</td>
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<tr>
<th>MOFs</th>
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<td>726</td>
<td>1241</td>
</tr>
<tr>
<td>MOF-909</td>
<td>82</td>
<td>114</td>
<td>199</td>
</tr>
</tbody>
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We also performed PBE calculations for the condensed phases of MOF-908 and MOF-909 to evaluate their relative stability with the projector-augmented wave (PAW) implemented in the Vienna Ab Initio Package.²⁻³⁻⁴ Those two structures were extremely large and sophisticated; therefore, we chose to simplify to model by substituting three acetylene residues into the position of three phenyls in BTB (the crystallographic data of original MOF-908 and MOF-909 as well as the modified structures are available in the SI). Such substitution was believed to alter the unit cell parameters insignificantly. To afford computational feasibility, plane-wave expansion was only done around the Γ point with a cut-off energy of 350 eV. After a simultaneous relaxation of unit cells and atomic positions, we calculated the C_{ij} elastic tensors for both systems by adopting the stress-strain relationship. It was observed that the obtained C_{ij} tensors of MOF-908 and MOF-909 satisfied the four conditions of mechanical stability of hexagonal unit cells. Moreover, the C_{ij} tensors of MOF-908 were much larger than those of MOF-909. To make a more quantitative justification, we then computed the shear (G), elongation (E), and Young’s (E) moduli.
bulk (K), and Young’s (E) moduli, as shown in Table 1 along with the C₄ quantities. Remarkably, each of the moduli of MOF-908 was six times larger than the corresponding modulus computed for MOF-909. Moreover, all G, K, and E of MOF-909 were below 200 kbar, which were relatively low for a large unit cell, and indicated that the framework of MOF-909 could suffer and collapse more easily. Such theoretical quantities clearly explain the experimental fact that MOF-909 actually partially collapsed after activation (PXRD pattern displayed the reduced intensity of the peaks located from higher than 7.5° 2θ, SI, Section 4). Additionally, MOF-908 is more mechanically stable than MOF-909, as proven by the pellet pressing test which clearly exhibits that MOF-908 framework still retains up to 11 tons cm⁻² of pressure while MOF-909 structure collapses at the pressure of 5 tons cm⁻² (SI, Section 4).

Conflicts of interest
There are no conflicts to declare.

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