



Development of Pyridine Phosphate-based Metal-Organic Frameworks

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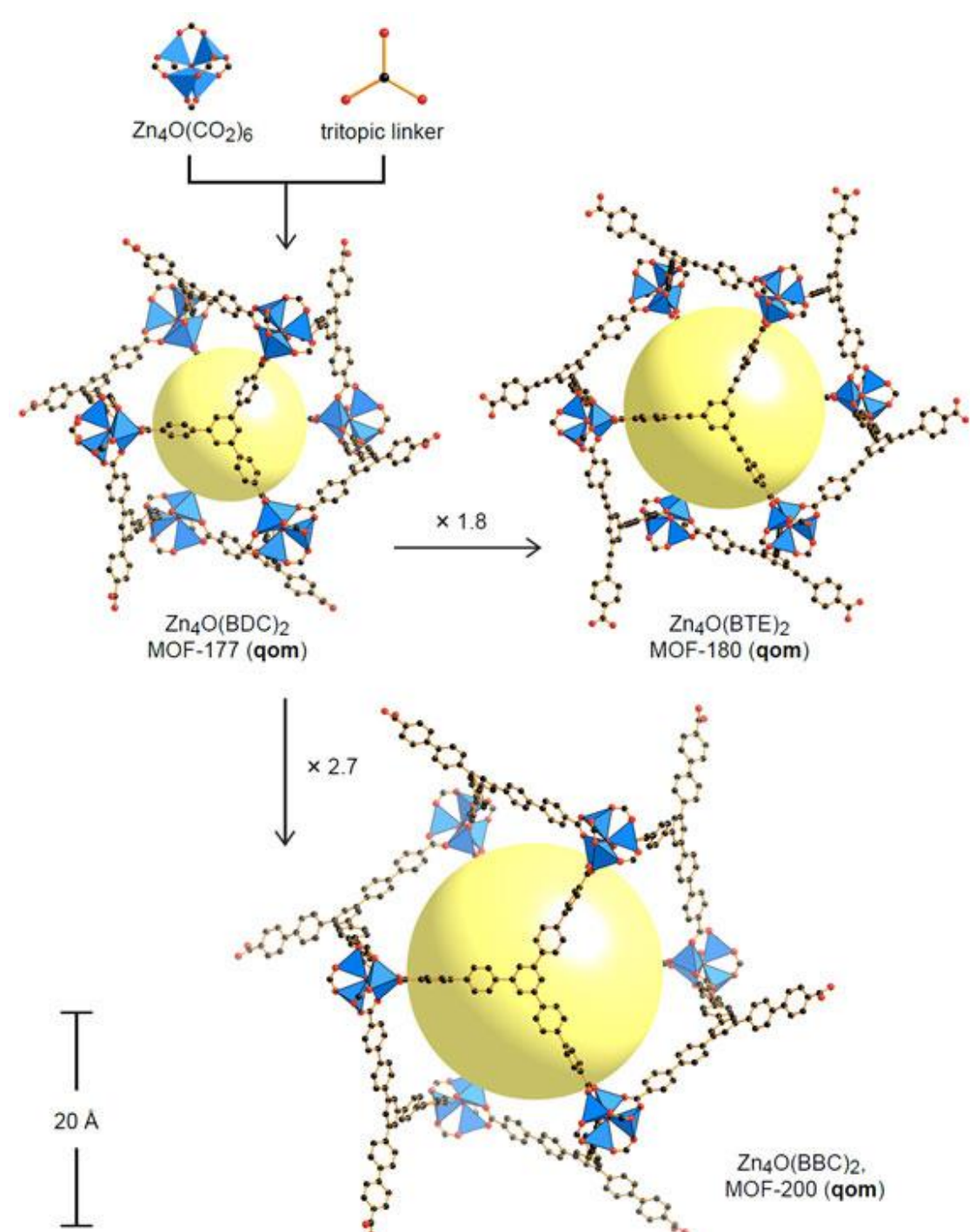
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Abstract

