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UNIVERSITY OF CALIFORNIA SAN DIEGO

**Tunable Transition-Metal-Linked Preyssler Type Polyoxometalate Frameworks:
Synthesis, Structural Characterization and Optical Properties**

A thesis submitted in partial satisfaction of the requirements for the degree
Master of Science

in

Chemistry

by

Linfeng Chen

Committee in charge:

Professor Alina M. Schimpf, Chair
Professor Jeffrey Rinehart
Professor Wei Xiong

2019

The thesis of Linfeng Chen is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

Chair

University of California San Diego

2019

DEDICATION

I dedicate this chapter of my life to my family and friends for the unconditional love and support over the years

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LIST OF SYMBOLS AND ABBREVIATIONS

!	Alpha
Å	Ångström; 10^{-10} m
Å ³	Cubic Ångström
atm	atmosphere (1 atm = 101.325 kPa)
"	Beta
°C	Degrees Celsius
ca.	Calculated
CO ₂	Carbon Dioxide
!	Chemical shift; ppm
!	Delta, heat
d	Doublet (NMR)
D ₂ O	Deuterated water
DMSO	Dimethylsulfoxide
ESI-MS	Electrospray Ionization mass spectrometry
Et ₂ O	Diethyl ether
EtOH	Ethanol
ee	Enantiomeric excess
FT-IR	Fourier transform infrared spectroscopy
\$	Gamma
g	Gram
h	Hour
H ₂	Hydrogen
HCl	Hydrochloric acid

H ₂ O	Water, hydrate
HPLC	High-Performance Liquid Chromatography
H ₂ SO ₄	Sulfuric acid
Hz	Hertz
<i>J</i>	Coupling constant
K	Kelvin
%	kappa
&''	Lambda; wavelength; nm
m	Multiplet
M	Molar; mol L ⁻¹
mg	Milligram
μL	Microliter
•m	Micrometers
mL	Milliliter
mm	Millimeter
mmol	Millimole
mmHg	Millimeters mercury
min	mintues
MHz	MegaHertz
MeOH	Methanol
MOF	Metal-Organic Framework
MS	Mass spectrometry
N ₂	Dinitrogen
&''	Lambda; wavelength; nm
m	Multiple

M	Molar; mol L ⁻¹
mg	Milligram
μL	Microliter
μm	Micrometers
mL	Milliliter
mm	Millimeter
mmol	Millimole
mmHg	Millimeters mercury
min	minutes
MHz	MegaHertz
MeOH	Methanol
MOF	Metal-Organic Framework
MS	Mass spectrometry
N ₂	Dinitrogen
NMR	Nuclear Magnetic Resonance spectroscopy
POM	Polyoxometalate
RT	Room temperature
S	Singlet (NMR)
SBU	Secondary Building Unit
SEM	Scanning electron microscopy
SiO ₂	Silica
(	Theta
TGA	Thermal gravimetric analysis
THF	Tetrahydrofuran
UV/VIS	Ultra-Violet/Visible

XRD	X-ray diffraction
V	Volume
wt%	Weight percent

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crystallography lab at UCSD and Dr. Jeffrey Rinehart and Benjamin H. Zhou aided in the conductivity measurement.

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Publications

1. **Linfeng Chen**, Michael J. Turo, Curtis E. Moore, Alina M. Schimpf, “Tunable transition-metal-linked Preyssler type polyoxometalate frameworks: Synthesis, structural characterization and optical properties.” In preparation.
2. Michael J. Turo, **Linfeng Chen**, Curtis E. Moore, Alina M. Schimpf, “Co²⁺-Linked [NaP₅W₃₀O₁₁₀]¹⁴⁻: A Redox-Active Metal Oxide Framework with High Electron Density”, *J. Am. Chem. Soc.*, Article ASAP
3. Weilai Yu, Shuai Zhang, Junxiang Chen, Pengfei Xia, Matthias H Richter, **Linfeng Chen**, Wei Xu, Jingpeng Jin, Shengli Chen, Tianyou Peng, “Biomimetic Z-scheme photocatalyst with a tandem solid-state electron flow catalyzing H₂ evolution” *J. Mater. Chem. A*, **2018**, *6*, 15668.
4. Weilai Yu, Junxiang Chen, Tongtong Shang, **Linfeng Chen**, Lin Gu, Tianyou Peng, “Direct Z-scheme g-C₃N₄/WO₃ photocatalyst with atomically defined junction for H₂ production”, *Appl. Catal. B: Environ.* **2017**, *219*, 693.
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by noble and 3d metals—a planar model electrode study for Li-O₂ battery”, *ACS Appl. Mater. Interfaces*, **2017**, *9*, 19800.

ABSTRACT OF THE THESIS

Tunable Transition-Metal-Linked Preyssler Type Polyoxometalate Frameworks: Synthesis, Structural Characterization and Optical Properties

by

Linfeng Chen

Master of Science in Chemistry

University of California San Diego, 2019

Professor Alina M. Schimpf, Chair

Polyoxometalates (POMs) are a class of molecularly defined transition-metal-oxide clusters (Cr, V, Mo, W, Nb) that have been explored for use in catalysis, magnetism, electronics, gas sensing, and drug delivery. frameworks.

In Chapter2, the general experimental methods have been introduced. The basic characterizations and experimental design are showed by figures and words.

The Chapter 3 focuses on using POMs as building blocks to create doped tungsten oxide frameworks. Specifically, I develop a strategy to synthesize six frameworks based on the Preyssler cluster $[P_5W_{30}O_{110}]^{15-}$ linked with various transition metals such as Mn, Fe, Co,

Ni, Cu and Zn. These cluster-based frameworks offer the advantage of precisely placed atoms and well-defined dopant W:O ratios. Additionally, bimetallic POM frameworks have been prepared in which the transition metals are distributed homogeneously within the crystals. The ability to synthesize frameworks with 6 different metals and combinations thereof enables tunable absorption that varies as a function of metal identity and content. I use diffuse reflectance and conductivity to characterize the effect of different metal linkers on the properties of the metal oxide.

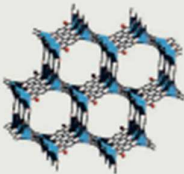
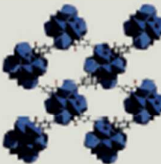
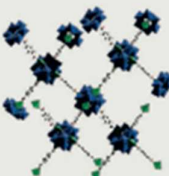
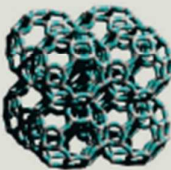
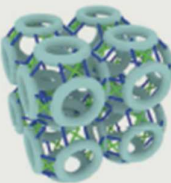
Chapter 1

Introduction to Polyoxometalate frameworks

1.1 Introduction to porous materials

Designing inorganic materials with a porous skeleton is attractive because the self-assembly process can be used to join small components into larger functional components.¹⁻² Porous inorganic materials such as metal organic frameworks (MOFs) and zeolites have been widely studied for various applications including catalysis, gas separation and storage, and energy conversion.³⁻⁶ MOFs and Zeolites are porous materials with multiple holes which helps them to capture different types of gas molecules.⁷⁻⁸ The sizes, shapes and distribution of the pores can be designed to satisfy different functional requirements (Table 1.1).⁹ Current routes toward porous materials include soft or hard templating, nanoparticle self-assembly, reinforced crystallization, or post-synthetic solid-solid crystallization.¹⁰ These methods however, often suffer from poor control over pore shape, size, or lose porosity when evacuated. It remains a great challenge to find a strategy to synthesize porous materials under mild conditions.

Table 1.1 The diversity of porous materials. Adapted with permission from ref 9.

Porous materials	Example of structure	Structural diversity	Inorganic content	Ability to delocalize electrons
Metal–organic frameworks (MOFs)	 MOF-74	High	Low	Low
Polyoxometalate-based open frameworks (POM-OFs)	 {MoLa}-based POM-OF	High	Low	Medium
Zeolitic POM-based MOFs (Z-POMOFs)	 Z-POMOF1	Low	Medium	High
Zeolites	 Zeolite A (LTA)	High	High	Low
POM-zeolites (POMzites)	 POMzite-3 (Mn)	High	High	High

1.2 Polyoxometalates

Recently, a new type of all-inorganic porous material has been developed by using polyoxometalates (POMs). POMs exhibit great properties in the field of redox chemistry, hydrolysable protons and anionic and oxygen-rich nature.¹¹⁻¹⁶ Base on these excellent properties, various applications in catalysis, magnetism, electronics, gas sensor,

supramolecular chemistry and drug deliver have been reported.¹⁷⁻²² Among these POMs, the Keggin structure, (Figure1.1) Dawson structure, (Figure1.2) and Preyssler structure (Figure1.3) are the most attractive.²³⁻²⁵

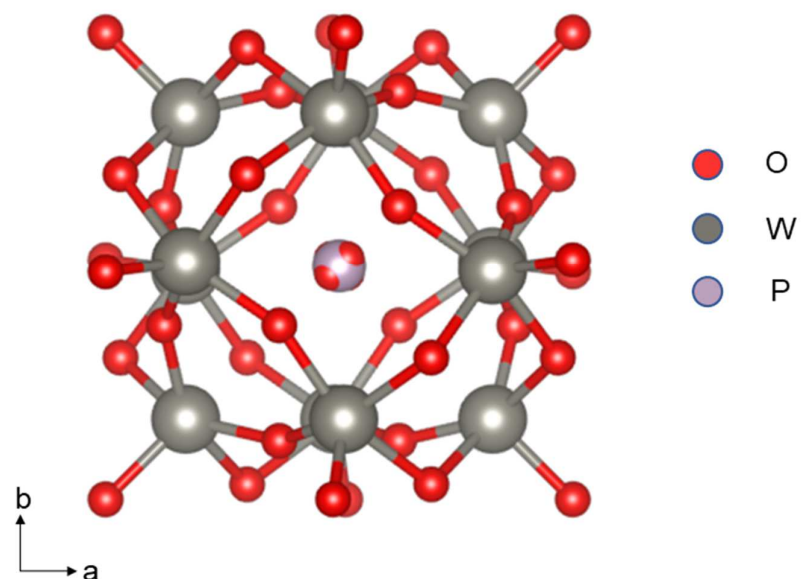


Figure. 1.1 Crystal structure of the Keggin anion.

