

Metal–metalloporphyrin frameworks (MMPF)

Composition:

MMPFs are a class of coordination networks composed of metal-containing secondary building units combined with metalloporphyrin ligands. The metal ion in the porphyrin core can be manipulated to generate different metalloporphyrin-based networks. The structure of a MMPF is essentially a cavity where the corners and edges are composed of metallic ions and ligands respectively, and the cavity functions as a space for many possible applications such as selective gas capture and catalysis. The varying electron densities in the metal-containing secondary building units and metalloporphyrin ligands contribute to the specificity of each MMPF and what molecule it might capture.

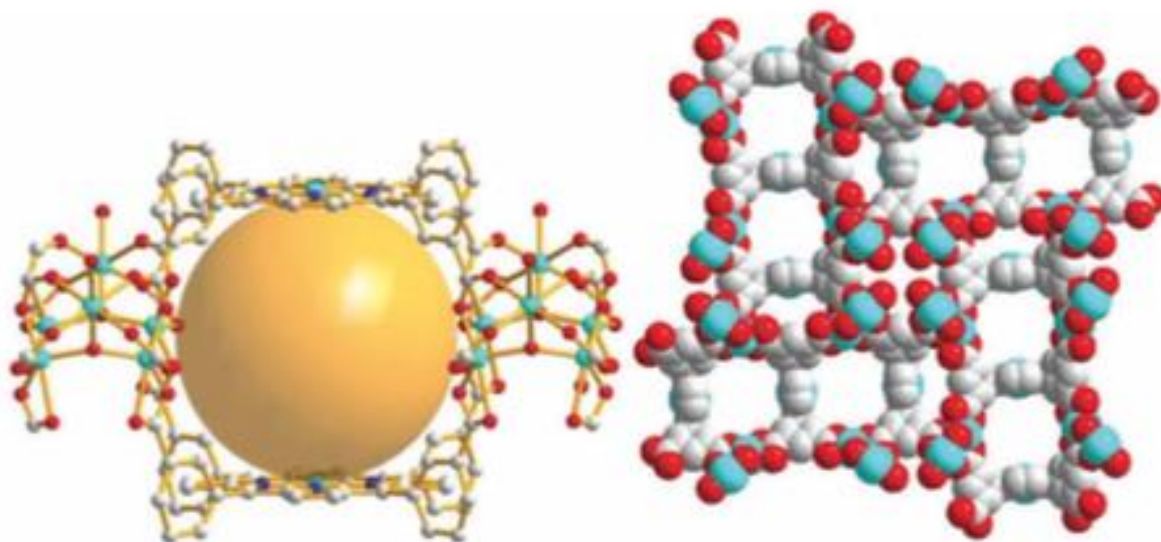


Figure 1. MMPF-2 with three cobalt porphyrins located in the “face-to-face” configuration. ^[1]

How it is made:

Frequently used synthetic strategies in constructing MMPFs include crystal engineering, pillared-layer strategy, and postsynthetic modification. Crystal engineering combines custom-designed ligands and metal-containing secondary building units using intermolecular forces and other factors rather than relying on the process of self-assembly. This method successfully created pre-defined networks. The pillared-layer strategy produces two-dimensional layers that may be linked to create three-dimensional structures. This method uses ditopic pillars and attractions between layers to create the MMPFs. Postsynthetic modification is the further modification of MMPFs after initial crystallization to confer more functional properties to the MMPF.

Its uses:

There are many applications of MMPFs such as guest molecule adsorption and separation and catalysis. Two important properties of MMPFs are the large internal surface area and pore volume, and through various strategies of synthesis, different porphyrin-derived ligands can be added to the framework. If the metalloporphyrin struts are aligned, the porphyrin metal centers become accessible to different guest molecules, many of them gases. This makes MMPFs a great potential porous material that can selectively filter and store various gasses from hydrogen to carbon dioxide. In addition, MMPFs are also able to catalyze certain reactions. These reactions include oxidation catalysis, Lewis acid catalysis, photocatalysis, biomimetic catalysis, and electrocatalysis. MMPFs have also been shown to capture CO₂ and synthesize it with other compounds to produce a final product, such as the synthesis of CO₂ with aziridine to produce 2-oxazolidinone (an antibacterial agent commonly found in pharmaceutical products).

Properties:

Research in MMPF molecules has grown rapidly in recent years because of its many remarkable properties. These include their high thermal and chemical stability, easy synthesis, and robust nature. MMPFs then are great potential building blocks of coordination polymers that have a range of applications from guest-molecule adsorption to catalysis. The internal surface areas and pore volume of MMPFs are also extremely large for the size of such a small crystal, and when combined with porphyrin metal centers, MMPFs can be customized to different guest molecules.

References

1. Metal–metalloporphyrin frameworks: a resurging class of functional materials (Chem. Soc. Rev., 2014, 43, 5841)
2. (Salen)chromium(III)/DMAP: An Efficient Catalyst System for the Selective Synthesis of 5-Substituted Oxazolidinones from Carbon Dioxide and Aziridines (ORGANIC LETTERS 2004 Vol. 6, No. 14 2301-2304)
3. Crystal Engineering of an nbo Topology Metal–Organic Framework for Chemical Fixation of CO₂ under Ambient Conditions (DOI: 10.1002)