Metal-organic frameworks (MOFs) are a group of porous crystalline materials formed from coordination complexes between organic and inorganic units. Due to their pores, MOFs can have impressively high surface areas, leading to potential valuable applications in gas storage, gas separation, and catalysis. MOFs are typically formed by the growth and accumulation of coordination complex crystals in solution. The goal of this project was to investigate if a crystalline complex could be formed with an organophosphate ligand instead of the more commonly-used carboxylate-based ligands. To do this, we first synthesized dipyridinediphosphonic acid (DPDPA). Afterwards, we paired the ligand up with a variety of metal cations, solvents, and pH ranges to determine the optimal condition for crystals to grow. We discovered that the best combination involved using 0.0500 mmol of DPDPA with 0.0500 mmol of copper (II) nitrate in 2.00 mL water and 0.10 mL triethanolamine (TEOA), forming blue-green microcrystals. Further tests could be performed with similar combinations to grow larger crystals for use in MOF-building.

Background

Metal-organic frameworks (MOFs) are an extensive class of highly-porous coordination polymers with huge internal surface areas. They consist of organic ligands coordinated to metal cations, and due to the enormous variety of compounds and metal ions that could be used as MOF components, a huge amount of different MOFs have been synthesized. Indeed, more than 20,000 different MOFs were reported within the past decade (Furukawa *et al.*).



The most basic units of a MOF is are secondary building units (SBUs) and linkers. SBUs are metal cation clusters or complexes, usually consisting of particular transition metal cations, since these can form a variety of interesting coordination complexes with oxidation numbers ranging from 2 to 7. Linkers are the organic units connecting SBUs to each other. Depending on the structure of the SBU and how it interacts with linkers, the resultant MOF can be one, two, or three-dimensional. See the chart below for how inorganic-organic hybrids are categorized by dimensionality.

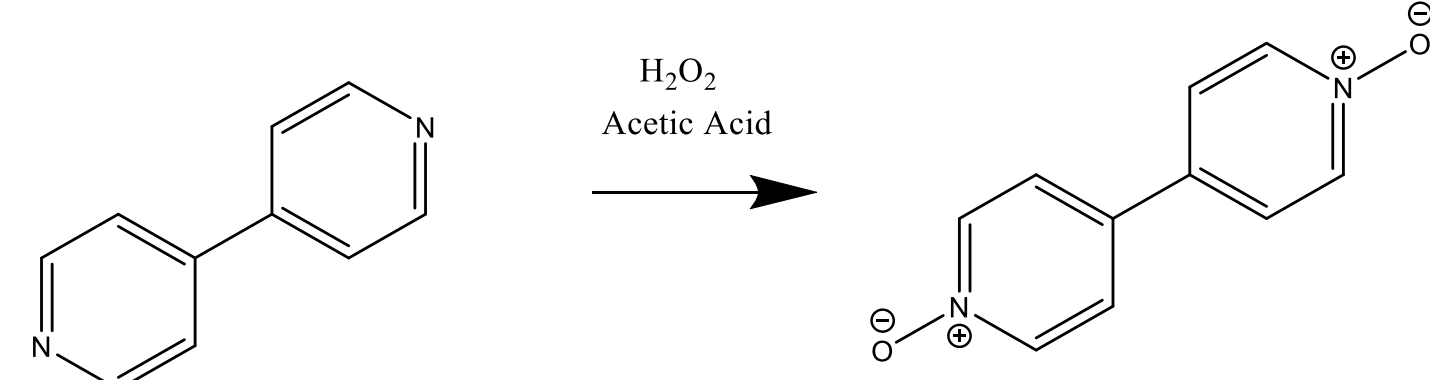
MOFs have attracted a considerable amount of interest since the 1990s due to their remarkable versatility. Because their features can be fine-tuned after synthesis without significantly affecting underlying topologies, MOFs can be precisely enhanced to suit a particular purpose, a flexibility that has not been achieved with other porous materials like zeolites and carbon-based structures.

Synthesis of MOFs is achieved almost exclusively through hydrothermal synthesis, in which crystals are grown from a solution under high pressure and temperature. These conditions mimic those found deep within Earth that cause natural crystals to form. In this situation, partial or complete dissolution of MOF ingredients is essential, since compounds must be able to easily travel through the solution to aggregate on a “seed” crystal.