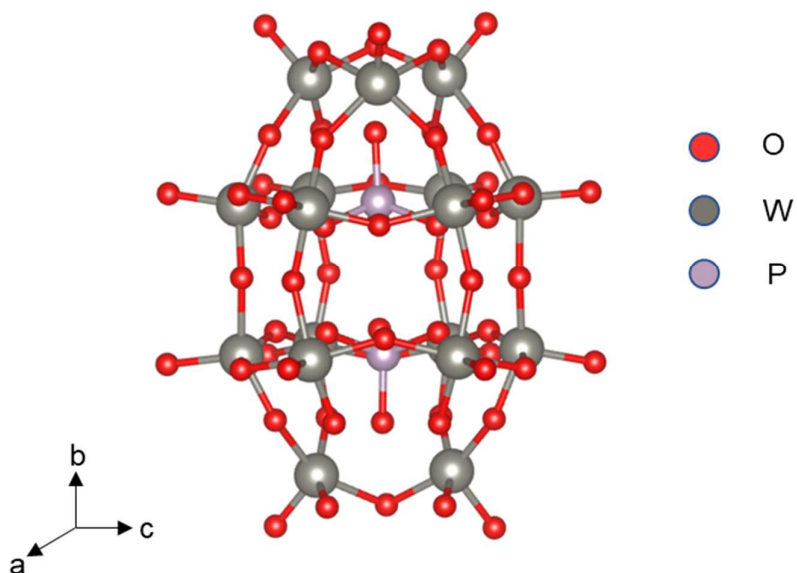


Figure. 1.2 Crystal structure of the Dawson anion.

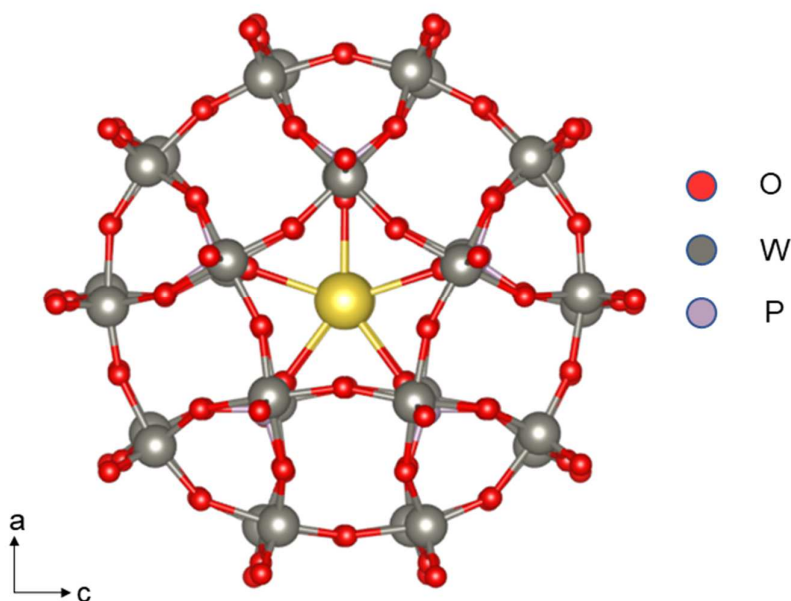


Figure. 1.3 Crystal structure of the Preyssler anion.

The Keggin structure based POMs was formed from twelve metal atoms ($M=V, Nb, Ta, Mo, W$) around one single heteroatom ($X=P, As, Si, Ge$), where $X/M=1:12$.²¹ This structure was first reported by Pauling²⁶ in 1929 and then characterized by X-ray diffraction in 1933. J.F. Keggin²⁷ named the structure of $PW_{12}O_{40}^{3-}$ as Keggin. In the Keggin structure, the heteroatom X is attached with four oxygen atoms to form a tetrahedron and six oxygen atoms linked with one metal atom to form octahedra. Three octahedra can yield a new M_3O_{13} group. And then this group can be connected with others atoms and the common site of M_3O_{13} is linked to the central heteroatom X . (Figure 1.4) The Keggin structure has generated large interest as oxidative catalysts. This is because by changing the constituent elements (other transition metals or main group metals), they can control their thermal and chemical stability and acidity properties at the atomic/molecule level without affecting the Keggin structure.²¹

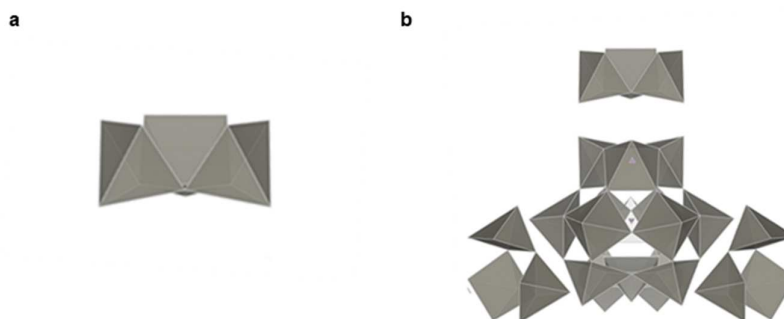


Figure. 1.4 (a) Combination of three octahedra to form a trimetallic group M_3O_{13} . (b) Structure of the Keggin type POM.

The Dawson structure-based POM was combined from two lacunary Keggin monomers $XW_9O_{34}^{2-}$, where $X/M=2/18$. In 1947, Souchay²⁸ synthesized a new POMs with the ratio $X/M=1:9$. Six years later, this structure was first characterized by Dawson so he named this structure as Dawson.²⁹ In Dawson POM, bimetallic groups (M_2O_{10}) are produced by the condensation of two octahedrons, the center of which is engaged by metal atoms and the vertices by oxygen atoms. (Figure 1.5) Wells–Dawson has been reported to be the best catalyst in the Prins cyclization alkenes. Compared with conventional catalytic systems, the high-reaction rate, mild conditions and improved selectivity are the features obtained in the systems.

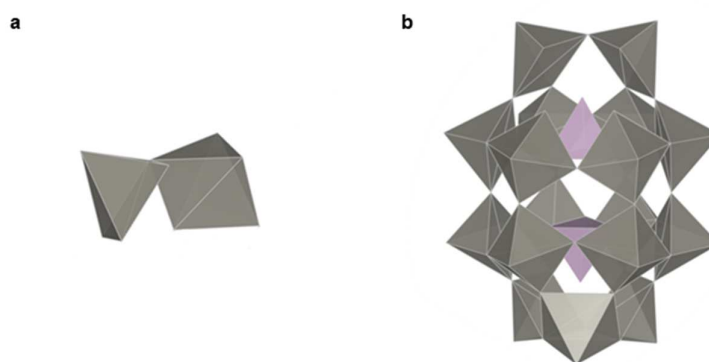


Figure. 1.5 (a) Combination of two octahedra to form a dimetallic group M_2O_{10} . (b) Structure of the Dawson type POM.

The Preyssler anion, $[NaP_5W_{30}O_{110}]^{14-}$, comprised of 5 $[PW_6O_{22}]^{3-}$ subunits grown around a central cation, is an electroactive cluster which is completely oxidized. Upon

switching out central cation, the electronic structure of the POM can be modulated, allowing for a tunable building block.³⁰⁻³¹ Up to 10 electrons can be admitted in the Preyssler anion in solution before the potential becomes reducing enough to reduce H₂O.³⁰ Easy preparation, stability in a wide pH range (0–11) and great electroactive properties led Preyssler to become an attractive building unit in POM family. Additionally, the central cation can be readily exchanged for various metal ions, such as Ca²⁺, Bi³⁺ and many of the trivalent lanthanoids, offering additional handles for controlling the properties of the assembled materials.³² Upon switching out the central cation the electronic structure of the Preyssler is changed, allowing for a tunable building block.³³

1.3 Tungsten oxide

POMs are molecularly defined transition metal-oxide clusters (TM= Cr, V, Mo, W, Nb). Among all POMs, tungsten oxide (WO_x) is the most attractive cluster for the researchers. The study of WO_x began from the 17th century when the LiWO₃ and WO₃ were found.¹⁸ Tungsten oxide is famous as nontoxic and photostable semiconductor with a narrow bandgap about 2.6 eV. A noteworthy part of visible light can be absorbed, hence, WO_x is a convincing photocatalyst for solar light harvesting¹⁹⁻²². Besides, WO_x also performed well in electrochromic display, gas sensors and optical devices.²¹⁻²³ Due to the narrow bandgap of WO_x, only the blue and near ultraviolet regions of the solar spectrum can be excited. The photocatalytic performance of WO_x can be increased by doping numerous elements to reduce bandgap effectively.²⁴⁻²⁵ Obtaining element doped WO_x has gained more and more attention in the application of WO_x although their synthesis is still challenging. However, POMs are a perfect candidate to solve these problems. POMs offer the advantage of precisely placed atoms and well-defined W:O ratios. Furthermore, POMs allow access to morphologies and compositions that may be otherwise difficult to achieve. POMs can be used as building blocks for frameworks in which the POMs are linked with organic or inorganic linkers, or a

combination of the two which are the great method to dope other elements..²⁶⁻²⁸ Indeed, numerous POM-based frameworks, containing POMs linked by organic ligands, have been reported, emulating the widely studied field of MOFs. All-inorganic frameworks, however, have high stability, high catalytic, photochemical and electrochemical activity.¹ Compared to hybrid materials that include organic linkers, all inorganic frameworks, in which the POM cluster is linked solely by metals, have not been widely explored.

