

# **Bachelor Thesis**

Use of a ligand containing a pyrazole functionality and two  
carboxylate groups to construct new MOFs for applications in gas  
storage

**Marton Stefano**

July 2023

# Summary

## CHAPTER 1: INTRODUCTION

Over the past 150 year supramolecular chemistry has grown at an exponential rate, with the field expanding to embrace a wide range of applications, in what can be the described as a new chemical space.

This chapter aims to provide a brief historical account of the most notable development in supramolecular chemistry, focusing on MOFs and 3D periodic structures as well as their implementation in gas adsorption and electrochemistry applications.

## CHAPTER 2: RESULT AND DISCUSSION

The construction of 3D periodic solid structure oriented towards specific gas adsorption remain a challenging synthetic problem for chemists, several problems related to their development and use must be accounted.

In this chapter will be reported the advancement in the synthesis of a pyrazole based ligand and the utilization of a 1,3-diketones ligand in electrochemistry oriented application.

## CHAPTER 3: EXPERIMENTAL SECTION

Several synthesis and characterization method as been applied, both in the synthesis of pyrazole based ligand and 1,3-diketones MOF electrochemistry exploration, in order to achieve the results discussed earlier.

They will be analyzed in great detail in this chapter.

## CHAPTER 4: TOOL DEVELOPMENT

During the time spent working on these wide range topics the need of small and reliable analytical tools raised. Being able to analyze and draw a comparison between obtained results in a fast manner has been very important.

Across this chapter will be presented a tiny python implementation for fast data analysis and graphs creation.

# Contents

0.0.1	CHAPTER 2: RESULT AND DISCUSSION . . . . .	1
0.0.2	CHAPTER 3: EXPERIMENTAL SECTION . . . . .	1
0.0.3	CHAPTER 4: TOOL DEVELOPMENT . . . . .	1
<b>1</b>	<b>Introduction</b>	<b>3</b>
1.1	Supramolecular Chemistry, why? . . . . .	3
1.1.1	Host-Guest Chemistry . . . . .	3
1.1.2	Metal-Organic Frameworks . . . . .	3
1.1.3	Carboxylate-Based Metal-Organic Frameworks . . . . .	4
<b>2</b>	<b>Result and discussion</b>	<b>5</b>
<b>3</b>	<b>Experimental section</b>	<b>6</b>
3.1	Dimethyl 4,4'-malonyldibenzoate . . . . .	6
3.1.1	Synthesis . . . . .	6
3.1.2	Characterization . . . . .	6
3.2	4,4'-(1H-pyrazole-3,5-diyl)dibenzoic acid Synthesis . . . . .	6
3.2.1	Synthesis . . . . .	6
3.2.2	Characterization . . . . .	7
3.3	4,4'-malonyldibenzonitrile Synthesis . . . . .	7
3.3.1	Synthesis . . . . .	7
3.3.2	Characterization . . . . .	7

# 1 Introduction

## 1.1 Supramolecular Chemistry, why?

Supramolecular chemistry can be classified as the branch of chemistry concerned about the interplay between designed molecular assemblies and intermolecular bonds, or more colloquially referred to as "chemistry beyond the molecule".

The discipline focuses on the design and synthesis of molecular architectures by relying on the complementary recognition, and subsequent assembly, of well-defined subunits. The products of complementary synthesis, the so-called "supermolecules" are sustained by non-covalent interactions such as hydrogen bonding, halogen bonding, coordination forces and  $\pi - \pi$ .

The emergence of supramolecular chemistry has directly influenced how efficiently chemists can design and synthesize desired frameworks. The development and application of the bottom up approach is widely successful, owing to the non-covalent forces that dictate structural and morphological properties, while producing structures that were previously inaccessible.

