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A Highly Stable Porphyrinic Zirconium Metal-Organic Framework with shp-a Topology

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Supporting Information Placeholder

ABSTRACT: Through a kinetically controlled synthetic process, we synthesized a new porphyrinic Zr-MOF (PCN-223). PCN-223 is constructed from the newly reported hexagonal prismatic twelve-connected Zr_6 cluster through an unusual disordered arrangement, which gives rise to the first example of the **shp-a** network in MOFs. With its extremely high connectivity, PCN-223 shows high stability in aqueous solutions with a wide range of pH values. After post synthetic treatment, the cationic PCN-223(Fe) is demonstrated to be an excellent recyclable heterogeneous catalyst for the hetero-Diels–Alder reaction.

Metal-organic-frameworks (MOFs), as an emerging class of highly ordered porous materials, have attracted great interest in the last few decades.[1] Their modular nature imparts structural diversity and tunable functionality within a single material, enabling promising potential applications in many areas, such as gas storage/separation, sensing and catalysis. [2]

Due to the readily adjustable nature of MOFs, one of the most convenient approaches to introduce functional moieties into the framework is to construct MOFs with those moieties or their derivatives as building units. As a solid state material with periodic structure and porosity, consequently, MOFs make those functional moieties well dispersed with extremely high accessibility, which will result in effective utilization of each individual unit. In other words, homogenous arrangement and the accessibility of functional moieties, which is one main advantage of homogenous liquid or gas systems, are almost completely realized in a heterogenous solid state material. Moreover, once stable MOFs are formed, they can be used under different media without concern for solubility, which tremendously diminishes the synthetic effort in some homogeneous catalytic systems where solubility and their working environment conflicts.

Porprhyrin derivatives have been substantially explored as organic linkers in MOFs due to their multifunctionality.[3]As one of the most frequently found species in biological systems, porphyrin derivatives can be used as light harvesting reagents, anti-cancer drugs, catalysts, sensors, nonlinear optical materials and DNA-binding or cleavage agents. After being introduced into MOFs, the dimerization of some porphyrinic species was eliminated. Meanwhile, as highly conjugated large molecules, most artificial porphyrinic species suffer solubility problems under either physiological conditions or unreactive organic solvents (mostly nonpolar). When immobilized into MOFs, porphyrinic species can be used in any media without considering their solubility. Despite that, the chemical stability of porphyrinic MOFs severely restricted wide applications for a long period when relatively soft Lewis acidic metal species were used as nodes. [3] The practice of using hard Lewis acidic species, such as Zr^{4+} and Al^{3+}, has successfully expanded the range of working environments for porphyrinic MOFs, especially in aqueous media, and thus greatly diversified the application of those MOFs.[4]

Porphyrinic Zr-MOFs are outstanding representatives with excellent chemical stability under harsh conditions for novel applications in the MOF field, such as biomimetic catalysis and pH sensing.[4a-4e] The variation of connecting numbers and symmetry provides many topological possibilities to form different frameworks with the same TCPP (tetrakis(4-carboxyphenyl) porphyrin) linker and Zr_6 node. These porphyrinic Zr-MOFs obtained from variation of synthetic conditions exhibit not only different pore sizes and shapes, but also different chemical stabilities, which offer eligible candidates for different applications. For example, the mesoporous PCN-222 (PCN stand for Porous Coordination Networks) has extremely high stability under acidic conditions, which makes it an ideal candidate for incorporation of large substrates or being applied under acidic environments.[4a] In comparison, PCN-224 has worse stability under acidic conditions but survives much better under basic conditions.[4e] Although there are already several different porphyrinic Zr-MOFs reported, the variable connectivity and symmetry of the Zr_6 cluster still provides topological possibilities to obtain more frameworks with different applicable properties. Therefore, exploration of novel porphyrinic Zr-MOFs might further expand the study of novel applications for MOFs.

Herein, through a kinetically controlled process, we synthesized a new porphyrinic Zr-MOF (PCN-223). PCN-223 contains the unprecedented D_{6h} symmetric twelve-connected Zr_6 cluster, which gives rise to the **shp-a** network, of which this is the first example in a MOF. PCN-223 has uniform one dimensional (1-D) triangular channels with porphyrinic walls. With the highest connectivity among the Zr-MOFs, PCN-223 shows excellent stability in aqueous environments with pH values ranging from 0 to 10. We generated a naked cationic iron(III) porphyrin center in PCN-223(Fe), which catalyzed the hetero-Diels–Alder reaction between unreactive aldehydes and a diene with very high yield and excellent recyclability.