1.4 POM Frameworks

POMs clusters represent an intermediate between molecular and nanosized metal oxides,³⁴ and comprise a vast library of building blocks for nano-, micro- or even millimeter sized metal oxide materials.^{11, 35} Due to structural diversity, POMs are ideal motifs for coordination polymers. POMs are molecularly defined metal-oxide clusters that can be used as building blocks for frameworks in which the POMs are linked with organic or inorganic linkers, or a combination of the two. Indeed, numerous POM-based frameworks (POM frameworks), containing POMs linked by organic ligands, have been reported, emulating the widely studied field of metal-organic frameworks (MOFs). All-inorganic frameworks have high stability, high catalytic, photochemical and electrochemical activity.³ Much less attention, however, has been given to all-inorganic POM frameworks, in which POM units are linked by transition metals (Figure 1.6)³⁶. Furthermore, most POM frameworks reports have focused on the development of novel topologies and architectures, while paying little heed to functionality. These materials, however, present an exciting opportunity to bridge the gap between MOFs and solid-state porous metal oxides, while taking advantage of the rich chemistry available in POMs. The potential synthetic versatility of POM frameworks offers access to quantized ternary metal oxide compositions not readily accessible via other synthetic strategies.

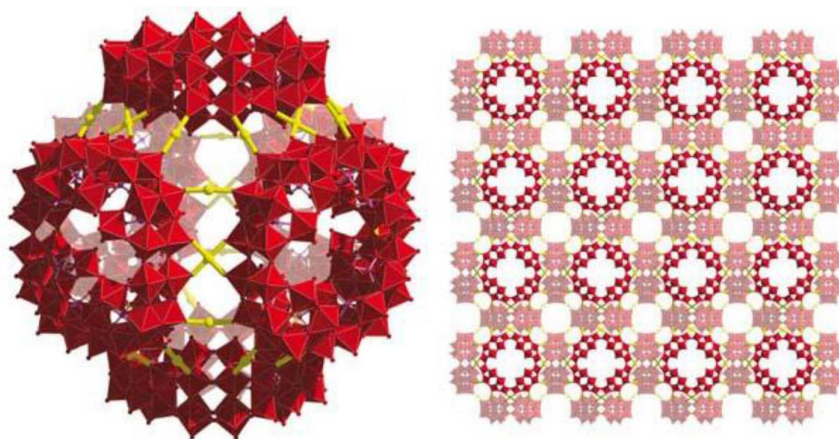


Figure 1.6 Face-directed assembly of Mn-linked $[\text{P}_8\text{W}_{48}\text{O}_{184}]^{40-}$ clusters to form $[\text{Mn}_8(\text{H}_2\text{O})_{48}\text{P}_8\text{W}_{48}\text{O}_{184} \cdot 108\text{H}_2\text{O}]^{24-}$. Adapted with permission from ref 36.

1.5 Topic selection and research ideas

According to the previous introduction, POMs are molecularly defined metal-oxide clusters that can be used as building blocks for frameworks in which the POMs are linked with organic or inorganic linkers, or a combination of the two. Compared to hybrid materials that include organic linkers, all inorganic frameworks, in which the POM cluster is linked solely by metals, have not been widely explored. The research focuses on the assembly of metal oxide clusters with transition-metal linkers, which can allow access to morphologies and compositions that may be difficult to achieve via traditional synthetic routes.

Here, this research will focus on Preyssler-based POM frameworks, although the Preyssler-based POM frameworks were not the good example of porous materials. The Preyssler-based POM frameworks which were stable over a wide pH range (0–11) and easy to synthesize are a good example to study the mechanism of POM frameworks formation and phase control. If researchers want to explore the world of POM frameworks, the Preyssler POM frameworks are the best example to start.

The goals of the research are three-fold:

First, this thesis will evaluate various synthetic conditions with many transition metals to determine the best way to make a variety of frameworks.

Second, the thesis will measure the effect of different linkers on properties such as absorption, and conductivity.

Third, the thesis will try to control the structure phases by adding different amount of cation.

Overall, the research hope to use POM-based frameworks to provide a unique path toward extending the library of porous inorganic metal oxide materials with tunable properties.

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Chapter 2.

General Experimental Methods

2.1 Experimental Design

POM frameworks were synthesized by similar to previous systems.¹ Briefly, in a 1 M LiCl solution adjusted to pH 1 using HCl (6M) the POM (130.0 mg, 0.016 mmol) was combined with CoCl₂ (156 mg, 0.663 mmol or various transition metals salt) and heated to 90 °C overnight. After the overnight reaction the solution was concentrated on a hot plate until half the volume of the original solution. Crystallizing the resulting solution resulted in the methanol the formation. Crystals were pink, black, green, yellow for Co, Fe, Ni and Mn respectively after 3 weeks.

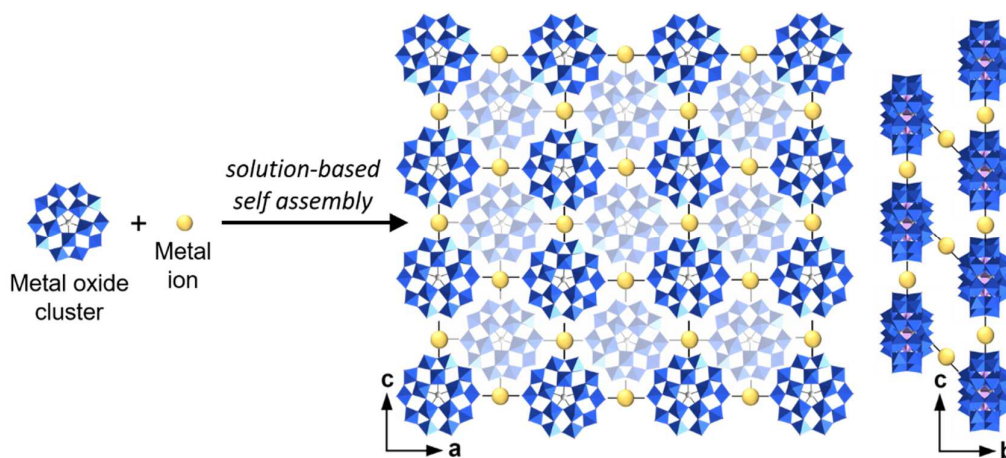


Figure 2.1 Assembly of a Preyssler cluster to form an extended metal oxide solid.

2.2 Experimental Method

Chemicals. Sodium chloride (NaCl, >99%), lithium chloride (LiCl, >99%), methanol and hydrochloric acid (HCl) were purchased from Fisher Chemical. Cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 98%) was purchased from TCI America. Manganous chloride 4-hydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, >95%) was purchased from J. T Baker. Cobalt(II) perchlorate hexahydrate ($\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, 95%), iron(II) chloride tetra-hydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 98%), manganese(II) perchlorate hexahydrate ($\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, >95%), iron(II) perchlorate hexahydrate ($\text{Fe}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$, >95%) and potassium chloride (KCl, 99%) were purchased from Alfa Aesar. Sodium tungsten oxide dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, 95%) and nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 98%) were purchased from Spectrum Chemical. Phosphoric acid (H_3PO_4 , 85%) was purchased from Acros Organics. All chemicals were used without further purification.

Synthesis of $\text{K}_{12.5}\text{Na}_{1.5}[\text{NaP}_5\text{W}_{30}\text{O}_{110}] \cdot 15\text{H}_2\text{O}$. The Preyssler cluster was synthesized following an improved literature procedure.¹ $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (9.90 g, 30 mmol), 85% H_3PO_4 (7.0 ml) and NaCl (1.17g, 20 mmol) were mixed with deionized water (9.0 ml) in a 43 ml Teflon-lined acid-digestion vessel. The reaction mixture was stirred until all reactants were dissolved at room temperature, and then the autoclave reactor was placed in an oven at 125 °C for 20 h. KCl (3.00g, 0.040 mol) was added to the solution mixture when the reaction was cooled to room temperature and stirred for 30 min. The pale-yellow solid was obtained by filtration. The resulting solid was dissolved and recrystallized in 10.0 ml of hot DI water overnight at 20 °C for 3 times. The final white crystals were collected by filtration and dried for 3 h. Yield: 1.8 g, 0.21 mmol, 21% based on W. Characteristic FTIR bands (cm^{-1}): 3403(s), 1620 (s), 1157 (s), 1075(m), 1016 (w), 904 (s), 704 (s). ^{31}P NMR (500 MHz, D_2O): δ -9.41 ppm (s).

Characterization. Inductive coupled plasma-mass spectrometry (ICP-MS) was

collected on a Thermo iCAP RQ ICP-MS. The samples were digested in a 1:1 mixture of 85% HNO₃ (Optima grade, Sigma Aldrich) and 30 % H₂O₂ (Trace metal grade, Sigma Aldrich) with sonication for 90 min. Thermogravimetric Analysis (TGA) was collected using a Perkin-Elmer STA 6000 thermogravimetric analyzer under N₂ and heating at a rate of 5 °C/s. The percent weight in water was determined by the mass loss from 30 °C to 400 °C. Infrared spectroscopy (IR) was collected using an Agilent Cary 630 ATR-FTIR. ³¹P NMR was collected on a JEOL ECA 500 MHz spectrometer with H₃PO₄ in a capillary as an internal standard. Scanning electron microscopy (SEM) images, EDX mapping and line scan profiles were obtained on FEI Quanta FEG 250 scanning electron microscope.

Single Crystals X-ray diffraction. The single crystal X-ray diffraction studies were carried out on a Bruker APEX-II Ultra CCD diffractometer equipped with Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$) 0.05 x 0.05 x 0.05 mm crystal was mounted on a Cryoloop with Fomblin Y oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ω scans. Crystal-to-detector distance was 45 mm and exposure time was 10 seconds per frame using a scan width of 0.75. Indexing and unit cell refinement indicated a primitive, orthorhombic lattice. The space group was found to be *Imma*. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure. All nonhydrogen atoms were refined anisotropic ally by full-matrix least-squares (SHELXL-2014).

Powder X-ray Diffraction. XRD data were collected on a Bruker K3 Kappa Vantec 500 diffractometer equipped with Cu K_α radiation ($\lambda = 1.5478$) at the UCSD X-ray Crystallography Facility, hydrated samples were collected in a sealed capillary. Diffraction images were merged/integrated in Diffrac. EVA V.4.2.2 (Bruker).

2.3 References

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Chapter 3.

