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Synthesis and characterization of two metal-organic frameworks

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SYNTHESIS AND CHARACTERIZATION

OF TWO METAL-ORGANIC FRAMEWORKS

A Thesis

by

ROXANNA SCHAFFINO MOORE

Submitted to the Graduate School of the
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May 2009

ABSTRACT

Moore, Roxanna Schaffino, <u>Synthesis and Characterization of Two Metal Organic Frameworks.</u> Master of Science (MS), May 2009, 34 pp., 2 tables, 23 figures, 31 references.

Herein, the design and synthesis of two metal-organic frameworks, $Zn_4O(FMA)_3$ (FMA = fumaric acid) and $Zn_2(CNC)_2(DPT)$ (CNC = 4-carboxycinnamic acid; DPT = 3,6-Di-4-pyridyl-1,2,4,5-tetrazine) via solvothermal methods are reported. $Zn_4O(FMA)_3$ was isolated as light yellow cubic crystals and $Zn_2(CNC)_2(DPT)$ as light pink-block shaped crystals. The structures of both MOFs were characterized by single X-ray diffraction. Integrity of both MOFs were determined via powder X-ray diffraction and thermal gravimetric analysis. $Zn_4O(FMA)_3$ is an isoreticular MOF exhibiting 6.8 Å pores taking up 5.2 wt % of hydrogen gas at 40 bar and 77K. $Zn_2(CNC)_2(DPT)$ is a 3D primative cubic net that exhibits 3.7 Å 1D pores taking up 1.28 wt % of hydrogen gas at 1 bar and 77 K.

DEDICATION

This thesis is dedicated to all of my family and friends that helped me through. First and foremost, I dedicate this to my mom, Esperanza Montes Fuentes, who has inspired me to seize any opportunities that have come my way. Also, to my dad, Octavio Schaffino, who has always beamed with pride with all that I do and has constantly been interested in my studies. I have been very blessed to have siblings, nieces, nephews, in-laws, and friends who may not have a clue what metal-organic frameworks are but cared enough to always ask how I was doing and provide the encouragement needed to finish. Finally, there is my husband, Cody Moore, who gave me the strength and energy when I was tired of long days of work and school or typing away yet another paper. Thanks for all the freshly baked cookies on those long days.

ACKNOWLEDGEMENTS

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CHAPTER I

INTRODUCTION

Porosity and high surface area are two properties that have been sought after for applications in catalysis and small molecule storage, sensing, and separation (Chen et al., 2006; Chen et al., 2007; Kitagawa, Kitaura, & Noro, 2004; Rosi et al., 2005; Rowsell & Yaghi, 2004; Walton & Snurr, 2007). Materials that exhibit these characteristics have proven useful in the industrial setting. Among these materials are metal-organic frameworks, otherwise known as MOFs (Rowsell & Yaghi, 2004). They first appeared in the mid-1990s when Omar Yaghi began to develop molecules which could be designed with a variety of metal ions and organic molecules (Walton & Snurr, 2007). This is an alternative to the ubiquitous zeolite which is commercially useful due to their porous nature. (Chen et al., 2006; Chen et al., 2007; Eddaoudi et al., 2001; Janiak, 2003; Kitagawa, Kitaura, & Noro, 2004; Llabres et al., 2007; Rosi et al., 2005; Rowsell & Yaghi, 2004; Walton & Snurr, 2007). They were discovered by Alex Fredrick Cronstedt in 1756 after he found that heating a mineral produced a vigorous bouncing effect as the water evaporated. Zeolites are microporous minerals that may be found naturally near volcanic areas or synthesized via the sol-gel process. Zeolites are part of the aluminosilicate family that contain cavities in their structure (Ghobarkar, Schaf, Massiani, & Knauth, 2007). As described by Ghobarkar, Schaf, Massiani, and Knauth (2007) and Zagorodni (2007), zeolites are currently, used as

ion exchange media in water softeners, detergents, and molecular adsorption for gas

chromatography and gas separation. The zeolite pores are also found useful in

heterogeneous catalysis to produce certain substances for selective synthesis

(Ghobarkar et al., 2003; Zagorodni, 2007; Kim, Kunieda, & Niwa, 1998). Figure 1,

shows an industrially important zeolite, ZSM – 5. It is used for its molecular sieves

that are shape selective. Kim, Kunieda, and Niwa (1998) describe o-xylene as a

substance used as an octane-booster and synthesized by using ZSM-5. Their research

also describes the size and shape of the sieve of ZSM-5 allowing only o-xylene to be

produced rather than to include m-xylene and p-xylene.As molecular sieves became

increasingly useful, developing materials with similar properties advanced. Thus,

synthesis of new, similar compounds continued to be on the rise.
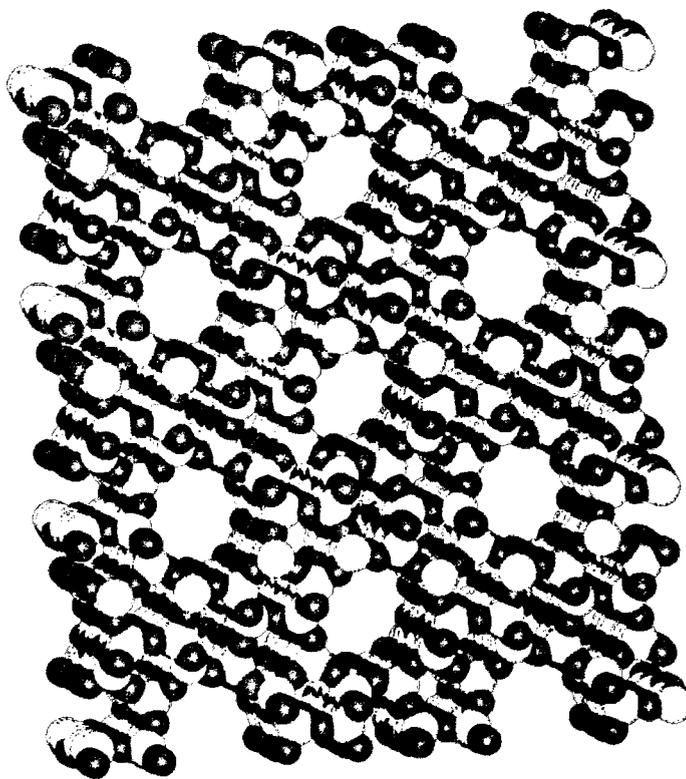
Figure 1 Structural framework of ZSM – 5. ZSM – 5 has molecular sieves which are suitable to selectively produce o-xylene without producing its countermolecules, m-xylene and p-xylene. (Zeolite, n.d.)

Metal-Organic Frameworks

Rowsell and Yaghi (2004) describe MOFs as structures made by choosing metal ions that will be linked to organic ligands. Rowsell and Yaghi (2004) continue to note that MOFs should exhibit a highly crystalline, open framework that have been developed via the building block approach to yield sturdy structures along with tunable pore size. Furthermore, strong bonds, accomodating ligands, and a well-defined crystalline structure are three characteristics that a material must exhibit to be considered a MOF. The starting materials are often inexpensive with high availability. Hydrated metallic nitrates and organic ligands with carboxylate functional groups are typically used (Rowsell & Yaghi, 2004). In addition, organic solvents are selected based on their electron withdrawing capacity. It should be stated that the materials are not limited to hydrated metallic nitrates or carboxylate groups. Once the selected components are mixed in a vial they are placed in an oven where temperatures range from 80°C to 250°C for twenty-four to forty-eight hours. This process of solvothermal synthesis allows deprotonation from the carboxylic group (that is, if the ligand has a carboxylate group) which then leads to the formation of the framework structures (Rowsell & Yaghi, 2004).

Chen et al. (2007) successfully developed a MOF based on the criteria described above. It was constructed with $Eu(NO_3)_3 \cdot 6H_2O$ and benzene-1,3,5-tricarboxylic acid (H_3BTC) dissolved in dimethylformamide, ethanol, and water was and is shown in Figure 2 (Chen et al., 2007). This mixture was placed in a sealed vial and heated at 80°C for twenty-four hours producing colorless needle crystals (Chen et al., 2007). The structure was characterized via X-ray crystallography.
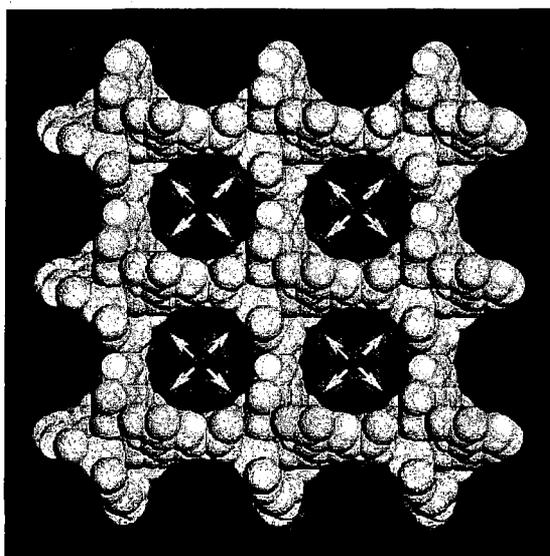
Figure 2 Structural framework of Eu(BTC)(H$_2$O)·1.5H$_2$O. Single-crystal X-ray diffraction revealed the above structure for metal-organic framework with the formula Eu(BTC)(H$_2$O)·1.5H$_2$O. (Chen et al., 2007).

