



METAL-ORGANIC FRAMEWORKS AND COVALENT ORGANIC FRAMEWORKS AS SINGLE SITE CATALYSTS FOR ORGANIC TRANSFORMATIONS

Luis Gutiérrez Victoriano

ADVERTIMENT. L'accés als continguts d'aquesta tesi doctoral i la seva utilització ha de respectar els drets de la persona autora. Pot ser utilitzada per a consulta o estudi personal, així com en activitats o materials d'investigació i docència en els termes establerts a l'art. 32 del Text Refós de la Llei de Propietat Intel·lectual (RDL 1/1996). Per altres utilitzacions es requereix l'autorització prèvia i expressa de la persona autora. En qualsevol cas, en la utilització dels seus continguts caldrà indicar de forma clara el nom i cognoms de la persona autora i el títol de la tesi doctoral. No s'autoritza la seva reproducció o altres formes d'explotació efectuades amb finalitats de lucre ni la seva comunicació pública des d'un lloc aliè al servei TDX. Tampoc s'autoritza la presentació del seu contingut en una finestra o marc aliè a TDX (framing). Aquesta reserva de drets afecta tant als continguts de la tesi com als seus resums i índexs.

ADVERTENCIA. El acceso a los contenidos de esta tesis doctoral y su utilización debe respetar los derechos de la persona autora. Puede ser utilizada para consulta o estudio personal, así como en actividades o materiales de investigación y docencia en los términos establecidos en el art. 32 del Texto Refundido de la Ley de Propiedad Intelectual (RDL 1/1996). Para otros usos se requiere la autorización previa y expresa de la persona autora. En cualquier caso, en la utilización de sus contenidos se deberá indicar de forma clara el nombre y apellidos de la persona autora y el título de la tesis doctoral. No se autoriza su reproducción u otras formas de explotación efectuadas con fines lucrativos ni su comunicación pública desde un sitio ajeno al servicio TDR. Tampoco se autoriza la presentación de su contenido en una ventana o marco ajeno a TDR (framing). Esta reserva de derechos afecta tanto al contenido de la tesis como a sus resúmenes e índices.

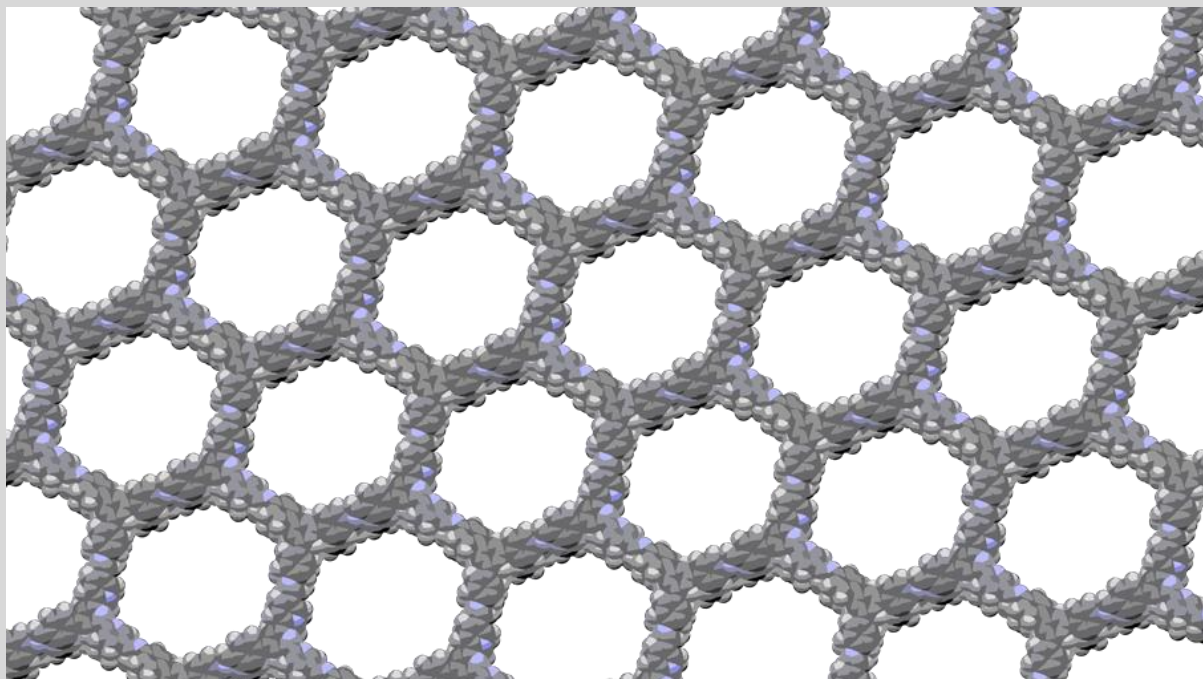
WARNING. Access to the contents of this doctoral thesis and its use must respect the rights of the author. It can be used for reference or private study, as well as research and learning activities or materials in the terms established by the 32nd article of the Spanish Consolidated Copyright Act (RDL 1/1996). Express and previous authorization of the author is required for any other uses. In any case, when using its content, full name of the author and title of the thesis must be clearly indicated. Reproduction or other forms of for profit use or public communication from outside TDX service is not allowed. Presentation of its content in a window or frame external to TDX (framing) is not authorized either. These rights affect both the content of the thesis and its abstracts and indexes.



UNIVERSITAT
ROVIRA I VIRGILI

Metal-Organic Frameworks and Covalent Organic Frameworks as single-site catalysts for organic transformations

Luis Gutiérrez Victoriano



**DOCTORAL THESIS
2022**

UNIVERSITAT ROVIRA I VIRGILI
METAL-ORGANIC FRAMEWORKS AND COVALENT ORGANIC FRAMEWORKS AS SINGLE SITE CATALYSTS
FOR ORGANIC TRANSFORMATIONS
Luis Gutiérrez Victoriano

UNIVERSITAT ROVIRA I VIRGILI
METAL-ORGANIC FRAMEWORKS AND COVALENT ORGANIC FRAMEWORKS AS SINGLE SITE CATALYSTS
FOR ORGANIC TRANSFORMATIONS
Luis Gutiérrez Victoriano

UNIVERSITAT ROVIRA I VIRGILI
METAL-ORGANIC FRAMEWORKS AND COVALENT ORGANIC FRAMEWORKS AS SINGLE SITE CATALYSTS
FOR ORGANIC TRANSFORMATIONS
Luis Gutiérrez Victoriano

Luis Gutiérrez Victoriano

Metal-Organic Frameworks and Covalent Organic Frameworks as single-site catalysts for organic transformations

Doctoral thesis

Supervised by Prof. Dr. Julio Lloret Fillol



UNIVERSITAT ROVIRA I VIRGILI



Tarragona, Spain

2022

UNIVERSITAT ROVIRA I VIRGILI
METAL-ORGANIC FRAMEWORKS AND COVALENT ORGANIC FRAMEWORKS AS SINGLE SITE CATALYSTS
FOR ORGANIC TRANSFORMATIONS
Luis Gutiérrez Victoriano

Prof. Dr. Julio Lloret Fillol, Group Leader of the Institut Català d'Investigació Química (ICIQ) and Research Professor of Institució Catalana de Recerca i Estudis Avançants (ICREA).

DECLARES that the present study entitled “Metal-Organic Frameworks and Covalent Organic Frameworks as single-site catalysts”, presented by Luis Gutiérrez Victoriano to receive the PhD degree in Chemistry, has been carried out under his supervision, in the Institut Català d'Investigació Química (ICIQ).

Tarragona, 1st November 2022

PhD Thesis Supervisor



Prof. Dr. Julio Lloret-Fillol

UNIVERSITAT ROVIRA I VIRGILI
METAL-ORGANIC FRAMEWORKS AND COVALENT ORGANIC FRAMEWORKS AS SINGLE SITE CATALYSTS
FOR ORGANIC TRANSFORMATIONS
Luis Gutiérrez Victoriano

Aknowledgments

First of all, I want to thank my supervisor Julio Lloret for inviting me to the research group and giving me the opportunity to learn a great deal of chemistry. Thank you very much.

I want to thank all the people that I have collaborated together in projects: Suvendu, Noufal, Felix, Alberto, Eduardo, Carla, Vlad and Manuel. Thanks to all the people in the lab for making a nice environment to be in and for helping me any time: Sergi, Miguel, Geyla, David, Fede, Gonell, Suyun, Jing, Liu, Ahmed and Lorenzo. Special thanks to Jordi for keeping me entertained with nerdy conversations.

Many thanks to my group of friends here in Tarragona: Ansgar, Laura, Ilario, Sofía, Alejandro and Iria. Thank you very much for all the good times and the many boardgame rounds. Special thanks to Laura for revising my thesis. Thanks to Alberto for keeping in touch through all these years.

Thanks to my family for supporting and believing in me.

UNIVERSITAT ROVIRA I VIRGILI
METAL-ORGANIC FRAMEWORKS AND COVALENT ORGANIC FRAMEWORKS AS SINGLE SITE CATALYSTS
FOR ORGANIC TRANSFORMATIONS
Luis Gutiérrez Victoriano

Financial Support

The present doctoral thesis has been made possible thanks to funding received from the ERC project (648304 — GREENLIGHT_REDCAT).



UNIVERSITAT ROVIRA I VIRGILI
METAL-ORGANIC FRAMEWORKS AND COVALENT ORGANIC FRAMEWORKS AS SINGLE SITE CATALYSTS
FOR ORGANIC TRANSFORMATIONS
Luis Gutiérrez Victoriano

LIST OF PUBLICATIONS

Luis Gutiérrez, Suwendu Sekhar Mondal, Alberto Bucci, Noufal Kandoth, Eduardo C. Escudero-Adán, Alexandr Shafir, and Julio Lloret-Fillol. “Crystal-to-Crystal Synthesis of Photocatalytic Metal– Organic Frameworks for Visible-Light Reductive Coupling and Mechanistic Investigations”, *ChemSusChem*. **2020**, 13, 1-12.
(10.1002/cssc.202000465).

UNIVERSITAT ROVIRA I VIRGILI
METAL-ORGANIC FRAMEWORKS AND COVALENT ORGANIC FRAMEWORKS AS SINGLE SITE CATALYSTS
FOR ORGANIC TRANSFORMATIONS
Luis Gutiérrez Victoriano

PREFACE

The work presented in this dissertation has been performed at the Institute of Chemical Research of Catalonia (ICIQ), during the period from October 2018 until December 2022 under the supervision of Professor Julio Lloret-Fillol. The thesis is divided into seven sections: a general introduction, the objectives of the thesis, four research chapters and a chapter in which the overall conclusions of the work are presented. Each of the research chapters includes a brief introduction on the topic, followed by the collected results and their discussion, the main conclusions, and finally a detailed experimental section. References and their numbering are independently organized by chapters.

UNIVERSITAT ROVIRA I VIRGILI
METAL-ORGANIC FRAMEWORKS AND COVALENT ORGANIC FRAMEWORKS AS SINGLE SITE CATALYSTS
FOR ORGANIC TRANSFORMATIONS
Luis Gutiérrez Victoriano

TABLE OF CONTENTS

Abstract	5
List of abbreviations.....	6
Chapter I: General Introduction	
1.1. Reticular chemistry	13
1.2. Metal-organic frameworks	15
1.2.1. Historical overview	16
1.2.2. Synthesis of MOFs	18
1.3. Covalent organic frameworks.....	20
1.3.1. Synthesis of COFs	21
1.4. MOFs and COFs as single-site heterogeneous catalysts	23
1.4.1. MOF catalysts	24
1.4.2. COF catalysts	28
1.2. Bibliography	35
Chapter II: Thesis Objectives.....	47
Chapter III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations	
3.1. General insight.....	51
3.2. Results and Discussion	56
3.2.1. Crystal-to-crystal modification of MOF-520.....	56
3.2.2. Characterization of bulk MOF-520-PCs.....	62
3.2.3. Pinacol coupling promoted by MOF-520-PCs	67
3.2.4. Substrate scope of aldehydes, ketones and imines ...	71
3.2.5. Catalyst recycling in batch.....	74
3.2.6. Photocatalysis in flow	75

3.2.7. Photophysical and electrochemical characterization.	78
3.2.8. Mechanistic studies.....	84
3.3. Conclusions	91
3.4. Experimental section	92
3.4.1. Materials and methods.....	92
3.4.2. Synthetic procedures.....	99
3.4.3. Catalytic experiments	104
3.5. Bibliography	126

Chapter IV: Development of imine Metal Covalent Organic Frameworks based on N-donor ligands

4.1. General insight.....	137
4.2. Results and Discussion	141
4.2.1. Synthesis and characterization of bipyridine COFs	141
4.2.2. Synthesis and characterization of terpyridine COFs	152
4.2.3. Synthesis and characterization of N,N-bispyridine-cyclohexyldiamine polymer.....	160
4.3. Conclusions	166
4.4. Experimental section	167
4.4.1. Materials and methods.....	167
4.4.2. Synthesis procedures	170
4.4.3. PXRD of tables 4.1 and 4.2	181
4.2. Bibliography	183

Chapter V: Low Oxidation State Cobalt Center Stabilized by a Covalent Organic Framework to promote Hydroboration of Olefins

5.1. General insight.....	193
5.2. Results and Discussion	201
5.2.1. Hydroboration catalysis with cobalt bipyridine COFs 201	
5.2.2. Alkene substrate scope	209
5.2.3. Catalyst recyclability	211
5.2.4. Study of the COF-BPY-1-Co reduced species	212
5.2.5. Mechanistic studies.....	219
5.2.6. Computational studies	222
5.2.7. Modification of the reactivity by a second ligand coordination.	225
5.2. Conclusions	232
5.3. Experimental section	233
5.3.1. Materials and methods.....	233
5.3.2. Synthetic procedures.....	236
5.3.3. Catalytic experiments	237
5.3.4. Computational details	249
5.4. Bibliography	250

Chapter VI: Terpyridine Covalent Organic Frameworks as efficient C-H borylation catalysts

6.1. General insight.....	265
6.2. Results and Discussion	272
6.2.1. Arylic and benzylic C-H borylation catalyzed by TPY-COFs	272
6.2.2. Arene substrate scope	276
6.2.3. Catalyst recycling	277

6.2.4. Study of the COF-BPY-1-Co reduced species and mechanistic studies	279
6.3. Conclusions	281
6.4. Experimental section	282
6.4.1. Materials and methods	282
6.4.1. Catalytic experiments	283
6.5. Bibliography	292
Chapter VII: General Conclusions.....	299

Abstract

Metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) are new porous materials that have attracted great attention due to their unique properties: high porosity, good chemical stability, well-ordered structures and remarkable structural tunability. Among their many possible applications, catalysis is one of the most promising due to the potential of MOFs and COFs to form single-site catalysts that are well-defined and remain accessible in the solid state. In this line of research, the current thesis aims to develop and study new MOF and COF-based catalysts for organic transformations.

The work presented in this thesis shows a simple method to immobilize photocatalytically active perylene ligands inside MOF-520, allowing this way to study the ligands as isolated units, and to employ the MOFs as heterogeneous photocatalysts for the reductive coupling of C=O and C=N bonds.

This thesis also describes the synthesis and characterization of a series of COFs bearing N-donor ligands in their structure. Incorporating cobalt centres into these structures resulted in MCOFs active as hydroboration and borylation catalysts. Finally, studies were performed to explore the single-site nature of the catalytic centers.

This work showcases the potential of MOFs and COFs as efficient and recyclable heterogeneous catalysts for organic transformations, and paves the way for the development of new single-site catalytic systems.

LIST OF ABBREVIATIONS

In this doctoral thesis, the abbreviations and acronyms most commonly used in organic chemistry are based on the recommendations of the ACS “Guidelines for authors” which can be found at https://pubs.acs.org/userimages/ContentEditor/1218717864819/joceah_abbreviations.pdf

General Abbreviations

2D	2 dimensional
3D	3 dimensional
[]	Concentration
Å	angstrom
abs	absorbance
Ac	acetyl
AcOH	acetic acid
Ac ₂ O	acetic anhydride
Anal.	combustion elemental analysis
anhyd	anhydrous
aq	aqueous
Ar	aryl
atm	atmosphere
A. U	arbitrary units
B3LYP	3-parameter hybrid Becke exchange/ Lee–Yang–Parr correlation functional
BET	Brunauer-Emmett-Teller (absorption isotherm)
Bipy	2,2'-bipyridine or 2,2'-bipyridyl
Bn	benzyl
Boc	<i>tert</i> -butoxycarbonyl
bp	boiling point
Bpin	pinacolborane
bpy	2,2'-bipyridine or 2,2'-bipyridyl
Bu	butyl

BuLi	butyl lithium (also <i>n</i> -BuLi)
°C	degrees Celsius
calcd	calculated (for MS analysis)
cat	catalytic
cc	cubic centimeters
COF	covalent organic framework
CI	chemical ionization
CIF	crystallographic information file
cm	centimeter
cm ⁻¹	wavenumbers(s)
¹³ C NMR	carbon NMR
cod	1,5-cyclooctadiene
Cp	cyclopentadienyl
CP/MAS	cross-polarization/magic angle spinning (NMR)
cryst	crystalline
CV	cyclic voltammetry
δ	chemical shift (ppm) downfield from TMS
d	days; doublet (spectral)
<i>d</i>	density
DCM	CH ₂ Cl ₂
DFT	density functional theory
DIPEA	<i>N,N</i> -diisopropylethylamine
DMA	dimethylacetamide
DMF	dimethylformamide
DMSO	dimethylsulfoxide
ε	molar absorptivity
E _{1/2}	electrochemical potential
ee	enantiomeric excess
EPR	electron paramagnetic resonance
eq or equiv	equivalent
ESI	electrospray ionization
Et	ethyl
et al.	and others (co-authors)

EtOH	ethanol
EXAFS	extended X-ray absorption fine structure
FT	Fourier transform
Fc	ferrocene
g	gram(s); gas
GC	gas chromatography
h	hours(s)
¹ H NMR	proton NMR
HPLC	high-performance liquid chromatography
HRMS	high-resolution mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectroscopy
IR	infrared
J	Joule
<i>J</i>	coupling constant in NMR
k	kilo
K	Kelvin
<i>K</i>	equilibrium constant
L	liter; ligand
λ_{max}	max UV-vis wavelength
m	meter; milli; multiplet (spectral)
M	molar (moles per liter)
M ⁺	parent molecular ion (in MS)
μ	micro
max	maximum
MCOF	metal covalent organic framework
MCP	dimethyl- bis(pyridinylmethyl)cyclohexane-1,2-diamine
Me	methyl
MeCN	acetonitrile
MeOH	Methanol
MHz	megahertz
min	minute(s); minimum
mL	milliliter
mm	millimeter

mM	millimolar (moles per liter)
mmol	millimole(s)
MOF	metal-organic framework
mp	melting point
MS	mass spectrometry; molecular sieves
M_w	weight average molecular weight
m/z	mass to charge ratio (in MS)
<i>n</i> -Bu	normal butyl (primary)
NBS	<i>N</i> -bromosuccinimide
NMP	<i>N</i> -methyl-2-pyrrolidinone
PC	photocatalyst
pH	proton log units
Ph	phenyl
ppm	part per million
Pr	propyl
PSM	post-synthetic modification
PTSA	<i>p</i> -toluenesulfonic acid
PXRD	powder x-ray diffraction
q	quartet (spectral)
quin	quintet (spectral)
<i>R</i>	gas constant
R	alkyl group
redox	reduction-oxidation
rt	room temperature
s	seconds; singlet (spectral); solid
SALI	solvent-assisted ligand incorporation
SBU	secondary building unit
<i>s</i> -Bu	<i>sec</i> -butyl
SEM	scanning electron microscope
SET	single electron transfer
sext	sextet (spectral)
τ	lifetime
t	triplet (spectral)

<i>t</i>	time or temp in °C
<i>T</i>	temperature in kelvin
TAS	transient absorption spectroscopy
<i>t</i> -Bu	<i>tert</i> -butyl
TBS	<i>tert</i> -butyldimethylsilyl
Tf	trifluoromethanesulfonyl
TFA	trifluoroacetic acid
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TMS	trimethylsilyl
Tol	toluene
TOF	turnover frequency
TON	turnover number
TPY	2,2':6',2''-terpyridine
UV-vis	ultraviolet-visible absorption spectroscopy
vol	volume
vs.	versus
v/v	volume to volume ratio
wt	weight
XPS	x-ray photoelectron spectroscopy
XRD	x-ray diffraction

Chapter I:

General Introduction

CHAPTER 1: General introduction

1.1. Reticular chemistry

Reticular chemistry is related to forming porous crystalline 2D and 3D frameworks such as metal-organic (MOFs) and covalent organic (COFs) by linking molecular building blocks by strong bonds.^{1,2} These structures were unknown and challenging due to the need to employ strong directional bonds to crystallise porous frameworks. However, the challenge was overcome by combining organic and inorganic synthesis concepts. Covalent bonding, typically employed in organic synthesis, facilitates complex molecules and polymers. However, the usual lack of microscopic reversibility makes the crystallisation of extended 2D and 3D lattices challenging. For this reason, organic synthesis was mainly restricted to 1D polymeric structures before the advent of reticular chemistry.^{3,4} On the other hand, inorganic synthesis facilitates the formation of highly symmetric extended structures from simple precursors in a single step. This reactivity favours the formation of dense crystals at the expense of complicating structures' rational design.

The development of the first MOFs (Figure 1.1) was enabled by combining aspects of organic and inorganic synthesis.^{5,6} In these first examples, the crystallisation of the material was achieved through the bond formation of the constituent inorganic secondary building units (SBUs). At the same time, the organic terephthalate linkers provided rigidity and opened up the structure, leading to materials with permanent porosity. The key to creating permanently porous frameworks with surface areas superior to previous materials was the linkage through strong (charged metal-carboxylate) and directional (bridging carboxylate binding mode) bonds.

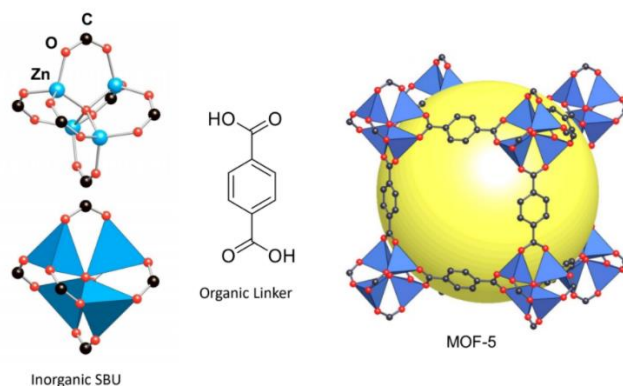


Figure 1.1. Structure of MOF-5. Reproduced with permission.⁷ Copyright 2004, Elsevier.

On the other hand, COFs are reticular materials formed entirely by organic building blocks connected through covalent bonds. The first synthesis of a COF (Figure 1.2) was achieved in 2005 by employing boronic esters as linkages between organic linkers.⁸ The reaction conditions allowed for the microscopic reversibility of covalent bond formation, enabling the crystallisation of a framework, while the rigid linkers led to the formation of open cavities with high surface areas.

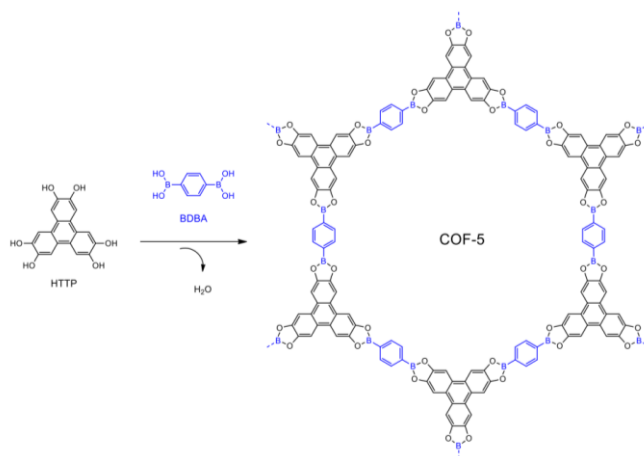


Figure 1.2. Structure of COF-5. Reproduced with permission.⁹ Copyright 2021, Elsevier.

The process of designing a reticular material begins with identifying a target structure, which is deconstructed into geometric units to determine the topology and identify the shape and connectivity of the components. Reticulation involves assembling these units through strong bonds, forming the desired crystalline structure.¹⁰ The structure can be optimised according to the isorecticular principle² and extra functionality can be introduced by post-synthetic modification.¹¹ Control over the structure in reticular materials can also be extended to the nanoscale (nanocrystals or films).¹²

1.2. Metal-organic frameworks

Metal-Organic Frameworks (MOFs) are two or three-dimensional porous crystalline materials formed by coordination bonds between metal cation salts or clusters and multidentate organic ligands (Figure 1.3).^{1,13} The large number of possible combinations of organic and inorganic building blocks that can be used to form MOFs means that there is a huge number of possible unique structures. Indeed, since their discovery in 1998, more than 20000 different MOFs have been synthesised and characterised.¹⁴ MOFs have been employed in a variety of fields such as gas storage, separation, sensors, biomedicine, and, of particular interest to this work, catalysis.^{13,15–}

18

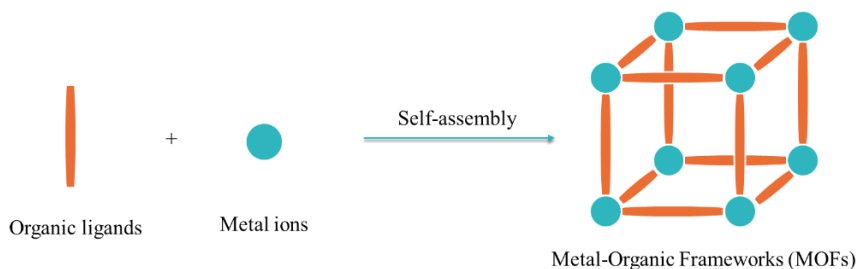


Figure 1.3. Schematic structure of a MOF.

One of the remarkable features of MOFs is their high porosity, presenting exceptional surface area values and very low density. These properties are

fundamental for gas storage applications but are also very important for other applications such as separation, sensors and catalysis. In addition, high porosity facilitates the diffusion of chemicals through the material and improves the accessibility of functional sites in the framework.

Compared to Zeolites, MOFs present more versatility and flexibility in their design. The framework topology, as well as the pore size, can be adjusted by the selection of organic linkers and metal nodes. This facilitates the tuning of host-guest interactions in the cavities of MOFs. The presence of well-defined functionalities can be employed to enhance properties like chemisorption, conductivity, chirality, stability, etc.^{19,20}

The strong bonds in MOFs endow the materials with high thermal stability, typically ranging from 250° to 500°C. However, chemical stability is harder to achieve due to the tendency of some MOFs to undergo link-displacement reactions when submerged in solvents over long periods or when treated with harsh chemicals. These limitations have been overcome by some MOFs, like the UiO-66 MOFs based on Zr(IV) cuboctahedral SBUs, which display good stability to acid or basic conditions.²¹

1.2.1. Historical overview

The origin of the modern field of synthetic metal-organic chemistry comes from coordination polymers.²² According to the IUPAC definitions, coordination polymers are ‘coordination compounds with repeating coordination entities extending in 1, 2, or 3 dimensions’, while MOFs are ‘coordination networks with organic ligands containing potential voids’. The first example of a coordination polymer was Prussian Blue, a blue pigment formed by cyanide and iron ions ($(\text{Fe}^{3+})_4 [\text{Fe}^{2+}(\text{CN})_6]_3 \cdot \text{H}_2\text{O}$) that was discovered at the beginning of the eighteenth century by Diesbach. Another early example of coordination polymer is the Hoffman clathrates,

first reported by Karl A. Hoffman in 1897.²³ The original Hofmann clathrate consists of 2D layers of alternating octahedral and square planar Ni^{2+} ions linked by CN^- ions. The layers are separated by benzene molecules, which act as a template. And consequently, the removal of benzene leads to a structural collapse of the clathrate. Although the field of coordination polymers progressed over the years, the occurrence of structural collapse after the evacuation of the pore content prevented the formation of materials with permanent microporosity until the 1990s.

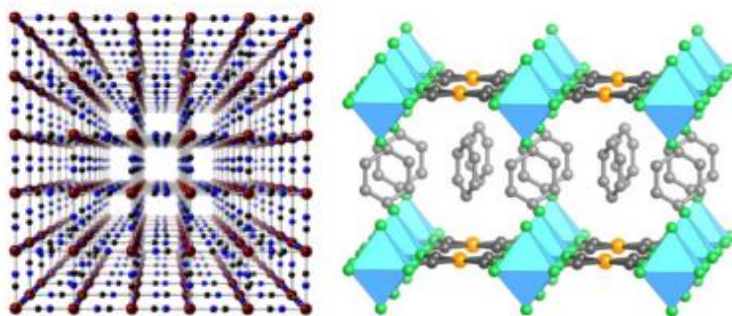


Figure 1.4. Structure of Prussian blue (left), the structure of Hofmann clathrate (right). Color code (right): Ni, blue and orange spheres; C, gray; N, green; benzene guest, light gray. Reproduced with permission.²² Copyright 2019, Wiley.

Two main features were necessary to establish permanent porosity in these materials: first, rigidity and directionality of the framework's constituents, and second, increased bond strength between them. During the 1990s there was great progress in this direction, culminating in the first MOF being reported by Yhagi in 1998 (Figure 1.5).⁵ The most significant difference between this new material and previous coordination polymers is the replacement of single metal ions by polynuclear clusters, referred to as secondary building units (SBU). The SBUs offered several advantages toward realising more robust structures: the chelation of metal ions to make polynuclear clusters provided rigidity and directionality, while the charge on the linker led to increased bond strength and the formation of neutral

frameworks. The increase in rigidity allowed the removal of the solvent molecules in the pores without causing structural collapse, which led to a material with high and permanent porosity. The proof of permanent porosity in Yhagi's MOF signalled a turning point in the chemistry of extended metal-organic solids and led to the use of the term MOF to emphasise their distinct stability and porosity.

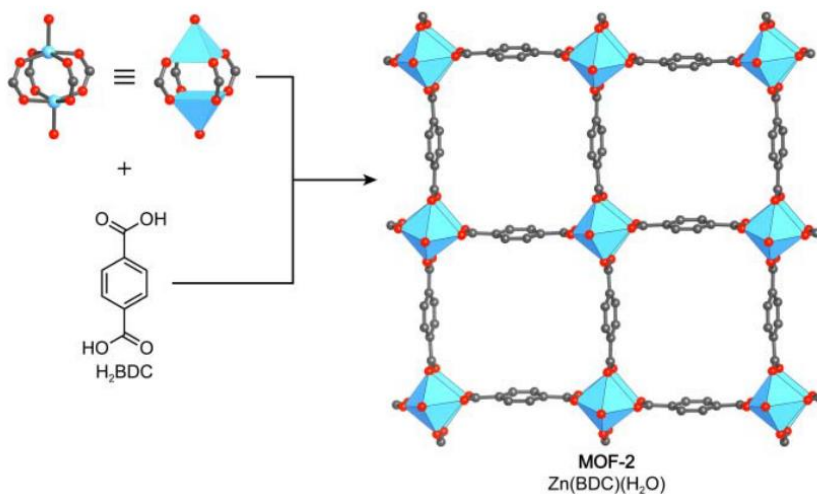


Figure 1.5. Crystal structure of MOF-2. Color code: Zn, blue; C, gray; N, green; O, red. Reproduced with permission.²² Copyright 2019, Wiley.

1.2.2. Synthesis of MOFs

MOFs are formed by combining a metal salt with an organic linker. Rigid molecules bearing carboxylic acid groups (Figure 1.6) are usually employed as linkers, although nitrogen-donor organic linkers such as pyridine andazole derivatives can also be employed.²⁴ Traditionally, MOFs are prepared by solvothermal synthesis, inspired by the conditions employed in synthesising zeolites. Solvothermal synthesis employs a closed vessel under heating above the boiling point of the solvent. However, other methods have also been developed for the synthesis of MOFs, including slow diffusion, mechanochemical and microwave synthesis.¹³

Most MOF synthesis procedures involve dissolving metal precursors, such as metal nitrates or chlorides, and organic linkers in an organic solvent. Polar aprotic solvents like DMF or DMA are very popular in MOF synthesis, but mixtures with alcohol or water can also be used. Optimisation of the synthesis variables (molar ratio of reactants, solvent, pH, concentration, type of reaction container, reaction time and temperature) is crucial. For this reason, high-throughput methods are used more frequently to screen synthesis conditions faster and more efficiently.

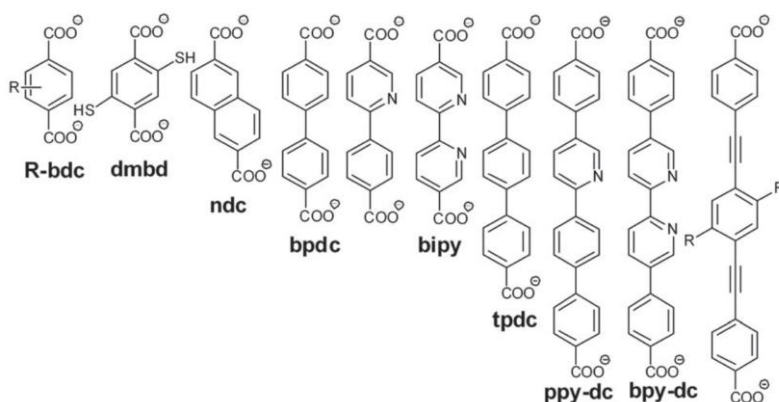


Figure 1.6. Examples of ditopic carboxylate linkers employed in the synthesis of UiO-MOFs. Reproduced with permission. ²⁴ Copyright 2014, Royal Society of Chemistry.

Additives play a crucial role in the synthesis of MOFs. They can be used to improve the crystallinity and porosity by controlling the reaction kinetics and the growth of the material. Carboxylic acid additives like benzoic acid, acetic acid or formic acid are usually employed as capping agents, which slow down the rate of nucleation and crystal growth rate by coordinating with the metal centres.²⁵

After synthesis, the pores of a MOF will be filled with guest molecules: solvents and starting materials. MOF are typically washed to remove the starting materials or to exchange high boiling point solvents like DMF with more volatile solvents. Volatile guest molecules can be easily removed by

heating under vacuum; however, in some cases, this leads to the collapse of the pores. Solvent removal with supercritical CO₂ presents a gentler alternative that usually results in a higher surface area of the MOF.²⁶

1.3. Covalent organic frameworks

Covalent organic frameworks (COFs) are crystalline and porous organic polymers constructed from light elements (C, N, H, O and B). These materials enable the integration of organic building blocks into well-defined structures, offering a platform for the design of periodically ordered organic structures. The choice of monomers and linkages determines the structure of the framework; thus, COFs are, in theory, fully predesignate and controllable.^{27–30}

The covalent bonds in COFs can grow in two or three dimensions (2D or 3D COFs). Most of the reported COF structures present 2D frameworks composed of layers stacked through non-covalent π – π interactions that lead to staggered or eclipsed stacking conformations. 2D COFs usually require planar and rigid linkers to restrict the growth of covalent bonds to a plane and facilitate the stacking of layers. 3D COFs are less common due to the difficulty synthesising building blocks with 3D symmetries. Additionally, it is challenging to control the interpenetration of structures in 3D COFs.²⁹

One of the most exciting properties of COFs is their porosity. COFs present very high surface area values and low density, similar to MOFs. However, the pore structure in 2D COFs is unique compared to other porous materials. 2D COFs present 1D channels perpendicular to the layers. These channels are entirely separated from each other due to the short interlayer distance, leading to independent channels free of interpenetration. The walls of these channels can support a high density of active sites that remain accessible to molecules diffusing through the pores.

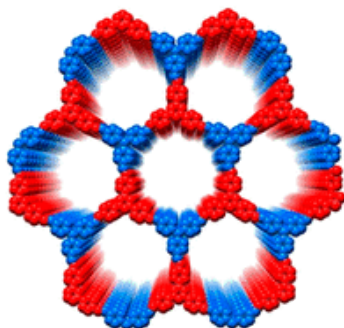


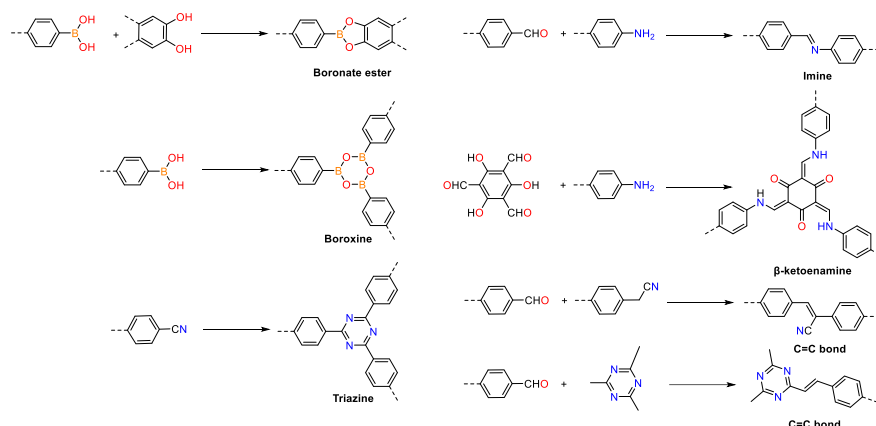
Figure 1.7. Typical structure of 1D channels present in COFs. Reproduced with permission.²⁸ Copyright 2020, Royal Society of Chemistry.

1.3.1. Synthesis of COFs

The synthesis of COFs, first described by Yaghi in 2005,⁸ relies on reversible covalent bonds to connect organic linkers. Reversibility of the bond formation under thermodynamic control allows error correction to afford the thermodynamically most stable product under certain reaction conditions. Employing this strategy, crystalline COFs can be obtained after self-healing and error-checking.

Most COFs are synthesised under solvothermal conditions, relying on high temperatures to achieve thermodynamic control over the reaction. Many reaction parameters like temperature, concentration, catalyst and reaction time will influence the crystallisation process of COFs.²⁹ The choice of solvent or solvent mixture plays a key role in this process as it determines the solubility of the monomers, and solvents can have a templating effect that improves COF crystallinity.³¹ Other methods for COF synthesis have been developed, including microwave and mechanochemical synthesis,^{32,33} and some catalysts or additives have been employed to develop room-temperature synthesis methods.^{34–36}

COFs are formed by connecting one or more types of building blocks in an organised manner through linkages. Several linkages have been employed in the design and synthesis of COFs. The most common ones are represented in Scheme 1.1.



Scheme 1.1. Common COF linkages

The linkages originally employed in COF synthesis, boroxine and boronate ester, are formed by self-condensation of boronic acids or by condensation of boronic acids and catechol derivatives. This type of linkage allows for the formation of highly crystalline COFs thanks to the high reversibility of the reaction. However, the high reversibility of the bonds also leads to lower chemical stability. Indeed, this type of COF is easily hydrolysed under humid or protic conditions.³⁷

Another type of linkage involves the formation of a triazine ring by cyclotrimerisation of nitrile groups. This has been used to form highly stable COFs, although the reported harsh conditions usually prevent the formation of crystalline and porous materials.³⁸

Imine COFs, formed by condensation between aromatic aldehydes and amines in the presence of an acid catalyst, represent the most widely used type of linkage. Their popularity can be attributed to a combination of high

crystallinity with good thermal and chemical stability.³⁹ Banerjee and co-workers improved even further the stability of imine COFs by employing 1,3,5-triformylphloroglucinol as aldehyde in the condensation reaction.⁴⁰ The resulting imine underwent irreversible proton tautomerism, resulting in the keto-enamine form. This form showed excellent stability in acidic and basic conditions.

More recently, there has been an increased interest in developing C=C linked fully π -conjugated COFs.^{41–44} This has been achieved via the Knoevenagel condensation of aldehydes and cyanides, or the reversible aldol condensation of aldehydes and s-triazine derivatives. The robust skeleton and the π -extended conjugation in olefin-linked COFs confer excellent thermal and chemical stability.

1.4. MOFs and COFs as single-site heterogeneous catalysts

Catalysis is one of the most predominant fields in chemistry. Developing new catalysts with improved efficiency, selectivity and stability is important in academia and industry to reduce costs, minimise waste and save energy. Given the importance of finding new catalysts, and especially solid ones, it is no surprise that heterogeneous catalysis was one of the earliest demonstrated applications of MOFs and COFs.^{16,18,45–55}

The characteristics of a MOF or COF-based catalyst can be considered as a mixture of homogeneous and heterogeneous catalysts. When looking at their structure, these materials present similar features to homogeneous catalysts but with the catalytic sites as isolated units in the framework. These catalytic sites are dispersed uniformly through the material thanks to the periodicity of the frameworks, and they are easily accessible by substrates and products due to their high porosity. On the other hand, being solid materials, MOFs/COFs have advantages similar to other

heterogeneous catalysts, such as recyclability, stability and robustness. Compared to traditional porous catalysts, such as zeolites, silica or activated carbon, MOFs/COFs present more diversified structures with pores of regular and tunable size.^{3,13,51,56}

Most MOF/COF catalysts can be considered single-site heterogeneous catalysts. These catalysts present isolated catalytic centres dispersed onto material support, possessing well-defined active sites at a nanoscale or sub-nanoscale.⁴⁵ The well-defined nature of the single-site catalytic centers and of the structure of the material is an important factor, since it facilitates the understanding of underlying mechanisms and makes it possible to establish relations between structure and catalytic performance. Another important factor is the isolated nature of the catalytic centers in MOF/COFs; the mechanical constraint imposed by the framework separates the catalytic centers from each other, preventing potentially undesirable interactions. In homogeneous catalysts, intermolecular interactions between metallic catalytic centers can form inactive species by processes like dimerisation, disproportionation or aggregation. Indeed, highly reactive metal complexes often require bulky ligands to protect the metal centers, but this steric protection can also become an unfavorable steric hindrance with the substrates, hampering their reactivity. Thus, single-site catalysts like MOFs and COFs offer a unique opportunity to stabilise reactive catalytic sites and to study them in detail.^{16,45,46}

In the following sections, some relevant examples of MOF and COF catalysts from the literature will be shown.^{47,51}

1.4.1. MOF catalysts

The strategies for creating MOFs with catalytic activity can be divided into three groups: 1) developing MOFs with intrinsic catalytic sites at their metal

nodes, 2) developing MOFs with intrinsic catalytic sites at their organic linkers, 3) introducing catalytic sites into MOFs through post-synthetic modification.

For catalysts in the first category, MOFs present metal ions in the SBU that are coordinated by organic linkers and terminal ligands like water or solvents. Solvents can be removed by heat or vacuum, forming open metal sites which can be used as catalytic sites. Figueroa, Cohen and co-workers reported an important example of this type of catalyst.⁵⁷ They developed a Mn MOF with open metal sites capable of catalysing the amination of activated C(sp³)-H bonds using a nitrene precursor, achieving TONs (up to 10⁵) and TOFs (above 10⁴/h) superior to benchmark homogeneous catalysts (Figure 1.8). The performance of the MOF catalyst is attributed to the site-isolation of the active sites, which prevents self-deactivation.

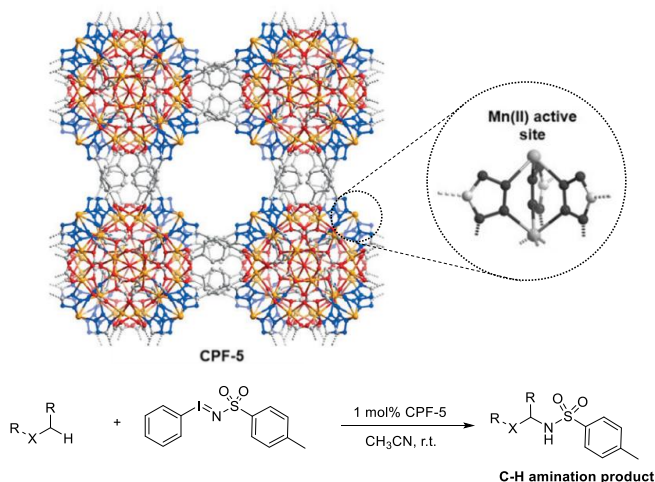


Figure 1.8. Structure of CPF-5 MOF with Mn (II) open sites (top). C-H amination catalysed by CPF-5. Reproduced with permission.⁵⁷ Copyright 2018, Wiley.

For the second category, synthesising MOFs with catalytically active linkers provides an opportunity to immobilise molecular catalysts. The immobilisation process can sometimes lead to the formation of catalysts

with selectivity different from homogeneous catalysts. This was observed by Ranocchiari and co-workers, who described a complete change in the selectivity of an organocatalyst when it is immobilised in a MOF.⁵⁸ The authors employed a MOF with amino groups in its organic linker as a co-catalyst on the Morita–Baylis–Hillman reaction. The MOF produced a drastic change in the reactivity, leading to an unexpected aldol-Tischenko product, while the same organic linker in solution did not affect the reactivity significantly (Figure 1.9). Mechanistic investigations revealed that the confinement of a reaction intermediate in the cavities of the material through noncovalent interactions was the cause of the change in selectivity when employing the MOF.

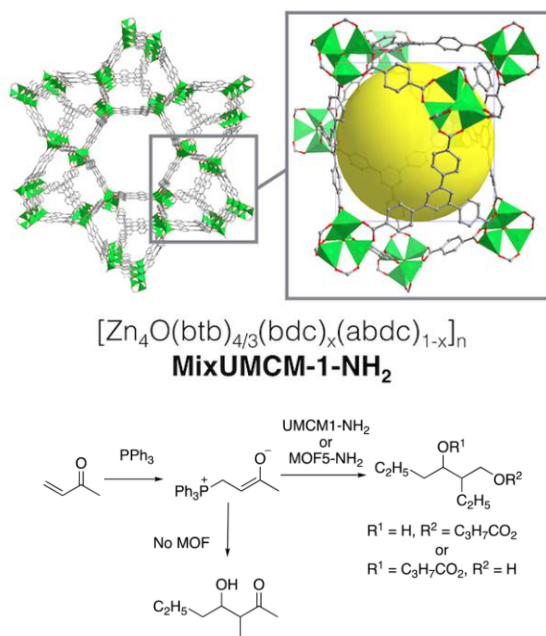


Figure 1.9. Structure of MIX-UMCM-1-NH₂ MOF (top), changes in reactivity in the presence or absence of MOF (bottom).⁵⁸

The introduction of catalytic sites through post-synthetic modification (PSM) presents a versatile approach to transforming inactive MOFs into efficient heterogeneous catalysts. Coordinating active metal moieties with

ligands in the MOF is a popular and simple way to achieve this. Lin and co-workers employed this strategy to stabilise Ir phosphine catalysts and prevent intermolecular deactivation processes in homogeneous catalysts.⁵⁹ In this work, a MOF with phosphine ligands (Zr-P1) was post-synthetically metalated with $[\text{Ir}(\text{COD})\text{Cl}]_2$ to generate Zr-P1-Ir (Figure 1.10). The metalated MOF was used as catalyst for the borylation of methane, a challenging reaction due to reactivity and selectivity issues. The Ir MOF outperformed other Ir catalysts, producing CH_3Bpin with a TON of 127.

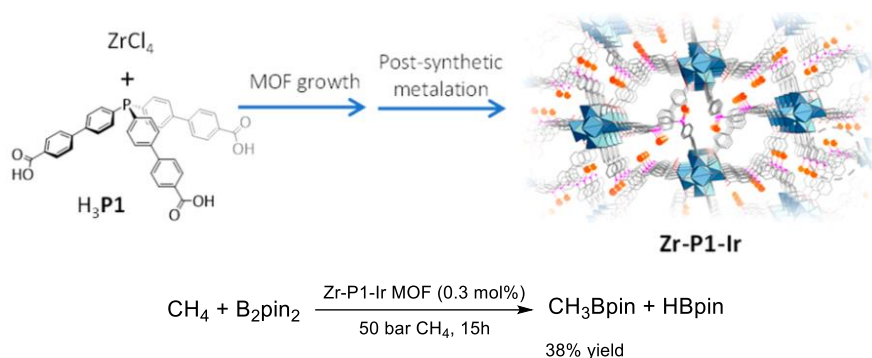


Figure 1.10. Synthesis and structure of Zr-P1-Ir MOF (top), methane borylation catalysed by Zr-P1-Ir MOF (bottom). Reproduced with permission.⁵⁹ Copyright 2019, American Chemical Society.

Another effective approach to introducing new catalytic sites through PSM involves the formation of covalent bonds. In this type of functionalisation, the organic linker usually has a functional group that is used as an anchoring point for new molecules to be immobilised by covalent bonds formed by classical organic reactions. A few functional groups used for this purpose are amines, alcohols, aldehydes and azides. However, deprotection reactions can also obtain functional groups incompatible with the synthesis conditions. One interesting example of covalent PSM used for MOF catalysis comes from Yaghi and co-workers, in which seven sequential reaction steps were performed on a MOF to create an enzyme-like catalyst (Figure 1.11).⁶⁰ A MOF containing an NHBoc group was subjected to a

series of deprotection and peptide coupling reactions, producing MOF-Ala-Gly-Pro-NH₂. This modified MOF could catalyse the cleavage of peptides in specific chain positions. The active sites in the material resemble the ones found in enzymes in their spatial arrangement and compositional heterogeneity. Indeed, this study suggests that the complexity achieved in this material can affect reactions that previously could only be achieved by enzymes.

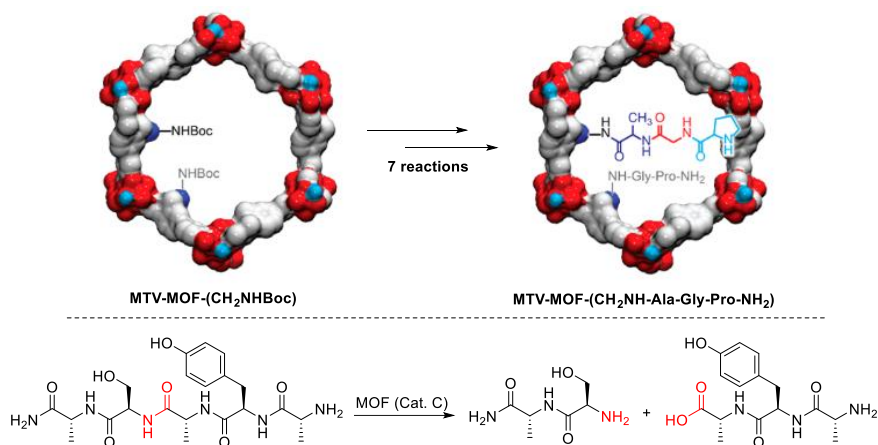


Figure 1.11. Post-synthetic modification on the pores of MTV-MOF to achieve enzyme-like complexity (top). Catalytic cleavage of pentapeptide 1 by Cat. C [MTV-IRMOF-74-III-(CH₃)_{0.6}(CH₂NH-Asp-His-Cys-NH₂)_{0.1}] in the specific sequence containing serine (bottom). Reproduced with permission.⁶⁰ Copyright 2016, American Chemical Society.

1.4.2. COF catalysts

COF catalysts can be divided into two categories. The first one encompasses COFs with intrinsic catalytic activity, and the second one includes COFs which have been functionalised through post-synthetic modification (PSM) to introduce catalytic activity.⁵¹

For the first category, the catalytic activity of the COF relies on the organic linkers that compose the structure of the framework. COFs in this category have been widely used as metal-free photocatalysts, although there are also

some examples of COFs used as acid or basic catalysts.^{51,52,61–64} In this context, Liu and co-workers developed a triazine-based COF photocatalyst (COF-JLU5) employed in the light-driven cross-dehydrogenative coupling of N-aryltetrahydroisoquinolines (Figure 1.12a).⁶⁵ This material presented an interesting photocatalytic system because of its periodic columnar p-array structure resulting from stacking the 2D COF sheets, which could allow for good exciton diffusion and migration. Additionally, the methoxide group improved the chemical stability of the linkage and the electron donor–acceptor structure enhanced the photocatalytic properties. Likewise, the same group later designed an imine COF (COF-JLU22) composed of an electron donor and acceptor (Figure 1.12b).⁶⁶ The combination of an electron-rich pyrene linker and an electron-poor benzothiadiazole linker led to a red shift in the absorption wavelength, which could improve the photocatalytic activity of the material. As a result, the COF was a highly efficient photocatalyst for the reductive dehalogenation of phenacyl bromide derivatives and α -alkylation of aldehydes under visible-light irradiation.

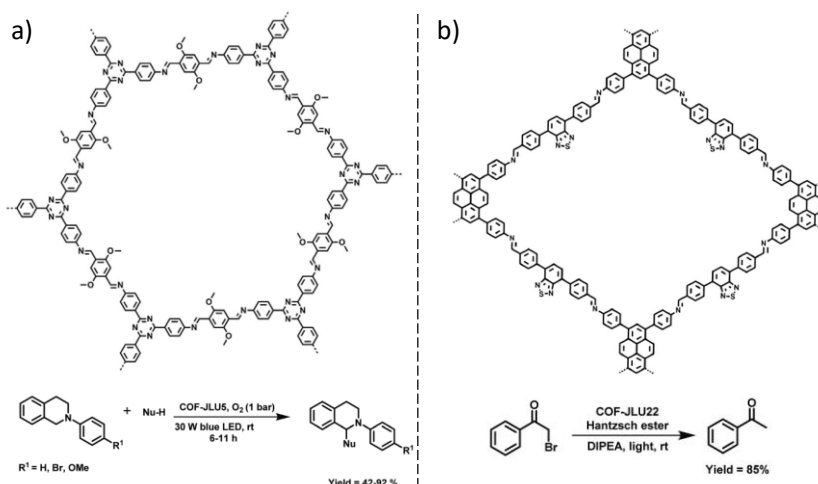


Figure 1.12. a) Structure of COF-JLU5 (top),⁶⁵ light-driven cross-dehydrogenative coupling catalysed by COF-JLU5 (bottom). b) Structure of COF-JLU22 (top),⁶⁶ light-driven reductive dehalogenation of phenacyl bromide catalysed by COF-JLU22 (bottom).

Post-synthetic modification (PSM) is a powerful tool that can introduce catalytic activity into an existing COF without dramatically altering its structure. This technique reduces the time spent finding the conditions for the synthesis of new COFs, since the same COF can be functionalised in many different ways, and allows for introducing functional groups and geometries incompatible with direct synthesis.⁶⁷ This strategy was employed by Jiang and co-workers to immobilise chiral organocatalysts in a COF (TPB-DMTP-COF, Figure 1.13).⁶⁸ In this work, a COF was designed with ethynyl units connected to one of the linkers. Pyrrolidine derivatives were immobilised through the reaction between ethynyl units and azide compounds using click chemistry. By adjusting the incorporation of organocatalytic sites on the material's walls, they obtained [(S)-Py]_{0.17}-TPB-DMTP-COF, which worked as an efficient chiral catalyst for the Michael reaction. The immobilised catalyst produced excellent enantiomeric excess values and could be recycled several times without losing catalytic activity or selectivity.

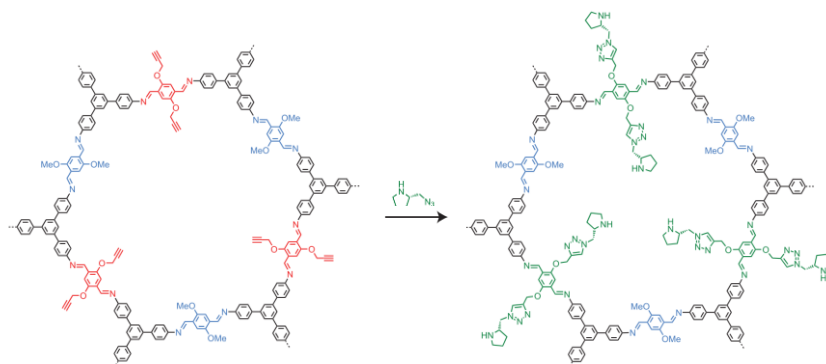


Figure 1.13. Post-synthetic modification of TPB-DMTP-COF. Reprinted with permission.⁶⁸
 Copyright 2015, Nature Publishing Group

The most common way to introduce catalytic sites into COFs is through the coordination of metal ions to organic ligands present in the framework, leading to metal-COFs (MCOFs) formation.^{50,56,69–80} The versatility of

COFs makes it possible to incorporate various molecular building blocks, which can be used as organic ligands uniformly distributed throughout COFs. Additionally, the uniform distribution of ligands with metal ions provides effective site isolation of the active catalytic sites at a molecular level. Many metal ions, including V, Mn, Fe, Co, Ni, Cu, Zn, Mo, Rh, Pd, Re, and Ir have been immobilised in COFs to form catalytically active MCOFs.⁶⁷ The first example of an organic reaction catalysed by a COF, in 2009, was developed by immobilising Pt^{2+} into a covalent triazine framework and employing it to oxidise methane into methanol. Another important example of MCOF catalysis was reported in 2011 by Wang and co-workers. They developed a 2D COF that could be easily metalated by post-treatment with $\text{Pd}(\text{AcO})_2$ to form Pd/COF-LZU1, which proved to be an efficient catalyst for the Suzuki–Miyaura coupling reaction (Figure 1.14). Pd/COF-LZU1 produced excellent yields of the coupling products with a wide substrate scope and good catalyst recyclability. The efficiency of the material was attributed to its well-ordered porous structure, which improves the accessibility of the catalytic sites and facilitates diffusion of reactants and products.

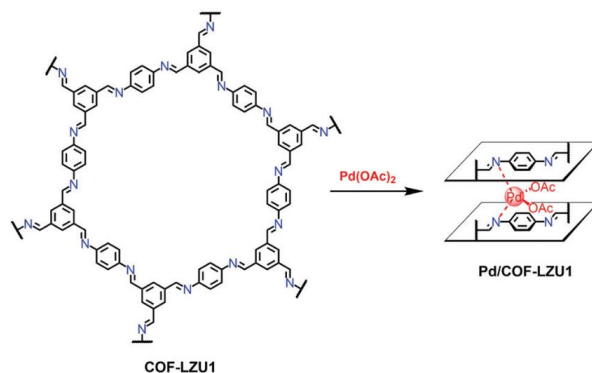


Figure 1.14. Schematic representation for the synthesis of Pd/COF-LZU1 materials. Reprinted with permission.⁶⁷ Copyright 2019, Royal Society of Chemistry.

When designing COF-based catalysts, the topology and dimensionality play a crucial role in the performance of the material. The work of Wang and co-workers clearly shows this.⁷⁰ The authors prepared a 2D and a 3D COF with Pd-porphyrin in their structure and compared the performance of the materials as photocatalysts for the oxidation of sulfides to sulfoxides (Figure 1.15). Interestingly, they found that the 2D COF produces much lower yields than the 3D COF, despite having the same type of catalytic centers. This difference was attributed to stacking the palladium porphyrin units in the 2D COF, which led to a fast quenching of the photocatalyst excited state. However, the 3D COF produced lower yields than the 2D COF when bulky substrates were employed due to the smaller cavities.

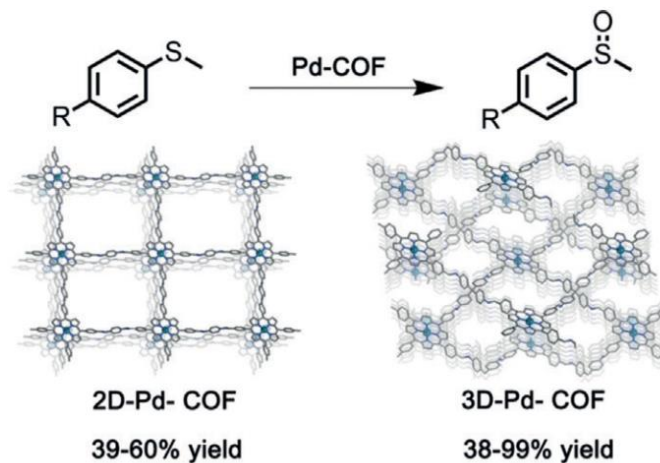


Figure 1.15. Photocatalytic selective oxidation of sulfides to sulfoxides by 2D and 3D Pd-COFs. Reprinted with permission.⁵⁶ Copyright 2020, Wiley.

Cooperation between photoredox catalysts and transition metal catalysts has become a very popular approach in synthetic methodology over the past decade.⁸¹ Van Der Voort and co-workers combined these two types of catalysts into one metallaphotoredox COF, presenting light harvesting triazine moieties within the framework plus nickel catalytic active sites (Figure 1.16).⁷⁶ The COF presented high catalytic activity in the visible-light-driven catalytic sulfur-carbon cross-coupling reaction, as well as good recyclability and stability due to the ordered structure and proximity of the photosensitiser and the nickel catalytic active sites.

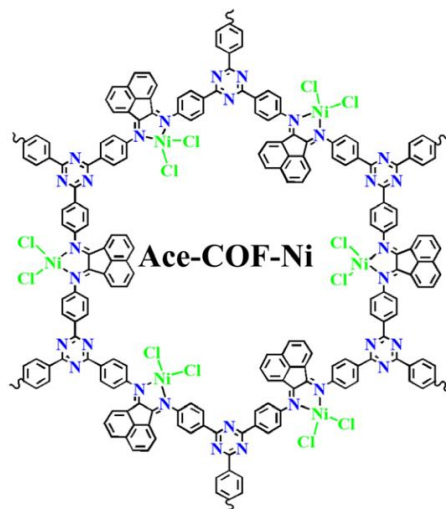


Figure 1.16. Structure of Ace-COF-Ni. Reprinted with permission.⁷⁶ Copyright 2021, Wiley.

Incorporating multiple metal centers in a COF is an attractive strategy that could allow for the development of more elaborate catalysts. However, obtaining a homogeneous distribution of different catalytic centers in close proximity is challenging while maintaining good crystallinity and porosity. Alemán and Mas-Ballesté employed this strategy to develop a sophisticated Ni/Ir COF photocatalyst (Figure 1.17).⁷⁹ The material was prepared by metalation of a phenanthroline COF with $[(dF(CF_3)ppy)_2Ir-\mu-Cl]_2$ and $NiCl_2 \cdot glyme$ in the presence of acetic acid. The dual metallic system proved an effective and recyclable photocatalyst for light-driven Csp^3-Csp^2 cross-couplings. In addition, the proximity of the Ni and Ir catalytic centers enhanced the efficiency of the combined system, while the separation between Ni centers prevented the formation of nanoparticles through the aggregation of reduced nickel species.

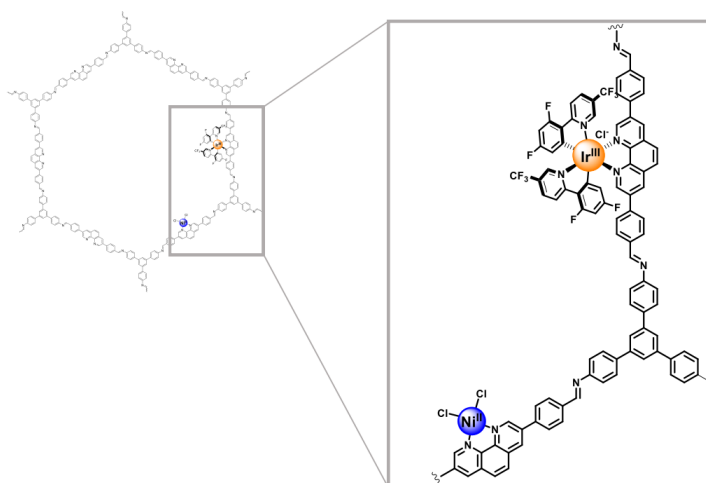


Figure 1.17. Structure of Ni-Ir COF photocatalyst employed in Csp³–Csp² cross-couplings.

79

1.2. Bibliography

- (1) Yaghi, O. M. Reticular Chemistry - Construction, Properties, and Precision Reactions of Frameworks. *J. Am. Chem. Soc.* **2016**, *138* (48), 15507–15509.
- (2) Jiang, H.; Alezi, D.; Eddaoudi, M. A Reticular Chemistry Guide for the Design of Periodic Solids. *Nat. Rev. Mater.* **2021**, *6* (6), 466–487.
- (3) Freund, R.; Canossa, S.; Cohen, S. M.; Yan, W.; Deng, H.; Guillermin, V.; Eddaoudi, M.; Madden, D. G.; Fairen-Jimenez, D.; Lyu, H.; Macreadie, L. K.; Ji, Z.; Zhang, Y.; Wang, B.; Haase, F.; Wöll, C.; Zaremba, O.; Andreo, J.; Wuttke, S.; Diercks, C. S. 25 Years of Reticular Chemistry. *Angew. Chemie - Int. Ed.* **2021**, *60* (45), 23946–23974.
- (4) Evans, A. M.; Strauss, M. J.; Corcos, A. R.; Hirani, Z.; Ji, W.; Hamachi, L. S.; Aguilar-Enriquez, X.; Chavez, A. D.; Smith, B. J.;

- Dichtel, W. R. Two-Dimensional Polymers and Polymerizations. *Chem. Rev.* **2022**, 122 (1), 442–564.
- (5) Li, H.; Eddaoudi, M.; Groy, T. L.; Yaghi, O. M. Establishing Microporosity in Open Metal–Organic Frameworks: Gas Sorption Isotherms for Zn(BDC) (BDC = 1,4-Benzenedicarboxylate). *J. Am. Chem. Soc.* **1998**, 120 (33), 8571–8572.
- (6) Li, H.; Eddaoudi, M.; O’Keeffe, M.; Yaghi, O. M. Design and Synthesis of an Exceptionally Stable and Highly Porous Metal–Organic Framework. *Nature* **1999**, 402 (6759), 276–279.
- (7) Rowsell, J. L. C.; Yaghi, O. M. Metal–Organic Frameworks: A New Class of Porous Materials. *Microporous Mesoporous Mater.* **2004**, 73 (1–2), 3–14.
- (8) Côté, A. P.; Benin, A. I.; Ockwig, N. W.; O’Keeffe, M.; Matzger, A. J.; Yaghi, O. M. Chemistry: Porous, Crystalline, Covalent Organic Frameworks. *Science* **2005**, 310 (5751), 1166–1170.
- (9) Altaf, A.; Baig, N.; Sohail, M.; Sher, M.; Ul-Hamid, A.; Altaf, M. Covalent Organic Frameworks: Advances in Synthesis and Applications. *Mater. Today Commun.* **2021**, 28, 102612.
- (10) Diercks, C. S.; Yaghi, O. M. The Atom, the Molecule, and the Covalent Organic Framework. *Science* **2017**, 355 (6328).
- (11) Mandal, S.; Natarajan, S.; Mani, P.; Pankajakshan, A. Post-Synthetic Modification of Metal–Organic Frameworks Toward Applications. *Adv. Funct. Mater.* **2021**, 31 (4), 1–22.
- (12) Haase, F.; Hirschle, P.; Freund, R.; Furukawa, S.; Ji, Z.; Wuttke, S. Beyond Frameworks: Structuring Reticular Materials across Nano-, Meso-, and Bulk Regimes. *Angew. Chemie - Int. Ed.* **2020**, 59 (50), 22350–22370.
- (13) Yuan, S.; Feng, L.; Wang, K.; Pang, J.; Bosch, M.; Lollar, C.; Sun,

- Y.; Qin, J.; Yang, X.; Zhang, P.; Wang, Q.; Zou, L.; Zhang, Y.; Zhang, L.; Fang, Y.; Li, J.; Zhou, H. C. Stable Metal–Organic Frameworks: Design, Synthesis, and Applications. *Adv. Mater.* **2018**, *30* (37), 1–35.
- (14) Yap, M. H.; Fow, K. L.; Chen, G. Z. Synthesis and Applications of MOF-Derived Porous Nanostructures. *Green Energy Environ.* **2017**, *2* (3), 218–245.
- (15) Cao, L.; Wang, C. Metal–Organic Layers for Electrocatalysis and Photocatalysis. *ACS Cent. Sci.* **2020**, *6* (12), 2149–2158.
- (16) Wei, Y.-S.; Zhang, M.; Zou, R.; Xu, Q. Metal–Organic Framework-Based Catalysts with Single Metal Sites. *Chem. Rev.* **2020**, *120* (21), 12089–12174.
- (17) Xiao, J.-D.; Jiang, H.-L. Metal–Organic Frameworks for Photocatalysis and Photothermal Catalysis. *Acc. Chem. Res.* **2019**, *52* (2), 356–366.
- (18) Jiao, L.; Wang, Y.; Jiang, H. L.; Xu, Q. Metal–Organic Frameworks as Platforms for Catalytic Applications. *Adv. Mater.* **2018**, *30* (37), 1–23.
- (19) Gong, W.; Chen, Z.; Dong, J.; Liu, Y.; Cui, Y. Chiral Metal–Organic Frameworks. *Chem. Rev.* **2022**, *122* (9), 9078–9144.
- (20) Xie, L. S.; Skorupskii, G.; Dincă, M. Electrically Conductive Metal–Organic Frameworks. *Chem. Rev.* **2020**, *120* (16), 8536–8580.
- (21) Ding, M.; Cai, X.; Jiang, H. L. Improving MOF Stability: Approaches and Applications. *Chem. Sci.* **2019**, *10* (44), 10209–10230.
- (22) Yaghi, O. M.; Kalmutzki, M. J.; Diercks, C. S. *Introduction to Reticular Chemistry*; 2019.
- (23) Hofmann, K. and Küspert, F. Verbindungen von

- Kohlenwasserstoffen Mit Metallsalzen. *Zeitschrift für Anorg. Chemie* **1897**, 15 (1): 20.
- (24) Lu, W.; Wei, Z.; Gu, Z. Y.; Liu, T. F.; Park, J.; Park, J.; Tian, J.; Zhang, M.; Zhang, Q.; Gentle, T.; Bosch, M.; Zhou, H. C. Tuning the Structure and Function of Metal-Organic Frameworks via Linker Design. *Chem. Soc. Rev.* **2014**, 43 (16), 5561–5593.
- (25) Schaate, A.; Roy, P.; Godt, A.; Lippke, J.; Waltz, F.; Wiebcke, M.; Behrens, P. Modulated Synthesis of Zr-Based Metal-Organic Frameworks: From Nano to Single Crystals. *Chem. A Eur. J.* **2011**, 17 (24), 6643–6651.
- (26) Nelson, A. P.; Farha, O. K.; Mulfort, K. L.; Hupp, J. T. Supercritical Processing as a Route to High Internal Surface Areas and Permanent Microporosity in Metal#organic Framework Materials. *J. Am. Chem. Soc.* **2009**, 131 (2), 458–460.
- (27) Liu, R.; Tan, K. T.; Gong, Y.; Chen, Y.; Li, Z.; Xie, S.; He, T.; Lu, Z.; Yang, H.; Jiang, D. Covalent Organic Frameworks: An Ideal Platform for Designing Ordered Materials and Advanced Applications. *Chem. Soc. Rev.* **2021**, 50 (1), 120–242.
- (28) Hu, J.; Gupta, S. K.; Ozdemir, J.; Beyzavi, M. H. Applications of Dynamic Covalent Chemistry Concept toward Tailored Covalent Organic Framework Nanomaterials: A Review. *ACS Appl. Nano Mater.* **2020**, 3 (7), 6239–6269.
- (29) Geng, K.; He, T.; Liu, R.; Dalapati, S.; Tan, K. T.; Li, Z.; Tao, S.; Gong, Y.; Jiang, Q.; Jiang, D. Covalent Organic Frameworks: Design, Synthesis, and Functions. *Chem. Rev.* **2020**, 120 (16), 8814–8933.
- (30) Kandambeth, S.; Dey, K.; Banerjee, R. Covalent Organic Frameworks: Chemistry beyond the Structure. *J. Am. Chem. Soc.*

2019, 141 (5), 1807–1822.