Tunable transition-metal-linked Preyssler type polyoxometalate frameworks: Synthesis, structural characterization and electronic properties

3.1 Introduction

Transition metals (TMs) are widely known for their redox and catalytic activity and semi-conductive properties because they have an incomplete inner subshell letting the valence electrons in a shell other than the outer shell.¹⁻⁷ TM linked POM frameworks are thermally stable and redox-active. Moreover, the TM linker of POM frameworks can be switchable with general retaining of the framework integrity. Many researchers have been working on the synthesis of TM linked POM frameworks. In 1999, Khan *et al.* reported a cubic $\{V_{18}\}$ cage with either Fe or Co to form two different frameworks.⁸ In 2007, Mizuno *et al.* assembled $M_3PW_{12}O_{40}$ ($M = Cs, Ag$) by controlling the crystallinity and porosity.⁹ In 2017, Cronin group revealed some new POM frameworks using $\{P_8W_{48}\}$ and Co, Ni or Mn. These materials followed the one-pot methodology which provided a synthetic route to better control over the ultimate framework topologies.¹⁰ (Figure 3.1)

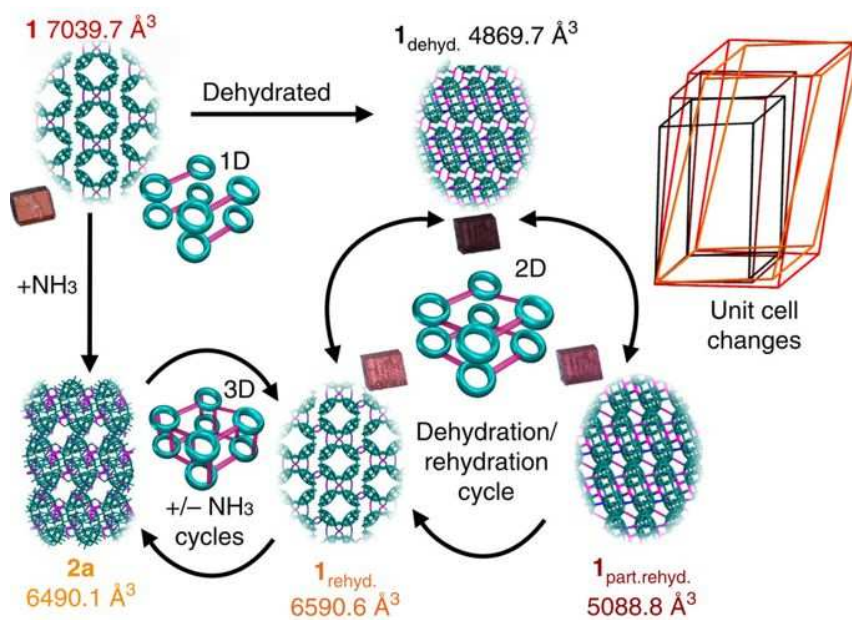


Figure 3.1 The crystal-to-crystal transformations when adding and deletion of small molecules initial from the original compound. Adapted with permission from ref 10.

Our previous work presented a new polyoxometalate framework comprised of Preyssler clusters linked with Co^{2+} . Using photochemical reduction the frameworks can be

reduced to electron densities of $\sim 2 \times 10^{21} \text{ cm}^{-3}$ without losing crystallinity. (Figure 3.2 and 3.3) The assembly of discrete metal oxide clusters thus presented a new approach to the development of tunable doped metal oxide functional materials. Based on the excellent performance of TM linked POM frameworks, it is very urgent to continue to explore their potential abilities.

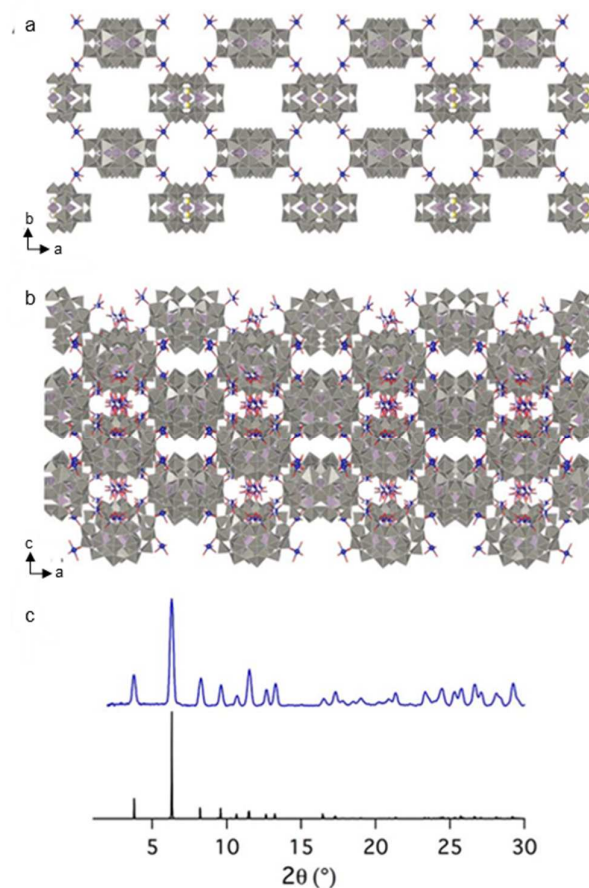


Figure 3.2 (a) Crystal structure of **Co-POM** framework showing the repeating belt to cap coordination of the Co atoms extending in the *ac* lattice plane. (b) Crystal structure of **Co-POM** framework showing assembly extends in 3D. (c) Experimental and simulated powder x-ray diffraction patterns. Counterions and water omitted for clarity.

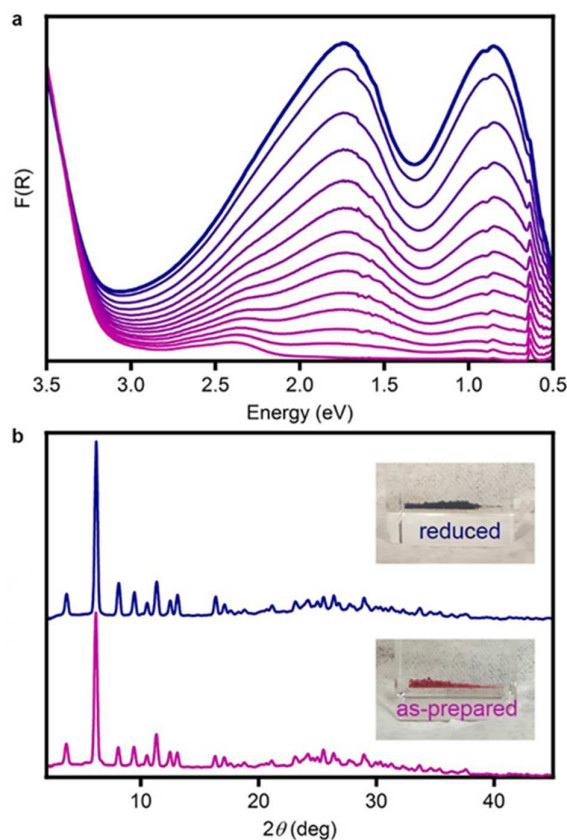


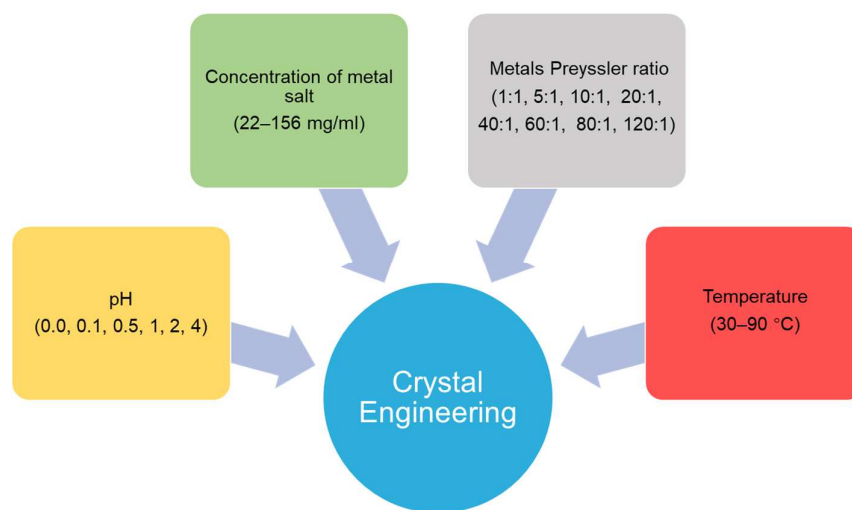
Figure 3.3 (a) Diffuse reflectance spectra show increased absorption in the visible/NIR with added electrons. The transition centered around 2.5 eV in the as-prepared sample is due to Co^{2+} $d-d$ absorption. (b) pXRD patterns before (1, bottom) and after (1R, top) reduction show no change in the crystal structure.

Here, this research improved a strategy to synthesize ten frameworks based on the Preyssler cluster linked with various transition metals such as Fe, Co, Mn and Ni.¹¹ this research performed systematic variation of synthetic conditions to obtain several different POM frameworks by varying the factors such as reaction time, temperature, concentration, pH, metal/Preyssler mole ratio and counterion identity. Moreover, bimetallic POM frameworks were obtained which were distributed homogeneously within all crystals of the sample. In addition, the metal/metal ratio was varied from 0 to 1, affording materials with absorption that varies as a function of metal identity and content. The diffuse reflectance from single metallic POM frameworks to bimetallic POM frameworks were shown to illustrate excellent optical properties of these POM frameworks. The presented approach

about tunable transition-metal-linked Preyssler type polyoxometalate frameworks will promote the current efforts of POM frameworks synthesis and practical applications.

3.2 Results and Discussion

All the reactions were performed in oil bath condition under ambient pressure. Different reaction conditions such as reaction temperature, concentration of metal salt, pH and metal/Preyssler mole ratio were explored in this work to synthesize different POM frameworks (Scheme 3.1). Reaction temperatures ranging from 30 to 90 °C, different concentrations of metal salt precursor (22, 44, 66, 88, 110, 132, 154 mg/ml), different pH (0.0, 0.1, 0.5, 1, 2, 4), metal to Preyssler ratio (1:1, 5:1, 10:1, 20:1, 40:1, 60:1, 80:1, 120:1) were studied to monitor their effects on the crystal structure.



