

A metal-organic framework assembled from T-shaped and octahedral nodes: A mixed-linker strategy to create a rare anatase TiO₂ topology

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A novel porphyrin paddlewheel framework (PPF-25), assembled from a Zn paddlewheel cluster and mixed-linkers (4,4'-bipyridyl; zinc 5,15-di(4-carboxyphenyl)-10,20-diphenylporphyrin), has been synthesized and structurally characterized. T-shaped organometallic nodes are generated, and the resulting structure is closely related to anatase, a polymorph of TiO₂.

The recent exponential growth in the synthesis and characterization of a new class of inorganic-organic hybrid materials, often referred to as metal-organic frameworks (MOFs), has been driven in part by their fascinating topologies and possible applications, ranging from gas storage to heterogeneous catalysts.¹⁻³ These MOFs are self-assembled from two different types of structural components (organic and inorganic nodes), and commonly form a 3D net topology found in solid-state materials.³⁻⁴ Among the many 3D nets identified in MOFs,⁴ framework structures with heteronodal nets are of particular interest.⁴⁻⁵ Examples include various (3,6) nets, such as rutile (**rtl**), anatase (**ant**), **qom**, and **pyr**, assembled from 3-connected organic linkers and 6-connected inorganic building blocks.⁶⁻¹¹

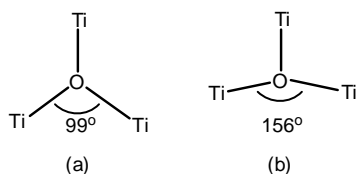
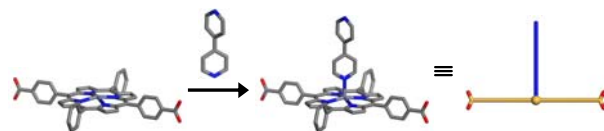


Figure 1. Coordination geometry around oxygen in (a) rutile and (b) anatase shown with 2θ (Ti-O-Ti) values of 99° and 156° , respectively.

Of these (3,6) nets, **rtl** and **ant** are polymorphs of TiO₂.¹²⁻¹³ A notable structural difference between the rutile and anatase architectures can be traced to the coordination geometry of the 3-connected oxygen atom.¹² The geometries around the oxygen atom in rutile and anatase are planar Y- and T-shapes, respectively (see Figure 1).¹² In both cases Ti atoms are surrounded by six oxygen atoms, forming an octahedral geometry.¹² To achieve these

net topologies in MOFs, tritopic Y-shaped organic linkers are frequently used; the most notable example is 1,3,5-benzenetricarboxylic acid (BTB).⁷⁻⁹ In contrast, T-shaped organic linkers are seldom used in MOF synthesis,¹⁴ possibly due to the difficulties encountered in the design and synthesis of such exotic ligands.^{14c}



Scheme 1. Schematic representation of the formation of a T-shaped organometallic node using *trans*-DCPP and bpy.

We previously reported a MOF called PPF-6 (PPF = porphyrin paddlewheel framework) with a (3,6)-connected, 2D CdI₂ topology using 5,10-di(4-carboxyphenyl)-15,20-diphenylporphyrin (*cis*-DCPP) and 4,4'-bipyridyl (bpy).^{15,16} In this CdI₂ topology, *cis*-ZnDCPP and bpy form an extraordinary trigonal-pyramidal metalloligand node.

In this communication, we use a different porphyrin ligand, 5,15-di(4-carboxyphenyl)-10,20-diphenylporphyrin (*trans*-DCPP) and bpy, and create a new T-shaped metalloligand node (Scheme 1). Combined with an octahedral Zn₂(COO)₄ secondary building unit, the resulting net is a rare example of a (3,6) **ant** topology. Such a mixed-linker approach is useful in creating a node geometry that is not easily accessible to MOF chemists.¹⁷