- (31) Emmerling, S. T.; Germann, L. S.; Julien, P. A.; Moudrakovski, I.; Etter, M.; Frišćić, T.; Dinnebier, R. E.; Lotsch, B. V. In Situ Monitoring of Mechanochemical Covalent Organic Framework Formation Reveals Templating Effect of Liquid Additive. *Chem* **2021**, 7 (6), 1639–1652.
- (32) Wei, H.; Chai, S.; Hu, N.; Yang, Z.; Wei, L.; Wang, L. The Microwave-Assisted Solvothermal Synthesis of a Crystalline Two-Dimensional Covalent Organic Framework with High CO₂ Capacity. *Chem. Commun.* **2015**, 51 (61), 12178–12181.
- (33) Biswal, B. P.; Chandra, S.; Kandambeth, S.; Lukose, B.; Heine, T.; Banerjee, R. Mechanochemical Synthesis of Chemically Stable Isorecticular Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2013**, 135 (14), 5328–5331.
- (34) Matsumoto, M.; Dasari, R. R.; Ji, W.; Feriante, C. H.; Parker, T. C.; Marder, S. R.; Dichtel, W. R. Rapid, Low Temperature Formation of Imine-Linked Covalent Organic Frameworks Catalyzed by Metal Triflates. *J. Am. Chem. Soc.* **2017**, 139 (14), 4999–5002.
- (35) Wang, K.; Yang, L. M.; Wang, X.; Guo, L.; Cheng, G.; Zhang, C.; Jin, S.; Tan, B.; Cooper, A. Covalent Triazine Frameworks via a Low-Temperature Polycondensation Approach. *Angew. Chemie - Int. Ed.* **2017**, 56 (45), 14149–14153.
- (36) Shiraki, T.; Kim, G.; Nakashima, N. Room-Temperature Synthesis of a Covalent Organic Framework with Enhanced Surface Area and Thermal Stability and Application to Nitrogen-Doped Graphite Synthesis. *Chem. Lett.* **2015**, 44 (11), 1488–1490.
- (37) Deblase, C. R.; Dichtel, W. R. Moving Beyond Boron: The Emergence of New Linkage Chemistries in Covalent Organic

- Frameworks. *Macromolecules* **2016**, 49 (15), 5297–5305.
- (38) Huang, W.; Byun, J.; Rörich, I.; Ramanan, C.; Blom, P. W. M.; Lu, H.; Wang, D.; Caire da Silva, L.; Li, R.; Wang, L.; Landfester, K.; Zhang, K. A. I. Asymmetric Covalent Triazine Framework for Enhanced Visible-Light Photoredox Catalysis via Energy Transfer Cascade. *Angew. Chemie - Int. Ed.* **2018**, 57 (27), 8316–8320.
- (39) Segura, J. L.; Mancheño, M. J.; Zamora, F. Covalent Organic Frameworks Based on Schiff-Base Chemistry: Synthesis, Properties and Potential Applications. *Chem. Soc. Rev.* **2016**, 45 (20), 5635–5671.
- (40) Kandambeth, S.; Mallick, A.; Lukose, B.; Mane, M. V.; Heine, T.; Banerjee, R. Construction of Crystalline 2D Covalent Organic Frameworks with Remarkable Chemical (Acid/Base) Stability via a Combined Reversible and Irreversible Route. *J. Am. Chem. Soc.* **2012**, 134 (48), 19524–19527.
- (41) Chen, R.; Shi, J.; Ma, Y.; Lin, G.; Lang, X.; Wang, C. Designed Synthesis of a 2D Porphyrin-Based Sp² Carbon-Conjugated Covalent Organic Framework for Heterogeneous Photocatalysis. *Angew. Chemie Int. Ed.* **2019**, 58 (19), 6430–6434.
- (42) Zhao, Y.; Liu, H.; Wu, C.; Zhang, Z.; Pan, Q.; Hu, F.; Wang, R.; Li, P.; Huang, X.; Li, Z. Fully Conjugated Two-Dimensional Sp² - Carbon Covalent Organic Frameworks as Artificial Photosystem I with High Efficiency. *Angew. Chemie Int. Ed.* **2019**, 58 (16), 5376–5381.
- (43) Jin, E.; Li, J.; Geng, K.; Jiang, Q.; Xu, H.; Xu, Q.; Jiang, D. Designed Synthesis of Stable Light-Emitting Two-Dimensional Sp² Carbon-Conjugated Covalent Organic Frameworks. *Nat. Commun.* **2018**, 9 (1), 1–10.

- (44) Becker, D.; Biswal, B. P.; Kaleńczuk, P.; Chandrasekhar, N.; Giebeler, L.; Addicoat, M.; Paasch, S.; Brunner, E.; Leo, K.; Dianat, A.; Cuniberti, G.; Berger, R.; Feng, X. Fully Sp²-Carbon-Linked Crystalline Two-Dimensional Conjugated Polymers: Insight into 2D Poly(Phenylenevinylene) Formation and Its Optoelectronic Properties. *Chem. – A Eur. J.* **2019**, 25 (26), 6562–6568.
- (45) Rogge, S. M. J.; Bavykina, A.; Hajek, J.; Garcia, H.; Olivos-Suarez, A. I.; Sepúlveda-Escribano, A.; Vimont, A.; Clet, G.; Bazin, P.; Kapteijn, F.; Daturi, M.; Ramos-Fernandez, E. V.; Llabrés Xamena, F. X. I.; Van Speybroeck, V.; Gascon, J. Metal-Organic and Covalent Organic Frameworks as Single-Site Catalysts. *Chem. Soc. Rev.* **2017**, 46 (11), 3134–3184.
- (46) Drake, T.; Ji, P.; Lin, W. Site Isolation in Metal-Organic Frameworks Enables Novel Transition Metal Catalysis. *Acc. Chem. Res.* **2018**, 51 (9), 2129–2138.
- (47) Pascanu, V.; González Miera, G.; Inge, A. K.; Martín-Matute, B. Metal–Organic Frameworks as Catalysts for Organic Synthesis: A Critical Perspective. *J. Am. Chem. Soc.* **2019**, 141 (18), 7223–7234.
- (48) Daliran, S.; Oveisi, A. R.; Peng, Y.; López-Magano, A.; Khajeh, M.; Mas-Ballesté, R.; Alemán, J.; Luque, R.; Garcia, H. Metal–Organic Framework (MOF)-, Covalent-Organic Framework (COF)-, and Porous-Organic Polymers (POP)-Catalyzed Selective C–H Bond Activation and Functionalization Reactions. *Chem. Soc. Rev.* **2022**, 51 (18), 7810–7882.
- (49) Abednatanzi, S.; Najafi, M.; Gohari Derakhshandeh, P.; Van Der Voort, P. Metal- and Covalent Organic Frameworks as Catalyst for Organic Transformation: Comparative Overview and Future Perspectives. *Coord. Chem. Rev.* **2022**, 451, 214259.

- (50) Hasija, V.; Patial, S.; Raizada, P.; Aslam Parwaz Khan, A.; Asiri, A. M.; Van Le, Q.; Nguyen, V. H.; Singh, P. Covalent Organic Frameworks Promoted Single Metal Atom Catalysis: Strategies and Applications. *Coord. Chem. Rev.* **2022**, 452, 214298.
- (51) Cheng, H. Y.; Wang, T. Covalent Organic Frameworks in Catalytic Organic Synthesis. *Adv. Synth. Catal.* **2021**, 363 (1), 144–193.
- (52) Sharma, R. K.; Yadav, P.; Yadav, M.; Gupta, R.; Rana, P.; Srivastava, A.; Zbořil, R.; Varma, R. S.; Antonietti, M.; Gawande, M. B. Recent Development of Covalent Organic Frameworks (COFs): Synthesis and Catalytic (Organic-Electro-Photo) Applications. *Mater. Horizons* **2020**, 7 (2), 411–454.
- (53) Lee, J.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. Metal-Organic Framework Materials as Catalysts. *Chem. Soc. Rev.* **2009**, 38 (5), 1450–1459.
- (54) García-García, P.; Müller, M.; Corma, A. MOF Catalysis in Relation to Their Homogeneous Counterparts and Conventional Solid Catalysts. *Chem. Sci.* **2014**, 5 (8), 2979–3007.
- (55) Liu, J.; Chen, L.; Cui, H.; Zhang, J.; Zhang, L.; Su, C. Y. Applications of Metal-Organic Frameworks in Heterogeneous Supramolecular Catalysis. *Chem. Soc. Rev.* **2014**, 43 (16), 6011–6061.
- (56) Dong, J.; Han, X.; Liu, Y.; Li, H.; Cui, Y. Metal–Covalent Organic Frameworks (MCOFs): A Bridge Between Metal–Organic Frameworks and Covalent Organic Frameworks. *Angew. Chemie Int. Ed.* **2020**, 59 (33), 13722–13733.
- (57) Wang, L.; Agnew, D. W.; Yu, X.; Figueroa, J. S.; Cohen, S. M. A Metal–Organic Framework with Exceptional Activity for C–H Bond Amination. *Angew. Chemie - Int. Ed.* **2018**, 57 (2), 511–515.

- (58) Bauer, G.; Ongari, D.; Xu, X.; Tiana, D.; Smit, B.; Ranocchiari, M. Metal-Organic Frameworks Invert Molecular Reactivity: Lewis Acidic Phosphonium Zwitterions Catalyze the Aldol-Tishchenko Reaction. *J. Am. Chem. Soc.* **2017**, *139* (50), 18166–18169.
- (59) Feng, X.; Song, Y.; Li, Z.; Kaufmann, M.; Pi, Y.; Chen, J. S.; Xu, Z.; Li, Z.; Wang, C.; Lin, W. Metal–Organic Framework Stabilizes a Low-Coordinate Iridium Complex for Catalytic Methane Borylation. *J. Am. Chem. Soc.* **2019**, *141* (28), 11196–11203.
- (60) Fracaroli, A. M.; Siman, P.; Nagib, D. A.; Suzuki, M.; Furukawa, H.; Toste, F. D.; Yaghi, O. M. Seven Post-Synthetic Covalent Reactions in Tandem Leading to Enzyme-like Complexity within Metal-Organic Framework Crystals. *J. Am. Chem. Soc.* **2016**, *138* (27), 8352–8355.
- (61) Lopez-Magano, A.; Jiménez-Almarza, A.; Aleman, J.; Mas-Ballesté, R. Metal–Organic Frameworks (MOFS) and Covalent Organic Frameworks (COFS) Applied to Photocatalytic Organic Transformations. *Catalysts* **2020**, *10* (7), 1–44.
- (62) Guo, L.; Jin, S. Stable Covalent Organic Frameworks for Photochemical Applications. *ChemPhotoChem* **2019**, *3* (10), 973–983.
- (63) López-Magano, A.; Salaverri, N.; Marzo, L.; Mas-Ballesté, R.; Alemán, J. Synergistic Combination of Triazine and Phenanthroline Moieties in a Covalent Triazine Framework Tailored for Heterogeneous Photocatalytic Metal-Free C-Br and C-Cl Activation. *Appl. Catal. B Environ.* **2022**, *317* (July), 121791.
- (64) Chen, D.; Chen, W.; Zhang, G.; Li, S.; Chen, W.; Xing, G.; Chen, L. N-Rich 2D Heptazine Covalent Organic Frameworks as Efficient Metal-Free Photocatalysts. *ACS Catal.* **2022**, *12* (1), 616–623.

- (65) Zhi, Y.; Li, Z.; Feng, X.; Xia, H.; Zhang, Y.; Shi, Z.; Mu, Y.; Liu, X. Covalent Organic Frameworks as Metal-Free Heterogeneous Photocatalysts for Organic Transformations. *J. Mater. Chem. A* **2017**, 5 (44), 22933–22938.
- (66) Li, Z.; Zhi, Y.; Shao, P.; Xia, H.; Li, G.; Feng, X.; Chen, X.; Shi, Z.; Liu, X. Covalent Organic Framework as an Efficient, Metal-Free, Heterogeneous Photocatalyst for Organic Transformations under Visible Light. *Appl. Catal. B Environ.* **2019**, 245 (October 2018), 334–342.
- (67) Segura, J. L.; Royuela, S.; Mar Ramos, M. Post-Synthetic Modification of Covalent Organic Frameworks. *Chem. Soc. Rev.* **2019**, 48 (14), 3903–3945.
- (68) Xu, H.; Gao, J.; Jiang, D. Stable, Crystalline, Porous, Covalent Organic Frameworks as a Platform for Chiral Organocatalysts. *Nat. Chem.* **2015**, 7 (11), 905–912.
- (69) Ma, H.-C.; Chen, G.-J.; Huang, F.; Dong, Y.-B. Homochiral Covalent Organic Framework for Catalytic Asymmetric Synthesis of a Drug Intermediate. *J. Am. Chem. Soc.* **2020**, 142 (29), 12574–12578.
- (70) Meng, Y.; Luo, Y.; Shi, J.-L.; Ding, H.; Lang, X.; Chen, W.; Zheng, A.; Sun, J.; Wang, C. 2D and 3D Porphyrinic Covalent Organic Frameworks: The Influence of Dimensionality on Functionality. *Angew. Chemie Int. Ed.* **2020**, 59 (9), 3624–3629.
- (71) Kang, X.; Wu, X.; Han, X.; Yuan, C.; Liu, Y.; Cui, Y. Rational Synthesis of Interpenetrated 3D Covalent Organic Frameworks for Asymmetric Photocatalysis. *Chem. Sci.* **2020**, 11 (6), 1494–1502.
- (72) Kang, X.; Wu, X.; Han, X.; Yuan, C.; Liu, Y.; Cui, Y. Rational Synthesis of Interpenetrated 3D Covalent Organic Frameworks for

- Asymmetric Photocatalysis. *Chem. Sci.* **2020**, *11* (6), 1494–1502.
- (73) Li, Y.; Yang, L.; He, H.; Sun, L.; Wang, H.; Fang, X.; Zhao, Y.; Zheng, D.; Qi, Y.; Li, Z.; Deng, W. In Situ Photodeposition of Platinum Clusters on a Covalent Organic Framework for Photocatalytic Hydrogen Production. *Nat. Commun.* **2022**, *13* (1), 1–9.
- (74) Jati, A.; Dey, K.; Nurhuda, M.; Addicoat, M. A.; Banerjee, R.; Maji, B. Dual Metalation in a Two-Dimensional Covalent Organic Framework for Photocatalytic C-N Cross-Coupling Reactions. *J. Am. Chem. Soc.* **2022**, *144* (17), 7822–7833.
- (75) Dong, W.; Yang, Y.; Xiang, Y.; Wang, S.; Wang, P.; Hu, J.; Rao, L.; Chen, H. A Highly Stable All-in-One Photocatalyst for Aryl Etherification: The Ni II Embedded Covalent Organic Framework. *Green Chem.* **2021**, *23* (16), 5797–5805.
- (76) Chen, H.; Liu, W.; Laemont, A.; Krishnaraj, C.; Feng, X.; Rohman, F.; Meledina, M.; Zhang, Q.; Van Deun, R.; Leus, K.; Van Der Voort, P. A Visible-Light-Harvesting Covalent Organic Framework Bearing Single Nickel Sites as a Highly Efficient Sulfur–Carbon Cross-Coupling Dual Catalyst. *Angew. Chemie Int. Ed.* **2021**, *60* (19), 10820–10827.
- (77) Bi, S.; Zhang, Z.; Meng, F.; Wu, D.; Chen, J. S.; Zhang, F. Heteroatom-Embedded Approach to Vinylene-Linked Covalent Organic Frameworks with Isoelectronic Structures for Photoredox Catalysis. *Angew. Chemie - Int. Ed.* **2021**, 202111627.
- (78) Vardhan, H.; Al-Enizi, A. M.; Nafady, A.; Pan, Y.; Yang, Z.; Gutiérrez, H. R.; Han, X.; Ma, S. Single-Pore versus Dual-Pore Bipyridine-Based Covalent–Organic Frameworks: An Insight into the Heterogeneous Catalytic Activity for Selective C–H Functionalization. *Small* **2021**, *17* (22), 2003970.

- (79) López-Magano, A.; Ortín-Rubio, B.; Imaz, I.; Maspoch, D.; Alemán, J.; Mas-Ballesté, R. Photoredox Heterobimetallic Dual Catalysis Using Engineered Covalent Organic Frameworks. *ACS Catal.* **2021**, *11* (19), 12344–12354.
- (80) Dong, Z.; Zhang, L.; Gong, J.; Zhao, Q. Covalent Organic Framework Nanorods Bearing Single Cu Sites for Efficient Photocatalysis. *Chem. Eng. J.* **2021**, *403*, 126383.
- (81) Chan, A. Y.; Perry, I. B.; Bissonnette, N. B.; Buksh, B. F.; Edwards, G. A.; Frye, L. I.; Garry, O. L.; Lavagnino, M. N.; Li, B. X.; Liang, Y.; Mao, E.; Millet, A.; Oakley, J. V.; Reed, N. L.; Sakai, H. A.; Seath, C. P.; MacMillan, D. W. C. Metallaphotoredox: The Merger of Photoredox and Transition Metal Catalysis. *Chem. Rev.* **2022**, *122* (2), 1485–1542.

Chapter II:

Thesis Objectives

Reticular materials like metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) are two emerging types of porous materials with excellent properties: high diversity of building blocks, tunable and predictable structure, high porosity, and good stability. Thanks to their unique properties, these materials have applications in various fields, particularly in catalysis. Therefore, MOFs and COFs could be ideal bridges between homogeneous and heterogeneous catalysts. However, further research is needed to understand how isolated catalytic sites in reticular materials behave to develop their full potential.

Based on these premises, the main objectives of the current thesis are:

- Study the immobilization of isolated photoactive organic ligands inside single-crystals of MOF-520 towards the development of MOF-based photocatalytic systems, in batch or flow conditions, for the reductive homocoupling of C=O and C=N bonds (**Chapter III**).
- Synthesize and characterize a series of COFs with single-catalytic sites based on cobalt. To this end, imine COFs will be formed by condensation between amine and aldehyde linkers with N-donor ligand moieties in their structure (bipyridine, terpyridine or bispyridine-cyclohexyldiamine), followed by coordination of cobalt to the frameworks through post-synthetic metalation (**Chapter IV**).
- Explore the catalytic activity of the developed COFs in the hydroboration and borylation of simple alkenes and arenes based on Co COFs (**Chapter V** and **Chapter VI**).

Chapter III:

Preparation of photocatalytically active
Metal-Organic Frameworks through
crystal-to-crystal transformations

3.1. General insight

Within the last decades, there has been an increased interest in the field of photocatalysis, in which electronically excited species created by light absorption are employed as catalysts of organic transformations.¹⁻⁵ A general photoredox catalytic cycle is shown in Figure 3.1. The reaction begins with the absorption of a photon by the photocatalyst (PC) to form the excited species PC*. If the excited state is long-lived ($\tau_{\text{deact}} > 10$ ns), it can undergo oxidative quenching ($^*PC^n \rightarrow PC^{n+1}$) by transferring an electron to an electron acceptor or reductive quenching ($^*PC^n \rightarrow PC^{n-1}$) by receiving an electron from an electron donor. The resulting oxidized (PC^{n+1}) or reduced (PC^{n-1}) photocatalyst can be reduced or oxidized back to the ground state (PC^n) in the presence of a suitable electron-donating or accepting molecule, closing in this way the photoredox cycle.

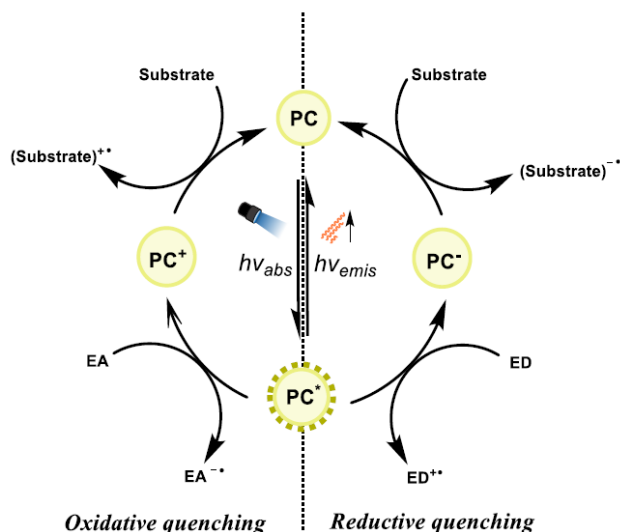


Figure 3.1. General photocatalytic cycle including reductive and oxidative electron-transfer quenching processes.

CHAPTER III: Preparation of photocatalytically active
Metal-Organic Frameworks through crystal-to-crystal
transformations

Ru and Ir iridium polypyridyl complexes compose among the most commonly used class of photocatalysts.^{1,3,4} Nevertheless, there are some drawbacks regarding the employed metal complexes, such as high cost and toxicity. Alternatively, organic photoredox catalysts present an exciting class of catalysts due to their relatively lower cost, wide availability, and properties that can, in some cases, outperform their inorganic and organometallic counterparts.^{6–10} The advantages of metal-free photocatalysts can be combined with the benefits of a MOF platform, such as porosity, modularity, tunability, high surface area, and crystallinity.¹¹ However, there is a limited number of examples of MOFs which contain organic photocatalysts in their structure.^{12–24}

In one of the earliest examples, Duan and co-workers reported a MOF (Zn-PY11) which combined a triphenylamine photoredox group with a stereoselective organocatalyst (pyrrolidin-2-ylimidazole) into a single framework (Figure 3.2a).¹⁶ The MOF could catalyze the asymmetric α -alkylation of aliphatic aldehydes under light irradiation, displaying superior enantioselectivity compared to the homogeneous control (Figure 3.2c). The same group later developed a MOF (Zn-PDI) constituted by perylene diimide ligands (PDI) (Figure 3.2b).¹⁵ This heterogeneous approach tackled several issues of PDI as a photocatalyst, like its poor solubility and tendency to aggregate. As a result, Zn-PDI MOF achieved excellent yields in the photoreduction of aryl halides (Figure 3.2d) and in the photooxidation of alcohols and amines.

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

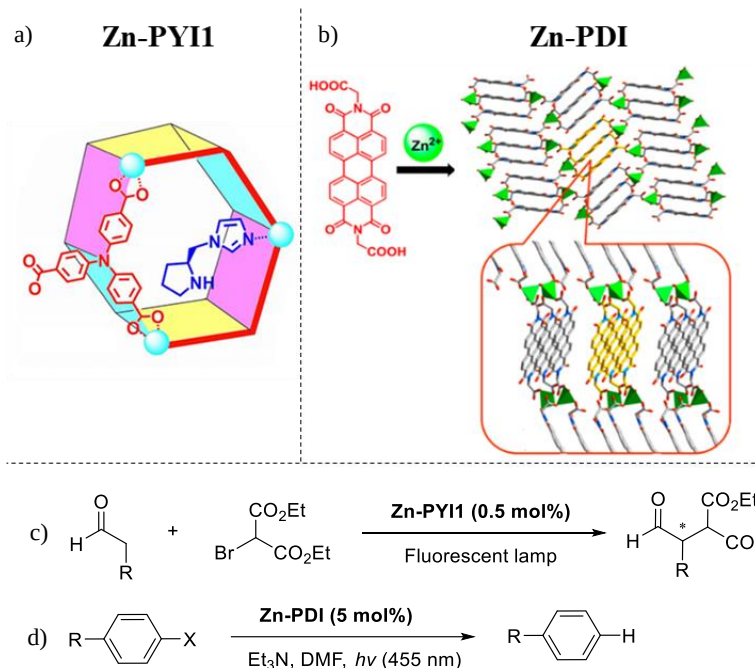


Figure 3.2. Illustration of Zn-MOFs with organic dyes in their structure: a) Zn-PYI1,¹⁶ b) Zn-PDI.¹⁵ Reactions photocatalyzed by the MOFs: c) asymmetric α -alkylation of aliphatic aldehydes, d) reduction of aryl halides.

The direct synthesis of MOFs with photoactive ligands has its limitations since the ligands need specific geometries and functional groups to form a well-ordered material.²⁵ Thus, only a fraction of the known photocatalysts can constitute the framework of a MOF.²⁶ A promising technique that can immobilize various ligands inside MOFs is solvent-assisted ligand incorporation (SALI).²⁷ The first example of functionalization via SALI entailed an acid–base reaction between a carboxylic acid ligand and a pair of terminal hydroxide ligands of the SBU in MOF-NU-1000, resulting in a material where the new charge compensating acid ligands are strongly bound to the NU-1000 node (Figure 3.3).^{28,29} Farha and co-workers demonstrated how this technique could attach several photoactive ligands inside MOF-NU-1000 (Figure 3.3c). After performing this

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

functionalization, the resulting MOFs were used as photocatalysts to degrade contaminants efficiently.^{22,23,30}

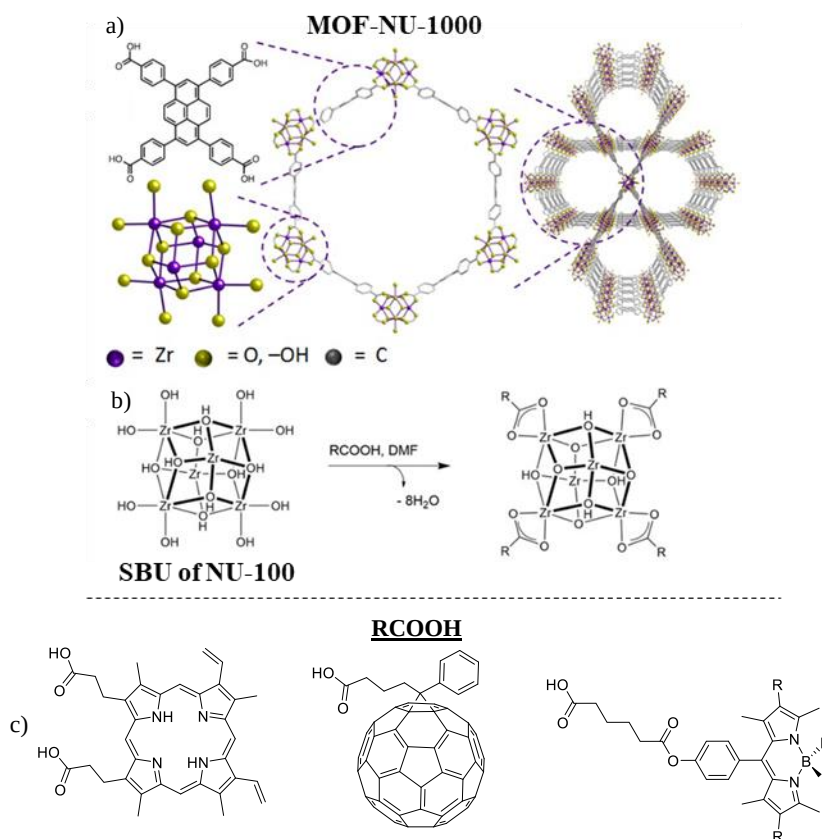


Figure 3.3. a) Structure of MOF-NU-1000,²⁸ b) coordination of carboxylic acid ligands via SALI, c) photoactive ligands included in NU-100 via SALI.

In 2016, O. Yaghi employed SALI to crystallize molecules inside the pores of MOF-520.³¹ The SBUs of this MOF contain formate ligands that can be replaced by other ligands like carboxylic acids or alcohols. After performing this transformation on crystals of MOF-520, the new ligands inside the cavities could be studied by single-crystal X-ray diffraction. The reduced motional degrees of freedom obtained with this coordinative alignment method facilitated the structural determination of the ligands, and

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

the chiral nature of the MOF made it possible to crystallize racemic mixtures of ligands enantioselectively. Later, this strategy expanded to include azolates, sulfur oxoacids and phosphorous oxoacids as ligands.³²

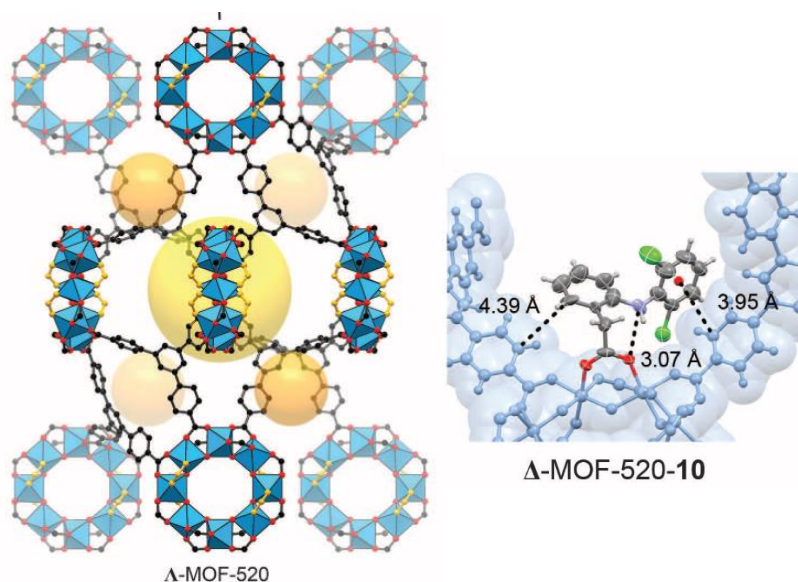


Figure 3.4. structure of **MOF-520** (left), an example of a molecule crystallized inside **MOF-520** (right).³¹

Inspired by these studies, we hypothesized the advantage of including photoredox catalysts in MOF-520. Coordination of the guest molecule into the SBU places the PC in a confined environment, which may allow for crystallographic characterization, and, therefore, aid in providing a mechanistic understanding. Another interesting aspect of the coordination of guest molecules into MOF-520 is that the material can be composed of a collection of isolated units, acting as single-site catalysts in a heterogeneous material. In general, mechanistic studies on heterogeneous phases are more challenging than those on homogeneous ones. However, heterogeneous reticular materials with well-defined single catalytic sites may clarify mechanistic aspects that are otherwise tough to address in a homogeneous

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

phase. For instance, it could be helpful to elucidate the active catalytic species in PCs based on π -conjugated molecules. The tendency to form π -stacking aggregates in solution introduces uncertainty into the catalytic species since the dynamics of excited states are very complex.³³ In those systems, the catalytic activity can result from the monomer, the dimer, larger aggregates, or a combination thereof.

In this chapter, we isolate a series of perylene ligands inside the cavities of MOF-520. Perylene is a polyaromatic hydrocarbon previously used as an efficient photoredox catalyst in the reductive coupling of aldehydes, ketones and imines.³⁴ Thus, immobilization of perylene in a MOF provides an interesting opportunity to study the PC as an isolated unit.

3.2. Results and Discussion

3.2.1. Crystal-to-crystal modification of MOF-520

Single crystals of **MOF-520** of adequate size were grown following the previously reported method with slight variations (Figure 3.5, see the experimental section for details).³¹ As previously reported, the X-ray analysis showed that the SBUs ($[\text{Al}_8(\mu\text{OH})_8(\text{HCOO})_4(\text{BTB})_4]$) are constituted by a ring of eight aluminum octahedra sharing corners through eight μ -OHs, twelve BTB linkers (4,4',4'',-benzene-1,3,5-triyl-tris(benzoic acid)) and four formate ligands, with wide window openings (13.7 Å) and cavities. Each BTB is connected to three SBUs to form a three-dimensional (3D) porous framework. The formates are exchangeable and offer anchoring points for other ligands with carboxylic acids.

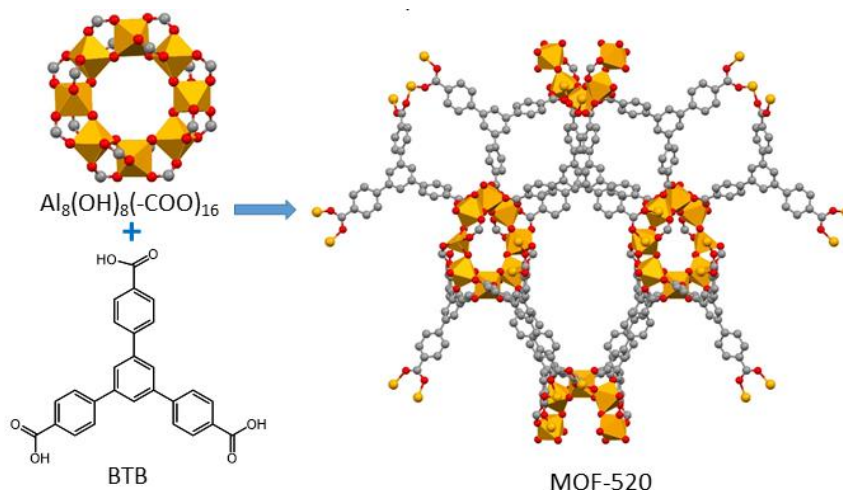
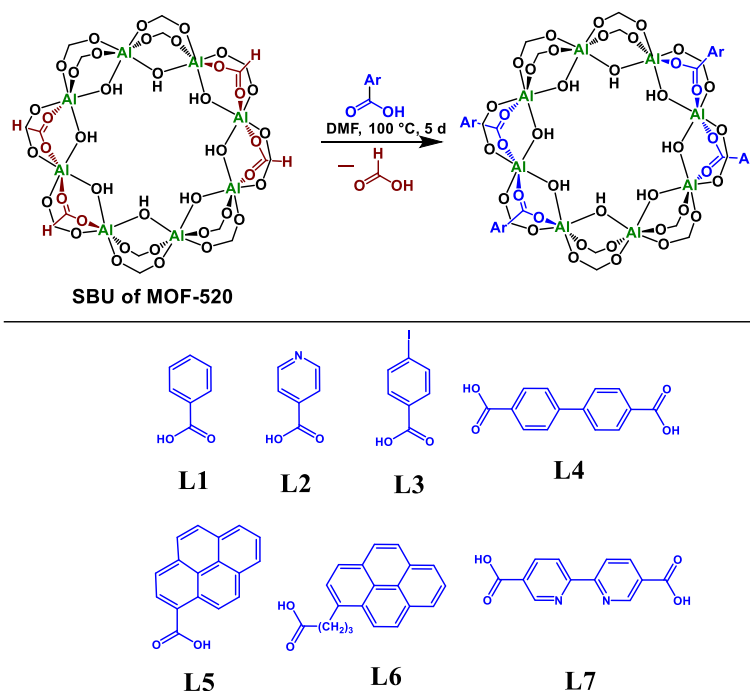


Figure 3.5. Structure and building blocks of **MOF-520**. H atoms and solvent molecules are omitted for clarity. Color code: gray, C; red, O; orange octahedra, Al.

The formates in the SBU were exchanged by incubating crystals of **MOF-520** in DMF at 100 °C for five days in the presence of an excess amount of a carboxylic acid ligand (Scheme 3.1). Then, the crystals were washed with DMF before SXRD measurements. A series of commercially available ligands (**L1-L6**) were incorporated into **MOF-520** to confirm the validity of this method for crystallizing molecules and to observe their arrangement in the cavities of the material.

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations



Scheme 3.1. Ligand exchange in **MOF-520**. Incoming ligands and outgoing formic acid are highlighted in red and blue, respectively.

The successful incorporation of ligands **L1**, **L2** and **L3** was confirmed by SXRD (Figure 3.6), validating this method for crystallizing small molecules. The occupancy factor of the ligands was determined to be 100%, corresponding to the coordination of 4 ligands on each SBU. The introduction of **L4** into the MOF resulted in a different coordination mode (Figure 3.6), in which the ligand was bonded to two adjacent SBUs in agreement with previous reports.³⁵ This arrangement is possible thanks to the similarity between the length of **L4** (10.1 Å), and the distance between formate ligands in adjacent SBUs (9.5 Å). Despite having a larger size, **L5** fits nicely into the MOF cavities, resulting in a 100% incorporation rate.

Interestingly, the pyrene ligands in adjacent SBUs formed π -stacking dimers with a distance of 3.58 Å (Figure 3.6), which is in good agreement

with crystal structure data of stacked pyrenes featuring a distance of 3.53 Å.^{36,37} Similarly, **L6** formed π -stacking dimers. However, other conformations were also detected due to the high degree of freedom of the alkyl chain (Figure 3.6). **L7** was successfully incorporated into MOF-520 and detected by XRD, presenting a similar coordination mode as **L4** (Figure 3.6). Then, MOF crystals modified with **L7** were placed in solutions of metal salts such as NiCl₂, NiNO₃, Ni(OTf)₂, Co(OTf)₂ and Fe(OTf)₂; to form bipyridine metallic complexes. However, the coordination of these metals could not be detected by XRD. The reason for this is not fully clear, and further work is needed to study these systems. Incorporation of larger nitrogen-donating ligands or phosphines was also unsuccessful (structures of all ligands are shown in the experimental section, Figure 3.25)

Next, we prepared a series of carboxylic acid-modified perylene ligands following reported procedures with modifications (Scheme 3.2). **III.1** was obtained by bromination of perylene with NBS. Then, an ester group was incorporated on the 3-position with *n*-BuLi, yielding **III.2**, which was hydrolyzed to produce **PC1**.³⁸ **III.3** was prepared by Friedel-Crafts acylation of perylene. Finally, reduction with hydrazine and hydrolysis of **III.3** afforded **PC2**.³⁹ **PC3**⁴⁰ was obtained by hydrolysis of bis(2-methylpropyl) perylene-dicarboxylate. The NMR spectra of all compounds agree with previously reported data^{38–40} (see the experimental section for details).

The perylene ligands were incorporated into crystals of **MOF-520** according to the conditions mentioned previously (Scheme 3.1), followed by SXRD analysis (Figure 3.7).

CHAPTER III: Preparation of photocatalytically active
 Metal-Organic Frameworks through crystal-to-crystal
 transformations

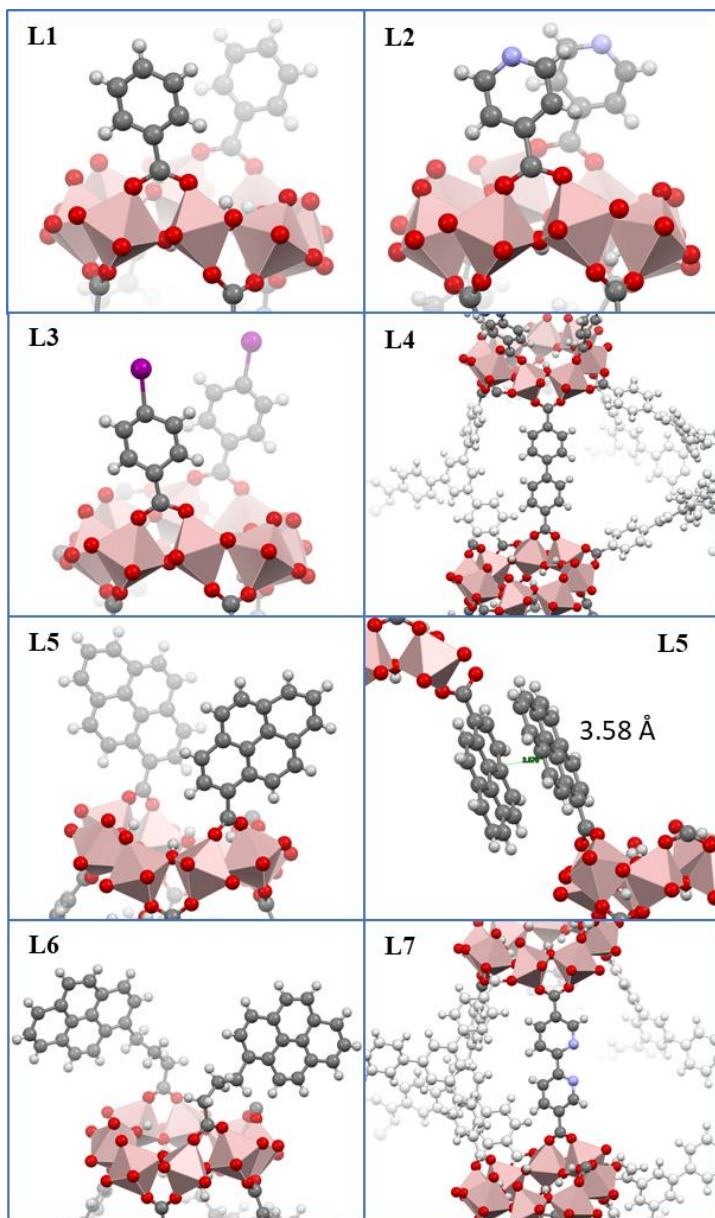
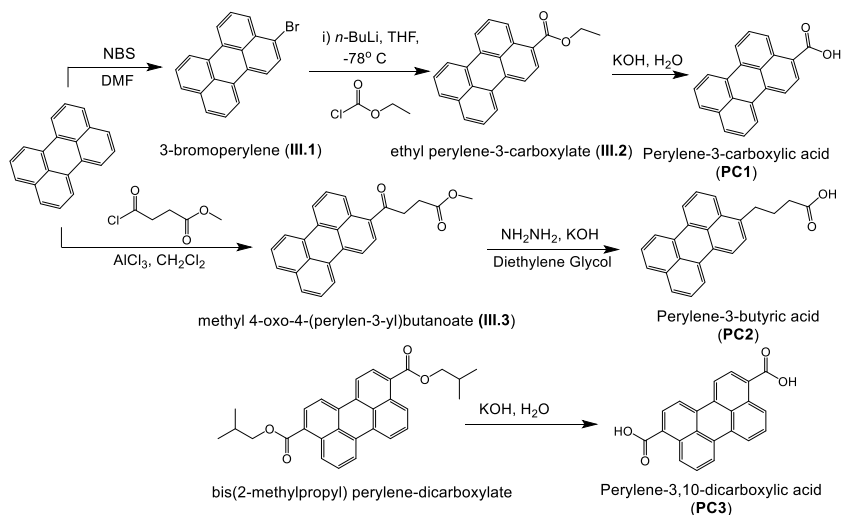


Figure 3.6. Representation of the single-crystal X-ray diffraction structures of ligands L1-L6 crystallized in **MOF-520**. BTB ligands and solvent molecules are omitted or painted white for clarity. In the case of positional disorder, only one conformation of bound molecules is shown for clarity. Color code: gray, C; red, O; white, H; blue, N; purple, I; pale red octahedra, Al.

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations



Scheme 3.2. Synthesis of perylene ligands **PC1**, **PC2** and **PC3**.^{38–40}

Although **PC1** and **L5** are pretty similar, the slightly larger perylene relative to pyrene leads to two interesting differences in the arrangement of molecules inside **MOF-520**. First, the larger size of **PC1** leads to steric hindrance from the BTB linker. This prevents the formation of perylene pi-stacking dimers, featuring a large distance of 6.35 Å between **PC1** molecules (Figure 3.7b). In contrast, the shortest distance between the BTB linker and perylene is only 3.2 Å. Second, the incorporation rate of **PC1** is only 40%, since the larger size of **PC1** prevents a second ligand from incorporating on the same SBU. The potential collision between **PC1** neighbouring positions within the same SBU is highlighted in Figure 3.7c. In the case of **PC2**, although single-crystal data collection was successful for detecting the ligand, it was impossible to resolve the structure, most probably due to the high degree of freedom of the flexible $-(\text{CH}_2)_3-$ units. However, x-ray analysis revealed that the ligand **PC3** was connected to two adjacent SBUs, acting as a bridge similar to **L4** (Figure 3.7d).

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

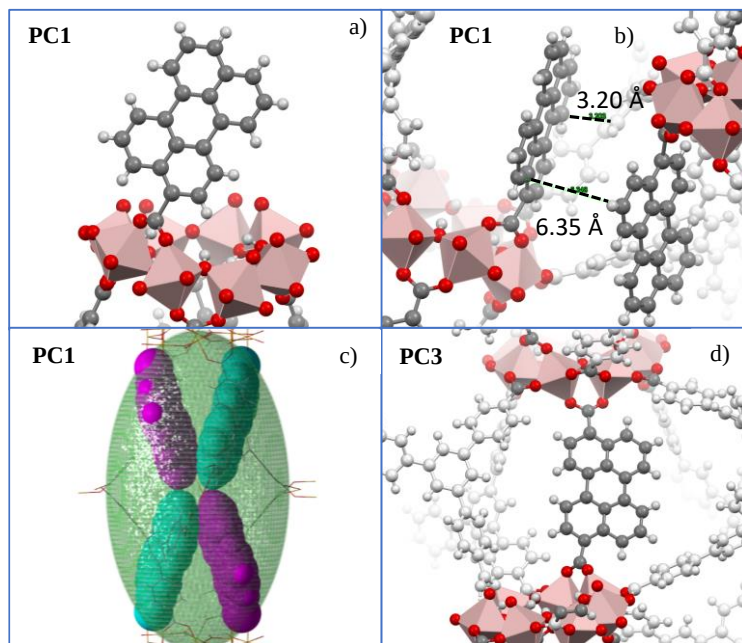


Figure 3.7. Representation of the single-crystal X-ray diffraction structure of ligands **PC1** (a-c) and **PC3** (d), crystallized in **MOF-520**. c) Representation of the structure of **MOF-520-PC1** highlighting the potential collision between **PC1** neighboring positions within the same SBU. X-ray single-crystal diffraction structure of **MOF-520-PC1** contains only green or purple **PC1**s

3.2.2. Characterization of bulk MOF-520-PCs

MOF-520-PC1, **MOF-520-PC2** and **MOF-520-PC3** were obtained as colored powders by incorporating **PC1**, **PC2** and **PC3**, respectively, into bulk **MOF-520** (Figure 3.8). The bulk materials were employed for further characterization and catalysis.

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

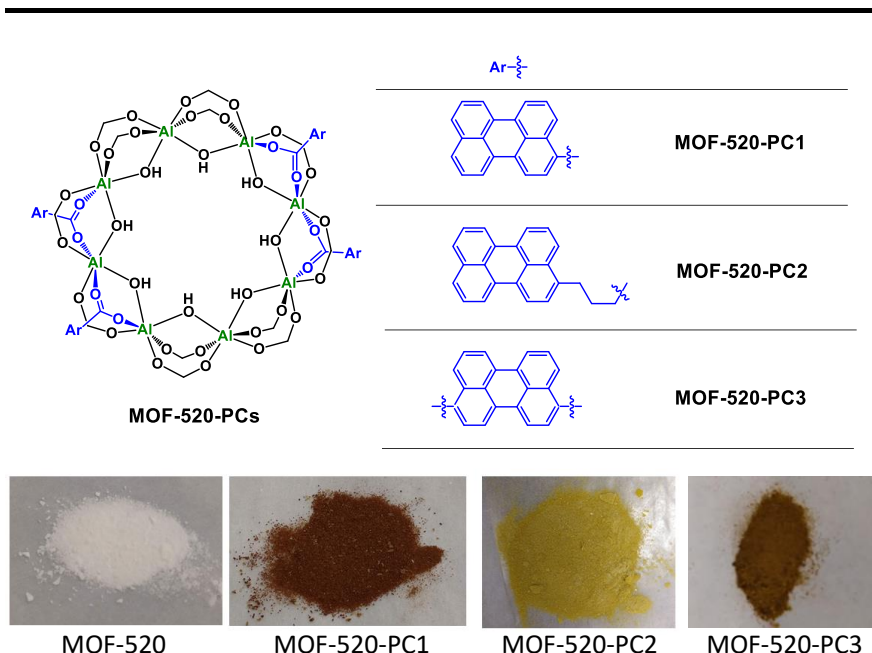


Figure 3.8. Structure of PC ligands incorporated into **MOF-520** (top), images of MOF-520-PCs in powder (bottom).

The powder X-Ray diffraction (PXRD) pattern of the MOF-520-PCs exhibited sharp diffraction peaks that were identical to those of **MOF-520**, which indicated that the porous framework maintained its crystalline integrity (Figure 3.9a). The stability of the MOF was tested by dispersing samples in acetone, tetrahydrofuran, methanol, acetonitrile, dichloromethane, or DMF for 3 days at room temperature. After such treatment, the materials maintained their crystalline integrity, as confirmed by PXRD (Figure 3.9b). Dinitrogen adsorption/desorption isotherms (77 K) of **MOF-520**, **MOF-520-PC1** and **MOF-520-PC2** indicate a porosity decrease in the materials after modification (Figure 3.9c), with BET surface areas determined to be 2438, 1448, and 1081 m²g⁻¹, respectively. The decrease of BET surface area is consistent with the steric bulk of guest perylene ligands residing in the pores of **MOF-520**. In contrast, **MOF-520-PC3** exhibited only a small porosity decrease, with a BET surface area of

2312 m²g⁻¹. The different behavior of **MOF-520-PC3** can be assigned to the lower number of perylene ligands per SBU and the different coordination modes of the dicarboxylic acid ligand.³⁵ Thermogravimetric analysis (TGA) of as-synthesized **MOF-520** exhibited an initial loss of mass at ~90 °C, likely due to the release of DMF molecules. All MOFs displayed a decomposition step beginning at 280 °C, and a second larger step at 530 °C, which could be assigned to the loss of the guest ligands or the BTB linkers (Figure 3.9d).

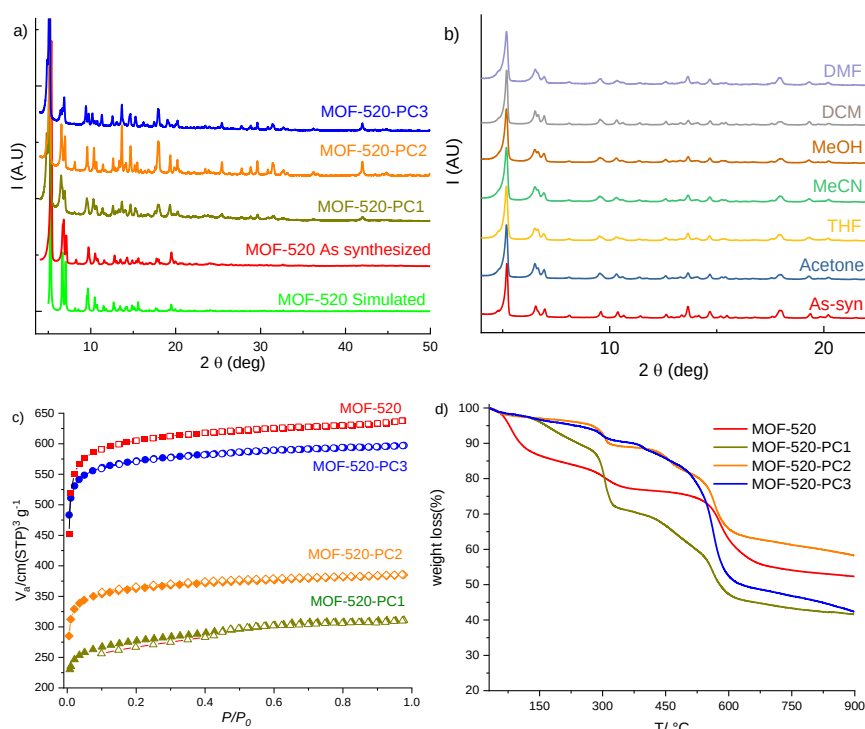


Figure 3.9. a) PXRD patterns of MOF-520-PCs, b) PXRD patterns of **MOF-520-PC2** collected during stability tests in different solvents at room temperature for three days, c) N₂ sorption isotherms at 77 K of MOF-520-PCs. d) TGA profile of MOF-520-PCs.

Solution ¹H-NMR spectroscopy of digested MOF-520-PCs samples was performed to quantify the amount of guest ligand binding in the bulk

CHAPTER III: Preparation of photocatalytically active
Metal-Organic Frameworks through crystal-to-crystal
transformations

materials (Figure 3.10). The samples were digested in a mixture of d₆-DMSO and NaOH 1M in D₂O, followed by heating at 120 °C over 18 h. The final clear solution was used to record the ¹H NMR spectrum. Perylene incorporation was determined by the ratio between the perylene and BTB linker measured in the digestion mixture (Figure 3.10). Based on the above results, we observed a 44%, 71% and 50% incorporation of **PC1**, **PC2** and **PC3**, respectively, postulating the formulas [Al₈(μ-OH)₈(HCOO)_{2.2}(**PC1**)_{1.8}(BTB)₄], [Al₈(μ-OH)₈(HCOO)_{1.2}(**PC2**)_{2.8}(BTB)₄] and [Al₈(μ-OH)₈(HCOO)₂(**PC3**)₁(BTB)₄], respectively.

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

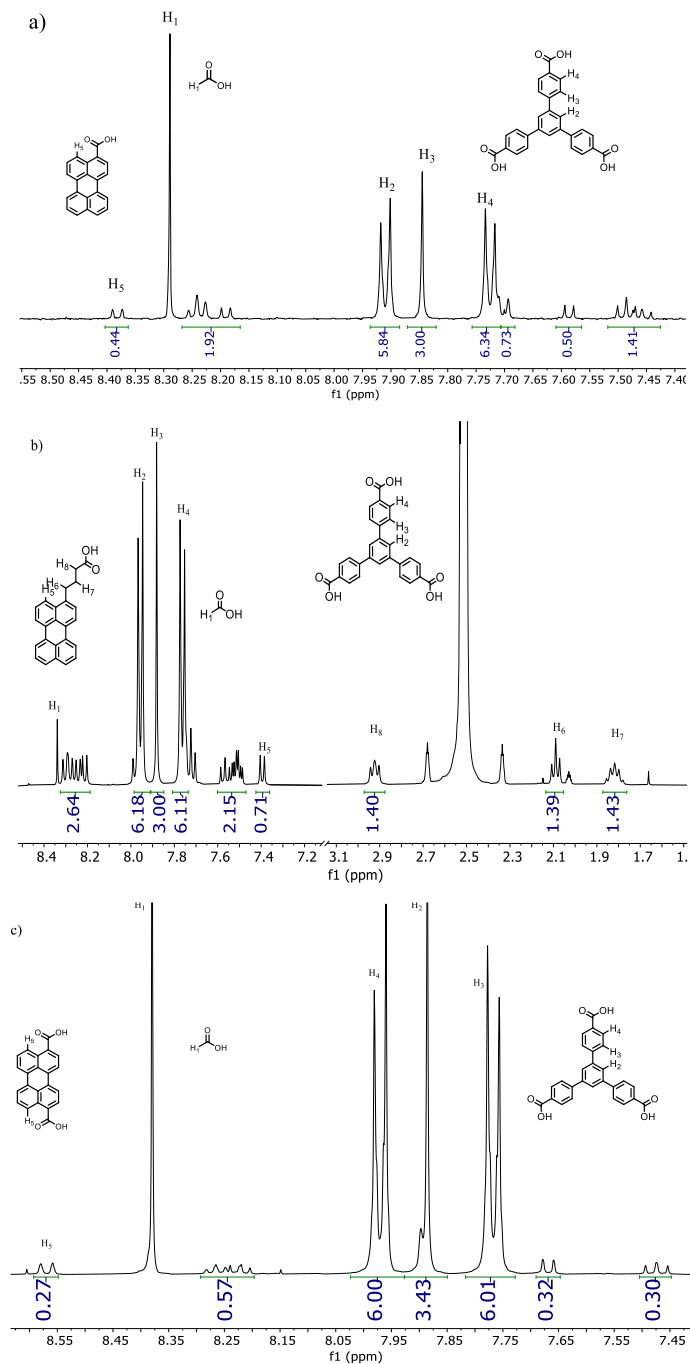


Figure 3.10. ¹H-NMR in d₆-DMSO of digested MOF-520-PCs: a) PC1, b) PC2, c) PC3.

3.2.3. Pinacol coupling promoted by MOF-520-PCs

To test the photocatalytic activity of the encapsulated perylene ligands inside the MOFs, we selected the light-driven pinacol coupling of 4-methylbenzaldehyde (**III.1a**) as a model reaction (Table 3.1). The reactions were performed under blue-led light irradiation over 16 h and with diisopropylethylamine (DIPEA) as electron donor. Moderate yields of **III.2a** were obtained when employing MeCN, MeOH or EtOH as solvents (Table 3.1, entries 1-9). DCM and THF, however, did not prove to be suitable solvents for this transformation (Table 3.1, entries 10-15). The yield was further improved by employing solvent mixtures of MeCN and MeOH or EtOH, achieving 82% yield with MeCN:MeOH (3:2, v:v) and 1% mol of **MOF-520-PC2** (mols of catalysts are calculated based on the formulas shown previously). Based on these results, the reactivity of the catalysts compares as follows: **MOF-520-PC2** > **MOF-520-PC1** > **MOF-520-PC3**. The differences in reactivity could be rationalized by the different incorporation rates and redox potentials (Section 3.2.7).

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

Table 3.1. Optimization of the homocoupling of **III.1a** catalyzed by MOF-520-PCs

III.1a $\xrightarrow[\text{DIPEA, solvent, 16 h, 30 °C, under N}_2]{\text{Photocatalyst Irradiation } (\lambda = 447 \text{ nm})}$ III.2a

Entry	Photocatalyst (mol%)	Solvent	DIPEA equiv.	Yield III.2a (%)
1	MOF-520-PC1 (1)	MeCN	14	17
2	MOF-520-PC2 (1)	MeCN	14	44
3	MOF-520-PC3 (1)	MeCN	14	14
4	MOF-520-PC1 (1)	MeOH	14	29
5	MOF-520-PC2 (1)	MeOH	14	45
6	MOF-520-PC3 (1)	MeOH	14	35
7	MOF-520-PC1 (1)	EtOH	14	30
8	MOF-520-PC2 (1)	EtOH	14	35
9	MOF-520-PC3 (1)	EtOH	14	27
10	MOF-520-PC1 (1)	DCM	14	0
11	MOF-520-PC2 (1)	DCM	14	0
12	MOF-520-PC3 (1)	DCM	14	0
13	MOF-520-PC1 (1)	THF	14	5
14	MOF-520-PC2 (1)	THF	14	4
15	MOF-520-PC3 (1)	THF	14	2
16	MOF-520-PC1 (1)	MeCN/MeOH 1/1	14	63
17	MOF-520-PC2 (1)	MeCN/MeOH 1/1	14	74
18	MOF-520-PC3 (1)	MeCN/MeOH 1/1	14	51
19	MOF-520-PC1 (1)	MeCN/EtOH 1/1	14	61
20	MOF-520-PC2 (1)	MeCN/EtOH 1/1	14	68
21	MOF-520-PC3 (1)	MeCN/EtOH 1/1	14	46
22	MOF-520-PC1 (1)	MeCN/MeOH 3/2	14	74
23	MOF-520-PC2 (1)	MeCN/MeOH 3/2	14	83
24	MOF-520-PC3 (1)	MeCN/MeOH 3/2	14	51
25	MOF-520-PC2 (1)	MeCN/MeOH 3/2	11	80
26	MOF-520-PC2 (1)	MeCN/MeOH 3/2	8	72
27	MOF-520-PC2 (1)	MeCN/MeOH 3/2	5	64
28	MOF-520-PC2 (1)	MeCN/MeOH 3/2	2	31
29	MOF-520-PC2 (2)	MeCN/MeOH 3/2	14	79
30	MOF-520-PC2 (0.7)	MeCN/MeOH 3/2	14	81
31	MOF-520-PC2 (0.4)	MeCN/MeOH 3/2	14	71

Conditions: Substrate **III.1a** (10.6 mg, 0.1 mmol), photocatalyst and DIPEA in a selected solvent (2 mL) was irradiated for 16 h (LED 1 W, $\lambda = 447 \pm 20$ nm). Yields calculated by ^1H NMR using an internal standard (1,3,5-trimethoxybenzene).

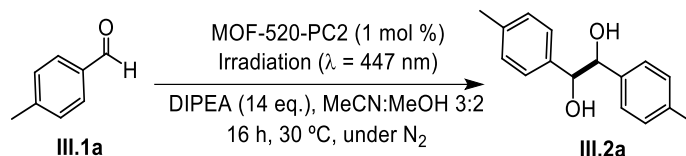
CHAPTER III: Preparation of photocatalytically active
Metal-Organic Frameworks through crystal-to-crystal
transformations

Blank experiments in the dark, without DIPEA, or without catalyst did not produce **III.2a**; and **MOF-520** (without PC) was equally inactive (Table 3.2, entries 2-6). Interestingly, the catalytic reaction mediated by **MOF-520-PC2** was also effective in an aerobic environment, with a similar catalytic performance as under anaerobic conditions. However, reductive transformations under aerobic conditions are uncommon and usually need to elaborate, sophisticated strategies to avoid the reaction of O₂ with the reduced catalyst.

Next, we directly compared the MOF-520-PCs with the corresponding homogeneous PCs under the optimized reaction conditions (Table 3.2, entries 7-11). Interestingly, the heterogeneous materials exhibit similar activity to the homogeneous counterparts. These results suggest that although immobilization of the catalysts has not improved their activity, most of the catalytic sites remain accessible. Additionally, the MOF does not seem to significantly quench or inhibit the PC.

CHAPTER III: Preparation of photocatalytically active
 Metal-Organic Frameworks through crystal-to-crystal
 transformations

Table 3.2. Control experiments



Entry	Deviation from standard conditions	%Yield
1	None	82
2	Under air	79
3	Under dark	0
4	Without DIPEA	0
5	No catalyst	0
6	MOF-520 as catalyst	0
7	MOF-520-PC1 as catalyst	74
8	MOF-520-PC3 as catalyst	51
9 ^a	PC-1 as catalyst	75
10 ^a	PC-2 as catalyst	81
11	PC-3 as catalyst	82

Conditions: Substrate **III.1a** (10.6 mg, 0.1 mmol), photocatalyst (1 μmol) and DIPEA (180 mg, 1.4 mmol) in a selected solvent (2 mL) was irradiated for 16 h (LED 1 W, $\lambda = 447 \pm 20$ nm). Yields calculated by $^1\text{H-NMR}$ using an internal standard (1,3,5-trimethoxybenzene).
^a2 μmol or 3 μmol of PC1 or PC2, respectively, were added.

Analysis of the *meso:dl* product ratio by NMR revealed that the coupling of **III.1a** proceeds with a slight preference for the *dl* diastereomer for all catalysts (Table 3.3). The source of this selectivity is not clear at present. In previous reports, the selectivity of this reaction has been linked to interactions between the amine electron donor and the carbonyl group,^{41,42} although the choice of catalyst and substrate also have a strong effect over the selectivity. Interestingly, all MOF-520-PCs show a small increase in *dl* selectivity compared to their respective homogeneous PCs. This small difference could be tentatively attributed to an effect of the cavities of the MOF.

Table 3.3. *meso:dl* product ratio for the coupling of **III.1a**.

Catalyst	<i>Meso:dl</i>
MOF-520-PC1	46:54
PC1	49:51
MOF-520-PC2	40:60
PC2	46:54
MOF-520-PC3	47:53
PC3	49:51

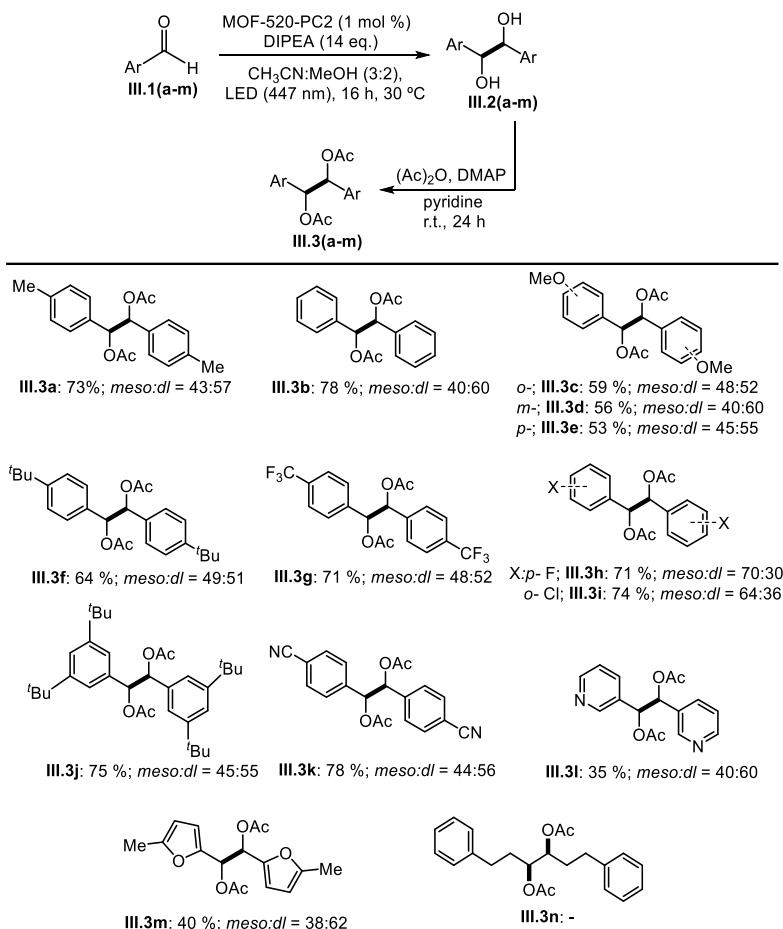
3.2.4. Substrate scope of aldehydes, ketones and imines

Next, we extended the reaction scope to include aromatic aldehydes with different substituents (Table 3.4). **MOF-520-PC2** was the chosen catalyst for the isolation of products because of the better yield compared to **MOF-520-PC1** and **MOF-520-PC3**. In order to facilitate the product isolation, the formed diols **III.2(a-m)** were converted into the corresponding diacetates **III.3(a-m)** using acetic anhydride. Moderate to excellent yields were obtained for the pinacol coupling with aromatic aldehydes bearing electron-donating and electron-withdrawing groups. Interestingly, products with bulky substituents (**III.3f** and **III.3j**) were obtained in good yield, indicating that diffusion through the cavities of the material is not excessively hampered by these substituents. Heteroaromatic aldehydes **III.1l** and **III.1m** were compatible with the reaction conditions, although only moderate to low yields were obtained. The developed methodology was incompatible with aliphatic aldehyde **III.1n**. Having outlined the scope for the homocoupling of aldehydes, we wanted to expand the reactivity to include the homocoupling of ketones and imines as well (Table 3.5). Benzophenones **III.4a-d** produced lower yields of the corresponding diols, despite the lower reduction potential of benzophenone ($E_{1/2}^{\text{red}} = -1.87$ V vs. Fc) compared to benzaldehyde ($E_{1/2}^{\text{red}} = -2.11$ V vs. Fc).⁴³ The lower yields are caused by a more prevalent competing H radical abstraction, generating

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

1,1-diphenylmethanol as a side product.³⁴ Acetophenone (**III.4e**) could not be reduced due to its higher potential ($E_{1/2}^{\text{red}} = -2.48 \text{ V vs. Fc}$) relative to benzaldehyde.⁴³ On the other hand, diamines **III.7a** and **III.7c** could be obtained in good yield using benzyl imines as substrates. Substrates **III.4d** and **III.6e** with electron rich -OMe substituents were not tolerated.

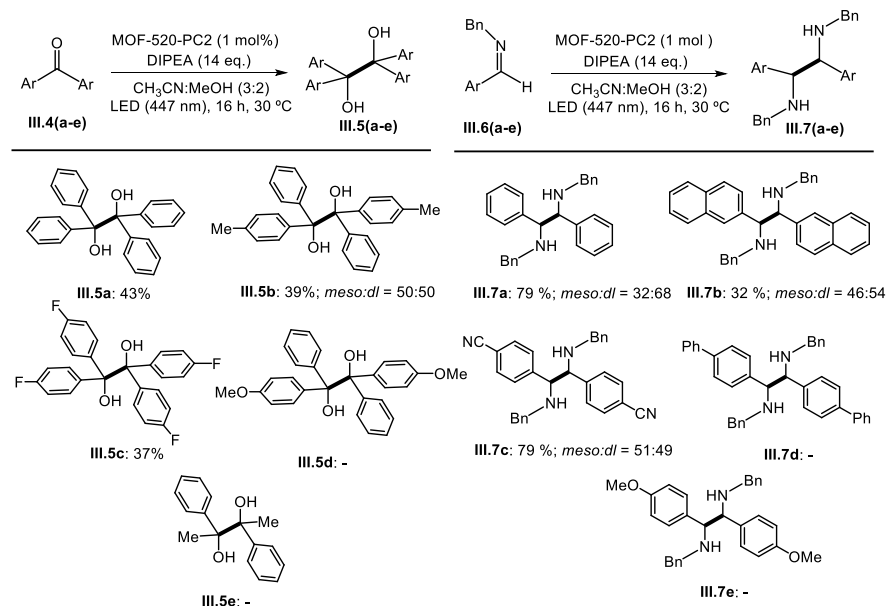
Table 3.4. Substrate scope of the homocoupling of aldehydes catalyzed by MOF-520-PC2.



Reaction conditions: **MOF-520-PC2** (3 mg, 1 mol%), aldehyde (0.1 mmol), DIPEA (180 mg, 1.4 mmol), in CH₃CN/CH₃OH (v:v = 3:2, 2 mL) at 30 °C, under N₂ during 16 h of irradiation (LED 447 nm). Yields are referred to isolated products.

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

Table 3.5 Substrate scope of the homocoupling of ketones and imines catalyzed by **MOF-520-PC2**.