Scheme 3.1 Various synthetic conditions will be systematically explored to optimize the crystallization of transition-metal-linked Preyssler frameworks.

POM frameworks were synthesized using our previously reported methods. The compound **1** was synthesized with CoCl_2 precursor and preyssler at pH 1 in 1 M LiCl for at least 4 hours at 90 °C. The pink crystals were obtained from resulting solution after 2 days via methanol diffusion with the formula $\text{HLi}_{1.5}\text{K}_{3.5}[\text{Co}_4\text{NaP}_5\text{W}_{30}\text{O}_{110}]\cdot 37\text{H}_2\text{O}$. The crystal structure was determined to be orthorhombic *Imma* unit cell with $a=52.05$ Å, $b=21.55$ Å and $c=26.18$ Å where the cluster was linked in three dimensions with 6 shared cobalt atoms (Figure 3.2). PXRD pattern of the bulk samples also confirmed the phase purity (Figure 3.4).

The PXRD pattern showed strong diffraction peaks at $2\theta=3.77, 6.29, 8.19, 9.57, 11.49$ and 16.43 , which were assigned to the lattice faces of (411), (811), (211), (411), (811), (211) respectively. The diffraction peak at $2\theta=3.77$ was the typical peak of Orthorhombic *Imma* structure. In addition to the Co framework, we were able to obtain several isostructural 3D POM frameworks with Fe, Mn and Ni. Compound **2–4** were synthesized like that of **1** by replacing CoCl_2 with FeCl_2 , MnCl_2 , NiCl_2 respectively. The PXRD patterns of these crystals in Figure 3.4. indicated that all the POM frameworks had same *Imma* structure.

The most fascinating feature of our approach was its extremely high tolerance to variation in experimental conditions. For instance, most syntheses were sensitive to the pH which can limit the potential application of these compounds. In our reactions, the crystals can be synthesized with pH range from 0 to 4 without affecting the crystal structure. The PXRD pattern shows that the resulting crystals are pure and have the same orthorhombic *Imma* structure. This was explained by the stability of the Preyssler in a wide pH range (0–11). Our POM framework system is also tolerant to metal/ Preyssler ratio from 5/1 to 120/1. Below 5/1 ratio, the pore site crystals were obtained and confirmed by PXRD. This was presumably due to the excess K^+ ions around preyssler, which in turn compete with Co^{2+} or other metal cations to link with preyssler cluster. Our Strategy shows no dependence on temperature variations from 60 to 90 °C. However, the pore site crystals were observed and confirmed by PXRD from 30 to 50 °C.

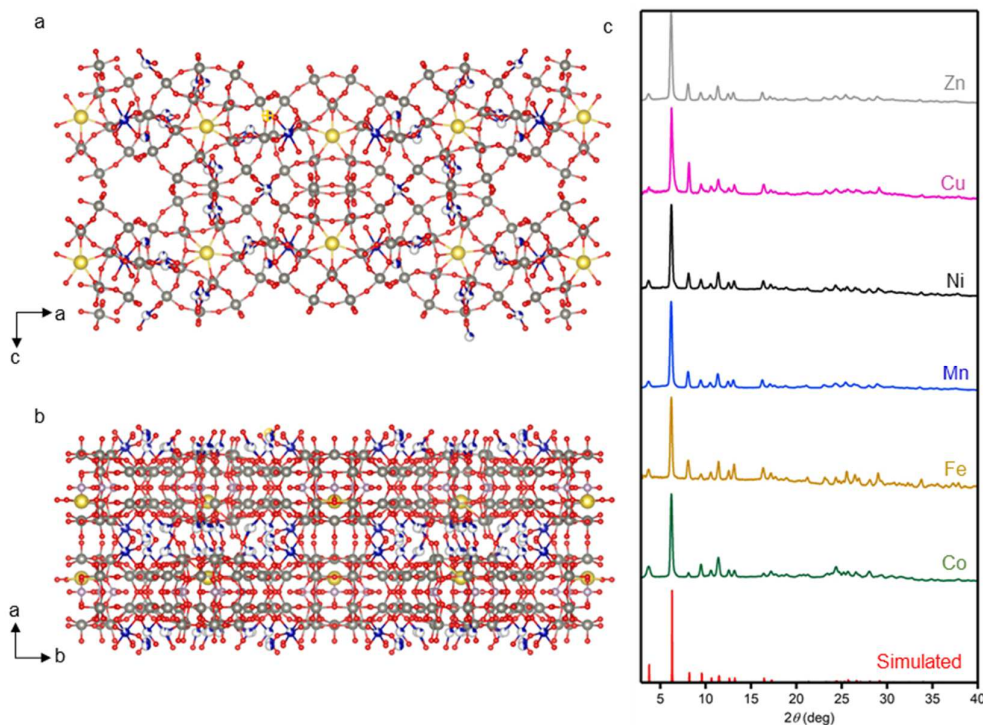


Figure 3.4 (a) Crystal structure of **1** showing the repeating belt to cap coordination of the Co atoms extending in the ac lattice plane. (b) Crystal structure of **1** showing assembly extends in 3D and potassium ions and water omitted for clarity. (c) Experimental powder x-ray diffraction patterns of Co-POM framework, Fe-POM framework, Mn-POM framework, Ni-POM framework, Cu-POM framework and Zn-POM framework.

Moreover, the concentration of metal salt is one of the crucial factors that can significantly affect the crystal growth quality. In our synthetic strategy, however, varying the concentration of metal salt did not influence the structure of the crystals. PXRD patterns show POM frameworks with concentration ranging from 22 to 156 mg/mL. All PXRD pattern matched with simulated *Imma* structure which indicates that the concentration of metal salt does not influence the crystal phase. Our observation under various experimental conditions demonstrated that there was a big growing window for crystal growth with our approach. This is undoubtedly an important advantage for practical applications and understanding of these new POM frameworks.

More exciting, our POM frameworks can be linked by multiple metals. Similar chemistry involving combinations of multiple metals in MOF structures is also under

development since the mixing of metals is widely regarded as an essential feature to achieve optimal catalysis, optical and electronic properties or even mimic the catalytic centers of proteins containing multiple metals. The various metal ions lie on the same crystallographic position so the similar synthesis strategies were used for bimetallic POM frameworks. One metal salt was instead of two different salts and then six new bimetallic POM frameworks (Co/Fe, Co/Mn, Co/Ni, Fe/Mn, Fe/Ni, Ni/Mn) were obtained.

In order to demonstrate metal ions dispersing uniformly within the crystal samples, we applied energy dispersive spectra (EDS) to map the presence of various metals using scanning electron microscopy (SEM). As shown in Figure 3.5, if it was a physical mixture of Co-POM framework and Fe-POM framework, we expected to observe the presence of Co and Fe in their corresponding crystal samples separately. However, the EDS mapping showed that both Co and Fe were distributed homogeneously within all crystals of the sample. This clearly indicated that this bimetallic POM framework was not a physical mixture. Similar observations were made for samples of Co/Mn-POM framework, Fe/Mn-POM framework. PXRD pattern of the bulk samples also confirmed the phase (Figure 3.6). The diffraction peak at $2\theta=3.77$ was observed which was the typical peak of Orthorhombic Imma structure.

The Preyssler cluster $[\text{NaP}_5\text{W}_{30}]^{14-}$, which contains the encapsulated single sodium cation inside the cavity, can be modified by exchanging the central Na cation with various alkali and alkaline earth metal cations. The exchange of central cation with lanthanide ions and other multivalent ions was first reported by Pope group.² Here, the central Na^+ was hydrothermally exchanged by multivalent cations such as Eu^{3+} , Sm^{3+} , and Bi^{3+} . The complete cation exchange was monitored by the Z^{n+} ion induced shift in ^{31}P NMR. The ^{31}P NMR spectra of all $[\text{ZP}_5\text{W}_{30}]^{14-}$ showed single line for five equivalent phosphorous atoms with chemical shifts of -9.495 ppm, 0.527 ppm, -9.616 ppm and -8.227 ppm for Na^+ , Eu^{3+} , Sm^{3+} , and Bi^{3+} preyssler respectively. (Figure 3.8).