The intermolecular forces between the metal and ligand determine the strength of the molecule (Rowsell & Yaghi, 2004). The Rowsell & Yaghi (2004) review of MOFs explain that the strongest possible bonds are attained when the researcher selects suitable ligands; however, the results are not always as predicted, making the selection process more challenging. In recent years, researchers have reported the formation of robust frameworks from metal-carboxylate bonds. Specifically, Rowsell and Yaghi (2004) have reported that MOFs with the generic formula, Zn$_4$O(L)$_3$, have sturdy structures. 'L' is defined as a rigid linear dicarboxylate. The metal-carboxylate bonds model the secondary building unit (SBU) concept of zeolites (Chen et al., 2006; Chen et al., 2005; Kim et al., 2001; Luo, Che, & Zheng, 2008; Rowsell & Yaghi, 2004; Rowsell & Yaghi, 2005; and Sudik, Cote, & Yaghi, 2005). SBUs afford the scientist with molecules that will extend the porous frameworks. SBUs have distinct shapes such as "paddle-wheel" or "pillared". The expansion of the framework is achieved by using longer organic linkers. Consequently, as nature does

not like vacancy, interpenetration occurs resulting in decreased pore size. The structures of MOFs can be characterized using X-ray crystallography (Rowsell & Yaghi, 2004). X-ray crystallography produces a three-dimensional structure of the MOF including all atoms and bonds. As progress in MOF design and synthesis continues, commonalities between structure and strength are revealed.

<center>Relevance of Metal-Organic Frameworks</center>

Pores are simply defined as voids within a structure. Porous materials have proven to be valuable in industrial processes (Chen et al., 2006; Chen et al., 2007; Kitagawa, Kitaura, & Noro, 2004; Rosi et al., 2005; Rowsell & Yaghi, 2004; Walton & Snurr, 2007). As previously mentioned, pore size and surface area are greatly important for applications in gas storage and separation, catalysis, and small molecule sensing (Chen et al., 2006; Chen et al., 2007; Kitagawa, Kitaura, & Noro, 2004; Rosi et al., 2005; Rowsell & Yaghi, 2004; Walton & Snurr, 2007). In the last decade, MOFs have been widely studied for applications in such areas, just like zeolites (Chen et al., 2006; Chen et al., 2007; Kitagawa, Kitaura, & Noro, 2004; Rosi et al., 2005; Rowsell & Yaghi, 2004; Walton & Snurr, 2007). MOFs are considered to be open frameworks in which molecules may move in and out. Most of the MOFs reported have been classified as mesoporous or microporous materials. Braga and Grepioni (2007) define microporous materials to have a pore diameter of 20 Å or less whereas mesoporous materials have a diameter between 20 Å and 50 Å. Braga and Grepioni (2007) also express that the pore diameter range of microporous and mesoporous materials have proven valuable for gas adsorption techniques.

Gas chromatography is a widely used technique for identification and/or separation of mixture components that do not decompose during vaporization. Figaure 3 shows a schematic diagram of a gas chromatograph. A sample is injected through a rubber septum which is immediately vaporized and passed through a column packed with liquid adsorbent particles via a carrier gas, as described by Pavia, Lampmann, Kriz, and Engel (1997).
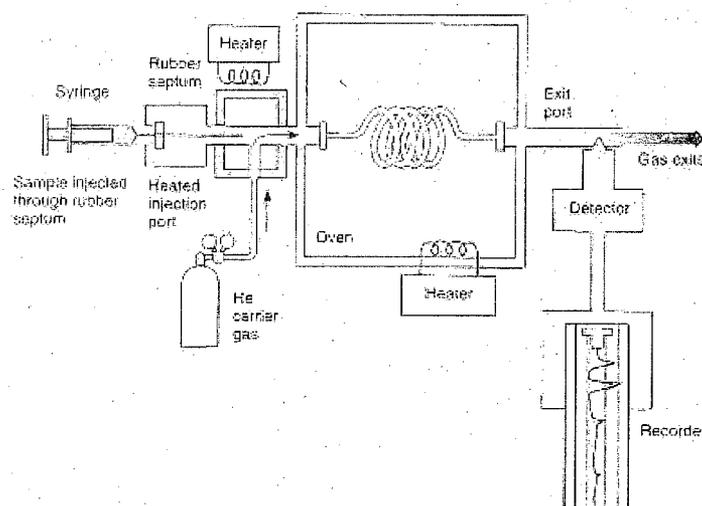
Figure 3 Schematic diagram of a gas chromatograph (Pavia et al., 1997).

The sample passes through a porous material to separate the various components. The column material must be thermally stable at high temperatures and can be solid or liquid. Also, the polarity of the substance is taken into consideration. Nonpolar packing material is used when separating or purifying nonpolar samples, and vice versa. Typical stationary phases include hydrocarbon greases, silicone oil, and diethylene glycol succinate (Pavia et al., 1997)

In 2006, Chen et al., reported a microporous MOF for the use as a novel packing material in gas chromatographs. MOF-508b, $Zn(BDC)(4,4'\text{-Bipy})_{0.5}$[1], shown

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[1] BDC = 1,4-benzenedicarboxylic acid, 4,4'-Bipy = 4,4'-bipyridine

in Figure 4, has been designed with tunable pores. MOF-508b molecules are released

when MOF-508a, $Zn(BDC)(4,4'-Bipy)_{0.5}(DMF)(H_2O)_{0.5}$, (DMF =

dimethylformamide) shown in Figure 4, is heated between 25-145°C.
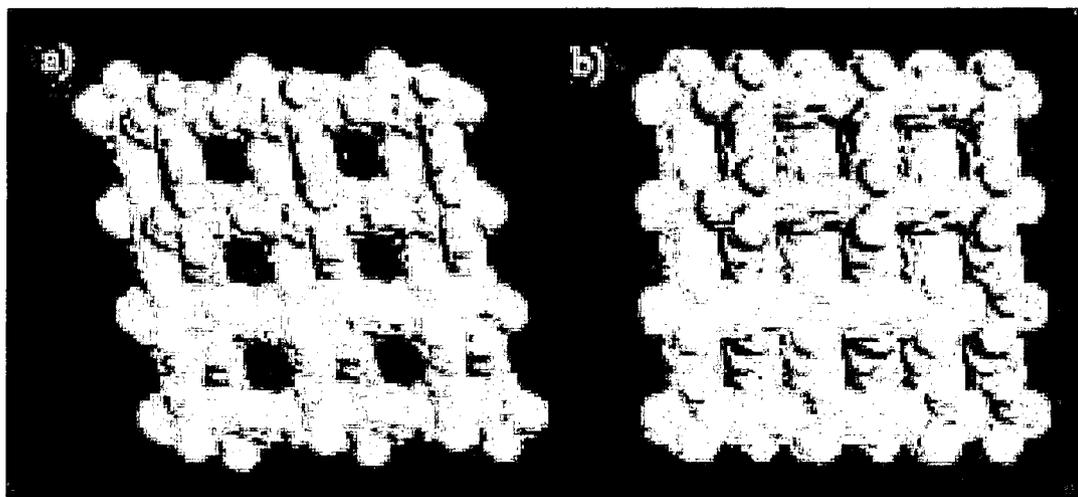
Figure 4 MOFs in gas chromatography. a) MOF-508a and b) MOF-508b (Chen et al., 2006).

Both of these structures are characterized by powder X-ray diffraction and are

determined to be different. Chen et al., (2006) describes MOF-508a as a paddle-

wheel structure with pillared units shaped by the 4,4'-Bipy which ends up looking

like a cubic lattice. In contrast, MOF-508b the pillared and the paddle-wheel

framework are dramatically contorted which results in a more dense structure. In the

study, MOF-508b may be converted back to MOF-508a by soaking it in a

DMF/ethanol mixture for one day. Furthermore, powder X-ray diffraction shows that

this simple soaking process expands MOF-508b back to MOF-508a without any

variation of its original framework. This process of compressing and expanding

extends the size of the MOF pores. As the MOF compresses, so do the pores and vice

versa. Furthermore, the expansion and compression of MOFs-508a and b can be

repeated while retaining the same structures. Therefore, MOFs that have tunable

pores at different temperatures can be used to separate alkanes of different sizes. The research by Chen et al., (2006) shows that alkanes have been separated from natural gas samples as the sample passes through the MOF-508 packed column. This led to further extensions, within the same research study, such as separating linear and branched isomers of other alkanes. *n-* Pentane and *n*-hexane are successfully separated via gas chromatography using the microporous MOF-508. Furthermore, *n*-hexane is separated from two of its isomers, 2,2-dimethylbutane and 2-methylpentane. Also, 2-methylbutane, an isomer of *n*-pentane, is successfully separated. Chen et al., (2006) describe the successful separation to the van der Waals interactions of the alkanes with the pores. Thus, MOFs potential may extend into the oil sector for sample analysis.

The American dependency on petroleum has recently been an increasing concern and has yielded many alternatives one of which is hydrogen fueled vehicles. This concern inspired President George W. Bush to develop the Hydrogen Fuel Initiative which was announced in 2003 and accelarated research in hydrogen storage is encouraged through the Initiative and the 2006 Advanced Energy Initiative as stated in the Hydrogen Overbook book set forth by the United States Department of Energy (2006).

Although hydrogen fueled vehicles have attained much support from the public and government, there are still barriers to overcome before they can become commercially available. One of the major challenges is storing the hydrogen. The United States Department of Energy (2006) has listed three approaches to store the

hydrogen: compression, liquid hydrogen, and hydrogen storage in solid-state materials.