The fully bridged Zr_6 $[Zr_6O_4OH_4(COO)_{12}]$ cluster reported in UiO-66 is a twelve-connected O_h symmetric node, which both symmetrically and in connectivity matches with the four-connected D_{4h} symmetric TCPP node. The combination of these two nodes gives rise to an **ftw-a** network. However, the relative position between the two nodes is not compatible with that in the **ftw-a** network unless a relatively high energy conformation is adopted for each node.[5] As a result, both the connectivity and the symmetry of the Zr$_6$ SBU always decrease to form other networks with the symmetry reduced TCPP ligands with a variety of dihedral angles between the central and peripheral rings. Despite the structural differences, the Zr porphyrinic MOFs are obtained under very similar reaction conditions, suggesting the lack of a thermodynamically dominant phase, providing opportunities to explore more new structures by tuning the synthetic conditions. By using less competing reagent (benzoic acid or acetic acid), which could accelerate the formation of MOFs while maintaining the crystallinity, we successfully obtained a kinetically favored phase of porphyrinic zirconium MOFs, PCN-223.

Solvothermal reactions of ZrCl$_4$, TCPP (free base or Fe coordinated) and the competing (modulating) reagent in DMF give rise to spindle-shaped crystals of PCN-223. Single crystal X-ray diffraction reveals that PCN-223(Fe) crystallizes in the *P6/m* space group. Originally, a twelve-connected Zr$_{18}$ cluster was observed, which has never been reported in either Zr carboxylates or Zr-MOFs (Figure 1a). However, the shortest Zr···Zr distance in the Zr$_{18}$ cluster is 2.45 Å, which is much shorter than that in the Zr$_6$ cluster (~2.70 Å) or other reported zirconium carboxylates. Considering Zr$_6$ is the absolutely dominant inorganic node in all the reported Zr-MOFs, we tried to confirm the discovery of this unusual Zr$_{18}$ cluster by measuring the ratio between Zr and the TCPP linker.[6] According to the result of energy dispersive X-ray spectroscopy (EDX), the Zr to Fe ratio in PCN-223(Fe) was determined to be 2:1, which suggests a twelve connected Zr$_6$ cluster instead of Zr$_{18}$ (supporting information section S4). To rationalize this result, we separated the Zr$_{18}$ cluster into three Zr$_6$ clusters oriented in different directions, which are periodically arranged in the framework and appear as a Zr$_{18}$ cluster through crystallographic disorder (Figure 1a). In each individual Zr$_6$ cluster, there are only eight carboxylates bridging adjacent Zr atoms while the other four chelating single Zr atoms (Figure 1b). In Zr-MOFs, this is a novel building unit different from the conventional twelve-connected Zr$_6$ cluster in UiO-66, in which all the carboxylates bridging adjacent Zr atoms (Figure 1b).[6a] After topological simplification (only carbon atoms on the carboxylates are considered), each twelve connected Zr$_6$ cluster in PCN-223 exhibits D_{6h} symmetry and overall gives rise to the first **shp-a** topology among all reported MOFs (Figure 2 c, 2d, and 2e). Along the c-axis, PCN-223 has uniform triangular 1-D channels of 12 Å; this arrangement is equivalent to separating the hexagonal channel in PCN-222 by six more TCPP linkers and an extra Zr$_6$ node (Figure 2a and 2b, supporting information section S3).

