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# **Engineering Flexible Metal-Organic Frameworks from Methylene-hinged Ligands**

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**A thesis submitted in fulfilment of the requirements for the**

**Degree**

**of**

**Doctor of Philosophy in Chemistry**

**in the**

**University of Adelaide**

**by**

**Witold M. Bloch**



**THE UNIVERSITY**  
*of* **ADELAIDE**

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**2013**



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## Acknowledgments

Firstly, I wish to sincerely thank my supervisor, A/Prof Christopher Sumby, who provided me with a great deal support and encouragement throughout this project. I also greatly appreciate his open door for help, and, what seemed to be, an unlimited time for discussing and interpreting research outcomes. I am grateful for experiencing research driven by curiosity, rather than ambitious goals; the lack of restrictions in this project has allowed me to develop a keen interest in areas which I would otherwise be unbeknown to. Without the guidance and support of A/Prof Christopher Sumby, this thesis would not be possible.

I would like to thank A/Prof Jonathan Morris for the helpful discussions on reagents and reaction mechanisms at the early stages of my project. I would also like to thank A/Prof Christian Doonan for his guidance and support, and for giving my later work much momentum. I would also like to express my gratitude to Dr Matthew Hill and Dr Ravichandar Babarao (CSIRO Melbourne) for their valued collaboration. I also thank Prof. Richard Keene for his continual support and encouragement.

I wish to thank Dr Antonio Avellaneda, who taught me various synthetic techniques during his time in our research group. The lab wouldn't be the same without Dr Alexandre Burgun, Dr Campbell Coghlan, Jesse Teo, Damien Rankine, and Dr Natasha Zaitseva, who have been great friends and have shared plenty of laughs with me over the past few years. Many thanks to everyone from Lab 5 – Dr Peter Valente, Jack Evans, Melanie Kitchin, Adrian Markwell-Heys, and Georgina Sylvia for their valued friendship. I would also like to extend my thanks to some of the previous members of our group – Dr Tony Keene, Dr Courtney Hollis, Dr Maisara Abdul-Kadir, Rachel Crees, and Stephanie Derwent-Smith. The friendship with these people has made my time truly memorable.

Lastly, but surely not the least, I wish to acknowledge the unconditional support, understanding, and love that my family has given me, especially over the past four years. I am endlessly grateful for them, and without their support, I would not be where I am.



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## Abbreviations

MOF	Metal-Organic Framework
<b>dpzm</b>	di-2-pyrazinylmethane
<b>dpm</b>	di-2-pyridylmethane
<b>dpym</b>	di-2-pyrazolylmethane
<b>bpy</b>	2,2'-bipyridine
<b>dcbpy</b>	2,2'-bipyridine-4,4'-dicarboxylic acid
<b>iBudcbpy</b>	bis(2-methylpropyl)-2,2'-bipyridine-4,4'-dicarboxylate
<b>dmb</b>	4,4'-dimethyl-2,2'-bipyridine
<b>pyrz</b>	pyrazine
<b>ppb</b>	[2,3- <i>a</i> :3',3'- <i>c</i> ]dipyridophenazine
<b>dpq</b>	2,3-di(2-pyridyl)quinoxaline
LDA	lithium diisopropylamide
EtOAc	ethyl acetate
DMF	<i>N,N</i> -dimethylformamide
DCM	dichloromethane
DMSO	dimethylsulfoxide
TFA	trifluoroacetic acid
THF	tetrahydrofuran
DSSC	Dye-Sensitised Solar Cells
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
PSM	post-synthetic modification
SC-SC	single-crystal to single-crystal
MH <sup>+</sup>	protonated molecular ion
NMR	Nuclear Magnetic Resonance
NOESY	Nuclear Overhauser effect spectroscopy
ROESY	Rotating frame nuclear Overhauser effect spectroscopy
TLC	Thin-layer Chromatography
UV	UltraViolet
IR	Infrared Spectroscopy
TGA	Thermal Gravimetric Analysis



## Abstract

This thesis focuses on the synthesis of functional materials composed of ligands that possess a methylene hinge – a flexible link between two coordinating groups – and the capacity to form a six-membered chelate ring with transition metals that moderates structural flexibility. A significant portion of this work characterises and explores the properties of a class of functional materials called metal-organic frameworks (MOFs). By utilising methylene-hinged ligands, MOFs are designed that contain intrinsic flexibility and consequently interesting guest exchange and gas adsorption properties.

The first methylene-hinged ligand described, di-2-pyrazinylmethane, exhibited an exceptionally rich coordination chemistry with silver(I). Appropriate conditions led to the crystallisation of three isostructural 3-D silver(I) MOFs with large 1-D channels. Although these materials lacked permanent porosity, they possessed the ability to undergo guest-induced structural contraction and expansion. This remarkable solid-state behaviour was related to the chemistry of the guest.

The theme of structural flexibility is continued in subsequent chapters which describe the structural flexibility and gas adsorption properties of several MOF materials composed of Cu(II), Co(II), Ni(II), or Mn(II) and the ligand bis(4-(4-carboxyphenyl)-1*H*-pyrazolyl)methane or bis(4-(4-carboxyphenyl)-3,5-dimethyl-1*H*-pyrazolyl)methane. Some of the work reported in chapter 3 that deserves particular attention is the exceptional CO<sub>2</sub>/N<sub>2</sub> selectivity of a Cu(II) MOF. This material undergoes post-synthetic structural contraction to achieve pore dimensions capable of discriminating between CO<sub>2</sub> and N<sub>2</sub> based on their respective kinetic diameters. Another noteworthy material is described in chapter 4; a flexible Mn(II) MOF capable of quantitative post-synthetic metal binding with preservation of single-crystallinity. The framework flexibility of this material allowed elucidation of the primary coordination sphere of the grafted metal ion and subsequent solid-state transformations by X-ray crystallography. A large portion of this thesis demonstrates and emphasises the positive impact of structural flexibility in MOFs as functional host materials.

Chapters 5 and 6 describe methylene-hinged compounds from the viewpoint of synthetic precursors to more complex ligands that contain a fused pyrazino[2,3-*b*]indolizine or indolizino[2,3-*b*]quinoxaline core. The synthesis, metal complexes, and corresponding solid-state structures of a series of these ligands are described.