The United States Department of Energy (2006) explains the compression of hydrogen gas that will allow more compact storage in the hydrogen gas tank. In the report, Hydrogen Overview Book, cryo-compressed tanks involve cooling the hydrogen from room temperature to -196°C at a constant pressure of 5,000 psi. Also, conformable tanks are investigated to sustain the high pressures of hydrogen storage while conveniently fitting into the vehicle (U.S. Department of Energy, 2006).

The second approach set forth by the United States Department of Energy (2006), involves cooling hydrogen to -253°C at which it will then become a liquid. In its liquid state, hydrogen is denser than its gaseous state which is beneficial because it contains higher energy content per volume. However, a tank must be designed to insulate the hydrogen to prevent loss due to evaporation. (U.S. Department of Energy, 2006).

Solid-state materials and chemical reaction storage of hydrogen are also proving to be front-runners. Metallic hydrides, chemical reactions, new materials, and carbon-based substances have been investigated due to their great potential in hydrogen storage (U.S. Department of Energy, 2006).

The United States Department of Energy (2006) suggests utilizing compounds such as lanthanum nickel hydride ($LaNi_5H_6$), produced by integrating hydrogen into the lattice framework of lanthanum and nickel ($LaNi_5$). The hydrogen atoms are released via desorption upon addition of heat to the lanthanum nickel hydride. Although the United States Department of Energy (2006) describes this as a valid

process, issues exist. The metallic hydrides have a low hydrogen capacity along with slow uptake and release. Furthermore, it is a high cost process compared to the existing gasoline powered vehicles (U.S. Department of Energy, 2006).

Metallic and nonmetallic hydrides may also be utilized as a means to store the hydrogen (U.S. Department of Energy, 2006). The details provided by the United States Department of Energy (2006), would have hydride compounds reacting with water or alcohols to release the hydrogen. Addition of hydrogen, heat, or other reagents, may be used to regenerate the reactants from the byproducts. Other methods such as hydrolysis of sodium borohydride ($NaBH_4$) have also been under investigation (U.S. Department of Energy, 2006). In the presence of a catalyst, $NaBH_4$ reacts with water producing hydrogen and sodium borate. Water, hydrogen and heat are utilized to convert the sodium borate back into $NaBH_4$. Catalysts may also be used with heat to release hydrogen from hydrocarbons such as decalin ($C_{10}H_{18}$) (U.S. Department of Energy, 2006).

Hydrogen can be adsorbed via carbon-based materials such as fullerenes and nanotubes (U.S. Department of Energy, 2006). MOFs also adsorb hydrogen at room and low temperatures. The secret of the adsorption lies in the structure of the MOF. (Rowsell & Yaghi, 2005). The MOF is a highly porous material that allows the hydrogen molecules to nest at the pores. Furthermore, MOFs exhibit large surface area which makes it desirable for storage (Rowsell & Yaghi, 2005). MOFs have some of the highest reported surface areas compared to other materials. This is highly critical as a higher surface area translates into more contact between the MOF and the guest molecule(s) (Rowsell & Yaghi, 2005; Walton & Snurr, 2007).
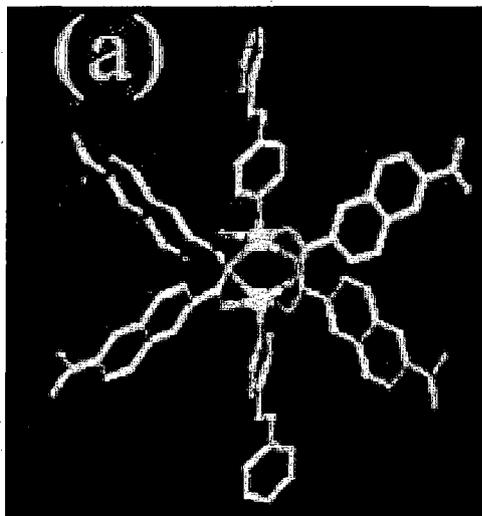
Figure 5 Paddle-wheel structure of $Zn_2(NDC)_2(4,4'-BPE)$. Zinc atoms are yellow, oxygen atoms are red, nitrogen atoms are blue, and carbon atoms are gray (Chen et al., 2006).

Chen, Ma, Zapata, Lobkovsky, and Yang (2006) recently reported hydrogen adsorption with MOF, $Zn(NDC)(4,4'-BPE)\cdot2.25DMF\cdot0.5H_2O$ shown in Figure 5 as the framework $Zn_2(NDC)_2(4,4'-BPE)$ unit, as a contender in the hydrogen storage race which has been reported a 2.0 wt % hydrogen uptake at 77 K and 40 bar. The percentage uptake decreases to 0.3% at 298 K and 65 bar as shown in Figure 6 (Chen et al., 2006).
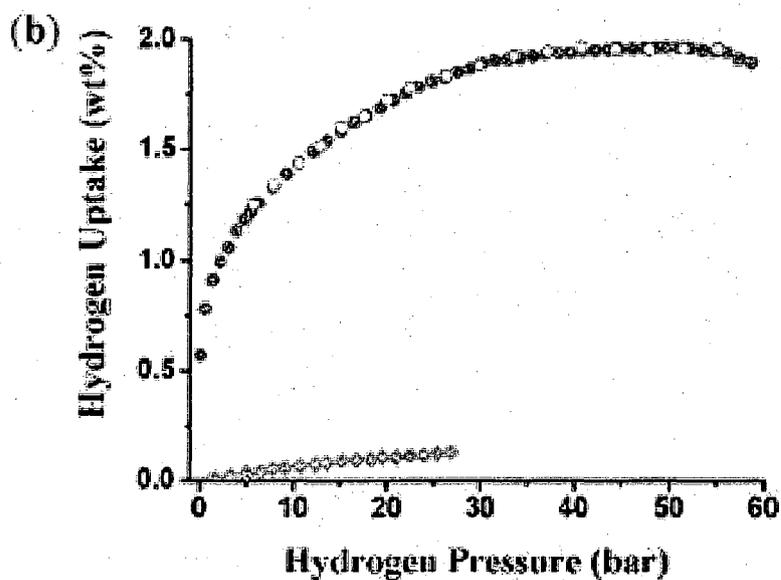

Figure 6 Hydrogen uptake of $Zn_2(NDC)_2(4,4'-BPE)$. The red isotherm shows hydrogen uptake at 77K and 298K for the green isotherm (Chen et al., 2006).

Additionally, other MOFs with similar hydrogen uptake have been synthesized, characterized, and reported. It has been a challenge for many researchers to develop an MOF that has a high hydrogen uptake at room temperature. The highest hydrogen uptake reported by MOF-77 is 7.5 wt % at 77 K and 70 bar (Chen et al., 2006). These porous MOFs; however, must meet the 9.0 wt % of hydrogen uptake by 2015 as set forth by the United States Department of Energy (2006).

MOFs also have the potential to be applied as catalysts (Chen et al., 2006; Chen et al., 2007; Kitagawa, Kitaura, & Noro, 2004; Llabres i Xamena, Abad, Corma, and Garcia, 2007; Rosi et al., 2005; Rowsell & Yaghi, 2004; Walton & Snurr, 2007). Typically, the organic ligands block the metal atoms from the outside. (Rowsell & Yaghi, 2004; Llabres i Xamena, Abad, Corma, & Garcia, 2007). Exposing the metal atoms in the MOF proved to be critical in the usage of catalysts. Llabres i Xamena et al. (2007) reported that a palladium containing MOF was successfully used for alcohol oxidation, Suzuki coupling, and olefin hydrogenation. Palladium-phosphine catalysts are used for the organic reaction previously mentioned; however, the solid is amorphous with irregular pores. (Llabres i Xamena et al., 2007). Thus, selectivity in size and shape could not be attained. On the other hand, Pd-MOF is a crystalline solid with a regular geometric pattern and thus having consistent pore shape and size as shown in Figure 7 (Llabres i Xamena et al., 2007). The prospect of shape selectivity may be attainable through the Pd-MOF. Llabres i Xamena et al., (2007) used phenylboronic acid and 4-bromoanisole as substrates for the Suzuki coupling reaction. In addition, potassium carbonate and o-xylene were

necessary in the study. The reaction was carried out for five hours at 150°C with the

Pd-MOF (Llabres i Xamena et al., 2007). The results of the study conducted the

Llabres i Xamena (2007), show that the reaction produced an 85% conversion to the

product, *p*-methoxybiphenyl with 99% selectivity. Moreover, cinnamyl alcohol was

used as the substrate for the alcohol oxidation reaction. After twenty hours of

exposure to air at atmospheric conditions, the cinnamyl alcohol was 99% converted

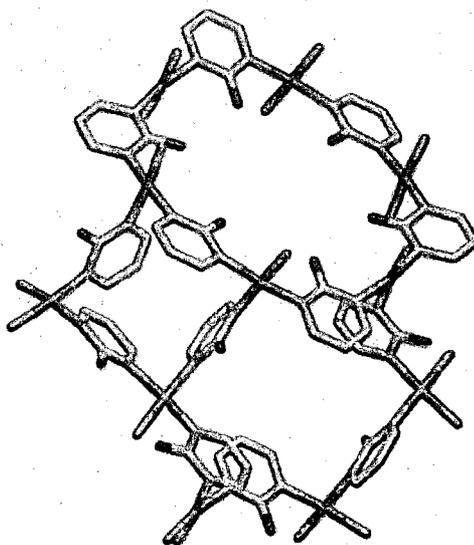to cinnamylaldehyde with 74% selectivity with the Pd-MOF (Llabres i Xamena et al.,

2007).