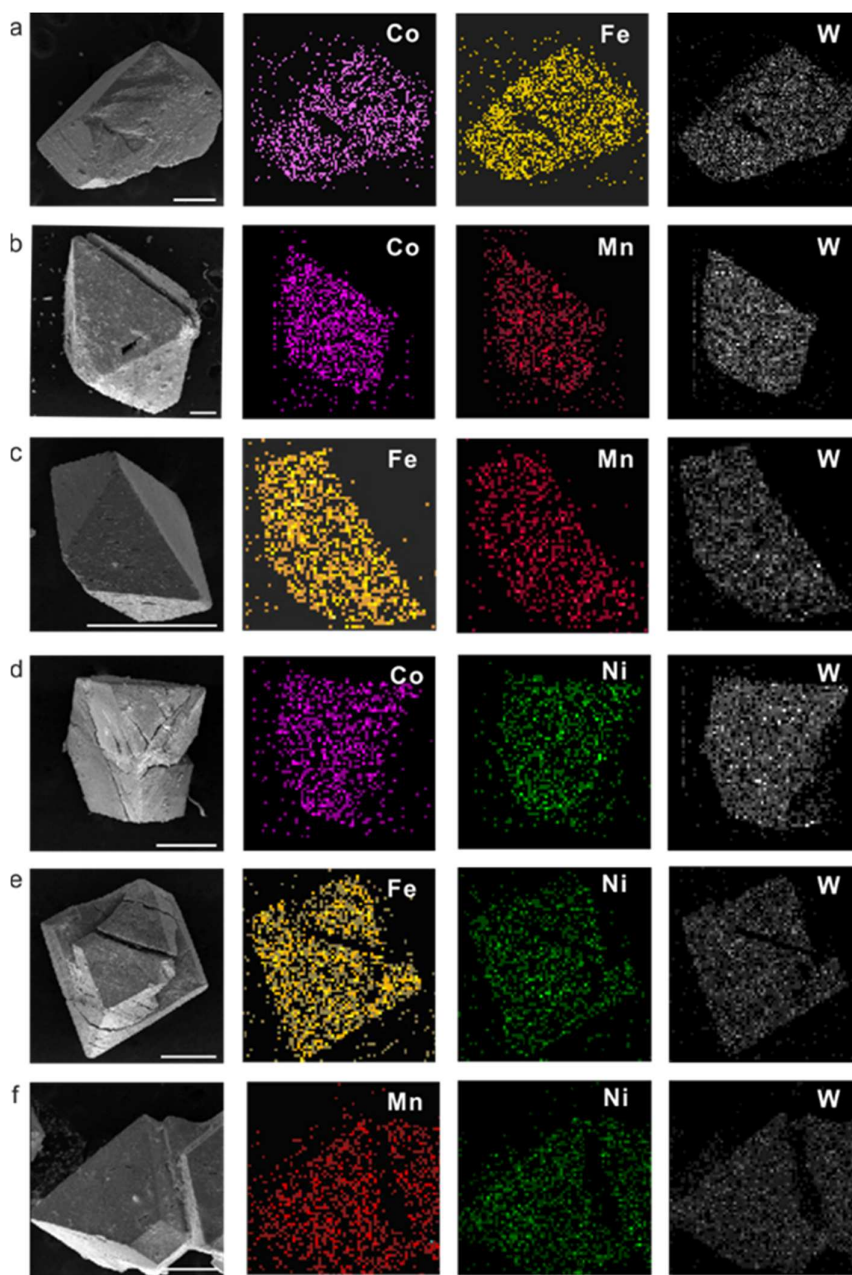


Figure 3.5 Dispersity of metal ions. SEM images (scale bar 250 μm) and the corresponding elemental maps for **(a)** Co/Fe-POM framework (The molar ratio of Co over Fe is 1 to 1), **(b)** Co/Mn-POM framework (The molar ratio of Co over Mn is 2 to 1), **(c)** Fe/Mn-POM framework (The molar ratio of Fe and Mn is 2 to 1), **(d)** Co/Ni-POM framework (The molar ratio of Co over Ni is 1 to 1), **(e)** Ni/Mn-POM framework (The molar ratio of Ni over Mn is 2 to 1), **(f)** Fe/Ni-POM framework (The molar ratio of Fe and Ni is 1 to 1). **(g)** Experimental powder x-ray diffraction patterns of Co/Fe-POM framework, Co/Mn-POM framework, Fe/Mn-POM framework, Co/Ni-POM framework, Ni/Fe-POM framework and Mn/Ni-POM framework.

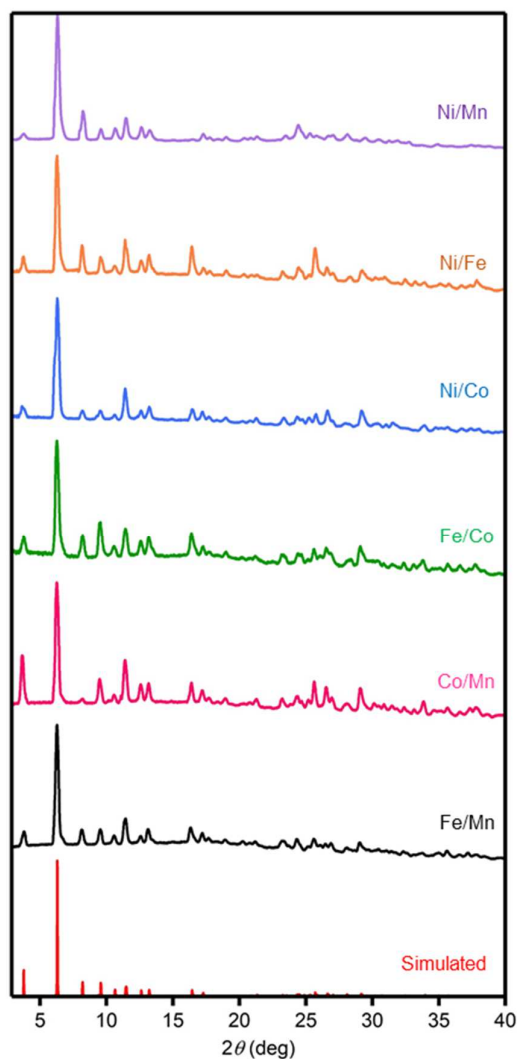


Figure 3.6 Powder x-ray diffraction patterns of Co/Fe-POM framework, Co/Mn-POM framework, Fe/Mn-POM framework, Co/Ni-POM framework, Ni/Mn-POM framework, Fe/Ni-POM framework and *Imma* simulated.

These modified clusters are then further reacted with CoCl_2 to obtain the transition metal linked framework. The resulting crystal structure is similar to the framework obtained by CoCl_2 , which is *Imma* structure. As shown in Figure 3.7, the PXRD pattern of the cavity ion exchanged Co POM framework match with the *Imma* simulated pattern. The photoluminescence spectrum of solid $[\text{EuP}_5\text{W}_{30}]$ excited at 405 nm showed two intense emission peaks for Eu^{3+} at 590 nm and 618 nm corresponding to $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ respectively. These emission peaks for Eu^{3+} are subsequently quenched by Co^{2+} ions in the

framework. The preyssler cluster served as the discrete building block, which can be easily modified to fine-tune various properties in these extended frameworks.

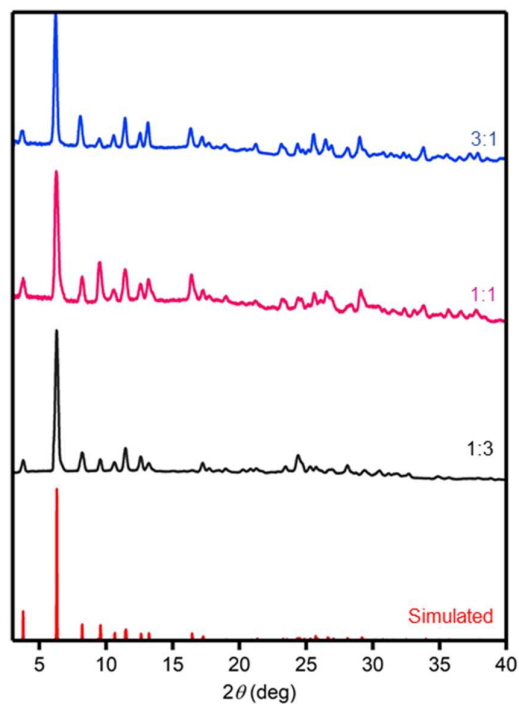


Figure 3.7 Powder x-ray diffraction patterns of Na-Preyssler, Sm-Preyssler, Bi-Preyssler, Eu-Preyssler and *Imma* simulated.

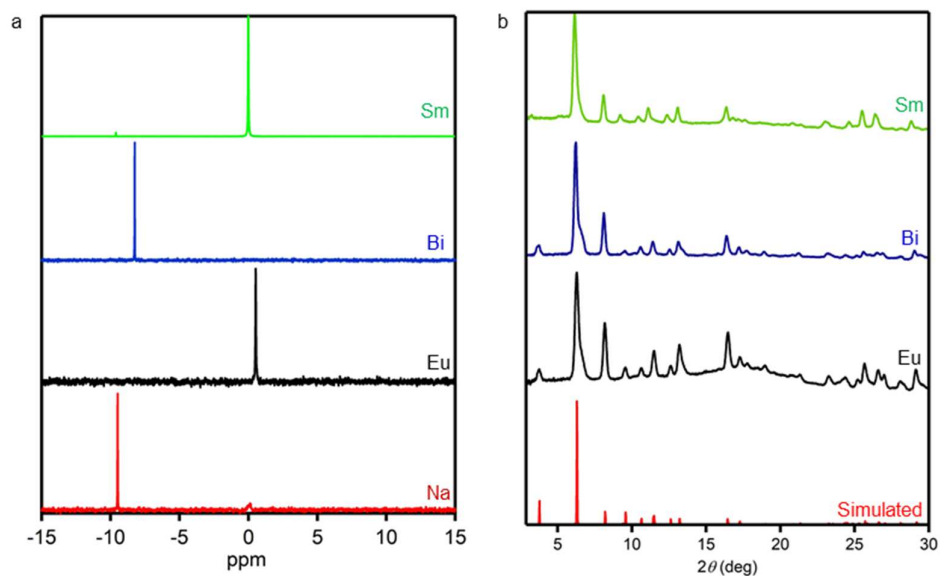


Figure 3.8 (a) Powder x-ray diffraction patterns of Co- {Sm-POM framework}, Co- {Bi-POM framework}, Co- {Eu-POM framework} and *Imma* simulated **(b)** ^{31}P NMR of Sm-Preyssler, Bi-Preyssler, Eu-Preyssler and Na-Preyssler

Conductivity was used to demonstrate the viability of the frameworks as functional electronic materials. For the measurements, powders of reduced-CoPOM framework were pressed into a pellet and fitted with wires using a silver epoxy (Figure 3.13). To reduced pellet-to-pellet variability the conductivity of CoPOM framework was determined by oxidizing the reduced pellets in ambient air for 1 week. After the oxidation, the conductivity of the framework decreased from $1.1 (\pm 0.1) \times 10^{-5}$ S/cm when reduced to $2.0 (\pm 0.2) \times 10^{-6}$ S/cm when oxidized back to native-CoPOM framework (Figure 3.9). This is the first reported conductivity measurements for POM frameworks, improvements of the conductivity may be achieved by using different transition metals as the linkers. Previous work on conductive MOFs have demonstrate that the transition metal used as the node plays a major role in the conductivity, ongoing work in our lab concerns extending this concept to all-inorganic POM frameworks.