Dimensionality of Inorganic Connectivity, I ⁿ (n = 0—3)					
Metal-organic metal connectivity, O ⁿ (n = 0—3)	0	1	2	3	
	0	Molecular complexes	Hybrid inorganic chains	Hybrid inorganic layers	3-D inorganic hybrids
	1	Chain coordination polymers	Mixed inorganic-organic layers	Mixed inorganic-organic 3-D framework	—
	2	Layered coordination polymers	Mixed inorganic-organic 3-D framework	—	—
	3	3-D coordination polymers	—	—	—

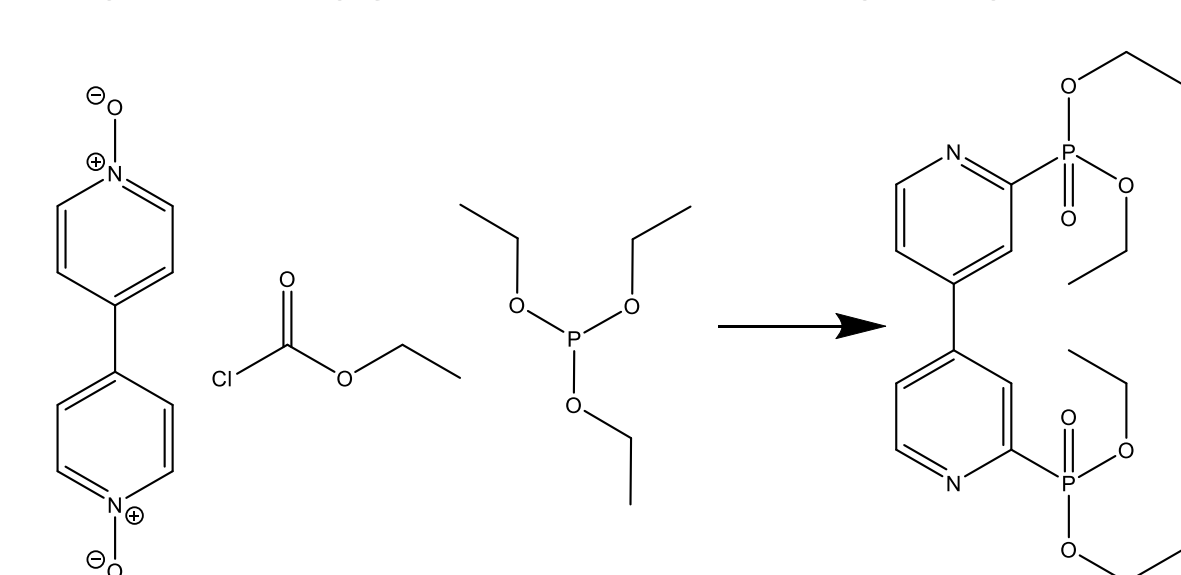
Synthesis of Dipyridinediphosphonic acid (DPDPA)

