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A Bioinspired Synthetic Approach for Building Metal−Organic Frameworks with Accessible Metal Centers

Paul M. Barron,[†,‡] Curtis A. Wray,[†,‡] Chunhua Hu,[⊥] Zhiyong Guo,[¶] and Wonyoung Choe*[,†,§]

[†]*Department of Chemistry, and* [§]*Nebraska Center for Materials and Nanoscience, University of Nebraska—Lincoln, Lincoln, Nebraska 68588-0304, United States,* [⊥]*Department of Chemistry, New York University, New York, New York 10003-6688, United States, and* [¶]*Department of Chemistry, University of Texas at San Antonio, San Antonio, Texas 78249-0698, United States.* [‡]*Equally contributed in this work.*

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We demonstrate how a bioinspired synthetic approach can help organic linkers distinguish between different types of metal centers in metal−organic frameworks (MOFs). Modification of an organic building unit with methyl groups enables the unit to selectively coordinate to one of the two metal sites present in the MOFs. We report four new porphyrin-based, pillared-paddlewheel frameworks: PPF-11-Zn/Zn, -Co/Co, -Mn/Zn, and -Fe/Zn, where the first and second metals indicate the metal center for the porphyrin core and paddlewheel cluster, respectively. These compounds exhibit 3D MOFs in which 2D layers are pillared by a sterically controlled bipyridine, leaving the metal centers inside the porphyrin structurally unconnected.

The development of metal−organic frameworks (MOFs) has become one of the most active research areas in materials science, partly because of their interesting properties in applications such as gas storage, drug delivery, separation, and catalysis.[1−5] In particular, pore surface engineering has become an important topic for MOF research because these self-assembled materials can easily incorporate structural or chemical features into pore walls to obtain specific properties.[6] One of the most desired features in MOFs is the implementation of various metal centers onto the pore surface[6] because this would open up new applications for MOF-based materials and improve their utility in established applications. However, a difficult challenge in this regard is the rational design of such materials. The self-assembly process of MOFs is intrinsically influenced by the coordination geometry of the metal building units and organic linkers.[7] The metal centers are commonly saturated with the linkers, leaving no accessible metal centers.[8] Accordingly, a new synthetic strategy is highly desirable in which the organic building units can distinguish between metal sites used for construction and those employed to attain the desired material properties.

Similar site recognition is commonly observed in biological systems. A good example is restriction enzymes, which are responsible for cleaving DNA along specific recognition sequences.[9,10] However, these enzymes bypass the host DNA with the targeted recognition sequence because the sites are methylated by a second enzyme called methylase.[10] Such methylation allows the restriction enzyme to distinguish between the recognition sites of the host and foreign DNAs. The components used in MOF synthesis are different from DNA cleavage, but the requirements are similar: the organic linkers are required to differentiate multiple types of metal centers in MOFs.

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*To whom correspondence should be addressed. E-mail: choe2@unl.edu. Phone: +1-402-472-0751. Fax: +1-402-472-7860.

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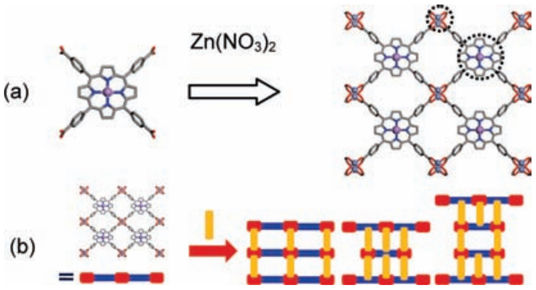
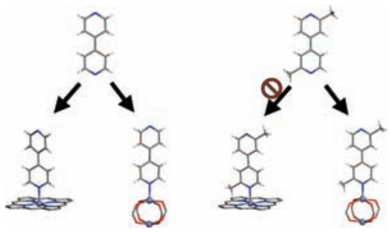


Figure 1. (a) 2D porphyrin grid assembled from a porphyrin building block and zinc paddlewheel secondary building units. Dotted circles represent two independent metal centers in the 2D porphyrin grid. (b) 3D pillared porphyrin frameworks controlled by the coordination geometry.[11,12].