Figure 7 Palladium-MOF. Palladium atoms are colored in pink, carbon atoms in gray, nitrogen atoms in blue, and oxygen atoms in red (Llabres i Xamena et al., 2007).
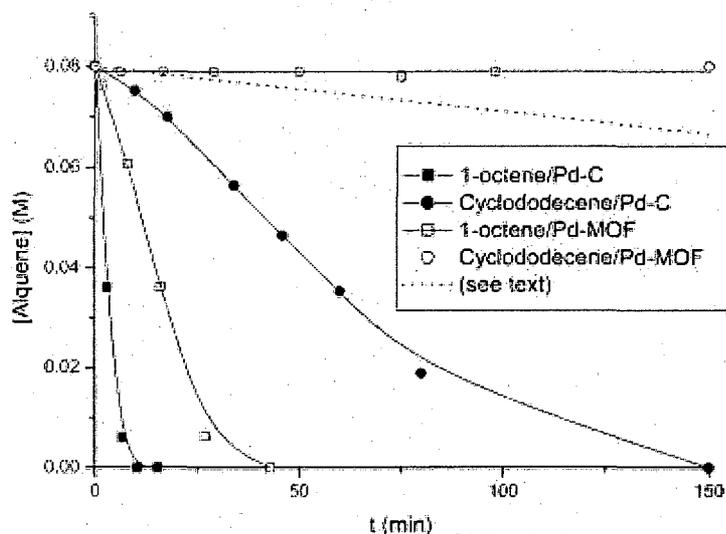

Figure 8 Traditional palladium catalyst versus palladium-MOF in hydrogenation (Llabres i Xamena et al., 2007).

Lastly, the alkene hydrogenation of 1-octene and cyclododecene were evaluated. Results obtained by Llabres i Xamena et al. (2007) are shown in Figure 8. Cylcododecene hydrogenation with the Pd-MOF is minimal whereas the traditional palladium catalyst was completely hydrogenated after two and a half hours. This shows that the pores in the Pd-MOF were too small for the cyclododecene to pass through. However, for 1-octene, hydrogenation did take place as the molecules could pass through the Pd-MOF pores (Llabres i Xamena et al., 2007). Therefore, shape selectivity is possible via the Pd-MOF molecular sieves (Llabres i Xamena et al., 2007).

It should be noted that the Pd-MOF is not synthesized via the solvothermal process (Llabres i Xamena et al., 2007). Llabres i Xamena et al. (2007), prepare a palladium complex, Pd(2-hydroxypyrimidine)$_2$Cl$_2$, in a one to two ratio of aqueous K$_2$PdCl$_4$ and aqueous 2-hydroxypyrimidine. This complex is then refluxed at a pH of 6.0 for five days and has the formula [Pd(2-pymo)2]$_n$·3H$_2$O and pore size of 8.8 angstroms in diameter (Llabres i Xamena et al., 2007). Pd-MOF is an appropriate replacement to the palladium catalysts currently used in the organic reactions (Llabres i Xamena et al., 2007).

Just as open metal sites are key to catalysis, they also prove significant for the sensing the molecules. MOFs intended to have open metal sites have been developed with lanthanide metals. For instance, Chen et al. (2007) reported MOF, Eu(BTC)[2] as a sensor of small molecules only when its parent structure, Eu(BTC)(H$_2$O)·1.5H$_2$O shown in Figure 2, is heated and the water is released at temperatures between 25-150°C and consequently revealing the europium. The pink atoms, in Figure 2,

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[2] BTC = benzene-1,3,5-tricarboxylate

represent europium atoms (Chen et al., 2007). Solvents such as DMF and acetone enhance the luminescent properties. Chen et al., describe in the literature that increasing aliquots of DMF are added to a constant concentration of Eu(BTC), containing 1-propanol utilized as a standard component, show an increase in the luminescent properties. Conversely, increasing aliquots of acetone actually decreased the luminescent properties. The interaction between the europium and solvents is a crucial concept in luminescent data acquired (Chen et al., 2007). Nonetheless, whether the luminescent properties increase or decrease the small molecules are sensed (Chen et al., 2007).

MOFs have proven staying power in the field of solid-state chemistry. Solvothermal production of MOFs has also proven to be economical. Furthermore, the reactants are readily available for purchase. The building-block approach is also very desirable because the scientist may pair a metal with a variety of organic linkers and/or solvents allowing endless combinations and properties (Rowsell & Yaghi, 2004). Characterization via X-ray diffraction has detected exact structures of the MOFs. Their crystalline structures and porosity have made way into the industrial world. MOFs are leading contenders in the hydrogen storage pursuit. Although no MOF has achieved the 9.0 wt % of hydrogen uptake, research is ongoing (Chen et al., 2006; Kitagawa et al., 2004; Ross, 2006; Rowsell & Yaghi, 2005; and United States Department of Energy, 2006). They are also making their way as packing material in gas chromatograph columns (Chen et al., 2006). MOFs can selectively separate linear and branched alkanes (Chen et al., 2006). This is useful for quality control and separation in mixtures. Not only have they proven to be selective in gas

chromatography, but in organic reactions replacing amorphous palladium complexes with Pd-MOFs (Llabres i Xamena et al., 2007). Llabres i Xamena et al. (2007) demonstrate Pd-MOF catalysts as having the potential to produce highly selective species due to their pore size and shape. The research conducted by Llabres i Xamena et al. (2007) and Chen et al. (2007) also revealed that catalysis and molecule recognition require open metal sites for maximum potential, respectively. The porous MOFs have potential in the area of sensing small molecules (Chen et al., 2007). The use of lanthanide metals has proven and important factor in monitoring luminescent properties as the small molecules are detected (Chen et al., 2007). In summary, zeolites have inspired a new class of microporous materials, that is MOFs, and are having an impact in industry as new, tailor-made framework structures.

CHAPTER II

EXPERIMENTAL DESIGN

MOFs are conveniently synthesized via a solvothermal, one-pot process (Rowsell & Yaghi, 2005). MOFs are designed via the building block approach as described by Rowsell and Yaghi (2004). That is, molecules are hand selected and combined for their properties. Thus, a myriad of MOFs may be developed via solvothermal synthesis by linking metallic ions with organic ligands.

MOF design begins by selecting metallic ions and organic linkers that will yield desired properties. A robust MOF with permanent porosity was the main goal of this research. Hydrated metallic nitrates, carboxylates, and organic solvents are typical reactants in the design of MOFs. Rowsell and Yaghi (2004) indicate that zinc ions are often chosen and connected to a dicarboxylate group which will inherit the general formula Zn_4O along with the remaining dicarboxylate. MOFs of this nature have exhibited a very rigid, highly crystalline structure (Rowsell & Yaghi, 2004). In addition, Rowsell and Yaghi (2004) describe the zinc-acetate clusters as secondary building units (SBUs). The SBUs Rowsell and Yaghi (2004) explain are "simple geometric figures", such as paddle-wheel, octahedral, or triangular (shown in Figure 9), that are utilized to predict the MOFs overall structure.
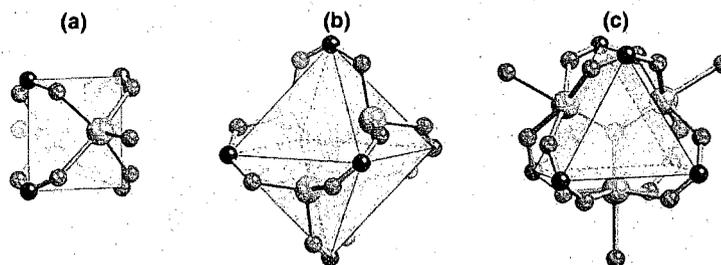
Figure 9 Secondary Building Units: a) square paddle-wheel, b) octahedral, and c) "trigonal prismatic oxo-centered trimer" (Rowsell & Yaghi, 2004).

Another organic linker is then chosen to be attached to form a netlike structure. For example, Figure 10 shows an octahedral MOF with various organic linkers that can be employed to yield MOFs with different functional groups and rigidity, known as isoreticular MOFs (Rowsell & Yaghi, 2004).
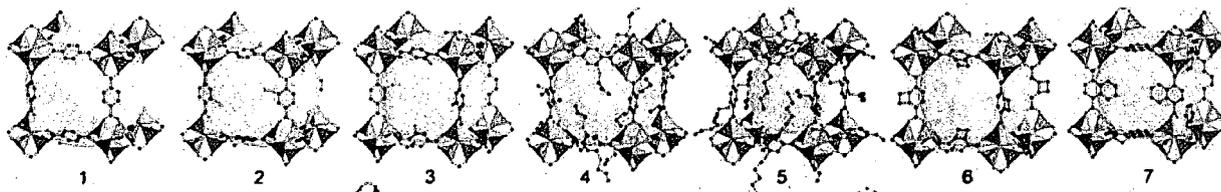

Figure 10 Isoreticular MOFs. MOFs 1-7 with the same octahedral SBU with different organic linkers (Rowsell & Yaghi, 2004).