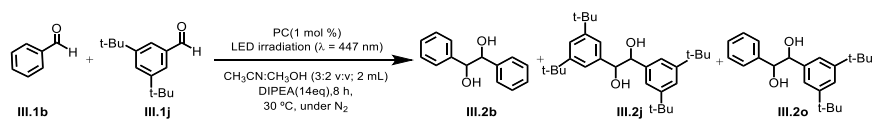
Reaction conditions: **MOF-520-PC2** (3 mg, 1 mol%), ketone or imine (0.1 mmol), **DIPEA** (180 mg, 1.4 mmol), $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ (v:v = 3:2, 2 mL) at 30 °C, under N_2 during 16 h of irradiation (LED 447 nm). Yields refer to isolated products.

Next, we wanted to ascertain if a size-exclusion effect from the cavities of the MOF could be employed to change the selectivity of a heterocoupling reaction. For this purpose, reactions were carried out using an equimolar mixture of a small substrate (**III.1b**) and a bulky substrate (**III.1j**). To observe better differences in reactivity, the reaction time was reduced to 8 h. In Table 3.6 is shown a comparison of the product distribution obtained when **MOF-520-PC2** or **PC2** are employed as catalysts. Although in both cases a mixture of homo- (**III.2j**, **III.2b**) and heterocoupling (**III.2o**) products were obtained, there was a remarkable difference in selectivity for the bulky substrate, **III.2j**. A product selectivity **III.2b/III.2j** value of 4.6 was obtained for **MOF-520-PC2**, whereas it was 1.0 for **PC2**. This 4.6-fold

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

increase for **III.2b** formation versus **III.2j** suggests a size-exclusion effect of the cavities of **MOF-520-PC2**.

Table 3.6. Light-induced pinacol coupling reaction between **III.1j** and **III.1b** promoted by **PC2** or **MOF-520-PC2**.



	Subs. (μmol)		Products (μmol)			Yield (%)	Selectivity	
	III.1b	III.1j	III.2b	III.2j	III.2o	III.2o	III.2b/ III.2j	III.2o/(III.2b+ III.2j)
PC2	100	100	19	19	22.5	23	1.0	0.6
MOF-520-PC2	100	100	16	3.5	20	21	4.6	1.0

Conditions: Substrate **III.1b** (0.1 mmol), substrate **III.1j** (0.1 mmol), photocatalyst (PC = **MOF-520-PC2** or **PC2**, 1 mol% regarding **III.1b**) and DIPEA (1.4 mmol) in MeCN/MeOH (3:2 v/v; 2 mL) irradiated for 8 h (LED 1 W, $\lambda = 447 \pm 20$ nm). Yields calculated by $^1\text{H-NMR}$ using an internal standard (1,3,5-trimethoxybenzene).

3.2.5. Catalyst recycling in batch

MOF-520-PC2 could be easily separated and recovered from the reaction mixture through filtration. Therefore, we studied the potential recycling of the catalyst after the pinacol coupling of **III.1a**. After washing twice with methanol and acetone, the recycled **MOF-520-PC2** was subjected to another catalytic run with the same substrate. The catalytic activity was maintained for the first two runs (79 and 75 %) and dropped in the third one to 34 % of **III.2a** (Figure 3.11a). This yield reduction was accompanied by a significant reduction in the crystallinity of the catalyst, as confirmed by PXRD analysis (Figure 3.11b). We rationalize that prolonged stirring under the catalytic conditions may be responsible for the structural degradation of **MOF-520-PC2**, which then diminishes the catalytic activity since the

catalytic sites are no longer accessible to the organic substrates. Indeed, MOF-520 has been previously reported to be mechanically fragile.³⁵ A very small amount of **PC2** was found in the filtered solution after catalysis. Quantification by UV-vis determined that only 1.3% of the photocatalyst had leached from the MOF. This suggests that the leaching of **PC2** into the solution is not the source of the diminishing catalytic activity of **MOF-520-PC2**.

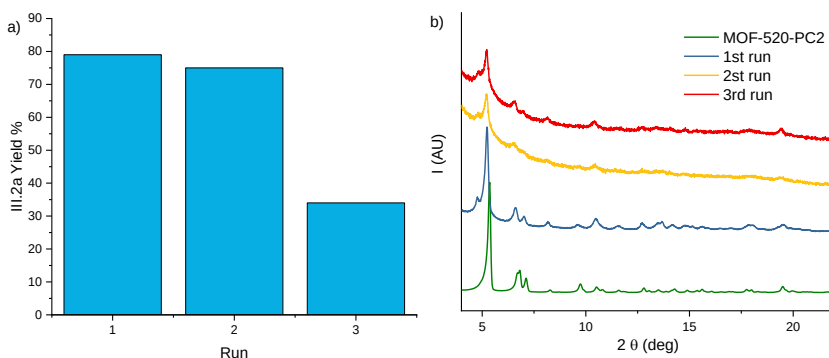


Figure 3.11. a) Yield for the pinacol coupling of **III.1a** catalyzed by **MOF-520-PC2** over several runs. The conditions employed are identical to Table 3.2. b) PXRD patterns of **MOF-520-PC2** after different catalytic runs.

3.2.6. Photocatalysis in flow

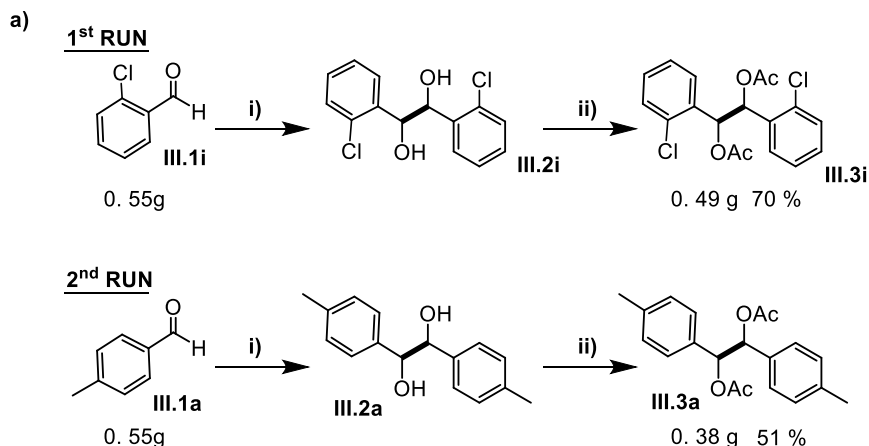
Taking advantage of the heterogeneous nature of MOF catalysts, we studied the potential use of **MOF-520-PC2** as a photocatalyst under flow conditions.^{44–46} Indeed, flow chemistry has many advantages, such as easy scaling and automation.⁴⁷ However, low light penetration is probably the reason for the few photocatalysis applications with heterogeneous materials under flow conditions.

The nature of the developed material (**MOF-520-PC2**) encouraged us to develop a heterogeneous photocatalytic system operative under flow conditions. We selected prototype substrates with different electronic

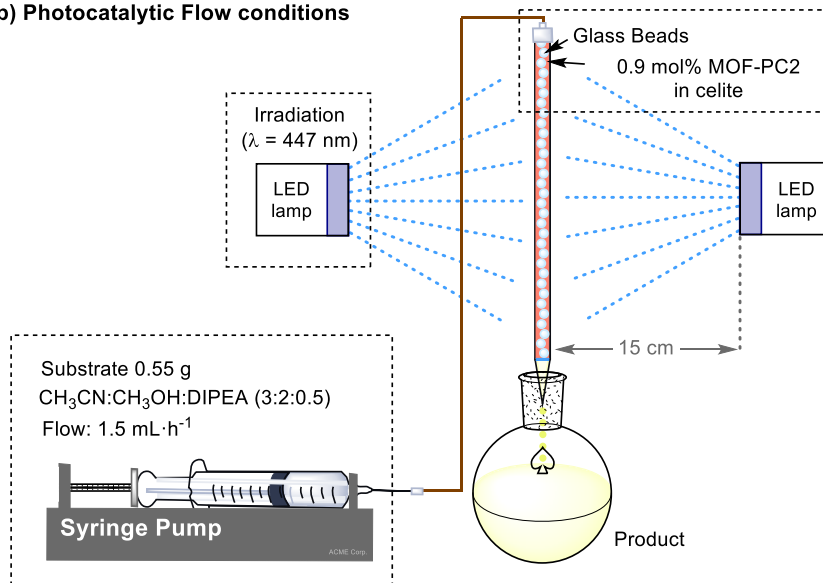
CHAPTER III: Preparation of photocatalytically active
Metal-Organic Frameworks through crystal-to-crystal
transformations

properties, **III.1i** and **III.1a**, for testing. To set up the flow reactor, we prepared a 1% dilution of **MOF-520-PC2** in Celite and directly packed it into a column (20x0.6 cm) with glass beads to facilitate light diffusion (Figure 3.12). Packing was carried out under aerobic conditions without any particular precautions. The reaction mixture contained the substrate and electron donor under identical conditions to those already discussed and optimized for batch reactions. The photoreactor was irradiated perpendicular to the surface from two light sources (Kessil lamp, $\lambda = 450$ nm) at 180 ° to each other (Figure 3.13). The first solution containing **III.1i** (0.55 g) was pumped through the photoreactor (flow rate of 1.5 mL·h⁻¹), followed by **III.1a** (0.55 g) after washing. Notably, sample preparation and photoreactions were performed in air, which further demonstrated the robustness of the catalytic system. As a result, the two consecutive 0.55 g scale reactions led to the isolation of products **III.3i** and **III.3a** in good overall yields (0.49 and 0.38 g, respectively, corresponding to 70 and 51% yield after two reactions, respectively), which validated the effectiveness of the system.

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations



b) Photocatalytic Flow conditions



ii) Acylation conditions: $(\text{Ac})_2\text{O}$, DMAP in pyridine at r.t. for 24 h

Figure 3.12. a) Consecutive photocatalytic reduction of aldehydes **III.1i** and **III.1a** to the corresponding pinacols in flow with the same **MOF-520-PC2/celite** packed column. b) Schematics of the experimental setup.

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

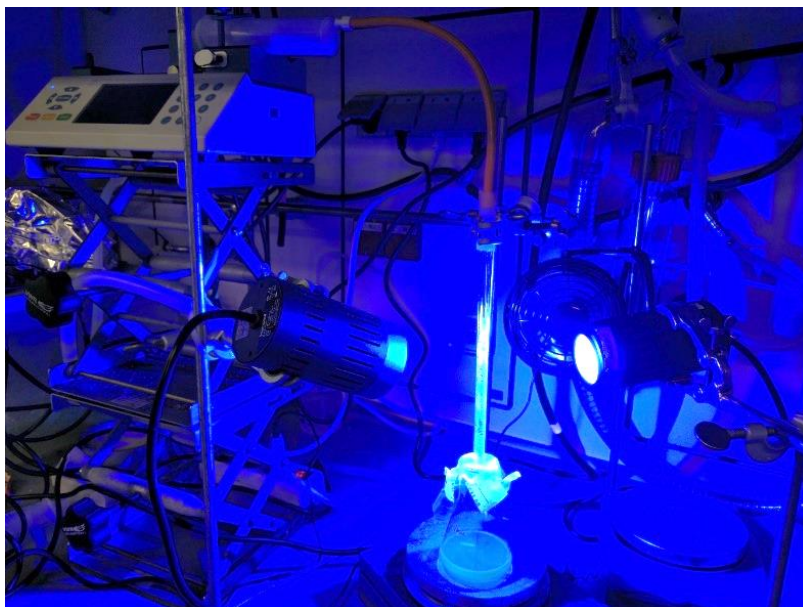


Figure 3.13. Image of the flow experimental setup.

3.2.7. Photophysical and electrochemical characterization.

To better understand the nature of the catalytic sites, we have investigated the photophysical and electrochemical properties of the materials, focusing on **MOF-520-PC1** and **MOF-520-PC2**, as well as their homogeneous analogues **PC1** and **PC2**

First, spectroscopic studies were performed to give insights into potential interactions between perylenes, or perylenes and the MOF matrix. Diffuse reflectance spectra of **PC1** and **PC2** showed broad absorption bands characteristic of the perylene monomer and a sharper band at $\lambda \approx 430$ nm (Figure 3.14).⁴⁸ In both cases, encapsulation in **MOF-520** only induced minor changes in absorbance, which suggested that the electronic structure of the PC was not significantly altered in the solid state.

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

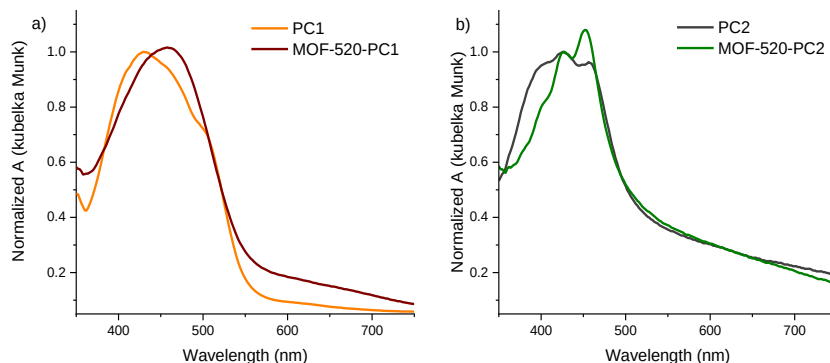


Figure 3.14. Solid-state absorption spectra of a) **PC1** and **MOF-520-PC1** and b) **PC2** and **MOF-520-PC2**, were obtained after normalizing the transmittance spectra with Kubelka Munk transformations.

Absorption and luminescence studies in solution, or suspensions in the case of MOFs, were more informative regarding potential aggregation processes. The UV/Vis features of **PC1** and **PC2** are located in the visible region, without overlap with the **MOF-520** absorption of the BTB linkers ($\lambda=276$ nm), facilitating analysis of the postmodified MOFs (Figure 3.15).

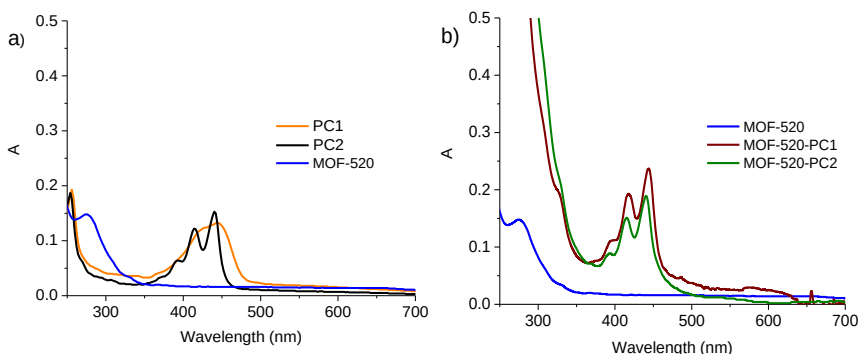


Figure 3.15. a) Absorption spectra of **PC1**, **PC2** and **MOF-520** in CH_3CN , $[\text{PC}] = 30\mu\text{M}$, b) the respective absorption spectra of **MOF-520**, **MOF-520-PC1** and **MOF-520-PC2** suspension in CH_3CN , $[\text{MOF-520-PCs}] = 1\text{ mg}\cdot\text{mL}^{-1}$.

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

The UV/Vis absorption spectra of **PC1** and **PC2** show broad bands ($\lambda = 360\text{--}470\text{ nm}$). In the case of **PC1** (Figure 3.16a), the characteristic vibrational fine structure of the perylene is not resolved, even at concentrations as low as $1\text{ }\mu\text{M}$, whereas, in the case of **PC2** (Figure 3.16a), the characteristic vibronic spectra of perylene monomers is present ($1\text{--}25\text{ }\mu\text{M}$). Presumably, the difference arises from the different capacities of **PC1** and **PC2** to form p-stacking structures, which is likely to be more favorable for **PC1**, since the formation of carboxylic acid homodimers duplicates the size of the p-conjugated structure. This agrees with the fact that the presence of a base, such as DIPEA (5 mM), resolves the characteristic vibronic spectra of perylene monomers for **PC1** (Figure 3.16a), since it disrupts the formation of homodimers. Interestingly, in the absorption spectra of the MOF-520-PCs, perylene vibronic features are present for both cases; this suggests negligible perylene–peryene interactions or MOF–peryene interactions.

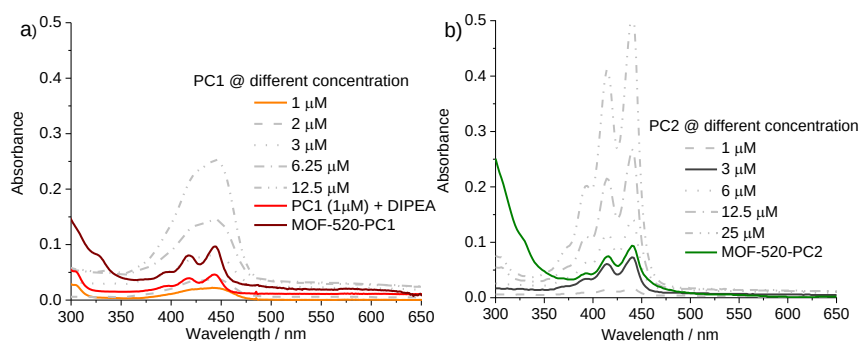


Figure 3.16. Absorption spectra of a) **PC1** b) **PC2** measured upon increasing its concentration and further compared with the same in the presence of DIPEA or with a suspension of a) **MOF-520-PC1** b) **MOF-520-PC2** (1 mg/mL), Solvent CH_3CN , DIPEA (5 mM).

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

To further understand the aggregation behavior of perylenes inside the MOF matrix, we also recorded fluorescence spectra of PCs in the concentration range from 1 to 100 μM , as well as suspensions of MOF-520-PCs (Figure 3.17). Similar to the UV/Vis absorption spectra, fluorescence spectra of **PC1** showed unresolved vibronic features, which appeared in the presence of DIPEA and perfectly matched the spectrum of the suspended **MOF-520-PC1** (Figure 3.17a). Also, the fluorescence spectra of **PC2** and **MOF-520-PC2** were informative (Figure 3.17b). As the concentration increases, the luminescence vibronic bands at $\lambda = 445 \text{ nm}$ decrease and the feature at $\lambda = 475 \text{ nm}$ rise, revealing an aggregation process between perylene units, which is not revealed in the studied UV/Vis spectral range (Figure 3.16b). The fluorescence spectrum of MOF-520-PC2 matches with that of **PC2** only at low concentration (1 μM photocatalyst), which indicates that **PC2** behaves as a monomer inside of the **MOF-520**.^{49–51}

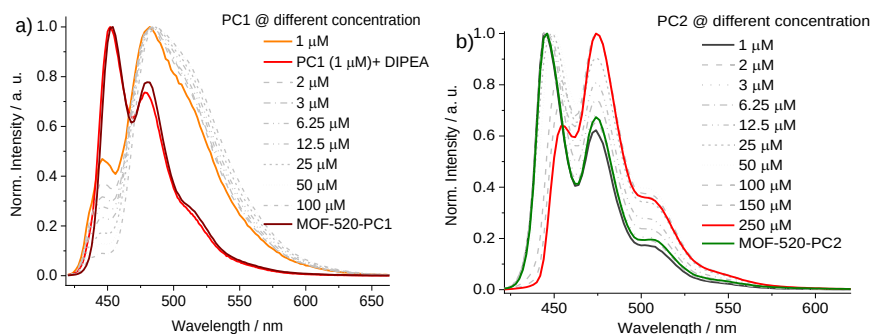


Figure 3.17. Fluorescence spectra of a) **PC1** b) **PC2** measured upon increasing its concentration and further compared with the same in the presence of DIPEA or with a suspension of a) **MOF-520-PC1** b) **MOF-520-PC2** (1 mg/mL), Solvent CH_3CN , DIPEA (5 mM), $\lambda_{\text{ex}} = 410 \text{ nm}$.

Cyclic voltammetry (CV) experiments showed apparent differences between perylene precursors (Figure 3.18a). The first reduction wave of **PC2** is shifted by 340 mV to more negative potentials than **PC1** ($E^0_{\text{PC2}} = -1.80$ V and $E^0_{\text{PC1}} = -1.45$ V, respectively). All redox values are given versus a standard calomel electrode (SCE), unless stated otherwise (Table 3.7). Although the cyclic voltammograms of the MOFs follow a similar trend to that of the perylene precursors, the interpretation is not straightforward. The CV results for **MOF-520** show two reduction waves that shift to positive and negative redox potentials in **MOF-520-PC1** and **MOF-520-PC2**, respectively (Figure 3.18b). We observed that the extension of the shifts depended on the perylene. The shift was more significant in the case of **MOF-520-PC1**, in which the perylene is electronically connected to the carboxylate and then to the aluminum centers. Conversely, for **MOF-520-PC2**, the perylene–Al centers are electronically disconnected by an alkyl spacer, which barely affects the redox process of the MOF.⁴⁸ Nevertheless, because the absorption and fluorescence spectra do not undergo significant changes, we estimate that the redox potentials of PCs within the MOF do not significantly deviate from those of the free PCs. Therefore, we hypothesize that the redox difference between the two materials can be ascribed as the main factor for the differences in catalysis.

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

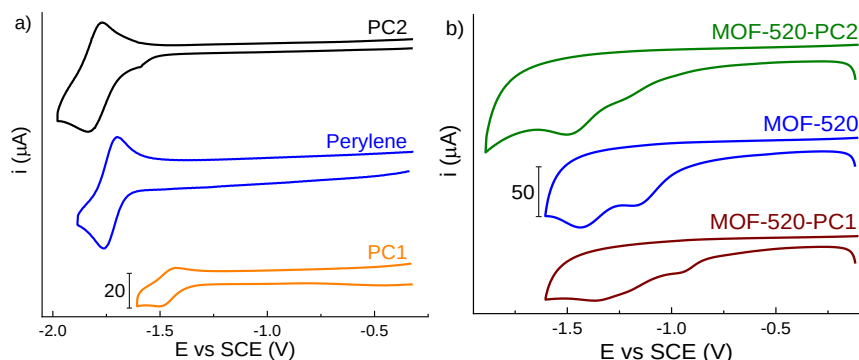


Figure 3.18. a) CV of **PC1**, **PC2** and perylene, b) CVs of **MOF-520-PC1**, **MOF-520-PC2** and **MOF-520**. Conditions are shown in the experimental section.

Finally, we characterized the excited states using time-correlated single-photon counting in the solid state (Figure 3.19). In both cases, the multiexponential lifetime decay of PCs is similar to that of the MOF-520-PCs (Table 3.7); the slowest $\tau_{1/2}$ is about 6 ns for **PC1** and 5 ns for **PC2**.^{50,52,53} This result, together with those previously reported, is in agreement with the fact that both PCs behave as isolated units inside the **MOF-520**.

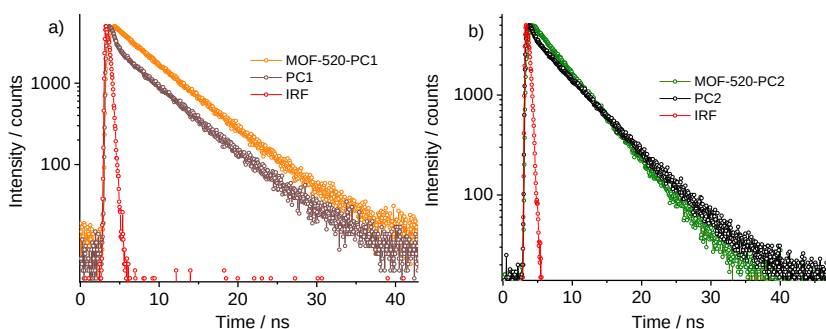


Figure 3.19. Normalized solid-state lifetime decay of a) **PC1**, **MOF-520-PC1**, and b) **PC2**, **MOF-520-PC2** measured by time-correlated single-photon counting and its exponential fits. $\lambda_{\text{ex}} = 470$ nm laser, $\lambda_{\text{em}} = 560$ nm. (IRF = instrument response function from the laser source). $[\text{PC}] = 50 \mu\text{M}$, $[\text{MOF-520-PC}] = 1 \text{ mg/ml}$. Solvent CH_3CN .

Table 3.7. Summary of the redox processes and excited-state lifetimes in solution.

Sample	λ_{abs}^a [nm]	λ_{em}^b [nm]	τ_l^c [ns]	$E_{1/2}^{(0/-)}$ [V vs. SCE]	$E^{(*/-)}^d$
PC1	442	452	5.5	-1.45	1.30
PC2	440	446	4.9	-1.80	0.98
MOF-520	275	390	-	-	-
MOF-520-PC1	445	454	6	-	-
MOF-520-PC2	440	448	5	-	-

^a Values obtained from the maximum absorption peak; ^b values obtained from the maximum fluorescence peak; ^c lifetime obtained from the single exponential function fit at the λ_{em} . Absorption and fluorescence spectra are collected CH₃CN/CH₃OH (v:v = 3:2). ^d Calculated as $E^o(*PC / PC^-) = E^o(PC / PC^-) + E_{0-0}$, Section 3.2.8.

3.2.8. Mechanistic studies

To gain insights into the reductive coupling reaction of aldehydes, we examined key steps of the catalytic cycle with the help of steady-state, time-resolved fluorescence quenching studies and transient spectroscopy experiments. To this end, we have focused on the model reaction of **III.1a** with **MOF-520-PC2**, in the absence and presence of DIPEA.

Quenching studies were performed on **MOF-520-PC1** and **MOF-520-PC2** by measuring the lifetime decay and fluorescence spectra with increasing amounts of DIPEA (Figure 3.20). The lifetime of the MOF-520-PCs* excited states was long enough to be quenched by DIPEA, as observed by the gradual decrease in lifetime and fluorescence intensity (Figure 3.20a and Figure 3.20d). Similar bimolecular quenching rate constants (k_q) were obtained by Stern-Volmer analysis (Figure 3.20c, Figure 3.20f and Table 3.8) for **MOF-520-PC1** ($6.0 \pm 0.3 \cdot 10^9 \text{ M}^{-1}\text{s}^{-1}$) and for **MOF-520-PC2** ($5.9 \pm 0.3 \cdot 10^9 \text{ M}^{-1}\text{s}^{-1}$, see experimental section for calculation details), suggesting that quenching occurs at similar speeds for both photocatalysts.

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

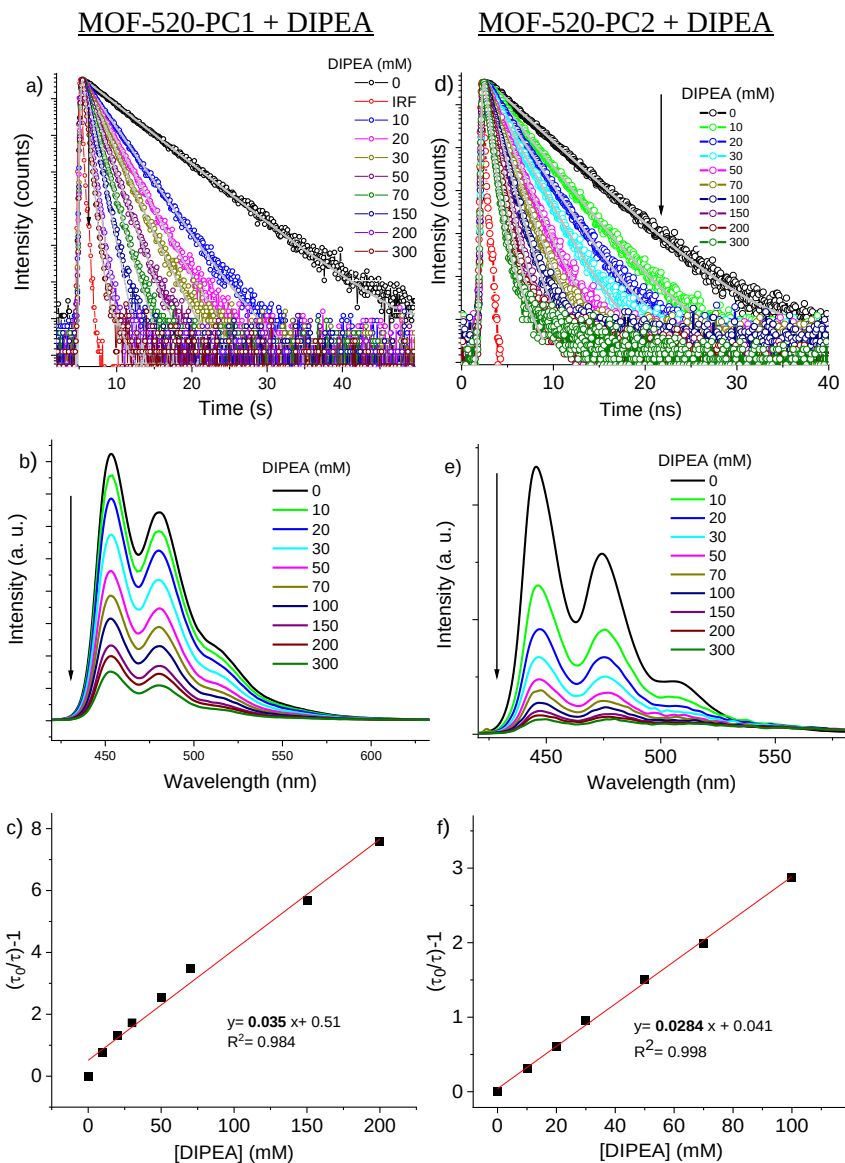


Figure 3.20. Titration lifetime decay (a,d); titration fluorescence decay (b,e) and Stern-Volmer quenching analysis (c,f) of **MOF-520-PC1** (a-c) and **MOF-520-PC2** (d-f) with DIPEA in CH₃CN/CH₃OH solvent mixture (v:v = 3:2, 2 mL). $\lambda_{ex} = 405$ nm laser, $\lambda_{em} = 460$ nm, [MOF-520-PCs]=1 mg/ml, cell path length 1 cm, T = 25 °C.

Table 3.8. Biexponential fitting parameters of excited state lifetime decay

DIPEA mM	MOF-520-PC1					MOF-520-PC2				
	τ_1 ns	A ₁ %	τ_2 ns	A ₂ %	χ^2	τ_1 (ns)	A ₁ (%)	τ_2 (ns)	A ₂ (%)	χ^2
0 ^a	6	100			1.2	5	100			1.2
10	0.04	5	3.4	95	1.1	0.77	4	3.8	96	1.2
20	0.03	6	2.64	94	1.2	0.72	6	3.12	94	1.2
30	0.0012	2	2.21	98	1.08	0.21	5	2.55	95	1.3
50	0.001	1	1.72	99	1.04	0.41	8	2.0	92	1.3
70	0.03	10	1.34	90	0.98	0.36	10	1.67	90	1.3
150	0.001	20	1.04	80	1.3	0.2	12	1.29	88	1.3
200	0.05	30	0.65	70	1.4	0.42	15	1.15	85	1.4

A₁ and A₂ correspond to the relative contributions of the two lifetimes, τ_1 and τ_2 .

Upon studying **III.1a** as a quencher, we could not observe quenching at concentrations relevant for catalysis (Figure 3.21). This shows that an electron transfer between the excited photocatalyst (PC*) and the substrate is not a relevant process for the catalytic cycle.

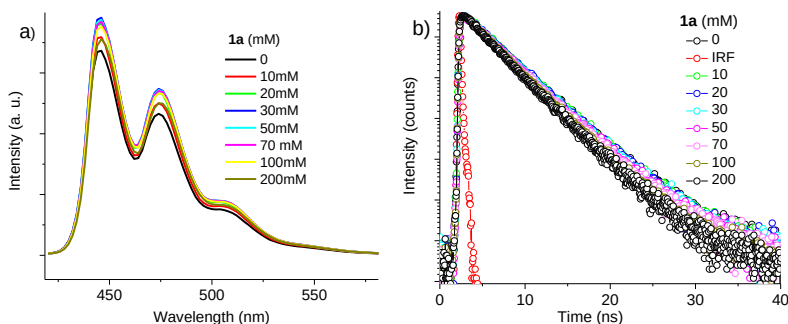


Figure 3.21. Oxidative electron transfer between **MOF-520-PC2** and substrate **III.1a**. a) Fluorescence spectra and b) Fluorescence lifetime changes during the titration of **MOF-520-PC2** with different amounts of **III.1a** (under constant stirring on the sample holder), solvent CH₃CN and MeOH (40 %) mixture, [**MOF-520-PC2**] = 1 mg/ml, λ_{ex} = 405 nm laser, λ_{em} = 460 nm, cell path length 1 cm, Temperature = 25 °C.

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

The excited state reduction potentials for the PCs were calculated as $E^{\circ}(*PC / PC^{-}) = E^{\circ}(PC / PC^{-}) + E_{0-0}$. The E_{0-0} energy was determined as 2.75 and 2.78 eV for **PC1** and **PC2**, respectively, based on the wavelength of the first emission peak (Table 3.7). Combining this result with the redox potentials in the ground state measured by CV (Table 3.7) produced the following redox values in the excited state: $E(*PC1/PC1^{-}) = 1.25$ V and $E(*PC2/PC2^{-}) = 1.0$ V. A comparison of these values with the redox potential of DIPEA ($E_{(DIPEA)}^0 = 0.72$ V)⁵⁴ suggests that a single electron transfer (SET) between DIPEA and PC* is thermodynamically feasible. Likewise, SET from DIPEA to MOF-520-PC* should also be thermodynamically feasible.^{55,56}

Transient absorption spectroscopy (TAS) was employed to study the formation and decay of the radical anion **PC2⁻** and **MOF-520-PC2⁻** (Figure 3.22, Table 3.9). In the case of **PC2**, laser excitation at $\lambda = 355$ nm in the presence of a large excess of DIPEA led to the formation of a new absorption band at $\lambda = 570$ nm, assigned to **PC2⁻** (Figure 3.22a). A negative band also appears at $\lambda = 450$ nm, corresponding to the consumption of **PC2**. As expected, the formation of the radical anion is not detected in the absence of DIPEA. Monitoring the radical anion at $\lambda = 570$ nm presented a biexponential decay time of about 0.75 and 3.6 ms (Figure 3.22c and Table 3.9), which could be rationalized as recombination on the millisecond timescale. Strangely, the negative signal at $\lambda = 450$ nm changes rapidly and becomes a positive signal after 0.15 ms, reaching a maximum at 0.6 ms and decaying slowly afterwards (Figure 3.22e). This could indicate that another transient species with an absorbance band at $\lambda = 450$ nm is being generated, although its identity is yet unknown. The TAS spectrum of **MOF-520-PC2** shows similar characteristics, with absorption bands at $\lambda = 450$ and 570 nm,

but presenting a shorter lifetime (Figure 3.22b and Table 3.9). Interestingly, the absorbance at $\lambda = 450$ increases much more rapidly in **MOF-520-PC2**, suggesting that immobilization of the PC has a strong effect over this process. Lastly, measurements were performed in the presence of **III.1a**, leading to shorter lifetimes for **PC2** and **MOF-520-PC2** (Figure 3.22c-d and Table 3.9). This is consistent with the occurrence of a SET between the radical anion (**PC2^{•-}**) and **III.1a**.

Table 3.9. Biexponential fitting parameters of transient absorption decay of **PC2** and **MOF-520-PC2** with DIPEA in the presence or absence of **III.1a**.

Sample	τ_1 ms	A_1 %	τ_2 ms	A_2 %	χ^2
PC2 +DIPEA	0.75	54	3.6	46	0.97
PC2 +DIPEA+ III.1a	0.44	63	3.0	37	0.95
MOF-520-PC2 +DIPEA	0.25	37	1.7	63	0.93
MOF-520-PC2 +DIPEA+ III.1a	0.25	50	2.3	50	0.66

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

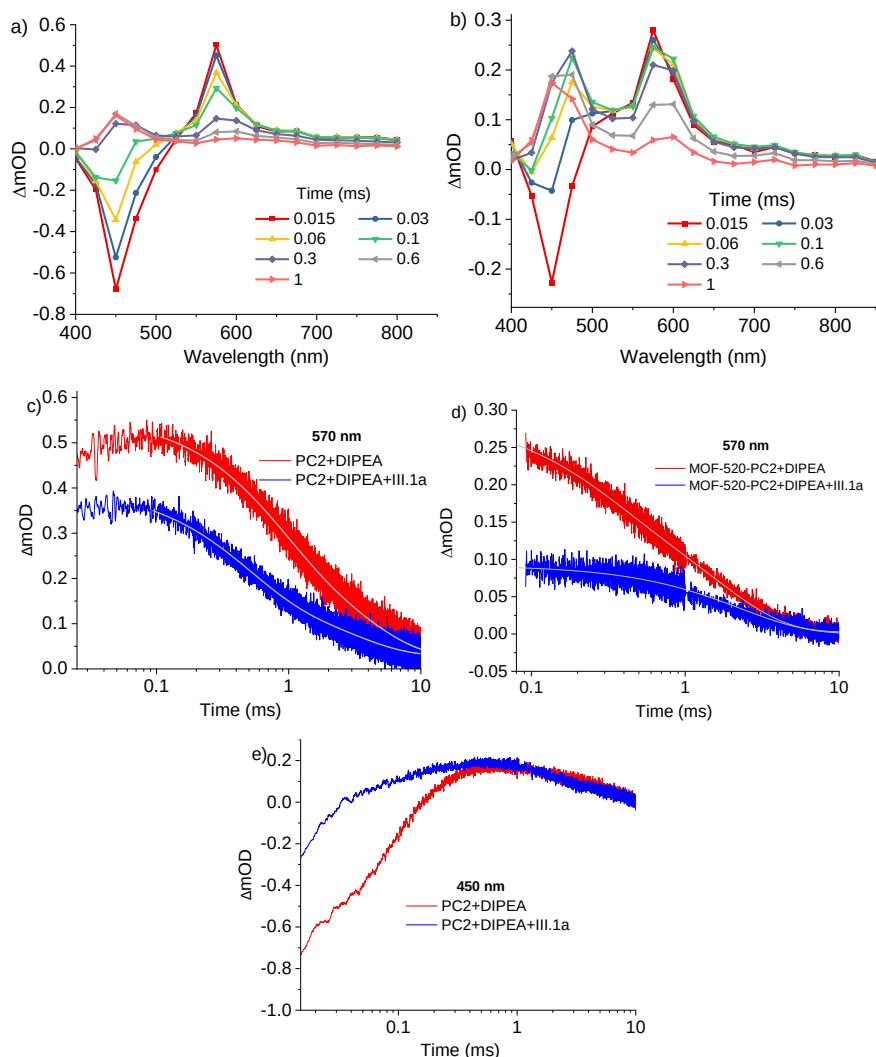
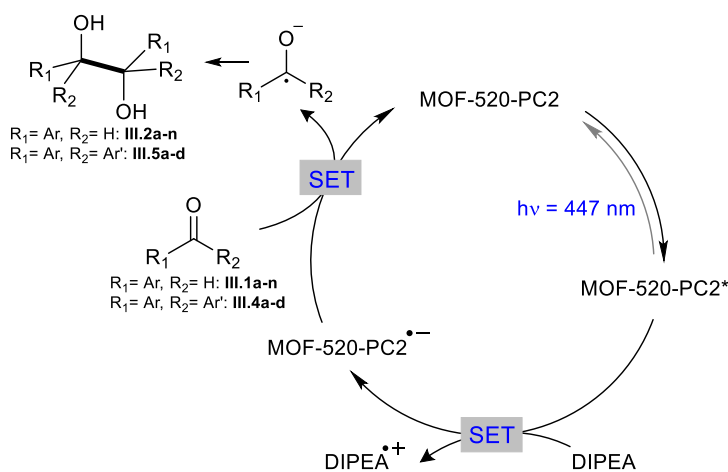


Figure 3.22. Transient absorption spectra for: a) PC2 (50 μM) and DIPEA (200 mM); b) MO-520-PC2 (50 μM) and DIPEA (200 mM). Transient absorption decay probed at 570 nm for: c) PC2 (50 μM), DIPEA (200 mM) and III.1a (40 mM), d) MOF-520-PC2 (1 mg/mL), DIPEA (200 mM) and III.1a (40 mM). All measurements were performed in CH₃CN under anaerobic condition. Laser excitation at 355 nm.

Based on the results shown in this section, a mechanism for the photocatalytic reductive coupling was proposed (Scheme 3.3). The reaction starts with the excitation of **MOF-520-PC2** ($\lambda = 447$ nm) into **MOF-520-PC2***. This process was studied by absorbance, fluorescence and lifetime decay experiments (Figure 3.15, Figure 3.16, Figure 3.17 and Figure 3.19). The excited state undergoes reductive quenching with DIPEA yielding **MOF-520-PC2^{•-}**, as shown by the quenching studies, the transient absorption measurements and the redox values (Figure 3.20, Figure 3.22, Table 3.8 and Table 3.9). A successive SET from **MOF-520-PC2^{•-}** onto the substrate (Figure 3.22) results in the reduction of the carbonyl group, followed by the C-C homocoupling reaction.⁴²



Scheme 3.3. Proposed mechanism of visible-light-driven reductive coupling reaction of aromatic aldehydes, acetophenones, and imines using MOF-520-PC2 photoredox catalyst.

3.3. Conclusions

In this chapter, we have shown a straightforward postsynthetic transformation of **MOF-520** with differently substituted perylene molecules to introduce a photoredox functionality to the material. As determined by the redox potential, differences in the catalytic activity between **MOF-520-PC1** and **MOF-520-PC2** can be ascribed to the redox potential differences between the reduced state of the PCs; **PC2** is more reductive than **PC1**.

The new heterogeneous organo-photocatalysts performed the light-driven reductive coupling of aldehydes, ketones, and imines efficiently to give 1,2-diols and 1,2-diamines, with similar catalytic activity to their homogeneous counterpart. Moreover, continuous-flow photocatalytic conditions highlight the potential of this technique to enhance the recyclability of the catalyst and to perform gram-scale reactions.

Combining steady-state and time-resolved spectroscopy revealed that perylenes immobilized in **MOF-520** acted as an isolated unit, and therefore, the catalytic activity could be exclusively ascribed to the perylene monomer, whereas in the homogeneous phase the potential aggregation of perylenes complicated the assignment of the real catalytically active species.

3.4. Experimental section

3.4.1. Materials and methods

Materials. Reagents and solvents were purchased from commercial sources and used as received unless otherwise stated. Aluminium nitrate nonahydrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, N,N-dimethylformamide (DMF) (purity $\geq 99.9\%$) and formic acid (ACS reagent, reagent grade, $\geq 98\%$) were purchased from Sigma Aldrich. 1,3,5-benzenetricarboxylic acid (H_3BTB) and perylene were purchased from Alfa Aesar and Fluorochem, respectively. All chemicals obtained were used without further purification. Scintillation vials (20 mL) and polypropylene caps with foil liner were purchased from Wheaton.

Nuclear magnetic resonance (NMR). NMR spectra were recorded on Bruker AV500/AV400 spectrometer using standard conditions (300 K). All ^1H chemical shifts are reported in ppm and have been internally calibrated to the residual protons of the deuterated solvent. The ^{13}C chemical shifts have been internally calibrated to the carbon atoms of the deuterated solvent. The coupling constants were measured in Hz.

Powder X-ray diffraction (PXRD). PXRD patterns were recorded on a D8 Advance Series 2Theta/Theta powder diffraction system using $\text{CuK}\alpha_1$ -radiation in transmission geometry. The system is equipped with a VÅNTEC-1 single-photon counting PSD, a Germanium monochromator, a ninety positions auto changer sample stage, fixed divergence slits and a radial soller.

Single X-ray diffraction (SXRD).

Sample preparation: The crystals used for structure determination were selected using a Zeiss stereomicroscope using polarized light and handled

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

under inert conditions immersed in perfluoropolyether as protecting oil for manipulation.

Data collection: Crystal structure determination for MOF samples were carried out using an Apex DUO Kappa 4-axis goniometer equipped with an APPEX 2 4K CCD area detector, a Microfocus Source E025 IuS using MoK α radiation, Quazar MX multilayer Optics as monochromator and an Oxford Cryosystems low-temperature device Cryostream 700 plus (T = -173 °C). Fullsphere data collection was used with ω and φ scans. Data collection was performed with APEX-2. Data reduction was performed with Bruker Saint V/.60A. Absorption correction was performed with SADABS.

Structure Solution and Refinement: Crystal structure solution was achieved using the computer program SHELXT. Visualization was performed with the program SHELXle. Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on F² using all measured intensities was carried out using the program SHELXL 2015. All non-hydrogen atoms were refined including anisotropic displacement parameters.

Thermogravimetric analysis (TGA). TGA curves were measured using Mettler Toledo TGA/SDTA/851 in N₂ with heating ramp 5 °C/min.

Gas Sorption. Nitrogen sorption isotherms were measured on Autosorb iQ adsorption analyzer (Quantachrome). Nitrogen measurements were performed at 77 K and the temperature was held constant using liquid N₂. The pressure range used to calculate the BET surface area was selected to fulfil the two “consistency criteria.”

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

In-house developed parallel photoreactor. *Light source:* The reactions were performed using Royal-Blue ($\lambda = 447 \pm 20$ nm) LUXEON Rebel ES LED, mounted on a 10mm Square Saber - 1030 mW @ 700 mA (Datasheet: <https://www.luxeonstar.com/assets/downloads/ds68.pdf>) as a light source. *Temperature Control:* Reaction temperature was controlled by a high precision thermoregulation Hubber K6 cryostat. Likewise, to guarantee stable irradiation the temperature of the LEDs was also controlled and set up at 30 °C. For the flow process was run with the Kessil LED lamp.

Photophysical Studies. UV-Vis measurements were carried out on a Shimadzu UV-2401PC spectrophotometer equipped with a photomultiplier tube (PMT) detector, double beam optics and D₂ and W light sources. The solid-state diffuse reflectance spectra (240-800 nm) were recorded by diluting the solid samples with BaSO₄ powder while equipped Shimadzu UV-2401PC spectrophotometer connected with a diffuse reflectance accessory. The samples were loaded in an integration sphere and utilized for all experiments.

Solid-state fluorescence measurements were carried out on an Aminco-Bowman Series 2 Luminescence spectrofluorometer equipped with a high voltage PMT detector and continuum Xe light source with detector under parallel mode. Sample preparation was the same as that of absorption experiments. Fluorescence lifetimes were determined using an Edinburgh Instruments LifeSpec-2 luminescence spectrometer equipped with a PMT detector, double subtractive monochromator and picosecond pulsed diode lasers source (470 nm). Exponential deconvolution fit was used to fit the emission decay by the FAST software from Edinburgh Instruments Ltd., with χ^2 values and intensity residuals used to determine goodness of fit. For all fitting results reported here, χ^2 values were close to unity. Where a single

exponential fit result was unsatisfactory, a dual-exponential fit was used. The sample preparation was the same as above.

Solid-state photophysical experiments were measured by loading a solid sample in 0.5 mm cuvette unless otherwise mentioned. The quenching experiments were performed by making fine heterogeneous suspension of MOFs in acetonitrile after sonication of 15 minutes. Prior to this, materials were ball milled for 15 minutes to get fine powders.

The lifetime decay is fitted with monoexponential or biexponential function depending on the absence or the presence of DIPEA in solvent acetonitrile and methanol suspension.

The Stern-Volmer analysis is based on eqs. 1-2:

$$\frac{I_0}{I_Q} \left(\text{or } \frac{\tau_0}{\tau_Q} \right) = 1 + K_{SV} [DIPEA] \quad (1)$$

$$K_{SV} = k_q \tau_0 \quad (2)$$

Where I_0 , I_Q , τ_0 and τ_Q are the luminescence intensities and excited-state lifetime at emission peak in the absence or in the presence of DIPEA, respectively, and K_{SV} is the Stern-Volmer quenching constant. The K_{SV} is calculated from the slope of the linear fitting of the plot, $\frac{I_0}{I_Q} \left(\text{or } \frac{\tau_0}{\tau_Q} \right) - 1$ versus DIPEA. The bimolecular quenching rate constant (k_q) is obtained from the value of K_{SV} and using the eq. (1), τ_0 is the lifetime of MOF-520-PC2 or MOF-520-PC1.

Laser Flash Photolysis. Laser flash photolysis was carried out by a pump-probe transient absorption spectroscopy (TAS) system involving Nd:YAG laser (355 nm, 6 ns pulse duration) from 25 ns to 100 ms. A two-monochromator setup with single wavelength detection was chosen to

minimize the samples exposition to probe light and to remove most of the fluorescence from the dye. A halogen bulb (640–890 nm) and a white light LED (500–640 nm), which provide very stable output power, were used as probing light sources. The light probe is selected by two Visible-IR motorized monochromators from Dongwoo Optron (DM500i model) placed before and after the sample holder. The probe light was detected with an amplified silicon photodiode (Hamamatsu S3883, 320–1000 nm spectral response range, 300 MHz bandwidth), and the dc signal was digitized with a 125 MHz bandwidth (200 MS/s, 16 bit resolution) transient recorder. The sample was stored in a sealed, 2 mm quartz cuvette under inert atmosphere and stirred between laser shots. The complete system was controlled by our home-build TAS software, and all kinetics were also processed by home-built software. The laser experiments were performed with fine heterogeneous suspension MOF-520-PC2 under constant stirring.

Electrochemical studies. Cyclic voltammetry (CV) experiments were carried out on a Biologic potentiostat/galvanostat connected to a three-electrode glass cell equipped with a glassy carbon as a working electrode, platinum wire as a counter electrode and an Ag/AgCl pseudo-reference electrode. A solution of tetrabutylammonium hexafluorophosphate (TBAPF₆) 0.1 M in CH₃CN was used as an electrolyte and kept under Ar flow during the measurements. For the CV of the perylene derivatives, a stock solution was obtained by dissolving the corresponding PC (ca. 0.8 mg, 3 μmol) and TBAPF₆ (38.7 mg, 0.1 mmol) in 1 mL of DMF. After that, 500 μL of this solution was injected to a 2.5 mL solution of electrolyte in CH₃CN (for a final concentration of 0.5 mM). The electrochemical measurements carried out on MOF-520 and MOF-520-PCs were realized with the same configuration as before, but this time a MOF suspension (1 mg of the powder in 200 μL of a solution (1:1) (Nafion/CH₃CN) was

CHAPTER III: Preparation of photocatalytically active
Metal-Organic Frameworks through crystal-to-crystal
transformations

sonicated 20-30 minutes before drop-casting 10 μL onto the surface of a glassy carbon electrode and allowing it to rest 2 hours to dry. CVs were recorded at a scan rate between 100 to 1000 mV/s. All the potentials were referred to ferrocene couple (Fc/Fc^+), measured by direct injecting 100 μL of a solution containing Fc (10 mM) and TBAPF_6 (0.1 M).

Photoreactor description: The photoreactor is made up of aluminium support with an array of 5x5 cavities where vials can be placed. At the bottom of each cavity there is a Royal-Blue ($\lambda = 447 \pm 20$ nm) LUXEON Rebel ES LED, mounted on a 20 mm Saber - 1030 mW @ 700 mA (Datasheet: <https://www.luxeonstar.com/assets/downloads/ds68.pdf>) as a light source. Reactions were performed at a current intensity of 700 mA per LED, which corresponds to a $2.05 \cdot 10^{-3}$ mmol $\cdot$ h $\cdot$ y/s photons per second through the vials at the volume of the reaction as reported.⁵⁷ The temperature around the vials is controlled by a high precision thermoregulation Hubber K6 cryostat, using a mixture of water/glycol as a cooling fluid. Likewise, aiming at ensuring stable irradiation, another cryostat is used to maintain the temperature of the LEDs at 22 $^{\circ}\text{C}$. The reactor sits on a mechanical stirrer, which is used to stir simultaneously all the vials placed on the reactor.

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations



Figure 3.24. In-house developed parallel photoreactors.

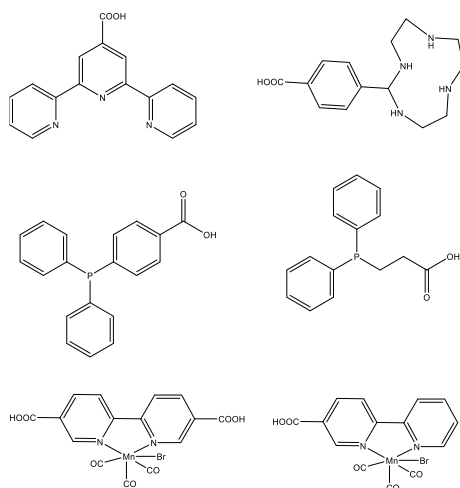
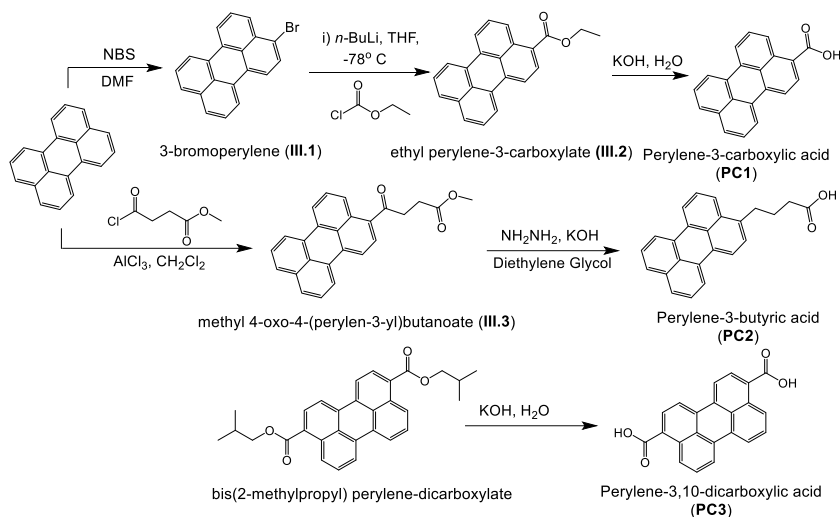


Figure 3.25. Failed attempts of incorporating ligands into MOF-520.

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

3.4.2. Synthetic procedures



3-Bromoperylene (III.1): III.1 was synthesized according to the published procedure.⁵⁸ Perylene (1.034 g, 4.106 mmol) was dissolved in dry *N,N*-Dimethylformamide (160 mL). After stirring for 15-20 minutes under nitrogen atmosphere, a solution of *N*-Bromosuccinimide (0.73 g, 4.101 mmol) in dry *N,N*-Dimethylformamide (30 mL) was injected through a syringe. The solution was stirred at room temperature for 24 h under a slow flow of nitrogen. Water (600 mL) was added, and the solution was stirred for 1 hour at room temperature. The resulting precipitate was separated through suction filtration, rinsed with water, and dried under vacuum. The precipitate was then recrystallized from hexane to afford 3-Bromoperylene as yellow crystals (yield: 1.27 mg, 93 %). ^1H NMR (500 MHz, CDCl_3) δ , ppm: 8.24-8.08 (m, 4H), 8.00-7.98 (d, 1H, $J = 8.1$ Hz), 7.77-7.75 (d, 1H, $J = 8.0$ Hz), 7.72-7.70 (m, 2H), 7.60-7.56 (m, 1H), 7.51-7.46 (m, 2H); ESI-MS : m/z (%): 331. (100) $[\text{M}+1]$.

Ethyl perylene-3-carboxylate (III.2): This compound was synthesized similarly to the procedure of pyrene-1-carboxylic acid.⁵⁹ Dry 3-

CHAPTER III: Preparation of photocatalytically active
 Metal-Organic Frameworks through crystal-to-crystal
 transformations

bromoperylene (0.5 g, 1.51 mmol) was dissolved in anhydrous THF (600 mL). This solution was placed into a Schlenk flask and cooled to $-78\text{ }^{\circ}\text{C}$ under argon. A solution of *n*-BuLi in hexane (1.6 M in hexanes, 1.0 mL) was added to the solution. The mixture obtained was stirred at $-78\text{ }^{\circ}\text{C}$ for 10 min, followed by addition of ethyl chloroformate (0.151 mL, 1.58 mmol) and stirring for 16 h at room temperature. After that, the reaction mixture was washed with an aqueous solution of NH_4Cl . The intermediate ethyl ester (**III.2**) was extracted with ethyl acetate ($3 \times 50\text{ mL}$). The extract was dried with anhydrous sodium sulfate. The solvents were evaporated at reduced pressure. The crude product was directly used for the next step, without further purification to yield **III.2** as a dark orange powder (0.357 g, 73 %). ^1H NMR (400 MHz, CDCl_3) δ , ppm: 8.84 (d, $J = 8.5\text{ Hz}$, 1H), 8.28-8.24 (m, 3H), 8.22-8.16 (m, 2H), 7.78-7.60 (m, 4H), 7.54-7.46 (m, 3H), 4.49 (q, 2H), 1.48 (t, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ , ppm: 167.6, 135.8, 134.6, 133.2, 131.4, 130.8, 130.5, 129.3, 128.2, 128.1, 127.0, 126.8, 126.7, 125.9, 121.9, 121.1, 120.7, 120.4, 119.1, 61.2, 14.6.; ESI-MS: m/z 324 (100) ($[\text{M}+1]$).

Perylene-3-carboxylic acid (PC1): Potassium hydroxide (1.5 g, 26.7 mmol) and ethyl perylene-3-carboxylate (0.250 g, 0.77 mmol) in water (10 mL) was added to ethanol (50 mL) and the mixture obtained was stirred with reflux for 24 h. The solution was filtered while hot. Water (100 mL) and hydrochloric acid (10% aqueous, to $\text{pH} = 4$) were sequentially added to the filtrate. A red precipitate was filtered off, washed with water several times, and dried in vacuum pump. The crude product was purified by column chromatography on silica gel, eluting with chloroform, to chloroform-methanol (15% chloroform) to give perylene-3-carboxylic acid (PC1) as a dark red powder (0.128 g, 56 %). m.p. $338\text{ }^{\circ}\text{C}$. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ , ppm: 13.25 (br, 1H), 8.81 (d, $J = 8.5\text{ Hz}$, 1H), 8.45-

CHAPTER III: Preparation of photocatalytically active
 Metal-Organic Frameworks through crystal-to-crystal
 transformations

8.40 (m, 4H), 8.14 (d, $J = 7.9$ Hz, 1H), 7.89-7.83 (m, 2H), 7.68 (dd, $J = 8.0$ Hz, 1H), 7.61-7.56 (m, 2H). ^{13}C NMR (101 MHz, DMSO- d_6) δ , ppm: 168.4, 134.5, 134.0, 132.4, 130.7, 130.5, 130.2, 129.5, 129.2, 128.3, 128.2, 128.0, 127.5, 127.1, 126.9, 125.5, 122.3, 121.5, 120.9, 119.7; ESI-MS: m/z 295 (100) ([M-1]).

3-perylenoylpropanoic acid methyl ester (III.3): This compound is synthesized according to the published procedure.³⁹ To a solution of methyl 4-chloro-4-oxobutrate (2.08 mL, 16.6 mmol) in dry dichloromethane (200 mL), was added aluminium chloride (2.54 g, 19.04 mmol) while stirring at 0 °C under nitrogen. The mixture was stirred at 0 °C for an hour before perylene (3.98 g, 15.84 mmol) was added. Then, the reaction mixture was stirred at room temperature for 18 hours. The solution was poured over ice (600 g) and acidified with concentrated hydrochloric acid. The product was extracted with dichloromethane (4 $\times$ 200 mL), and washed with water (2 $\times$ 50 mL). The organic layer was dried over MgSO_4 and filtered before removing the solvent under vacuum. The crude yellow solid was purified by column chromatography on silica gel, eluting with chloroform, to give **III.3** as a dark orange powder (5.08 g, 88%). ^1H NMR, (400 MHz, CDCl_3) δ : ppm: 8.57 (1H, d, $J = 8.5$ Hz), 8.28-8.19 (4H, m), 7.97 (1H, d, $J = 7.9$ Hz), 7.93 (1H, d, $J = 8.0$ Hz, Ar- H), 7.78-7.71 (2H, m), 7.62-7.58 (1H, m), 7.55-7.50 (2H, m), 3.75 (3H, s), 3.31 (2H, t, $J = 6.5$ Hz), 2.86 (2H, t, $J = 6.6$ Hz); ^{13}C NMR (CDCl_3 , 101 MHz) δ , ppm: 201.5, 173.9, 135.6, 134.6, 134.2, 132.0, 131.3, 131.1, 130.3, 130.2, 129.3, 128.8, 128.4 (2C), 128.3, 127.0, 126.7, 125.9, 121.9, 122.2, 120.9, 118.9, 52.0, 36.5, 28.7.

Perylene-3-butyric acid (PC2): PC2 was synthesized according to the published procedure.³⁹ To a suspension of 3-perylenoylpropanoic acid methyl ester (1.20 g, 3.27 mmol) in diethylene glycol (20 mL), hydrazine

CHAPTER III: Preparation of photocatalytically active
 Metal-Organic Frameworks through crystal-to-crystal
 transformations

hydrate (0.49 g, 9.85 mmol) and powdered potassium hydroxide (1.38 g, 24.58 mmol) were added under nitrogen. The reaction mixture was heated to 140 °C for 2 hours, before heating at 190 °C for 18 hours. The solution was cooled to room temperature and diluted with water (100 mL) before acidifying with concentrated hydrochloric acid (5 mL). The resulting precipitate was filtered off and washed with water to pH 7.0, followed by acetone. The filtrate was then washed with a mixture of chloroform and methanol (8:2, v/v), and concentrated under *vacuum*. The crude dark solid was purified by flash chromatography, eluting by gradient with chloroform to chloroform/methanol (8:2) to give perylene-3-butyric acid (0.67 g, 61%); m.p. 338 °C. ¹H NMR, (CDCl₃, 400 MHz δ, ppm = 8.23-8.12 (4H, m, Ar-*H*), 7.90 (1H, appt d, *J* = 8.5 Hz, Ar-*H*), 7.68-7.65 (2H, m, Ar-*H*), 7.53-7.47 (3H, m, Ar-*H*), 7.35 (1H, d, *J* = 7.5 Hz, Ar-*H*), 3.10 (2H, t, *J* = 7.5 Hz, CCH₂CH₂CH₂C(O)), 2.50 (2H, t, *J* = 7.0 Hz, CCH₂CH₂CH₂C(O)), 2.13 (2H, quin, *J* = 8.0 Hz, CCH₂CH₂CH₂C(O)); ¹³C NMR (CDCl₃, 101 MHz) δ, ppm: 180.0, 142.7, 139.3, 137.7, 136.9, 134.1, 133.6, 133.0, 132.7, 132.5, 132.2, 131.8, 131.5, 131.4, 131.3, 128.7, 124.9, 124.8, 124.5, 38.5, 37.3, 30.3; ESI-MS: *m/z* 337 (100) ([M-1].

Perylene-3,9-dicarboxylic acid (PC3): Perylene-3,9-dicarboxylic acid was synthesized with slight modification of the published procedure. Solvent green 5 (1 g, 2.2 mmol) and KOH (0.369 g, 6.6 mmol) were taken in 5 ml EtOH and 5 ml water, and heated to reflux for 16 h. After cooling down, the mixture was neutralized with 2 N HCl. The resulting red solid was washed with water (3 × 10 mL) and dried over vacuum. Yield: 0.821 g (89 %). ¹H NMR (400 MHz, DMSO) δ 8.87 (dd, *J* = 31.2, 8.4 Hz, 2H), 8.61 – 8.49 (m, 4H), 8.19 (dd, *J* = 8.0, 2.6 Hz, 2H), 7.74 (dt, *J* = 8.5, 7.0 Hz, 2H).

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

Synthesis of MOF-520 single crystals: MOF-520 was synthesized with a slight modification of the published procedure of Yaghi et al.³⁹ In a 20 mL scintillation vial, the mixture solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (30 mg, 0.080 mmol), H_3BTB (25 mg, 0.056 mmol), formic acid (450 μL , 119 mmol) in DMF (4 mL) was prepared. The vial was capped and incubated at 140 °C for 5 days. Block shaped clear single crystals were obtained. The single crystals were first washed with DMF (5 mL) two times per day for two days to remove the unreacted reagents in the pores. These crystals were used directly for the inclusion of guest molecules. Moreover, DMF solvent in the pore was exchanged with anhydrous acetone by washing the crystals with anhydrous acetone (5 mL) two times per day for three days.

Bulk scale synthesis: In the same vial type, a mixture containing $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (90.0 mg, 0.240 mmol), H_3BTB (75.0 mg, 0.170 mmol) in DMF (18 mL) was prepared. The vial was sonicated for 1 min and formic acid (1.40 mL, 0.037 mol) was added under air atmosphere. The vial was capped and placed in a preheated oven to 140 °C for 5 days. The crystalline MOF-520 material was washed as above and collected.

Ligand exchange of MOF-520: 0.01 mmol of the corresponding carboxylic acid ligand was dissolved in DMF (0.5 mL) in a GC vial. Good quality crystals of MOF-520 (1.0 mg) were added to the solution. The vial was capped and placed pre-heated oven at 50°C for 5 days. SXRD data was collected with a single crystal from this vial.

Bulk scale synthesis of MOF-520-PCs: the synthesis was run in a sealed 20 mL scintillation vial containing either PC1, PC2 or PC3 (300 mg), and bulk MOF-520 (100 mg) in DMF as a solvent for 5 days at 100 °C. The crystalline material was collected and washed with DMF and acetone for

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

two times per day for three days to remove unreacted linker. The bulk material was dried in vacuum.

3.4.3. Catalytic experiments

General procedure for catalysis: All the catalytic reactions were conducted in a 10 mL septum-capped vial placed in an orbital stirrer using in-house developed parallel photoreactor equipped with a LED light ($\lambda = 447 \pm 20$ nm) in a nitrogen atmosphere at 30 °C, unless otherwise indicated. III.1a (0.1 mmol, 12 mg), catalyst (1 μ mol), DIPEA (180 mg, 1.4 mmol) and the solvent (1.25 mL MeCN, 0.75 mL MeOH) were added to the vial. After irradiating the vials for 18 h, the solution was concentrated under reduced pressure. A known amount of 1,3,5-trimethoxybenzene, internal standard (I.S.) was added before measuring ^1H -NMR spectra for quantification.

Leaching test: After carrying out a catalytic reaction following the general procedure with MOF-520-PC1 or MOF-520-PC2 as catalyst (3 mg, 1 μ mol), the solution was filtered to remove the catalyst and the solvent was evaporated. The residue was dissolved in 2 mL of acetonitrile and an aliquot of this solution was diluted 80:1 (v:v). The quantification of PC's leaching was performed by calculating the concentration of the PCs in the diluted solution from the absorption spectra (peak position at 435 nm). According to the Beer-Lambert law, the PCs concentration in the supernatant is approx. 0.24 μM for both ($\epsilon = 10^5 \text{ M}^{-1}\text{cm}^{-1}$), that corresponds to overall concentration of 19.2 μM (due to the 80:1 dilution). Since the concentration of the MOF-520-PCs in the reaction vial is 0.47 mM (corresponding to 0.95 μmol in 2 mL of solvent mixture), the total concentration of the PCs in the MOF, based on a 44% and 71% incorporation of PC1 and PC2, respectively, is $[\text{PC1}] = 0.83 \text{ mM}$ and $[\text{PC2}] = 1.33 \text{ mM}$. Therefore, the

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

percentage of leaching corresponds to 2.3 % and 1.4 % for MOF-520-PC1 and MOF-520-PC2, respectively.

Recyclability test: The reductive coupling of 4-methylbenzaldehyde (**III.1a**) was carried out over 6 hours under the general conditions using MOF-520-PC2 as a catalyst. The catalyst was recovered from the reaction medium by filtration and it was washed with methanol and acetone twice. Several samples of MOF-520-PC2 obtained this way were combined in order to have more amount of sample. Part of the solid sample was submitted for PXRD analysis and the rest was used for the next catalytic cycle. This process was repeated three times.

Flow chemistry: MOF-520-PC2 (247 mg), celite (257 mg) and glass dust (494 mg) (weight ratio = 1:1:2) are mixed together to make a homogeneous mixture. Glass balls are used to enhance the reflection of light. A glass tube (20 cm long and the diameter 0.6 cm) is added first with glass wool at the bottom part and then with the glass balls (size: 2.5-3.5 mm, company: VWR) up to 15 cm. The solid mixture was filled in the void space of the tube containing glass balls. This glass tube is connected with a flow pump. Under illumination of light with two Kessil lamps ($\lambda=450$ nm), the fluid is moved at the rate of $1.5 \text{ mL} \cdot \text{h}^{-1}$ into the column under aerobic conditions.

General procedure of reductive coupling for aromatic aldehydes. Aromatic aldehyde **III.1(a-m)** (0.1 mmol), MOF-520-PC2 (1 mol%, 3 mg), DIPEA (180 mg, 14 equivalents respect to the substrate), and CH_3CN (1.2 ml) and MeOH (0.8 ml) were added to a 5 mL vial under N_2 . The resulting solution was irradiated using a LED light ($\lambda = 447$ nm) under stirring at 30 °C. After 16 h, the solution was concentrated under reduced pressure to obtain a mixture containing diol **III.2(a-m)**. To the mixture, acetic anhydride (2 mL), pyridine (2 mL), and DMAP (2 mg) were added, and the

CHAPTER III: Preparation of photocatalytically active
Metal-Organic Frameworks through crystal-to-crystal
transformations

solution was left at room temperature for 16 h. Then, it was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (Eluent: Hexane/EtOAc 9/1). The fractions were combined and concentrated under reduced pressure, affording diacetate **III.3(a-m)**. Each substrate was run in three vials in parallel reactions and combined together after the end of the reaction for isolation.

Reductive coupling reaction of 4-methylbenzaldehyde (III.1a). The reductive coupling reaction of **III.1a** (36 mg, 0.30 mmol) was performed under the same conditions as mentioned in the general procedure. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate), furnishing **III.3a** (mixture of *dl*- and *meso*-diastereomers; 36 mg, 73% yield) as yellow solid. ¹H NMR (CDCl₃, 400 MHz) δ, ppm: 7.14-7.04 (m, 16H), 6.06 (*meso*, s, 2H), 6.04 (*dl*, s, 2H), 2.35 (*meso*, s, 6H), 2.30 (*dl*, s, 6H), 2.09 (*dl*, s, 6H), 2.01 (*meso*, s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ, ppm: 169.84, 169.61, 138.08, 138.04, 133.26, 133.22, 128.91, 128.75, 127.57, 127.55, 77.21, 76.36, 21.20, 21.17, 21.07, 20.98

Reductive coupling reaction of benzaldehyde (III.1b). The reductive coupling reaction of **III.1b** (32 mg, 0.30 mmol) was performed under the same conditions as mentioned in the general procedure. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate), furnishing **III.3b** (mixture of *dl*- and *meso*-diastereomers; 35 mg, 78% yield) as pale-yellow solid. ¹H NMR (400 MHz, CDCl₃) δ, ppm: 7.63-7.59 (m, 4H), 7.57-7.54 (m, 8H), 7.36-7.31 (m, 4H), 6.19 (*meso*, s, 2H), 6.16(*dl*, s, 2H), 2.15 (*dl*, s, 6H), 2.08 (*meso*, s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ, ppm: 169.84, 169.67, 135.13, 135.03, 128.80, 128.76, 128.08, 128.03, 127.08, 127.05, 76.87, 76.27, 21.09, 21.02.