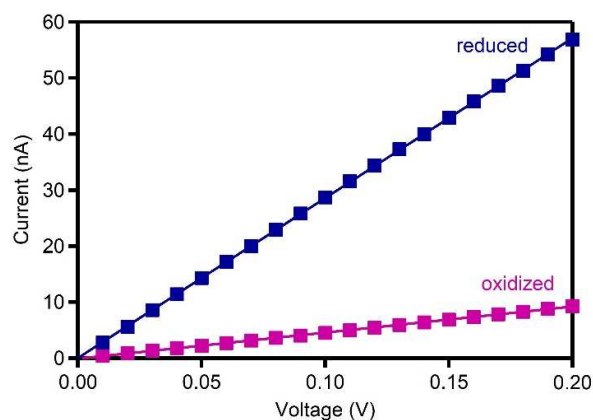


Figure 3.9 IV curve of native-CoPOM framework and reduced-CoPOM framework.

3.3 Conclusion

This research presented a strategy to synthesize nine frameworks based on the Preyssler cluster linked by transition metals such as Fe, Co, Mn and Ni and further explored the crystal engineering for tunable transition-metal-linked polyoxometalate frameworks by controlling the reaction time, temperature, concentration, pH, and metal/Preyssler mole ratio. In addition, bimetallic POM frameworks were obtained which were distributed homogeneously within all crystals of the sample. What's more, the metal/metal ratio was varied from 0 to 1, affording materials with absorption that varies as a function of metal identity and content. The presented approach about tunable transition-metal-linked Preyssler type polyoxometalate frameworks will promote the current efforts of POM frameworks synthesis and practical applications.

3.4 Experimental Methods

Synthesis of $[\text{ZP}_5\text{W}_{30}\text{O}_{110}]^{n-}$. The Preyssler cluster (1g, 0.125 mmol) was dissolved in 12 mL of DI water and one equivalent of metal salt dissolved in DI water (3 ml) was added and stirred for 15–20 mins. The solution mixture was then transferred to the Teflon-lined digestion bomb and heated to 160 °C overnight. Solid KCl (4g) was added to the solution after it had cooled to room temperature. The white product was isolated by filtration and air dried.

Synthesis of Co-POM frameworks (1). $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (156.0 mg, 0.656 mmol) and $\text{K}_{12.5}\text{Na}_{1.5}[\text{NaP}_5\text{W}_{30}\text{O}_{110}] \cdot 15\text{H}_2\text{O}$ (130.0 mg, 0.015 mmol) were dissolved in 7.0 ml of 1 M LiCl buffer solution (pH 1.0, adjusted by 4M HCl) and placed in a 25 ml round-bottom flask equipped with a reflux condenser. The resulting pink solution was heated and stirred for 20 h. After the reaction, the solution was transferred to a 20 ml vial and concentrated on a hot plate at 80 °C until the volume of the solution was approximately 2 ml, taking about 3 hours. Pink crystals were obtained the next day by slow diffusion of methanol. The samples were cleaned for further studies by washing with methanol 3 times to remove any chloride salt impurities. The purity of the samples was checked by EDS. Yield: 105.5 mg, 0.123 mmol, 82% based on $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$. ICP–MS analysis for partially dehydrated material, $\text{H}_{76}\text{Li}_{0.875}\text{K}_{1.75}\text{Co}_{5.75}\text{Na}_{1.25}\text{P}_5\text{W}_{30}\text{O}_{148}$, MW 8564.717 g/mol. Calculated values (found values in parenthesis Li 0.071 (0.069) K 0.68 (0.71), Co 3.97 (3.94), Na 0.30 (0.30), P 1.81 (1.73), W 64.55 (64.63). Thermogravimetric analysis (TGA) for water loss from 30°C to 400°C, calculated (found): 7.99 (7.97) %. Characteristic FTIR bands (cm^{-1}): 3363(s), 1616(s), 1157 (s), 1075(m), 1014 (w), 981 (w), 901 (s), 695(s).

Synthesis of Mn-POM framework (2). Preparation of 2 was similar to that of 1, except that $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (130.0 mg, 0.685 mmol) was used instead of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. Pale yellow crystals were isolated overnight and used for further studies. Yield: 95.3mg, 0.111 mmol,

74% based on $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$. Thermogravimetric analysis (TGA) for water loss from 30°C to 400°C, calculated (found): 7.86 %. Characteristic FTIR bands (cm^{-1}): 3363(s), 1616(s), 1157 (s), 1075(m), 1014 (w), 981 (w), 901 (s), 695(s).

Synthesis of Fe-POM framework (3). Preparation of 3 was similar to that of 1, except that $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (130.0 mg, 0.685 mmol) was used instead of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. Pale black crystals were isolated overnight and used for further studies. Yield: 73.5 mg, 0.086 mmol, 57% based on $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$. Thermogravimetric analysis (TGA) for water loss from 30°C to 400°C, calculated (found): 7.91 (7.91) %. Characteristic FTIR bands (cm^{-1}): 3363(s), 1616(s), 1157 (s), 1075(m), 1014 (w), 981 (w), 901 (s), 695(s).

Synthesis of Ni-POM framework (4). Preparation of 4 was similar to that of 1, except that $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (156.0 mg, 0.691 mmol) was used instead of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. Pale green crystals were isolated overnight and used for further studies. Yield: 115.3 mg, 0.133 mmol, 88% based on $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$. Thermogravimetric analysis (TGA) for water loss from 30°C to 400°C, calculated (found): 8.06 %. Characteristic FTIR bands (cm^{-1}): 3363(s), 1616(s), 1157 (s), 1075(m), 1014 (w), 981 (w), 901 (s), 695(s).

Synthesis of Co/Mn-POM framework (5). Preparation of 5 was similar to that of 1, except that the mix of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (78.0 mg, 0.345 mmol) and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (65.0 mg, 0.342 mmol) was used instead of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. Pale pink crystals were isolated overnight and used for further studies. Yield: 93.1 mg, 0.108 mmol, 72% based on $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$. Characteristic FTIR bands (cm^{-1}): 3363(s), 1616(s), 1157 (s), 1075(m), 1014 (w), 981 (w), 901 (s), 695(s).

Synthesis of Co/Ni-POM framework (6). Preparation of 5 was similar to that of 1, except that the mix of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (78.0 mg, 0.345 mmol) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (78.0 mg, 0.345 mmol) was used instead of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. Pale pink crystals were isolated overnight and used for further studies. Yield: 92.5 mg, 0.106 mmol, 71% based on $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$.

Characteristic FTIR bands (cm^{-1}): 3363(s), 1616(s), 1157 (s), 1075(m), 1014 (w), 981 (w), 901 (s), 695(s).

Synthesis of Co/Fe-POM framework (7). Preparation of 5 was similar to that of 1, except that the mix of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (78.0 mg, 0.345 mmol) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (65.0 mg, 0.342 mmol) was used instead of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. Brown crystals were isolated overnight and used for further studies. Yield: 99.5 mg, 0.116 mmol, 77% based on $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$.

Characteristic FTIR bands (cm^{-1}): 3363(s), 1616(s), 1157 (s), 1075(m), 1014 (w), 981 (w), 901 (s), 695(s).

Synthesis of Ni/Mn-POM framework (8). Preparation of 5 was similar to that of 1, except that the mix of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (78.0 mg, 0.345 mmol) and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (65.0 mg, 0.342 mmol) was used instead of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. Pale green crystals were isolated overnight and used for further studies. Yield: 108.5 mg, 0.126 mmol, 84% based on $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$.

Characteristic FTIR bands (cm^{-1}): 3363(s), 1616(s), 1157 (s), 1075(m), 1014 (w), 981 (w), 901 (s), 695(s).

Synthesis of Fe/Mn-POM framework (9). Preparation of 5 was similar to that of 1, except that the mix of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (65.0 mg, 0.342 mmol) and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (65.0 mg, 0.342 mmol) was used instead of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. Brown crystals were isolated overnight and used for further studies. Yield: 111.5 mg, 0.130 mmol, 87% based on $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$. Characteristic FTIR bands (cm^{-1}): 3363(s), 1616(s), 1157 (s), 1075(m), 1014 (w), 981 (w), 901 (s), 695(s).

Synthesis of Fe/Ni-POM framework (10). Preparation of 5 was similar to that of 1, except that the mix of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (65.0 mg, 0.342 mmol) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (78.0 mg, 0.345 mmol) was used instead of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. Brown crystals were isolated overnight and used for further studies. Yield: 105.1 mg, 0.122 mmol, 82% based on $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$. Characteristic FTIR bands (cm^{-1}): 3363(s), 1616(s), 1157 (s), 1075(m), 1014 (w), 981 (w), 901 (s), 695(s).

Photodoping. In a nitrogen-filled glovebox, ~500 mg (~60 mol) of finely powdered

sample and 3 ml 5:1 toluene/methanol were added to a quartz screw-cap cuvette. Samples were photochemically reduced by illumination with a Phoseon FireEdge LED (365 nm, 10.5 W/cm²) for ~2 h with frequent mixing. Following photodoping, the samples were brought back into the glovebox and the solvent removed under vacuum. This dried stock powder was split up for diffuse reflectance spectroscopy, powder x-ray diffraction and titrations. For diffuse reflectance, samples were prepped in the glovebox by mixing ~200 mg with BaSO₄ (1:10 wt%). Spectra were measured as the samples re-oxidized using a Cary 5000 equipped with a DRA-2500 internal diffuse reflectance accessory.

Electrical conductivity and photoconductivity. For the electrical measurements, ~50 mg of powdered crystals was pressed into a pellet. The pellet was made by packing the powder in a 7-mm pellet die (Specac GS03950), and pressed under 462 MPa for 1 hour in a Specac GS03940 mini-pellet press. The thickness of the pellet was measured by a digital caliper. Gold wires (Alfa Aesar, 100 μ m diameter) were then pasted onto the pellet in using silver epoxy (Epo-Tek H20E). The pellet was placed in an oven at 120 °C for 15 min to cure the epoxy. Gold wires were soldered to the sample rod of the Electrical Transport Option for the Quantum Design MPMS3 superconducting interference device magnetometer.