Step 1: 4,4'-bipyridine to N-oxide



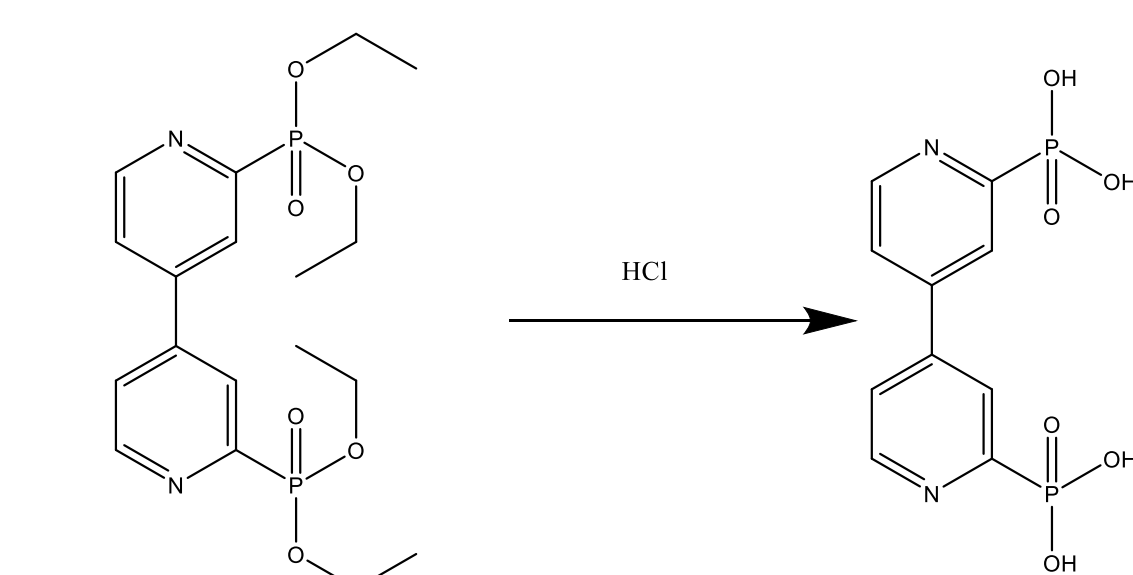
To a 250 mL round-bottomed flask was added 15.5 g of 4,4'-pyridine, 41 mL of 30% H₂O₂, and 80.0 mL of glacial acetic acid. The mixture was heated while stirring at 80°C for 4 hours. Then another 41 mL of 30% H₂O₂ was added, and the mixture was heated at 80°C for another 12 hours. After that, the flask was cooled to room temperature, and the unreacted H₂O₂ and acetic acid were evaporated under reduced pressure. 40 mL of water was added to the residue, and the mixture was evaporated again under reduced pressure. Then 200 mL of acetone was added to form a yellow precipitate that was then filtered and washed with acetone. Finally, 4,4'-pyridine N-oxide was recrystallized from ethanol at an 86% yield.

Step 2: 4,4'-pyridine N-oxide to phosphodiester