CHAPTER III: Preparation of photocatalytically active
Metal-Organic Frameworks through crystal-to-crystal
transformations

Reductive coupling reaction of 2-methoxybenzaldehyde (III.1c). The reductive coupling reaction of **III.1c** (41 mg, 0.30 mmol) was performed under the same conditions as mentioned in the general procedure. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate), furnishing **III.3c** (mixture of *dl*- and *meso*-diastereomers; 32 mg, 59% yield) as yellow solid. ^1H NMR (400 MHz, CDCl_3) δ , ppm: 7.39 (d, $J = 7.6$ Hz, 2H), 7.21 (dd, $J = 8.3, 5.5$ Hz, 4H), 7.05 (d, $J = 7.7$ Hz, 2H), 6.92 (t, $J = 7.5$ Hz, 2H), 6.83 (t, $J = 7.5$ Hz, 2H), 6.75 (t, $J = 8.3$ Hz, 4H), 6.67 (*meso*, s, 2H), 6.63 (*dl*, s, 2H), 3.74 (*dl*, s, 6H), 3.58 (*meso*, s, 6H), 2.13 (*meso*, s, 6H), 2.01 (*dl*, s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.67, 169.63, 156.75, 156.45, 128.98, 128.82, 127.79, 127.62, 125.37, 124.69, 119.89, 119.76, 110.28, 109.78, 70.62, 69.70, 55.46, 55.25, 21.11, 20.89.

Reductive coupling reaction of 3-methoxybenzaldehyde (III.1d). The reductive coupling reaction of **III.1d** (41 mg, 0.30 mmol) was performed under the same conditions as mentioned in the general procedure. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate), furnishing **III.3d** (mixture of *dl*- and *meso*-diastereomers; 30 mg, 56% yield) as yellow oil. ^1H NMR (400 MHz, CDCl_3) δ , ppm: 7.24-7.14 (m, 4H), 6.86-6.69 (m, 12H), 6.07 (*meso*, s, 2H), 6.02 (*dl*, s, 2H), 3.77 (*meso*, s, 6H), 3.73 (*dl*, s, 6H), 2.11 (*meso*, s, 6H), 2.05 (*dl*, s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ , ppm: 169.76, 169.57, 159.36, 159.28, 137.68, 137.51, 129.25, 129.06, 119.98, 119.83, 114.08, 113.99, 113.12, 112.98, 77.21, 76.24, 55.21 (2C), 21.04, 20.97.

CHAPTER III: Preparation of photocatalytically active
Metal-Organic Frameworks through crystal-to-crystal
transformations

Reductive coupling reaction of 4-methoxybenzaldehyde (III.1e). The reductive coupling reaction of **III.1e** (41 mg, 0.30 mmol) was performed under the same conditions as mentioned in the general procedure. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate), furnishing **III.3e** (mixture of *dl*- and *meso*-diastereomers; 28 mg, 53% yield) as yellow solid. ^1H NMR (400 MHz, CDCl_3) δ , ppm: 7.16 (*meso*, d, $J = 8.7$ Hz, 4H), 7.09 (*dl*, d, $J = 8.7$ Hz, 4H), 6.84 (*meso*, d, $J = 8.7$ Hz, 4H), 6.76 (*dl*, d, $J = 8.7$ Hz, 4H), 6.03 (*meso*, s, 2H), 6.02 (*dl*, s, 2H), 3.82 (*meso*, s, 6H), 3.77 (*dl*, s, 6H), 2.09 (*dl*, s, 6H), 2.01 (*meso*, s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ , ppm: 169.89, 169.62, 159.53, 159.47, 128.98, 128.93, 128.40, 128.34, 113.62, 113.46, 76.83, 76.12, 55.21, 55.16, 21.11, 21.00.

Reductive coupling reaction of 4-(tert-butyl)benzaldehyde (III.1f). The reductive coupling reaction of **III.1f** (49 mg, 0.30 mmol) was performed under the same conditions as mentioned in the general procedure. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate), furnishing **III.3f** (mixture of *dl*- and *meso*-diastereomers; 39 mg, 64% yield) as pale-yellow solid. ^1H NMR (400 MHz, CDCl_3) δ , ppm: 7.32-7.28 (m, 4H), 7.24-7.20 (m, 4H), 7.19-7.15 (m, 4H), 7.10-7.06 (m, 4H), 6.06 (*meso*, s, 2H), 6.04 (*dl*, s, 2H), 2.07 (*dl*, s, 6H), 1.97 (*meso*, s, 6H), 1.31 (*meso*, s, 18H), 1.26 (*dl*, s, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ , ppm: 170.00, 169.77, 151.37, 151.34, 133.41, 127.51, 127.31, 125.12, 125.06, 76.40, 34.69, 34.62, 31.44, 31.38, 21.21, 21.10.

Reductive coupling reaction 4-(trifluoromethyl)benzaldehyde (III.1g). The reductive coupling reaction of **III.1g** (52 mg, 0.30 mmol) was performed under the same conditions as mentioned in the general

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

procedure. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate), furnishing **III.3g** (mixture of *dl*- and *meso*-diastereomers; 49 mg, 75% yield) as light-yellow solid. ¹H NMR (400 MHz, CDCl₃) δ, ppm: 7.59-7.50 (m, 8H), 7.32-7.27 (m, 8H), 6.13 (*meso*, s, 2H), 6.08 (*dl*, s, 2H), 2.10 (*dl*, s, 6H), 2.06 (*meso*, s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ, ppm: 169.58, 169.51, 139.86, 139.63, 127.98, 127.90, 125.55, 125.51, 125.40, 125.36, 76.12, 75.76, 20.98, 20.96.

Reductive coupling reaction 4-fluorobenzaldehyde (III.1h). The reductive coupling reaction of **III.1h** (36 mg, 0.30 mmol) was performed under the same conditions as mentioned in the general procedure. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate), furnishing **III.3h** (mixture of *dl*- and *meso*-diastereomers; 36 mg, 71% yield) as pale-yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ, ppm: 7.19-7.13 (m, 9H), 7.13-7.07 (m, 4H), 7.02-6.88 (m, 14H), 6.02 (*meso*, s, 2.3x 2H), 5.99 (*dl*, s, 2H), 2.09 (*dl*, s, 6H), 2.02 (*meso*, s, 2.3x 6H). ¹³C NMR (101 MHz, CDCl₃) δ, ppm: 169.81, 169.61, 164.06, 161.60, 131.84, 131.81, 129.51, 129.43, 115.40, 115.19, 76.50, 75.82, 21.05.

Reductive coupling reaction 4-chlorobenzaldehyde (III.1i). The reductive coupling reaction of **III.1i** (42 mg, 0.30 mmol) was performed under the same conditions as mentioned in the general procedure. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate), furnishing **III.3i** (mixture of *dl*- and *meso*-diastereomers; 41 mg, 74% yield) as pale-yellow solid. ¹H NMR (400 MHz, CDCl₃) δ, ppm: 7.52-7.48 (m, 4H), 7.33-7.28 (m, 6H), 7.25-7.19 (m, 14H), 6.64 (s, 4H), 2.07 (*dl*, s, 6H), 2.01 (*meso*, s, 1.6x 6H). ¹³C NMR (101 MHz,

CHAPTER III: Preparation of photocatalytically active
Metal-Organic Frameworks through crystal-to-crystal
transformations

CDCl₃) δ , ppm: 169.28, 169.23, 134.14, 134.12, 133.81, 133.13, 129.69, 129.67, 129.62, 129.29, 129.21, 128.91, 126.71, 126.53, 72.06, 71.97, 20.97, 20.83.

Reductive coupling reaction 3,5-di-tert-butylbenzaldehyde (III.1j). The reductive coupling reaction of **III.1j** (41 mg, 0.20 mmol) was performed under the same conditions as mentioned in the general procedure. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate), furnishing **III.3j** (mixture of *dl*- and *meso*-diastereomers; 39 mg, 75% yield) as white solid. ¹H NMR (400 MHz, CDCl₃) δ , ppm: 7.30 (*meso*, t, *J* = 1.8 Hz, 2H), 7.21 (*dl*, t, *J* = 1.8 Hz, 2H), 7.02 (*meso*, d, *J* = 1.8 Hz, 4H), 6.89 (*dl*, d, *J* = 1.8 Hz, 4H), 6.16 (*meso*, s, 2H), 6.03 (*dl*, s, 2H), 2.14 (*dl*, s, 6H), 2.07 (*meso*, s, 6H), 1.27 (*meso*, s, 36H), 1.20 (*dl*, s, 36H). ¹³C NMR (101 MHz, CDCl₃) δ , ppm: 170.07, 169.72, 150.48, 150.27, 135.39, 134.99, 121.81, 121.65, 78.64, 76.82, 34.74, 34.68, 31.42, 31.40, 21.24, 21.07.

Reductive coupling reaction 4-cyanobenzaldehyde (III.1k). The reductive coupling reaction of **III.1k** (39 mg, 0.30 mmol) was performed under the same conditions as mentioned in the general procedure. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate), furnishing **III.3k** (mixture of *dl*- and *meso*-diastereomers; 41 mg, 78% yield) as pale-yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ , ppm: 7.67-7.55 (m, 14H), 7.25-7.20 (m, 5H), 6.09 (*meso*, s, 2H), 6.04 (*dl*, s, 2H), 2.10 (*dl*, s, 6H), 2.07 (*meso*, s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ , ppm: 169.40, 140.86, 140.60, 132.40, 132.27, 128.23, 128.12, 126.54, 126.52, 113.00, 112.96, 75.78, 75.47, 20.92.

CHAPTER III: Preparation of photocatalytically active
Metal-Organic Frameworks through crystal-to-crystal
transformations

Reductive coupling reaction nicotinaldehyde (III.1l). The reductive coupling reaction of **III.1l** (32 mg, 0.30 mmol) was performed under the same conditions as mentioned in the general procedure. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate), furnishing **III.3l** (mixture of *dl*- and *meso*-diastereomers; 16 mg, 35% yield) as a yellow solid. ^1H NMR (400 MHz, CDCl_3) δ 8.55 (*meso*, d, $J = 4.8$ Hz, 2H), 8.50 (*dl*, d, $J = 4.8$ Hz, 2H), 8.47 (*meso*, d, $J = 2.3$ Hz, 2H), 8.42 (*dl*, d, $J = 2.4$ Hz, 2H), 7.47 (*meso*, dt, $J = 7.9, 2.0$ Hz, 2H), 7.43 (*dl*, dt, $J = 7.9, 2.0$ Hz, 2H), 7.24-7.21 (*meso*, m, 2H), 7.20-7.16 (*dl*, m, 2H), 6.09 (*meso*, s, 2H), 6.07 (*dl*, s, 2H), 2.10 (*dl*, s, 6H), 2.04 (*meso*, s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.22, 149.17, 149.02, 135.13, 131.54, 123.40, 74.53, 74.24, 20.96, 20.92.

Reductive coupling reaction 4-Methyl-3-furancarboxaldehyde (III.1m). The reductive coupling reaction of **III.1m** (22 mg, 0.20 mmol) was performed under the same conditions as mentioned in the general procedure. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate), furnishing **III.3m** (mixture of *dl*- and *meso*-diastereomers; 12 mg, 40% yield) as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ , ppm: 6.36 (*dl*, s, 2H), 6.30 (*meso*, d, $J = 3.2$ Hz, 2H), 6.27 (*meso*, s, 2H), 6.18 (*dl*, d, $J = 3.1$ Hz, 2H), 5.93 (*meso*, d, $J = 3.1$ Hz, 2H), 5.84 (*dl*, d, $J = 3.1$, 2H), 2.29 (*meso*, s, 6H), 2.25 (*dl*, s, 6H), 2.10 (*dl*, s, 6H), 1.99 (*meso*, s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ , ppm: 169.80, 169.37, 152.83, 152.76, 147.43, 146.85, 111.24, 111.06, 106.37, 106.29, 67.85, 67.42, 20.96, 20.80, 13.55, 13.52.

General procedure of reductive coupling for aromatic ketones and imines. Aromatic ketone **III.4(a-c)** or imine **III.6(a-c)** (1 equiv), MOF-

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

520-PC2 (1 mol%), DIPEA (14 equiv), CH₃CN (1.2 ml) and MeOH (0.8 ml) were added to a 5 mL vial under N₂. The resulting solution was irradiated using a LED light (λ = 447 nm) under stirring at 30 °C. After 16 h, the solution was concentrated under reduced pressure and the residue was purified by silica gel column chromatography (Eluent: Hexane/EtOAc 9/1). The fractions were combined and concentrated under reduced pressure, affording diol **III.5(a-c)** or diamine **III.7(a-c)**. Each substrate was run in two vials in parallel reactions and combined together after the end of the reaction for isolation.

Reductive coupling reaction benzophenone (III.4a). The reductive coupling reaction of **III.4a** (18 mg, 0.10 mmol) was performed under the same conditions as mentioned in the general procedure. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate), furnishing **III.5a** (mixture of *dl*- and *meso*-diastereomers; 7.8 mg, 43% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ , ppm: 7.35-7.30 (m, 8H), 7.23-7.17 (m, 12H), 3.06 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ , ppm: 144.18, 128.61, 127.30, 126.96, 83.04.

Reductive coupling reaction 4-Benzoyltoluene (III.4b). The reductive coupling reaction of **III.4b** (19.6 mg, 0.10 mmol) was performed under the same conditions as mentioned in the general procedure. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate), furnishing **III.5b** (mixture of *dl*- and *meso*-diastereomers; 7.8 mg, 39% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ , ppm: 7.37-7.31 (m, 8H), 7.23-7.12 (m, 20H), 7.00 (t, *J* = 7.9 Hz, 8H), 3.01 (s, 4H), 2.31 (s, 6H), 2.30 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ , ppm: 144.44, 141.24,

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

136.59, 136.49, 128.62, 128.57, 128.51, 128.46, 128.05, 128.02, 127.23, 127.20, 126.80, 126.73, 82.93, 20.97.

Reductive coupling reaction 4,4'-Difluorobenzophenone (III.4c). The reductive coupling reaction of **III.4c** (21.8 mg, 0.10 mmol) was performed under the same conditions as mentioned in the general procedure. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate), furnishing **III.5c** (mixture of *dl*- and *meso*-diastereomers; 8.2 mg, 37% yield) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ , ppm: 7.30-7.24 (m, 8H), 6.94-6.86 (m, 8H), 2.87 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ , ppm: 161.81 (d, $J = 247.4$ Hz), 139.64 (d, $J = 3.5$ Hz), 130.28 (d, $J = 8.0$ Hz), 114.31 (d, $J = 21.2$ Hz), 82.57. ^{19}F NMR (376 MHz, CDCl_3) δ , ppm: -115.11.

Reductive coupling reaction N-Benzylidenebenzylamine (III.6a). The reductive coupling reaction of **III.6a** (39 mg, 0.20 mmol) was performed under the same conditions as mentioned in the general procedure. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate), furnishing **III.7a** (mixture of *dl*- and *meso*-diastereomers; 31 mg, 79% yield) as a colorless solid. ^1H NMR (400 MHz, CDCl_3) δ , ppm: 7.44-7.16 (m, 68H), 7.12-7.07 (*meso*, m, 4H), 7.05-6.99 (*dl*, m, 9H), 3.81 (*dl*, s, 2.1x 2H), 3.77 (*meso*, s, 2H), 3.72 (*meso*, d, $J = 13.3$ Hz, 2H), 3.59 (*dl*, d, $J = 13.7$ Hz, 2.1x 2H), 3.55 (*meso*, d, $J = 13.4$ Hz, 2H), 3.35 (*dl*, d, $J = 13.7$ Hz, 2.1x 2H), 1.97 (s, 7.39H). ^{13}C NMR (101 MHz, CDCl_3) δ , ppm: 140.91, 140.43, 129.28, 128.74, 128.51, 128.48, 128.46, 128.37, 128.34, 128.32, 128.26, 128.13, 128.08, 128.04, 127.79, 127.11, 126.96, 126.82, 68.43, 67.33, 51.46, 51.09.

CHAPTER III: Preparation of photocatalytically active
Metal-Organic Frameworks through crystal-to-crystal
transformations

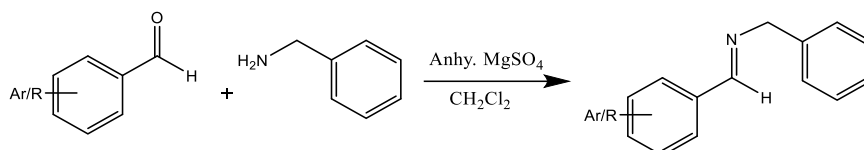
Reductive coupling reaction N-benzyl-1-(naphthalen-2-yl)methanimine (III.6b). The reductive coupling reaction of **III.6b** (49 mg, 0.20 mmol) was performed under the same conditions as mentioned in the general procedure. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate), furnishing **III.7b** (mixture of *dl*- and *meso*-diastereomers; 16 mg, 32% yield) as a yellow solid. ^1H NMR (400 MHz, CDCl_3) δ , ppm: 7.96-7.81 (m, 8H), 7.80-7.73 (m, 2H), 7.73-7.65 (m, 4H), 7.62-7.51 (m, 8H), 7.42 (d, $J = 6.2$ Hz, 4H), 7.35-7.29 (m, 6H), 7.28-7.23 (m, 6H), 7.21-7.15 (m, 6H), 6.95-6.89 (m, 4H), 4.07 (*dl*, s, 2H), 4.05 (*meso*, s, 2H), 3.74 (d, $J = 13.4$ Hz, 2H), 3.57 (d, $J = 13.5$ Hz, 4H), 3.34 (d, $J = 13.9$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ , ppm: 140.47, 140.12, 138.58, 138.34, 133.36, 133.32, 133.19, 132.80, 128.44, 128.35, 128.18, 128.13, 127.95, 127.93, 127.84, 127.80, 127.74, 127.56, 127.13, 126.84, 126.70, 126.07, 125.96, 125.91, 125.88, 125.77, 125.49, 67.99, 67.05, 51.36, 50.90.

Reductive coupling reaction 4-((benzylimino)methyl)benzonitrile (III.6c). The reductive coupling reaction of **III.6c** (44 mg, 0.20 mmol) was performed under the same conditions as mentioned in the general procedure. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate), furnishing **III.7c** (mixture of *dl*- and *meso*-diastereomers; 35 mg, 79% yield) as a pale-yellow solid. ^1H NMR (400 MHz, CDCl_3) δ , ppm: 7.60-7.56 (m, 4H), 7.51-7.47 (m, 4H), 7.36-7.23 (m, 16H), 7.23-7.18 (m, 4H), 7.17-7.11 (m, 4H), 7.09-7.04 (m, 4H), 3.89 (*dl*, s, 2H), 3.73 (*meso*, s, 2H), 3.66 (*meso*, d, $J = 13.3$ Hz, 2H), 3.60 (*dl*, d, $J = 13.6$ Hz, 2H), 3.48 (*meso*, d, $J = 13.3$ Hz, 2H), 3.37 (*dl*, d, $J = 13.6$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ , ppm: 146.35, 145.57, 139.55, 139.41,

CHAPTER III: Preparation of photocatalytically active Metal-Organic Frameworks through crystal-to-crystal transformations

132.08, 132.01, 129.18, 128.60, 128.51, 128.49, 128.01, 127.92, 127.24, 127.22, 118.69, 118.57, 111.65, 111.36, 67.82, 66.31, 51.33, 51.15.

Synthesis of aromatic imines



Aromatic imines were synthesized with slight modification of the published procedure.³⁴ A flame-dried round-bottom flask was charged with the appropriate aldehyde (20 mmol, 1.0 equiv), benzylamine (21 mmol, 1.05 equiv), and anhy. MgSO₄ (2 equiv) in CH₂Cl₂ (20 ml). The reaction mixture was allowed to stir vigorously at room temperature from 6 to 8 hours. After filtration over Celite the collected organic layers were evaporated to dry and stored at -5 °C. Spectroscopic and physical data for substrates **III.6(a-c)** were in accordance with those previously reported.³⁴

Synthesis of **N-Benzylidenebenzylamine (III.6a)** was carried out following the general procedure. The product was obtained as a colorless solid in 96 % yield. ¹H NMR (400 MHz, CDCl₃) δ, ppm: 8.41 (t, 1H), 7.80 – 7.78 (m, 2H), 7.44 – 7.41 (m, 2H), 7.36(s, 2H), 7.34 (s, 2H), 7.29-7.26(m, 1H), 4.84 (d, J = 1.3 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ, ppm: 162.15, 139.4, 136.6, 130.9, 128.75, 128.64, 128.43, 128.13, 127.13, 65.2.

Synthesis of **N-benzyl-1-(naphthalen-2-yl)methanimine (III.6b)** was carried out following the general procedure. The product was obtained as a pale-yellow solid in 92 % yield. ¹H NMR (400 MHz, CDCl₃) δ, ppm: 8.56 (t, 1H), 8.09 – 8.04 (m, 2H), 7.91 – 7.85 (m, 3H), 7.55 – 7.49 (m, 2H), 7.40 – 7.34 (m, 4H), 7.30 – 7.28 (m, 1H), 4.89 (d, J = 1.2 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ, ppm: 162.19, 139.46, 134.92, 134.0, 133.2, 130.25,

128.76, 128.67, 128.6, 128.18, 128.02, 127.31, 127.17, 126.6, 124.11, 65.28.

Synthesis of **4-((benzylimino)methyl)benzonitrile (III.6c)** was carried out following the general procedure. The product was obtained as a pale-yellow solid in 91 % yield. ¹H NMR (400 MHz, CDCl₃) δ, ppm: 8.41 (s, 1H), 7.89 – 7.87 (m, 2H), 7.71 – 7.69 (m, 2H), 7.38 – 7.33 (m, 4H), 7.30 – 7.27 (m, 1H), 4.87 (s, 2H); ¹³C NMR (101 MHz, CDCl₃) δ, ppm: 160.0, 140.1, 138.68, 132.56, 128.8, 128.76, 128.17, 127.41, 118.64, 114.16, 65.26.

Crystal data and structure refinement for MOF-520-PC3.

Identification code	MOF-520-PC3 (mo_ssm637_0m)
Empirical formula	C37.70 H25.10 Al2 N0.50 O10.50
Formula weight	707.04
Temperature	100(2)K
Wavelength	0.71073 Å
Crystal system	tetragonal
Space group	P 42 21 2
Unit cell dimensions	a = 19.1731(7)Å, a= 90° b = 19.1731(7)Å, b =90° c = 36.1245(14)Å, g = 90°
Volume	13279.6(11) Å ³
Z	8
Density (calculated)	0.707 Mg/m ³
Absorption coefficient	0.076 mm ⁻¹
F(000)	2918
Crystal size	0.100 x 0.080 x 0.080 mm ³
Theta range for data collection	1.502 to 25.430°.
Index ranges	-23<=h<=23,-23<=k<=23,-43<=l<=43
Reflections collected	277952
Independent reflections	12259[R(int) = 0.1104]
Completeness to theta =25.430°	99.7%
Absorption correction	Multi-scan
Max. and min. transmission	0.74 and 0.71
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	12259/ 1438/ 854
Goodness-of-fit on F ²	0.973
Final R indices [I>2sigma(I)]	R1 = 0.0476, wR2 = 0.1283
R indices (all data)	R1 = 0.0643, wR2 = 0.1378
Flack parameter	x =0.07(4)
Largest diff. peak and hole	0.243 and -0.327 e.Å ⁻³

Crystal data and structure refinement for MOF520.

Identification code	MOF520_GOOD
Empirical formula	C28.06 H20.48 Al2 O11.18
Formula weight	590.48
Temperature	100(2)K
Wavelength	0.71073 Å
Crystal system	tetragonal
Space group	P 42 21 2
Unit cell dimensions	a = 19.10876(18)Å α= 90°. b = 19.10876(18)Å β =90°. c = 36.7026(6)Å γ = 90°.
Volume	13279.6(11) Å ³
Z	8
Density (calculated)	0.707 Mg/m ³
Absorption coefficient	0.076 mm ⁻¹
F(000)	2918
Crystal size	13401.7(3) Å ³
Theta range for data collection	8
Index ranges	0.585 Mg/m ³
Reflections collected	0.069 mm ⁻¹
Independent reflections	2434
Completeness to theta =25.430°	0.100 x 0.100 x 0.050 mm ³
Absorption correction	1.872 to 31.343°.
Max. and min. transmission	-27<=h<=27,-27<=k<=27,-47<=l<=53
Refinement method	111785
Data / restraints / parameters	20672[R(int) = 0.0326]
Goodness-of-fit on F ²	96.0%
Final R indices [I>2sigma(I)]	Multi-scan
R indices (all data)	1.00 and 0.90
Flack parameter	Full-matrix least-squares on F ²
Largest diff. peak and hole	20672/ 56/ 444

Crystal data and structure refinement for MOF-520-L2

Identification code	MOF-520-L2(SSM186a)
Empirical formula	C33 H21 Al2 N O10
Formula weight	645.47
Temperature	100(2)K
Wavelength	0.71073 Å
Crystal system	tetragonal
Space group	P 42 21 2
Unit cell dimensions	a = 18.5347(3)Å α = 90°. b = 18.5347(3)Å β = 90°. c = 37.2612(8)Å γ = 90°.
Volume	12800.6(5) Å ³
Z	8
Density (calculated)	0.670 Mg/m ³
Absorption coefficient	0.075 mm ⁻¹
F(000)	2656
Crystal size	0.150 x 0.150 x 0.150 mm ³
Theta range for data collection	2.265 to 29.006°.
Index ranges	-24<= <i>h</i> <=24,-24<= <i>k</i> <=25,-50<= <i>l</i> <=46
Reflections collected	122624
Independent reflections	15610[R(int) = 0.0634]
Completeness to theta =25.430°	93.4%
Absorption correction	Multi-scan
Max. and min. transmission	1.00 and 0.95
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	15610/ 168/ 446
Goodness-of-fit on F ²	0.682
Final R indices [I>2sigma(I)]	R1 = 0.0355, wR2 = 0.0944
R indices (all data)	R1 = 0.0593, wR2 = 0.1086
Flack parameter	x =0.20(4)
Largest diff. peak and hole	0.245 and -0.388 e.Å ⁻³

Crystal data and structure refinement for MOF520-L3.

Identification code	MOF520-L3 (ssm204)
Empirical formula	C34.75 H22.25 Al2 I O10
Formula weight	780.63
Temperature	100(2)K
Wavelength	0.71073 Å
Crystal system	tetragonal
Space group	P 42 21 2
Unit cell dimensions	a = 18.6530(3)Å α= 90°. b = 18.6530(3)Å β= 90°. c = 37.2688(9)Å γ = 90°.
Volume	12967.1(5) Å ³
Z	8
Density (calculated)	0.800 Mg/m ³
Absorption coefficient	0.551 mm ⁻¹
F(000)	3118
Crystal size	0.150 x 0.150 x 0.150 mm ³
Theta range for data collection	2.251 to 27.790°.
Index ranges	-23<=h<=23,-24<=k<=21,-48<=l<=48
Reflections collected	87150
Independent reflections	13951[R(int) = 0.0722]
Completeness to theta =25.430°	93.5%
Absorption correction	Multi-scan
Max. and min. transmission	1.00 and 0.89
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	13951/ 420/ 553
Goodness-of-fit on F ²	0.717
Final R indices [I>2sigma(I)]	R1 = 0.0396, wR2 = 0.0989
R indices (all data)	R1 = 0.0677, wR2 = 0.1127
Flack parameter	x =0.322(17)
Largest diff. peak and hole	0.319 and -0.461 e.Å ⁻³

Crystal data and structure refinement for MOF-520-L5

Identification code	MOF-520-L5 (SSM206_twin1_hklf5)
Empirical formula	C44.50 H29.75 Al2 O11.35
Formula weight	799.99
Temperature	100(2)K
Wavelength	0.71073 Å
Crystal system	tetragonal
Space group	P 42 21 2
Unit cell dimensions	a = 18.2060(6)Å α= 90°. b = 18.2060(6)Å β = 90°. c = 37.7556(15)Å γ = 90°.
Volume	12514.4(10) Å ³
Z	8
Density (calculated)	0.849 Mg/m ³
Absorption coefficient	0.087 mm ⁻¹
F(000)	3308
Crystal size	0.075 x 0.075 x 0.050 mm ³
Theta range for data collection	2.431 to 24.707°.
Index ranges	-21<=h<=21,-21<=k<=21,-44<=l<=44
Reflections collected	55408
Independent reflections	10669[R(int) = 0.3143]
Completeness to theta =25.430°	99.8%
Absorption correction	Multi-scan
Max. and min. transmission	1.00 and 0.71
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	10669/ 395/ 669
Goodness-of-fit on F ²	1.019
Final R indices [I>2sigma(I)]	R1 = 0.0825, wR2 = 0.1922
R indices (all data)	R1 = 0.1107, wR2 = 0.2077
Flack parameter	x =0.04(19)
Largest diff. peak and hole	0.305 and -0.274 e.Å ⁻³

Crystal data and structure refinement for MOF520-L6

Identification code	MOF520-L6 (SSM210)
Empirical formula	C _{48.10} H _{34.20} Al ₂ O ₁₀
Formula weight	826.11
Temperature	100(2)K
Wavelength	0.71073 Å
Crystal system	tetragonal
Space group	P 42 21 2
Unit cell dimensions	a = 18.6043(6)Å α = 90°. b = 18.6043(6)Å β = 90°. c = 37.2073(15)Å γ = 90°.
Volume	12878.2(10) Å ³
Z	8
Density (calculated)	0.852 Mg/m ³
Absorption coefficient	0.084 mm ⁻¹
F(000)	3430
Crystal size	0.100 x 0.100 x 0.100 mm ³
Theta range for data collection	2.257 to 23.256°.
Index ranges	-18<= <i>h</i> <=19, -20<= <i>k</i> <=19, -40<= <i>l</i> <=40
Reflections collected	39114
Independent reflections	9038[R(int) = 0.1159]
Completeness to theta =25.430°	98.5%
Absorption correction	Multi-scan
Max. and min. transmission	1.00 and 0.96
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	9038/ 386/ 708
Goodness-of-fit on F ²	0.991
Final R indices [I>2sigma(I)]	R1 = 0.0639, wR2 = 0.1505
R indices (all data)	R1 = 0.1049, wR2 = 0.1661
Flack parameter	x = -0.02(13)
Largest diff. peak and hole	0.469 and -0.320 e.Å ⁻³

Crystal data and structure refinement for MOF-520-L4.

Identification code	MOF-520-L4 (SSM352)
Empirical formula	C34 H21.37 Al2 O10
Formula weight	643.84
Temperature	100(2)K
Wavelength	0.71073 Å
Crystal system	tetragonal
Space group	P 42 21 2
Unit cell dimensions	a = 18.9350(2)Å α= 90°. b = 18.9350(2)Å β= 90°. c = 36.7974(5)Å γ = 90°.
Volume	13193.1(4) Å ³
Z	8
Density (calculated)	0.648 Mg/m ³
Absorption coefficient	0.072 mm ⁻¹
F(000)	2651
Crystal size	0.100 x 0.100 x 0.100 mm ³
Theta range for data collection	1.978 to 32.208°.
Index ranges	-21<=h<=27,-27<=k<=27,-49<=l<=53
Reflections collected	81126
Independent reflections	21803[R(int) = 0.0366]
Completeness to theta =25.430°	95.6%
Absorption correction	Multi-scan
Max. and min. transmission	1.00 and 0.91
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	21803/ 108/ 480
Goodness-of-fit on F ²	0.671
Final R indices [I>2sigma(I)]	R1 = 0.0319, wR2 = 0.0884
R indices (all data)	R1 = 0.0412, wR2 = 0.0944
Flack parameter	x =0.28(3)
Largest diff. peak and hole	0.209 and -0.392 e.Å ⁻³

Crystal data and structure refinement for MOF520-L1

Identification code	MOF520-L1 (ssm611)
Empirical formula	C32.75 H21.50 Al2 O10
Formula weight	628.96
Temperature	100(2)K
Wavelength	0.71073 Å
Crystal system	tetragonal
Space group	P 42 21 2
Unit cell dimensions	a = 18.80977(17)Å α= 90°. b = 18.80977(17)Å β = 90°. c = 36.9016(5)Å γ = 90°.
Volume	13056.0(3) Å ³
Z	8
Density (calculated)	0.640 Mg/m ³
Absorption coefficient	0.072 mm ⁻¹
F(000)	2592
Crystal size	0.100 x 0.100 x 0.100 mm ³
Theta range for data collection	1.978 to 27.308°.
Index ranges	-23<=h<=23,-23<=k<=24,-46<=l<=47
Reflections collected	232638
Independent reflections	13972[R(int) = 0.0617]
Completeness to theta =25.430°	96.4%
Absorption correction	Multi-scan
Max. and min. transmission	1.00 and 0.68
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	13972/ 867/ 642
Goodness-of-fit on F ²	0.813
Final R indices [I>2sigma(I)]	R1 = 0.0372, wR2 = 0.1040
R indices (all data)	R1 = 0.0517, wR2 = 0.1113
Flack parameter	x =0.11(3)
Largest diff. peak and hole	0.235 and -0.340 e.Å ⁻³

Crystal data and structure refinement for MOF520-PC1

Identification code	MOF520-PC1 (ssm704af_sq)
Empirical formula	C36 H23 Al2 O10.50
Formula weight	677.50
Temperature	100(2)K
Wavelength	0.71073 Å
Crystal system	tetragonal
Space group	P 42 21 2
Unit cell dimensions	a = 18.7463(3)Å α= 90°. b = 18.7463(3)Å β = 90°. c = 36.9186(6)Å γ = 90°.
Volume	12974.0(4) Å ³
Z	8
Density (calculated)	0.694 Mg/m ³
Absorption coefficient	0.076 mm ⁻¹
F(000)	2792
Crystal size	0.150 x 0.100 x 0.080 mm ³
Theta range for data collection	2.173 to 27.253°.
Index ranges	-22<=h<=23,-23<=k<=23,-47<=l<=47
Reflections collected	219112
Independent reflections	13705[R(int) = 0.0904]
Completeness to theta =25.430°	96.1%
Absorption correction	Multi-scan
Max. and min. transmission	1.00 and 0.72
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	13705/ 748/ 677
Goodness-of-fit on F ²	1.004
Final R indices [I>2sigma(I)]	R1 = 0.0739, wR2 = 0.2042
R indices (all data)	R1 = 0.1363, wR2 = 0.2435
Largest diff. peak and hole	0.716 and -0.264 e.Å ⁻³

3.5. Bibliography

- (1) Narayanam, J. M. R.; Stephenson, C. R. J. Visible Light Photoredox Catalysis: Applications in Organic Synthesis. *Chem. Soc. Rev.* **2011**, 40 (1), 102–113.
- (2) Schultz, D. M.; Yoon, T. P. Solar Synthesis: Prospects in Visible Light Photocatalysis. *Science* **2014**, 343 (6174).
- (3) Marzo, L.; Pagire, S. K.; Reiser, O.; König, B. Visible-Light Photocatalysis: Does It Make a Difference in Organic Synthesis? *Angew. Chemie - Int. Ed.* **2018**, 57 (32), 10034–10072.
- (4) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis. *Chem. Rev.* **2013**, 113 (7), 5322–5363.
- (5) Xi, Y.; Yi, H.; Lei, A. Synthetic Applications of Photoredox Catalysis with Visible Light. *Org. Biomol. Chem.* **2013**, 11 (15), 2387.
- (6) Ravelli, D.; Fagnoni, M.; Albini, A. Photoorganocatalysis. What For? *Chem. Soc. Rev.* **2013**, 42 (1), 97–113.
- (7) Vega-Peñaloza, A.; Mateos, J.; Companyó, X.; Escudero-Casao, M.; Dell’Amico, L. A Rational Approach to Organo-Photocatalysis: Novel Designs and Structure-Property Relationships. *Angew. Chemie - Int. Ed.* **2021**, 60 (3), 1082–1097.
- (8) Nicewicz, D. A.; Nguyen, T. M. Recent Applications of Organic Dyes as Photoredox Catalysts in Organic Synthesis. *ACS Catal.* **2014**, 4 (1), 355–360.
- (9) Sideri, I. K.; Voutyritsa, E.; Kokotos, C. G. Photoorganocatalysis, Small Organic Molecules and Light in the Service of Organic

CHAPTER III: Preparation of photocatalytically active
Metal-Organic Frameworks through crystal-to-crystal
transformations

- Synthesis: The Awakening of a Sleeping Giant. *Org. Biomol. Chem.* **2018**, *16* (25), 4596–4614.
- (10) Romero, N. A.; Nicewicz, D. A. Organic Photoredox Catalysis. *Chem. Rev.* **2016**, *116* (17), 10075–10166.
- (11) Dolgoplova, E. A.; Rice, A. M.; Martin, C. R.; Shustova, N. B. Photochemistry and Photophysics of MOFs: Steps towards MOF-Based Sensing Enhancements. *Chem. Soc. Rev.* **2018**, *47* (13), 4710–4728.
- (12) Tang, Y.; Zhao, L.; Ji, G.; Zhang, Y.; He, C.; Wang, Y.; Wei, J.; Duan, C. Ligand-Regulated Metal–Organic Frameworks for Synergistic Photoredox and Nickel Catalysis. *Inorg. Chem. Front.* **2022**, *9* (13), 3116–3129.
- (13) Hou, L.; Jing, X.; Huang, H.; Duan, C. Merging Charge Transfer into Metal-Organic Frameworks to Achieve High Reduction Potentials via Multiphoton Excitation. *ACS Appl. Mater. Interfaces* **2022**, *14* (13), 15307–15316.
- (14) Li, Q. Y.; Ma, Z.; Zhang, W. Q.; Xu, J. L.; Wei, W.; Lu, H.; Zhao, X.; Wang, X. J. AIE-Active Tetraphenylethene Functionalized Metal-Organic Framework for Selective Detection of Nitroaromatic Explosives and Organic Photocatalysis. *Chem. Commun.* **2016**, *52* (75), 11284–11287.
- (15) Zeng, L.; Liu, T.; He, C.; Shi, D.; Zhang, F.; Duan, C. Organized Aggregation Makes Insoluble Perylene Diimide Efficient for the Reduction of Aryl Halides via Consecutive Visible Light-Induced Electron-Transfer Processes. *J. Am. Chem. Soc.* **2016**, *138* (12), 3958–3961.
- (16) Wu, P.; He, C.; Wang, J.; Peng, X.; Li, X.; An, Y.; Duan, C.

CHAPTER III: Preparation of photocatalytically active
Metal-Organic Frameworks through crystal-to-crystal
transformations

- Photoactive Chiral Metal-Organic Frameworks for Light-Driven Asymmetric α -Alkylation of Aldehydes. *J. Am. Chem. Soc.* **2012**, *134* (36), 14991–14999.
- (17) Quan, Y.; Shi, W.; Song, Y.; Jiang, X.; Wang, C.; Lin, W. Bifunctional Metal–Organic Layer with Organic Dyes and Iron Centers for Synergistic Photoredox Catalysis. *J. Am. Chem. Soc.* **2021**, *143* (8), 3075–3080.
- (18) Zhao, L.; Du, Z.; Ji, G.; Wang, Y.; Cai, W.; He, C.; Duan, C. Eosin Y-Containing Metal–Organic Framework as a Heterogeneous Catalyst for Direct Photoactivation of Inert C–H Bonds. *Inorg. Chem.* **2022**, *61* (19), 7256–7265.
- (19) Wang, Z.; Zeng, L.; He, C.; Duan, C. Photocatalytic C–H Activation with Alcohol as a Hydrogen Atom Transfer Agent in a 9-Fluorenone Based Metal-Organic Framework. *ACS Appl. Mater. Interfaces* **2021**, *13* (22), 25898–25905.
- (20) Cai, P.; Xu, M.; Meng, S. S.; Lin, Z.; Yan, T.; Drake, H. F.; Zhang, P.; Pang, J.; Gu, Z. Y.; Zhou, H. C. Precise Spatial-Designed Metal-Organic-Framework Nanosheets for Efficient Energy Transfer and Photocatalysis. *Angew. Chemie - Int. Ed.* **2021**, *60* (52), 27258–27263.
- (21) Li, H.; Yang, Y.; He, C.; Zeng, L.; Duan, C. Mixed-Ligand Metal-Organic Framework for Two-Photon Responsive Photocatalytic C–N and C–C Coupling Reactions. *ACS Catal.* **2019**, *9* (1), 422–430.
- (22) Atilgan, A.; Islamoglu, T.; Howarth, A. J.; Hupp, J. T.; Farha, O. K. Detoxification of a Sulfur Mustard Simulant Using a BODIPY-Functionalized Zirconium-Based Metal-Organic Framework. *ACS Appl. Mater. Interfaces* **2017**, *9* (29), 24555–24560.

CHAPTER III: Preparation of photocatalytically active
Metal-Organic Frameworks through crystal-to-crystal
transformations

- (23) Howarth, A. J.; Buru, C. T.; Liu, Y.; Ploskonka, A. M.; Hartlieb, K. J.; McEntee, M.; Mahle, J. J.; Buchanan, J. H.; Durke, E. M.; Al-Juaid, S. S.; Stoddart, J. F.; DeCoste, J. B.; Hupp, J. T.; Farha, O. K. Postsynthetic Incorporation of a Singlet Oxygen Photosensitizer in a Metal–Organic Framework for Fast and Selective Oxidative Detoxification of Sulfur Mustard. *Chem. A Eur. J.* **2017**, 23 (1), 214–218.
- (24) Zhang, Y.; Guo, J.; Shi, L.; Zhu, Y.; Hou, K.; Zheng, Y.; Tang, Z. Tunable Chiral Metal Organic Frameworks toward Visible Light–Driven Asymmetric Catalysis. *Sci. Adv.* **2017**, 3 (8), 1–8.
- (25) Stock, N.; Biswas, S. Synthesis of Metal-Organic Frameworks (MOFs): Routes to Various MOF Topologies, Morphologies, and Composites. *Chem. Rev.* **2012**, 112 (2), 933–969.
- (26) Wu, C.-D.; Zhao, M. Incorporation of Molecular Catalysts in Metal-Organic Frameworks for Highly Efficient Heterogeneous Catalysis. *Adv. Mater.* **2017**, 29 (14), 1605446.
- (27) Mandal, S.; Natarajan, S.; Mani, P.; Pankajakshan, A. Post-Synthetic Modification of Metal–Organic Frameworks Toward Applications. *Adv. Funct. Mater.* **2021**, 31 (4), 1–22.
- (28) Deria, P.; Mondloch, J. E.; Tylianakis, E.; Ghosh, P.; Bury, W.; Snurr, R. Q.; Hupp, J. T.; Farha, O. K. Perfluoroalkane Functionalization of NU-1000 via Solvent-Assisted Ligand Incorporation: Synthesis and CO₂ Adsorption Studies. *J. Am. Chem. Soc.* **2013**, 135 (45), 16801–16804.
- (29) Deria, P.; Bury, W.; Hupp, J. T.; Farha, O. K. Versatile Functionalization of the Nu-1000 Platform by Solvent-Assisted Ligand Incorporation. *Chem. Commun.* **2014**, 50 (16), 1965–1968.

CHAPTER III: Preparation of photocatalytically active
Metal-Organic Frameworks through crystal-to-crystal
transformations

- (30) Lee, M. S.; Garibay, S. J.; Ploskonka, A. M.; DeCoste, J. B. Bioderived Protoporphyrin IX Incorporation into a Metal-Organic Framework for Enhanced Photocatalytic Degradation of Chemical Warfare Agents. *MRS Commun.* **2019**, 9 (2), 464–473.
- (31) Lee, S.; Kapustin, E. A.; Yaghi, O. M. Coordinative Alignment of Molecules in Chiral Metal-Organic Frameworks. *Science* **2016**, 353 (6301), 808–811.
- (32) Pei, X.; Bürgi, H.-B.; Kapustin, E. A.; Liu, Y.; Yaghi, O. M. Coordinative Alignment in the Pores of MOFs for the Structural Determination of N-, S-, and P-Containing Organic Compounds Including Complex Chiral Molecules. *J. Am. Chem. Soc.* **2019**, 141 (47), 18862–18869.
- (33) Winnik, F. M. Photophysics of Preassociated Pyrenes in Aqueous Polymer Solutions and in Other Organized Media. *Chem. Rev.* **1993**, 93 (2), 587–614.
- (34) Okamoto, S.; Kojiyama, K.; Tsujioka, H.; Sudo, A. Metal-Free Reductive Coupling of CO and CN Bonds Driven by Visible Light: Use of Perylene as a Simple Photoredox Catalyst. *Chem. Commun.* **2016**, 52 (76), 11339–11342.
- (35) Kapustin, E. A.; Lee, S.; Alshammari, A. S.; Yaghi, O. M. Molecular Retrofitting Adapts a Metal–Organic Framework to Extreme Pressure. *ACS Cent. Sci.* **2017**, 3 (6), 662–667.
- (36) Birks, J. B. Excimers. *Reports Prog. Phys.* **1975**, 38 (8), 903–974.
- (37) Haedler, A. T.; Misslitz, H.; Buehlmeyer, C.; Albuquerque, R. Q.; Köhler, A.; Schmidt, H. W. Controlling the π -Stacking Behavior of Pyrene Derivatives: Influence of H-Bonding and Steric Effects in Different States of Aggregation. *ChemPhysChem* **2013**, 14 (9),

CHAPTER III: Preparation of photocatalytically active
Metal-Organic Frameworks through crystal-to-crystal
transformations

1818–1829.

- (38) Bag, S. S.; Saito, Y.; Hanawa, K.; Kodate, S.; Suzuka, I.; Saito, I. Intelligent Fluorescent Nucleoside in Sensing Cytosine Base: Importance of Hydrophobic Nature of Perylene Fluorophore. *Bioorg. Med. Chem. Lett.* **2006**, *16* (24), 6338–6341.
- (39) Hart, L. R.; Harries, J. L.; Greenland, B. W.; Colquhoun, H. M.; Hayes, W. Supramolecular Approach to New Inkjet Printing Inks. *ACS Appl. Mater. Interfaces* **2015**, *7* (16), 8906–8914.
- (40) Li, J.; Yuan, S.; Qin, J.-S.; Huang, L.; Bose, R.; Pang, J.; Zhang, P.; Xiao, Z.; Tan, K.; Malko, A. V.; Cagin, T.; Zhou, H.-C. Fluorescence Enhancement in the Solid State by Isolating Perylene Fluorophores in Metal–Organic Frameworks. *ACS Appl. Mater. Interfaces* **2020**, *12* (23), 26727–26732.
- (41) Okamoto, S.; Kojiyama, K.; Tsujioka, H.; Sudo, A. Metal-Free Reductive Coupling of C=O and C=N Bonds Driven by Visible Light: Use of Perylene as a Simple Photoredox Catalyst. *Chem. Commun.* **2016**, *52* (76), 11339–11342.
- (42) Nakajima, M.; Fava, E.; Loescher, S.; Jiang, Z.; Rueping, M. Photoredox-Catalyzed Reductive Coupling of Aldehydes, Ketones, and Imines with Visible Light. *Angew. Chemie - Int. Ed.* **2015**, *54* (30), 8828–8832.
- (43) Izutsu, K. *Electrochemistry in Nonaqueous Solutions*; Wiley, 2009.
- (44) Sachse, A.; Ameloot, R.; Coq, B.; Fajula, F.; Coasne, B.; De Vos, D.; Galameau, A. In Situ Synthesis of Cu-BTC (HKUST-1) in Macro-/Mesoporous Silica Monoliths for Continuous Flow Catalysis. *Chem. Commun.* **2012**, *48* (39), 4749–4751.
- (45) Pascanu, V.; Hansen, P. R.; Bermejo Gómez, A.; Ayats, C.; Platero-

CHAPTER III: Preparation of photocatalytically active
Metal-Organic Frameworks through crystal-to-crystal
transformations

- Prats, A. E.; Johansson, M. J.; Pericàs, M.; Martín-Matute, B. Highly Functionalized Biaryls via Suzuki-Miyaura Cross-Coupling Catalyzed by Pd@MOF under Batch and Continuous Flow Regimes. *ChemSusChem* **2015**, 8 (1), 123–130.
- (46) Cambié, D.; Bottecchia, C.; Straathof, N. J. W.; Hessel, V.; Noël, T. Applications of Continuous-Flow Photochemistry in Organic Synthesis, Material Science, and Water Treatment. *Chem. Rev.* **2016**, 116 (17), 10276–10341.
- (47) Sambiagio, C.; Noël, T. Flow Photochemistry: Shine Some Light on Those Tubes! *Trends Chem.* **2020**, 2 (2), 92–106.
- (48) Merz, J.; Steffen, A.; Nitsch, J.; Fink, J.; Schürger, C. B.; Friedrich, A.; Krummenacher, I.; Braunschweig, H.; Moos, M.; Mims, D.; Lambert, C.; Marder, T. B. Synthesis, Photophysical and Electronic Properties of Tetra-Donor- or Acceptor-Substituted: Ortho - Perylenes Displaying Four Reversible Oxidations or Reductions. *Chem. Sci.* **2019**, 10 (32), 7516–7534.
- (49) Allendorf, M. D.; Bauer, C. A.; Bhakta, R. K.; Houk, R. J. T. Luminescent Metal-Organic Frameworks. *Chem. Soc. Rev.* **2009**, 38 (5), 1330–1352.
- (50) Chaudhari, A. K.; Tan, J. C. Mechanochromic MOF Nanoplates: Spatial Molecular Isolation of Light-Emitting Guests in a Sodalite Framework Structure. *Nanoscale* **2018**, 10 (8), 3953–3960.
- (51) Fedorov, I. A.; Zhuravlev, Y. N.; Berveno, V. P. Structural and Electronic Properties of Perylene from First Principles Calculations. *J. Chem. Phys.* **2013**, 138 (9), 1–6.
- (52) Müller, M.; Devaux, A.; Yang, C. H.; De Cola, L.; Fischer, R. A. Highly Emissive Metal-Organic Framework Composites by Host-

CHAPTER III: Preparation of photocatalytically active
 Metal-Organic Frameworks through crystal-to-crystal
 transformations

- Guest Chemistry. *Photochem. Photobiol. Sci.* **2010**, 9 (6), 846–853.
- (53) Dietl, C.; Hintz, H.; Rühle, B.; Auf Der Ginne, S. J.; Langhals, H.; Wuttke, S. Switch-On Fluorescence of a Perylene-Dye-Functionalized Metal-Organic Framework through Postsynthetic Modification. *Chem. A Eur. J.* **2015**, 21 (30), 10714–10720.
- (54) Barbante, G. J.; Kebede, N.; Hindson, C. M.; Doeven, E. H.; Zammit, E. M.; Hanson, G. R.; Hogan, C. F.; Francis, P. S. Control of Excitation and Quenching in Multi-Colour Electrogenerated Chemiluminescence Systems through Choice of Co-Reactant. *Chem. A Eur. J.* **2014**, 20 (43), 14026–14031.
- (55) Pal, A. K.; Li, C.; Hanan, G. S.; Zysman-Colman, E. Blue-Emissive Cobalt(III) Complexes and Their Use in the Photocatalytic Trifluoromethylation of Polycyclic Aromatic Hydrocarbons. *Angew. Chemie - Int. Ed.* **2018**, 57 (27), 8027–8031.
- (56) Beckwith, J. S.; Lang, B.; Grilj, J.; Vauthey, E. Ion-Pair Dynamics upon Photoinduced Electron Transfer Monitored by Pump-Pump-Probe Spectroscopy. *J. Phys. Chem. Lett.* **2019**, 10 (13), 3688–3693.
- (57) Call, A.; Franco, F.; Kandoth, N.; Fernández, S.; González-Béjar, M.; Pérez-Prieto, J.; Luis, J. M.; Lloret-Fillol, J. Understanding Light-Driven H₂ Evolution through the Electronic Tuning of Aminopyridine Cobalt Complexes. *Chem. Sci.* **2018**, 9 (9), 2609–2619.
- (58) Beyer, C.; Wagenknecht, H.-A. Synthesis of Spiropyrans As Building Blocks for Molecular Switches and Dyads. *J. Org. Chem.* **2010**, 75 (8), 2752–2755.
- (59) Kovalev, I. S.; Slovesnova, N. V.; Kopchuk, D. S.; Zyryanov, G. V.; Taniya, O. S.; Rusinov, V. L.; Chupakhin, O. N. Synthesis of 1-

Functionalized Pyrenes from 1-Lithiopyrene, and Their Application
as Fluorescent Probes for the Components of the Ginkgo Biloba L.
Leaves Extract. *Russ. Chem. Bull.* **2014**, 63 (6), 1312–1316.

Chapter IV:

Development of imine Metal Covalent
Organic Frameworks based on N-donor
ligands

4.1. General insight

Over the last two decades, metal-organic frameworks (MOFs) and, later on, covalent organic frameworks (COFs) have emerged as powerful catalysts, capable of bridging the gap between homogeneous and heterogeneous catalysis due to their ability to expand the precision of the discrete molecular entities to extended frameworks.¹⁻³ In this regard, MOFs possess great potential due to the versatility of their structures and the presence of open metal sites. However, their application is sometimes restricted by the relative stability of the coordination bonds connecting the framework, especially under harsh conditions.⁴ Indeed, in Chapter III of this work, we observed that **MOF-520-PC-2** presents limited catalyst recyclability due to its instability.

On the other hand, COFs have been proposed as an appealing alternative due to their high stability to harsh chemical environments, including boiling water, strong acids and bases, and oxidation and reduction conditions.^{2,5} Using COFs as metal-free catalysts is an interesting approach, but their reactivity is limited compared to the catalytic ability of transition metals. In order to overcome these limitations, metal ions can be introduced into COFs to form metal-covalent organic frameworks (MCOFs). Considering the catalytic properties, MCOFs can be seen as a bridge between MOFs and COFs, exhibiting a combination of stability, porosity, crystallinity and tuneability.⁶

The most common approach to obtain MCOFs is by post-treatment of COFs with metal salts, taking advantage of metal–ligand coordination, although it is also possible to form MCOFs by employing metal complexes as monomers, or to form the complexes *in-situ* during the polymerization. However, the latter strategies require metal-complexes stable to the synthetic COFs conditions, which usually are too aggressive for these

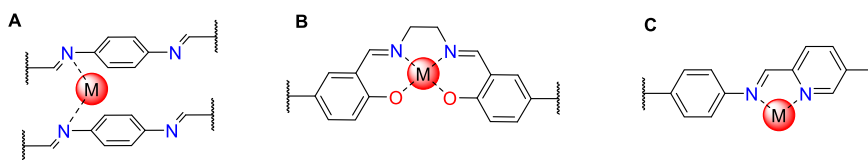
systems.⁷ Therefore, a successful strategy for designing MCOFs is to develop frameworks with linkages that can act as ligands by the coordination with metal salts (Figure 4.1a-c). In one of the earliest examples of MCOF catalysis, imine pairs in adjacent layers formed during the condensation of an imine COF could be used as ligands to coordinate to Pd(AcO)₂ (Figure 4.1a), which was used as a recyclable catalyst in the Suzuki Miyaura Coupling reaction.⁸ The imine groups of a COF can also be combined with alcohol groups to obtain **salen** ligands⁹ (Figure 4.1b) or with pyridine rings to form imino pyridine ligands¹⁰ within the framework (Figure 4.1c). MCOFs with **salen** ligands have been employed as chiral catalysts in a variety of reactions, including the cyanation of aldehydes, the epoxidation of alkenes, and the aminolysis of epoxides.¹¹

A different approach to obtain more diverse ligand structures in COFs is to use monomers that can already function as ligands by themselves (Figure 4.1d-h). Some examples of ligands used this way include biphenol¹² (Figure 4.1d), dehydrobenzoannulene¹³ (Figure 4.1e) and phenantroline¹⁴ (Figure 4.1f). We can highlight porphyrin¹⁵ (Figure 4.1g) and bipyridine¹⁶ (Figure 4.1h) as two of the most commonly found ligands in the design of MCOFs. These two ligands have shown excellent versatility, being used as catalysts in a variety of reactions ranging from CO₂ reduction to Suzuki cross-couplings.^{17–26}

Despite the progress in developing these materials, a comparison of the functional groups, coordination environments and geometries present in MCOFs *versus* molecular complexes, clearly shows that the diversity of MCOFs is still much more limited.⁶ This is not only because the development and study of COFs is relatively young (The first COF and the first catalytic COF were reported in 2005²⁷ and 2009,²⁸ respectively), but more importantly because not all ligands are suitable monomers for the

formation of COFs.²⁹ The ligands need to have specific geometries and functional groups to be able to form well-ordered COFs. For example, ligands usually need to be flat to facilitate stacking of the material, and they cannot have functional groups that would interfere with the polymerization reaction. Nevertheless, MCOFs like the one formed with bis-phenanthroline complexes show that this limitation can be overcome with particular designs. For these reasons, developing new MCOFs is still quite challenging and requires careful design to obtain materials with the desired properties.

Linkage-based ligands



Monomer-based ligands

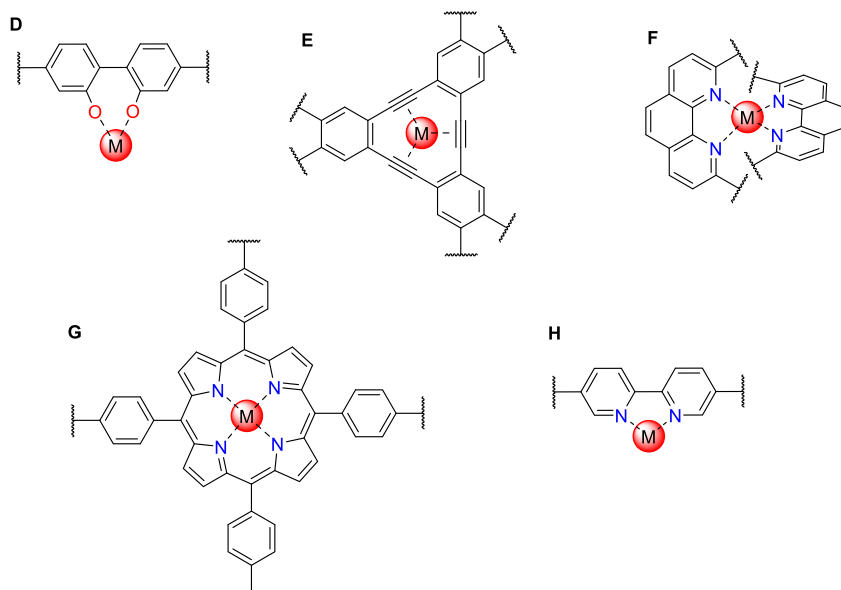


Figure 4.1. Examples of ligands used in MCOFs.

Previously, our group reported the coordination of a molecular $\{\text{Mn}(\text{CO})_3\text{Br}\}$ moiety onto an imine-linked 2D pyrene-bipyridine COF for electrochemical CO_2 reduction in water.³⁰ The study shows how the mechanical constraint imposed by the framework prevents the formation of metallic dimers after the reduction of the manganese centers (Figure 4.2). This is an important feature of the manganese MCOF, which leads to superior performance compared with analogous homogenous catalysts. Furthermore, this work highlights the potential of MCOFs to stabilize reactive metal species that can be employed as active catalysts.

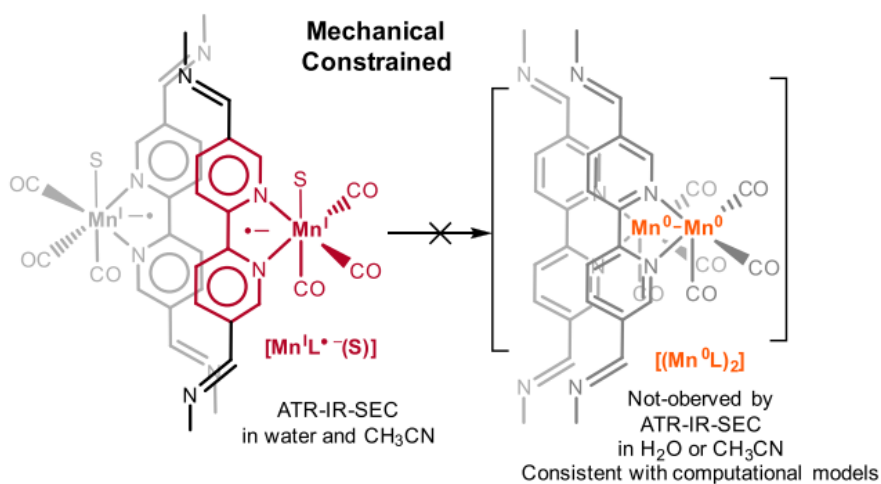


Figure 4.2. Mechanical constrain within COF_{bpy}.³⁰

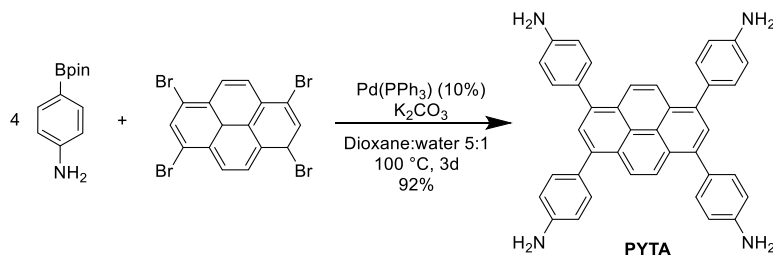
In this chapter, we address the synthesis and characterization of imine COFs with nitrogen ligands in their structure, which are used to immobilize cobalt in the framework for further use as catalysts of organic transformations. In this first part of the chapter, we studied the synthesis of two different COFs based on bipyridine (BPY) as the monomer ligand (**COF-BPY-1** and **COF-BPY-2**) due to its versatility and capacity to form highly crystalline COFs. Then, we selected terpyridine (TPY) as the monomer ligand (**COF-TPY-1** and **COF-TPY-2**). Although terpyridine is commonly used in molecular

complexes, there is only one previous example of a terpyridine MCOF.³¹ We hypothesized this ligand has excellent potential for MCOFs, since it has a flat geometry, a strong chelating effect and a non-innocent ligand behavior.³² Lastly, we selected a bipyridine-cyclohexyldiamine-based ligand for the final COF (**MCP-polymer**). This type of tetradentate ligand has been previously employed to stabilize high-valent metal-oxo intermediates in oxidation catalysis,^{33,34} or to create highly active Co^I and Ni^I species,³⁵ but it has not been used in MCOFs. Additionally, this ligand can be chiral, and potentially useful for asymmetric catalytic transformations or chiral separations.³⁶

4.2. Results and Discussion

4.2.1. Synthesis and characterization of bipyridine COFs

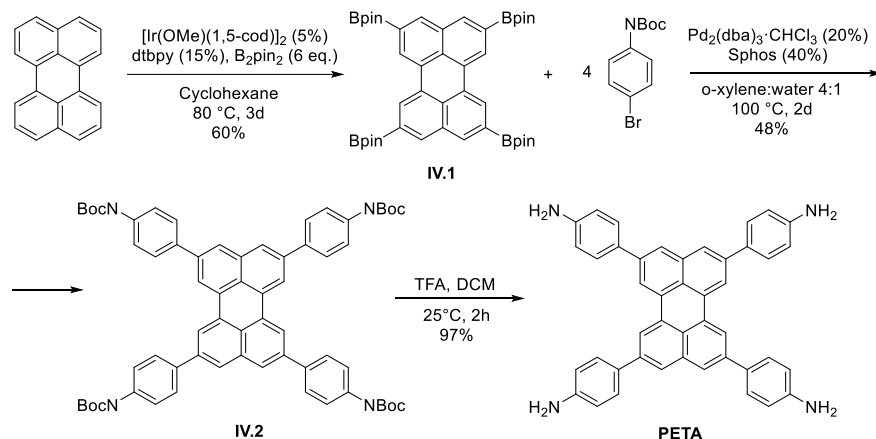
Prior to the synthesis of the bipyridine COFs, the amine linkers 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetraaniline (**PYTA**) and 4,4',4'',4'''-(perylene-2,5,8,11-tetrayl)tetraaniline (**PETA**) were prepared. Following the reported procedure,¹⁶ PYTA was obtained in good yield after a Suzuki cross-coupling reaction between commercially available tetrabromopyrene and aminophenylboronic acid pinacol ester (Scheme 4.1).



Scheme 4.1. PYTA synthetic route.¹⁶

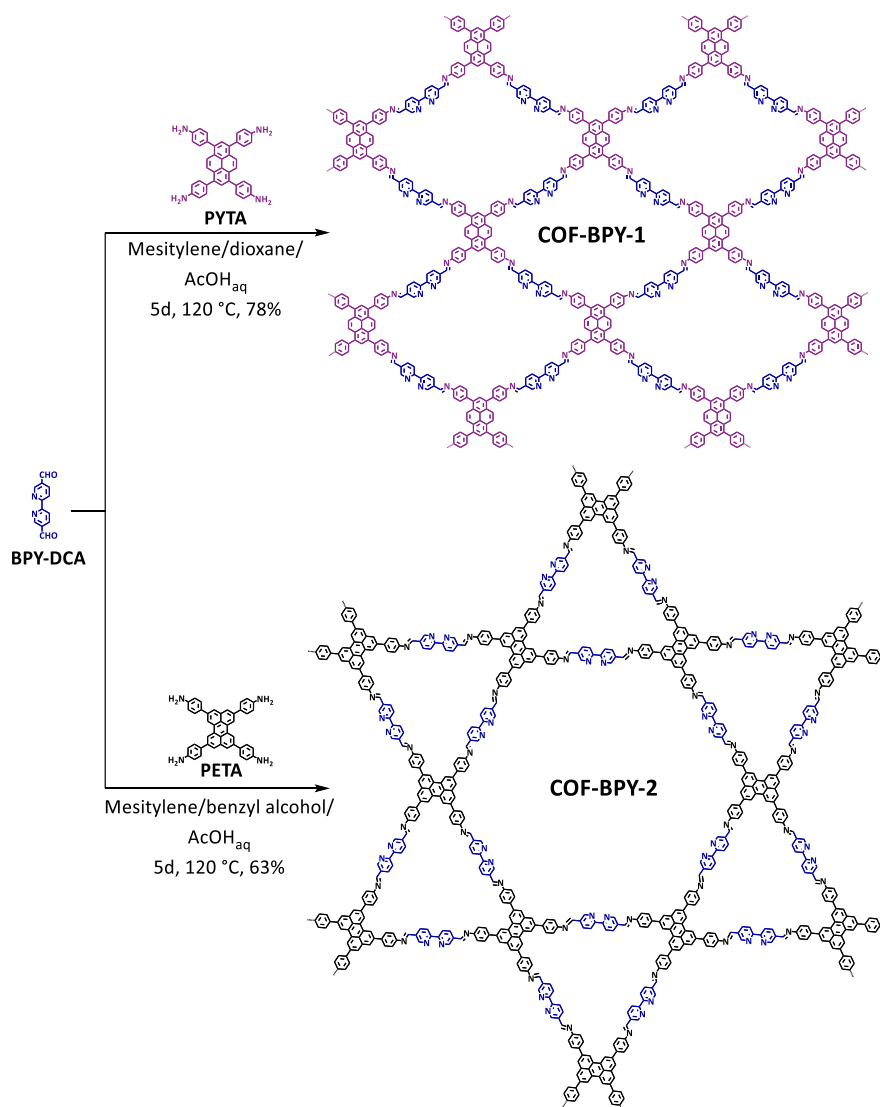
PETA was synthesized as previously reported,³⁷ following the synthetic rout shown in Scheme 4.2. Commercially available perylene was borylated at the 2-, 5-, 8- and 11- positions with an iridium catalyst, affording

compound **IV.1**. This was followed by a cross-coupling reaction with Boc-protected aniline bromide to produce **IV.2**. Deprotection of the amines with trifluoroacetic acid afforded **PETA**. The ^1H NMR and ^{13}C NMR spectra of both amine ligands agree with previously reported data^{16,37} (see experimental section for details).



Scheme 4.2. PETA synthetic route.³⁷

The bipyridine COFs were synthesized by a conventional two-component condensation catalyzed by acetic acid between 2,2'-bipyridine-5,5'-dicarbaldehyde (**BPY-DCA**, commercially available) and an amine linker (Scheme 4.3). For the first COF (**COF-BPY-1**), we selected **PYTA** as the amine linker. For the second COF (**COF-BPY-2**) we selected **PETA** as the amine linker. Although the **PYTA** and **PETA** linkers have similar structures, we expected to obtain two COFs with very different topologies since **PYTA** combined with bitopic aldehyde linkers seems to produce exclusively rhombic frameworks,¹⁶ while **PETA** combined with bitopic aldehyde linkers generates star-shaped COFs (kagome skeleton) with small trigonal and large hexagonal pores.^{37,38}



Scheme 4.3. Synthesis of **COF-BPY-1** and **COF-BPY-2**.

Following the reported conditions¹⁶ [5:5:1 (v/v) mixture of mesitylene/1,4-dioxane/(aqueous 6 M AcOH) at 120 °C for 5 d], **COF-BPY-1** was isolated in 78% yield as a fine orange powder. To obtain the novel **COF-BPY-2** as a crystalline material, we performed a screening of conditions (Table 4.1). The starting reaction conditions employed for **COF-BPY-1** were gradually

modified to form materials with sharp PXRD peaks, which indicate crystallinity (PXRD diffractograms for all materials are shown in section 4.4.3). Solvent mixture, catalyst (AcOH) concentration and temperature were the variables adjusted in this screening of conditions due to their strong effect over the materials formation. As a general trend, mixtures of mesitylene with 1,4-dioxane or benzyl alcohol (BnOH) produced the best crystallinity results, which could be improved by increasing the catalyst concentration (Table 4.1, entry 16). Under the optimized conditions [4:2:1 (v/v) mixture of mesitylene/BnOH/(aqueous 6 M AcOH) at 120 °C for 5 d], **COF-BPY-2** was isolated in 63% yield as a fine brown powder with moderate crystallinity.