### 1.1.1 Host-Guest Chemistry

In supramolecular chemistry, host-guest chemistry describes complexes that are composed of two or more molecules or ions that are held together in unique structural relationships by forces other than those of full covalent bonds. Host-guest chemistry encompasses the idea of molecular recognition and interactions through non-covalent bonding. Non-covalent bonding is critical in maintaining the 3D structure of large molecules, such as proteins and is involved in many biological processes in which large molecules bind specifically but transiently to one another.

Host-guest interaction has raised dramatic attention since it was discovered. It is an important field, because many biological processes require the host-guest interaction, and it can be useful in some material designs.

### 1.1.2 Metal-Organic Frameworks

Metal-Organic Frameworks represent an exciting and rapidly growing area of research within the field of supramolecular chemistry.

MOFs' chemistry is a specific type of supramolecular chemistry that involve the coordination of metal ions with organic ligands to form highly porous and crystalline materials with a unique structure. The metal ions act as nodes that are connected by the organic ligands to create a three-dimensional framework. The resulting structure has a large internal surface area and can adsorb gases and other molecules with high efficiency, making MOFs useful in a variety of applications, such as gas storage, catalysis, and drug delivery.

### 1.1.3 Carboxylate-Based Metal-Organic Frameworks

The divalent metal carboxylate based frameworks MOF-5 and HKUST-1 are examples of prototypical MOF materials and triggered a huge growth in the field of metal-organic frameworks.

## 2 Result and discussion

## 3 Experimental section

### 3.1 Dimethyl 4,4'-malonyldibenzoate

#### 3.1.1 Synthesis

In a flask, 1.132 g of NaH dispersion in mineral oil are washed with anhydrous THF (15 mL x 2). 4.0 g of methyl 4-acetyl benzoate and 4.4 g of dimethyl terephthalate are dissolved in 45 mL of anhydrous THF, and then NaH suspension in THF is added.

The mixture is heated to reflux overnight.

Evaporation of the solvent under vacuum gives a dark brown compound. The solid is taken up in water and acidified with HCl 20% in an ice bath. Taking care to leave it to react for a few hours and checking the pH to make sure it is acid. More water is added if mixing is particularly difficult. The raw product is recovered as a yellow solid by filtration with a Buchner funnel. To eliminate the impurities of the remaining reagents the solid is washed with chloroform and with diethyl ether. The solid is lastly collected on a Buchner funnel and dried. Yield: 92%.

#### 3.1.2 Characterization

NMR

IR

### 3.2 4,4'-(1H-pyrazole-3,5-diyl)dibenzoic acid Synthesis

#### 3.2.1 Synthesis

EtOH

A typical synthesis is described here: 500 mg of dimethyl 4,4'-malonyldibenzoate is suspended in 20 mL of EtOH in a 50 mL flask. The mixture is left in ultrasonic bath for 30'. 350  $\mu$ L of hydrazine monohydrate are slowly added to the mixture that is then heated to reflux overnight.

The compound is collected as a pale yellow solid on a teflon funnel. Yield: 25%.

DMF

500 mg of dimethyl 4,4'-malonyldibenzoate is suspended in 15 mL of DMF in a 50 mL flask. The mixture is left in ultrasonic bath for 30'. 350  $\mu$ L of hydrazine monohydrate are slowly added to the mixture that is then heated to 150°C overnight.

Evaporation of the solvent under vacuum gives a white ivory solid. The compound is then washed

adding 25 mL of ethanol and heat to reflux for 2 hours. Pure solid is collected on a Buchner funnel. Yield: 48%.

### DMSO

500 mg of dimethyl 4,4'-malonyldibenzoate is solubilized in 20 mL of DMSO in a 50 mL flask. The mixture is left in ultrasonic bath for 30'. 350  $\mu$ L of hydrazine monohydrate are slowly added to the mixture that is then heated to 150°C overnight.

### 3.2.2 Characterization

NMR

IR

## 3.3 4,4'-malonyldibenzonitrile Synthesis

### 3.3.1 Synthesis

### 3.3.2 Characterization

NMR

IR