Scheme 1. Schematic Illustration of the Binding Modes of (a) 4,4′-Bipyridine Pillar and (b) A Sterically Hindered dmbpy Pillar to Metalloporphyrins and Paddlewheel Clusters



The first step in the realization of site recognition in MOFs is to create a material with multiple metal centers. Previously, we reported a new series of MOFs, 3D porphyrin paddlewheel frameworks (PPFs), in which the basic structure unit is a 2D porphyrin grid (Figure 1).[11,12] This grid is constructed from tetrakis(4-carboxyphenyl)porphyrin (TCPP) linkers and $Zn_2(COO)_4$ paddlewheel secondary building units at a 1:1 ratio of porphyrin to paddlewheel. Interestingly, this porphyrin sheet contains two distinct metal centers: one in the porphyrin core and the other in the axial positions of the paddlewheel cluster; both are available for additional coordination (Figure 1). For example, an organic pillar, 4,4′-bipyridine, can be used to link these metal sites and form various PPFs with three main stacking sequences: AA, AB, and ABBA.[11] The stacking sequences in these PPFs could be controlled by the coordination geometry of the metal center inside the porphyrin core.[11,12] Although these PPFs contain two distinct metal centers, the pillar molecules are coordinating to all available coordination sites. Consequently, no site recognition by 4,4′-bipyridine has been observed.[11]

The goal in constructing the next series of PPFs is to maintain the framework topology independently of the porphyrin metal center. To achieve this goal, we utilize a 2,2′-dimethyl-4,4′-bipyridine (hereafter, dmbpy) pillar in place of the nonsubstituted pillar used in the previous studies.[11,12] The rationale behind this modified pillar is to exploit the different physical environments of the two metal centers (see Scheme 1). When nonsubstituted pillar molecules are used, no selectivity is observed between the paddlewheel and porphyrin metal centers, as exemplified by more than 10 PPF structures,.[11,12] We hypothesize that steric repulsion of the methyl group in dmbpy will drastically lower the association constant of the pyridyl group to the metal center inside the porphyrin,[13] leading to preferential coordination to paddlewheel metal sites, which are sterically available.

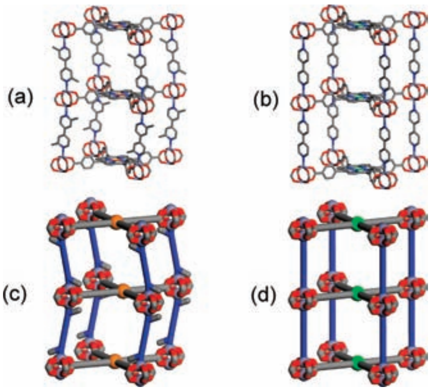


Figure 2. Comparison of the AA packing pattern seen in (a) PPF-11-Zn/Zn with that in the previously reported PPF-5-Pd/Co series (b). (c and d) Simplified representations of the framework structures in parts a and b, respectively. The metal centers in porphyrins are highlighted in orange (Zn) and green (Pd). The water molecules are omitted for clarity.

Here, we demonstrate how a simple methylation can help organic linkers distinguish two different types of metal centers. Modification of an organic building unit with methyl groups enables the unit to selectively coordinate to just one of the two metal sites present in the MOFs. We report a series of PPFs that demonstrate such a site recognition. Site recognition in the PPF series is a key step toward the engineering of pores decorated with accessible metal centers.

The PPF-11-Zn/Zn framework was synthesized via a solvothermal reaction of $Zn(NO_3)_2 \cdot 6H_2O$ (8.9 mg, 0.03 mmol), *meso*-TCPP (8.0 mg, 0.01 mmol), dmbpy (3.8 mg, 0.02 mmol), *N*,*N*-dimethylformamide (1.5 mL), and ethanol (0.5 mL) at 80 °C for 24 h.[14] The purity of the resulting crystals was confirmed by elemental analysis and powder X-ray diffraction. A single crystal suitable for single-crystal X-ray diffraction was obtained for PPF-11-Zn/Zn (in this nomenclature, the first metal indicates the metal center for the porphyrin core and the second is the metal used in the paddlewheel cluster).[15]

Figure 2 shows the AA stacking sequence of PPF-11-Zn/Zn, a structural analogue to the previously reported PPF-5 series (see Table S1 in the Supporting Information for crystallographic data).[11,12] The 2D porphyrinic layers are pillared by dmbpy molecules, coordinating solely to the paddlewheel metal sites as designed. The AA stacking in the PPF-11 structure is directed by the pillar molecule (dmbpy), not the coordination geometry of the metal center in the porphyrin core.

The zinc metal center in porphyrin prefers a five-coordinate square-pyramidal geometry, as seen in PPF-4.[11] In PPF-11-Zn/Zn, a water molecule is coordinated to the zinc porphyrin metal center. The steric hindrance imposed by

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[14] For details, see the Supporting Information.