16 g of 4,4'-pyridine N-oxide was added to a 1000 mL round-bottomed flask with 800 mL CH₂Cl₂. Then 48.6 mL anhydrous ethyl chloroformate was added and stirred for 10 minutes under nitrogen atmosphere. Following that, 89 mL triethyl phosphite was added dropwise, and the mixture was then stirred for an additional 30 minutes under nitrogen atmosphere. The resulting solution was washed with saturated NaHCO₃, water, and then brine, with excess liquid evaporated under reduced pressure. The organic product left behind was dried with silica, run on a column with CH₂Cl₂ and methanol, and evaporated under reduced pressure again to form a yellow solid (the phosphodiester) at 67% yield.

Step 3: 4,4'-pyridine phosphodiester to phosphate

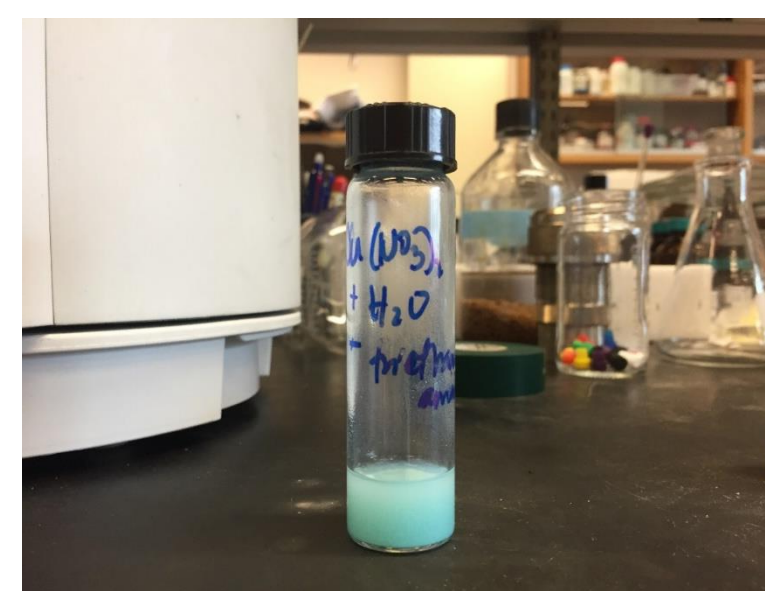
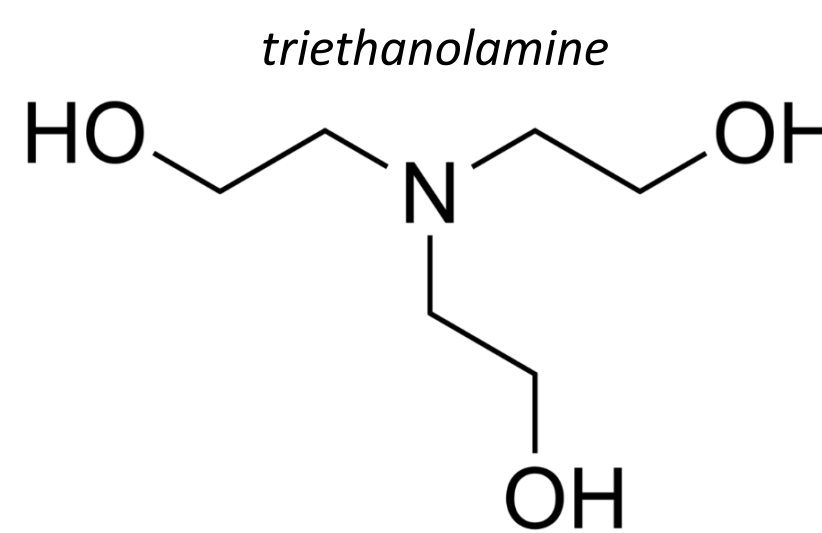