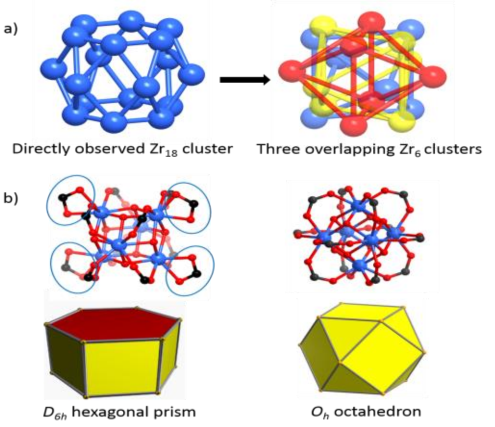


Figure 1. (**a**) Directly observed Zr$_{18}$ cluster (left) and overlapping Zr$_6$ clusters (right), each exhibiting partial crystallographic occupancy. (**b**) The unusual twelve-connected Zr$_6$ cluster (left) and the conventional twelve-connected O_h symmetric Zr$_6$ cluster

It is worth noting that such a shp-a network is one of the three predicted edge-transitive (4,12)-c nets by O'Keeffe and coworkers.[5b] Interestingly, another (4,12)-c net, ftw-a, has also been realized in porphyrinic Zr-MOFs (MOF-525 and PCN-221). In comparison, MOF-525 was obtained with a much higher acid to ligand ratio and a longer reaction time, suggesting that PCN-223 may be more kinetically favored. Compared with the **shp-a** net, the ftw-a net shows more a regular arrangement (higher symmetry). To obtain the latter requires a longer time for the assembly and crystal growth procedures. Moreover, less or weaker competing reagent is needed for PCN-223 compared to PCN-222, which not only kinetically accelerates MOF growth but also facilitates the formation of an entropically favored product.[7]

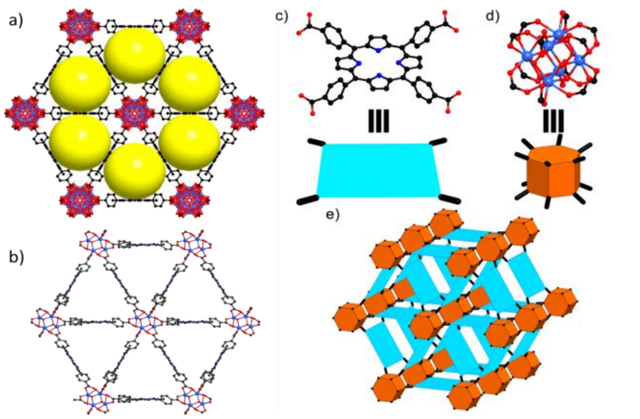


Figure 2*.* PCN-223 viewed along c axis with uniformed triangular 1-D channels observed in the structure (**a**) and after removing disorder (**b**). Topology analysis of PCN-223(**c-e**).

In order to assess the porosity of PCN-223(No metal and Fe), we performed N$_2$ sorption measurements at 77 K (Figure 3b). Both PCN-223(Free base) and PCN-223(Fe) show N$_2$ uptake around 430 cm^3/g at 1 bar. The experimental Brunauer-Emmett-Teller (BET) surface area of PCN-223(Free base) and PCN-223(Fe) is around 1600m^2/g and porosity is 0.6cm^3/g, values of which are in good agreement with the calculated results using the non-disordered structure. When the Zr$_{18}$ cluster model is used, the simulated results of both would be lower than experimental data, which further confirms our structural rationalization. The single crystal structure of PCN-223 is finally validated with powder X-ray diffraction results (Supporting information Figure S6). Since the **shp-a** network has one of the highest connectivity among all the reported MOFs, we expected high chemical stability for PCN-223 and tested that under aqueous solutions with different pH values.[7] After soaking in different solutions for 24h hours, the PXRD patterns of PCN-223(No metal) are completely maintained from 1M HCl solution to pH = 10 aqueous solution (Figure 3a). Meanwhile, the N$_2$ uptakes of PCN-223(Free base) samples after different treatments are almost the same as that of the pristine sample, which is evidence for the stability of the framework under harsh chemical conditions (Figure 3b). Although the stability of PCN-223 under acidic conditions is not as good as PCN-222, PCN-223 exhibits much better stability in basic environments, allowing its application under different conditions. Moreover, PCN-223 shows excellent thermal stability (Figure S11 and Figure S12).

Due to the high concentration of porphyrinic centers in the framework as well as excellent chemical stability for PCN-223, we therefore studied its catalytic activity for the hetero-Diels–Alder reaction between unreactive aldehydes and a diene, confirming PCN-223 as a recyclable heterogeneous catalyst.