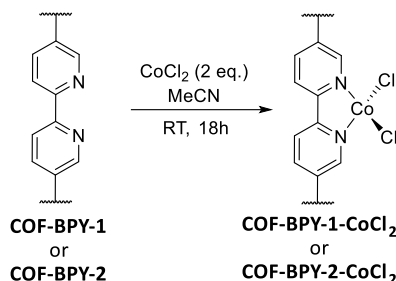
Table 4.1. Screening of conditions for the synthesis of **COF-BPY-2**.

Nº	Solvent mixture	aq. AcOH 6 M (V %)	Temp. (°C)	Yield (%)	Crystallinity
1	Mesitylene:dioxane 1:1	9	120	79	Low
2	Mesitylene:dioxane 1:2	9	120	73	Low
3	Mesitylene:dioxane 2:1	9	120	69	Amorphous
4	Mesitylene:dioxane 1:1	15	120	73	Low
5	Mesitylene:dioxane 2:1	15	150	44	Amorphous
6	Mesitylene:dioxane 2:1	15	150	42	Amorphous
7	Mesitylene:NMP 1:2	15	120	48	Amorphous
8	Mesitylene:EtOH 1:2	15	120	44	Amorphous
9	<i>o</i> -DCB:dioxane 2:1	15	120	57	Amorphous
10	<i>o</i> -DCB:dioxane 1:2	15	120	48	Amorphous
11	<i>o</i> -DCB: <i>n</i> -BuOH 2:1	15	120	51	Amorphous
12	<i>o</i> -DCB: <i>n</i> -BuOH 1:2	15	120	55	Amorphous
13	<i>o</i> -DCB: <i>n</i> -BuOH 2:1	9	120	50	Amorphous
14	Mesitylene:BnOH 1:2	9	120	71	Low
15	Mesitylene:BnOH 1:2	15	120	60	Moderate
16	Mesitylene:BnOH 2:1	15	120	63	Moderate
17	Mesitylene:BnOH 1:2	15	90	71	Low
18	Mesitylene: <i>n</i> -BuOH 1:2	15	120	64	Amorphous
19	<i>o</i> -DCB:BnOH 2:1	15	120	73	Amorphous
20	<i>o</i> -DCB:BnOH 2:1	9	120	51	Amorphous

Reaction conditions: PETA (12mg, 0.02 mmol), BPY-DCA (8.5 mg, 0.04 mmol), solvent mixture (0.5 mL), aqueous AcOH 6M, 120 °C for 5 d. Crystallinity was estimated based on the intensity of the PXRD peaks (Section 4.4.3).

Post-synthetic metalation of the materials was performed by placing them in a CoCl₂ solution in MeCN at room temperature for over 18 h, producing

COF-BPY-1-CoCl₂ and **COF-BPY-2-CoCl₂** after thorough washing and vacuum drying (Scheme 4.4).



Scheme 4.4. Post-synthetic metalation of **COF-BPY-1** and **COF-BPY-2**.

Next, the pristine and metalated COFs were characterized. FT-IR of **COF-BPY-1** revealed the disappearance of the characteristic C=O stretching band centered at 1696 cm⁻¹ and the appearance of a new C=N band around 1626 cm⁻¹, confirming the condensation reaction (Figure 4.4a). The same band is present in **COF-BPY-1-CoCl₂**, suggesting that the imine bond is not affected by the metalation. In contrast, the signals on the spectra of **COF-BPY-2** are more problematic to assign due to overlapping. The consumption of the initial aldehyde can be observed by the disappearance of the C-H aldehyde vibration bands at 2810 cm⁻¹, while the band at 1612 cm⁻¹ could be assigned to the new C=N bond (Figure 4.4b). The PXRD pattern of **COF-BPY-1** shows intense diffraction peaks at 3.16°, 4.58°, 6.38°, 9.74°, 12.98° and 24.26° assigned to the (110), (020), (220), (330), (440) and (001) facets, matching with the reported structure (Figure 4.4c).¹⁶ This structure is mostly unaffected by the metalation, since **COF-BPY-1-CoCl₂** presents the same diffraction peaks, although the intensity of the peaks is reduced. Simulations based on an eclipsed stacking model of the 2D layers in **COF-BPY-1** (Figure 4.3) reproduced the PXRD peak positions and intensity obtained experimentally (Figure 4.4c). This suggests

that the material presents a layer staking that leads to open 1D channels, which could facilitate the diffusion of reagents.

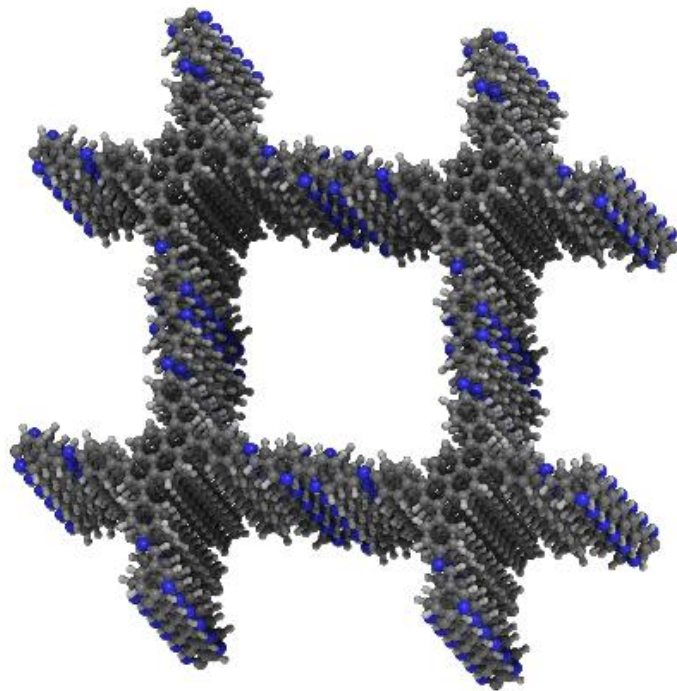


Figure 4.3. Eclipsed model of **COF-BPY-1**.

COF-BPY-2 shows weak diffraction peaks centered at 1.72° , 3.22° and 6.25° , which can be tentatively assigned to (100), (200) and (300) facets by comparison with an eclipsed model of **COF-BPY-2** (Figure 4.4d). The position and relative intensity of the peaks also match the previous report for a star-shaped perylene COF.³⁷ Based on the intensity and width of the PXRD signals, it appears that **COF-BPY-2** is much less crystalline than **COF-BPY-1**. This result could be rationalized by the low solubility of **PETA**, which could hamper the correct formation and purification of the material. In addition, the PXRD signals are no longer visible after metalation with CoCl_2 , suggesting that the crystallinity is being reduced due to the metalation.

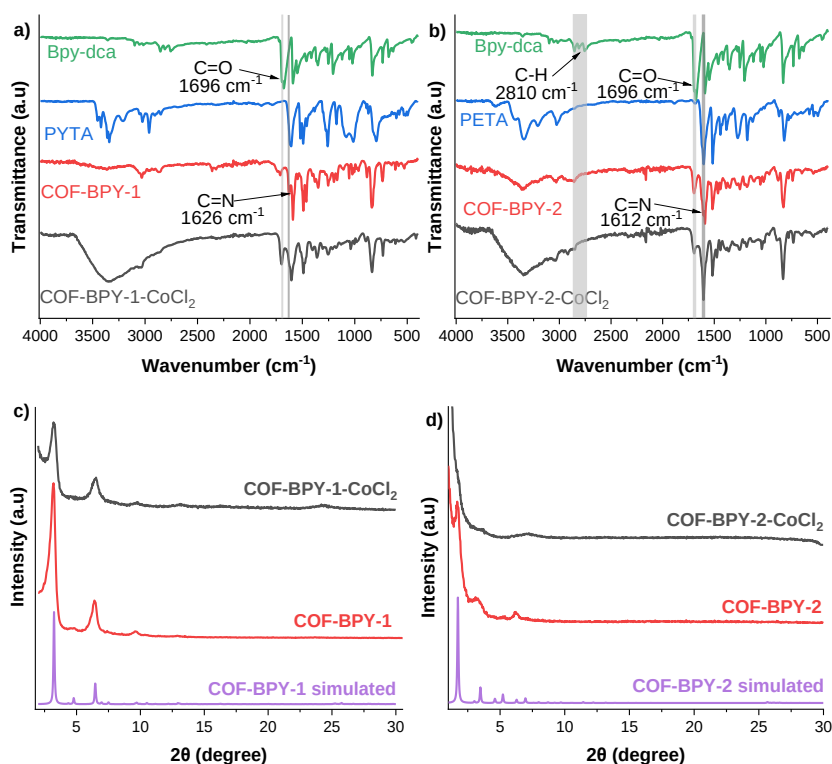


Figure 4.4. a-b) Comparison of FT-IR spectra of the bipyridine COFs and their precursors. c-d) Comparison of PXRD diffractograms of the bipyridine COFs.

Previous computational analysis of **COF-BPY-1** performed in our group indicated that the most stable stacked structure has the layers rotated by 180° along the perpendicular axes of the 2D COF, pointing the bipyridyl groups toward different pores.³⁰ This particular disposition of the bipyridines in adjacent layers of **COF-BPY-1**, pointing towards opposite directions, can prevent repulsion between coordinated metal centers in the bipyridines. This 3D packing avoids the repulsion between close CoCl₂ units, explaining the large metal loading (95%) measured by ICP-OES for the **COF-BPY-1-CoCl₂** relative to the bipyridine units in the COF (7.60 wt% Co). This metal loading is high relative to other metal-COFs reported, typically 20-50%.^{21,39-41} **COF-BPY-2-CoCl₂** presented a slightly lower metal loading, with an occupancy rate of 72% (6.1 wt% Co). The COFs were also

successfully metalated with other cobalt salts. Metalation of **COF-BPY-1** with $\text{Co}(\text{AcO})_2$ resulted in a slightly lower metal content (6.0 wt% Co), and metalation with $\text{Co}(\text{OTf})_2$ resulted in even lower metal content (3.7 wt% Co), which could be caused by the larger anions size.

COF-BPY-1 and **COF-BPY-1-CoCl₂** show isotherms characteristic of mesoporous materials, with high values of BET surface areas of 1953 and 1519 m^2g^{-1} , respectively, and total pore volumes of 1.21 and 0.87 cm^3g^{-1} (Figure 4.5a). The decrease in surface area and volume after metalation is consistent with the volume of the pores being partially occupied by CoCl_2 . In contrast, the porosity of **COF-BPY-2** and **COF-BPY-2-CoCl₂** is almost negligible, with BET surface areas of only 44 and 47 m^2g^{-1} , and pore volumes of 0.146 and 0.135 cm^3g^{-1} , respectively. The low porosity and low crystallinity of these materials suggest that the structure could be collapsed. It is also possible that insoluble oligomers are blocking the cavities. Nonlocal density functional theory (NLDFT) was used to calculate the distribution of pore widths, revealing a maximum at 2.8 and 2.3 nm for **COF-BPY-1** and **COF-BPY-1-CoCl₂**, respectively (Figure 4.5b). The reduction of the pore size by 5 Å could be associated with the high loading of CoCl_2 , reducing the effective pore size. The pore width of **COF-BPY-1** matches well with the cavity diameter calculated from PXRD data (2.79 nm). Smaller pores could be also observed (1.4 and 1.3 nm), possibly due to defects. The distribution of pore widths for the BPY-2 COFs was not calculated due to the low BET values.

TGA results showed excellent thermal stability up to 500°C and 400°C for **COF-BPY-1** and **COF-BPY-1-CoCl₂**, respectively (Figure 4.5c). Additionally, a 20% mass loss between 30-80°C was detected for **COF-BPY-1-CoCl₂**. Since all COFs were dried under vacuum at 80°C before measurements, this mass loss is assigned to the loss of water captured from

CHAPTER IV: Development of imine Metal Covalent Organic Frameworks based on N-donor ligands

the air during the analysis preparation. **COF-BPY-2** and **COF-BPY-2-CoCl₂** showed similar stability, with a gradual loss of mass beginning around 500°C (Figure 4.5d).

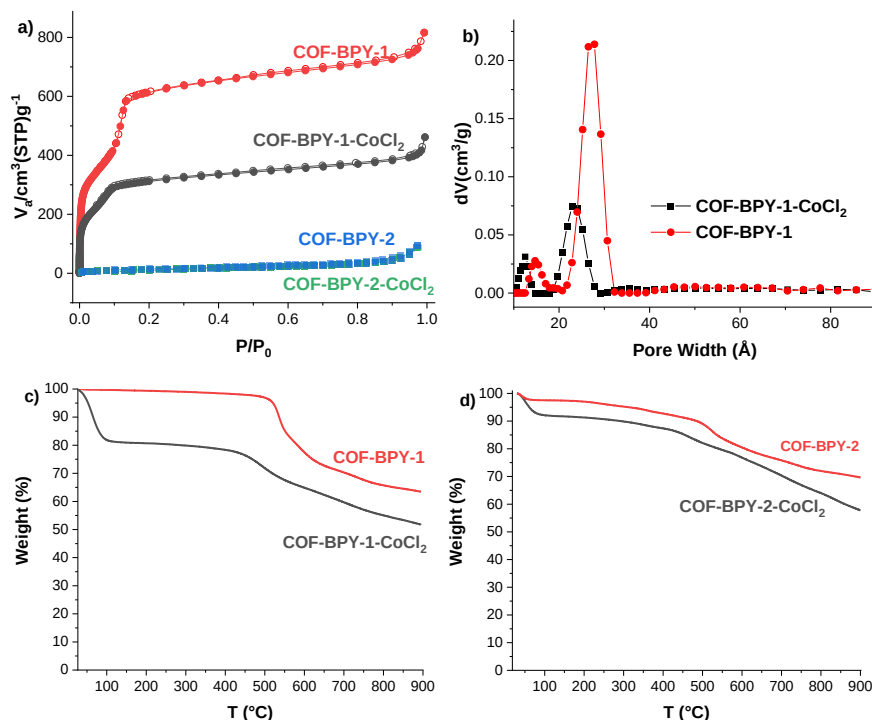


Figure 4.5. a-b) Nitrogen adsorption isotherms of the bipyridine COFs, c-d) TGA under nitrogen atmosphere of the bipyridine COFs.

TEM images of **COF-BPY-1** and **COF-BPY-1-CoCl₂** showed sheet-like structures, with some globular features of a few hundred nanometers in size (Figure 4.6). Additionally, the square grid structure of the framework could be appreciated at higher magnifications. STEM HAADF images and EDX elemental mapping of **COF-BPY-1-CoCl₂** showed no signs of metallic nanoparticles (Figure 4.7). In some parts of **COF-BPY-2** and **COF-BPY-2-CoCl₂**, large hexagonal pores could be observed by TEM images, in agreement with the expected structure (Figure 4.8).

Having synthesized and characterized the two cobalt bipyridine COFs, they were employed as catalysts in the hydroboration of alkenes. This reactivity study is covered in chapter V.

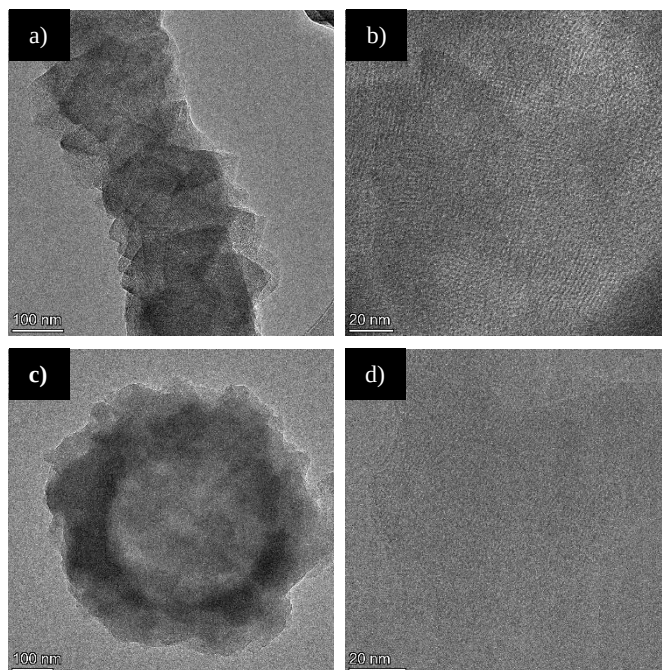


Figure 4.6. TEM images of a-b) **COF-BPY-1**, c-d) **COF-BPY-1-CoCl₂**.

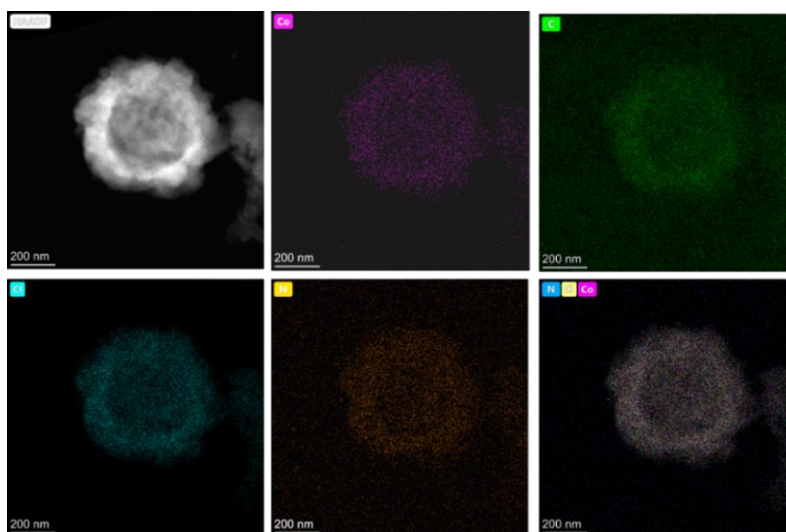


Figure 4.7. STEM HAADF images and EDX elemental mapping of **COF-BPY-1-CoCl₂**.

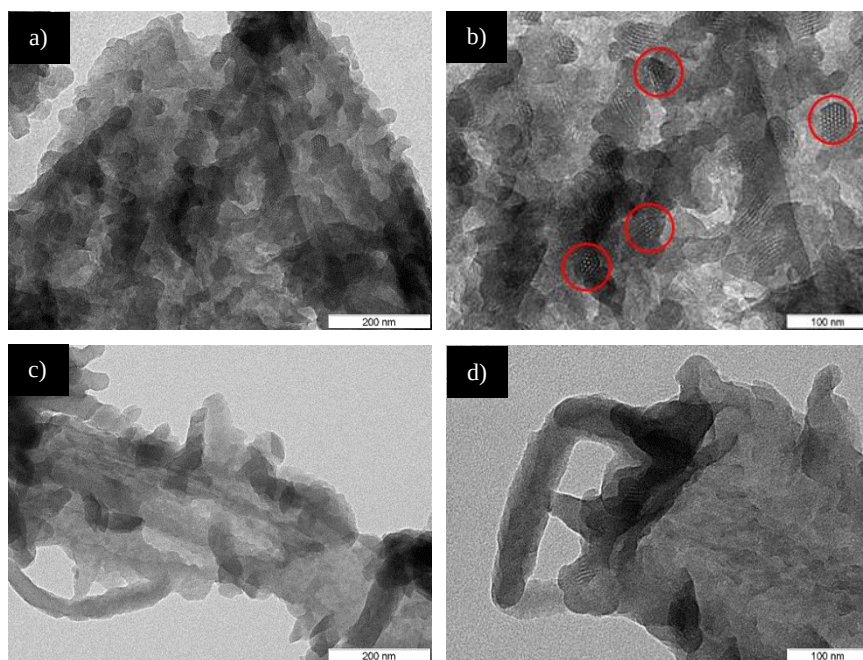
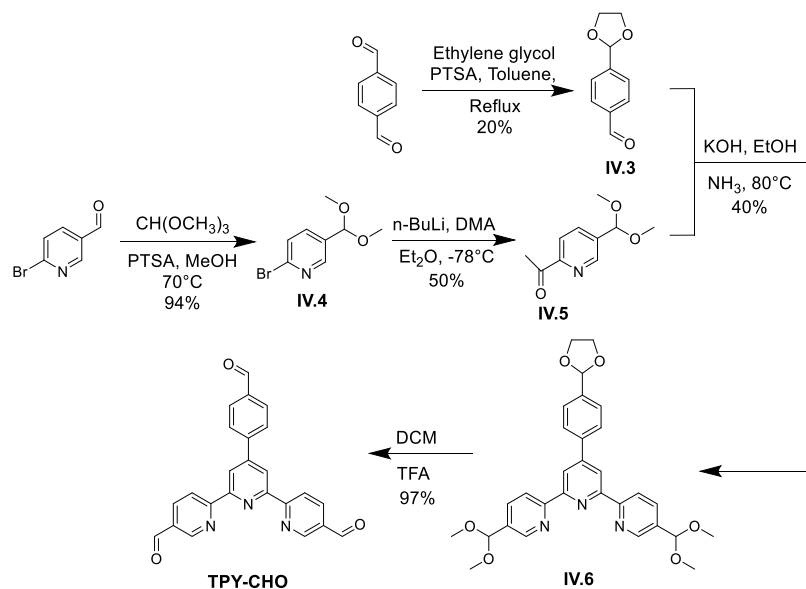


Figure 4.8. TEM images of a-b) **COF-BPY-2**, c-d) **COF-BPY-2-CoCl₂**. Well-defined hexagonal pores are highlighted by a red circle.

4.2.2. Synthesis and characterization of terpyridine COFs

The formation of terpyridine COFs was initiated by the synthesis of a new aldehyde terpyridine linker: 4'-(4-formylphenyl)-[2,2':6',2''-terpyridine]-5,5''-dicarbaldehyde (**TPY-CHO**) (Scheme 4.5). Terephthalaldehyde and bromonicotinaldehyde were protected as acetals with ethylene glycol or trimethyl orthoformate to produce **IV.3**⁴² and **IV.4**,⁴³ respectively. **IV.5**⁴⁴ was obtained by acylation of **IV.4** with *n*-BuLi and DMA. Combining **IV.3** with **IV.5** and NH₃ in a Kröhnke reaction formed terpyridine **IV.6**, which was deprotected by TFA treatment to produce **TPY-CHO**. The proper formation of the aldehyde ligand was confirmed by the two ¹H NMR signals corresponding to aldehyde groups (10.26 and 10.17 ppm, see the experimental section for details), and by the mass of the product (MS (ESI) *m/z*: calcd for C₂₄H₁₅N₃O₄ [M+H]⁺ 394.4; found, 394.1).



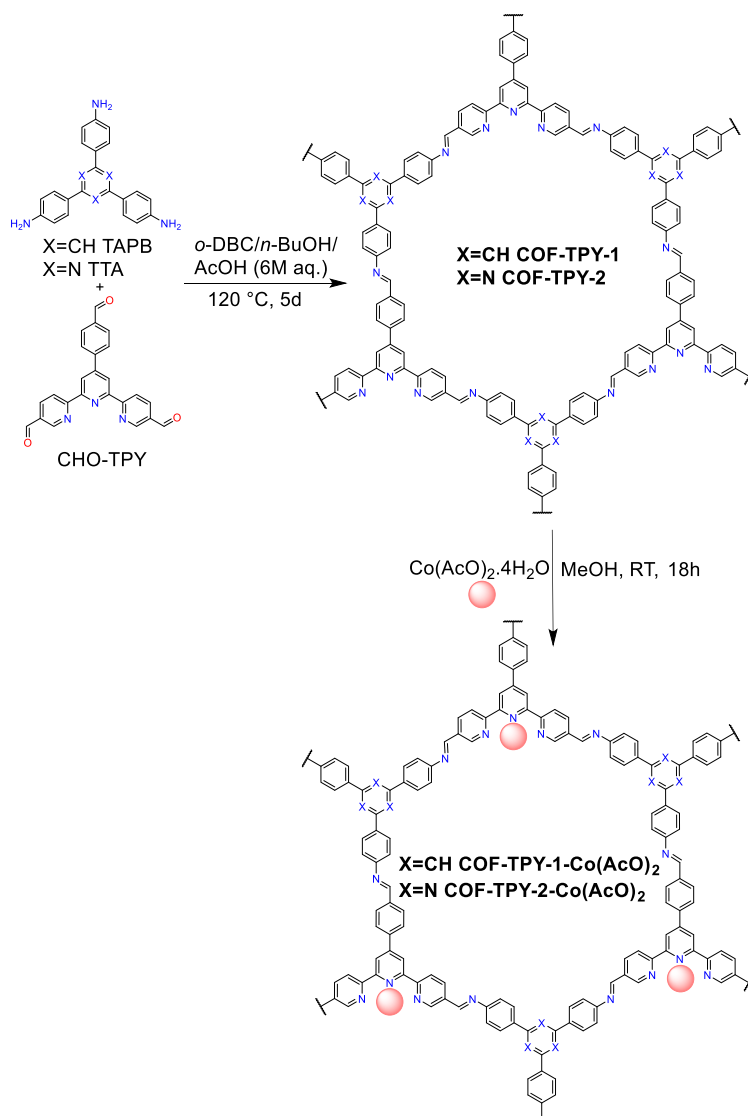
Scheme 4.5. **TPY-CHO** synthetic route.

PYTA and **PETA** (Section 4.2.1) were not selected as amine linkers for forming COFs with **TPY-CHO**, since a fully condensed 2D framework

cannot be envisaged from a combination of molecules with such symmetries,⁴⁵ and could result in the formation of amorphous materials. Similar to the previous section, **COF-TPY-1** and **COF-TPY-2** were synthesized under solvothermal conditions by condensation between **TPY-CHO** and the commercially available amine ligands 1,3,5-tris(4-aminophenyl)benzene (**TAPB**) or 4,4',4''-(1,3,5-triazine-2,4,6-triyl)trianiline (**TTA**), respectively (Scheme 4.6).

COF-TPY-1 and **COF-TPY-2** were obtained as yellow powders in 85% and 75% yield, respectively, under the optimized conditions [5:5:1 (v/v) mixture of *o*-DCB/*n*-BuOH/(aqueous 6 M AcOH), 120 °C, 5 d for **COF-TPY-1**, 3:7:1 (v/v) mixture of *o*-DCB/*n*-BuOH/(aqueous 6 M AcOH), 120 °C, 5 d for **COF-TPY-2**]. Afterward, the COFs were metalated by Co(AcO)₂·6H₂O in MeOH, forming **COF-TPY-1-Co(AcO)₂** and **COF-TPY-2-Co(AcO)₂** as orange solids. Co(AcO)₂·6H₂O was selected as the metal salt due to the good stability and high activity of Co(II) carboxylate borylation catalysts previously reported, which is our targeted transformation.⁴⁶⁻⁵⁰

CHAPTER IV: Development of imine Metal Covalent Organic Frameworks based on N-donor ligands



Scheme 4.6. Synthesis and metalation of the terpyridine COFs.

Fourier-transform infrared spectroscopy (FT-IR) of **COF-TPY-1** and **2** revealed the disappearance of the characteristic C=O stretching band at 1693 cm^{-1} and the appearance of a new C=N band around 1626 cm^{-1} , confirming the condensation reaction (Figure 4.9a-b). After metalation, **COF-TPY-1-Co(AcO)₂** presented new bands around 1552 and 1404 cm^{-1}

assigned to the acetate anions. The acetate bands could not be easily observed in **COF-TPY-2-Co(AcO)₂**, possibly due to the lower metal loading. The powder X-ray diffraction (PXRD) pattern of **COF-TPY-1** showed sharp peaks indicative of a crystalline structure, with signals centered at 4.01°, 6.96°, 8.05°, 10.64°, 14.47° and 24.86° (Figure 4.9c). **COF-TPY-2** presented a diffraction pattern with very similar angles (Figure 4.9d), except for the band around ~25°, which is slightly shifted to a higher angle (Figure 4.9e. The band is centered at 24.86° and 25.60° for **COF-TPY-1** and **COF-TPY-2**, respectively). The change in position of this band, usually associated with the (001) facet, suggests an increase in the interlayer distance of 0.1 Å (The interlayer distance for **COF-TPY-1** and **COF-TPY-2** is 3.58 and 3.48 Å, respectively). This change could be rationalized by the slightly different geometries of the linkers; TTA is entirely flat, which facilitates stacking, but TAPB presents a dihedral angle between the aryl rings.⁵¹

The identical PXRD pattern for the metalated COFs suggests that the structure of the framework remains unchanged after cobalt incorporation. PXRD predictions using an eclipsed model of **COF-TPY-1** and **COF-TPY-2** matched well with the experimental diffractograms (Figure 4.9c-d). Additionally, preliminary DFT studies tentatively suggested that stacking the **COF-TPY-1** layers in an alternating fashion is more energetically favorable compared to stacking identical layers, resulting in **TABP** linkers stacked on top of **TPY-CHO** linkers (Figure 4.10).

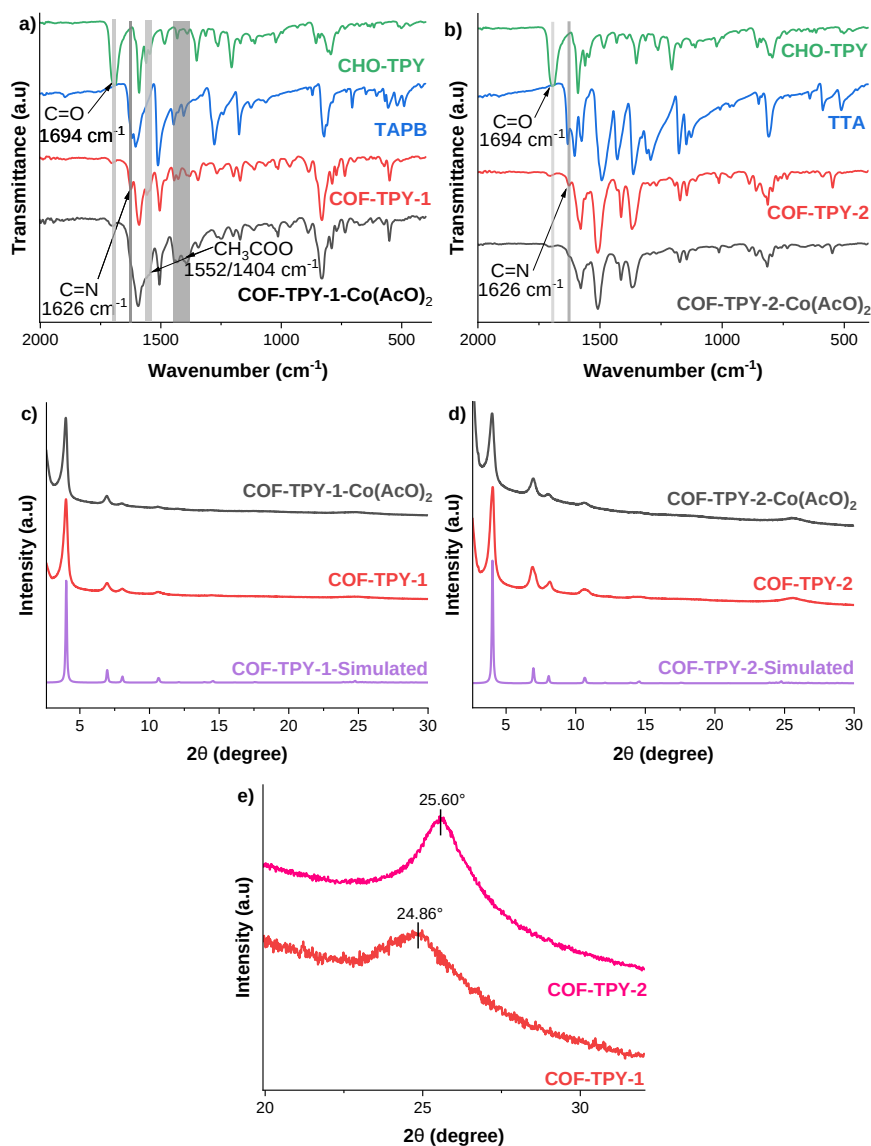


Figure 4.9. a-b) Comparison of FT-IR spectra of the terpyridine COFs and their precursors. c-e) Comparison of PXRD diffractograms of the terpyridine COFs.

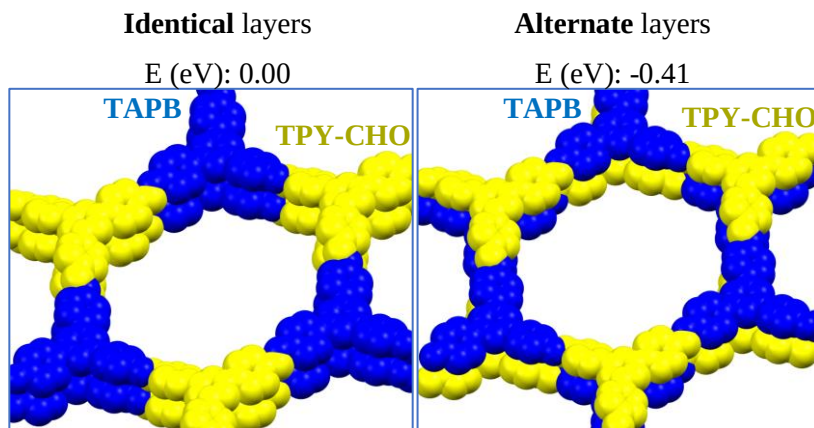


Figure 4.10. Comparison of the eclipsed model of **COF-TPY-1** with identical or alternate layers. TAPB and TPY-CHO linkers are colored blue and yellow, respectively.

The presence of cobalt in the metalated COFs was confirmed by ICP-OES analysis, with a 3.8 wt% Co for **COF-TPY-1-Co(AcO)₂** and a 2.9 wt% Co for **COF-TPY-2-Co(AcO)₂**, corresponding to an occupancy of 50% and 37% of the terpyridine, respectively.

High BET surface areas of 1768 and 2100 cm²/g were measured for **COF-TPY-1** and **COF-TPY-2**, respectively, based on N₂ isotherms (Figure 4.11a-b). Additionally, the porosity of the materials remains high after metalation (1347 and 1519 cm²/g for **COF-TPY-1-Co(AcO)₂** and **COF-TPY-2-Co(AcO)₂**, respectively). The total pore volumes were calculated as 1.22 cm³g⁻¹, 1.74 cm³g⁻¹, 0.84 cm³g⁻¹ and 0.88 cm³g⁻¹ for **COF-TPY-1**, **COF-TPY-2**, **COF-TPY-1-Co(AcO)₂** and **COF-TPY-2-Co(AcO)₂**, respectively. Thermogravimetric analysis (TGA) showed that the COFs possess good thermal stability up to 500 °C, while the metalated COFs are stable up to 300 °C. An initial loss of water at around 50 °C was also observed for **COF-TPY-1-Co(AcO)₂** and **COF-TPY-2-Co(AcO)₂** (Figure 4.11c-d).

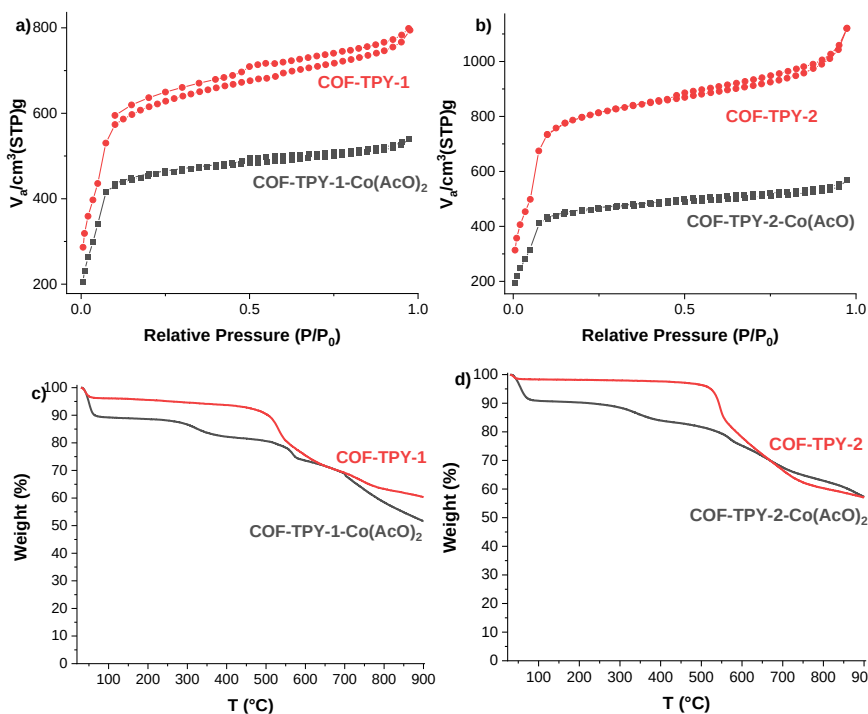


Figure 4.11. a-b) Nitrogen adsorption isotherms of the terpyridine COFs, c-d) TGA under N_2 of the terpyridine COFs

The COFs were also characterized with transmission electron microscopy (TEM, Figure 4.12 and Figure 4.13), revealing small rod-shaped crystalline features with extended porous channels for **COF-TPY-2** and **COF-TPY-2-Co(AcO)₂**. The line profile suggests a pore size of 2 nm, which is shorter than the unit cell ($a = 2.61$ nm, $b = 2.63$ nm). On the other hand, the porous channels of **COF-TPY-1** and **COF-TPY-1-Co(AcO)₂** were harder to detect due to having more agglomerated structures.

After being characterized, the two cobalt terpyridine COFs were employed as catalysts in the borylation of arenes. This topic is covered in Chapter VI of this thesis.

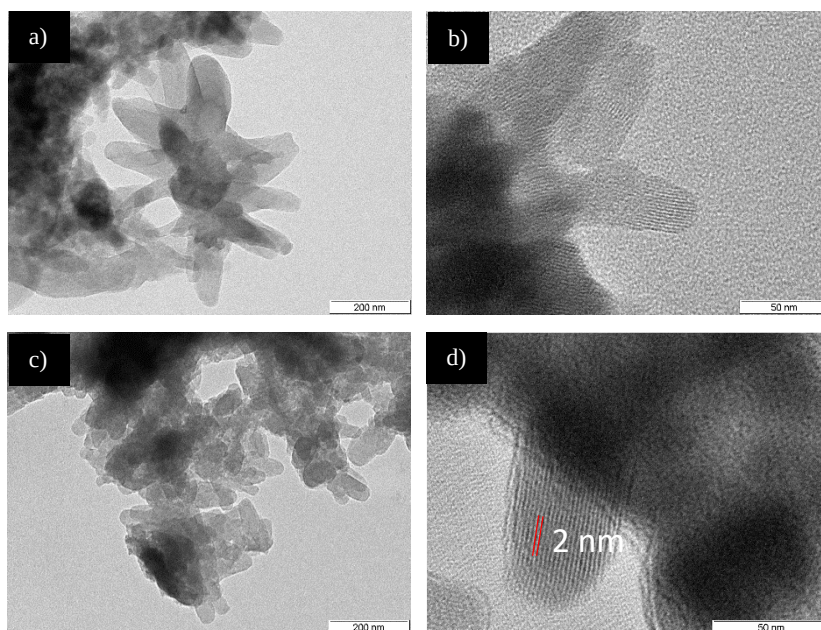


Figure 4.12. TEM images of a-b) COF-TPY-2, c-d) COF-TPY-2-Co(AcO)₂.

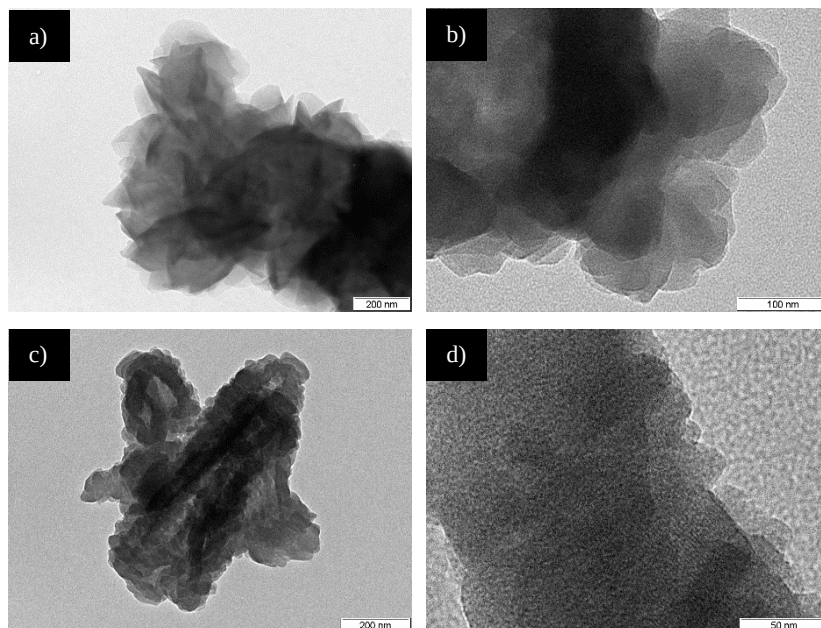
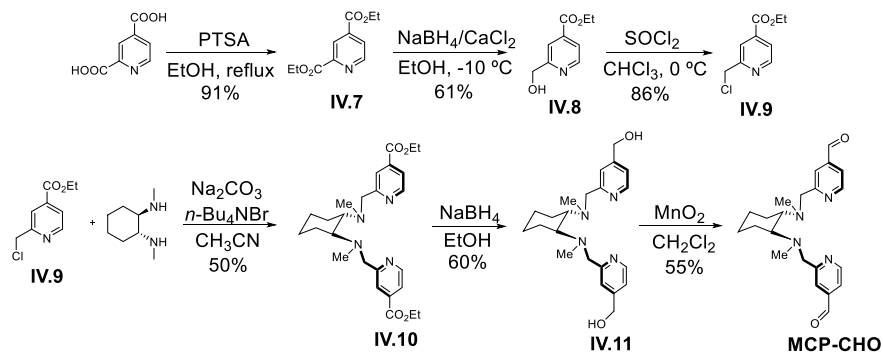


Figure 4.13. TEM images of a-b) COF-TPY-1, c-d) COF-TPY-1-Co(AcO)₂.

4.2.3. Synthesis and characterization of N,N-bispyridine-cyclohexyldiamine polymer

A novel tetradentate ligand based on a bispyridine-cyclohexyldiamine scaffold with two aldehyde groups (**MCP-CHO**) was synthesized following the synthetic path shown in Scheme 4.7. Compound **IV.7**⁵² was prepared by esterification of commercially available pyridine-2,4-dicarboxylic acid, followed by a selective reduction of the ester group on the 2-position by NaBH₄, affording **IV.8**.⁵² Chlorination of this compound with SOCl₂ yielded **IV.9**.⁵² The NMR spectra of **IV.7-IV.9** agree with previously reported data.⁵² The tetradentate ester ligand **IV.10** was formed by combining (1S,2S)-N,N'-Dimethyl-1,2-cyclohexane-diamine with **IV.9** through nucleophilic substitution. The incorporation of two pyridine rings in **IV.10** was confirmed by the integration of cyclohexyl to pyridine ¹H NMR signals. Reduction of the ester groups **IV.10** in with NaBH₄ resulted in the formation of **IV.11**, as evidenced by the appearance of a -CH₂OH ¹H NMR signal at 5.27 ppm. Finally, the alcohol groups in **IV.11** were oxidized by MnO₂, producing **MCP-CHO** as an orange oil. The disappearance of the -CH₂OH signal and the appearance of a new -CHO signal at 9.94 ppm on the ¹H-NMR spectrum confirmed the correct formation of the aldehyde groups (See experimental section for details).

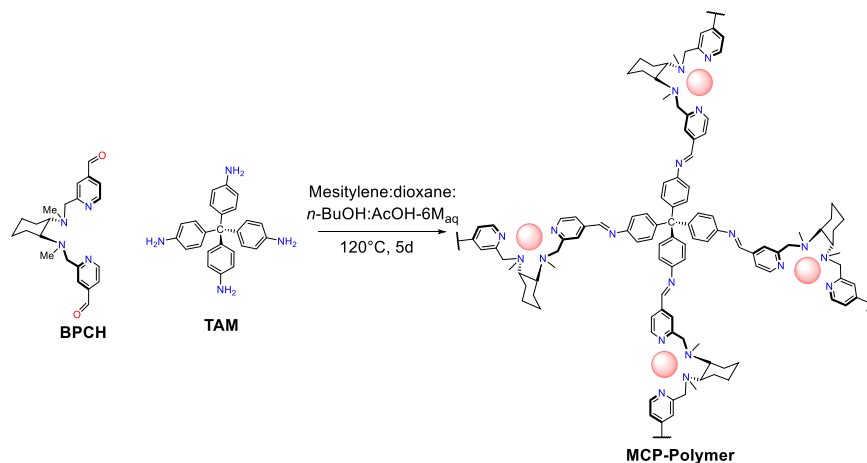


Scheme 4.7. MCP-CHO synthetic route.

Similar to previous sections, **MCP-CHO** was combined with different amine linkers through condensation reactions to form a COF. A screening of reaction conditions was performed to improve the product yield and crystallinity (Table 4.2).

Unlike the rest of the linkers used in this chapter, MCP-CHO is quite flexible and can adopt several conformations, which makes the synthesis of a well-ordered COF much more challenging. A potential solution for this issue, which has been previously used for challenging COFs,¹¹ is to add a metal salt to the reaction medium to form *in-situ* a rigid coordination complex. Thus, metal salts were included as an additive in the screening.

Different amine linkers were also employed in the screening (**PYTA**, **TAPB** and **TAM**), to ascertain which linker is more suitable for obtaining an ordered material. Despite the extensive screening (Table 4.2), all entries produced amorphous solids or liquids. The conditions on entry 24 were selected for the synthesis of the **MCP-polymer** (Scheme 4.8) due to the high yield (84 %) and the presence of cobalt in the material. **MCP-polymer** was obtained as a purple powder, characterized and employed in catalytic tests.



Scheme 4.8. Formation of **MCP-polymer**.

Table 4.2. Conditions screening for the synthesis of **MCP-Polymer**.

Nº	Solvent mixture	Amine linker	Metal salt	aq. AcOH 6 M (V %)	Temp. (°C)	Yield (%)	Result
1	Mesitylene:dioxane 1:1	PYTA	-	9	120	9	Amorphous
2	<i>o</i> -DCB: <i>n</i> -BuOH 1:1	PYTA	-	9	120	-	Liquid
3	Mesitylene:dioxane 1:1	PYTA	Zn(AcO) ₂	9	120	61	Amorphous
4	<i>o</i> -DCB: <i>n</i> -BuOH 1:1	PYTA	Zn(AcO) ₂	9	120	39	Amorphous
5	<i>o</i> -DCB:dioxane 1:1	PYTA	Zn(AcO) ₂	9	150	64	Amorphous
6	Mesitylene: <i>n</i> -BuOH 1:1	PYTA	Zn(AcO) ₂	9	150	-	Liquid
7	DMF: <i>n</i> -BuOH 1:1	PYTA	Zn(AcO) ₂	9	120	-	Liquid
8	Dioxane	PYTA	Zn(AcO) ₂	9	120	18	Amorphous
9	Mesitylene:dioxane 1:1	TAPB		9	120	68	Amorphous
10	<i>o</i> -DCB: <i>n</i> -BuOH 1:1	TAPB		9	120	-	Liquid
11	Mesitylene:dioxane 1:1	TAPB	Zn(AcO) ₂	9	120	74	Amorphous
12	<i>o</i> -DCB: <i>n</i> -BuOH 1:1	TAPB	Zn(AcO) ₂	9	120	-	Liquid
13	Mesitylene:dioxane 1:1	TAPB	Zn(AcO) ₂	15	120	-	Liquid
14	Mesitylene:dioxane 1:1	TAPB		15	120	-	Liquid
15	Mesitylene:dioxane 3:1	TAPB	Zn(AcO) ₂	9	120	51	Amorphous
16	Mesitylene:dioxane 1:3	TAPB	Zn(AcO) ₂	9	120	45	Amorphous
17	Mesitylene:dioxane 1:3	TAPB		9	90	66	Amorphous
18	Mesitylene:dioxane 3:1	TAPB		9	120	-	Liquid
19	Mesitylene:dioxane: <i>n</i> -BuOH 2:2:1	TAPB	Zn(AcO) ₂	9	120	69	Amorphous
20	Mesitylene:dioxane: <i>n</i> -BuOH 2:2:1	TAM		9	120	70	Amorphous
21	Mesitylene:dioxane: <i>n</i> -BuOH 2:2:1	TAM	Zn(AcO) ₂	9	120	74	Amorphous
22	Mesitylene:dioxane: <i>n</i> -BuOH 2:2:1	TAM		9	120	69	Amorphous
23	Mesitylene:dioxane 1:1	TAM	Zn(AcO) ₂	9	120	76	Amorphous
24	Mesitylene:dioxane:<i>n</i>-BuOH 2:2:1	TAM	CoCl₂	9	120	84	Amorphous
25	Mesitylene:dioxane: <i>n</i> -BuOH 2:2:1	TAM	CoCl ₂	15	120	64	Amorphous
26	Mesitylene:dioxane: <i>n</i> -BuOH 3:1:1	TAM	CoCl ₂	9	120	68	Amorphous
27	Mesitylene:dioxane: <i>n</i> -BuOH 1:3:1	TAM	CoCl ₂	9	120	80	Amorphous
28	<i>o</i> -DCB:dioxane: <i>n</i> -BuOH 2:2:1	TAM	CoCl ₂	9	120	73	Amorphous
29	<i>o</i> -DCB:dioxane: <i>n</i> -BuOH 3:1:1	TAM	CoCl ₂	9	120	69	Amorphous

Reaction conditions: amine linker, MCP-CHO (10 mg, 0.026 mmol), solvent mixture (0.5 mL), aqueous AcOH 6M, metal salt (0.4 mmol), 120 °C for 5 d. Crystallinity was estimated based on the intensity of the PXRD peaks (Section 4.4.3).

The occurrence of the condensation reaction was checked by FT-IR, which displays the disappearance of the C=O band at 1703 cm^{-1} (Figure 4.14a). The peak at 1615 cm^{-1} could be assigned to the imine bond, although the assignment is not clear due to overlapping. The broad signals of the PXRD pattern indicate that the material is an amorphous polymer and thus cannot be classified as a COF (Figure 4.14b). ICP-OES analysis of the **MCP-polymer** revealed a metal content of 5.0 wt% Co, corresponding to a 66% loading of the ligands. N_2 adsorption isotherms showed that the material is non-porous, with a BET area of only $17\text{ m}^2\text{g}^{-1}$ and a pore volume of $0.05\text{ cm}^3\text{g}^{-1}$ (Figure 4.14c). TGA showed an initial loss of water around 80°C and a sharp loss of mass around 400°C due to decomposition (Figure 4.14d). TEM images of the material revealed the presence of metal nanoparticles, possibly formed due to aggregation of Co during the synthesis (Figure 4.14e-f). This result contrasts with the previous COFs of this chapter, which shows no signs of metal nanoparticles.

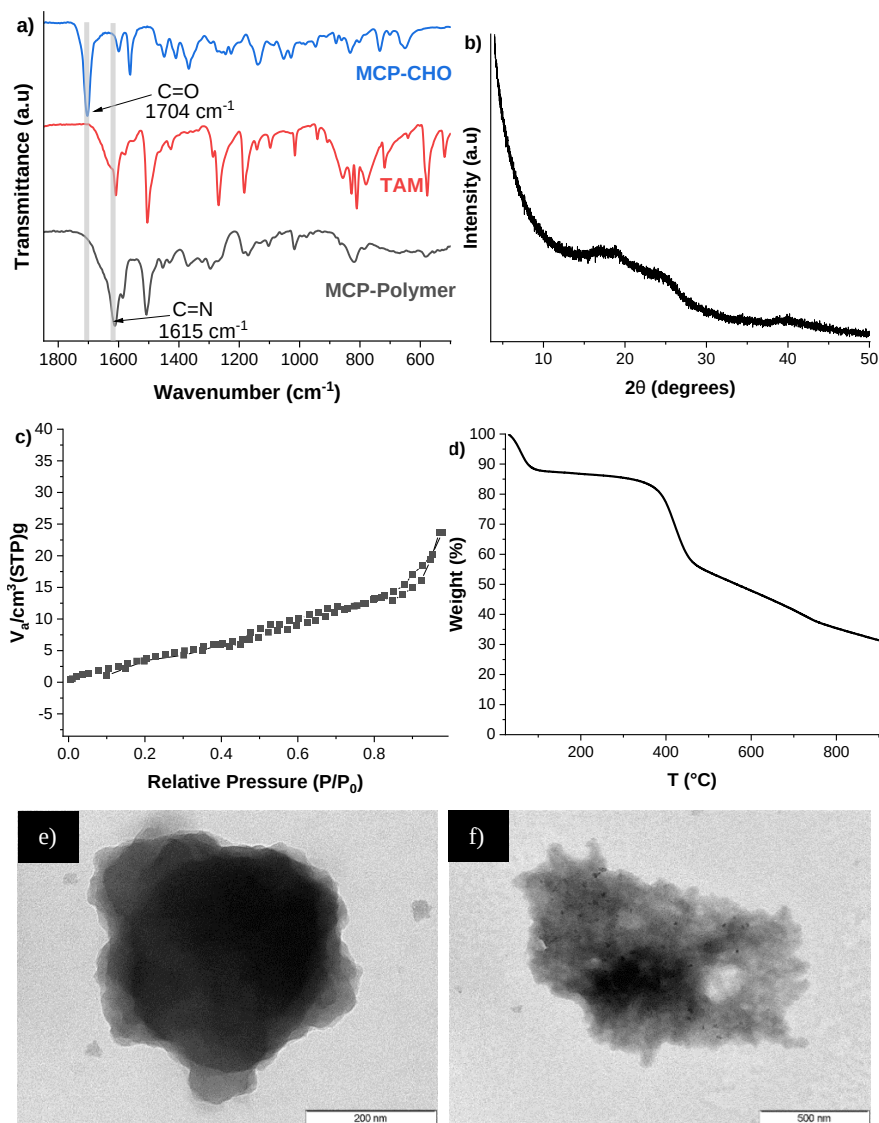


Figure 4.14. Characterization of **MCP-polymer**: a) FT-IR, b) PXRD, c) Gas adsorption, d) TGA, e-f) TEM.

The catalytic performance of the material was evaluated by performing preliminary experiments on the hydroboration or borylation of alkenes and arenes catalyzed by **MCP-polymer** (Table 4.3). No product was detected for the borylation of toluene, while only traces of product were found for

the hydroboration of 1-octene or styrene. This result could be slightly improved by activating the catalyst with NaBEt₃H before the reaction, but the yields were still below 10% (Table 4.3, entry 2). The poor performance of **MCP-polymer** in the reactions tested could be attributed to the low porosity of the material which reduces the accessibility of reagents towards the catalytic sites, or it could be caused by the agglomeration of the Co catalytic centers into nanoparticles.

Table 4.3. Evaluation of **BPCH-polymer** as catalyst.

$\text{R}-\text{CH}=\text{CH}_2$ or Ar-H <math>\xrightarrow[\text{Neat substrate, 24h}]{\text{MCP-Polymer (1.5 mol\% [Co]) HBpin or B}_2\text{pin}_2}</math> $\text{R}-\text{CH}_2-\text{CH}_2-\text{Bpin}$ or Ar-Bpin						
Entry	Substrate	Boron source	Activator	Temperature	Conv. %	Yield %
1	1-octene	HBpin	-	25 °C	6	1
2	1-octene	HBpin	NaBEt ₃ H	25 °C	19	9
3	Styrene	HBpin	-	25 °C	5	1
4	Styrene	HBpin	NaBEt ₃ H	25 °C	4	2
5	Toluene	HBpin	-	100 °C	-	0
6	Toluene	HBpin	NaBEt ₃ H	100 °C	-	0
7	Toluene	B ₂ pin ₂	-	100 °C	4	0
8	Toluene	B ₂ pin ₂	NaBEt ₃ H	100 °C	0	0

Reaction conditions for entries 1-4: 0.25 mmol 1-octene or styrene, 0.32 mmol HBpin, 3.75 μmol Co, 25 °C, 24 h, under N₂. Reaction conditions for entries 5-8: 0.5 mL toluene, 0.3 mmol B₂pin₂, 3.75 μmol Co, 100 °C, 24 h, under N₂. Conversion and yield were determined by GC. On entries where NaBEt₃H is used as an activator, MCP-polymer was placed in a NaBEt₃H (10 eq.) solution in THF for 1 h, then filtered and washed with THF and used as a catalyst.

4.3. Conclusions

In this chapter, we have synthesized a series of imine COFs by condensation between aldehyde and amine linkers, followed by metalation with cobalt through coordination of the ligands present in the structure of the materials. FT-IR, PXRD, gas adsorption, TGA, TEM, and ICP-OES were employed to characterize all materials.

First, we synthesized two bipyridine-based COFs. The synthesis of **COF-BPY-1** was successfully reproduced, while the synthesis of **COF-BPY-2** was described for the first time in this work by employing a perylene amine linker (**PETA**). Both COFs could be effectively metalated with CoCl_2 in solution. However, **COF-BPY-2** showed much lower crystallinity and porosity, possibly indicating that the structure collapsed or did not properly form. We also prepared two terpyridine COFs (**COF-TPY-1** and **COF-TPY-2**) by employing a new terpyridine aldehyde linker (**TPY-CHO**). This linker allowed for the facile synthesis of highly crystalline and porous COFs with terpyridine moieties that were metalated afterward with $\text{Co}(\text{AcO})_2$. Finally, a bipyridine-cyclohexyldiamine ligand with aldehyde groups was prepared (**MCP-CHO**). The materials prepared with this ligand were amorphous and non-porous (**MCP-polymer**), which explains their poor catalytic activity in the reactions tested. This result could be assigned to the flexibility of the ligand, which hinders the formation of a well-ordered material.

4.4. Experimental section

4.4.1. Materials and methods

Materials. Commercial reagents were purchased from Sigma Aldrich, Alfa Aesar, TCI Chemicals, Fluorochem or abcr and used as received without further purification. All solvents were purified by a SPS-400, Innovative Technology solvent purification system and stored under argon with activated 4 Å molecular sieves after degassing.

Nuclear magnetic resonance (NMR). NMR spectra were recorded on Bruker AV500/AV400 spectrometer using standard conditions (300 K). All ^1H chemical shifts are reported in ppm and have been internally calibrated to the residual protons of the deuterated solvent. The ^{13}C chemical shifts have been internally calibrated to the carbon atoms of the deuterated solvent. The coupling constants were measured in Hz.

Powder X-ray diffraction (PXRD). Powder X-Ray Diffraction (PXRD) PXRD measurements were made using a Siemens D5000 diffractometer (Bragg-Brentano parafocusing geometry and vertical θ - θ goniometer) fitted with a curved graphite diffracted-beam monochromator, incident and diffracted -beam Soller slits, a 0.06° receiving slit and scintillation counter as a detector. The angular 2θ diffraction range was between 2 and 40° . The data was collected with an angular step of 0.02° at 12s per step and sample rotation. A low background Si(510) wafer was used as sample holder. $\text{Cu}_{\text{K}\alpha}$ radiation was obtained from a copper X-ray tube operated at 40 kV and 30 mA.

Gas Sorption. Nitrogen sorption isotherms were measured on Autosorb iQ adsorption analyzer (Quantachrome). Samples were degassed under vacuum at 100°C over 24h. Nitrogen measurements were performed at 77 K and the temperature was held constant using liquid N_2 . The pressure

range used to calculate the BET surface area was selected to fulfill the two “consistency criteria.”

Scanning Electron Microscopy-Energy Dispersed X-ray Spectroscopy (SEM-EDX). The ESEM is from FEI company, model Quanta 600 in low vacuum mode (vacuum pressure 0.68 Torr). The EDX is from Oxford Instruments. The conditions for the ESEM are 20 kV accelerating voltage and a working distance close to 10 mm.

Inductively Coupled Plasma Optical Emisión Spectrometry (ICP-OES). ICP-OES measurement was performed on the Perkin Elmer Optical Emission Spectrometer Optima 5300 DV (Scott-Chamber/Cross-Flow-Nebulizer).

Fourier-Transformed Infrared (FTIR). Spectroscopy FTIR measurements were measured using a Bruker Optics FT-IR Alpha spectrometer equipped with a DTGS detector, KBr beamsplitter at 4 cm⁻¹ resolution using a one bounce ATR accessory with diamond windows.

Thermogravimetric Analysis (TGA). TGA curves were measured using Mettler Toledo TGA/SDTA/851 in N₂, heating ramp 10 °C /min.

Transmission Electron Microscopy (TEM). Transmission electron microscopy (TEM) images were collected using a Thermo Scientific (FEI) Talos F200X G2 TEM operating at 200 kV. TEM images were acquired using a Ceta 16M CMOS camera. Samples were prepared by applying 5 µL of the suspended sample in an aqueous solution onto continuous carbon 300 mesh Cu grids. Alternatively, TEM images were collected using a JEOL 1011 Transmission Electron Microscope operating at 80 kV. Samples were dispersed in ethanol and a drop of resultant suspensions was poured on carbon coated-copper grids.

Computational details. Periodic simulations were performed at the Density Functional Theory (DFT) level using the PBE functional and Grimme's D3 dispersion scheme as implemented in the Vienna Ab Initio Simulation Package (VASP).⁵³ Core electrons were described by projector augmented wave (PAW) and valence electrons by plane waves with a kinetic energy cutoff of 600 eV. The models are composed by two layers, with a and $b > 25 \text{ \AA}$ and $c \approx 7 \text{ \AA}$. The Brillouin zone was thus sampled at $1 \times 1 \times 3$ through the Monkhorst-Pack method.⁵³ PXRD spectra was simulated with the VESTA software.⁵³

Calculation of ligand occupancy rates: Occupancy rates for the MCOFs were calculated based on the following equation, where MW_{COF} is the molecular weight of a unit cell of the COF containing one ligand, MW_M is the atomic weight of the metal, MW_{ML} is the molecular weight of the metal plus anions plus coordinated solvents, and $\frac{g_M}{g_{MCOF}}$ is the cobalt content determined by ICP-OES.

$$Occupancy = \frac{\frac{MW_{COF}}{MW_M} \frac{g_M}{g_{MCOF}}}{1 - \frac{MW_{ML}}{MW_M} \frac{g_M}{g_{MCOF}}} \quad (eq. 1)$$

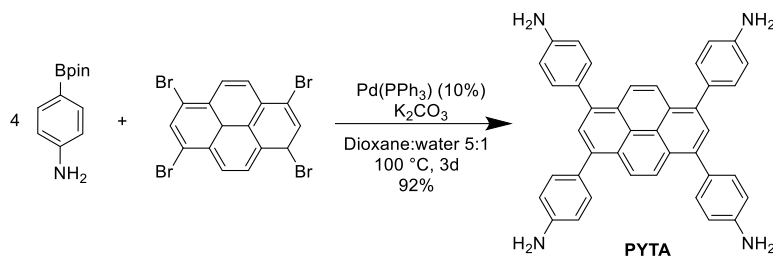
Eq. 1 was obtained the following way:

$$Occupancy = \frac{Mol_M}{Mol_{MCOF}} = \frac{\frac{g_M}{MW_M}}{\frac{g_{MCOF}}{MW_{MCOF}}} = \frac{\frac{g_M}{MW_M}}{\frac{g_{MCOF}}{MW_{COF} + MW_{ML} \times Occupancy}} \quad (eq. 2)$$

Table 4.4. Calculation of occupancy rates in MCOFs.

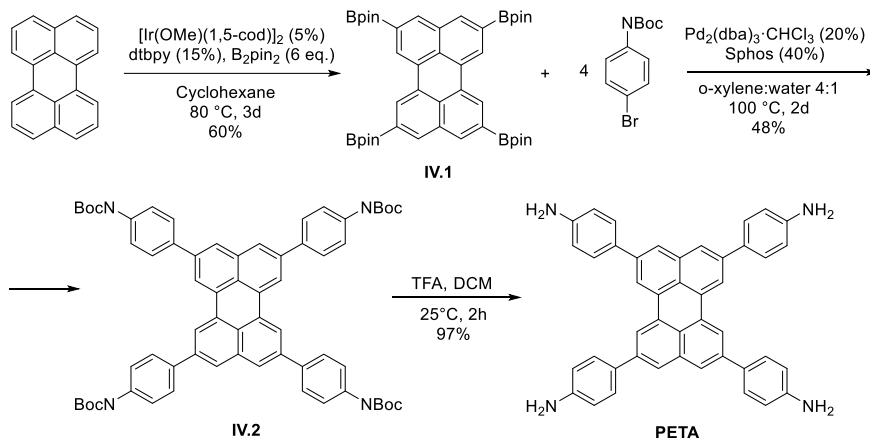
	MW_M	$\frac{g_M}{g_{MCOF}}$	MW_{COF}	MW_{ML}	Occupancy
COF-BPY-1- CoCl ₂	58.9	0.076	458	293	0.95
COF-BPY-2- CoCl ₂	58.9	0.061	484	293	0.72
COF-TPY-1- Co(AcO) ₂	58.9	0.038	691	177	0.50
COF-TPY-2- Co(AcO) ₂	58.9	0.029	693	177	0.37
MCP- Polymer	58.9	0.05	534	130	0.51

4.4.2. Synthesis procedures

**Scheme 4.9.** PYTA synthetic route.¹⁶

4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetraaniline (PYTA)¹⁶: This compound was synthesized according to a modified version of the published procedure. 1,3,6,8-Tetrabromopyrene (1.24 g, 2.39 mmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (2.51 g, 11.4 mmol), palladium tetrakis(triphenyl phosphine) (0.28 g, 0.24 mmol), and potassium carbonate (1.81 g, 13.3 mmol) were added to 20 mL dioxane and 4 mL water in a 100 mL round bottom flask. The mixture was stirred under reflux in Ar for 3 days. After cooling to room temperature, 30 mL of water were added. The precipitate was filtered, washed with water and methanol. The solid was dissolved in acetone and filtered through a short silica gel plug. The solvent was removed to afford the product in 92% yield. ¹H NMR

(DMSO, 400 MHz): δ (ppm) 8.09 (s, 4H), 7.75 (s, 2H), 7.32-7.29 (d, 8H), 6.74-6.72 (d, 8H), 5.28 (s, 8H). ^{13}C NMR (DMSO, 101 MHz): δ (ppm) 148.3, 137.6, 131.6, 129.5, 128.4, 127.2, 126.6, 125.0, 114.7.



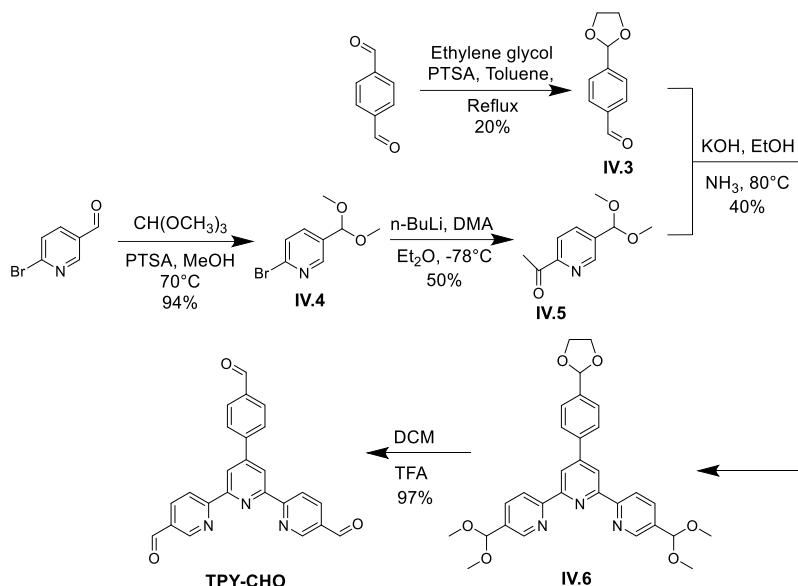
Scheme 4.10. PETA synthetic route.³⁷

2,5,8,11-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)peryene (IV.1)³⁷: Under nitrogen protection, into a 100 mL round bottom flask was added perylene (1.7 g, 6.74 mmol, 1.0 eq.), B₂pin₂ (7.53 g, 29.6 mmol, 4.4 eq.), [Ir(OMe)COD]₂ (45 mg, 0.067 mmol, 1 mol%), 4,4'-dimethyl-2,2'-bipyridyl (36 mg, 0.135 mmol, 2 mol%) and THF (30 mL). Then the mixture was heated at 80°C for 16 h. The reaction mixture cooled to room temperature, and upon addition of methanol (100 mL) a solid precipitated. The material was collected by vacuum filtration and washed with methanol to give 6.43 g of 2,5,8,11-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)peryene as a light yellow solid (4.85 g, 95%). ^1H NMR (300 MHz, CDCl₃) δ 8.62 (s, 4H), 8.25 (s, 4H), 1.43 (s, 48H).

2,5,8,11-tetrakis(4-Boc-aminophenyl)peryene (IV.2)³⁷: A reaction mixture containing compound IV.1 (1512 mg, 2.00 mmol, 1.0 eq.), N-Boc-4-bromoaniline (8708 mg, 32.0 mmol, 16 eq.), K₂CO₃ (2211 mg, 16.0 mmol, 8.0 eq.), Pd₂(dba)₃·CHCl₃ (414 mg, 0.40 mmol, 20 mol%), and

Sphos (328 mg, 0.80 mmol, 40 mol%) in 64 mL o-xylene and 16 mL H₂O was stirred under a static argon atmosphere at 100 °C for 40 h. After cooling to room temperature, 20 mL MeOH was added to form a homogeneous suspension. The precipitate was collected by filtration and washed with H₂O and MeOH until the washings were clear. The greenish solid was dissolved in a 6:4 DCM/EtOAc mixture and passed through a short plug of silica gel. The solution was concentrated to ca. 20 mL under reduced pressure, causing the product to precipitate. The precipitate was collected by filtration and washed successively with 10 mL MeOH and 10 mL DCM. For further purification, the product was dispersed in 600 mL EtOAc and sonicated for 30 min. The suspension was concentrated to ca. 20 mL under reduced pressure. The solids were collected by filtration, washed successively with 10 mL EtOAc and 10 mL DCM, and dried under high vacuum to yield the title compound as a greenish-yellow powder (1 g, 0.96 mmol, 48%). ¹H NMR (400 MHz, DMSO-d₆): 9.52 (s, 4H), 8.73 (s, 4H), 8.14 (s, 4H), 7.92 (d, *J* = 8.6 Hz, 8H), 7.66 (d, *J* = 8.3 Hz, 8H), 1.52 (s, 36H)

4,4',4'',4'''-(perylene-2,5,8,11-tetrayl)tetraaniline (PETA)³⁷: To a suspension of compound **IV.2** (829 mg, 0.82 mmol, 1.0 eq.) in 30 mL of anhydrous DCM was added 10 mL TFA. The resulting dark yellow solution was stirred for 2 h at room temperature. The reaction mixture was neutralized by slowly adding a saturated NaHCO₃ solution in argon-saturated H₂O, causing the product to precipitate as a dark orange solid. The solids were collected by filtration, washed with 500 mL argon-saturated H₂O and dried under high vacuum to yield the title compound as a bright orange powder (487 mg, 0.79 mmol, 97%). ¹H NMR (400 MHz, DMSO) δ 8.56 (s, 4H), 7.97 (s, 4H), 7.69 (d, *J* = 8.5 Hz, 8H), 6.79 – 6.72 (m, 8H), 5.32 (s, 8H). ¹³C NMR (126 MHz, DMSO) δ 149.52, 139.97, 136.44, 131.52, 128.59, 127.95, 126.03, 124.50, 119.25, 115.07.