The title compound, PPF-25, was synthesized by a solvothermal reaction of zinc nitrate hexahydrate (5.8 mg, 0.02 mmol), *trans*-DCPP (7.0 mg, 0.01 mmol), and bpy (2.3 mg, 0.015 mmol) in a mixture of DMF and ethanol (2.0 mL, v/v 3:1). The mixture was sealed in a small capped vial and sonicated for 30 seconds to assure homogeneity. The vial then was heated at 80 °C in an oven for 24 h, followed by slow cooling to room temperature for 9 h, yielding square purple crystals. The structure of PPF-25 was determined by X-ray single crystal diffraction¹⁸ and its purity was confirmed by elemental analysis and X-ray powder diffraction (see Figure S1).¹⁹

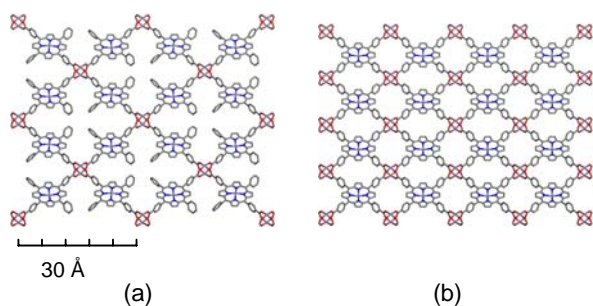


Figure 2. 2D porphyrinic (4,4) grids found in (a) *trans*-DCPP (PPF-25) and (b) TCPP (TCPP = 5,10,15,20-tetrakis(4-carboxyl)-21H,23H-porphine, PPF-1)²⁰ linkers.

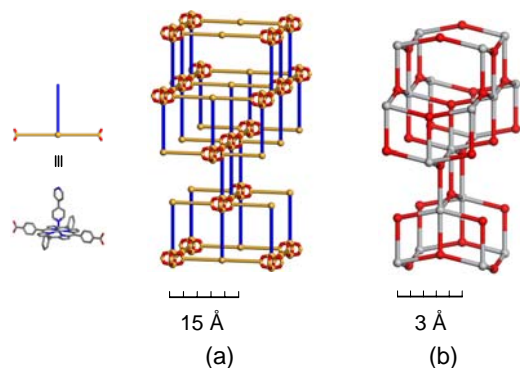


Figure 3. Crystal structures of (a) PPF-25 and (b) its parent topology anatase (**ant**), showing the isostructural relationship.

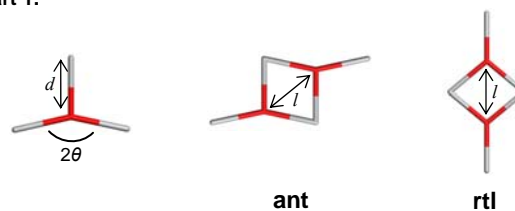
The PPF-25 structure can be explained in the following manner. The structure is based on 2D porphyrin sheets (Figure 2a) assembled from *trans*-DCPP linkers and dinuclear $Zn_2(COO)_4$ paddlewheel secondary building unit at a ratio of 2:1. Here, dinuclear paddlewheel Zn atoms are connected by four *trans*-ZnDCPP, forming a 2D square (4,4) grid pattern. This ratio is different from the 1:1 ratio found in other tetratopic porphyrin-based MOFs, and can be compared with PPF-1 (Figure 2b).²⁰ Therefore, the 2D pattern of PPF-25 can be considered a 'defective-paddlewheel' structure of PPF-1. As shown in Figure 2, PPF-25 is an open framework structure. The distance between the nearest paddlewheels is 23.6 Å and the diagonal distances are 31.9 and 34.8 Å (the corresponding distances for PPF-1 are 23.6 and 33.3 Å), slightly distorted from the regular square grid pattern. The framework density calculated from X-ray single crystal data is 0.45 cm³/g, with a solvent-accessible volume of 42738 Å³ (72% of the unit cell volume in PPF-25), based on a PLATON calculation.

