

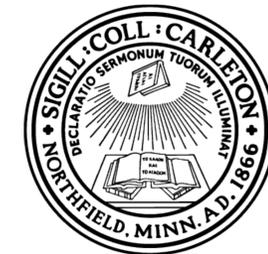


# Hydrothermal synthesis of three-dimensional frameworks from molybdophosphonate building blocks

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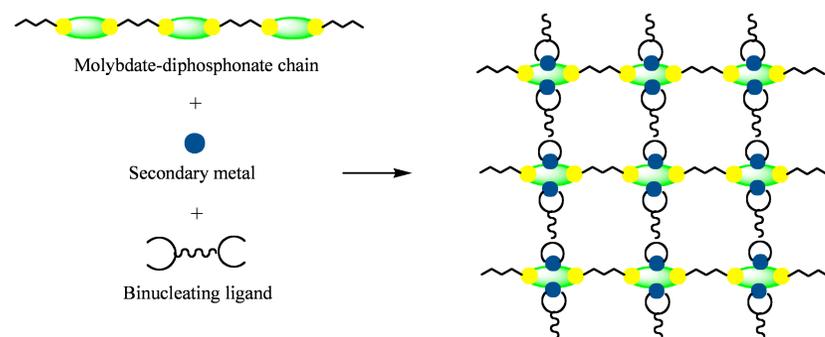
## ABSTRACT:

The hydrothermal reaction of molybdenum(VI) oxide, copper(II) acetate, heptyl didipicolylamine, and butane-1,4-diphosphonic acid in an aqueous solution with HF yielded a three-dimensional open-framework using  $\{Mo_5O_{15}\{O_3P(CH_2)_4PO_3\}_2\}^{4-}$  building blocks. The synthesized material,  $\{[Cu_2(\text{didipicolylamine})]Mo_5O_{15}\{O_3P(CH_2)_4PO_3\}_2\} \cdot 2H_2O$ , falls into the family of copper-molybdophosphonate coordination polymers. Anionic molybdophosphonate clusters are charge compensated by  $\{Cu_2(\text{didipicolylamine})\}^{4+}$  ligand-cations. Three-dimensionality is achieved by copper oxide corner sharing linking one-dimensional molybdenum/diphosphonate chains, while the secondary didipicolylamine ligands simply bridge neighboring phosphomolybdate clusters. This structure was characterized by single-crystal x-ray crystallography

## INTRODUCTION:

The versatility in both structure and function of inorganic oxides has sparked great interest in harnessing their potential for various applications. Inorganic oxides can exhibit magnetic, electronic, optical, and several other properties, characteristics that can be exploited for industrial and scientific purposes.<sup>1</sup> The introduction of organic guest molecules as structural guides to inorganic oxide arrangements, particularly oxometallic clusters, has become a stepping stone into the novel design of oxide architectures.<sup>1,2</sup> Due to the interaction of the inorganic and organic components, these hybrid materials exhibit unique physical and chemical properties, including high porosity and luminescence. Potential applications for these materials involve gas sorption, gas purification, and catalysis.<sup>3</sup>

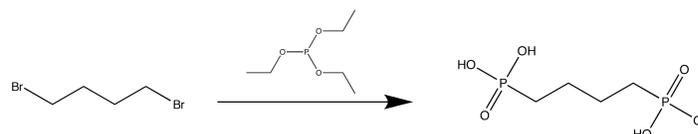
The design of novel materials from polyoxomolybdate clusters as building blocks is well documented. Molybdenum clusters are linked by organophosphonate primary ligands to form one-dimensional chains, while entrained secondary copper(II) bidentate ligands link these chains to provide two- or three-dimensionality<sup>4</sup>, as seen in **Figure 1**.



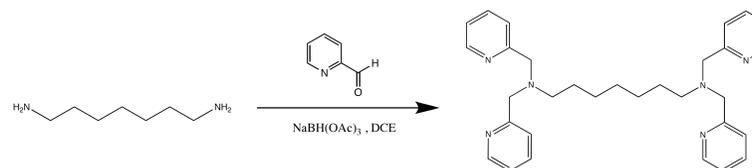
**Figure 1** Basic structural scheme of a molybdophosphonate coordination polymer. Phosphomolybdate clusters are bound together by an organic tether, forming one-dimensional chains. Secondary metal sites decorate the clusters, linked by a binucleating ligand.

Structures of this variety are produced in hydrothermal conditions to overcome the hurdle of differential solubility.

The syntheses of the primary diphosphonic acid (**Figure 2**) and the secondary didipicolylamine ligand (**Figure 3**) were relatively straightforward one-step reactions:

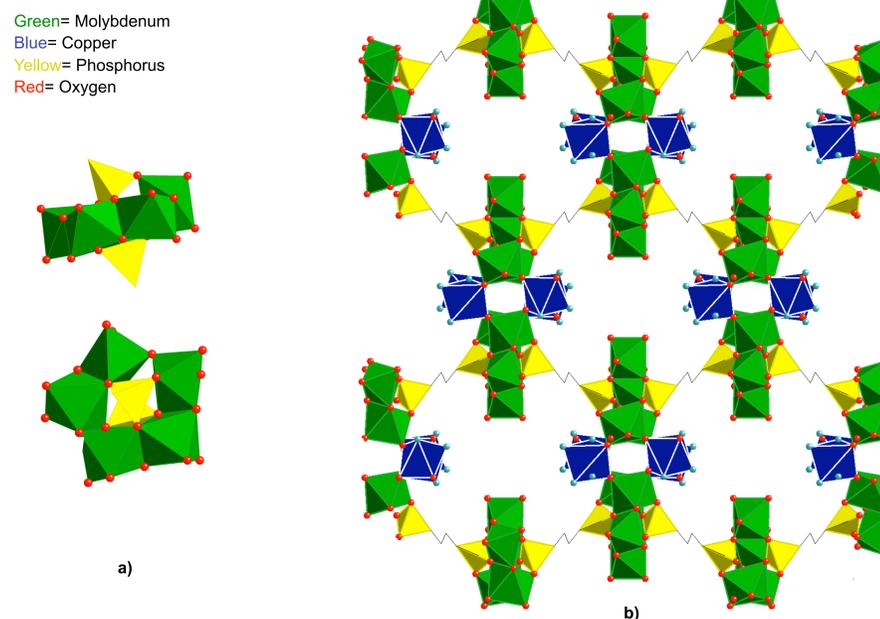


**Figure 2** 1,4-dibromobutane was treated in a solution of triethylphosphite to form butane-1,4-diphosphonic acid, the primary ligand.



**Figure 3** Heptane-1,7-diamine was treated with picolinaldehyde and sodium acetoxyborohydride in dichloroethane to form heptyl didipicolylamine, the secondary ligand.

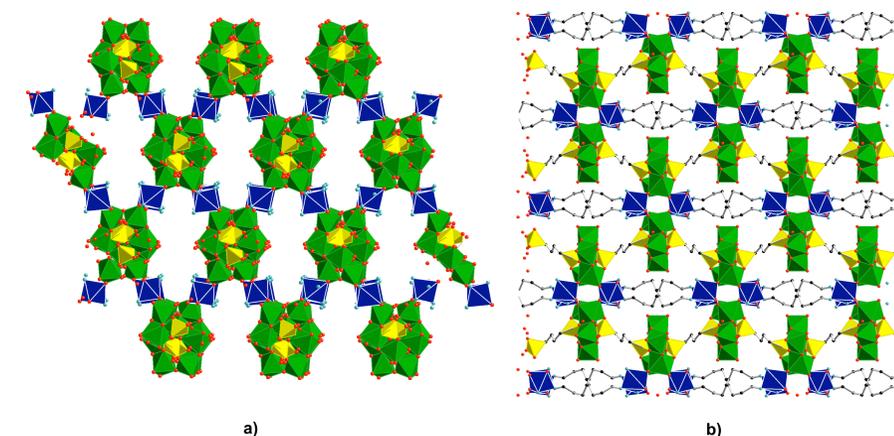
**Figure 4a** shows the phosphomolybdate clusters as they are assembled in  $\{[Cu_2(\text{didipicolylamine})]Mo_5O_{15}\{O_3P(CH_2)_4PO_3\}_2\} \cdot 2H_2O$ . These pentamolybdate clusters are corner-sharing with the phosphorus ends of the primary ligand. This coordination forms one-dimensional phosphomolybdate chains, as predicted by the experimental design. These chains are clearly visible in **Figure 4b**. The peculiarity of this structure is that the link between the one-dimensional phosphomolybdate chains is not provided by the secondary ligand, but rather by corner-sharing copper atoms, as seen in **Figure 4b**.



**Figure 4** a) A polyhedral representation of the pentanuclear molybdophosphonate clusters formed in the structure. b) A side view of the one-dimensional chain linking through corner sharing coppers.

This structure uses corner-sharing coppers to expand three-dimensionally as well. **Figure 5a** shows a view of the framework looking down the one-dimensional molybdophosphonate chains. The linking coppers' binding position allows perpendicular expansion for the open framework.

When the secondary heptyl didipicolylamine ligand is shown, it is apparent that it does not behave in the way in which the experimental design predicted. Rather, the ligands tether the molybdenum clusters diagonally, thus reducing pore size as shown in **Figure 5b**.

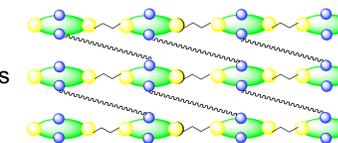


**Figure 5** a) A view of the framework structure with the one-dimensional phosphomolybdate chains running into the page. It is apparent that the parallel chains are linked in a staggered formation, which makes the framework three-dimensional, as the one-dimensional chains are tethered laterally and downward. b) The same view as in figure 4b with secondary copper ligands incorporated within the structure. The ligands run diagonally out of the page.

## CONCLUSION & FUTURE WORK:

The hydrothermal experimentation with butane-1,4-diphosphonic acid and heptyl didipicolylamine was able to yield a 3D framework, and therefore was a success. However, the functionality of this material is limited due to the arrangement of the secondary ligand, which decreases pore size. Therefore, using long aliphatic ligands does not necessarily allow for larger pore size, since the structure can "accordion," as seen in **Figure 6**.

Future work includes experimentation with different secondary metals/ligands and further characterization of these materials for magnetic, luminescent, electronic, and other properties.



**Figure 6** The "accordion" effect of longer ligands.

## ACKNOWLEDGEMENTS:

This work was supported by a grant from the National Science Foundation (CHE-0850756). Special thanks to Mark Bartholomä and Jon Zubieta.

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