Scheme 4.11. TPY-CHO synthetic route.

Synthesis of 4-(1,3-dioxolan-2-yl)benzaldehyde (VI.3)⁴²: To a solution of terephthalaldehyde (7 g, 52.2 mmol) and p-toluenesulfonic acid (100 mg, 0.5 mmol) in toluene (200 mL) was added slowly ethylene glycol (2.9 mL, 52.2 mmol). After heating at reflux for 6 h under a Dean-Stark trap, the solution was cooled down to room temperature. Then, 100 mL of water was added and the aqueous layers were extracted with dichloromethane. The combined organic solution was washed with brine, dried with MgSO₄ and the solvent was evaporated. The crude was purified by silica column chromatography using hexane/ethyl acetate 95/5 as eluent (1.91 g, 52.2 mmol, 20%). ¹H NMR (400 MHz, CDCl₃) δ 10.06 (s, 1H), 7.92 (d, J = 8.3 Hz, 2H), 7.67 (d, J = 8.2 Hz, 2H), 5.90 (s, 1H), 4.12 (dd, J = 20.6, 7.5 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 190.2, 144.1, 135.3, 129.5, 128.5, 114.7, 72.3.

Synthesis of 2-Bromo-5-(dimethoxymethyl)pyridine (VI.4)⁴³: 2-Bromo-5-formylpyridine (10 g, 54.2 mmol), p toluenesulphonic acid (204 mg, cat.), and trimethylorthoformate (25 mL) were added to a flask and sparged with nitrogen. After 100 mL dry methanol was injected with syringe, the mixture was refluxed at 68 °C for 4 h. The solution was cooled down to room temperature, 80 mL of dichloromethane was added, and the mixture was washed with sat. Na₂CO₃ and water. The aqueous layers were extracted with dichloromethane. The combined organic solution was washed with brine, dried with MgSO₄, and finally evaporated to yield a yellow oil (11.45 g, 92%). ¹H NMR (300 MHz, CDCl₃) δ 8.45 (dd, J = 2.4, 0.7 Hz, 1H), 7.64 (dd, J = 8.2, 2.5 Hz, 1H), 7.50 (d, J = 8.3 Hz, 1H), 5.44 (s, 1H), 3.34 (s, 6H).

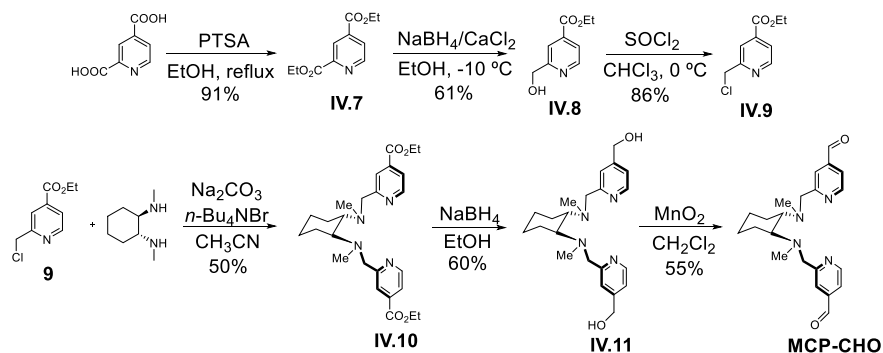
Synthesis of 1-(5-(dimethoxymethyl)pyridin-2-yl)ethan-1-one (VI.5)⁴⁴: 2-bromo-5-(dimethoxymethyl)pyridine (11.4 g, 49 mmol) was dissolved in 80 mL Et₂O and cooled to -78 °C, then 33.8 mL 1.6 M n-BuLi in hexane was added dropwise over 30 min. The mixture was stirred at -78 °C for 90 min, then 5.7 mL dimethylacetamide was added dropwise over 30 min and stirred for another 3 h. The mixture was quenched with NH₄Cl (aq.) slowly. The reaction mixture was evaporated to obtain the crude product and then purified by flash chromatographic column (hexane/ethyl acetate 90/10) to afford **3** (5 g, 49 mmol, 50%) ¹H NMR (300 MHz, CDCl₃) δ 8.76 (d, J = 2.0 Hz, 1H), 8.06 (dd, J = 8.1, 0.9 Hz, 1H), 7.93 (dd, J = 8.1, 2.1 Hz, 1H), 5.52 (s, 1H), 3.37 (s, 6H), 2.75 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 199.85, 153.53, 147.92, 137.15, 135.42, 121.20, 100.82, 52.69, 25.85.

Synthesis of 4'-(4-(1,3-dioxolan-2-yl)phenyl)-5,5''-bis(dimethoxymethyl)-2,2':6',2''-terpyridine (VI.6): 1-(5-(dimethoxymethyl)pyridin-2-yl)ethan-1-one (3.1 g, 16 mmol) and 4-(1,3-dioxolan-2-yl)benzaldehyde (1.4 g, 7.9 mmol) were dissolved in 130 mL of ethanol, followed by the addition of KOH (0.88 g, 16 mmol) and aqueous

CHAPTER IV: Development of imine Metal Covalent Organic Frameworks based on N-donor ligands

ammonia solution (34 mL, 30%). The reaction was refluxed for 72 h. After cooling to room temperature, water was added and the precipitate was filtered and washed with water and cold ethanol. The product was recrystallized from ethanol (1.7 g, 7.9 mmol, 41%). ^1H NMR (400 MHz, CDCl_3) δ 8.83 – 8.80 (m, 2H), 8.78 (s, 2H), 8.69 (d, J = 8.0 Hz, 2H), 8.01 – 7.93 (m, 4H), 7.69 – 7.63 (m, 2H), 5.93 (s, 1H), 5.59 (s, 2H), 4.22 – 4.07 (m, 4H), 3.41 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.22, 155.73, 149.92, 148.00, 139.23, 138.83, 135.57, 133.75, 127.38, 127.09, 120.92, 119.19, 103.41, 101.29, 65.37, 52.65.

Synthesis of 5,5''-bis(dimethoxymethyl)-4'-(4-(dimethoxymethyl)phenyl)-2,2':6',2''-terpyridine (TPY-CHO): 4'-(4-(1,3-dioxolan-2-yl)phenyl)-5,5''-bis(dimethoxymethyl)-2,2':6',2''-terpyridine (0.42 g, 0.79 mmol) was dissolved in THF (25 mL) and an HCl aqueous solution (24.5 mL, 5%) was added slowly. After stirring the reaction overnight, it was quenched with NaHCO_3 (aq.). The solid was filtered and washed with water and ethanol. (0.30 g, 0.79 mmol, 97%). ^1H NMR (400 MHz, CDCl_3) δ 10.26 (s, 2H), 10.17 (s, 1H), 9.25 – 9.20 (m, 2H), 8.99 (s, 2H), 8.91 (d, J = 8.3 Hz, 2H), 8.42 (dd, J = 8.2, 2.1 Hz, 2H), 8.11 (s, 4H). ^{13}C NMR spectra could not be measured due to low solubility. MS (ESI) m/z : calcd for $\text{C}_{24}\text{H}_{15}\text{N}_3\text{O}_4$ $[\text{M}+\text{H}]^+$ 394.4; found, 394.1



Scheme 4.12. MCP-CHO synthetic route.

Diethyl pyridine-2,4-dicarboxylate (IV.7)⁵²: To a solution of pyridine-2,4-dicarboxylic acid (4,87 g, 29,1 mmol) in EtOH (250 mL) was added PTsOH (11,64 g, 61,2 mmol) and the mixture was refluxed for 24 h. The mixture was allowed to reach ambient temperature. Then the solvent was removed under reduced pressure and CHCl₃ (100 mL) was added followed by sat. aq. Na₂CO₃ (60 mL). The organic layer was separated and the aq. layer was extracted with CHCl₃ (3*30 mL). The combined organic extracts were dried over MgSO₄ and the solvent was removed under reduced pressure to yield the title compound as a colorless oil (6.42 g, 99%). ¹H-NMR (400 MHz, CDCl₃): 8.91 (dd, J = 4.9, 0.9 Hz, 1H), 8.64 (dd, J = 1.6, 0.9 Hz, 1H), 8.03 (dd, J = 4.9, 1.6 Hz, 1H), 4.51 (q, J = 7.1 Hz, 2H), 4.45 (q, J = 7.1 Hz, 2H), 1.46 (t, 3H), 1.43 (t, J = 6.5 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): 148.7, 139.1, 135.6, 130.7, 127.8, 127.1, 125.2, 123.7, 118.4, 114.2.

Ethyl 2-(hydroxymethyl)isonicotinate (IV.8)⁵²: diethyl pyridine-2,4-dicarboxylate (IV.7) (1 g, 4,48 mmol) was dissolved in anhydrous EtOH (30 mL) and cooled to -10 °C. NaBH₄ (0.119 g, 3.14 mmol) was added in three portions, and a solution of CaCl₂ (11 mL, 0.5 M in EtOH) was added over the course of 4 h. The mixture was stirred for another hour at the indicated temperature. The reaction was quenched by the addition of H₂O (10 mL) and allowed to reach ambient temperature. The mixture was diluted with CHCl₃ (15 mL) and extracted with CHCl₃ (3*10 mL). The combined organic extracts were dried over MgSO₄ and the solvent was removed under reduced pressure. The crude product was used directly for the next step. ¹H-NMR (400 MHz, CDCl₃): 8.70 (dd, J = 5.2, 1.2 Hz, 1H), 7.83 (dt, J = 1.7, 0.8 Hz, 1H), 7.76 (ddd, J = 5.1, 1.6, 0.8 Hz, 1H), 4.84 (s, 2H), 4.42 (dq, J = 7.1 Hz, 2H), 1.41 (td, J = 7.1, 0.6 Hz, 3H), 1.43 (t, J = 6.5 Hz, 3H).

Ethyl 2-(chloromethyl)isonicotinate*HCl (IV.9)⁵²: ethyl 2-(hydroxymethyl)isonicotinate (**IV.8**) (2.2 g) was dissolved in CHCl₃ (50 mL) and cooled to 0 °C. A solution of thionyl chloride (3.5 mL, 48,6 mmol) in CHCl₃ (6 mL) was added dropwise at 0 °C. After complete addition stirring was continued for 20 h. The solvent was removed under reduced pressure and the crude material (1.7 g, 86%) was used directly for the next step.

Bis-(4-CO₂EtPy)-(1S,2S)-N1,N2-dimethylcyclohexyldiamine (IV.10): ethyl 2-(chloromethyl)isonicotinate*HCl (**IV.9**) (0.2 g, 1 mmol, 2 eq.) and (1S, 2S)-N1, N2-dimethylcyclohexane-1,2-diamine (0.071 g, 0.5 mmol, 1 eq) were dissolved in acetonitrile (4 mL). To the mixture was added Na₂CO₃ (0.563 g, 5.31 mmol, 5.3 eq) and TBABr (10 mg, 5% mol). The mixture was refluxed for 24 h, then, was filtered through sintered glass and the filtercake was washed several times with acetonitrile. The filtrate was collected and the solvent was removed to yield an oil. The material was purified by FCC (neutral Al₂O₃, Merck) 20%-50% EtOAc in hexane. The product is an orange oil. (0.33 g, 50%). ¹H-NMR (400 MHz, CDCl₃): 8.62 (dd, J = 5.1, 0.9 Hz, 2H), 8.14 (dd, J = 1.7, 0.9 Hz, 2H), 7.66 (dd, J = 5.1, 1.7, 1.7 Hz, 2H), 4.24 (m, 4H), 3.98 (d, J = 14.4 Hz, 2H), 3.82 (d, J = 14.4 Hz, 2H), 2.74-2.64 (m, 2H), 2.32 (s, 6H), 2.04-1.97 (m, 2H), 1.78 (d, J = 8.4 Hz, 2H), 1.22 (t, J = 7.1 Hz, 6H), 1.35-1.25 (m, 2H).

Bis-(4-hydroxymethylPy)-(1S,2S)-N1,N2-dimethylcyclohexyldiamine (IV.11): Diether (**IV.10**) (340 mg, 0.73 mmol, 1 eq.) was dissolved in anhydrous EtOH (20 mL) and NaBH₄ (220 mg, 5.8 mmol, 8 eq.) was added at 0 °C in three portions. The mixture was stirred for 1h at r.t. and then at 60 °C for another hour. The mixture was allowed to reach ambient temperature and the reaction was quenched by acetone (15 mL). The solvent was removed under reduced pressure and the crude material was purified by

FCC (DCM, 0-15% MeOH) The product is a light-yellow foam. (0.17 g, 60%). ¹H-NMR (400 MHz, CDCl₃): 8.32 (d, J = 5.1 Hz, 2H), 7.70 (s, 2H), 7.08 (dd, J = 5.2, 1.7 Hz, 2H), 5.27 (s, 4H), 4.68-4.58 (m, 4H), 3.85-3.73 (m, 4H), 2.66-2.56 (m, 2H), 2.30 (s, 6H), 1.97 (d, J = 12.1 Hz, 2H), 1.80-1.72 (m, 2H), 1.46-1.05 (m, 1H).

Bis-(4-carbonylPy)-(1S,2S)-N1,N2-dimethylcyclohexyldiamine (MCP-CHO): Alcohol (**IV.11**) (320 mg, 0.32 mmol, 1 eq.) was dissolved in CH₂Cl₂ (30 mL) and the mixture was cooled to 0 °C. MnO₂ (2.17 g, 24.97 mmol, 30 eq.) was added and the cooling bath was removed. The black suspension was stirred for 18 h at room temperature. The suspension was filtered and the solvent was removed under reduced pressure. The yellow oil was taken up with DCM (5 mL) and filtered again. The solvent was removed, hexane (3 mL) was added and the solvent was removed. The procedure was repeated two times. The product was obtained as an orange oil (0.2 g, 55%). ¹H NMR (400 MHz, CDCl₃) δ 9.94 (s, 2H), 8.76 (d, J = 4.9 Hz, 2H), 8.01 (s, 2H), 7.56 (d, J = 4.7 Hz, 2H), 4.03 (d, J = 14.8 Hz, 2H), 3.89 (d, J = 14.8 Hz, 2H), 2.74 (d, J = 9.0 Hz, 2H), 2.35 (s, 6H), 2.05 (d, J = 12.3 Hz, 2H), 1.83 (d, J = 8.7 Hz, 3H), 1.26 (td, J = 21.7, 21.0, 14.6 Hz, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 192.08, 150.04, 142.15, 122.06, 119.83, 77.38, 77.06, 76.74, 64.79, 59.95, 36.83, 25.75, 25.52, 1.02

COF-BPY-1¹⁶: The compound was synthesized following the reported procedure. **PYTA** (0.02 mmol, 11.3 mg) and 2,2'-bipyridyl-5,5'-dialdehyde (**bpy-CHO**) (0.04 mmol, 8.5 mg) linkers were placed in a Schlenk tube (10 mL) under nitrogen, followed by adding a solution of mesitylene/dioxane/6 M AcOH (5/5/1 by vol.; 1.1 mL). The mixture was sonicated for 10 min, then it was heated at 120 °C for 5 days yielding an orange precipitate, which was isolated by filtration. The wet sample was then transferred to a Soxhlet extractor and thoroughly washed with THF (24 h) and acetone (24 h). The

powder was dried at 120 °C under vacuum overnight to give an isolated yield of 78%.

COF-BPY-2: The material was prepared in a similar way to **COF-BPY-1**. **PETA** (0.02 mmol, 12 mg) and 2,2'-bipyridyl-5,5'-dialdehyde (**bpy-CHO**) (0.04 mmol, 8.5 mg) linkers were placed in a Schlenk tube (10 mL) under nitrogen, followed by adding a 0.7 mL of a 4:2:1 (v/v) mixture of mesitylene/BnOH/(aqueous 6 M AcOH). The mixture was sonicated for 10 min, then it was heated at 120 °C for 5 days yielding an orange precipitate, which was isolated by filtration. The wet sample was then transferred to a Soxhlet extractor and thoroughly washed with THF (24 h) and acetone (24 h). The powder was dried at 120 °C under vacuum overnight to give an isolated yield of 63%.

COF-TPY-1: The material was prepared in a similar way to **COF-BPY-1**. **TAPB** (0.047 mmol, 16.3 mg) and **TPY-CHO** (0.047 mmol, 18.3 mg) linkers were placed in a Schlenk tube (10 mL) under nitrogen, followed by adding a solution of *o*-DCB:*n*-BuOH:AcOH-6M_{aq} (5:5:1, 2.2 mL). The mixture was sonicated for 10 min, then it was heated at 120 °C for 5 days yielding an orange precipitate, which was isolated by filtration. The wet sample was then transferred to a Soxhlet extractor and thoroughly washed with THF (24 h) and acetone (24 h). The powder was dried at 120 °C under vacuum overnight to give an isolated yield of 85%.

COF-TPY-2: The material was prepared in a similar way to **COF-BPY-1**. **TTA** (0.047 mmol, 16.5 mg) and **TPY-CHO** (0.047 mmol, 18.3 mg) linkers were placed in a Schlenk tube (10 mL) under nitrogen, followed by adding a solution of *o*-DCB:*n*-BuOH:AcOH-6M_{aq} (3:7:1, 2.2 mL). The mixture was sonicated for 10 min, then it was heated at 120 °C for 5 days yielding an orange precipitate, which was isolated by filtration. The wet

sample was then transferred to a Soxhlet extractor and thoroughly washed with THF (24 h) and acetone (24 h). The powder was dried at 120 °C under vacuum overnight to give an isolated yield of 75%.

MCP-Polymer: **MCP-CHO** (0.05 mmol, 20.0 mg), **TAM** (0.025 mmol, 10.0 mg) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (27 mg, 0.10 mmol) were placed in a Schlenk tube (10 mL) under nitrogen and the mixture was dissolved in n-BuOH (0.4 mL). After 15 min, dioxane (1 mL), mesitylene (1 mL) and AcOH (6M 0.3 mL) were added. The mixture was sonicated for 10 min, then it was heated at 120 °C for 5 days yielding a purple precipitate, which was isolated by filtration. The wet sample was then transferred to a Soxhlet extractor and thoroughly washed with THF (24 h) and acetone (24 h). The powder was dried at 120 °C under vacuum overnight to give an isolated yield of 84%.

COF-BPY-1- CoCl_2 : Inside a glovebox, **COF-BPY-1** (60 mg) was added to CoCl_2 (30 mg, 0.23 mmol, 2 eq.) in MeCN (7 mL), which caused the solid to quickly turn a darker color. After stirring overnight, the mixture was filtered and the solid was washed with MeCN until the washings were clear. The solid was dried at 80 °C under vacuum overnight to give **COF-BPY-1- CoCl_2** as a dark red powder. (89%)

COF-BPY-2- CoCl_2 : Inside a glovebox, **COF-BPY-2** (30 mg) was added to CoCl_2 (15 mg, 0.11 mmol, 2 eq.) in MeCN (3 mL). After stirring overnight, the mixture was filtered and the solid was washed with MeCN until the washings were clear. The solid was dried at 80 °C under vacuum overnight to give **COF-BPY-1- CoCl_2** as a brown powder. (88%)

COF-TPY-1- $\text{Co}(\text{AcO})_2$: **COF-TPY-1** (60 mg) was added to $\text{Co}(\text{AcO})_2 \cdot 6\text{H}_2\text{O}$ (43 mg, 0.17 mmol, 2 eq.) in MeOH (6 mL). After stirring overnight, the mixture was filtered and the solid was washed with MeOH

until the washings were clear. The solid was dried at 80 °C under vacuum overnight to give **COF-TPY-1-Co(AcO)₂** as an orange powder. (94%)

COF-TPY-2-Co(AcO)₂: **COF-TPY-2** (60 mg) was added to Co(AcO)₂·6H₂O (43 mg, 0.17 mmol, 2 eq.) in MeOH (6 mL). After stirring overnight, the mixture was filtered and the solid was washed with MeOH until the washings were clear. The solid was dried at 80 °C under vacuum overnight to give **COF-TPY-2-Co(AcO)₂** as an orange powder. (90%)

4.4.3. PXRD of tables 4.1 and 4.2

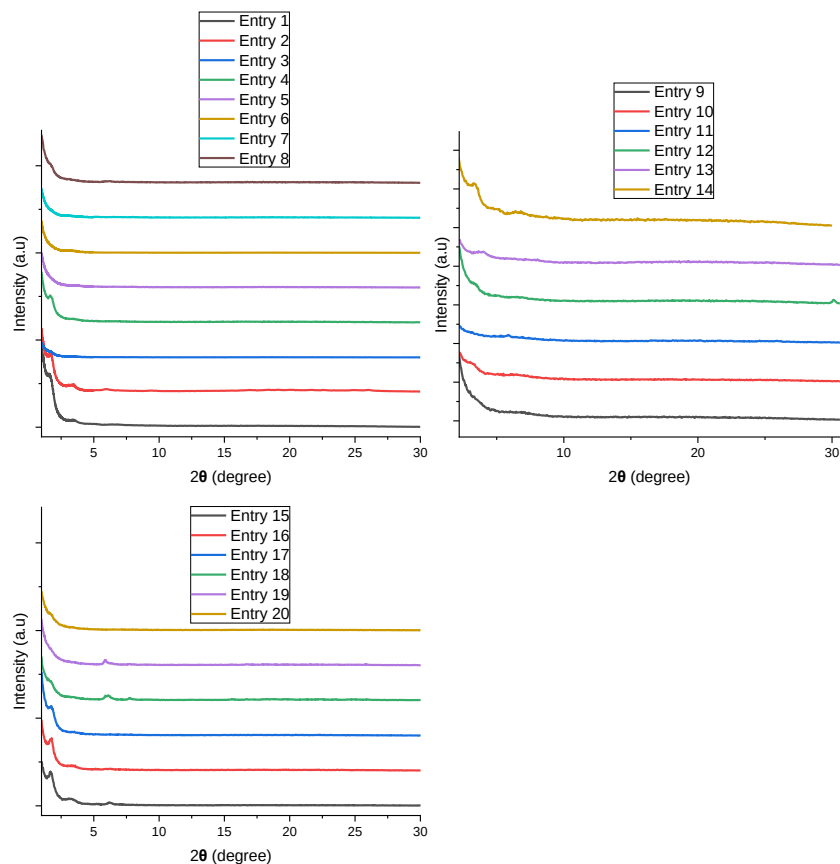


Figure 4.15. PXRDs of samples obtained in table 4.1.

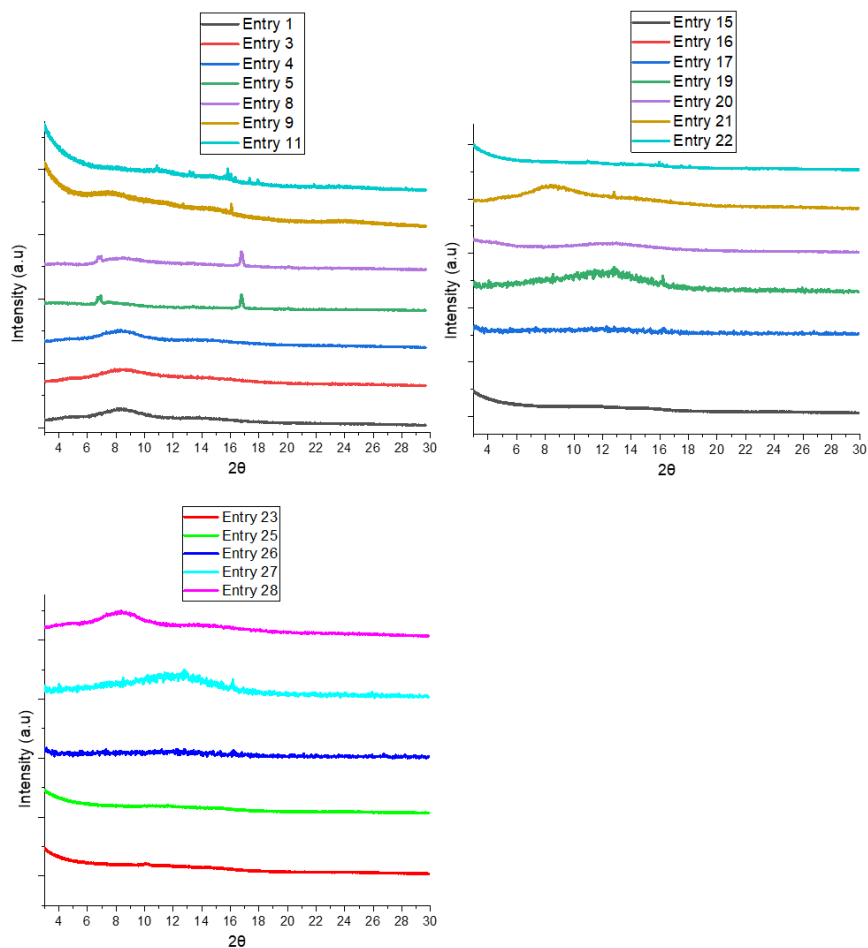


Figure 4.16. PXRDs of samples obtained in table 4.2.

4.2. Bibliography

- (1) Yaghi, O. M. Reticular Chemistry in All Dimensions. *ACS Cent. Sci.* **2019**, 5 (8), 1295–1300.
- (2) Kandambeth, S.; Dey, K.; Banerjee, R. Covalent Organic Frameworks: Chemistry beyond the Structure. *J. Am. Chem. Soc.* **2019**, 141 (5), 1807–1822.
- (3) Yuan, S.; Feng, L.; Wang, K.; Pang, J.; Bosch, M.; Lollar, C.; Sun, Y.; Qin, J.; Yang, X.; Zhang, P.; Wang, Q.; Zou, L.; Zhang, Y.; Zhang, L.; Fang, Y.; Li, J.; Zhou, H. C. Stable Metal–Organic Frameworks: Design, Synthesis, and Applications. *Adv. Mater.* **2018**, 30 (37), 1–35.
- (4) Vikrant, K.; Kumar, V.; Kim, K. H.; Kukkar, D. Metal–Organic Frameworks (MOFs): Potential and Challenges for Capture and Abatement of Ammonia. *J. Mater. Chem. A* **2017**, 5 (44), 22877–22896.
- (5) Guan, X.; Li, H.; Ma, Y.; Xue, M.; Fang, Q.; Yan, Y.; Valtchev, V.; Qiu, S. Chemically Stable Polyarylether-Based Covalent Organic Frameworks. *Nat. Chem.* **2019**, 11 (6), 587–594.
- (6) Dong, J.; Han, X.; Liu, Y.; Li, H.; Cui, Y. Metal–Covalent Organic Frameworks (MCOFs): A Bridge Between Metal–Organic Frameworks and Covalent Organic Frameworks. *Angew. Chemie Int. Ed.* **2020**, 59 (33), 13722–13733.
- (7) Segura, J. L.; Royuela, S.; Mar Ramos, M. Post-Synthetic Modification of Covalent Organic Frameworks. *Chem. Soc. Rev.* **2019**, 48 (14), 3903–3945.
- (8) Ding, S.-Y.; Gao, J.; Wang, Q.; Zhang, Y.; Song, W.-G.; Su, C.-Y.; Wang, W. Construction of Covalent Organic Framework for Catalysis: Pd/COF-LZU1 in Suzuki–Miyaura Coupling Reaction. *J.*

- Am. Chem. Soc.* **2011**, 133 (49), 19816–19822.
- (9) Li, L. H.; Feng, X. L.; Cui, X. H.; Ma, Y. X.; Ding, S. Y.; Wang, W. Salen-Based Covalent Organic Framework. *J. Am. Chem. Soc.* **2017**, 139 (17), 6042–6045.
 - (10) Feng, T.; Sun, B.; Hao, Q.; Li, J.; Xu, Y.; Shang, H.; Wang, D. Ambient Synthesis of Metal–Covalent Organic Frameworks with Fe-Iminopyridine Linkages. *Chem. Commun.* **2022**, 58 (63), 8830–8833.
 - (11) Han, X.; Xia, Q.; Huang, J.; Liu, Y.; Tan, C.; Cui, Y. Chiral Covalent Organic Frameworks with High Chemical Stability for Heterogeneous Asymmetric Catalysis. *J. Am. Chem. Soc.* **2017**, 139 (25), 8693–8697.
 - (12) Vardhan, H.; Verma, G.; Ramani, S.; Nafady, A.; Al-Enizi, A. M.; Pan, Y.; Yang, Z.; Yang, H.; Ma, S. Covalent Organic Framework Decorated with Vanadium as a New Platform for Prins Reaction and Sulfide Oxidation. *ACS Appl. Mater. Interfaces* **2019**, 11 (3), 3070–3079.
 - (13) Baldwin, L. A.; Crowe, J. W.; Pyles, D. A.; McGrier, P. L. Metalation of a Mesoporous Three-Dimensional Covalent Organic Framework. *J. Am. Chem. Soc.* **2016**, 138 (46), 15134–15137.
 - (14) Liu, Y.; Ma, Y.; Zhao, Y.; Sun, X.; Gándara, F.; Furukawa, H.; Liu, Z.; Zhu, H.; Zhu, C.; Suenaga, K.; Oleynikov, P.; Alshammari, A. S.; Zhang, X.; Terasaki, O.; Yaghi, O. M. Weaving of Organic Threads into a Crystalline Covalent Organic Framework. *Science* **2016**, 351 (6271), 365–369.
 - (15) Lin, S.; Diercks, C. S.; Zhang, Y.-B.; Kornienko, N.; Nichols, E. M.; Zhao, Y.; Paris, A. R.; Kim, D.; Yang, P.; Yaghi, O. M.; Chang, C. J. Covalent Organic Frameworks Comprising Cobalt Porphyrins for

- Catalytic CO₂ Reduction in Water. *Science* **2015**, 349 (6253), 1208–1213.
- (16) Chen, X.; Huang, N.; Gao, J.; Xu, H.; Xu, F.; Jiang, D. Towards Covalent Organic Frameworks with Predesignable and Aligned Open Docking Sites. *Chem. Commun.* **2014**, 50 (46), 6161–6163.
- (17) Feng, X.; Ren, Y.; Jiang, H. Metal-Bipyridine/Phenanthroline-Functionalized Porous Crystalline Materials: Synthesis and Catalysis. *Coord. Chem. Rev.* **2021**, 438, 213907.
- (18) Leng, W.; Peng, Y.; Zhang, J.; Lu, H.; Feng, X.; Ge, R.; Dong, B.; Wang, B.; Hu, X.; Gao, Y. Sophisticated Design of Covalent Organic Frameworks with Controllable Bimetallic Docking for a Cascade Reaction. *Chem. A Eur. J.* **2016**, 22 (27), 9087–9091.
- (19) Zhang, J.; Peng, Y.; Leng, W.; Gao, Y.; Xu, F.; Chai, J. Nitrogen Ligands in Two-Dimensional Covalent Organic Frameworks for Metal Catalysis. *Chinese J. Catal.* **2016**, 37 (4), 468–475.
- (20) Jia, J.; Bu, X.; Yang, X. A Cobalt Covalent Organic Framework: A Dual-Functional Atomic-Level Catalyst for Visible-Light-Driven C–H Annulation of Amides with Alkynes. *J. Mater. Chem. A* **2022**, 10 (21), 11514–11523.
- (21) Vardhan, H.; Al-Enizi, A. M.; Nafady, A.; Pan, Y.; Yang, Z.; Gutiérrez, H. R.; Han, X.; Ma, S. Single-Pore versus Dual-Pore Bipyridine-Based Covalent–Organic Frameworks: An Insight into the Heterogeneous Catalytic Activity for Selective C–H Functionalization. *Small* **2021**, 17 (22), 2003970.
- (22) Leng, W.; Ge, R.; Dong, B.; Wang, C.; Gao, Y. Bimetallic Docked Covalent Organic Frameworks with High Catalytic Performance towards Tandem Reactions. *RSC Adv.* **2016**, 6 (44), 37403–37406.
- (23) Johnson, E. M.; Haiges, R.; Marinescu, S. C. Covalent-Organic

- Frameworks Composed of Rhenium Bipyridine and Metal Porphyrins: Designing Heterobimetallic Frameworks with Two Distinct Metal Sites. *ACS Appl. Mater. Interfaces* **2018**, 10 (44), 37919–37927.
- (24) Meng, Y.; Luo, Y.; Shi, J.-L.; Ding, H.; Lang, X.; Chen, W.; Zheng, A.; Sun, J.; Wang, C. 2D and 3D Porphyrinic Covalent Organic Frameworks: The Influence of Dimensionality on Functionality. *Angew. Chemie Int. Ed.* **2020**, 59 (9), 3624–3629.
- (25) Chen, R.; Shi, J.; Ma, Y.; Lin, G.; Lang, X.; Wang, C. Designed Synthesis of a 2D Porphyrin-Based Sp² Carbon-Conjugated Covalent Organic Framework for Heterogeneous Photocatalysis. *Angew. Chemie Int. Ed.* **2019**, 58 (19), 6430–6434.
- (26) Seo, W.; White, D. L.; Star, A. Fabrication of Holey Graphene: Catalytic Oxidation by Metalloporphyrin-Based Covalent Organic Framework Immobilized on Highly Ordered Pyrolytic Graphite. *Chem. A Eur. J.* **2017**, 23 (24), 5652–5657.
- (27) Côté, A. P.; Benin, A. I.; Ockwig, N. W.; O’Keeffe, M.; Matzger, A. J.; Yaghi, O. M. Chemistry: Porous, Crystalline, Covalent Organic Frameworks. *Science* **2005**, 310 (5751), 1166–1170.
- (28) Palkovits, R.; Antonietti, M.; Kuhn, P.; Thomas, A.; Schüth, F. Solid Catalysts for the Selective Low-Temperature Oxidation of Methane to Methanol. *Angew. Chemie - Int. Ed.* **2009**, 48 (37), 6909–6912.
- (29) Segura, J. L.; Mancheño, M. J.; Zamora, F. Covalent Organic Frameworks Based on Schiff-Base Chemistry: Synthesis, Properties and Potential Applications. *Chem. Soc. Rev.* **2016**, 45 (20), 5635–5671.
- (30) Dubed Bandomo, G. C.; Mondal, S. S.; Franco, F.; Bucci, A.;

- Martin-Diaconescu, V.; Ortuño, M. A.; van Langevelde, P. H.; Shafir, A.; López, N.; Lloret-Fillol, J. Mechanically Constrained Catalytic Mn(CO)₃Br Single Sites in a Two-Dimensional Covalent Organic Framework for CO₂ Electroreduction in H₂O. *ACS Catal.* **2021**, *11* (12), 7210–7222.
- (31) Dong, Z.; Zhang, L.; Gong, J.; Zhao, Q. Covalent Organic Framework Nanorods Bearing Single Cu Sites for Efficient Photocatalysis. *Chem. Eng. J.* **2021**, *403*, 126383.
- (32) Wei, C.; He, Y.; Shi, X.; Song, Z. Terpyridine-Metal Complexes: Applications in Catalysis and Supramolecular Chemistry. *Coord. Chem. Rev.* **2019**, *385*, 1–19.
- (33) Murphy, A.; Dubois, G.; Stack, T. D. P. Efficient Epoxidation of Electron-Deficient Olefins with a Cationic Manganese Complex. *J. Am. Chem. Soc.* **2003**, *125* (18), 5250–5251.
- (34) Shehata, M. F.; Ayer, S. K.; Roizen, J. L. Iron(MCP) Complexes Catalyze Aziridination with Olefins As Limiting Reagents. *J. Org. Chem.* **2018**, *83* (9), 5072–5081.
- (35) Claros, M.; Ungeheuer, F.; Franco, F.; Martin-Diaconescu, V.; Casitas, A.; Lloret-Fillol, J. Reductive Cyclization of Unactivated Alkyl Chlorides with Tethered Alkenes under Visible-Light Photoredox Catalysis. *Angew. Chemie Int. Ed.* **2019**, *58* (15), 4869–4874.
- (36) Liu, G.; Sheng, J.; Zhao, Y. Chiral Covalent Organic Frameworks for Asymmetric Catalysis and Chiral Separation. *Sci. China Chem.* **2017**, *60* (8), 1015–1022.
- (37) Ascherl, L.; Evans, E. W.; Gorman, J.; Orsborne, S.; Bessinger, D.; Bein, T.; Friend, R. H.; Auras, F. Perylene-Based Covalent Organic Frameworks for Acid Vapor Sensing. *J. Am. Chem. Soc.* **2019**, *141*

- (39), 15693–15699.
- (38) Geng, K.; He, T.; Liu, R.; Dalapati, S.; Tan, K. T.; Li, Z.; Tao, S.; Gong, Y.; Jiang, Q.; Jiang, D. Covalent Organic Frameworks: Design, Synthesis, and Functions. *Chem. Rev.* **2020**, *120* (16), 8814–8933.
- (39) Dong, W.; Yang, Y.; Xiang, Y.; Wang, S.; Wang, P.; Hu, J.; Rao, L.; Chen, H. A Highly Stable All-in-One Photocatalyst for Aryl Etherification: The Ni II Embedded Covalent Organic Framework. *Green Chem.* **2021**, *23* (16), 5797–5805.
- (40) Chen, H.; Liu, W.; Laemont, A.; Krishnaraj, C.; Feng, X.; Rohman, F.; Meledina, M.; Zhang, Q.; Van Deun, R.; Leus, K.; Van Der Voort, P. A Visible-Light-Harvesting Covalent Organic Framework Bearing Single Nickel Sites as a Highly Efficient Sulfur–Carbon Cross-Coupling Dual Catalyst. *Angew. Chemie Int. Ed.* **2021**, *60* (19), 10820–10827.
- (41) Jati, A.; Dey, K.; Nurhuda, M.; Addicoat, M. A.; Banerjee, R.; Maji, B. Dual Metalation in a Two-Dimensional Covalent Organic Framework for Photocatalytic C-N Cross-Coupling Reactions. *J. Am. Chem. Soc.* **2022**, *144* (17), 7822–7833.
- (42) Isaad, J.; El Achari, A. BODIPY Modified Silica Coated Magnetite Nanoparticles as Fluorescent Hybrid Material for Cu (II) Detection in Aqueous Medium. *Dye. Pigment.* **2013**, *99* (3), 878–886.
- (43) Yang, Y.; Pei, X.-L.; Wang, Q.-M. Postclustering Dynamic Covalent Modification for Chirality Control and Chiral Sensing. *J. Am. Chem. Soc.* **2013**, *135* (43), 16184–16191.
- (44) Zhang, L.; Wang, S.; Zhou, Y.; Wang, C.; Zhang, X.; Deng, H. Covalent Organic Frameworks as Favorable Constructs for Photodynamic Therapy. *Angew. Chemie Int. Ed.* **2019**, *58* (40),

14213–14218.

- (45) Banerjee, T.; Haase, F.; Trenker, S.; Biswal, B. P.; Savasci, G.; Duppel, V.; Moudrakovski, I.; Ochsenfeld, C.; Lotsch, B. V. Sub-Stoichiometric 2D Covalent Organic Frameworks from Tri- and Tetratopic Linkers. *Nat. Commun.* **2019**, *10* (1), 1–10.
- (46) Jayasundara, C. R. K.; Sabasovs, D.; Staples, R. J.; Oppenheimer, J.; Smith, M. R.; Maleczka, R. E. Cobalt-Catalyzed C-H Borylation of Alkyl Arenes and Heteroarenes Including the First Selective Borylations of Secondary Benzylic C-H Bonds. *Organometallics* **2018**, *37* (10), 1567–1574.
- (47) Léonard, N. G.; Bezdek, M. J.; Chirik, P. J. Cobalt-Catalyzed C(Sp²)–H Borylation with an Air-Stable, Readily Prepared Terpyridine Cobalt(II) Bis(Acetate) Precatalyst. *Organometallics* **2017**, *36* (1), 142–150.
- (48) Obligacion, J. V.; Bezdek, M. J.; Chirik, P. J. C(Sp²)–H Borylation of Fluorinated Arenes Using an Air-Stable Cobalt Precatalyst: Electronically Enhanced Site Selectivity Enables Synthetic Opportunities. *J. Am. Chem. Soc.* **2017**, *139* (7), 2825–2832.
- (49) Obligacion, J. V.; Zhong, H.; Chirik, P. J. Insights into Activation of Cobalt Pre-Catalysts for C(Sp²)–H Functionalization. *Isr. J. Chem.* **2017**, *57* (10), 1032–1036.
- (50) Palmer, W. N.; Obligacion, J. V.; Pappas, I.; Chirik, P. J. Cobalt-Catalyzed Benzylic Borylation: Enabling Polyborylation and Functionalization of Remote, Unactivated C(Sp³)–H Bonds. *J. Am. Chem. Soc.* **2016**, *138* (3), 766–769.
- (51) Vyas, V. S.; Haase, F.; Stegbauer, L.; Savasci, G.; Podjaski, F.; Ochsenfeld, C.; Lotsch, B. V. A Tunable Azine Covalent Organic Framework Platform for Visible Light-Induced Hydrogen

- Generation. *Nat. Commun.* **2015**, 6 (1), 8508.
- (52) Kojima, T.; Hayashi, K. I.; Iizuka, S. Y.; Tani, F.; Naruta, Y.; Kawano, M.; Ohashi, Y.; Hirai, Y.; Ohkubo, K.; Matsuda, Y.; Fukuzumi, S. Synthesis and Characterization of Mononuclear Ruthenium(III) Pyridylamine Complexes and Mechanistic Insights into Their Catalytic Alkane Functionalization with m-Chloroperbenzoic Acid. *Chem. A Eur. J.* **2007**, 13 (29), 8212–8222.
- (53) Björkman, T. CIF2Cell: Generating Geometries for Electronic Structure Programs. *Comput. Phys. Commun.* **2011**, 182 (5), 1183–1186.

Chapter V:

Low Oxidation State Cobalt Center
Stabilized by a Covalent Organic
Framework to promote Hydroboration of
Olefins

5.1. General insight

The hydroboration reaction is among the most widely used transformations for upgrading commodity alkenes and producing organoboranes. These products are commonly used as building blocks for cross-coupling reactions, and are necessary for the synthesis of biologically active molecules and materials.¹ The reaction involves the addition of a H atom and a boron group across the π - system of an unsaturated substrate. Originally, highly reactive boranes such as diborane (B_2H_6) and the borane–tetrahydrofuran complex ($BH_3 \cdot THF$) were employed.² Although these boranes could be used in hydroborations without catalyst, the products are extremely air sensitive and incompatible with chromatographic purification. Using instead dialkoxyboranes like pinacolborane (HBpin) is much more attractive due to the higher stability of the products. However, the lower reactivity of dialkoxyboranes means that catalysts are usually required. Thus, the development and study of new hydroboration catalysts is an important topic.³

The field of hydroboration catalysis has been traditionally dominated by complexes based on precious metals like Ru and Ir.^{4,5} In this context, Wilkinson's catalyst $[(Ph_3P)_3RhCl]$ is one of the most well studied alkene hydroboration catalysts. The proposed reaction mechanism for this catalyst has been described as follows (Figure 5.1): the reaction starts with dissociation of one of the phosphine ligands followed by oxidative addition of the B-H bond to the coordinatively unsaturated rhodium center.³ Then, an alkene is coordinated and inserted into the Rh-H bond. The final organoboronate ester product is released after reductive elimination.

CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by a Covalent Organic Framework to promote Hydroboration of Olefins

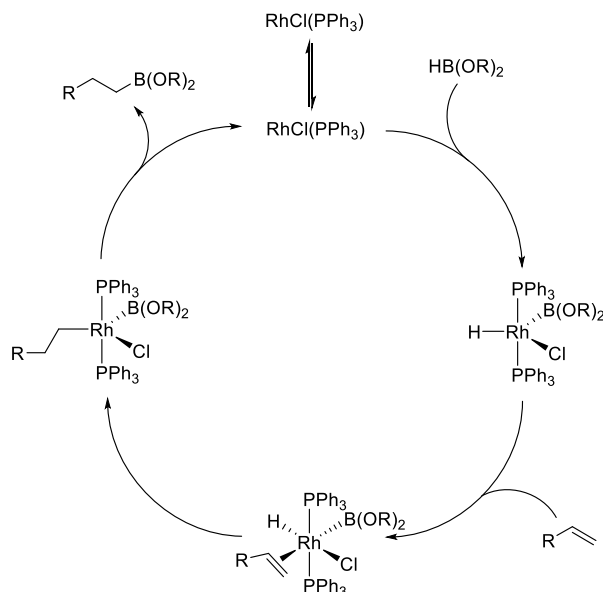
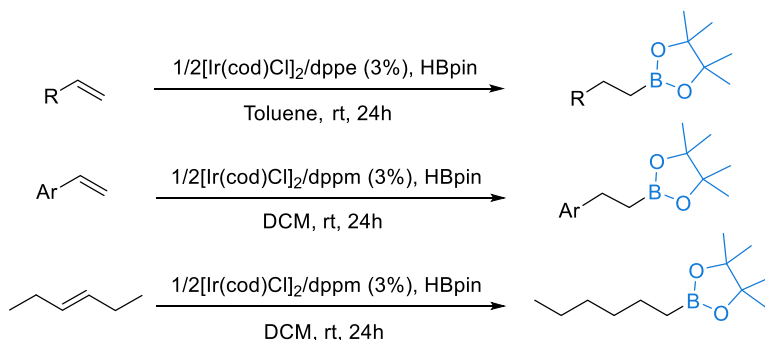


Figure 5.1. A proposed mechanism for the rhodium-catalyzed alkene hydroboration.

We can highlight the work published by Miyaura and coworkers,⁶ in which an iridium (I) complex with bidentate phosphine ligands (ddpm = Bis(diphenylphosphino)methane or dppe = Bis(diphenylphosphino)ethane) was employed as a hydroboration catalyst of alkenes with HBpin. Using this catalytic system, they achieved high yields and selectivity in the hydroboration of internal or terminal aliphatic alkenes, as well as aromatic alkenes (Scheme 5.1).



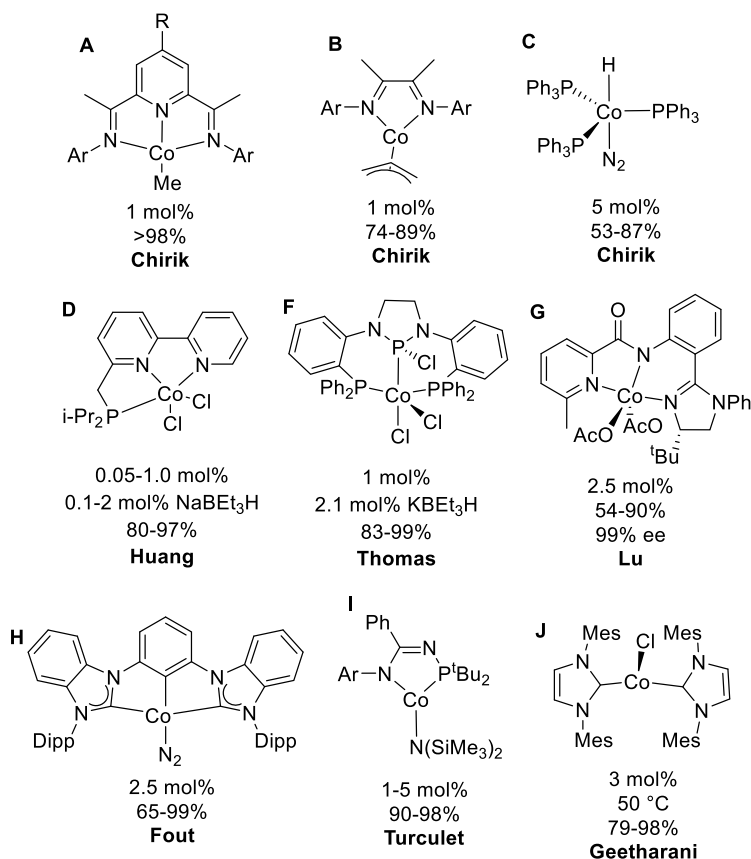
Scheme 5.1. Iridium-catalyzed hydroboration.⁶

In recent years there has been an increased interest in replacing precious metal catalysts with earth-abundant ones, due to their natural abundance, low toxicity and ready availability.⁷ Moreover, earth-abundant metals offer the opportunity to develop new reactivity and overcome limitations presented by precious metal complexes. In this context, several groups have demonstrated the capacity of cobalt complexes to catalyze the hydroboration of alkenes.⁸⁻¹⁶ In Scheme 5.2 is shown a list of selected examples of molecular Co catalysts.

One of the earliest examples of Co-catalyzed alkene hydroboration was reported by Chirik and coworkers (**A**).¹⁶ The authors presented several bis(imino)pyridine cobalt methyl complexes capable of catalyzing the transformation of terminal or internal alkenes into terminal boronates, achieving high selectivity and good group tolerance. However, the large aryl substituents present in these complexes limited their scope, showing poor performance for cyclic alkenes such as cyclohexene and cyclooctene due to steric hinderance.⁷ This work was followed by a study of α -diimine Co catalysts (**B**), which present a more open coordination sphere.¹⁴ Although these catalysts were more active towards trisubstituted substituted alkenes, they showed poor performance with styrenes and dienes due to the formation of inactive $[(^{\text{dipp}}\text{DI})\text{Co}(\eta^6\text{-arene})]$ and $[(^{\text{dipp}}\text{DI})\text{Co}(\eta^3\text{-allyl})]$ complexes. In order to achieve a different selectivity, Chirik employed $[(\text{Ph}_3\text{P})_3\text{CoH}(\text{N}_2)]$ (**C**) as an isomerization-hydroboration catalyst.¹³ **C** can isomerize terminal alkenes into the thermodynamically preferred internal isomers, which then are transformed into internal boronate esters. Huang and coworkers reported an extremely active catalyst based on a Co pincer complex (**D**) that becomes active after reduction with NaBEt_3H .¹⁵ The activated catalyst could achieve TONs as high as 19800, surpassing in performance even the best precious-metal catalysts. Additionally, the

CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by a Covalent Organic Framework to promote Hydroboration of Olefins

catalytic system presented a wide scope of aromatic and aliphatic alkenes. Similarly, Thomas and coworkers reported a Co pincer complex (**E**) activated by a hydride (KBET_3H).⁸ The catalyst showed good activity but limited scope, moreover, it becomes deactivated by dimerization into $[(\text{PPP})\text{CoH}]_2$ species. Enantioselective hydroboration catalysis has also attracted great attention. For examples, Lu and coworkers developed a chiral Co complex (**F**) that could perform asymmetric isomerization/hydroboration transformations from terminal alkenes into internal boronate esters with excellent values of enantiomeric excess.⁹



Scheme 5.2. Selected examples of molecular Co hydroboration catalysts.⁸⁻¹⁶

Regarding the mechanism of base-metal-catalyzed alkene hydroborations, Fout and coworkers studied a $\text{Co}(\text{N}_2)$ catalyst (**H**) and proposed a mechanism analogous to the one shown in Figure 5.1: oxidative addition of HBpin to Co is followed by insertion of an alkene into the Co-H bond, finishing with reductive elimination of the alkyl boronate ester.¹¹ Chirik and coworkers proposed a slightly different mechanism for the hydroboration of internal alkenes with $[(\text{PDI})\text{Co}(\text{CH}_3)]$ complexes (Figure 5.2).¹⁶ Entry into the catalytic cycle starts with a reaction between the Co-Me complex and HBpin to generate a Co-H complex. Then, an internal alkene is inserted into the Co-H bond, followed by a chain-walking process through rapid β -hydrogen elimination–olefin reinsertion steps. One Co is coordinated to the terminal position of the chain, it generates the alkyl boronate ester by reaction with HBpin through σ -bond metathesis or through oxidative addition followed by reductive elimination.

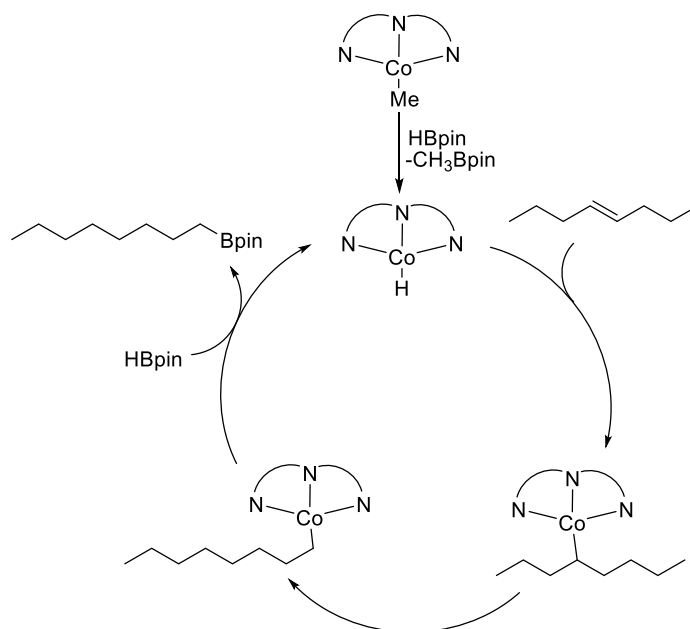
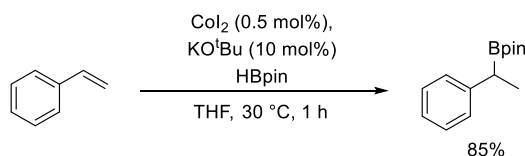


Figure 5.2. Proposed mechanism for Co-catalyzed hydroboration of internal alkenes.¹⁶

Apart from cobalt, other earth-abundant metal complexes including copper,^{17–20} manganese,^{21–24} and iron^{12,23,25–31} have shown promising results as alkene hydroboration catalysts. In particular, [(^{Ar}PDI)Fe(N₂)] complexes are highly active and can transform internal alkenes into terminal boronate esters, but the complexes have yet to find practical use owing to air sensitivity and challenging syntheses.⁷

The low oxidation state metal centers required for this type of reactivity are usually susceptible to catalyst deactivation pathways *via* bimolecular dimerization, disproportionation, and aggregation processes.^{32–35} A clear example of this behavior was shown by Wang and coworkers, who reported a ligand-free cobalt hydroboration catalytic system (Scheme 5.3).³⁶ The authors employed an active cobalt species generated *in situ* by reaction with a boron ‘ate’ reductive species,²³ and obtained good yields in the hydroboration of aromatic alkenes. However, due to the lack of steric protection, the catalyst deactivated in the first few minutes of the reaction by aggregation into larger nanoparticles, thus limiting the potential of the catalytic system.



Scheme 5.3. Ligand-free alkene hydroboration cobalt catalysis.³⁶

Intermolecular deactivation processes like the one shown previously can be minimized by employing bulky ligands. Indeed, many of the complexes presented in Scheme 5.2 contain bulky substituents for this purpose. However, their production generally requires multiple steps in elaborated synthetic processes, and the added steric hindrance to minimize the decomposition pathways can also turn into unfavorable steric hindrance

with the substrates.³⁷⁻⁴⁴ A potential solution for stabilizing low coordinated metal complexes with a low oxidation state without hampering their reactivity is to isolate them in solid matrices. In this case, the metal centers behave like single catalytic sites that do not require steric protection while maintaining low coordination indexes and thus enhancing their reactivity. Additionally, heterogenization of the catalysts could facilitate recovery and recycling of the materials, since homogeneous catalysts are challenging to recycle.⁴⁵

Following this strategy, Lin and coworkers have developed a series of single-site catalysts by isolating metal centers within MOFs. The catalysts developed this way could outperform their homogeneous counterparts in terms of catalyst stability, catalytic activity, recyclability and reusability.⁴⁶ Among these catalysts, Lin reported a series of MOFs with bipyridine or phenantroline groups capable of stabilizing reduced cobalt species (Figure 5.3a).⁴⁷ The MOFs could be used as catalysts for different reactions, including the hydroboration of alkenes, producing excellent TONs thanks to the isolated nature of the catalytic centers. Similarly, Manna and coworkers reported a phosphine MOF-supported cobalt catalyst for alkene hydroborations and arene borylations (Figure 5.3b).⁴⁸ However, the alkene scope presented for both MOF catalysts was limited.

CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by a Covalent Organic Framework to promote Hydroboration of Olefins

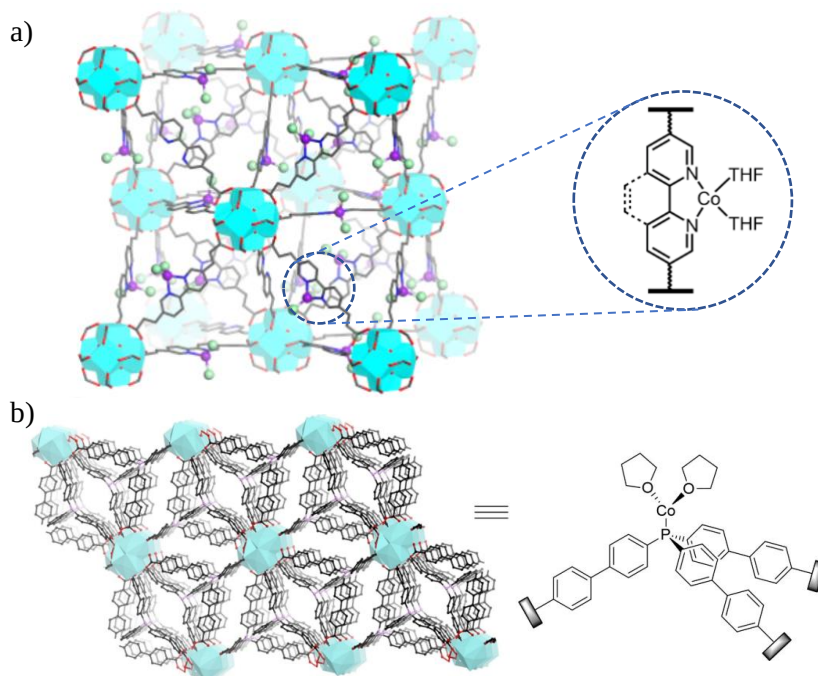


Figure 5.3. MOF-based single-site alkene hydroboration Co catalysts. Reproduced with permission.^{47,48} Copyright 2016, American Chemical Society.

Despite the great potential shown by these systems, there are few examples of this strategy being expanded to other materials in order to obtain alkene hydroboration catalysts. Sawamura employed a polystyrene-cross-linking bisphosphine coordinated with Co or Cu (Figure 5.4a) to hydroborate alkenes in good yields, showing a superior performance to homogeneous analogs.⁴⁹ S.Zheng reported a cobalt terpyridine 1D coordination polymer (Figure 5.4b) that could achieve excellent TOFs in the markovnikov-selective hydroboration of aromatic alkenes.⁵⁰ Even so, recyclability was a limitation in both cases.

CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by a Covalent Organic Framework to promote Hydroboration of Olefins

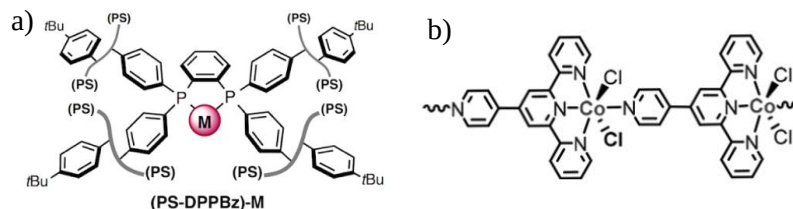


Figure 5.4. Materials used as single-site alkene hydroboration catalysts.^{49,50}

We hypothesized that covalent organic frameworks (COFs), owing to their well-defined structure, high porosity, stability, and tunable properties,^{51–53} could also support single-site reduced metal catalysts. However, in most 2D-COFs, the stacked layered structure locates metal centers of adjacent layers close enough to engage in interactions, opening potential decomposition pathways. In this line, our group has previously studied a 2D bipyridine COF, showing that the M-M interactions between immobilized $\{Mn(CO)_3Br\}$ centers were prevented by the mechanical constraints imposed by the framework.⁵⁴ Therefore, we envision that COFs could be used to design efficient catalysts based on cobalt for the hydroboration of alkenes, a known reaction that requires cobalt centers in low oxidation states that are difficult to stabilize against bimolecular decomposition processes.⁷

5.2. Results and Discussion

5.2.1. Hydroboration catalysis with cobalt bipyridine COFs

To study the catalytic activity of the bipyridine COFs obtained in the section 4.2.1 of chapter 4, we selected the hydroboration of 1-octene (**V.1a**) with pinacolborane (**HBpin**) as a model reaction (Table 5.1). The *anti*-Markovnikov product **V.2a** was obtained in low yield when using 1 mol% of **COF-BPY-1-CoCl₂** or **COF-BPY-2-CoCl₂** in THF (Table 5.1, entries 1-2). To improve this result, different additives were added to the reaction

CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by
 a Covalent Organic Framework to promote Hydroboration of
 Olefins

medium (Table 5.1, entries 3-7). The expected role of these additives is to reduce the cobalt catalyst in order to form *in-situ* low-valent cobalt species which are much more reactive in catalysis. A clear increase in the reactivity was observed when using NaBEt₃H, MeMgCl or sodium naphthalene as reductants. Notably, the reactions presented very high conversions because a large portion of the substrate had been isomerized into a mixture of octene isomers that were detected as byproducts by GC-MS.

Table 5.1. Additive screening for the hydroboration of **V.1a**.

V.1a + 1.2 eq. HBpin $\xrightarrow[25^\circ\text{C, 24h, under N}_2]{\text{Catalyst (1 mol\%), Additive (10 mol\%), THF}}$ V.2a

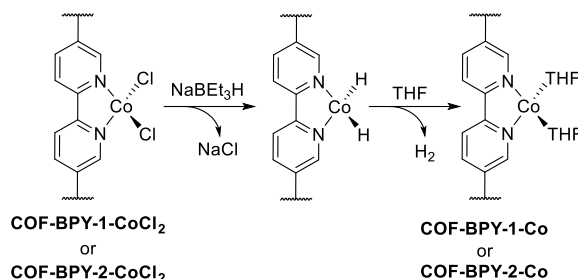
Entry	Catalyst (mol%)	Additive	Solvent	Conversion (%)	Yield (%)
1	COF-BPY-1-CoCl ₂ (1%)	-	THF	12	7
2	COF-BPY-2-CoCl ₂ (1%)	-	THF	10	2
3	COF-BPY-1-CoCl₂ (1%)	NaBEt₃H	THF	87	25
4	COF-BPY-2-CoCl ₂ (1%)	NaBEt ₃ H	THF	78	15
5	COF-BPY-1-CoCl ₂ (1%)	MeMgCl	THF	89	19
6	COF-BPY-1-CoCl ₂ (1%)	Sodium naphthalene	THF	90	18
7	COF-BPY-1-CoCl ₂ (1%)	<i>t</i> -BuOK	THF	20	6

General reaction conditions: **V.1a** (0.2 M), HBpin (0.24 M), **COF-BPY-1-CoCl₂** or **COF-BPY-2-CoCl₂** (1 mol% [Co]), additive (10 mol%), THF, 25 °C for 24 h. Conversion and yield were determined by GC using biphenyl as an internal standard.

Since the best results in catalysis were obtained using NaBEt₃H as additive, we wanted to isolate the reduced catalyst species that was being formed. To accomplish this, a mixture of **COF-BPY-1-CoCl₂** and NaBEt₃H (10 eq.) in THF was stirred for 1 h. The resulting solid was filtered and washed with THF, followed by drying under vacuum to produce **COF-BPY-1-Co** as a black powder. We propose that a bis-cobalt hydride intermediate is being formed when **COF-BPY-1-CoCl₂** reacts with NaBEt₃H, which quickly undergoes reductive elimination to form **COF-BPY-1-Co** as cobalt species

CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by a Covalent Organic Framework to promote Hydroboration of Olefins

in a formal oxidation state zero (Scheme 5.4). This reduced cobalt species is studied in section 5.2.4 of this chapter.



Scheme 5.4. Reduction of **COF-BPY-CoCl₂** with NaBEt₃H.

For the next experiments **COF-BPY-1-Co** was used as catalyst instead of generating it *in-situ*, as this produces slightly better yields (Table 5.2). After testing several solvents, we observed a significant yield increase by performing the reaction without solvent, in a neat mixture of 1-octene:HBpin (1:1.2), producing **V.2a** in 76% yield (Table 5.2, entry 6). In contrast, only 21% yield was obtained when using **COF-BPY-2-Co** instead of **COF-BPY-1-Co** (Table 5.2, entry 7). This large difference in reactivity could be rationalized by the superior porosity and crystallinity of **COF-BPY-1-CoCl₂**.

CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by
 a Covalent Organic Framework to promote Hydroboration of
 Olefins

Table 5.2. Solvent screening for the hydroboration of **V.1a**.

V.1a + **HBpin** (1.2 eq.) $\xrightarrow[25^\circ\text{C, 24h, under N}_2]{\text{Catalyst (1 mol\%), Additive (10 mol\%)}}$ **V.2a**

Entry	Catalyst (mol%)	Additive	Solvent	Conversion (%)	Yield (%)
1	COF-BPY-1-CoCl ₂ (1%)	NaBEt ₃ H	THF	87	25
2	COF-BPY-1-Co (1%)	-	THF	100	34
3	COF-BPY-1-Co (1%)	-	DCM	40	8
4	COF-BPY-1-Co (1%)	-	Toluene	70	14
5	COF-BPY-1-Co (1%)	-	MeCN	34	10
6	COF-BPY-1-Co (1%)	-	Neat substrate	100	76
7	COF-BPY-2-Co (1%)	-	Neat substrate	74	19

General reaction conditions: **V.1a** (0.2 M), HBpin (0.24 M), catalyst (1 mol% [Co]), solvent, 25 °C for 24 h. Conversion and yield were determined by GC using biphenyl as an internal standard.

Further screening of conditions was performed by increasing the catalyst loading, the temperature, or the number of equivalents of HBpin, however, no significant increase in the yield of the reaction was observed (Table 5.3). After these screenings of variables, we define **COF-BPY-1-Co** (1 mol% [Co]), **V.1a** (neat), HBpin (neat, 1.2 eq.), 25 °C, for 24 h, as the optimal conditions for the model reaction.

CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by a Covalent Organic Framework to promote Hydroboration of Olefins

Table 5.3. Screening for the hydroboration of **V.1a** with **COF-BPY-1-Co** under neat conditions.

V.1a + 1.2 eq. **HBpin** $\xrightarrow[24\text{h, under N}_2]{\text{COF-BPY-1-Co}}$ **V.2a**

Entry	Catalyst (mol%)	N° equiv. HBpin	Temp. (°C)	Conv. (%)	Yield (%)
1	COF-BPY-1-Co (0.5%)	1.2	25	100	69
2	COF-BPY-1-Co (1%)	1.2	25	100	74
3	COF-BPY-1-Co (2%)	1.2	25	100	78
4	COF-BPY-1-Co (1%)	1.2	35	100	74
5	COF-BPY-1-Co (1%)	1.2	50	100	79
6	COF-BPY-1-Co (1%)	1	25	100	70
7	COF-BPY-1-Co (1%)	1.5	25	100	75

General reaction conditions: **V.1a** (0.25 mmol), HBpin (0.3 mmol), **COF-BPY-1-Co** (2 mg, 1 mol% [Co]), 25 °C for 24 h. Conversion and yield were determined by GC using biphenyl as an internal standard.

Next, we compared the catalytic activity of **COF-BPY-1-Co** and molecular complexes (Table 5.4). Cobalt chloride complexes formed with 2,2-bipyridine, 6,6-dimethyl-2,2-bipyridine or 2,2-bipyridine-5,5-dicarbaldehyde produced very low yields, even after activation with NaBEt_3H (Table 5.4, entries 6-8). The poor activity of these catalysts has been previously attributed to the low stability of the reduced cobalt bipyridine complexes, which quickly undergo ligand disproportionation to produce bis-bipyridine cobalt complexes and metal nanoparticles.⁴⁷ Based on these results, we can rationalize that the site-isolation of the cobalt sites within **COF-BPY-1-Co** prevents this type of intermolecular deactivation from happening, leading to a superior performance in catalysis relative to the homogeneous analogs.

Table 5.4. Catalyst comparison.

Entry	Catalyst	%Yield (Conv.)
1	COF-BPY-1-Co	77 (100)
2	(bpy)CoCl ₂	0 (3)
3	(BPY-DCA)CoCl ₂	0 (4)
4	(^{Me2} bpy)CoCl ₂	0 (5)
5	CoCl ₂	1 (6)
6	(bpy)CoCl ₂ + NaBEt ₃ H	11 (100)
7	(BPY-DCA)CoCl ₂ + NaBEt ₃ H	5 (71)
8	(^{Me2} bpy)CoCl ₂ + NaBEt ₃ H	13 (100)
9	CoCl ₂ + NaBEt ₃ H	7 (72)
10	NaBEt ₃ H	4 (16)
11	COF-BPY-1	0 (5)

General reaction conditions: **V.1a** (0.25 mmol), HBpin (0.3 mmol), 1 mol% catalyst, 25 °C for 24 h. Conversion and yield were determined by GC using biphenyl as an internal standard.

In order to test the possible catalytic activity of nanoparticles trapped inside **COF-BPY-1-Co**, control experiments were performed with cobalt nanoparticles trapped inside **COF Py-1P**,⁵⁵ which has a similar structure to **COF-BPY-1** but it does not contain bipyridine groups (Figure 5.5). Since this COF has no ligands to coordinate strongly to the cobalt ions, any cobalt present inside the material during the reduction could agglomerate into nanoparticles. To form the trapped nanoparticles, **COF Py-1P** was soaked in a THF solution of CoCl₂. After stirring for 1h, NaBEt₃H was added to the mixture. The nanoparticles formed in the COF could be seen by TEM (Figure 5.5). This mixture of COF and nanoparticles produced a very low yield (13%) when used as catalysts for the hydroboration of **V.1a**. Assuming that trapped nanoparticles in **COF Py-1P** and **COF-BPY-1-Co** behave similarly, then the results suggest that trapped nanoparticles could only have a small contribution to the catalytic activity of **COF-BPY-1-Co**.

CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by a Covalent Organic Framework to promote Hydroboration of Olefins

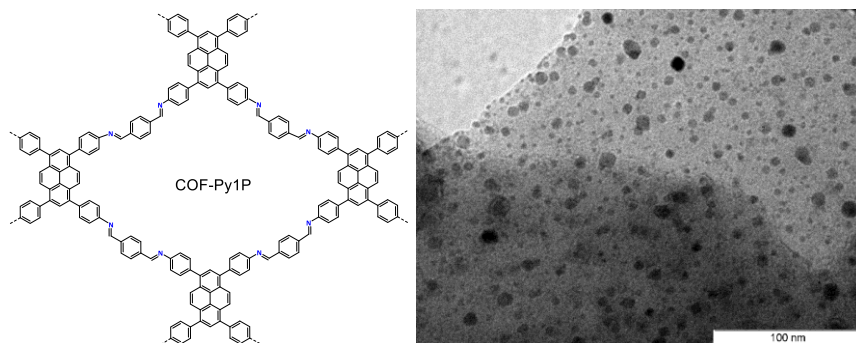


Figure 5.5. Schematic representation of COF-Py1P (left), TEM image of nanoparticles formed from the reduction of COF-Py1P+CoCl₂ (right).

The catalysis of **V.1a** with **COF-BPY-1-Co** was monitored over time to gain insight into the formation of **V.2a** and the byproducts over time (Figure 5.6). Interestingly, during the first 3 min of the reaction, a quick isomerization of 1-octene into *Z*-2-octene and *E*-2-octene was observed, followed by isomerization to more internal olefins (Scheme 5.5). Despite the great abundance of internal alkenes over terminal ones, the hydroboration was mostly selective towards terminal alkenes, occurring in only 10% of the internal alkenes. By the end of the reaction, almost all internal alkenes had been consumed by walk-chain isomerization back into 1-octene. A minor product from alkene hydrogenation (14%) was also detected. Based on these results, it should be possible to obtain terminal alkyl boronates starting from internal alkenes thanks to the isomerization reaction.

CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by
 a Covalent Organic Framework to promote Hydroboration of
 Olefins

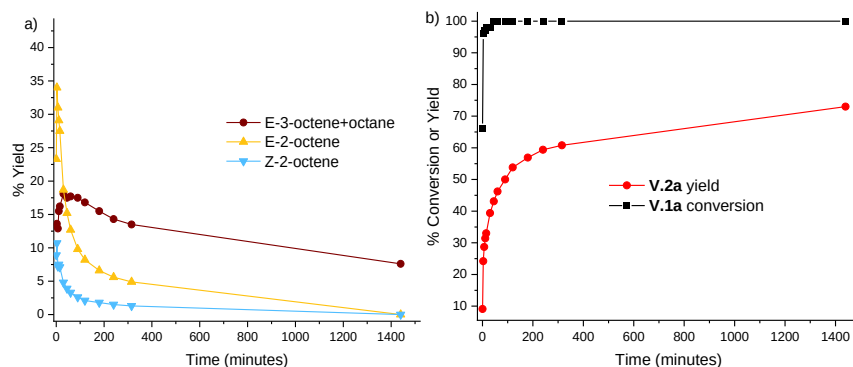
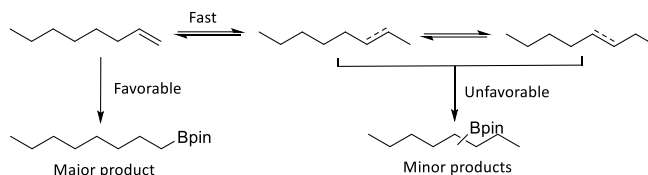


Figure 5.6. a) Yield for the byproducts of catalysis with **V.1a** over time, b) yield for **V.2a** and conversion of **V.1a** over time.



Scheme 5.5. Isomerization-hydroboration of 1-octene.

To understand better the possible low coordinated nature of the active sites in the COFs, we added increasing amounts of bipyridine in solution (0.1 to 1 eq.) to a catalytic mixture with preformed **COF-BPY-1-Co** (Figure 5.7). Interestingly, we observed a gradual decrease in yield from 76% to 11% for **V.2a**. We rationalized that the most active catalytic species in **COF-BPY-1-Co** should be unsaturated cobalt centers, which are inhibited by a second bpy coordination. No leaching from bpyCo species was detected by ICP-OES.

CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by
 a Covalent Organic Framework to promote Hydroboration of
 Olefins

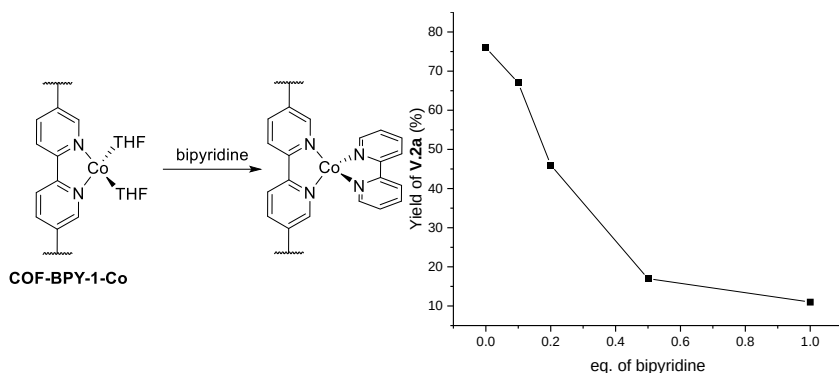


Figure 5.7. Proposed coordination of bipyridine to **COF-BPY-1-Co** (left). Yield of **V.2a** for catalysis in the presence of bipyridine (right). Number of equivalents relative to cobalt. Reaction conditions: 0.25 mmol **V.1a**, 0.3 mmol HBpin, **COF-BPY-1-Co** (1% Co), bipyridine, 24 h, 25 °C, under N₂.

5.2.2. Alkene substrate scope

Next, we explored the capacity of **COF-BPY-1-Co** to hydroborate different alkenes (Table 5.5). Good to excellent yields were obtained for simple terminal alkenes (**V.1a-V.1c**). Thanks to the isomerization process observed previously, terminal alkyl boronates **V.2d** and **V.2e** were obtained in good yields starting from internal alkenes **V.1d** and **V.1e**. This type of remote functionalization is potentially useful for obtaining single products starting from olefin mixtures such as the ones obtained by cracking processes.^{56,57} Despite being internal alkenes, cyclic substrates **V.1f** and **V.1g** underwent hydroboration with excellent yields. On the other hand, substrates with functional groups such as chloride (**V.1h**), silyl ether (**V.1i**) or epoxide (**V.1j**) were hydroborated with moderate to low yields. Aromatic olefins such as styrene (**V.1k**) also underwent hydroboration, but the reaction had poor selectivity with a 30:70 ratio of linear to branched product (l:b). Unprotected alcohols and carbonyls (Table 5.5, entries 12-14) were not compatible with the catalyst, since only traces of the boronated products were detected.

CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by
 a Covalent Organic Framework to promote Hydroboration of
 Olefins

Table 5.5. Hydroboration of terminal and internal alkenes with COF-BPY-1-Co.^[a]

Entry	Alkene	Product	Yield ^[b] (V.2) (%)	l:b ^[c]
1			69 (V.2a)	90:10
2			95 (V.2b)	99:1
3			77 (V.2c)	85:15
4			62 (V.2d)	81:19
5			60 (V.2e)	85:15
6			77 (V.2f)	-
7			90 (V.2g)	-
8			63 ^[d] (V.2h)	94:6
9			51 ^[d] (V.2i)	98:2
10			25 (V.2j)	92:8
11			49 ^[e] (V.2k)	30:70
12		-	-	-
13		-	-	-
14		-	-	-

^[a]Reaction conditions: alkene (0.25 mmol), HBpin (38.4 mg, 0.3 mmol), **COF-BPY-1-Co** (2 mg, 2.5 μ mol), 24 h, 25 $^{\circ}$ C, under N₂. ^[b]Yield of products isolated by silica gel column chromatography. ^[c]Linear to branched product ratio (l:b) determined by GC. ^[d]Reaction time increased to 48 h. ^[e]Total yield of both hydroboration products determined by ¹H-NMR

5.2.3. Catalyst recyclability

Recyclability experiments of **COF-BPY-1-Co** were conducted by separating the catalyst from the reaction medium through centrifugation, followed by washing, and then re-employing it for the hydroboration of **V.1a**. The catalyst showed good recyclability up to six times without losing activity or selectivity (Figure 5.8). Additionally, the catalyst did not suffer from leaching, as an ICP-OES analysis of the filtered organic phase did not show detectable cobalt traces (<0.005 mg/mL). TEM and SEM images of the material recovered from catalysis did not show changes compared to the pristine COF (Figure 5.9).

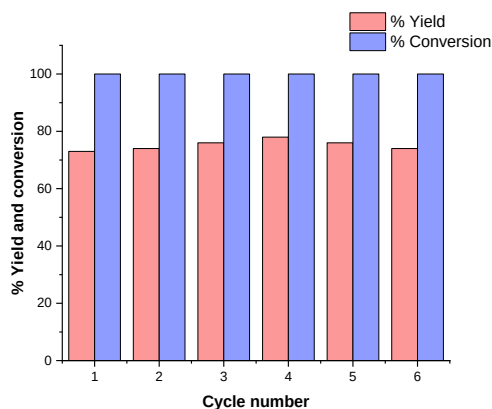
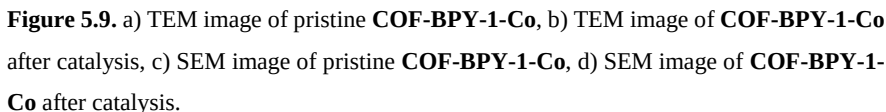
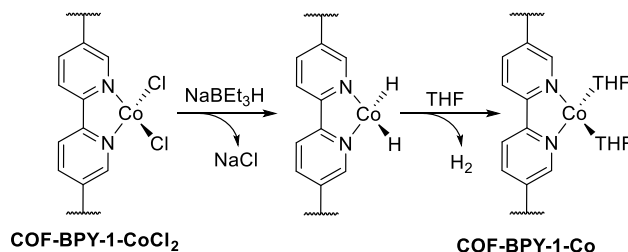


Figure 5.8. Yield and conversion determined by GC for catalysis with recycled **COF-BPY-1-Co**. Reaction conditions: 0.25 mmol **V.1a**, 0.3 mmol HBpin, 1% Co, 24 h, 25 °C, under N₂.



The reduction of **COF-BPY-1-CoCl₂** was investigated to understand the nature of the catalytic species better. First, gas chromatography (GC) analysis of the reaction headspace of **COF-BPY-1-CoCl₂** with NaBEt₃H revealed the formation of ca. 1 eq. of H₂ versus cobalt centers in the COF. A metal reduction by a hydride source with concomitant formation of 1 eq. H₂ is typically interpreted as a two-electron reduction process due to a bis-hydride reductive elimination reaction.^{47,58} As mentioned previously, this suggests that a bis-cobalt hydride intermediate is being formed when **COF-BPY-1-CoCl₂** reacts with NaBEt₃H, which quickly undergoes reductive elimination to form a cobalt species in a formal oxidation state zero (Scheme 5.6).



Scheme 5.6. Reduction of **COF-BPY-1-CoCl₂** with NaBEt₃H

Monitoring the reduction process by UV-vis showed a gradual decrease in the absorption band at 650 nm assigned to the consumption of the initial cobalt species, along with the growth of a new band at 950 nm assigned to the new reduced cobalt species⁴⁷ (Figure 5.10).

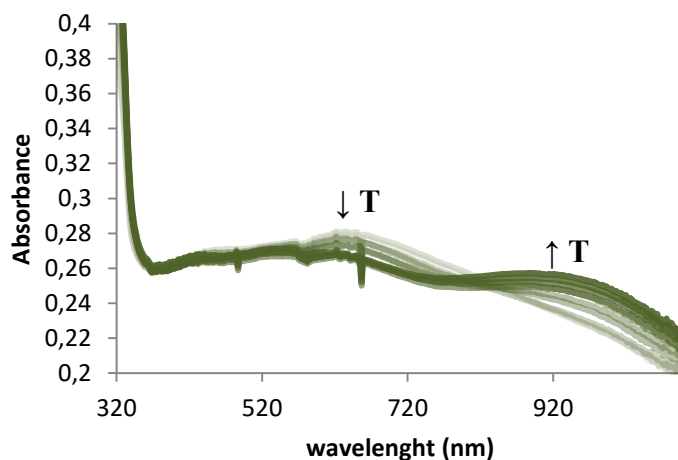


Figure 5.10. UV-vis monitoring of a suspension of **COF-BPY-1-CoCl₂** in THF (28 µg/ml) over 15 minutes after addition of NaBEt₃H (6 equivalents). Over time the band at 650 nm decreases in intensity and the band at 950 nm increases in intensity.

FTIR analysis showed that the imine bonds of **COF-BPY-1** are being reduced to amines during the reaction with NaBEt₃H, since the characteristic imine band at 1626 cm⁻¹ disappears (Figure 5.11a). The reduction of the COF also leads to the disappearance of the PXRD peaks (Figure 5.11b). This loss of crystallinity has been previously reported for

imine COFs, where the reduction of the imines leads to a disordered structure, while the connectivity of the material remains intact.^{59,60} Although this loss of crystallinity complicates the study of the structure after reduction of the framework, it does not appear to hamper the catalytic activity of the material, as it remains active through several catalytic runs.

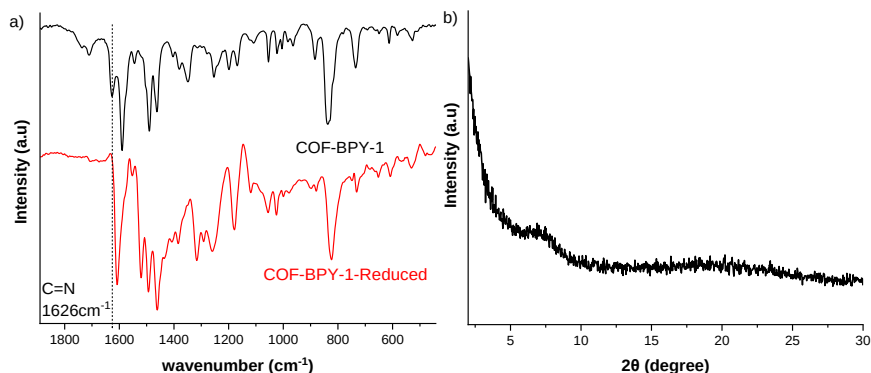


Figure 5.11. a) FT-IR and b) PXRD spectrum of **COF-BPY-1** reduced by NaBEt_3H .

EXAFS studies were conducted on **COF-BPY-1-CoCl₂** and the reference complex **Co(^{Me₂bpy})Cl₂**, before and after reduction, to gain insights into the coordination environment of the Co center (Figure 5.12). **Co(^{Me₂bpy})Cl₂** undergoes ligand disproportionation after being reduced, producing a reduced bis-bipyridine complex **Co(^{Me₂bpy})₂** and cobalt nanoparticles (Scheme 5.7).⁴⁷

In contrast to **Co(^{Me₂bpy})Cl₂**, which shows an intense pre-edge feature at 7710.3 eV consistent with a coordinate tetrahedral environment, **COF-BPY-1-CoCl₂** has a very weak pre-edge indicating a centrosymmetric environment (Figure 5.12a, Figure 5.13, Table 5.7). A lack of a shoulder on the rising edge together with the EXAFS analysis indicates a pseudo-octahedral environment dominated by N/O scattering atoms. Nevertheless, EXAFS analysis indicates the coordination of the bpy ligand to the Co center in the COF, as highlighted both by EXAFS fitting as well as the

CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by a Covalent Organic Framework to promote Hydroboration of Olefins

feature at 3.5 Å in r-space with a maximum 4.5 Å⁻¹ in k-space, clearly visible both in **Co**(^{Me2}bpy)Cl₂ and the reduced analog **Co**(^{Me2}bpy)₂ (Figure 5.12c). These results are consistent with the presence of {[bpy]Co(MeCN)₄}Cl₂ metal sites in **COF-BPY-1-CoCl₂**. Upon reduction, **COF-BPY-1-CoCl₂** undergoes a coordination environment change, resulting in a similar profile to **Co**(^{Me2}bpy)₂, having a 4 coordinate first coordination sphere dominated by N/O scattering atoms. In addition, the XANES spectra is comparable to the previously reported 4 coordinate MOF-bpy based Co encapsulated centers with two coordinating THF solvent molecules.⁴⁷ Based on these results, we propose that {(bpy)Co(THF)₂} is the main metallic species present in **COF-BPY-1-Co**.

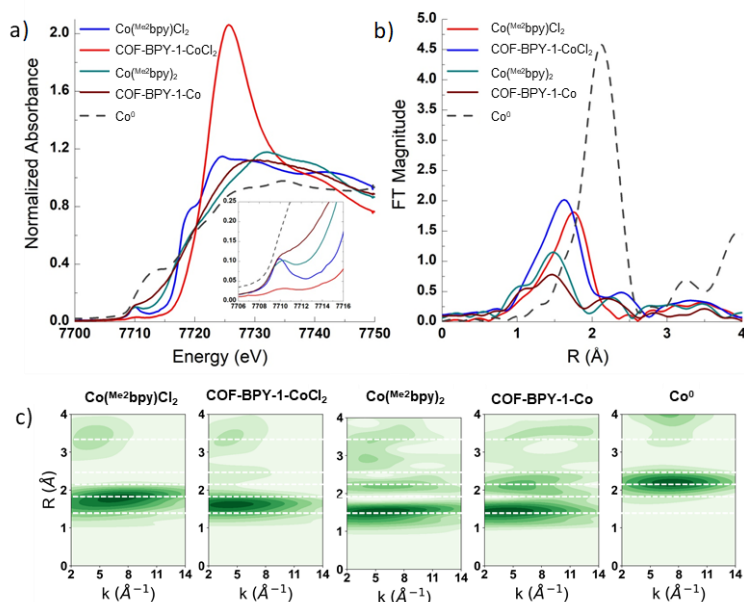
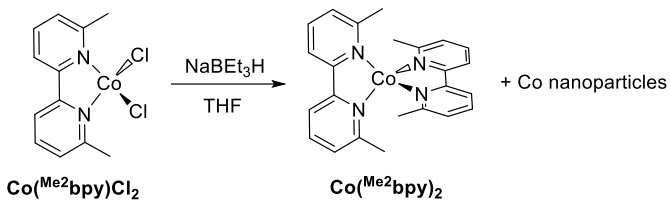


Figure 5.12. (a) XANES region XAS spectra highlighting the rising edges, with inset showing the pre-edge region due to 1s→3d transitions; (b) Fourier transformed (FT) EXAFS spectra; (c) Cauchy wavelet transform of EXAFS spectra highlighting signal dependence on both r- and k- space.



Scheme 5.7. Reduction of the $\text{Co}(\text{Me}_2\text{bpy})\text{Cl}_2$ reference complex into $\text{Co}(\text{Me}_2\text{bpy})_2$.

Table 5.6. Co K-edge XAS samples and spectral parameters (1s→3d refers to the pre-edge transitions; $E_0^{1/2}$ is the rising edge energy at half intensity, E_0' is the rising edge energy at the inflection point of the first derivative).

Sample	E_0' (eV)	$E_0\text{_{half}}$ (eV)	Pre-edge Energy (eV)	Pre-edge Energy Fit Error	Pre-edge Area	Pre-edge Area Fit Error
$\text{Co}(\text{Me}_2\text{bpy})\text{Cl}_2$	7717.4	7717.5	7710.0	0.0	0.17	0.00
COF-BPY-1- CoCl_2	7722.4	7719.7	7710.3	0.0	0.035	0.01
$\text{Co}(\text{Me}_2\text{bpy})_2$	7716.3	7717.8	7709.9	0.1	0.22	0.06
COF-BPY-1-Co	7718.3	7718.2	7710.3	-	-	-

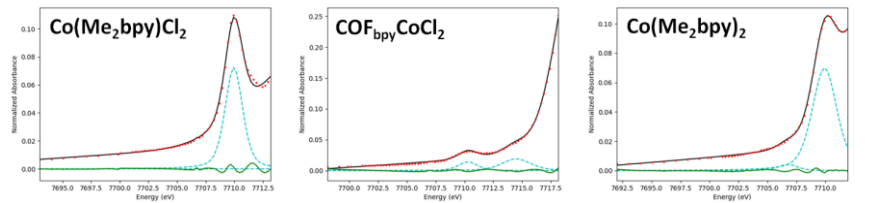


Figure 5.13. Pre-edge fits for $\text{Co}(\text{Me}_2\text{bpy})\text{Cl}_2$, COF-BPY-1- CoCl_2 , and $\text{Co}(\text{Me}_2\text{bpy})_2$.

Table 5.7. k^3 -weighted fits carried out in r-space using a Hanning window (dk 1), and an $S_0 = 0.9$ was chosen. Bond distances and disorder parameters (Δr_{eff} and σ^2) were allowed to float having initial values of 0.0 Å and 0.003 Å² respectively, with a universal E_0 and $\Delta E_0 = 0$ eV. Plots of fits are presented below.

Sample	Δk	Δr	R_{factor}	χ^2_{v}	ΔE_0	M-N/C/O			M-Cl			M-Co			M-C			M-C-C			M-C-C		
						N	r(Å)	σ^2	N	r(Å)	σ^2	N	r(Å)	σ^2	N	r(Å)	σ^2	N	r(Å)	σ^2	N	r(Å)	σ^2
$\text{Co}(\text{Me}_2\text{bpy})\text{Cl}_2$	2.5-13	1-4.0	0.011	57.5	2.7	2	2.04	0.006	2	2.23	0.002	-	-	-	4	2.92	0.007	8	3.07	0.007	14	4.29	0.008
COF-BPY-1- CoCl_2	2.5-13	1-4.0	0.029	1009	-2.9	5	2.1	0.006	1	2.37	0.004	-	-	-	7.5	2.95	0.008	-	-	-	16	4.40	0.008
$\text{Co}(\text{Me}_2\text{bpy})_2$	2.5-13	1-4.0	0.023	50	2.5	3.8	1.95	0.003	-	-	-	0.3	2.48	0.006	5.7	2.95	0.007	11.3	3.09	0.007	13.2	4.22	0.010
COF-BPY-1-Co	2.5-13	1-3.2	0.018	9	-0.7	3.6	1.96	0.009	-	-	-	1.1	2.46	0.009	3.6	2.97	0.007	7.2	3.11	0.008	-	-	-

CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by a Covalent Organic Framework to promote Hydroboration of Olefins

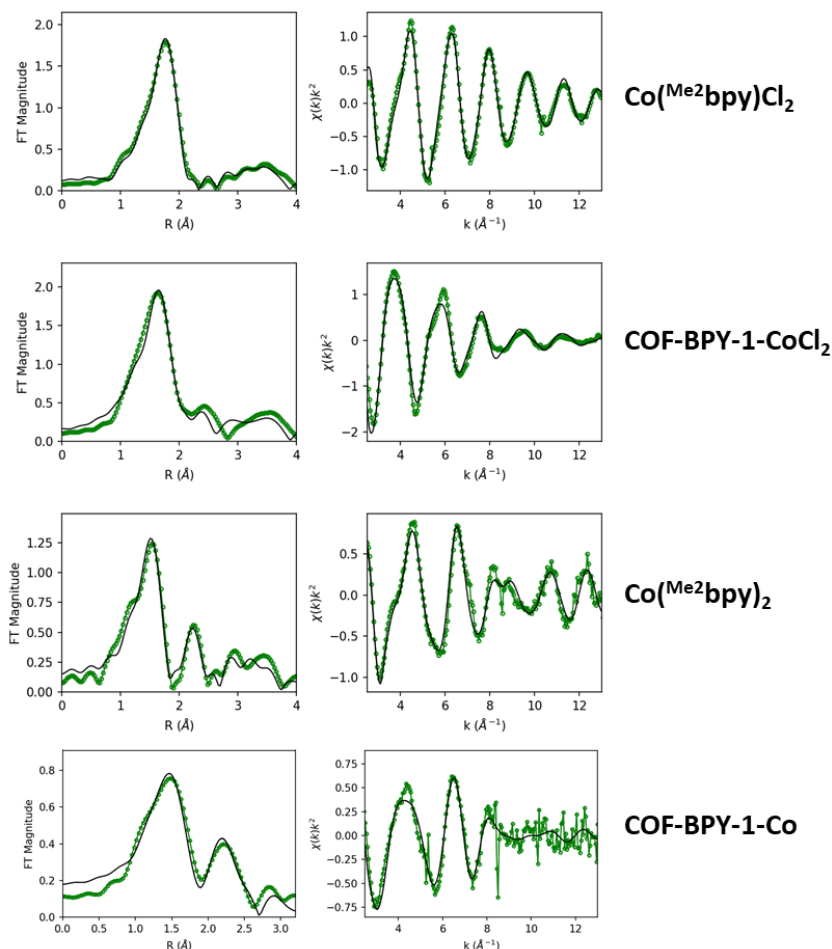


Figure 5.14. R-space and k-space of data (green) and fits (black) for samples from Table 5.7.

From the EXAFS results, it is evident in both, in the case of **Co(Me₂bpy)₂** and the reduced **COF-BPY-1-Co** that the formation of small nanoparticles in minor amounts is present upon reduction. Based on EXAFS fitting, Co-Co scattering coordinations of 0.3 and 1.1 for **Co(Me₂bpy)₂**, and **COF-BPY-1-Co**, respectively, are observed at 2.47 Å (Table 5.7), which is consistent with the presence of a minor amount of disordered Co nanoparticles. XPS characterization of **COF-BPY-1-Co** showed no clear spectral signal for

metallic Co (Figure 5.15). However, there is a significant increase in the signal width compared to the pristine sample **COF-BPY-1-CoCl₂**. Therefore, a small contribution from metallic cobalt could be fitted in the spectrum of **COF-BPY-1-Co**. The distribution of cobalt in **COF-BPY-1-Co** determined by STEM-HAADF could also be consistent with the presence of small quantity agglomerated cobalt and cobalt single sites (Figure 5.16). We interpreted that the formation of a small number of nanoparticles is facilitated by the high cobalt loading in the COF, but without essential consequences for the outcome of the catalytic experiments. Indeed, blank experiments suggested that cobalt nanoparticles in a COF (Section 5.2.1) lead to poor catalytic performances. Therefore, the catalytically active sites should be the cobalt bipyridine single-sites $\{(bpy)Co(THF)_2\}$.

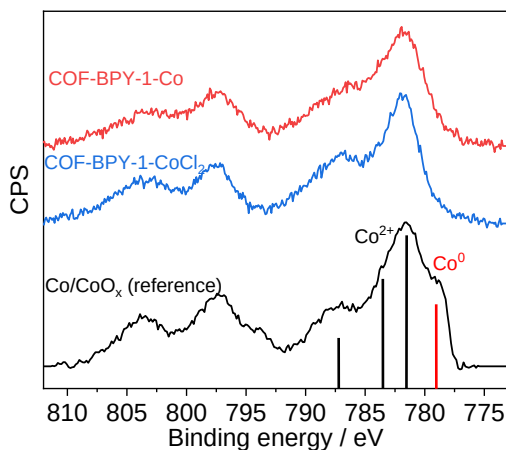


Figure 5.15. XPS of **COF-BPY-1-CoCl₂** and **COF-BPY-1-Co**.

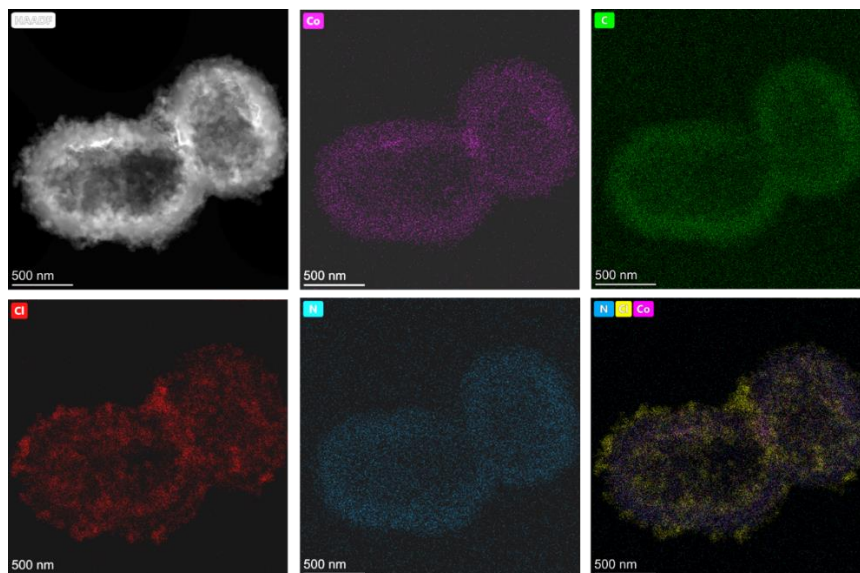
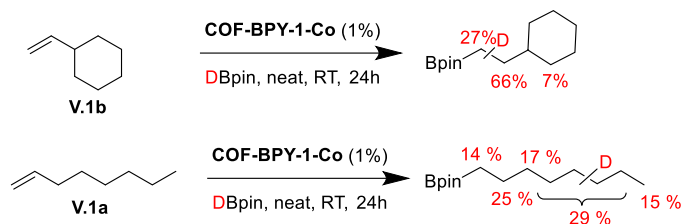


Figure 5.16. STEM HAADF images and EDX elemental mapping of **COF-BPY-1-Co**.

5.2.5. Mechanistic studies

To gain insight into the reaction mechanism, labeling studies were performed with deuterated DBpin (Scheme 5.8). **V.1b** was used as the first substrate for these studies since the cyclohexyl group hinders the isomerization, which simplifies the analysis of the results. ^2H -NMR analysis of the products established partial incorporation of deuterium at the 1- and 2-positions in 27% and 66%, respectively, due to 2,1- and 1,2-insertions. The overwhelming selectivity for the linear borane product over the branched one (99:1) suggests that although the 2,1-insertion happens about 1/4 of the time (27% D incorporation), it is not a productive pathway to form the borane product. Moreover, repeating the experiment with the linear substrate **V.1a** established partial deuterium incorporation along the alkyl chain, indicating that a chain walking process occurred.

CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by a Covalent Organic Framework to promote Hydroboration of Olefins



Scheme 5.8. Deuterium-labeled experiments.

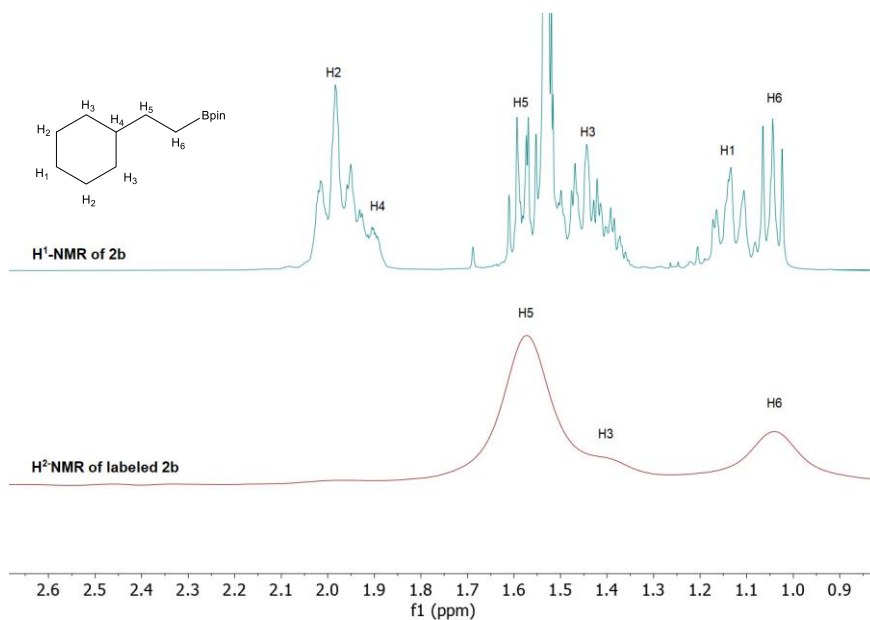


Figure 5.17. ¹H-NMR of **V.2b** and ²H-NMR of labeled **V.2b**.

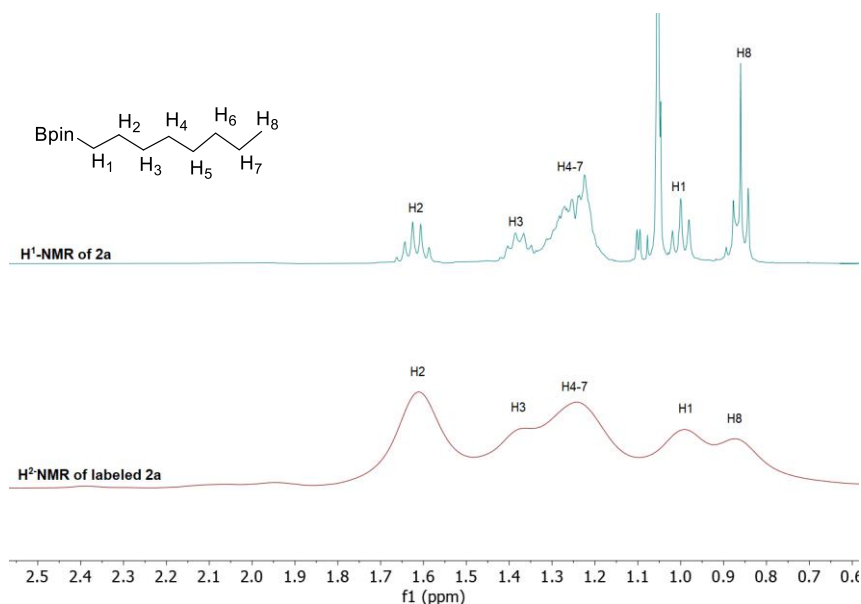


Figure 5.18. ¹H-NMR of **V.2a** and ²H-NMR of labeled **V.2a**.

The empirical rate law of the reaction for HBpin, **V.1b** and **COF-BPY-1-Co** was determined by kinetic studies (Figure 5.19). Plots of initial rates versus catalyst concentration showed a first-order rate dependence (1.22), while the rate dependence for **V.1b** and HBpin was close to zero-order (0.25 and 0.24, respectively). The almost independent reaction order versus **V.1b** and HBpin may imply that potential pre-equilibrium processes between **COF-BPY-1-Co** single sites and **V.1b** and HBpin are shifted towards a {Co(**V.1b**)(HBpin)} intermediate species, and then becoming their concentrations kinetically not relevant. We hypothesize that the high concentrations of substrate employed could be saturating the catalytic centers, or that the COF is helping to pre-concentrate the substrate in their pores, increasing the local substrate concentration in the neighborhood of the cobalt centers, shifting the pre-equilibrium coordination to the products.

CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by a Covalent Organic Framework to promote Hydroboration of Olefins

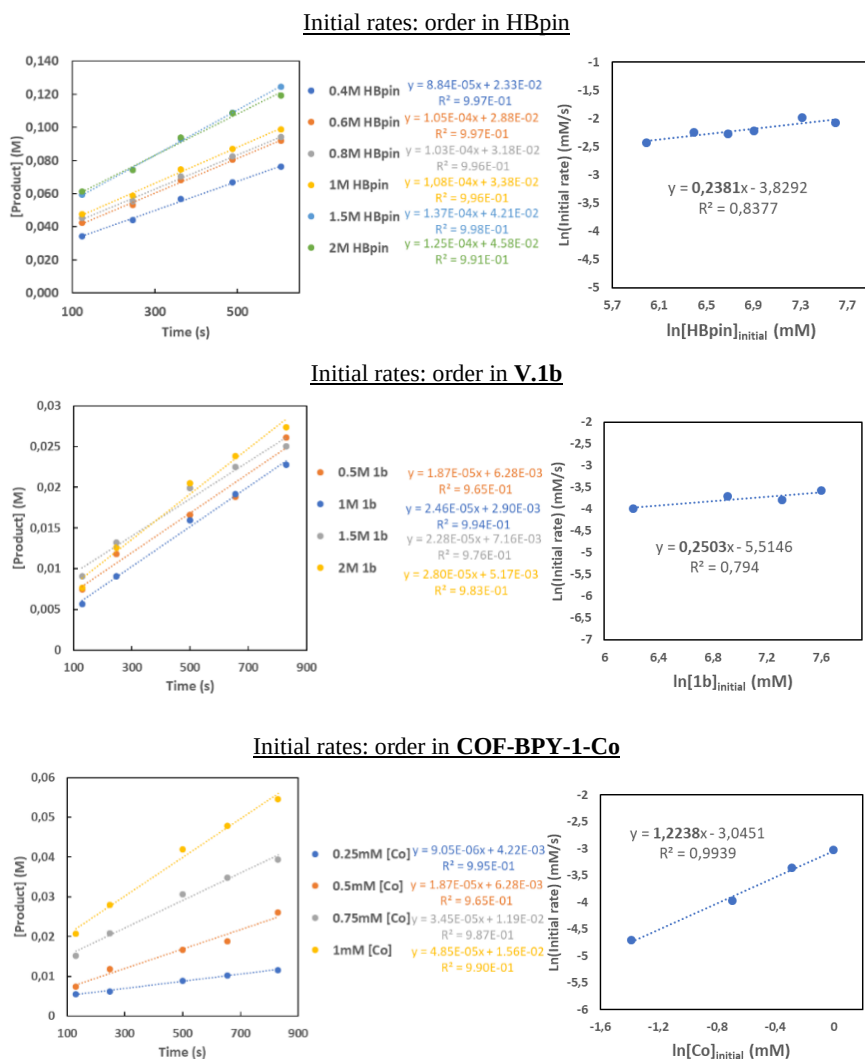


Figure 5.19. Determination of order in substrates and catalyst by the initial rates method for the hydroboration of 1b with HBpin using **COF-BPY-1-Co** as catalyst in THF.

5.2.6. Computational studies

Density functional theory (DFT) simulations were performed to propose a feasible reaction mechanism for the single-site Co-catalyzed hydroboration of alkenes. All calculations were carried out with the M06-L⁶¹ density functional as implemented in Gaussian 16.⁶² A cluster model comprised of

bipyridine with methyl-aniline groups (to account for imine reduction under experimental conditions) was employed to simulate the COF material. HBpin and 1-pentene were used as reactants. All structures can be freely consulted through the ioChem-BD platform⁶³ in the following link.⁶⁴ Full computational methods are detailed in Section 5.3.4.

We first study the electronic structure of **COF-BPY-1-Co** models with a formal Co(0) center in doublet and quartet spin states, namely **3**. The resulting structures and spin densities of the metal (Co) and the bpy-derived ligand (L) are shown in Figure 5.20. For the quartet, there are two unpaired e^- on Co and one unpaired e^- on L. Similarly, for the doublet, two unpaired e^- are present on Co and one unpaired e^- is placed antiferromagnetically on L (broken symmetry solution). Overall, these models indicate a Co(I) center bound to a non-innocent COF fragment. Although spin state energetics are sensitive to the density functional (Table 5.8), previous studies demonstrated that M06-L is suitable for first-row transition metals,⁶⁵ including bpy complexes⁶⁶ and neutral low-valent species with non-innocent ligands.⁶⁷ Thus, we continue the mechanistic study at this level of theory.

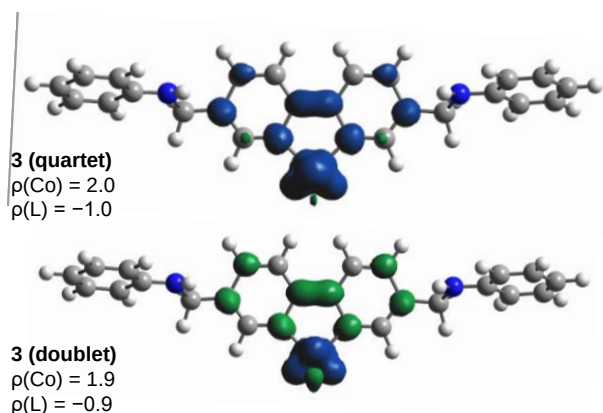


Figure 5.20. Spin density surfaces (isovalue = 0.004) of **3** for quartet and doublet spin states; up (blue) and down (green).

Table 5.8. Spin-state energetics and spin densities for species 3 according to different density functionals.

Species 3	quartet		doublet	
Density functional	ΔG / kcal mol ⁻¹	$\rho(\text{Co}) \rho(\text{L})$ / a.u.	ΔG / kcal mol ⁻¹	$\rho(\text{Co}) \rho(\text{L})$ / a.u.
PBE-D3	0.0	2.4 0.6	-5.0	1.5 -0.5
PBE0-D3	0.0	2.0 1.0	5.8	1.9 -0.9
B3LYP-D3	0.0	2.0 1.0	3.6	1.8 -0.8
M06-L	0.0	2.0 1.0	1.4	1.9 -0.9
M06	0.0	2.0 1.0	5.1	1.8 -0.8

The computed reaction mechanism and Gibbs energies are shown in Figure 5.21. Considering the previous kinetic studies, we start with a Co center bound to HBpin and 1-pentene, as in species **4**. The doublet exhibits a square-pyramidal structure and is taken as zero of energies. The quartet spin state spontaneously dissociates HBpin, thus from now on all intermediates and transition states correspond to the doublet. The first step concerns an oxidative boryl migration⁶⁸ via **TS4** (22.2 kcal/mol) to form the terminal boryl-alkyl complex **5** (anti-Markovnikov product) with H in apical position. The isomeric process giving rise to an internal boryl-alkyl intermediate (Markovnikov product) via **TS4a** (23.4 kcal/mol) is slightly higher in energy, which is in line with the l:b ratio reported experimentally (Table 2, 90:10 for 1-octene and 85:15 for 4-methyl-1-pentene). Alternative pathways involving oxidative hydrogen migrations are also higher in energy (Figure 5.22). Then species **5**, which is very transient, quickly isomerizes via **TS5** (20.9 kcal/mol) to the more stable intermediate **6** with H in equatorial position. The subsequent reductive elimination occurs easily via **TS6** (16.2 kcal/mol). Finally, the product releases and the new reactants coordinate to Co through an exoergic process. Overall, the rate-determining step corresponds to the oxidative boryl migration and demands 22.2 kcal/mol.

CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by a Covalent Organic Framework to promote Hydroboration of Olefins

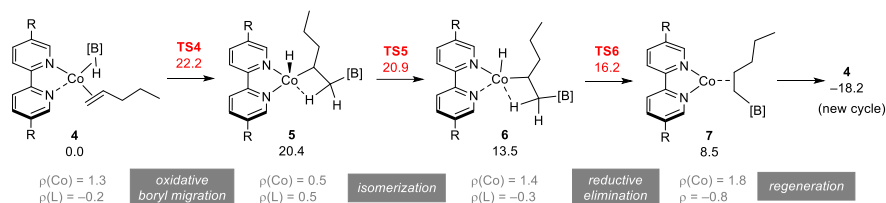


Figure 5.21. Computed reaction mechanism for the Co-catalyzed hydroboration of 1-pentene with HBpin ([B] = Bpin). Gibbs energies in kcal/mol.

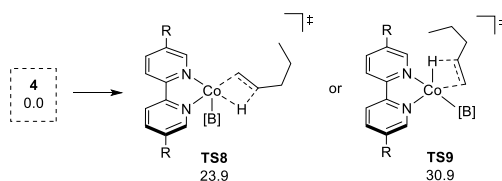


Figure 5.22. Transition states for oxidative hydrogen migration processes. Gibbs energies in kcal/mol.

Regarding oxidation states, it is quite challenging to unequivocally assign them in such complex systems. By inspecting relative spin density trends, we propose that: (i) the oxidative boryl migration provokes a $1-e^-$ oxidation of Co and $1-e^-$ oxidation of L; (ii) the isomerization involves a $1-e^-$ transfer from Co to L; (iii) the reductive elimination induces a $1-e^-$ reduction of Co and $1-e^-$ reduction of L; and (iv) the regeneration via reactants coordination triggers a $1-e^-$ transfer from L to Co. These data suggest that the reaction occurs through a series of $1-e^-$ processes assisted by the non-innocent COF.

5.2.7. Modification of the reactivity by a second ligand coordination.

The experiments shown in Figure 5.7 suggested that it could be possible to coordinate a second ligand to **COF-BPY-1-Co** in order to change the catalytic activity of the material. The idea of adding in solution a ligand to an unsaturated metal in a MCOF is quite interesting, since it would allow to modify easily the coordination environment without having to perform

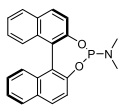
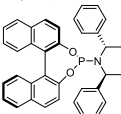
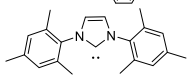
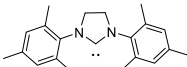
changes in the structure of the COF. To explore this idea further, **COF-BPY-1-Co** was mixed with different ligands and then it was used in catalysis. The hydrosilylation of styrene (**V.3a**) with SiH_2Ph_2 was selected as the model reaction for this catalysis, in order to observe the effect of different ligands over the selectivity of the linear vs branched products. To prevent saturation of the cobalt centers, only monodentate ligands were selected for the screening (Table 5.9).

The reaction catalyzed by **COF-BPY-1-Co** without any added ligands resulted in approximately a 1:1 ratio of linear (**V.4a**) to branched (**V.5a**) products plus a small amount of dehydrogenative silylation product (**V.6a**) (Table 5.9, entry 1). The addition of different ligands had a strong effect over the selectivity of the reaction, however the yields were too low (less than 10%) for each product (Entries 2-9). To try to improve these results, further screening was performed by changing the metal from Co to Ni. **COF-BPY-1-Ni** was prepared and reduced following the same procedure as **COF-BPY-1-Co** but using NiCl_2 as metal salt instead (9.2 wt% Ni for **COF-BPY-1-NiCl₂**). The use of **COF-BPY-1-Ni** as catalyst resulted in approximately a 1:2 ratio of **V.4a** to **V.5a**. Surprisingly, addition of PPh_3 as a ligand had a drastic effect on the reactivity of the catalyst, producing **V.4a** in 54% yield with a ~8:1 ratio of **V.4a** to **V.5a** (Entry 11). After increasing the catalyst loading, **V.4a** was obtained with 86% yield and 89% selectivity using **COF-BPY-1-Ni** (2 mol%) and PPh_3 (2.4 mol%) as catalyst.

Table 5.9. Ligand screening for the hydrosilylation of **V.3a**.

Entry	Catalyst	Ligand	Yield% V.4a	Yield% V.5a	Yield% V.6a
1	COF-BPY-1-Co	-	11	10	2
2	COF-BPY-1-Co		3	1	2
3	COF-BPY-1-Co		6	4	5
4	COF-BPY-1-Co		0	0	0
5	COF-BPY-1-Co		0	0	0
6	COF-BPY-1-Co		6	3	3
7	COF-BPY-1-Co		9	3	4
8	COF-BPY-1-Co		6	3	4
9	COF-BPY-1-Co		5	4	4
10	COF-BPY-1-Ni	-	6	10	0
11	COF-BPY-1-Ni		54	7	1
12	COF-BPY-1-Ni		5	9	0
13	COF-BPY-1-Ni		5	8	1
14	COF-BPY-1-Ni		3	7	0

CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by
 a Covalent Organic Framework to promote Hydroboration of
 Olefins

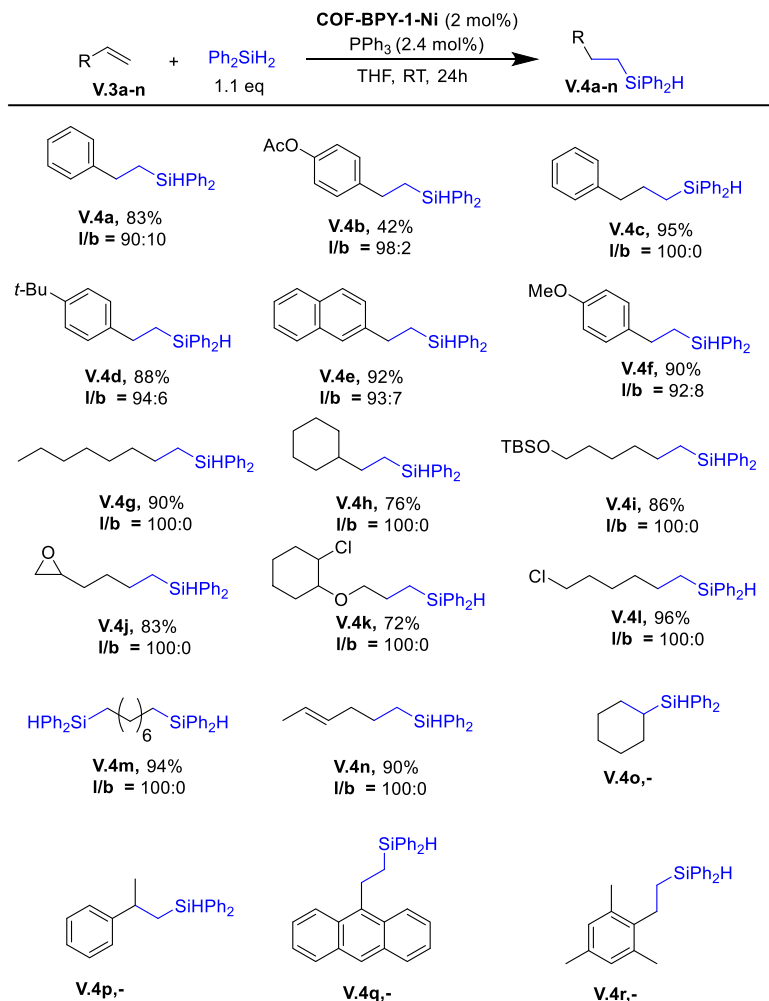
15	COF-BPY-1-Ni		4	2	0
16	COF-BPY-1-Ni		3	1	0
17	COF-BPY-1-Ni		7	9	0
18	COF-BPY-1-Ni		2	1	0

Reaction conditions: **V.3a** (0.1 mmol, 1M), SiPh₂H₂ (0.11 mmol), **COF-BPY-1-Co** or **COF-BPY-1-Ni** (1 μmol), ligand (1 μmol), THF, 24 h, 25 °C, under N₂. Yield of products determined by GC.

Encouraged by the previous results, we used the **COF-BPY-1-Ni**/PPh₃ system for the hydrosilylation of a variety of aliphatic and aromatic alkenes (Table 5.10). Aromatic alkenes (**V.3a-3f**) underwent hydrosilylation with moderate to excellent yields and good selectivity, with a linear to branched ratio for all aromatic products of more than 9:1. For aliphatic alkenes (**V.3g-3n**) good to excellent yields were obtained for the linear products. The system also showed excellent selectivity, with no branched products detected. Interestingly, 1,7-octadiene could be functionalized twice by the addition of 2eq. of silane, giving 94% yield for the disilane **V.4m**. On the other hand, 1,4-hexadiene (**V.3n**) was only functionalized in the terminal double bond, leaving the internal bond intact thanks to the high selectivity of the catalyst towards terminal olefins. Sterically demanding substrates (**V.3o-3r**) were not compatible with the catalytic system.

CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by a Covalent Organic Framework to promote Hydroboration of Olefins

Table 5.10. Hydrosilylation of aromatic and aliphatic alkenes with **COF-BPY-1-Ni** and PPh_3 .



Reaction conditions: alkene (0.1 mmol, 1 M), SiPh_2H_2 (20.2 mg, 0.11 mmol), **COF-BPY-1-Ni** (1.3 mg, 2 μmol), PPh_3 (0.6 mg, 2.4 μmol), THF, 24 h, 25 $^\circ\text{C}$, under N_2 . Yield of products isolated by silica gel column chromatography. l/b: linear to branched ratio of products determined by GC.

COF-BPY-1-Ni/PPh₃ was recovered from the reaction with **V.3a** by centrifugation and reused several times to check the recyclability of the catalyst (Figure 5.23). After the first cycle, the yield of **V.4a** suffered a reduction of 17%, followed by even lower yields for the next cycles. This result indicates that the catalyst is being quickly deactivated or it suffers from leaching.

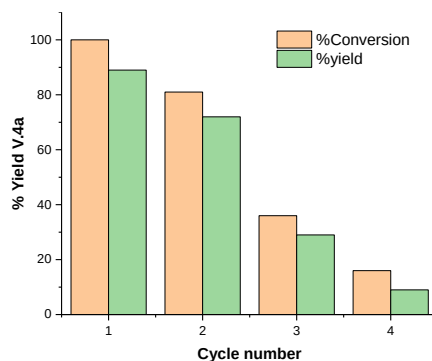


Figure 5.23. Recyclability test for **COF-BPY-1-Ni**/PPh₃. Reaction conditions: **V.3a** (10.4 mg, 0.1 mmol, 1 M), SiPh₂H₂ (20.2 mg, 0.11 mmol), **COF-BPY-1-Ni** (1.3 mg, 2 μmol), PPh₃ (0.6 mg, 2.4 μmol), THF, 24 h, 25 °C, under N₂. Yield determined by GC.

ICP-OES analysis of the filtered solution after catalysis revealed that 15% of the nickel in **COF-BPY-1-Ni** was being leached out after the first cycle. The gradual loss of metal from the COF could explain the loss of catalytic activity after a few cycles. In order to find if the leached-out Ni is active in catalysis, a hot filtration test was performed on the hydrosilylation of styrene (Figure 5.24). After 90 minutes of reaction (29% yield), **COF-BPY-1-Ni** was removed by filtration and the reaction was continued. The speed of the reaction was reduced after filtration, and the yield reached 49% after 20 hours. These results show that the leached-out nickel is active in catalysis and contributes partially to the overall yield of the reaction.

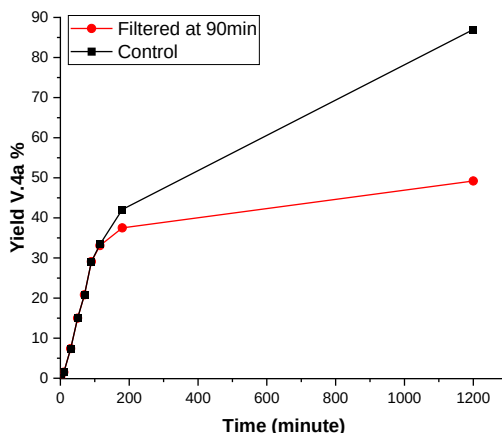


Figure 5.24. Hot filtration test for **COF-BPY-1-Ni/PPh₃**. Reaction conditions: **V.3a** (10.4 mg, 0.1 mmol, 1M), SiPh₂H₂ (20.2 mg, 0.11 mmol), **COF-BPY-1-Ni** (1.3 mg, 2 μ mol), PPh₃ (0.6 mg, 2.4 μ mol), THF, 24 h, 25 $^{\circ}$ C, under N₂.

In order to find if the leached-out nickel is forming phosphine complexes, the ³¹P-NMR spectrum of the filtrate after catalysis with **COF-BPY-1-Ni/PPh₃** was measured, and compared to the ³¹P-NMR spectrum obtained when Ni(PPh₃)₄ is used as catalyst instead (Figure 5.25). The reaction with **COF-BPY-1-Ni/PPh₃** showed peaks at -1.5 and 27.7 ppm assigned to PPh₃ and its oxide, and two doublets at 37.2 and 32.8 ppm which could be attributed to a nickel phosphine complex. These last two signals are also present in the spectrum of the reaction with Ni(PPh₃)₄, suggesting that in both cases the same nickel phosphine complex is being formed in solution during catalysis.

Based on these results, it is difficult to ascertain if the changes in reactivity of the catalyst after addition of PPh₃ to **COF-BPY-1-Ni** are caused by coordination of the phosphine ligands to the Ni sites immobilized in the framework, or whether they are caused by leaching of catalytically active Ni phosphine complexes into solution.

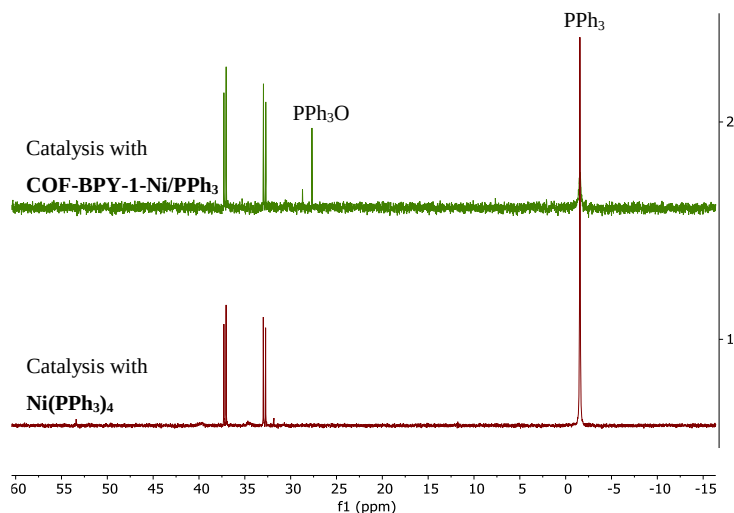


Figure 5.25. ^{31}P -NMR of the hydrosilylation catalysis with **COF-BPY-1-Ni/PPh₃** or with **Ni(PPh₃)₄**

5.2. Conclusions

In this chapter, we have developed a new single-site cobalt hydroboration catalyst isolated within a covalent organic framework. After reducing the cobalt centers with a hydride, the material can effectively transform terminal and internal alkenes into terminal boronate esters. Differences in reactivity between **COF-BPY-1-Co** and **COF-BPY-2-Co** can be ascribed to the superior crystallinity and porosity of **COF-BPY-1**. Compared to homogeneous analogs, **COF-BPY-1-Co** showed better performance in catalysis thanks to the isolated nature of the metal centers, preventing intermolecular deactivation. Additionally, the catalyst remained active after being reused several times. Based on experimental and theoretical studies, a highly reactive $(\text{bpy}^{\cdot-})\text{Co}^{\text{I}}(\text{THF})_2$ species was suggested as the primary catalytic species. DFT calculations were used to propose a reaction mechanism, beginning with oxidative boryl migration of HBpin and alkene onto the cobalt center, followed by isomerization and reductive elimination

of the alkyl boronate ester. Finally, catalytic experiments were performed in the presence of a phosphine ligand in solution, but the results were inconclusive due to excessive leaching. This work highlights the benefits of isolating unstable catalytic species within a COF, as a way to obtain new and efficient catalytic materials.

5.3. Experimental section

5.3.1. Materials and methods

Materials. Commercial reagents were purchased from Sigma Aldrich, Alfa Aesar, TCI Chemicals, Fluorochem or abcr and used as received without further purification. All solvents were purified by a SPS-400, Innovative Technology solvent purification system and stored under argon with activated 4 Å molecular sieves after degassing.

Nuclear magnetic resonance (NMR). NMR spectra were recorded on Bruker AV500/AV400 spectrometer using standard conditions (300 K). All ^1H chemical shifts are reported in ppm and have been internally calibrated to the residual protons of the deuterated solvent. The ^{13}C chemical shifts have been internally calibrated to the carbon atoms of the deuterated solvent. The coupling constants were measured in Hz.

Powder X-ray diffraction (PXRD). Powder X-Ray Diffraction (PXRD) PXRD measurements were made using a Siemens D5000 diffractometer (Bragg-Brentano parafocusing geometry and vertical θ - θ goniometer) fitted with a curved graphite diffracted-beam monochromator, incident and diffracted -beam Soller slits, a 0.06° receiving slit and scintillation counter as a detector. The angular 2θ diffraction range was between 2 and 40° . The data was collected with an angular step of 0.02° at 12 s per step and sample

rotation. A low background Si(510) wafer was used as sample holder. $\text{Cu}_{\text{K}\alpha}$ radiation was obtained from a copper X-ray tube operated at 40 kV and 30 mA

Scanning Electron Microscopy-Energy Dispersed X-ray Spectroscopy (SEM-EDX). The ESEM is from FEI company, model Quanta 600 in low vacuum mode (vacuum pressure 0.68 Torr). The EDX is from Oxford Instruments. The conditions for the ESEM are 20 kV accelerating voltage and a working distance close to 10 mm.

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). ICP-OES measurement was performed on the Perkin Elmer Optical Emission Spectrometer Optima 5300 DV (Scott-Chamber/Cross-Flow-Nebulizer).

Fourier-Transformed Infrared (FTIR). Spectroscopy FTIR measurements were measured using a Bruker Optics FT-IR Alpha spectrometer equipped with a DTGS detector, KBr beamsplitter at 4 cm^{-1} resolution using a one bounce ATR accessory with diamond windows.

XAFS analysis: Data was collected at the ALBA synchrotron CLAES beamline at cryogenic temperatures (80 K) using a Si311 double crystal monochromator. Samples of COF encapsulated single site Co centers (**COF-BPY-1-CoCl₂**) and the reference complex **Co(Me₂bpy)Cl₂** were prepared as powders diluted in boron nitride with spectra collected in transmission mode. Data was also collected on samples of **COF-BPY-1-Co** and **Co(Me₂bpy)Cl₂**. These latter samples were run as suspensions in THF with spectra acquired in fluorescence mode using a 5 channel SDD detector. The Athena⁶⁹ software package was used for data averaging, normalization and energy scale calibration. The energy was calibrated to the first inflection point of Co foil taken as 7709.5 eV. EXAFS data was

extracted using the AUTOBK algorithm having a spline in the 0 to 16 Å⁻¹ region and an R_{bkg} of 1.1, unless otherwise specified. The FEFF6 code^{70,71} was used for scattering path generation, and multi k^{1,2,3}-weighted fits of the data were carried out in r-space as specified in the text, using Larch.⁷² The S₀² value was set to 0.9, and a global ΔE₀ was employed with the initial E₀ value set to the inflection point of the rising edge. Single scattering paths were fit in terms of a Δr_{eff} and σ² as previously described.⁷³ To assess the goodness of the fits both the R_{factor} (%R) and the reduced χ² (χ²_v) were minimized, ensuring that the data was not over-fit. Pre-edge features were fit using a Gaussian-Lorentzian sum function with 50% Gaussian character.

X-ray photoelectron spectroscopy (XPS). X-ray photoelectron spectra were recorded with a lab-based spectrometer (SPECS GmbH, Berlin) using monochromated Al Kα source (hν = 1486.6 eV) operated at 50W as excitation source. In the spectrometer, the X-ray is focused with a μ-FOCUS 600 monochromator onto a 300 μm spot on the sample, and the data is recorded with a PHOIBOS 150 NAP 1D-DLD analyser in fixed analyser transmission (FAT) mode. The pass energy was set to 40 eV for survey scans and 20 eV for high-resolution regions. The binding energy scale was calibrated using Au 4f_{7/2} (84.01 eV) and Ag 3d_{5/2} (368.20 eV). Charge compensation was required for data collection. Recorded spectra were additionally calibrated against the C 1s internal reference. Data interpretation was done with Casa XPS. Shirley or two-point linear (for the Co 2p region) background were used depending on the spectrum shape. Surface chemical analysis was done based on the peak area of high-resolution spectra and the CasaXPS sensitivity factors (where RSF of C 1s = 1.000).

Transmission Electron Microscopy (TEM). Transmission electron microscopy (TEM) images were collected using a Thermo Scientific (FEI) Talos F200X G2 TEM operating at 200 kV. TEM images were acquired using a Ceta 16M CMOS camera. Samples were prepared by applying 5 μ L of the suspended sample in an aqueous solution onto continuous carbon 300 mesh Cu grids.

UV-vis absorption. UV-Vis measurements were carried out on a Shimadzu UV-2401PC spectrophotometer equipped with a photomultiplier tube (PMT) detector, double beam optics and D2 and W light sources.

5.3.2. Synthetic procedures

DBpin⁷⁴: The compound was synthesized following the reported procedure. In a round-bottomed flask connected with a dropping funnel and an N₂ inlet was charged with NaBD₄ (0.65 g, 15.5 mmol) in 15 mL of diglyme. The flask containing NaBD₄ was connected through a Teflon cannula to a second flask containing a solution of pinacol (0.61 g, 5.2 mmol) in 10 mL of anhydrous THF, maintaining 0 °C temperature. The flask containing pinacol was vented through a Teflon cannula bubbling into THF. The diglyme solution (10 mL) of I₂ (1.90 g, 7.5 mmol) was loaded in a dropping funnel and was allowed to add dropwise for over an hour. The steam of N₂ was continued for an additional 2 h after the addition of I₂. This step allowed complete elimination of any excess trace of polydeuterated diborane in the solution of DBPin. The removal of excess THF by a continuous flow of N₂ steam resulted in pure DBpin (0.43g, 8mmol, 42%). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 1.28 (s, 12H). ¹¹B NMR (CDCl₃, 160 MHz): δ (ppm) 28, 22.

Co(^{Me2}bpy)Cl₂⁷⁵: The compound was synthesized following the reported procedure. A solution of 6,6'-dmbipy (0.25 g, 1.34 mmol) in methanol (15

ml) was added to a solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.37 g, 1.34 mmol) in acetonitrile (15 ml) and the resulting blue solution was stirred for 15 min at 313 K. This solution was left to evaporate slowly at room temperature (yield: 0.35 g, 84%).

COF-BPY-1-Co: Inside a glovebox, NaBEt_3H (0.1 ml, 1M in THF) was added under stirring to a suspension of **COF-BPY-1-CoCl₂** (10 mg) in THF (1ml). After stirring for 1h, the solid was filtered and washed with THF 3 times. Due to the air sensibility of the material, **COF-BPY-1-Co** was stored in the glovebox or consumed directly in catalysis.

COF-BPY-1-Ni: Inside a glovebox, NaBEt_3H (0.1 ml, 1M in THF) was added under stirring to a suspension of **COF-BPY-1-NiCl₂** (10 mg) in THF (1ml). After stirring for 1h, the solid was filtered and washed with THF 3 times. Due to the air sensibility of the material, **COF-BPY-1-Ni** was stored in the glovebox or consumed directly in catalysis.

5.3.3. Catalytic experiments

General procedure for catalysis. Inside a glovebox, the catalyst was placed on a small vial with a stirring bar. After adding HBpin (38.3 mg, 43.4 μL , 0.3 mmol) and 1-octene (28 mg, 0.25 mmol), the vial was sealed. After stirring for 24 h the vial was opened to air and a known quantity of 1,3,5-trimethoxybenzene was added. The solid was removed by centrifugation and an aliquot of the solution was taken to be analyzed by GC.

Control experiments with trapped nanoparticles. In order to test the possible catalytic activity of nanoparticles trapped inside **COF-BPY-1-Co**, control experiments were performed with cobalt nanoparticles trapped inside **COF Py-1P**,⁵⁵ which has a similar structure to **COF-BPY-1** but it does not contain bipyridine groups. Since this COF has no ligands to

coordinate strongly to the cobalt ions, any cobalt present inside the material during the reduction will agglomerate into nanoparticles. To form the trapped nanoparticles, **COF Py-1P** (3 mg) was soaked in a THF solution of CoCl_2 (1mg, 7.7 μmol). After stirring for 1h, NaBEt_3H was added to the mixture (10 eq. relative to Co). The nanoparticles formed in the COF could be seen by TEM (Figure S16). This mixture of COF and nanoparticles produced a meager yield (13%) for the hydroboration catalysis. These results suggest that trapped nanoparticles could only have a small contribution to the catalytic activity of **COF-BPY-1-Co**.

Procedure for catalyst recycling. The catalysis was set up following the general procedure: inside a glovebox, **COF-BPY-1-Co** (2 mg, 2.5 μmol) was placed on a small vial with a stirring bar. After adding HBpin (38.3 mg, 43.4 μL , 0.3 mmol) and 1-octene (28 mg, 0.25 mmol), the vial was sealed. After stirring for 24 h, the vial was opened inside a glovebox and trimethoxybenzene was added as an internal standard. The solid was separated by centrifugation, and the solution analyzed by GC to determine the yield of **V.2a**. Next, the solid was washed with THF and centrifuged again. Then, the catalyst was reused for subsequent reactions.

Procedure for determining the reaction order in the hydroboration of vinylcyclohexane catalyzed by COF-BPY-1-Co. The kinetic reactions were performed in THF, keeping the total volume constant at 400 μL . First, the reactions were stirred inside a glovebox at room temperature for an appropriate time. Then they were stopped by the removal of the catalyst through filtration. The concentration of the product was determined by GC using 1,3,5-trimethoxybenzene as the internal standard. To determine the rate of HBpin, the concentration of HBpin was varied between 0.4 - 2 M while keeping constant the concentration of vinylcyclohexane at 0.5 M and the concentration of Co at 0.5 mM. To determine the rate of

vinylcyclohexane, the concentration of vinylcyclohexane was varied between 0.5 - 2 M while keeping constant the concentration of HBpin at 0.5 M and the concentration of Co at 2 mM. To determine the rate of Co, the concentration of Co was varied between 0.25 - 1 mM while keeping constant the concentration of HBpin at 0.5 M and the concentration of vinylcyclohexane at 0.5M.

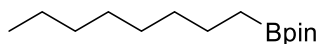
Procedure for quantification of H₂ during reduction of COF-BPY-1-CoCl₂. Inside a glovebox, NaBEt₃H (75 µl, 1M in THF, 10 equiv) was added under stirring to a suspension of **COF-BPY-1-CoCl₂** (5.8 mg, 7.55 µmol) in THF (1ml) in a closed vial. After stirring for 30 min, the headspace gas was analyzed by GC. The amount of H₂ produced was calculated as 7.93 µmol. Repeating the same experiment with **COF-BPY-1** produced traces of H₂.

General procedure for alkene hydroboration catalysis scope. Inside a glovebox, **COF-BPY-1-Co** (2 mg, 2.5 µmol) was placed on a small vial with a stirring bar. After adding HBpin (38.3 mg, 43.4 µL, 0.3 mmol) and the alkene (0.25 mmol), the vial was sealed. After stirring for 24 h the vial was opened to air and the solid was removed from the solution by filtration. The solution was purified by silica gel column chromatography using a hexane/ethyl acetate 97/3 mixture as eluent. After removing the solvent, **V.2a-j** was obtained as the product.