Once the starting materials are selected, crystallization takes place via solvothermal synthesis. Solvothermal synthesis allows deportation of the carboxylate group and attachment to the metal being used which yields a strong metal-carboxylate bond (Eddaouidi et al., 2002; Hirscher & Panella, 2007; Rosi et al., 2002; Rosi et al., 2005; Rowsell & Yaghi, 2004). The solvent molecules aid in defining the openings of the MOF (Eddaouidi et al., 2002; Hirscher & Panella, 2007; Rosi et al., 2002; Rosi et al., 2005; Rowsell & Yaghi, 2004). They occupy the framework's space to form identical channels and are referred to as "guest molecules" (Eddaouidi et al., 2002; Hirscher & Panella, 2007; Rosi et al., 2002; Rosi et al., 2005; Rowsell & Yaghi, 2004). As the unbound solvent molecules are removed, the MOF structure may collapse and lose its stability (Chen et al., 2007; Rowsell & Yaghi, 2004). Therefore,

it becomes more challenging to prepare a MOF whose structure does not cave in as the solvent molecules are removed. For this reason MOFs are not considered porous but rather an open framework in which the solvent molecules are flowing freely throughout the channels (Rowsell & Yaghi, 2004). The guest molecules may be removed by heating the MOF (Rowsell & Yaghi, 2004). Furthermore, it has been reported that the "guest-free" MOF may be converted back by soaking it in the originally used solvents (Chen et al., 2006; Rowsell & Yaghi, 2004). Rowsell and Yaghi (2004) explain that the integrity of the MOF structure, as the free solvent molecules are released, are most commonly analyzed utilizing powder X-ray diffraction (PXRD) in conjunction with thermal gravimetric analysis (TGA). Additionally, the PXRD of the MOFs before and after release of its solvent molecules may confirm similarities of both structures.

Creation of a MOF begins by hand-selecting the starting materials. Moreover, by employing the concepts of SBUs, one should acquire robust, highly crystalline MOFs. The next section describes the synthesis of two newly developed MOFs based on these principles.

Experimental Procedures

General: All chemicals were used in this research as purchased from the following companies: Acros Organics, Alfa-Aesar Lacaste, Fluka, Sigma-Aldrich, TCI America, and TCI Tokyo Kasei. Masses of substances were carried out using the same Denver Instrument (max 220g) balance, to assure consistency. A Bruker SMART CCD diffractometer was utilized to conduct X-ray crystallography. Either

SHELXL97 or SHELXTL programs were employed to refine structures. Selected bond lengths for both MOFs are located in the appendix.

The following metallic nitrates were used in this research: zinc nitrate hexahydrate, cobalt (II) nitrate hexahydrate, copper (II) nitrate dihydrate, cadmium nitrate hexahydrate, and nickel (II) nitrate hexahydrate. In addition, these metals were combined with different dicarboxylates and other organic linkers of various lengths which are shown in Table 1. The hydrated metallic nitrates, dicarboxylates, and other organic linker were combined either in a 2:2:1 or 3:3:1 ratio, respectively. Solvents of choice are alkyl formamides and pyrrolidinones. In specific, N,N-dimethyformamide, N,N-diethylformamide, 1-methyl-2-pyrrolidone, water, ethanol, cyclohexanol, acetone, methanol, and ethylene glycol have been used in this research as solvents. In addition, the temperature ranged from 80°C to 120°C over a twenty-four to forty-eight hour period. A Fisher Scientific Isotemp Oven was used as part of this research and is shown below in Figure 11.
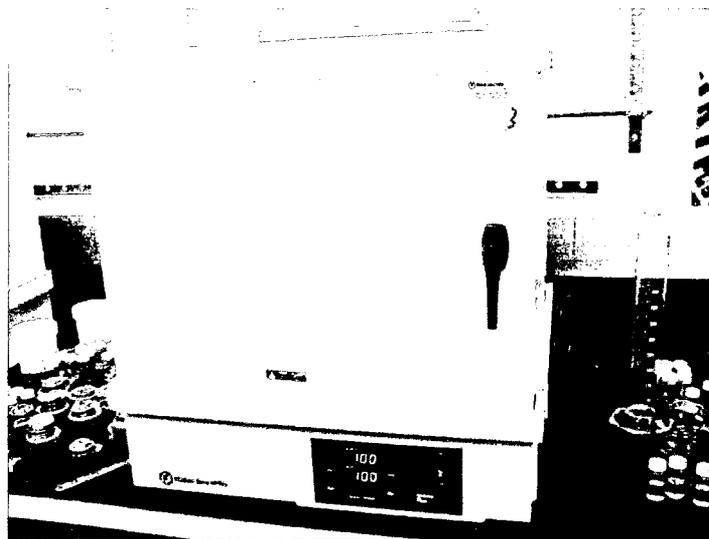
Figure 11 Fisher Scientific Isotemp Oven.

Once the MOFs have crystallized, a Fisher Scientific Stereomaster is used to analyze the crystals. We are looking for nice crystals with a geometric pattern. For instance, sample RSM-145 was synthesized using zinc nitrate hexahydrate, terephthalic acid, and DPT in a 2:2:1 mole ratio, respectively. Solvents used for this sample were N,N-dimethylformamide and ethanol. All of the starting materials were placed in a vial and after twenty-four hours at 100°C, light pink crystals were observed along with light green transparent crystals as shown in Figure 14. Although the MOF reagents yielded a mixture of two different crystals, it is worth taking a closer look at the reaction conditions and reagents. This sample was not successfully characterized via X-ray diffraction.

a) b)
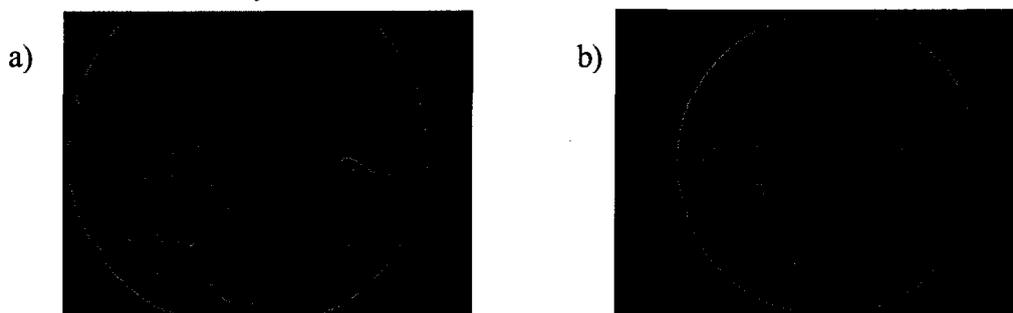
Figure 12 Sample RSM-145: a) yields light pink crystals along with b) light green transparent crystals.

Sample RSM-41J was prepared using zinc nitrate hexahydrate, azobenzene-4,4'-dicarboxylic acid, and 4,4'-Dipyridyl in a 3:3:1 ratio, respectively. These reagents were placed in a vial and dissolved with dimethylformamide and water. Bright orange crystals appeared after twenty-four hours in a 100°C oven as shown in Figure 15a. A similar experiment was conducted for sample RSM-81 using cadmium nitrate hexahydrate, azobenzene-4,4'-dicarboxylic acid, and 4,4'-Dipyridyl in a 3:3:1 ratio, respectively. Also, dimethylformamide was the only solvent used. The crystals were grown in a 100°C oven for a twenty-four hour period which yielded bright

orange crystals as shown in Figure 15b. Under the microscope the two are very similar in structure; however, they are not identical as shown in Figure 8. Further analysis may reveal differences between the two structures. These samples, among others, were not successfully characterized via X-ray diffraction.
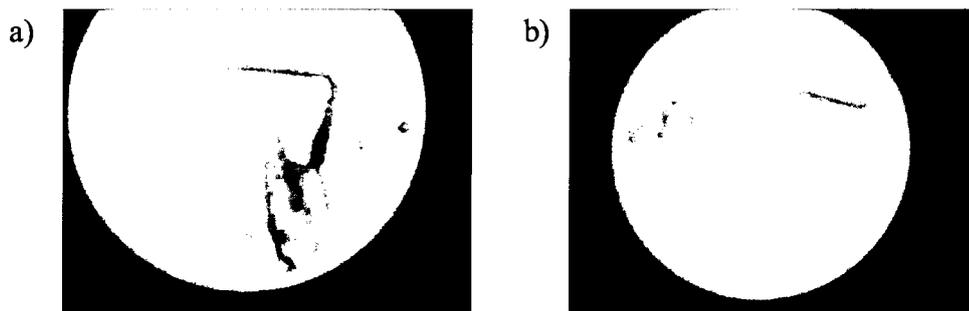

Figure 13 Samples RSM – 41J and RSM – 81: a) RSM-41J orange crystals which are very similar to b) RSM-81 orange crystals.

Not all samples produced crystals such as RSM-153. Nickel (II) nitrate hexahydrate, terephthalic acid, and BPE in a 3:3:1 ratio, respectively, were placed in a vial and dissolved in N,N-dimethylformamide and ethylene glycol. After twenty-four hours in a 100°C oven, a pink cloudy mixture was observed as shown in Figure 16a. A closer look under the microscope reveals lack of crystalline structure as shown in Figure 16b. It may be necessary for a milder temperature allowing for slower crystal growth. Sample RSM-153 and others like it, were not analyzed via X-ray crystallography.
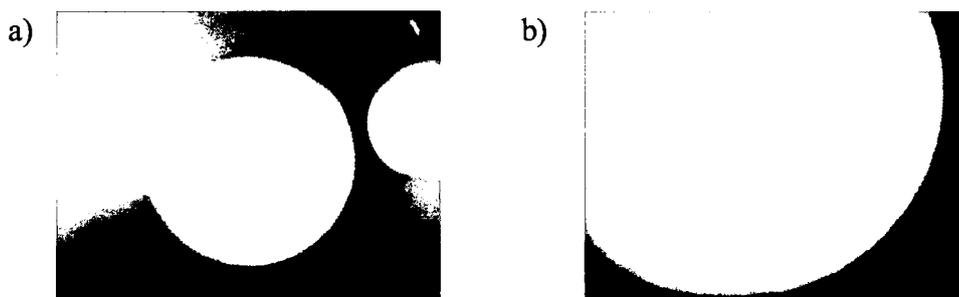
Figure 14 Sample RSM-153: a) a top view of the vial after twenty-four hours yielded a pink opaque mixture and b) lacks of crystalline structure.