[15] The solvent-accessible volumes calculated by *PLATON* for PPF-11-Zn/Zn and -Co/Co are 72.8% and 73.1%, respectively. These values are significantly higher than those from previously reported AB (PPF-3-Mn/Zn, 51.3%) and ABBA (PPF-4-Zn/Zn, 68.6%) stacking patterns but comparable to the bpy-substituted AA pattern (PPF-5-Pd/Co, 74.7%).[11,16]

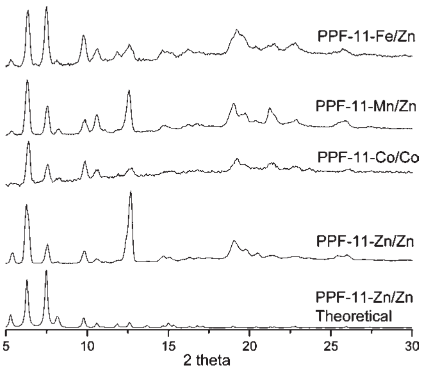

Figure 3. X-ray diffraction patterns for the isostructural PPF-11 series.

the methyl group prevents dmbpy from coordinating to the metal center in the porphyrin. Evidence of steric strain imposed by the methyl group can be seen in paddlewheel pillar coordination in the crystal structure. The methyl group is positioned between two arms on the paddlewheel building unit, where the steric hindrance is minimized. In addition, the pillaring dmbpy ligand is slightly tilted (6.8°) from the ideal vertical position, thereby reducing the overall crystal symmetry. PPF-11-Zn/Zn is orthorhombic (*Cmcm*), while the PPF-5-type compounds previously reported are tetragonal (*P*4/*mmm*).

To further demonstrate the utility of this design strategy, three additional PPFs were synthesized using the methylated pillar dmbpy. In each of these additional frameworks, we use octahedral metals, such as manganese, iron, and cobalt, inside the porphyrin. Such octahedral metals have exclusively yielded AB stacking patterns previously.[11,12] However, the assembly process for PPF-11 is independent of the metal geometry in the porphyrin core. As a result, square-planar (4), square-pyramidal (5), and octahedral (6) metal centers can be used to build the same AA stacking sequence, provided the paddlewheel secondary building unit has an available coordination site. This is demonstrated by the framework PPF-11-Co/Co, which contains a $Co_2(COO)_4$ paddlewheel and a cobalt porphyrin metal center (see Table S1 in the Supporting Information for crystallographic data). In contrast to zinc porphyrin, cobalt porphyrin prefers octahedral coordination. One notable difference is that there are now two water molecules coordinated to the axial positions of the porphyrin. The two additional PPF-11 frameworks developed in the present study are heterobimetallic PPFs, in which the porphyrin metal and paddlewheel metals are different. The resulting PPF-11-Mn/Zn and PPF-11-Fe/Zn were assembled from the corresponding metalated TCPPs. In these two cases, we have been unable to obtain crystals suitable for single-crystal X-ray data collection. However, the obtained powder X-ray diffraction patterns (Figures 3 and S3 in the Supporting Information) and elemental analysis are consistent with the expected AA stacking pattern.[14]

Thermogravimetric analysis (TGA) of PPF-11-Zn/Zn shows thermal stability up to 350 °C (Figure S1 in the Supporting Information). As expected, the three other PPF compounds show thermal stability similar to that of PPF-11-Zn/Zn (Figures S1 and S2 in the Supporting Information). Therefore, the solvent molecules can be removed from accessible metal centers by thermal treatment to create unsaturated metal centers.[8] Testing the sorption of PPF-11-Zn/Zn for H_2, N_2, and CO_2 sorption showed that the structure only had a very small amount of porosity after activation and, as a result, poor gas uptake (Figure S4 in the Supporting Information).[15,16]

Molecular recognition in the restriction–modification process is an elegant example of nature finding a relatively simple solution to a complex problem. By methylation of the recognition sites, enough steric interaction is introduced into the system to block the restriction of DNA, yet the modification is not drastic enough to affect the overall assembly and function of the host DNA. The dmbpy ligand in this work also uses methyl modification to impart metal site selectivity. The synthetic conditions for assembly do not significantly deviate from those of previous PPF systems.

In summary, we demonstrate how metal centers can be incorporated onto MOFs via a new bioinspired synthetic strategy. This metal site recognition is accomplished by functionalization of the organic pillar. The resulting AA stacking structure is directed by pillaring ligands, not by the metal coordination geometry of metal centers in the porphyrin. The ability to distinguish between the metals used for structure assembly and those used for functionality is a critical step in the assembly of next-generation functional MOF materials.

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Supporting Information Available: Synthetic conditions, powder X-ray diffraction patterns, CIF files, TGA data, and sorption data. This material is available free of charge via the Internet at http://pubs.acs.org.

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