The 2D sheet of PPF-25 is further coordinated by bpy linkers. One of the pyridyl ends of bpy binds to the Zn center in the porphyrin core. The overall geometry of this metalloligand node becomes T-shaped because of the strong preference of the Zn atom inside the porphyrin to be five-coordinated.²¹ The bpy-Zn(DCPP) interaction shows a Zn-N interaction of 2.148 Å, consistent with that of other five-coordinated Zn porphyrins.²¹ This T-shaped organometallic node offers two carboxylate groups and one

pyridyl group to the Zn paddlewheel SBU. In contrast, the Zn paddlewheel SBU can accept four carboxylate and two pyridyl groups. Therefore, the ratio of T-shaped nodes to Zn paddlewheel SBU in the PPF-25 structure is 2:1. The pyridyl group in this T-shaped node binds to the axial coordination site in the Zn paddlewheel, while the carboxylate sites are connected to equatorial Zn paddlewheels. The resulting structure is a non-interpenetrating **ant** topology (Figure 3).⁸ 1D ladders formed from the T-shaped nodes and octahedral paddlewheel nodes are evident in Figure 3. These 1D ladders are stacked in an *ABCD* fashion (Figure S2 in Supporting Information). Such ladder motifs are commonly found in MOFs.¹⁴

Compared with other (3,6)-coordinated nets, **ant** is a rare topology in MOFs: to the best of our knowledge, only two other structures have been reported in the literature.⁸ A noteworthy example with **ant** topology is the Zn/BTB **ant** compound, assembled from trigonal Y-shaped linkers (BTB).⁸ To adopt the **ant** topology, the Zn_4O octahedral node in this compound is severely distorted to link trigonal BTB linkers.²² As exemplified by this case and PPF-25, the **ant** topology can accept both Y- and T-shaped nodes.

Chart 1.



In contrast, another (3,6) topology, **rtl**, is not flexible regarding the choice of trigonal nodes. To illustrate this, the distance (*l*) between trigonal nodes are estimated as $2d\sin(\theta/2)$ and $2d\cos\theta$, in **ant** and **rtl** topologies, respectively (where *d* is the distance between trigonal and octahedral nodes, and 2θ is the angle of the trigonal node).^{22c} When the trigonal node becomes T-shaped ($2\theta = 180^\circ$) in an ideal **rtl** topology, the distance between the adjacent trigonal nodes becomes zero, suggesting that the construction of an **rtl** topology using T-shaped nodes becomes unfavorable due to such steric effect.²³ In PPF-25, the **ant** topology is favored. The competing **rtl** topology cannot accommodate a T-shaped linker, which suggests that the shape of the trigonal linker plays an important role in the framework assembly of (3,6) nets.²⁴

T-shaped nodes, and their use in MOF design, have been of interest in recent decades.^{14,25} More than 30 years ago, Wells noted that framework architectures can be built using T-shaped nodes to form extraordinary architectures such as brick wall, herringbone, bilayer, and basket weave.^{25a} The T-shaped nodes previously established in MOFs are mainly metallic nodes.¹⁴ Utilizing a new type of organometallic node composed of mixed linkers could represent an important strategy in uncovering a variety of uninodal or heteronodal net patterns that have been predicted theoretically but that are difficult to achieve experimentally. A detailed analysis of the binding mode

and symmetry of nodes is a key component of achieving rare topologies in MOFs.^{23,26}

Finally, we compare two topologies: the **ant** topology found in the title compound PPF-25 assembled from *trans*-DCPP, and the CdI₂ topology constructed from *cis*-DCPP reported previously in PPF-6.¹⁵ The 3-connected organometallic nodes form either cubic closest packing (**ant**) or hexagonal closest packing (CdI₂) lattices, and the octahedral nodes are distributed in a zig-zag pattern (**ant**) or in alternating 2D sheets (CdI₂).^{12d,15} In both cases, a mixed-linker synthetic strategy has been proven to be useful in yielding extremely rare topologies in MOFs.²⁷ We are currently investigating the photoluminescence properties of PPF-25.

In summary, we have demonstrated that a porphyrin linker can be used to create T-shaped nodes composed of mixed linkers, thereby forming a rare anatase (**ant**) topology.

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Supporting Information Available: X-ray powder pattern, TGA data, additional figures, table listing TiO₂ topologies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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