The hetero-Diels–Alder reaction is one of the most powerful synthetic approaches for the construction of six-membered heterocyclic compounds. In particular, the cyclo-addition of aldehydes to dienes has been widely applied in the preparation of natural products.[8a] However, most of these reactions involve the use of activated aldehydes such as glyoxylates or electron-rich dienes such as Danishefsky's diene to reach a high yield. Only a small number of hetero-Diels–Alder reactions have been reported using unactivated aldehydes and simple dienes.[8b] Moreover, the use of very strong Brønsted acids or Lewis acids is always necessary to activate the poorly reactive hetero-dienophile to compensate for the low reactivity of simple dienes, which severely restricts the choice of functional groups that can be tolerated under such harsh reaction conditions. Recently, Fujiwara *et al* reported the catalysis of the hetero-Diels–Alder reaction with unactivated aldehydes and simple dienes by using an iron(III) porphyrinic cation, which shows high catalytic performance as well as robustness in the reaction.[8c]

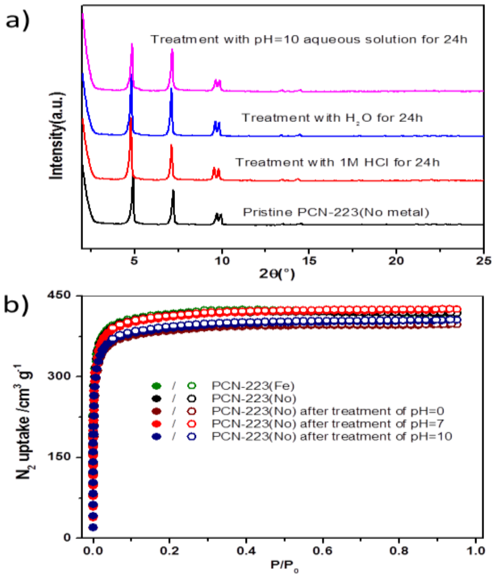
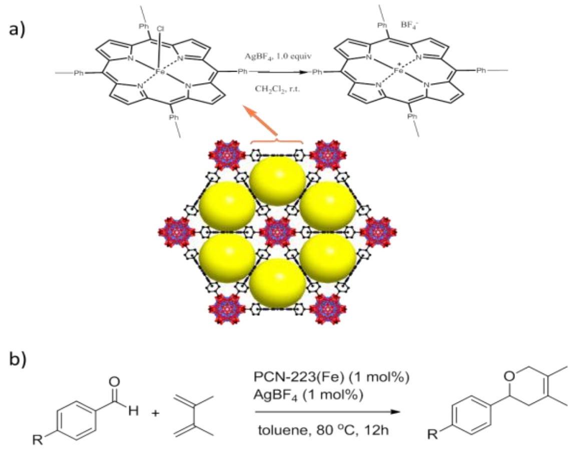


Figure 3. (**a**) Powder X-ray diffraction of PCN-223(No metal) under different conditions and (**b**) N_2 adsorption isotherms for PCN-223(Fe) and PCN-223(Free base) after harsh treatments to show the excellent stability.