In a 1000 mL round-bottom flask was placed 24.2 g of 4,4'-pyridine phosphodiester and 300 mL of 8 M HCl. The mixture was refluxed over 18 hours, then evaporated under reduced pressure, and then suspended in water and filtered. The resulting product was washed with water twice before let to dry at room temperature. The result is an off-white cakey solid, DPDPA, and it was obtained at 87% yield.

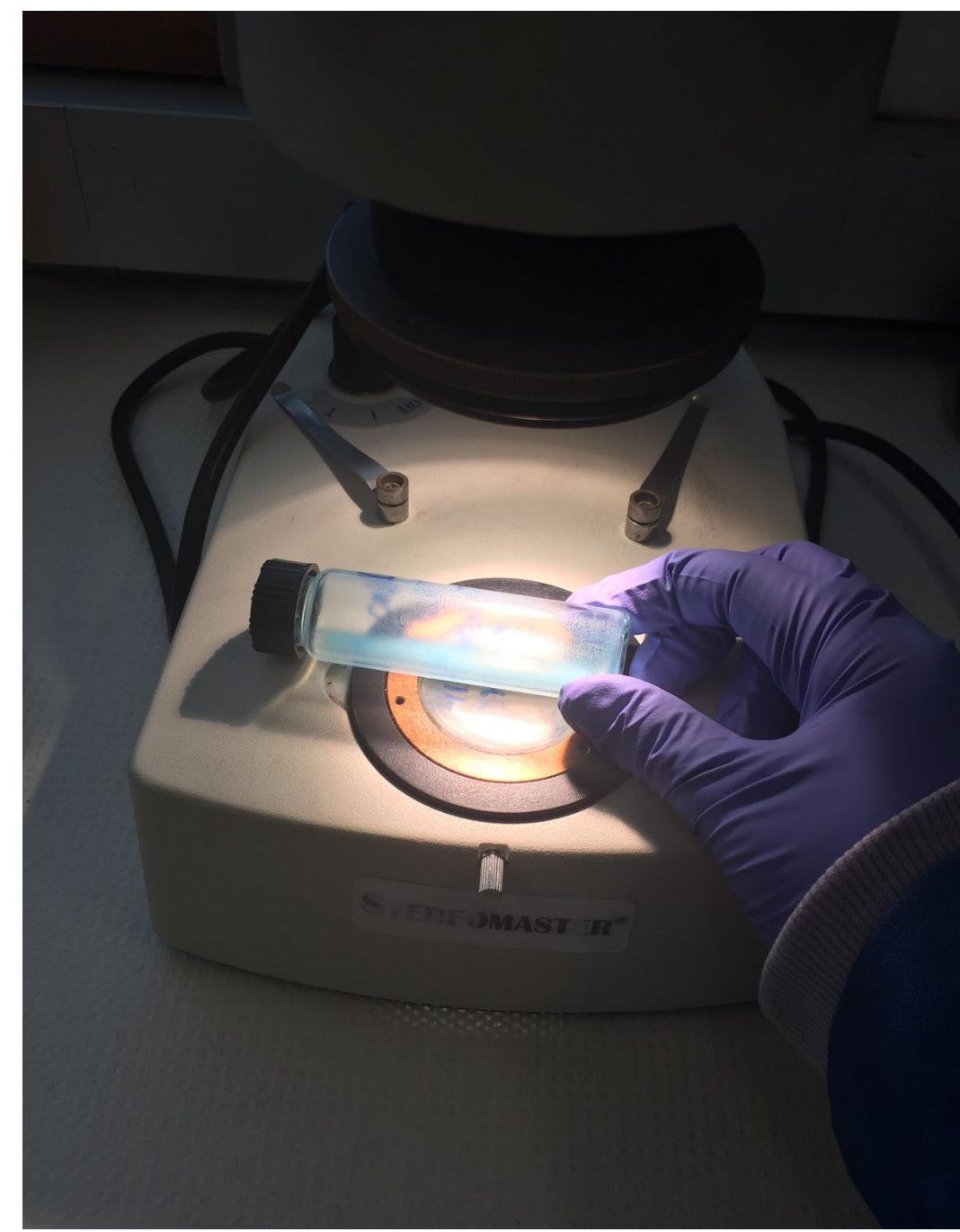
Making the Crystals

Several trials were run, with different metal cations (Mn²⁺, Co²⁺, Cu²⁺, Ni²⁺, Zn²⁺), metal-ligand ratios, pH, solvents (water, N-methyl-2-pyrrolidone, methanol, dimethylformamide), and time in oven, before a combination that yields crystals was found. A detailed table of all trials can be found here: <https://goo.gl/a6BBBF>.

In the successful trial, 11.7 mg (0.0500 mmol) of Cu(NO₃)₂ was added to a screw-top vial containing 15.8 mg (0.0500 mmol) of DPDPA, 2.00 mL deionized water, and 0.10 mL triethanolamine (TEOA). The vial was sonicated until the solution inside became clear. Afterwards, it was heated for 8 hours in a sand bath in an oven at 120°C. After being removed from the oven, the vial was allowed to slowly cool down to room temperature, so the complexes within would continue to form crystals without disturbance. Finally, the vial was examined under a microscope.