3.5 Appendix

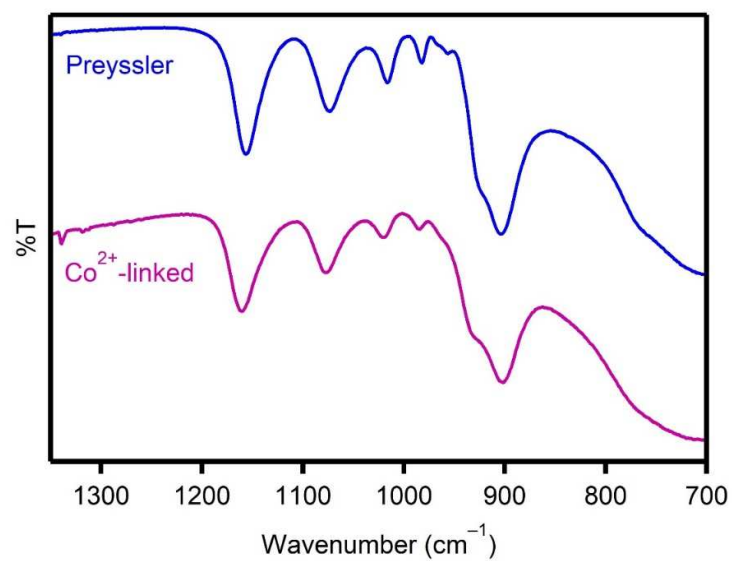


Figure 3.10: IR of the Preyssler POM (red) and **1** (black), the Preyssler structure is not altered during the synthesis of the framework.

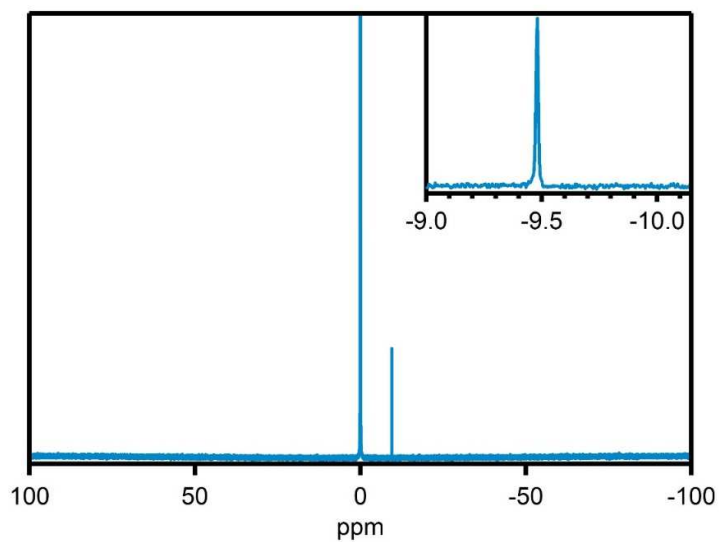


Figure 3.11: ³¹P NMR of Preyssler

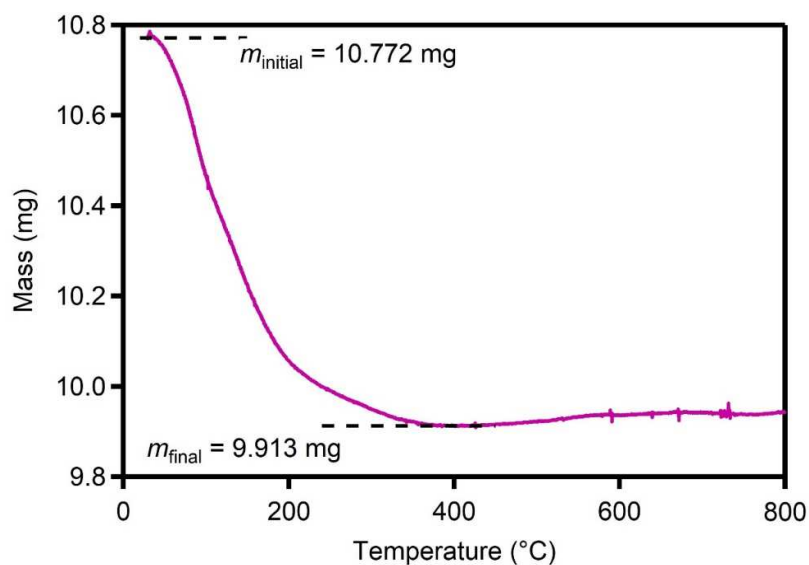


Figure 3.12: Thermogravimetric analysis of Co linked POM framework. The loss of mass from room temperature to 400 °C was used to determine the water content of the crystals.

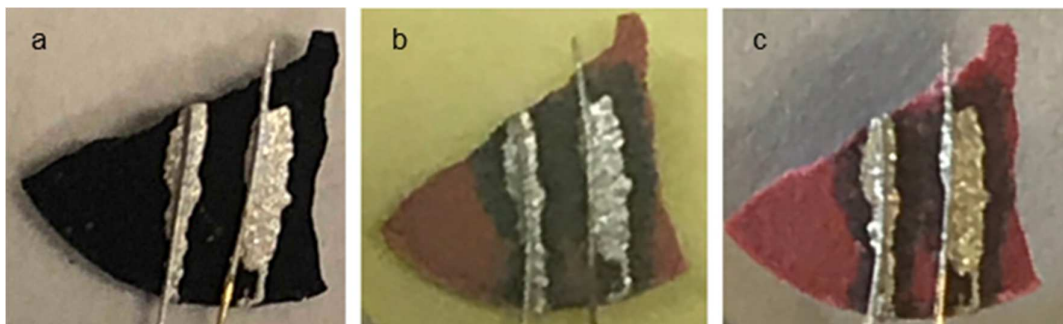


Figure 3.13: Picture of the pressed pellet of reduced-Co-POM framework (a), the same pellet after 1 week in an ambient environment (b) and after 2 weeks in an ambient environment (c). After 1 week, the pellet does not appear to complete return to the pink color of the native crystals, however, little change was observed in the conductivity following 2 weeks of exposure to air compared to after only 1 week in air.

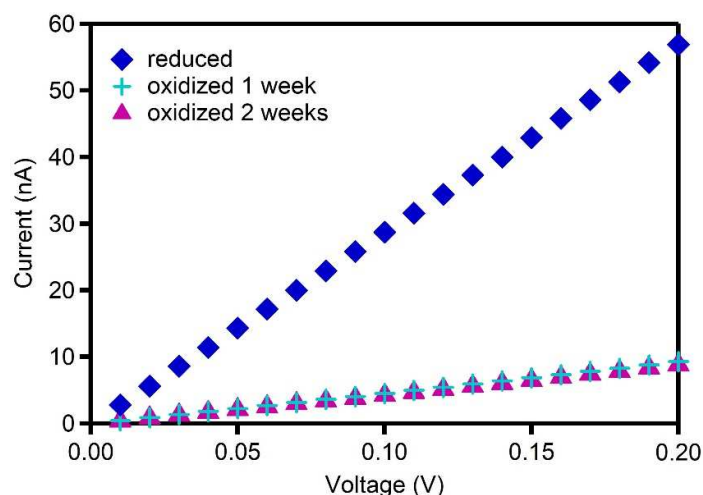


Figure 3.14: I-V curve for the reduced Co-POM framework, after 1 week exposed to air and 2 weeks exposed to air.

Sample Calculations:

Conductivity

The conductivity of the samples was calculated using the method outlined by Sun, L. *et al.* for two points pressed pellet measurements.² Figure 3.13 shows a sample pellet used for the conductivity calculations with the highlighted irregular shape and the corresponding measurements. For this sample the thickness (t) was measured to be 0.031 cm using a digital caliper and the resistance (R) was determined to be $3.50 \times 10^6 \Omega$ from the I-V curve.

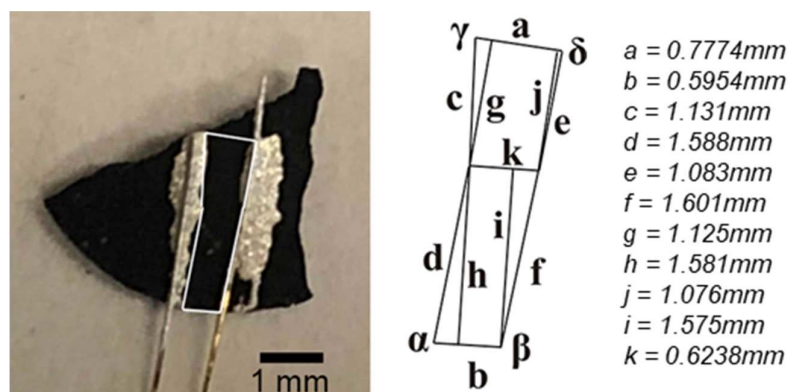


Figure 3.15: Picture of the pressed pellet of **1** used for the conductivity measurements highlighting the irregular shape of the channel used to calculate the conductivity and the values for the different measured dimensions.

$$dR = \frac{1}{\sigma} \frac{1}{tdx_b} \frac{1}{\sigma} \frac{b-x_b \cot\alpha - x_b \cot\beta}{tdx} \left(\cot\alpha = \frac{\sqrt{d^2-h^2}}{h}, \cot\beta = \frac{\sqrt{f^2-j^2}}{j} \right)$$

$$\frac{1}{R_b} = \int \frac{1}{dR} = \int_0^h \sigma t \frac{dx_b}{b-x_b \cot\alpha - x_b \cot\beta}$$

$$\frac{1}{R_a} = \int \frac{1}{dR} = \int_0^g \sigma t \frac{dx_a}{a-x_a \cot\gamma - x_a \cot\delta}$$

Therefore,

$$\frac{1}{R} = \frac{1}{R_b} + \frac{1}{R_a} = \int_0^h \sigma t \frac{dx_b}{b-x_b \cot\alpha - x_b \cot\beta} + \int_0^g \sigma t \frac{dx_b}{a-x_a \cot\gamma - x_a \cot\delta}$$

$$\sigma = \frac{1}{Rt} \frac{1}{\ln\left(\frac{b}{k}\right) / \left(\frac{\sqrt{d^2-h^2}}{h} + \frac{\sqrt{f^2-j^2}}{j} \right) + \ln\left(\frac{a}{k}\right) / \left(\frac{\sqrt{c^2-g^2}}{g} + \frac{\sqrt{e^2-i^2}}{i} \right)} = 1.1 \times 10^{-5} \text{ S/cm}$$

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