Since the cationic iron (III) porphyrin has very strong affinity to all electron donating species, the synthesis and handling have to be conducted under an inert environment. However, when porphyrinic MOFs are used, the catalysts can be conveniently recycled, which could save a lot of effort for making new catalyst and for product separation. Following the synthetic procedure in the reported homogeneous system, we made the cationic Fe(III) porphyrin center in PCN-223(Fe) and tested its catalytic performance using the same substrates (Scheme 1). The potential block of cationic sites and pores of PCN-223(Fe) due to the generation of AgCl precipitates is highly concerned but could not be directly measured because of the high activity of cationic PCN-223(Fe). Remarkably, the reaction of benzaldehyde with 2,3-dimethyl-1,3-butadiene reached 99% yield confirmed by both column chromatography (NMR) and GC (Table 1), which is even higher than that reported in the optimal homogeneous system. It is also worth noting that we employed toluene as the solvent instead of the carcinogenic benzene, which is the optimized solvent in the reported homogenous system. Since the catalytic mechanism is to use the naked cationic iron (III) center to polarize the aldehyde species, electron withdrawing groups on the porphyrin should increase the polarization ability of the iron center and thus enhance the catalytic activity. To eliminate other possible reactive centers, two control experiments were performed with PCN-223(Free base) and PCN-223(Fe) with no $AgBF_4$ additives to confirm that only the cationic PCN-223(Fe) is active towards the catalysis of the hetero-Diels-Alder reaction. Therefore, the higher catalytic activity in cationic PCN-223(Fe) than the homogeneous system could be ascribed to two possible reasons: carboxylate itself is an electron withdrawing group, which could decrease the electron density on the iron center; meanwhile, due to its high (Z/r) value, zirconium could be considered as an extremely effective electron withdrawing group, which would dramatically decease the electron density on the porphyrin after bonding to the carboxylates. Both effects could further increase the polarization ability of the iron center and increase the overall catalytic activity. Such an extraordinary result also highlights the advantages of using MOFs as a heterogeneous system. Because of the porous framework, MOFs can be used as heterogeneous catalysts in any solvent despite the solubility of the catalyst, compared to homogenous systems that always require extra synthetic effort to find the appropriate solvents, which greatly limits the scope of the catalytic reaction. For instance, although carboxylate groups might enhance the catalytic activity, TCPP has very low solubility in nonpolar solvents, so it cannot be used alone in benzene or toluene. Furthermore, the inorganic units could further increase the activity of the linker instead of acting as pure spectators; however, these inorganic clusters would be useless in a homogeneous system due to their limited solubility in common organic solvents. This illustrates that when MOFs are applied in a suitable system, the metal-containing nodes, organic linkers, and framework porosity can be most effectively integrated to enhance the utility of a catalytic system. Of course, it should be pointed out that optimizing reaction conditions, such as temperature, substrate solubility, and even substrate diffusion from the solvent towards the porous catalyst, are still necessary.



Scheme1. (**a**) The preparation of cationic iron porphyrin center in PCN-223(Fe). (**b**) Hetero-Diels–Alder reaction catalyzed by PCN-223(Fe)

Table 1. Hetero-Diels–Alder reaction based on different benzaldehydes.

Entry	R	GC yield (%)	Isolated yield(%)
1	H	>99	>99
2	CH_3	98	96
3	CN	28	30
4	Ph	51	56

Three other functionalized benzaldehydes were also tested (Table 1) 4-methylbenzaldehyde is almost completely converted to product while 4-phenylbenzaldehyde and 4-cyanobenzaldehyde show relatively low yields, which are presumably caused by the electron withdrawing effect of the functional groups. To evaluate the recyclability, the PCN-223(Fe) catalyst was recovered after each reaction (4-methylbenzaldehyde and 12 h) by simple centrifugation and the recovered catalyst was reused for the next reaction. The catalytic activity was well maintained; the yield of the reaction (12 h) is still higher than 90% after 5 cycles, which demonstrates the excellent recyclability of PCN-223(Fe) (Table 2).

Table 2. Recyclability test of PCN-223(Fe) using 4-methylbenzaldehyde (12 h reaction time).

Cycles	**R**	**GC yield (%)**
1	CH_3	98
2	CH_3	95
3	CH_3	96
4	CH_3	94
5	CH_3	90

In conclusion, through a kinetically controlled synthetic process, we synthesized a new porphyrinic Zr-MOF (PCN-223). PCN-223 is constructed from a new hexagonal prismatic twelve-connected Zr_6 cluster, which gives rise to the first example of a **shp-a** network in MOFs. After post synthetic treatment, the cationic PCN-223(Fe) is demonstrated to be an excellent recyclable heterogeneous catalyst for the hetero-Diels–Alder reaction.

ASSOCIATED CONTENT

Supporting Information

Full details for sample preparation and characterization results, crystallographic data of the precursor, structure (CIF), N_2 adsorption, thermal stability, and chemical stability and catalytic activity tests are in the supporting information. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Author Contributions

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Notes

The authors declare no competing financial interest.

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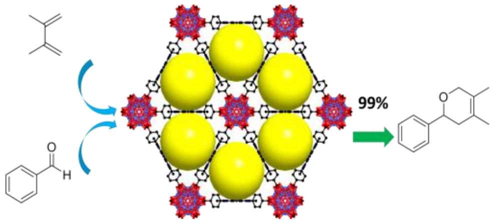
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