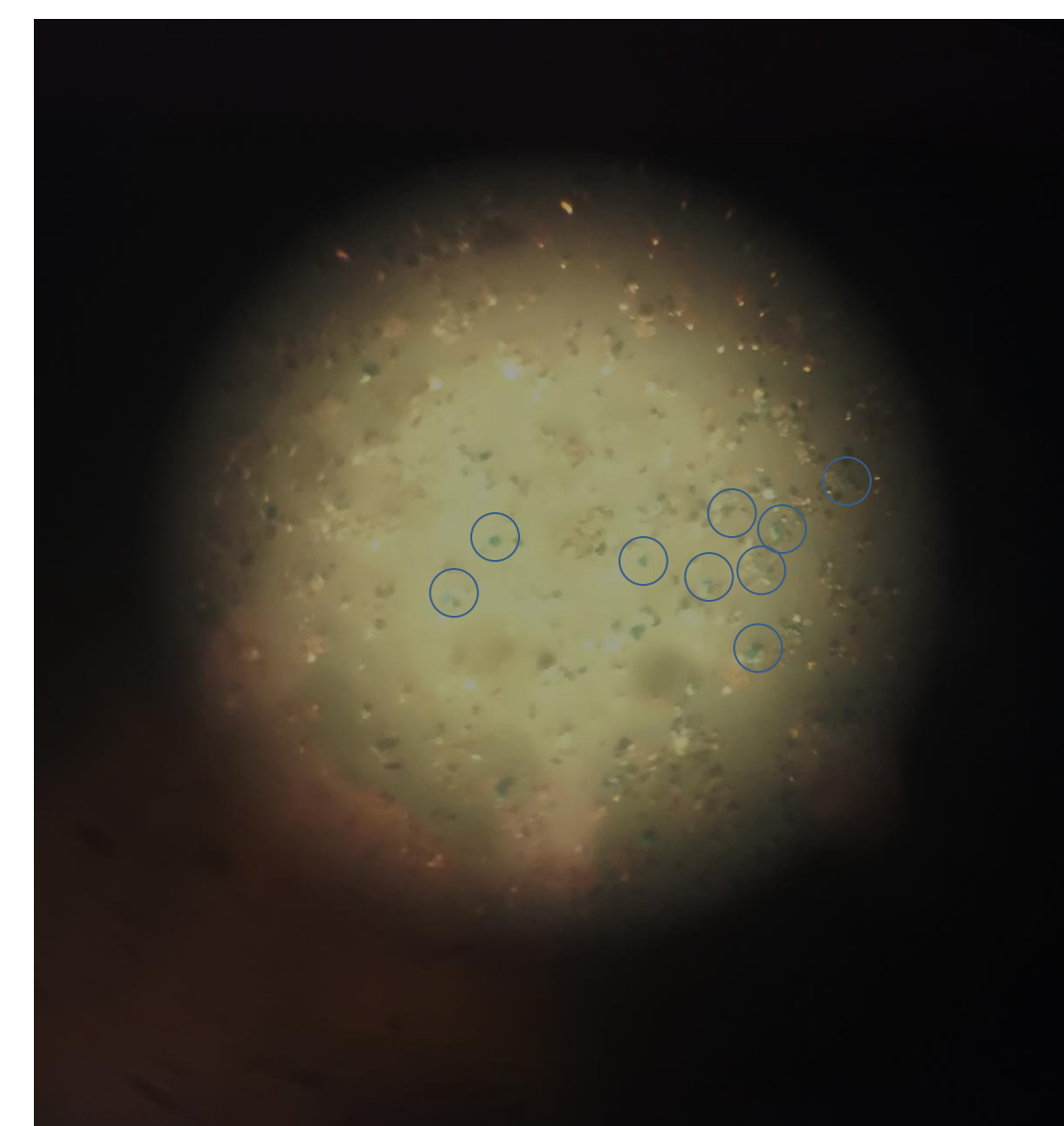


Vial after removal from oven



Examining the crystals

Results



Microcrystals under a microscope (circled)

The ligand by itself was insoluble in all solvents used, so base (NaOH or TEOA) was added to deprotonate it. The metal cations did not precipitate as metal hydroxides when TEOA was added, which made it a better base to use than NaOH. Out of all solvents, water was best at keeping both metal and the deprotonated ligand in solution. Also, combinations with copper and nickel dissolved with the most ease.

Most trials were unsuccessful — the ligand may have settled out, or simply remained in solution without binding to the cation, or a powder may have been produced. The trial that produced crystals involved 0.0500 mmol of DPDPA paired with 0.0500 mmol of Cu in 2.00 mL water and 0.10 mL TEOA. The blue-green microcrystals that formed had a diameter of < 10 μm. Since they were so small, however, we could not determine the crystal structure with X-ray crystallography.

Discussion, Conclusion, and Future Studies

Condition Screening

By solvent	By pH	By metal-ligand ratio	By temperature	By time	By cation
H ₂ O, NMP, MeOH, DMF	3-5 to 8-10	1:2 to 3:1	120°C or 160-180°C	8 h to 70 h	Mn ²⁺ , Co ²⁺ , Cu ²⁺ , Ni ²⁺ , Zn ²⁺

Reflection

Organophosphonic acids are notoriously insoluble in most organic solvents, as is the DPDPA. This in turn means it is difficult to form MOFs, using this linker, as most MOF syntheses rely on organic solvents. For this reason, water was used as solvent instead, as DPDPA can dissolve in water at basic pH. Other factors preventing the formation of large crystals may include a too-high pH as well as a metal-ligand ratio that is not optimal. Most MOF structures seem to grow in a pH range of 5-8; however, since we added the strong base TEOA to dissolve the DPDPA, the pH in our vials exceeded the limits of that range. With respect to the metal-ligand ratio being unoptimized, structures that form may not crystallize into an ordered crystal lattice. As for the trials where only a clear solution with no crystal formation resulted, the TEOA may have chelated the cation, preventing it from being coordinated by the ligand.

Due to time and resource constraints, I was unable to fine-tune the component ratios within the vial so that larger crystals would form. Future efforts will focus on this. DPDPA's phosphodiester precursor could also serve as a ligand for MOF formation, since it is much more water-soluble. For now, this is a promising start to a MOF with pyridine-phosphate ligands.

References

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