Synthesis and Characterization

Zn₄O(FMA)₃: Synthesis of $Zn_4O(FMA)_3$ was successfully synthesized and characterized as follows. $Zn(NO_3)_2 \cdot 6H_2O$ (0.279g, 1mmol) and FMA (0.116g, 1mmol) were combined in a 400 mL vial along with 100 mL DEF. The crystals formed via solvothermal reaction at 100°C for 24 hours. The light yellow cubic crystals, shown in Figure 15, were collected washed with DEF. The crystals were air-dried to give 0.34g, an 85% yield of the light yellow crystalline solid
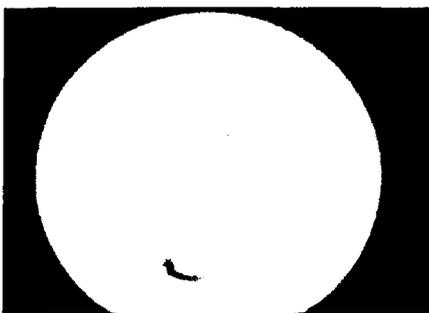
Figure 15 $Zn_4O(FMA)_3$ crystals.

Zn₂(CNC)₂(DPT)(DMF)₁.₅(H₂O): Similarly, $Zn_2(CNC)_2(DPT)(DMF)_{1.5}(H_2O)$ was also successfully synthesized and characterized. $Zn(NO_3)_2 \cdot 6H_2O$ (0.279g, 1mmol), CNC (0.200g, 1 mmol), and DPT (0.12g, 0.5 mmol) were placed in a 400 mL vial along with 100 mL of DMF. The mixture was heated in an isotemp oven at 80°C for 24 hours producing light pink, block shaped crystals, as shown in Figure 16. The crystals were collected, washed with DMF, and air-dried with a yield of 60%.
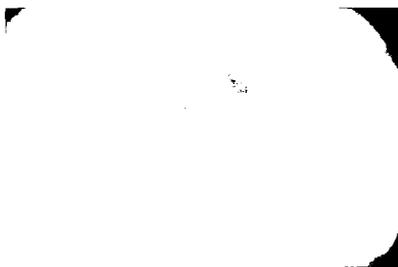
Figure 16 $Zn_2(CNC)_2(DPT)(DMF)_{1.5}(H_2O)$ crystals.

Supporting Information: X-Ray crystal structures for $Zn_4O(FMA)_3$ and

$Zn_2(CNC)_2(DPT)\cdot(DMF)_{1.5}(H_2O)$ are shown in Figures 17 and 18, respectively.

Selected crystallography data for both MOFs are located in the appendix (Xue,
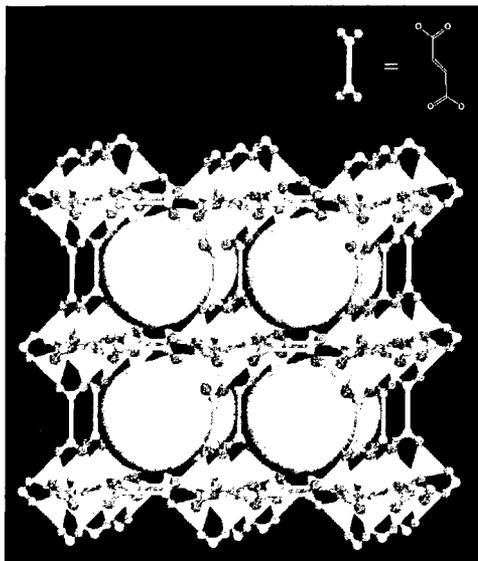
Schaffino Moore, et al., 2008, 2009).

Figure 17 X-ray crystal structure of $Zn_4O(FMA)_3$: cubic nets with pore size of 6.8 Å. (zinc is pink; oxygen is red; guest molecules are green) (Xue, Schaffino Moore, et al., 2009).
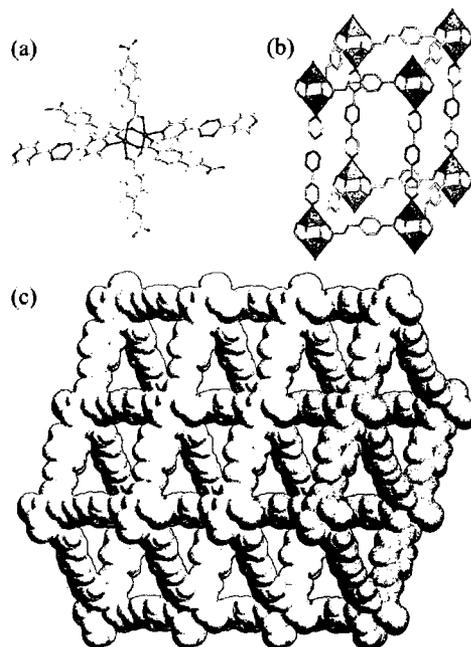

Figure 18 X-ray crystal structure of $Zn_2(CNC)_2(DPT)$: (a) the paddle-wheel geometry (b) the cubic net and 3.7 Å channels. (zinc is green; carbon is grey; nitrogen is blue; oxygen is red; and hydrogen is white) and (c) a 3.7 Å 1D pore as shown along the rectangular diagonal (Xue, Schaffino Moore, et al., 2008).

CHAPTER III

RESULTS AND DISCUSSION

In this research, IRMOF $Zn_4O(FMA)_3$ was rationally designed. That is the short organic ligand, fumaric acid, was combined with zinc nitrate hexahydrate in such a manner that it would produce the expected octahedral Zn_4O units bridged by FMA. The non-interpenetrated structure is robust with high porosity. Gas adsorption studies were conducted at high pressure and at a range of temperatures. The studies reveal that $Zn_4O(FMA)_3$ has a hydrogen uptake of 71 mg/g at 30 K and 3.5 bar, and 52 mg/g at 77 K and 39 bar. Although the IRMOF has a small surface area, 1700 m^2/g, it can store quite a bit of hydrogen. However, at room temperature it can only uptake 0.32 wt % at 40 bar as shown in Figure 19.
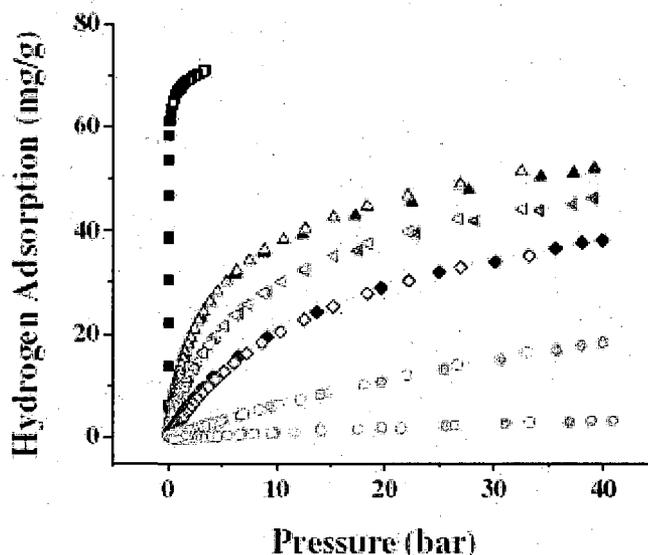
Figure 19 Hydrogen sorption isotherms for $Zn_4O(FMA)_3$: at 30 K (black), 77 K (blue), 87 K (magenta), 100 K (navy), 150 K (green), and 300 K (orange) (solid shapes represent adsorption; open shapes represent desorption) (Xue, Schaffino Moore, et al., 2009).

Zn₄O(FMA)₃ can take up a considerable amount of small gaseous molecules such as

methane and carbon dioxide. At 28 bar and 300K, it can adsorb 8.6 wt % of methane

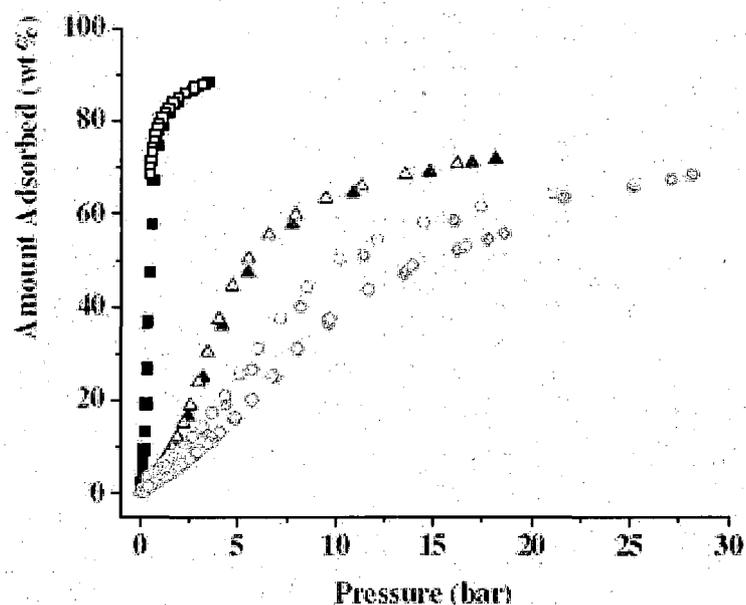and 69 wt % of carbon dioxide as shown in Figure 20.

a)
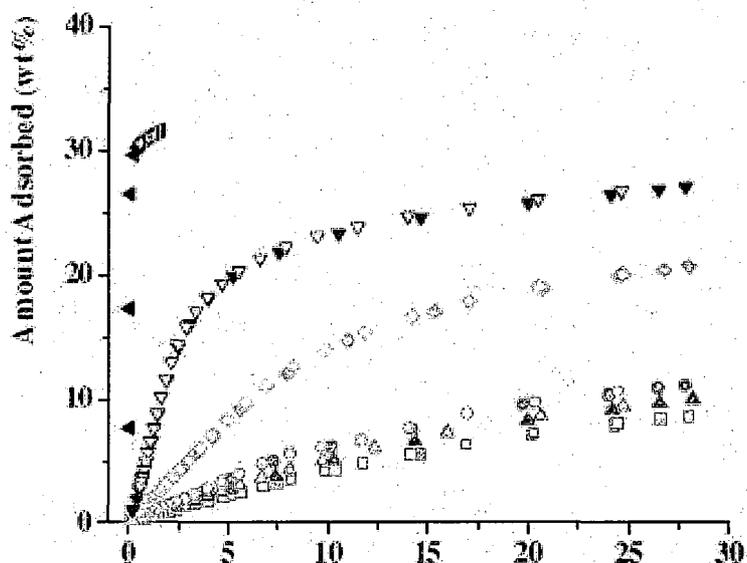
b)

Figure 20 Methane and Carbon dioxide sorption isotherms for Zn₄O(FMA)₃: a) Methane sorption isotherms: 125 K (black), 200 K (blue), 240 K (green), 280 K (magenta), 290 K (red) and 300 K (orange) and b) Carbon dioxide sorption isotherms: 220 K (black), 280 K (blue), 300 K (green), 310 K (orange) (solid shapes represent adsorption; open shapes represent desorption) (Xue, Schaffino Moore, et al., 2009).

The integrity of IRMOF $Zn_4O(FMA)$ was determined via PXRD. PXRD

assesses the phase homogeneity of the crystalline products. Figure 21 below shows,

the PXRD data revealing a structurally pure crystalline structure. TGA also revealed
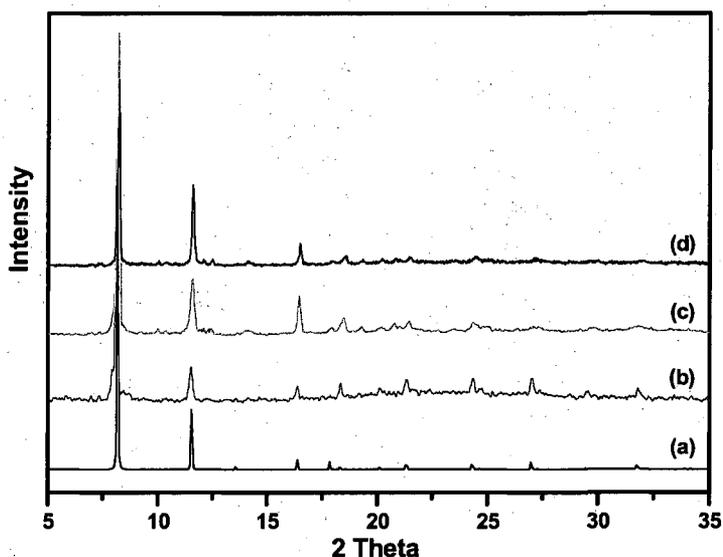
structure stability up to 300°C.

Figure 21 PXRD data for IRMOF $Zn_4O(FMA)_3$: A) single crystal structure (black); b) as synthesized (red), c) anhydrous CH_2Cl_2 exchange (green), and d) guest free sample (blue) (Xue, Schaffino Moore, et al., 2009).

The solvothermal synthesis of zinc nitrate hexahydrate, CNC and DMF

yielded red-block shaped crystals of $Zn_2(CNC)_2(DPT)(DMF)_{1.5}(H_2O)$. The structures

also demonstrate rigidity as it forms a rare triply penetrated framework which is

favored by the long DPT ligand. It has been reported that short linkers tend to form

rigid doubly interpenetrated frameworks and longer linker forming flexible doubly

interpenetrated frameworks. Thus, the triply interpenetrated network is unique. The

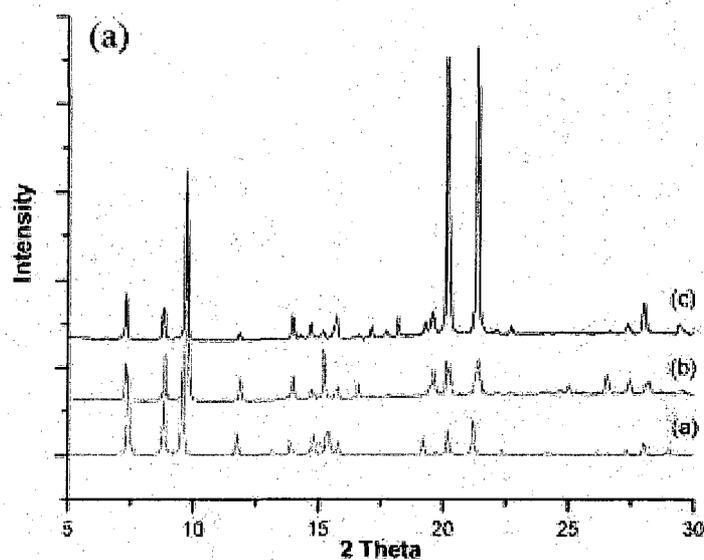robust MOF is proven via PXRD as shown in Figure 22.

Figure 22 PXRD data for $Zn_2(CNC)_2(DPT)\cdot(DMF)_{1.5}(H_2O)$. a) single crystal structure (red); b) methanol-exchanged (green); c) activated guest free sample (black) (Xue, Schaffino Moore, et al., 2008).

The guest free form of $Zn_2(CNC)_2(DPT)\cdot(DMF)_{1.5}(H_2O)$, $Zn_2(CNC)_2(DPT)$,

has a high hydrogen adsorption of 1.28 wt % at 1 atm for a MOF that with low

porosity as shown in Figure 23. However, it has a low adsorption for nitrogen, also

shown in Figure 23. The hydrogen storage density of the MOF is 0.0674 g/cm^3,

which is relative high based on its pore volume of 0.19 cm^3/g. Considering the

density of liquid hydrogen is 0.0708 g/cm^3, the pores are filled with 95.2% at 1 atm

and 77 K.
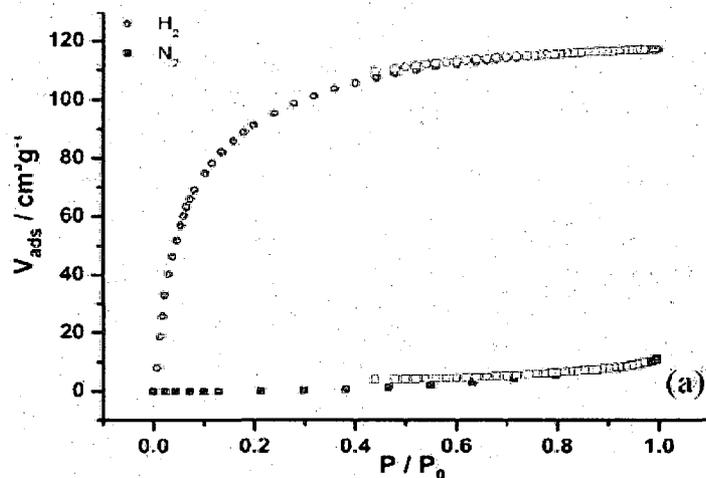
Figure 23 Hydrogen and nitrogen adsorption isotherms for $Zn_2(CNC)_2(DPT)$: at 77 K where hydrogen is green and nitrogen is blue (solid shapes represent adsorption; open shapes represent desorption) (Xue, Schaffino Moore, et al., 2008).

Zn$_2$(CNC)$_2$(DPT) also displays selective sorptions behavior. As shown in Figure 24, a high sorption of carbon dioxide (3.3A) was exhibited over methane (3.8A). This is important as Zn$_2$(CNC)$_2$(DPT) interacts more so with the smaller carbon dioxide molecules (Xue, Schaffino Moore, et al., 2008, 2009).
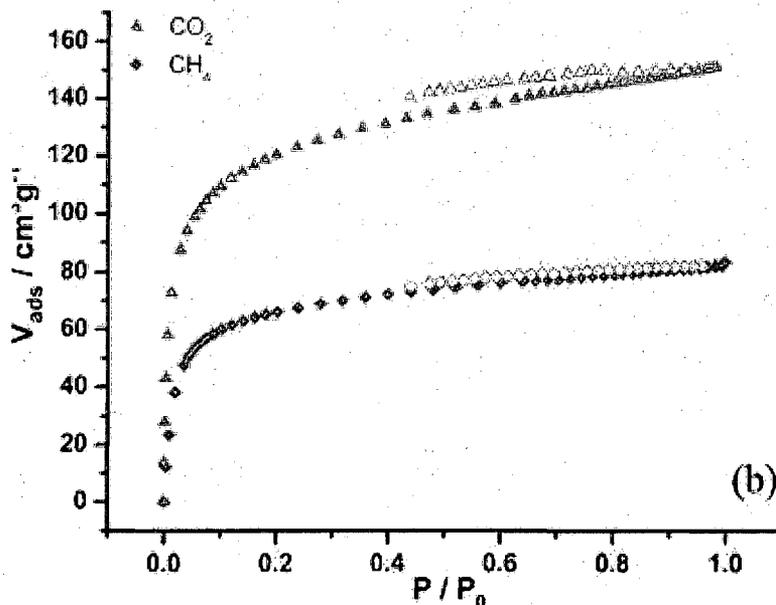

Figure 24 Carbon dioxide and methane adsorption isotherms for Zn$_2$(CNC)$_2$(DPT): at 195 K where carbon dioxide is red and methane is purple (solid shapes represent adsorption; open shapes represent desorption) (Xue, Schaffino Moore, et al., 2008).

CHAPTER IV

CONCLUSION

Zn$_4$O(FMA)$_3$ is a newly synthesized, novel IRMOF. The hand selected units of zinc nitrate hexahydrate and fumaric acid were expected to form octahedral Zn$_4$O units that would link to the fumarate ions. The highly rigid, crystalline structure was developed using fumaric acid, a highly available and economic substance. The 3D primitive cubic net exhibited intersecting pores of 6.8 x 6.8 Å. It can adsorb 5.2 wt % of hydrogen at 77K and 39 bar despite its relatively small surface area of 1700 m^2/g.

Zn$_2$(CNC)$_2$(DPT) was also successfully developed as a robust, triply interpenetrated MOF. The dinuclear Zn$_2$(COO)$_4$ units exhibit a paddle-wheel geometry that are connected to CNC ligands producing a 2D square. A 3D primitive cubic net is formed from the DPT pillars. The 1D triangular micropores, 3.7 Å, which can take up 1.28 wt % hydrogen gas at 77K and 1 bar.

Solvothermal synthesis was carried out using a variety of hydrated metallic nitrates, organic molecules, solvents, and conditions. Many combinations of the previously mentioned were conducted. However, only two MOFs were successfully characterized: Zn$_4$O(FMA)$_3$ and Zn$_2$(CNC)$_2$(DPT). Both MOFs exhibit a highly crystalline, robust structure along with adjustable organic units all of which are determining characteristics of MOFs (Xue, Schaffino Moore, et al., 2008, 2009).

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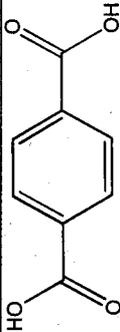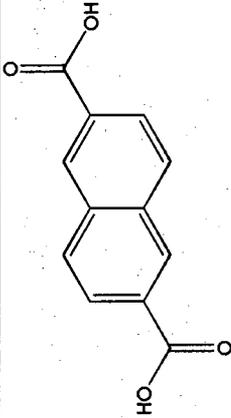Xue, M., Ma S., Schaffino R.M., Zhu G., Lobkovsky E., Qiu S., Chen B. *Inorganic Chemistry* **2008**, *47* 6825-6828.

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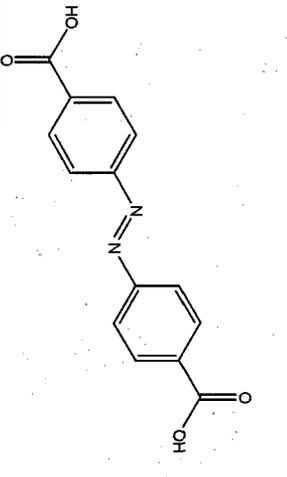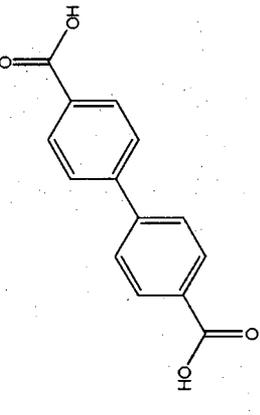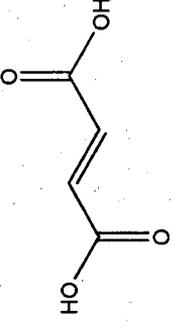
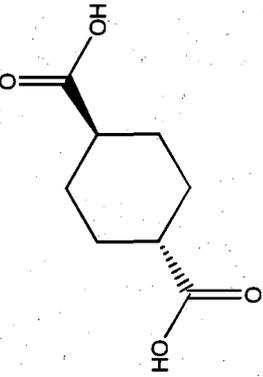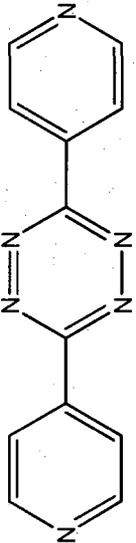Zeolite. (n.d). In *Wikipedia*. Retrieved January 17, 2008, from http://en.wikipedia.org
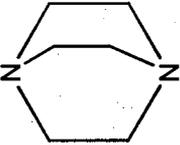
APPENDIX

Table 1 [3] Molecular abbreviations, formulas, and structures.

Organic Ligand	Abbreviation	Molecular Formula	Molecular Structure
a) terephthalic acid	H_2BDC	$C_6H_4(COOH)_2$	
b) 2,6-naphthalenedicarboxylic acid	NDC	$C_{10}H_6(COOH)_2$	
c) 4,4'-stiben-4,4'-dicarboxylic acid	SDA	$C_6H_4CH=CHC_6H_4(COOH)_2$	

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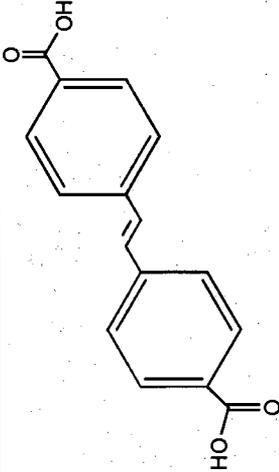
[3] All chemical structures were drawn using ChemDraw.

d) azobenzene-4,4'-dicarboxylic acid	ADA	$C_6H_4N=NC_6H_4(COOH)_2$	
e) 4,4'-biphenyldicarboxylic acid	BBA	$C_6H_4C_6H_4(COOH)_2$	
f) fumaric acid	FMA	HOOCCH=CHCOOH	
g) trans,trans-muconic acid	-----	HOOCCH=CHCH=CHCOOH	
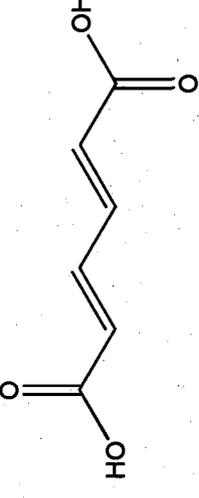
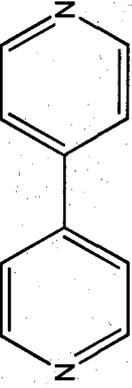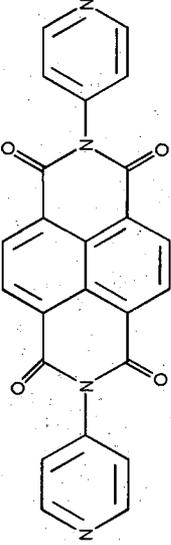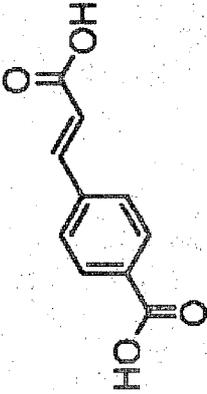|			
h) trans-1,4-cyclohexanedicarboxylic acid	CDC	$C_6H_{10}(COOH)_2$	
i) 3,6-Di-4-pyridyl-1,2,4,5-tetrazine	DPT	$C_{12}H_8N_6$	
j) 1,4-Diazabicyclo[2.2.2.]octane	DAB	$C_6H_{12}N_2$	
k) 1,2-Di(4-pyridyl)ethylene	BPE	$C_{12}H_{10}N_2$	
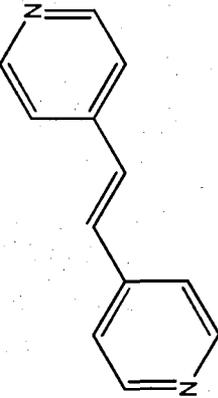
l) 4,4'-Bipyridyl	Bipy	$C_{10}H_8N_2$	
m) N,N-Bis(4-pyridyl)naphthalene-3,4	diPyNI	$C_{24}H_{12}N_4O_4$	
n) 4-carboxycinnamic acid	CNC	$C_6H_4CH=CH(COOH)_2$	

Table 2 Crystallography data for $Zn_4O(FMA)_3$ and $Zn_2(CNC)_2(DPT)$.

	$Zn_4O(FMA)_3$	$Zn_2(CNC)_2(DPT)$
Formula	$C_{12}H_6O_{13}Zn_4$	$C_{35}H_{27}N_7O_9Zn_2$
a, Å	21.639(3)	7.9273(16)
b, Å	21.639(3)	10.556(2)
c, Å	21.639(3)	13.155(3)
R1 [$I > 2\sigma(I)$]	0.0688	0.0687
$R_w{}^b$	0.1212	0.1832

BIOGRAPHICAL SKETCH

Roxanna Schaffino Moore was born in Santa Ana, California to Esperanza and Octavio Schaffino on October 15, 1982. She attended La Feria High School and graduated in May 2000. She attended the University of Texas – Pan American in Edinburg, Texas and transferred to Texas A&M University in College Station, Texas in 2002. In December 2004, she graduated from Texas A&M with a bachelor's of arts in chemistry with secondary teacher certification. She began working at Harlingen High School South as a chemistry teacher in January 2005. In August 2006, Roxanna enrolled in the Master's chemistry program at the University of Texas – Pan American. Currently, she continues to teach chemistry at Harlingen High School South in Harlingen, Texas.

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