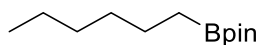
Hydroboration of 1-octene (1a) or E-3-octene (V.1b): The reaction was performed following the general procedure using **V.1a** (28 mg, 0.25 mmol) or **V.1b** (28 mg, 0.25 mmol) as substrate to produce **V.2a**. (41.4 mg, 0.17 mmol, 69% for reaction with **V.1a**), (37.2 mg, 0.16 mmol, 62% for reaction with **V.1b**). ¹H NMR (400 MHz, CDCl₃) δ, ppm: 1.49-1.35 (m, 2H), 1.34 – 1.25 (m, 10H), 1.25 (s, 12H), 0.93 – 0.82 (m, 3H), 0.77 (t, *J* = 7.6 Hz, 2H).

CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by
a Covalent Organic Framework to promote Hydroboration of
Olefins

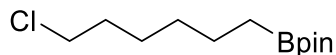
^{13}C NMR (101 MHz, CDCl_3) δ , ppm: 82.78, 32.42, 31.88, 29.36, 29.24, 24.78, 23.98, 22.66, 14.08.



Hydroboration of Z-3-hexene (V.1c): The reaction was performed following the general procedure using **V.1c** (21 mg, 0.25 mmol) as substrate to produce **V.2c** (33.9 mg, 0.16 mmol, 62%). ^1H NMR (400 MHz, CDCl_3) δ , ppm: 1.46-1.37 (m, 2H), 1.34-1.27 (m, 6H), 1.26 (s, 12H), 0.92–0.86 (m, 3H), 0.78 (t, $J = 7.7$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 82.80, 32.09, 31.64, 24.80, 23.96, 22.58, 14.07.



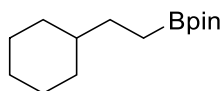
Hydroboration of 6-chloro-1-hexene (V.1d): The reaction was performed following the general procedure using **V.1d** (29.5 mg, 0.25 mmol) as substrate to produce **V.2d** (30.8 mg, 0.13 mmol, 50%). ^1H NMR (400 MHz, CDCl_3) δ , ppm: 3.54 (t, $J = 6.8$ Hz, 2H), 1.92-1.75 (m, 2H), 1.48 – 1.41 (m, 4H), 1.27 (s, 12H), 0.92 – 0.87 (m, 4H), 0.80 (t, $J = 7.7$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ , ppm: 82.90, 45.14, 32.54, 31.53, 26.63, 24.81, 23.78.



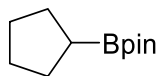
Hydroboration of vinyl-cyclohexane (V.1e): The reaction was performed following the general procedure using **V.1e** (27.5 mg, 0.25 mmol) as substrate to produce **V.2e** (56.5 mg, 0.24 mmol, 95%). ^1H NMR (400 MHz, CDCl_3) δ , ppm: 1.78-1.60 (m, 5H), 1.35-1.28 (m, 2H), 1.26 (s, 12H), 0.91

CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by
a Covalent Organic Framework to promote Hydroboration of
Olefins

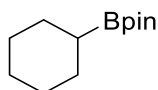
– 0.81 (m, 2H), 0.83 – 0.73 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ , ppm:
82.79, 39.94, 32.97, 31.35, 26.76, 26.43, 24.78.



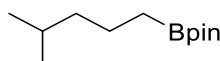
Hydroboration of cyclopentene (V.1f): The reaction was performed following the general procedure using **V.1f** (17 mg, 0.25 mmol) as substrate to produce **V.2f** (37.7 mg, 0.19 mmol, 77%). ^1H NMR (400 MHz, CDCl_3) δ , ppm: 1.82-1.71 (m, 2H), 1.70-1.57 (m, 2H), 1.56 – 1.40 (m, 4H), 1.25 (s, 12H), 1.21 – 1.15 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ , ppm: 82.76, 28.50, 26.82, 24.72.



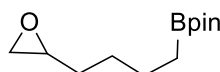
Hydroboration of cyclohexene (V.1g): The reaction was performed following the general procedure using **V.1g** (20.5 mg, 0.25 mmol) as substrate to produce **V.2g** (47.2 mg, 0.23 mmol, 90%). ^1H NMR (400 MHz, CDCl_3) δ , ppm: 1.72-1.58 (m, 6H), 1.38-1.28 (m, 4H), 1.25 (s, 12H), 1.05 – 0.95 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ , ppm: 82.72, 27.97, 27.14, 26.77, 24.75.



Hydroboration of 4-methyl-1-pentene (V.1h): The reaction was performed following the general procedure using **V.1h** (20.5 mg, 0.25 mmol) as substrate to produce **V.2h** (40.4 mg, 0.19 mmol, 77%). (36.0 mg, 0.15 mmol, 60%). ^1H NMR (400 MHz, CDCl_3) δ , ppm: 1.59-1.51 (m, 2H), 1.42 (p, $J = 8.2$ Hz, 2H), 1.27 (s, 12H), 1.22 – 1.15 (m, 2H), 0.88 (d, $J = 6.7$ Hz, 6H), 0.77 (t, $J = 7.9$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ , ppm: 82.82, 41.94, 27.78, 24.81, 24.78, 22.63, 21.77.



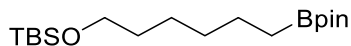
Hydroboration of 5,6-epoxy-1-hexene (V.1i): The reaction was performed following the general procedure using **V.1i** (24.5 mg, 0.25 mmol) as substrate to produce **V.2i** (14.1 mg, 0.06 mmol, 25%). ^1H NMR (400 MHz, CDCl_3) δ , ppm: 2.95-2.89 (m, 1H), 2.75 (dd, $J = 5.1, 3.9$ Hz, 1H), 2.47 (dd, $J = 5.1, 2.7$ Hz, 1H), 1.56-1.44 (m, 6H), 1.26 (s, 12H), 0.84 – 0.77 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 82.93, 52.35, 47.13, 32.26, 30.90, 28.58, 24.81, 23.84.



Hydroboration of tert-butyl(hex-5-en-1-yloxy)dimethylsilane (V.1j): The reaction was performed following the general procedure using **V.1j** (53.5 mg, 0.25 mmol) as substrate to produce **V.2j** (43.6 mg, 0.13 mmol, 51%). ^1H NMR (400 MHz, CDCl_3) δ , ppm: 3.60 (t, $J = 6.7$ Hz, 2 H), 1.58-1.47 (m, 2 H), 1.47-1.37 (m, 2 H), 1.36-1.29 (m, 4 H), 1.26 (s, 12 H), 0.90

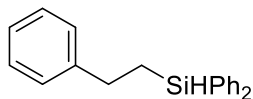
CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by
 a Covalent Organic Framework to promote Hydroboration of
 Olefins

(s, 9 H), 0.78 (t, $J = 7.7$ Hz, 2 H), 0.06 (s, 6 H). ^{13}C NMR (101 MHz, CDCl_3)
 δ , ppm: 82.83, 63.34, 32.84, 32.24, 25.98, 25.58, 24.80, 24.00, 18.37, -5.27.

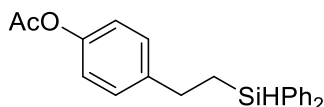


General procedure for alkene hydrosilylation catalysis scope: Inside a glovebox, **COF-BPY-1-Ni** (1.3 mg, 2 μmol) was placed on a small vial with a stirring bar. THF (0.13 mL) and PPh_3 (0.5 mg, 2 μmol) were added and the mixture was stirred for 30min. After adding SiH_2Ph_2 (40.5 mg, 0.22 mmol) and the alkene (0.20 mmol), the vial was sealed. After stirring for 18 hours the vial was opened to air and the solid was removed from the solution by filtration. The solution was purified by silica gel column chromatography using a hexane/ethyl acetate 97/3 mixture as eluent. After removing the solvent, **V.4 (a-n)** was obtained as the product.

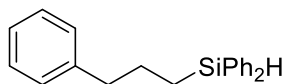
Hydrosilylation of styrene (V.3a): The reaction was performed following the general procedure using **V.3a** (21.2 mg, 0.20 mmol) as substrate to produce **V.4a** (47.9mg, 0.17 mmol, 83%). ^1H NMR (400 MHz, CDCl_3) δ , ppm: 7.70 – 7.63 (m, 4H), 7.50 – 7.42 (m, 6H), 7.37 – 7.31 (m, 2H), 7.29 – 7.22 (m, 3H), 4.99 (t, $J = 3.7$ Hz, 1H), 2.89 – 2.81 (m, 2H), 1.64 – 1.54 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ : 144.39, 135.19, 134.13, 129.68, 128.38, 128.08, 127.88, 125.75, 30.47, 14.30.



Hydrosilylation of 4-vinylphenyl acetate (V.3b): The reaction was performed following the general procedure using **V.3b** (32.8 mg, 0.20 mmol) as substrate to produce **V.4b** (29.1 mg, 0.08 mmol, 42%). ^1H NMR (400 MHz, CDCl_3) δ , ppm: 7.64 – 7.58 (m, 4H), 7.47 – 7.38 (m, 6H), 7.24 – 7.19 (m, 2H), 7.05 – 6.98 (m, 2H), 4.94 (t, $J = 3.7$ Hz, 1H), 2.86 – 2.75 (m, 2H), 2.32 (s, 3H), 1.60 – 1.48 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ : 169.67, 148.70, 141.91, 135.16, 133.98, 129.72, 128.77, 128.10, 121.33, 29.87, 21.15, 14.24.

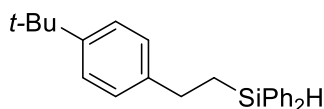


Hydrosilylation of allylbenzene (V.3c): The reaction was performed following the general procedure using **V.3c** (24 mg, 0.20 mmol) as substrate to produce **V.4c** (58.7mg, 0.19 mmol, 95%). ^1H NMR (400 MHz, CDCl_3) δ , ppm: 7.64 (dd, $J = 7.6$, 1.8 Hz, 4H), 7.46 (dq, $J = 8.0$, 6.2, 5.6 Hz, 6H), 7.36 (t, $J = 7.4$ Hz, 2H), 7.31 – 7.20 (m, 3H), 4.99 (t, $J = 3.7$ Hz, 1H), 2.78 (t, $J = 7.6$ Hz, 2H), 1.95 – 1.83 (m, 2H), 1.34 – 1.24 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ : 142.24, 135.23, 134.46, 129.64, 128.62, 128.34, 128.08, 125.82, 39.32, 26.39, 11.94.

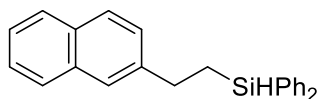


Hydrosilylation 1-(tert-butyl)-4-vinylbenzene (V.3d): The reaction was performed following the general procedure using **V.3d** (32.4 mg, 0.20 mmol) as substrate to produce **V.4d** (60.6 mg, 0.18 mmol, 88%). ^1H NMR

(400 MHz, CDCl_3) δ , ppm: 7.69 – 7.64 (m, 4H), 7.50 – 7.43 (m, 6H), 7.40 – 7.36 (m, 2H), 7.24 – 7.19 (m, 2H), 5.01 (t, $J = 3.7$ Hz, 1H), 2.91 – 2.80 (m, 2H), 1.67 – 1.59 (m, 2H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ : 148.59, 141.35, 135.24, 134.27, 129.69, 128.11, 127.57, 125.29, 34.42, 31.52, 29.93, 14.21.

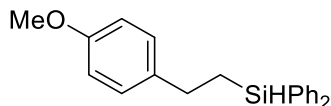


Hydrosilylation 2-vinylnaphthalene (V.3e): The reaction was performed following the general procedure using **V.3e** (31.2 mg, 0.20 mmol) as substrate to produce **V.4e** (62.2 mg, 0.18 mmol, 92%). ^1H NMR (400 MHz, CDCl_3) δ , ppm: 7.89 – 7.79 (m, 3H), 7.70 – 7.65 (m, 5H), 7.52 – 7.37 (m, 9H), 5.01 (td, $J = 3.7, 1.0$ Hz, 1H), 3.05 – 2.96 (m, 2H), 1.74 – 1.60 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ : 141.87, 135.24, 134.13, 133.72, 132.05, 129.74, 128.13, 127.96, 127.65, 127.50, 127.04, 125.92, 125.68, 125.14, 30.70, 14.23.

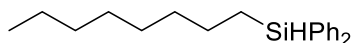


Hydrosilylation 1-methoxy-4-vinylbenzene (V.3f): The reaction was performed following the general procedure using **V.3f** (27.2 mg, 0.20 mmol) as substrate to produce **V.4f** (57.3 mg, 0.18 mmol, 90%). ^1H NMR (400 MHz, CDCl_3) δ , ppm: 7.68 – 7.64 (m, 4H), 7.50 – 7.41 (m, 6H), 7.21 – 7.15 (m, 2H), 6.93 – 6.87 (m, 2H), 4.98 (t, $J = 3.7$ Hz, 1H), 3.91 – 3.78 (m, 3H), 2.88 – 2.77 (m, 2H), 1.65 – 1.52 (m, 2H). ^{13}C NMR (101 MHz,

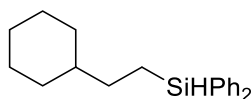
CDCl_3) δ : 157.75, 136.49, 135.19, 134.21, 129.65, 128.77, 128.06, 113.79, 55.30, 29.57, 14.55.



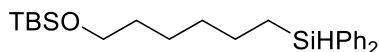
Hydrosilylation of 1-octene (V.3g): The reaction was performed following the general procedure using **V.3g** (24 mg, 0.20 mmol) as substrate to produce **V.4g** (53.3 mg, 0.18 mmol, 90%). ^1H NMR (400 MHz, CDCl_3) δ , ppm: 7.69 – 7.58 (m, 4H), 7.51 – 7.29 (m, 6H), 4.93 (t, J = 3.7 Hz, 1H), 1.62 – 1.49 (m, 2H), 1.49 – 1.40 (m, 2H), 1.38 – 1.29 (m, 8H), 1.27 – 1.17 (m, 2H), 0.99 – 0.91 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ : 135.20, 134.80, 129.51, 128.00, 33.25, 31.95, 29.28, 29.25, 24.47, 22.73, 14.18, 12.22.



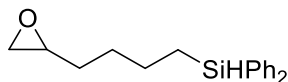
Hydrosilylation of vinyl cyclohexane (V.3h): The reaction was performed following the general procedure using **V.3h** (22.0 mg, 0.20 mmol) as substrate to produce **V.4h** (44.8 mg, 0.15 mmol, 90%). ^1H NMR (400 MHz, CDCl_3) δ , ppm: 7.69 – 7.57 (m, 4H), 7.50 – 7.36 (m, 6H), 4.91 (t, J = 3.6 Hz, 1H), 1.89 – 1.65 (m, 5H), 1.47 – 1.36 (m, 2H), 1.35 – 1.12 (m, 6H), 1.01 – 0.84 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ : 135.19, 134.79, 129.51, 128.00, 40.54, 32.97, 31.90, 26.81, 26.46, 9.26.



Hydrosilylation of vinyl cyclohexane (V.3i): The reaction was performed following the general procedure using **V.3i** (42.8 mg, 0.20 mmol) as substrate to produce **V.4i** (68.5 mg, 0.17 mmol, 86%). ^1H NMR (400 MHz, CDCl_3) δ , ppm: 7.63 (dd, $J = 7.6, 1.9$ Hz, 4H), 7.49 – 7.38 (m, 6H), 4.94 (t, $J = 3.7$ Hz, 1H), 3.65 (t, $J = 6.6$ Hz, 2H), 1.58 – 1.37 (m, 8H), 1.27 – 1.18 (m, 2H), 0.98 (s, 9H), 0.12 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ : 135.19, 134.73, 129.54, 128.02, 63.34, 33.01, 32.82, 26.08, 25.46, 24.46, 18.45, 12.19, -5.16.



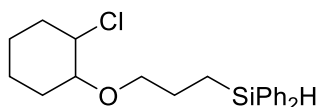
Hydrosilylation of 5,6-epoxy-1-Hexene (V.3j): The reaction was performed following the general procedure using **V.3j** (19.6 mg, 0.20 mmol) as substrate to produce **V.4j** (48.0 mg, 0.17 mmol, 83%). ^1H NMR (400 MHz, CDCl_3) δ , ppm: 7.65 – 7.60 (m, 4H), 7.48 – 7.39 (m, 6H), 4.93 (t, $J = 3.7$ Hz, 1H), 2.92 (dt, $J = 4.1, 2.1$ Hz, 1H), 2.76 (dd, $J = 5.0, 3.9$ Hz, 1H), 2.47 (dd, $J = 5.1, 2.7$ Hz, 1H), 1.59 (td, $J = 6.9, 6.2, 3.7$ Hz, 6H), 1.28 – 1.19 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ : 135.17, 134.47, 129.63, 128.06, 52.26, 47.11, 32.12, 29.41, 24.34, 12.21.



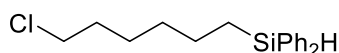
Hydrosilylation of 1-(allyloxy)-2-chlorocyclohexane (V.3k): The reaction was performed following the general procedure using **V.3k** (35.6 mg, 0.20 mmol) as substrate to produce **V.4k** (51.7 mg, 0.14 mmol, 72%).

CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by
 a Covalent Organic Framework to promote Hydroboration of
 Olefins

^1H NMR (400 MHz, CDCl_3) δ , ppm: 7.66 – 7.59 (m, 4H), 7.48 – 7.37 (m, 6H), 4.94 (t, J = 3.7 Hz, 1H), 3.87 (ddd, J = 9.6, 8.0, 4.3 Hz, 1H), 3.68 – 3.53 (m, 2H), 3.25 (td, J = 8.4, 4.2 Hz, 1H), 2.29 – 2.01 (m, 2H), 1.86 – 1.64 (m, 5H), 1.42 – 1.20 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ : 135.21, 134.36, 129.61, 128.03, 81.61, 72.04, 62.76, 34.60, 30.34, 25.05, 24.29, 23.15, 8.45.

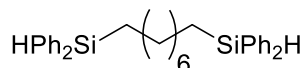


Hydrosilylation of 6-chloro-1-hexene (V.3l): The reaction was performed following the general procedure using **V.3l** (21 mg, 0.20 mmol) as substrate to produce **V.4l** (58.2 mg, 0.19 mmol, 96%). ^1H NMR (400 MHz, CDCl_3) δ , ppm: δ 7.68 – 7.61 (m, 4H), 7.48 – 7.41 (m, 6H), 4.95 (t, J = 3.7 Hz, 1H), 3.56 (t, J = 6.7 Hz, 2H), 1.79 (td, J = 9.1, 8.1, 5.7 Hz, 2H), 1.64 – 1.52 (m, 2H), 1.48 (tp, J = 6.6, 3.3 Hz, 4H), 1.29 – 1.20 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ : 135.19, 134.60, 129.61, 128.06, 45.15, 32.57, 32.38, 26.53, 24.34, 12.16.

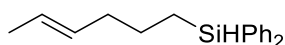


Hydrosilylation of 1,7-octadiene (V.3m): The reaction was performed following the general procedure using **V.3m** (22 mg, 0.20 mmol) as substrate to produce **V.4m** (76.8 mg, 0.19 mmol, 94%). ^1H NMR (400 MHz, CDCl_3) δ , ppm: 7.74 – 7.69 (m, 8H), 7.53 – 7.46 (m, 12H), 5.03 (t, J = 3.7 Hz, 2H), 1.66 – 1.55 (m, 4H), 1.49 (dq, J = 12.9, 6.7 Hz, 4H), 1.43 –

1.36 (m, 4H), 1.35 – 1.24 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ : 135.29, 134.86, 129.62, 128.11, 33.28, 29.21, 24.53, 12.31.



Hydrosilylation of 1,4-hexadiene (V.3n): The reaction was performed following the general procedure using **V.3n** (16.8 mg, 0.20 mmol) as substrate to produce **V.4n** (47.9 mg, 0.18 mmol, 90%). ^1H NMR (400 MHz, CDCl_3) δ , ppm: 7.61 (dq, J = 6.5, 2.4 Hz, 4H), 7.48 – 7.37 (m, 6H), 5.51 – 5.38 (m, 2H), 4.91 (t, J = 3.7 Hz, 1H), 2.10 (tdt, J = 8.5, 5.2, 1.4 Hz, 2H), 1.68 (dt, J = 5.1, 1.3 Hz, 3H), 1.61 – 1.52 (m, 2H), 1.25 – 1.16 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ : 135.18, 134.63, 131.01, 129.52, 127.98, 125.35, 35.99, 24.48, 17.96, 11.74.



5.3.4. Computational details

Calculations were carried out at density functional theory (DFT) level using the M06-L density functional⁶¹ as implemented in Gaussian 16.⁶² Co atoms were described with def2-TZVP and the rest of atoms with def2-SVP (basis set BS-1).⁷⁶ Numerical integrations were performed with an ultrafine grid. When necessary, doublet spin states were corrected for spin contamination.⁷⁷ Geometry optimizations were performed without restrictions and analytical frequency calculations were computed to confirm the nature of minima (intermediates) and maxima (transition states, one imaginary frequency). Gibbs energies are reported in gas phase at 298.15

K and 1 M. All frequencies below 50 cm⁻¹ were replaced by 50 cm⁻¹ when computing vibrational partition functions⁷⁸ with the GoodVibes script.⁷⁹ Single point calculations were performed on previously optimized geometries using def2-TZVP for all atoms (basis set BS-2).⁷⁶ Final Gibbs energies are obtained as follows:

$$\Delta G = \Delta E(\text{BS-2}) + [\Delta G(\text{BS-1}) - \Delta E(\text{BS-1})]$$

Additional density functionals were used to evaluate quartet-doublet spin state splitting: PBE⁸⁰ and PBE0⁸¹ with dispersion D3,⁸² B3LYP⁸³ with dispersion D3,⁸² and M06.⁸⁴ All inputs and outputs are available from the open access ioChem-BD platform⁶³ in the following database.⁶⁴

5.4. Bibliography

- (1) *Contemporary Boron Chemistry*; Davidson, M. G., Wade, K., Marder, T. B., Hughes, A. K., Eds.; Special Publications; Royal Society of Chemistry: Cambridge, 2007.
- (2) Carroll, A.-M.; O'Sullivan, T.; Guiry, P. The Development of Enantioselective Rhodium-Catalysed Hydroboration of Olefins. *Adv. Synth. Catal.* **2005**, 347 (5), 609–631.
- (3) Beletskaya, I.; Pelter, A. Hydroborations Catalysed by Transition Metal Complexes. *Tetrahedron* **1997**, 53 (14), 4957–5026.
- (4) Burgess, K.; Ohlmeyer, M. J. Transition-Metal Promoted Hydroborations of Alkenes, Emerging Methodology for Organic Transformations. *Chem. Rev.* **1991**, 91 (6), 1179–1191.
- (5) Vogels, C.; Westcott, S. Recent Advances in Organic Synthesis Using Transition Metal-Catalyzed Hydroborations. *Curr. Org.*

- Chem.* **2005**, 9 (7), 687–699.
- (6) Yamamoto, Y.; Fujikawa, R.; Umemoto, T.; Miyaura, N. Iridium-Catalyzed Hydroboration of Alkenes with Pinacolborane. *Tetrahedron* **2004**, 60 (47), 10695–10700.
 - (7) Obligacion, J. V.; Chirik, P. J. Earth-Abundant Transition Metal Catalysts for Alkene Hydrosilylation and Hydroboration. *Nat. Rev. Chem.* **2018**, 2 (5), 15–34.
 - (8) Poitras, A. M.; Oliemuller, L. K.; Hatzis, G. P.; Thomas, C. M. Highly Selective Hydroboration of Terminal Alkenes Catalyzed by a Cobalt Pincer Complex Featuring a Central Reactive N-Heterocyclic Phosphido Fragment. *Organometallics* **2021**, 40 (8), 1025–1031.
 - (9) Chen, X.; Cheng, Z.; Guo, J.; Lu, Z. Asymmetric Remote C-H Borylation of Internal Alkenes via Alkene Isomerization. *Nat. Commun.* **2018**, 9 (1), 3939.
 - (10) Verma, P. K.; Sethulekshmi, A.; Geetharani, K. Markovnikov-Selective Co(I)-Catalyzed Hydroboration of Vinylarenes and Carbonyl Compounds. *Org. Lett.* **2018**, 20 (24), 7840–7845.
 - (11) Ibrahim, A. D.; Entsminger, S. W.; Fout, A. R. Insights into a Chemoselective Cobalt Catalyst for the Hydroboration of Alkenes and Nitriles. *ACS Catal.* **2017**, 7 (5), 3730–3734.
 - (12) Ogawa, T.; Ruddy, A. J.; Sydora, O. L.; Stradiotto, M.; Turculet, L. Cobalt- and Iron-Catalyzed Isomerization–Hydroboration of Branched Alkenes: Terminal Hydroboration with Pinacolborane and 1,3,2-Diazaborolanes. *Organometallics* **2017**, 36 (2), 417–423.

CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by
a Covalent Organic Framework to promote Hydroboration of
Olefins

- (13) Scheuermann, M. L.; Johnson, E. J.; Chirik, P. J. Alkene Isomerization-Hydroboration Promoted by Phosphine-Ligated Cobalt Catalysts. *Org. Lett.* **2015**, *17* (11), 2716–2719.
- (14) Palmer, W. N.; Diao, T.; Pappas, I.; Chirik, P. J. High-Activity Cobalt Catalysts for Alkene Hydroboration with Electronically Responsive Terpyridine and α -Diimine Ligands. *ACS Catal.* **2015**, *5* (2), 622–626.
- (15) Zhang, L.; Zuo, Z.; Leng, X.; Huang, Z. A Cobalt-Catalyzed Alkene Hydroboration with Pinacolborane. *Angew. Chemie Int. Ed.* **2014**, *53* (10), 2696–2700.
- (16) Obligacion, J. V.; Chirik, P. J. Bis(Imino)Pyridine Cobalt-Catalyzed Alkene Isomerization–Hydroboration: A Strategy for Remote Hydrofunctionalization with Terminal Selectivity. *J. Am. Chem. Soc.* **2013**, *135* (51), 19107–19110.
- (17) Jang, W. J.; Song, S. M.; Moon, J. H.; Lee, J. Y.; Yun, J. Copper-Catalyzed Enantioselective Hydroboration of Unactivated 1, 1-Disubstituted Alkenes. *J. Am. Chem. Soc.* **2017**, *139* (39), 13660–13663.
- (18) Kerchner, H. A.; Montgomery, J. Synthesis of Secondary and Tertiary Alkylboranes via Formal Hydroboration of Terminal and 1,1-Disubstituted Alkenes. *Org. Lett.* **2016**, *18* (21), 5760–5763.
- (19) Liu, S.; Zeng, X.; Xu, B. CuII-Catalyzed Regioselective Borylation of Alkynes and Alkenes. *Tetrahedron Lett.* **2016**, *57* (33), 3706–3710.
- (20) Carroll, T. G.; Ryan, D. E.; Erickson, J. D.; Bullock, R. M.; Tran, B. L. Isolation of a Cu-H Monomer Enabled by Remote Steric

- Substitution of a N-Heterocyclic Carbene Ligand: Stoichiometric Insertion and Catalytic Hydroboration of Internal Alkenes. *J. Am. Chem. Soc.* **2022**, *144* (30), 13865–13873.
- (21) Garhwal, S.; Kroeger, A. A.; Thenarukandiyil, R.; Fridman, N.; Karton, A.; De Ruiter, G. Manganese-Catalyzed Hydroboration of Terminal Olefins and Metal-Dependent Selectivity in Internal Olefin Isomerization-Hydroboration. *Inorg. Chem.* **2021**, *60* (1), 494–504.
- (22) Carney, J. R.; Dillon, B. R.; Campbell, L.; Thomas, S. P. Manganese-Catalyzed Hydrofunctionalization of Alkenes. *Angew. Chemie Int. Ed.* **2018**, *57* (33), 10620–10624.
- (23) Docherty, J. H.; Peng, J.; Dominey, A. P.; Thomas, S. P. Activation and Discovery of Earth-Abundant Metal Catalysts Using Sodium Tert-Butoxide. *Nat. Chem.* **2017**, *9* (6), 595–600.
- (24) Zhang, G.; Zeng, H.; Wu, J.; Yin, Z.; Zheng, S.; Fettingner, J. C. Highly Selective Hydroboration of Alkenes, Ketones and Aldehydes Catalyzed by a Well-Defined Manganese Complex. *Angew. Chemie - Int. Ed.* **2016**, *55* (46), 14369–14372.
- (25) Wu, J. Y.; Moreau, B.; Ritter, T. Iron-Catalyzed 1,4-Hydroboration of 1,3-Dienes. *J. Am. Chem. Soc.* **2009**, *131* (36), 12915–12917.
- (26) Zhang, L.; Peng, D.; Leng, X.; Huang, Z. Iron-Catalyzed, Atom-Economical, Chemo- and Regioselective Alkene Hydroboration with Pinacolborane. *Angew. Chemie Int. Ed.* **2013**, *52* (13), 3676–3680.
- (27) Obligacion, J. V.; Chirik, P. J. Highly Selective Bis(Imino)Pyridine Iron-Catalyzed Alkene Hydroboration. *Org. Lett.* **2013**, *15* (11),

2680–2683.

- (28) Zheng, J.; Sortais, J.-B.; Darcel, C. [(NHC)Fe(CO)₄] Efficient Pre-Catalyst for Selective Hydroboration of Alkenes. *ChemCatChem* **2014**, 6 (3), 763–766.
- (29) Espinal-Viguri, M.; Woof, C. R.; Webster, R. L. Iron-Catalyzed Hydroboration: Unlocking Reactivity through Ligand Modulation. *Chem. A Eur. J.* **2016**, 22 (33), 11605–11608.
- (30) Chen, X.; Cheng, Z.; Lu, Z. Iron-Catalyzed, Markovnikov-Selective Hydroboration of Styrenes. *Org. Lett.* **2017**, 19 (5), 969–971.
- (31) Macaulay, C. M.; Gustafson, S. J.; Fuller, J. T.; Kwon, D. H.; Ogawa, T.; Ferguson, M. J.; McDonald, R.; Lumsden, M. D.; Bischof, S. M.; Sydora, O. L.; Ess, D. H.; Stradiotto, M.; Turculet, L. Alkene Isomerization-Hydroboration Catalyzed by First-Row Transition-Metal (Mn, Fe, Co, and Ni) N-Phosphinoamidinate Complexes: Origin of Reactivity and Selectivity. *ACS Catal.* **2018**, 8 (11), 9907–9925.
- (32) Van Leeuwen, P.W.N.M.; Chadwick, J. . *Homogeneous Catalysts Activity-Stability-Deactivation*; Wiley-VCH: Weinheim, Germany, 2011.
- (33) Alberico; Möller; Horstmann; Drexler; Heller. Activation, Deactivation and Reversibility Phenomena in Homogeneous Catalysis: A Showcase Based on the Chemistry of Rhodium/Phosphine Catalysts. *Catalysts* **2019**, 9 (7), 582.
- (34) Crabtree, R. H. Deactivation in Homogeneous Transition Metal Catalysis: Causes, Avoidance, and Cure. *Chem. Rev.* **2015**, 115 (1), 127–150.

CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by
a Covalent Organic Framework to promote Hydroboration of
Olefins

- (35) de Vries, H.G.; Elsevier, C., E. Catalyst Inhibition and Deactivation in Homogeneous Hydrogenation. In *Handbook of Homogeneous Hydrogenation*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2007; pp 1483–1516.
- (36) Li, C.; Song, S.; Li, Y.; Xu, C.; Luo, Q.; Guo, Y.; Wang, X. Selective Hydroboration of Unsaturated Bonds by an Easily Accessible Heterotopic Cobalt Catalyst. *Nat. Commun.* **2021**, *12* (1), 1–8.
- (37) Gao, K.; Yoshikai, N. Low-Valent Cobalt Catalysis: New Opportunities for C–H Functionalization. *Acc. Chem. Res.* **2014**, *47* (4), 1208–1219.
- (38) Tondreau, A. M.; Atienza, C. C. H.; Weller, K. J.; Nye, S. A.; Lewis, K. M.; Delis, J. G. P.; Chirik, P. J. Iron Catalysts for Selective Anti-Markovnikov Alkene Hydrosilylation Using Tertiary Silanes. *Science* **2012**, *335* (6068), 567–570.
- (39) Enthaler, S.; Junge, K.; Beller, M. Sustainable Metal Catalysis with Iron: From Rust to a Rising Star? *Angew. Chemie - Int. Ed.* **2008**, *47* (18), 3317–3321.
- (40) Hennessy, E. T.; Betley, T. A. Complex N-Heterocycle Synthesis via Iron-Catalyzed, Direct C–H Bond Amination. *Science* **2013**, *340* (6132), 591–595.
- (41) Friedfeld, M. R.; Shevlin, M.; Hoyt, J. M.; Krska, S. W.; Tudge, M. T.; Chirik, P. J. Cobalt Precursors for High-Throughput Discovery of Base Metal Asymmetric Alkene Hydrogenation Catalysts. *Science* **2013**, *342* (6162), 1076–1080.
- (42) Kundu, S.; Choliy, Y.; Zhuo, G.; Ahuja, R.; Emge, T. J.; Warmuth,

- R.; Brookhart, M.; Krogh-Jespersen, K.; Goldman, A. S. Rational Design and Synthesis of Highly Active Pincer-Iridium Catalysts for Alkane Dehydrogenation. *Organometallics* **2009**, 28 (18), 5432–5444.
- (43) Schaefer, B. A.; Margulieux, G. W.; Small, B. L.; Chirik, P. J. Evaluation of Cobalt Complexes Bearing Tridentate Pincer Ligands for Catalytic C-H Borylation. *Organometallics* **2015**, 34 (7), 1307–1320.
- (44) Léonard, N. G.; Bezdek, M. J.; Chirik, P. J. Cobalt-Catalyzed C(Sp²)–H Borylation with an Air-Stable, Readily Prepared Terpyridine Cobalt(II) Bis(Acetate) Precatalyst. *Organometallics* **2017**, 36 (1), 142–150.
- (45) Molnár, Á.; Papp, A. Catalyst Recycling—A Survey of Recent Progress and Current Status. *Coord. Chem. Rev.* **2017**, 349, 1–65.
- (46) Drake, T.; Ji, P.; Lin, W. Site Isolation in Metal-Organic Frameworks Enables Novel Transition Metal Catalysis. *Acc. Chem. Res.* **2018**, 51 (9), 2129–2138.
- (47) Zhang, T.; Manna, K.; Lin, W. Metal–Organic Frameworks Stabilize Solution-Inaccessible Cobalt Catalysts for Highly Efficient Broad-Scope Organic Transformations. *J. Am. Chem. Soc.* **2016**, 138 (9), 3241–3249.
- (48) Newar, R.; Begum, W.; Akhtar, N.; Antil, N.; Chauhan, M.; Kumar, A.; Gupta, P.; Malik, J.; Balendra; Manna, K. Mono-Phosphine Metal-Organic Framework-Supported Cobalt Catalyst for Efficient Borylation Reactions. *Eur. J. Inorg. Chem.* **2022**, 2022 (10), 3–9.
- (49) Iwai, T.; Harada, T.; Shimada, H.; Asano, K.; Sawamura, M. A

CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by
 a Covalent Organic Framework to promote Hydroboration of
 Olefins

- Polystyrene-Cross-Linking Bisphosphine: Controlled Metal Monochelation and Ligand-Enabled First-Row Transition Metal Catalysis. *ACS Catal.* **2017**, 7 (3), 1681–1692.
- (50) Zhang, G.; Wu, J.; Li, S.; Cass, S.; Zheng, S. Markovnikov-Selective Hydroboration of Vinylarenes Catalyzed by a Cobalt(II) Coordination Polymer. *Org. Lett.* **2018**, 20 (24), 7893–7897.
- (51) Segura, J. L.; Mancheño, M. J.; Zamora, F. Covalent Organic Frameworks Based on Schiff-Base Chemistry: Synthesis, Properties and Potential Applications. *Chem. Soc. Rev.* **2016**, 45 (20), 5635–5671.
- (52) Cheng, H. Y.; Wang, T. Covalent Organic Frameworks in Catalytic Organic Synthesis. *Adv. Synth. Catal.* **2021**, 363 (1), 144–193.
- (53) Sharma, R. K.; Yadav, P.; Yadav, M.; Gupta, R.; Rana, P.; Srivastava, A.; Zbořil, R.; Varma, R. S.; Antonietti, M.; Gawande, M. B. Recent Development of Covalent Organic Frameworks (COFs): Synthesis and Catalytic (Organic-Electro-Photo) Applications. *Mater. Horizons* **2020**, 7 (2), 411–454.
- (54) Dubed Bandomo, G. C.; Mondal, S. S.; Franco, F.; Bucci, A.; Martin-Diaconescu, V.; Ortuño, M. A.; van Langevelde, P. H.; Shafir, A.; López, N.; Lloret-Fillol, J. Mechanically Constrained Catalytic Mn(CO)₃Br Single Sites in a Two-Dimensional Covalent Organic Framework for CO₂ Electroreduction in H₂O. *ACS Catal.* **2021**, 11 (12), 7210–7222.
- (55) Auras, F.; Ascherl, L.; Hakimioun, A. H.; Margraf, J. T.; Hanusch, F. C.; Reuter, S.; Bessinger, D.; Döblinger, M.; Hettstedt, C.; Karaghiosoff, K.; Herbert, S.; Knochel, P.; Clark, T.; Bein, T.

- Synchronized Offset Stacking: A Concept for Growing Large-Domain and Highly Crystalline 2D Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2016**, *138* (51), 16703–16710.
- (56) Sommer, H.; Juliá-Hernández, F.; Martin, R.; Marek, I. Walking Metals for Remote Functionalization. *ACS Cent. Sci.* **2018**, *4* (2), 153–165.
- (57) Juliá-Hernández, F.; Moragas, T.; Cornella, J.; Martin, R. Remote Carboxylation of Halogenated Aliphatic Hydrocarbons with Carbon Dioxide. *Nature* **2017**, *545* (7652), 84–88.
- (58) Newar, R.; Begum, W.; Antil, N.; Shukla, S.; Kumar, A.; Akhtar, N.; Balendra; Manna, K. Single-Site Cobalt-Catalyst Ligated with Pyridylimine-Functionalized Metal–Organic Frameworks for Arene and Benzylic Borylation. *Inorg. Chem.* **2020**, *59* (15), 10473–10481.
- (59) Lyle, S. J.; Osborn Popp, T. M.; Waller, P. J.; Pei, X.; Reimer, J. A.; Yaghi, O. M. Multistep Solid-State Organic Synthesis of Carbamate-Linked Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2019**, *141* (28), 11253–11258.
- (60) Grunenberg, L.; Savasci, G.; Terban, M. W.; Duppel, V.; Moudrakovski, I.; Etter, M.; Dinnebier, R. E.; Ochsenfeld, C.; Lotsch, B. V. Amine-Linked Covalent Organic Frameworks as a Platform for Postsynthetic Structure Interconversion and Pore-Wall Modification. *J. Am. Chem. Soc.* **2021**, *143* (9), 3430–3438.
- (61) Zhao, Y.; Truhlar, D. G. A New Local Density Functional for Main-Group Thermochemistry, Transition Metal Bonding, Thermochemical Kinetics, and Noncovalent Interactions. *J. Chem.*

- Phys.* **2006**, 125 (19), 194101.
- (62) *Gaussian 16, Revision C.01. Frisch M. J. et Al. Gaussian Inc., Wallingford CT, 2016.*
- (63) Álvarez-Moreno, M.; de Graaf, C.; López, N.; Maseras, F.; Poblet, J. M.; Bo, C. Managing the Computational Chemistry Big Data Problem: The IoChem-BD Platform. *J. Chem. Inf. Model.* **2015**, 55 (1), 95–103.
- (64) <https://iochem-bd.bsc.es/browse/review-collection/100/216299/f63c805975676b70c8667e96>.
- (65) Verma, P.; Varga, Z.; Klein, J. E. M. N.; Cramer, C. J.; Que, L.; Truhlar, D. G. Assessment of Electronic Structure Methods for the Determination of the Ground Spin States of Fe(II), Fe(III) and Fe(IV) Complexes. *Phys. Chem. Chem. Phys.* **2017**, 19 (20), 13049–13069.
- (66) Milko, P.; Iron, M. A. On the Innocence of Bipyridine Ligands: How Well Do DFT Functionals Fare for These Challenging Spin Systems? *J. Chem. Theory Comput.* **2014**, 10 (1), 220–235.
- (67) Ortuño, M. A.; Cramer, C. J. Multireference Electronic Structures of Fe–Pyridine(Diimine) Complexes over Multiple Oxidation States. *J. Phys. Chem. A* **2017**, 121 (31), 5932–5939.
- (68) Liu, Y.; Jiang, Z.; Chen, J. Origin of the Ligand Effect in the Cobalt Catalyzed Regioselective Hydroboration of 1,3-Diene. *Org. Biomol. Chem.* **2020**, 18 (19), 3747–3753.
- (69) Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: Data Analysis for X-Ray Absorption Spectroscopy Using IFEFFIT.

- J. Synchrotron Radiat.* **2005**, 12 (4), 537–541.
- (70) Newville, M. EXAFS Analysis Using FEFF and FEFFIT. *J. Synchrotron Radiat.* **2001**, 8 (2), 96–100.
- (71) Rehr, J. J.; Albers, R. C. Theoretical Approaches to X-Ray Absorption Fine Structure. *Rev. Mod. Phys.* **2000**, 72 (3), 621–654.
- (72) Newville, M. Larch: An Analysis Package for XAFS and Related Spectroscopies. *J. Phys. Conf. Ser.* **2013**, 430 (1), 012007.
- (73) Martin-Diaconescu, V.; Bellucci, M.; Musiani, F.; Ciurli, S.; Maroney, M. J. Unraveling the *Helicobacter Pylori* UreG Zinc Binding Site Using X-Ray Absorption Spectroscopy (XAS) and Structural Modeling. *J. Biol. Inorg. Chem.* **2012**, 17 (3), 353–361.
- (74) Ghatak, T.; Makarov, K.; Fridman, N.; Eisen, M. S. Catalytic Regeneration of a Th-H Bond from a Th-O Bond through a Mild and Chemoselective Carbonyl Hydroboration. *Chem. Commun.* **2018**, 54 (78), 11001–11004.
- (75) Akbarzadeh Torbati, N.; Rezvani, A. R.; Safari, N.; Saravani, H.; Amani, V. Dichlorido(6,6'-Dimethyl-2,2'-Bipyridine- κ^2 N, N')Cobalt(II). *Acta Crystallogr. Sect. E Struct. Reports Online* **2010**, 66 (10), m1284–m1284.
- (76) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, 7 (18), 3297.
- (77) Yamaguchi, K.; Jensen, F.; Dorigo, A.; Houk, K. N. A Spin Correction Procedure for Unrestricted Hartree-Fock and Møller-

- Plesset Wavefunctions for Singlet Diradicals and Polyradicals. *Chem. Phys. Lett.* **1988**, *149* (5–6), 537–542.
- (78) Grimme, S. Supramolecular Binding Thermodynamics by Dispersion-Corrected Density Functional Theory. *Chem. A Eur. J.* **2012**, *18* (32), 9955–9964.
- (79) Luchini, G.; Alegre-Requena, J. V.; Funes-Ardoiz, I.; Paton, R. S. GoodVibes: Automated Thermochemistry for Heterogeneous Computational Chemistry Data. *F1000Research* **2020**, *9*, 291.
- (80) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865–3868.
- (81) Adamo, C.; Barone, V. Toward Reliable Density Functional Methods without Adjustable Parameters: The PBE0 Model. *J. Chem. Phys.* **1999**, *110* (13), 6158–6170.
- (82) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H–Pu. *J. Chem. Phys.* **2010**, *132* (15), 154104.
- (83) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. *Phys. Rev. A* **1988**, *38* (6), 3098–3100.
- (84) Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Function. *Theor. Chem. Acc.* **2008**, *120*

CHAPTER 5: Low Oxidation State Cobalt Center Stabilized by
a Covalent Organic Framework to promote Hydroboration of
Olefins

(1–3), 215–241.

Chapter VI:

Terpyridine Covalent Organic Frameworks as efficient C-H borylation catalysts

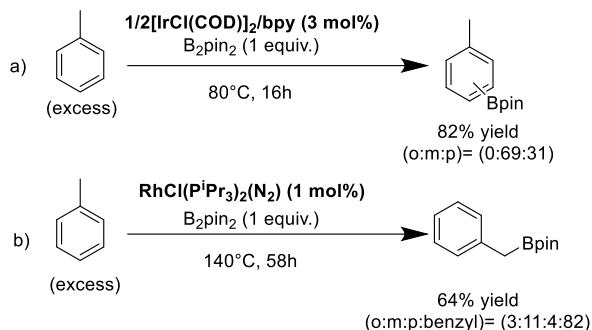
6.1. General insight

Carbon-hydrogen (C-H) bonds are some of the most common type of bonds present in organic compounds, and methods for their direct activation and functionalization present attractive ways to efficiently achieve more complex molecular entities.¹⁻⁷ In particular, the borylation of aromatic C-H bonds is highly important due to the versatile aryl boronic ester products, which are valuable building blocks employed in cross-coupling reactions to produce fine chemicals.⁸ Indeed, aryl boronic esters present properties that make them ideal coupling partners: air stability, low toxicity and ease of handling or storing. Although the direct borylation of C-H bonds is a very efficient approach, it is challenging to achieve due to the relatively unreactive nature of C-H bonds, and the presence of multiple C-H bonds that can lead to selectivity issues. To overcome these challenges, many research groups have worked towards the development of catalysts capable of borylating arenes with high efficiency and selectivity.^{9,10}

Initial studies from Smith and co-workers employed Cp*Ir complexes as catalysts for the borylation of benzene.¹¹ This was followed by many investigations into Ir catalysts. Notably, the groups of Hartwig and Miyaura developed a series of efficient arene borylation catalysts based on the Ir^I dimer [$\{\text{Ir}(\text{OMe})(\text{cod})\}_2$] combined with bipyridine ligands, achieving TONs as high as 20000.¹²⁻¹⁴ For this type of catalysts, the borylation of substituted arenes occurs with regioselectivity controlled by steric effects (Scheme 6.1a).¹⁵ The reaction at the *o*-position occurs with difficulty due to steric hindrance, while the selectivity of the *m*- or *p*- the statistical ratio mostly determines positions. B₂pin₂ or HBpin are usually employed as boron sources for this reactivity due to their stability and ease of handling. Other catalysts based on Rh or Pt complexes showed a different selectivity,

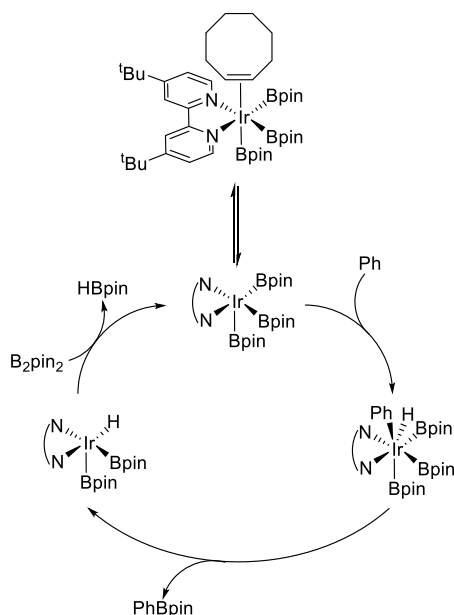
CHAPTER VI: Terpyridine Covalent Organic Frameworks as efficient C-H borylation catalysts

activating the Csp³-H bond at the benzylic position in toluene (Scheme 6.1b).^{16,17}



Scheme 6.1. a) Iridium-catalyzed¹¹²⁻¹⁴ and b) Rhodium-catalyzed¹⁶ borylation of toluene.

The mechanism of the Ir-catalyzed borylation was studied systematically by Hartwig and Miyaura.¹³ Their proposed catalytic cycle starts with the species $[\text{Ir}(\text{dtbpy})(\text{COE})(\text{Bpin})_3]$, which is formed by reaction from $[\text{Ir}(\text{COD})(\text{OMe})]_2$, dtbpy, COE, and HBpin. A reversible dissociation of COE is followed by oxidative addition of the arene onto the Ir (I) center. Reductive elimination then forms the aryl boronate ester product, and the catalyst is regenerated by reaction with B_2pin_2 to form the HBpin by-product.



Scheme 6.2. Proposed mechanism for the Ir-catalyzed borylation of arenes.¹³

The challenge of separating and recycling homogeneous catalysts from the reaction medium encouraged researchers to immobilize borylation catalysts onto silica.^{18–21} Sawamura and co-workers employed a silicon-constrained monodentate alkylphosphine (SMAP) ligand to immobilize an Ir catalyst (Figure 6.1a).¹⁸ The resulting heterogeneous catalyst produced excellent TONs in the borylation of substituted arenes. Additionally, the borylation of methyl benzoate derivatives was *o*-selective. This selectivity was achieved by employing substrates with directing groups and a phosphine ligand (SMAP) with low steric hinderance. However, the catalysts showed decreased activity after being recovered from the reaction medium because of partial decomposition during the recycling process. Likewise, Jones and co-workers developed an Ir-bipyridine catalyst attached to mesoporous silica through an alkyl linker (Figure 6.1b).²⁰ The catalyst showed moderate to good catalytic activity in the aromatic C–H borylation of a variety of substrates, but it also suffered loss of activity after being recycled.

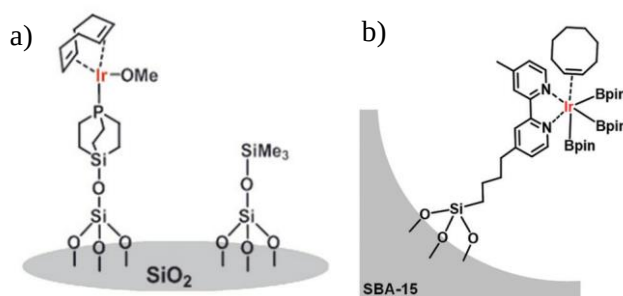


Figure 6.1. a) Silica-SMAP-Ir catalyst. b) silica-supported Ir-bipyridine catalyst. Figure reproduced with permission.²¹ Copyright 2021, Thieme.

The development of MOFs presented an attractive alternative support for catalysts. Compared to silica supports, MOFs offer higher porosity, well-defined structure, controlled molecular tailoring and good stability. Lin's group has extensively studied using MOFs as single-site catalysts, developing several MOF-based borylation catalysts.^{22–28} In 2014 Lin and co-workers reported the post-synthetic metalation of a bipyridyl-containing UiO-type MOF with Ir (Figure 6.2).²³ The Ir-MOF was used as a catalyst in several reactions, including the borylation of arenes. The catalyst showed enhanced activity relative to homogeneous analogues, and it could be reused many times due to its high stability. The same group later developed other Ir-MOF catalysts with phenantroline or phosphine ligands capable of performing arene borylations.^{24,27}

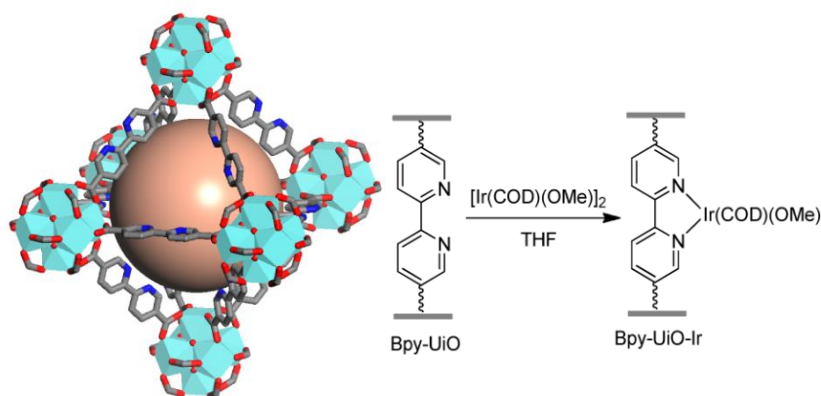


Figure 6.2. Structure of bpy-UiO MOF (left), Ir metalation of bpy-UiO MOF. Reproduced with permission.²³ Copyright 2014, American Chemical Society.

Replacing precious metal catalysts with earth-abundant metal catalysts has attracted considerable attention because of issues attached to precious metals like high cost, low abundance and high toxicity.^{2,4,6} In this context, Lin's group has developed several Co-MOF borylation catalysts.^{25,26,28} In 2016, they reported the metalation of MOF secondary building units (SBUs) with cobalt salts affording highly active and reusable single-site solid catalysts for a range of organic reactions (Figure 6.3a). After being activated with NaBEt_3H , UiO-Co-MOF could catalyze the borylation of methyl arenes with good selectivity towards the benzylic position. The selectivity was attributed to a steric effect from the cavities, while the high activity and recyclability were attributed to the site-isolated nature of the catalytic centres, which prevents intermolecular deactivation processes. The same group later developed a terpyridine metal-organic layer (MOL) metalated with cobalt that was active as a benzylic or aryl borylation catalyst (Figure 6.3b).²⁸ In this work, the authors proposed a diradical terpyridine complex $\text{Co}^{\text{II}}(\text{THF})_2(\text{TPY}^{\bullet})^{2-}$ as the catalytically active species generated by reduction with NaBEt_3H .

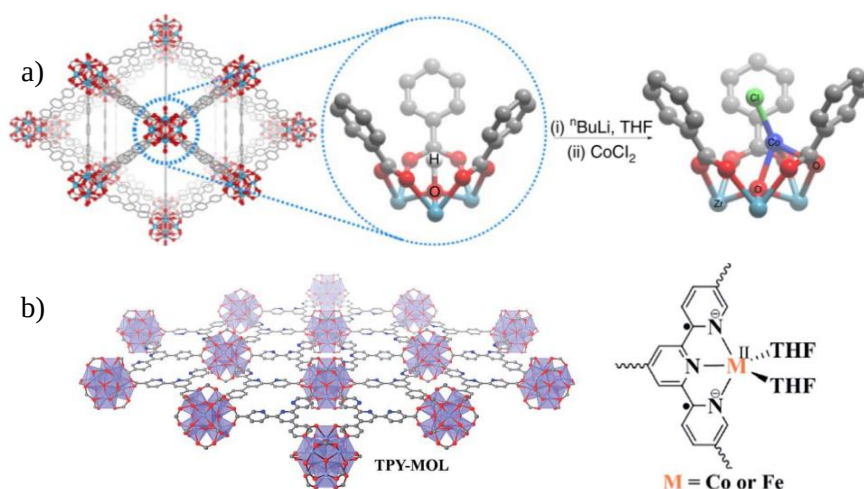


Figure 6.3. Structure of UiO-Co-MOF²⁵ (a). Structure of Co(THF)₂·TPY-MOL²⁸ (b). Reproduced with permission.²⁵

Manna and co-workers have also worked on the development of MOF-based borylation catalysts.^{29,30} They reported the introduction of a pyridylimine ligand into a MOF through PMS, followed by metallation with CoCl₂ (Figure 6.4a). Upon reduction with NaBEt₃H, the Co-MOF produced excellent TONs in the borylation of arene C-H bonds, as well as benzylic C-H bonds. The catalyst presented a broad substrate scope, as well as good recyclability.²⁹ The authors proposed a reaction mechanism slightly different from that presented in Scheme 6.2: First, B₂pin₂ undergoes oxidative addition to the (Pyrim⁺)-Co^I(THF) species. Then, a σ -bond metathesis of Co-Bpin and arene C-H produces the aryl boronate ester product. Finally, the catalyst is regenerated by reductive elimination of HBpin (Figure 6.4b).

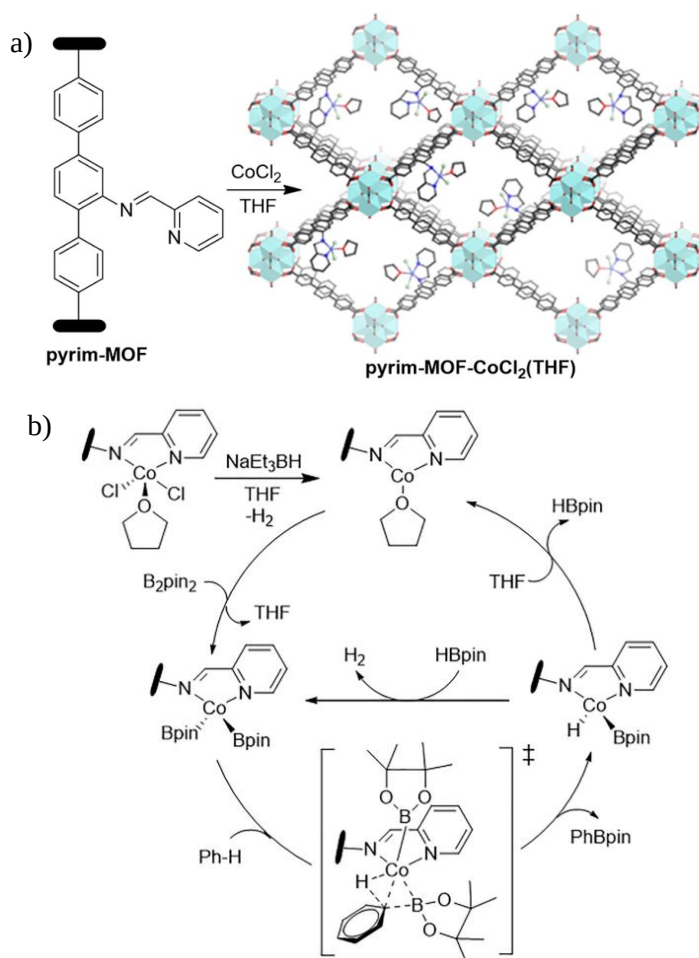


Figure 6.4. a) Structure of pyrim-MOF-CoCl_2 . b) Proposed reaction mechanism for the MOF-catalyzed borylation. Figures reproduced with permission.²⁹ Copyright 2020, American Chemical Society.

COFs, owing to their well-defined structure, high porosity, stability, and tunable properties, can also make excellent supports for borylation catalysts. Cui and co-workers reported a series of COFs with different alkyl substituents that were used to control the interlayer stacking of the sheets in the material.³¹ The bipyridine COFs were metallated with $[\{\text{Ir}(\text{OMe})(\text{cod})\}_2]$ and used as catalysts for the borylation of arenes. Interestingly, the COF functionalized with isopropyl chains, which formed

into an ABC stacking mode, was more catalytically active than the other COFs with AA staking (Figure 6.5). This was attributed to its higher porosity and superior stability. Likewise, Ma and co-workers also developed an Ir-bipyridine COF for arene borylation.³²

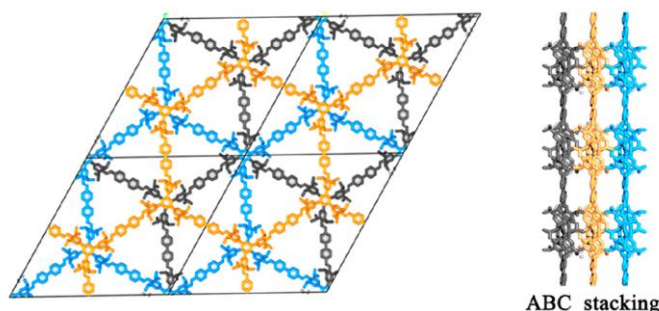


Figure 6.5. Structure and stacking mode of 4-iPr COF. Reproduced with permission.³¹ Copyright 2018, American Chemical Society.

So far, the use of COFs as borylation catalysts has been limited to precious metal catalysis. Thus, in this chapter, we sought to explore using a cobalt-terpyridine COF as an arene borylation catalyst. We envision that the site isolation of the COF could stabilize reactive metal species, and the heterogeneous nature of the material could facilitate recycling.

6.2. Results and Discussion

6.2.1. Arylic and benzylic C-H borylation catalyzed by TPY-COFs

The cobalt-terpyridine COFs presented in chapter 4 (**COF-TPY-1-Co(AcO)₂** and **COF-TPY-1-Co(AcO)₂**) were initially evaluated as catalysts for the borylation of toluene. Reactions were performed with B₂pin₂ and an excess of toluene at 100°C over 24 h. Using only 1 mol% catalyst loading, **COF-TPY-1-Co(AcO)₂** and **COF-TPY-2-Co(AcO)₂** could achieve 92% and 95% yield, respectively, of borylated products (Yields relative to 1 equiv. of B₂pin₂, Table 6.1, entries 1 and 2). Within the

first 30 min of the reaction, a colour change from yellow to black was observed for the cobalt COFs, indicative of catalyst activation. Interestingly, the catalysts did not require additives like NaBEt_3H or LiOMe to be activated, and their addition did not improve the reaction (Table 6.1, entries 3-6). By contrast, most Co(II) borylation catalysts require strong reductants or bases to become active or to prevent deactivation.^{26,28,29,33-37} Low yields were obtained when THF or hexane was employed as solvents instead of neat toluene (Table 6.1, entries 7-8). This result could be improved by employing a mixture of 1:1 hexane and toluene (Table 6.1, entry 9). The results suggest that a high concentration of arene is required for the reaction to proceed smoothly. *Meta*- and *para*-substituted toluene boronates were obtained in approximately a 3:1 ratio for all reactions. Additionally, *benzyl*-**VI.2d** was detected as a minor product, presenting a rare case of benzylic C-H activation.

CHAPTER VI: Terpyridine Covalent Organic Frameworks as efficient C-H borylation catalysts

Table 6.1. Optimization of toluene borylation^a

Cc1ccccc1 (VI.1d, Excess) $\xrightarrow[\text{100}^\circ\text{C, 24h, -HBpin}]{\text{Catalyst B}_2\text{pin}_2, \text{Neat toluene}}$ Cc1cccc(Bpin)c1 (*m*-VI.2d) + Cc1ccc(Bpin)cc1 (*p*-VI.2d) + Cc1ccccc1CBpin (benzyl-VI.2d)

Entry	Catalyst (mol%)	Additive	Solvent	Arene equiv.	Total borylation yield (%)	Selectivity (m:p:benzyl)
1	COF-TPY-1-Co(AcO) ₂ (1)		Toluene	25	92	66:20:14
2	COF-TPY-2-Co(AcO) ₂ (1)		Toluene	25	95	69:20:11
3 ^b	COF-TPY-1-Co(AcO) ₂ (1)	NaBEt ₃ H	Toluene	25	76	64:20:16
4 ^b	COF-TPY-1-Co(AcO) ₂ (1)	LiOMe	Toluene	25	93	66:20:14
5 ^b	COF-TPY-2-Co(AcO) ₂ (1)	NaBEt ₃ H	Toluene	25	69	64:21:15
6 ^b	COF-TPY-2-Co(AcO) ₂ (1)	LiOMe	Toluene	25	94	68:20:12
7 ^c	COF-TPY-1-Co(AcO) ₂ (1)		THF	1	6	58:21:21
8 ^c	COF-TPY-1-Co(AcO) ₂ (1)		Hexane	1	37	68:20:12
9 ^d	COF-TPY-1-Co(AcO) ₂ (1)		Hexane/ Toluene 1/1	6	91	61:21:17

^aReactions were conducted using **VI.1d** (7.5 mmol), B₂pin₂ (0.3 mmol) and catalyst (1.2 μmol) for 24 h at 100°C. ^b10 mol% of additive (NaBEt₃H or LiOMe) relative to B₂pin₂ was added. ^c0.5 mL of THF or hexane was added. ^d0.2ml of hexane and toluene were added. Borylation yields were determined by GC employing 1,3,5-trimethoxybenzene as an internal stand.

For the subsequent reactions, 2,6-lutidine (**VI.1l**) was employed as a more challenging substrate to convert. Interestingly, **COF-TPY-2-Co(AcO)₂** produced better yields than **COF-TPY-1-Co(AcO)₂** for the borylation of **VI.1l** (Table 6.2, entries 1 and 2). Since both catalysts present almost identical structure and porosity, this difference in reactivity and the slight difference in selectivity could be attributed to an electronic effect from the **TAPB** or **TTA** linkers. Lowering the excess of arene positively affected the reaction, achieving 98% yield of **VI.2l** with 1 mol% **COF-TPY-2-Co(AcO)₂** (Table 6.2, entries 3 and 4). Under the optimized conditions, the

CHAPTER VI: Terpyridine Covalent Organic Frameworks as efficient C-H borylation catalysts

catalyst loading could be reduced to 0.4 mol% without affecting the yield (Table 6.2, entry 5).

Table 6.2. Optimization of **VI.11** borylation.^a

Entry	Catalyst (mol%)	Solvent	Arene equiv.	Total borylation yield (%)
1	COF-TPY-1-Co(AcO) ₂ (1)	VI.11	25	55
2	COF-TPY-2-Co(AcO) ₂ (1)	VI.11	25	75
3 ^b	COF-TPY-1-Co(AcO) ₂ (1)	VI.11	2.5	69
4 ^b	COF-TPY-2-Co(AcO) ₂ (1)	VI.11	2.5	98
5 ^b	COF-TPY-2-Co(AcO) ₂ (0.4)	VI.11	2.5	96

^aReactions were conducted using **11** (7.5 mmol), B₂pin₂ (0.3 mmol) and catalyst (1.2 μmol) for 24 h at 100°C. ^b0.75 mmol of **11** were employed. Borylation yields were determined by NMR employing 1,3,5-trimethoxybenzene as an internal stand.

Next, the catalytic activity of **COF-TPY-2-Co(AcO)₂** was compared against analogous homogeneous catalysts (Table 6.3). A molecular complex formed from terpyridine and Co(AcO)₂ produced only 4% yield, while a complex with the terpyridine aldehyde linker employed in the synthesis of the COF (**TPY-CHO**) only gave traces of borylation products (Table 6.3, entries 2 and 3). This significant difference in reactivity between the COF and a molecular catalyst could be attributed to site isolation of the catalytic sites within the COFs. Interestingly, the bipyridine COFs studied in chapter 5 of this thesis were not active for this reaction, even after reduction (Table 6.3, entries 4 and 5). Using HBpin instead of B₂pin₂ produced 10% yield (Table 6.3, entry 6). Since HBpin is obtained as a by-product of the reactions with B₂pin₂. This result suggests that some HBpin by-products can be consumed as a boron source.

Table 6.3. Control experiments

VI.1d $\xrightarrow[100^{\circ}\text{C}, 24\text{h}]{\text{Catalyst B}_2\text{pin}_2, \text{-HBpin}}$ *m*-VI.2d + *p*-VI.2d + benzyl-VI.2d

Entry	Deviation from standard conditions	Total borylation yield (%)	Selectivity (m:p:benzyl)
1	None	102	69:20:11
2	Co(AcO) ₂ .tpy as catalyst	4	55:29:16
3	Co(AcO) ₂ .TPY-CHO as catalyst	-	-
4	COF-BPY-1-CoCl ₂ as catalyst	-	-
5	COF-BPY-1-Co as catalyst	-	-
6	HBpin as boron source	10	57:24:19

^aReactions were conducted using **VI.1i** (7.5 mmol), B₂pin₂ (0.3 mmol) and catalyst (1.2 μmol) for 24 h at 100°C. ^b0.75 mmol of **VI.1i** were employed. Borylation yields were determined by GC employing 1,3,5-trimethoxybenzene as an internal stand.

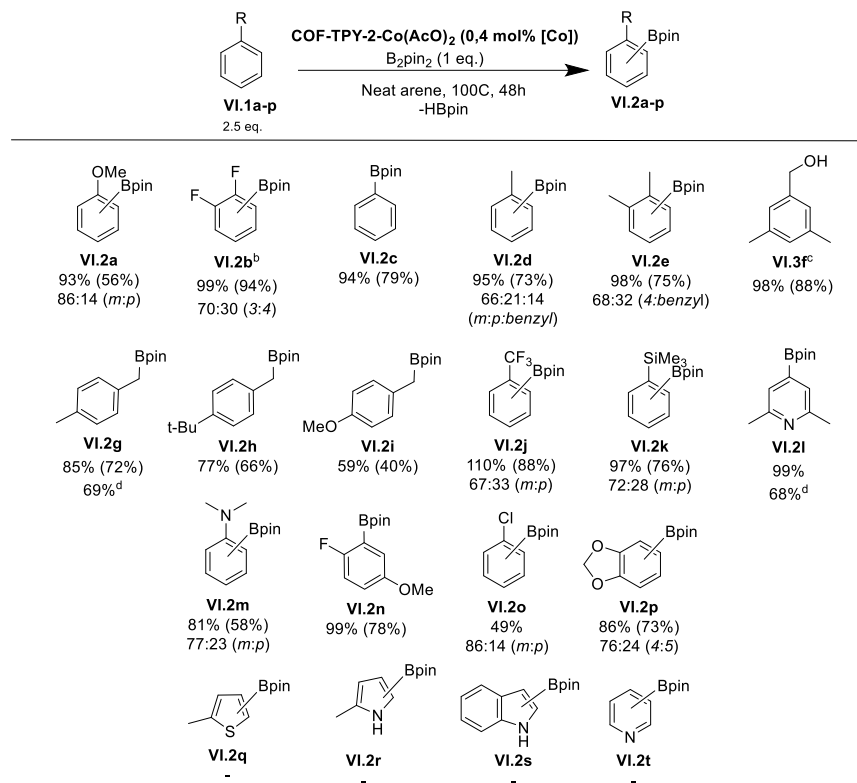
6.2.2. Arene substrate scope

The catalytic activity of the COFs was further investigated by expanding the scope of the reaction, obtaining good to excellent yields with arenes and methylarenes (Table 6.4). For methylarenes (**VI.1d-1i**), the selectivity of the reaction was strongly influenced by steric hinderance. *m*- and *p*-substituted methylarenes (**VI.1f-1i**) became selectively borylated at the benzylic position due to the steric effect of the substituents, while non-substituted or *m*-substituted methylarenes (**VI.1d-1e**) produced mixtures of benzylic and aromatic borylation products. Interestingly, the borylation of **VI.1j** produced more than 1 eq. of aryl boronate relative to B₂pin₂, suggesting that some of the HBpin released as a by-product was consumed as a boron source. A small amount of 2-fluorophenyl boronate ester (9%) pinacol ester and 3-fluorophenyl boronate ester (3%) were detected as products from the borylation of **VI.1b**, likely due to defluorination-borylation.³⁶ None of the heterocycles tested in this screening (**VI.1q-t**) were compatible with the methodology, except for **VI.1L**. We rationalize that coordination of the heterocycles to the catalyst as N-donors stops the

CHAPTER VI: Terpyridine Covalent Organic Frameworks as efficient C-H borylation catalysts

reaction, but **VI.1L** presents two methyl groups which prevent coordination through steric hindrance.

Table 6.4. Substrate scope for arene borylation.^a



^aReported numbers are yields relative to B₂pin₂ based on ¹H-NMR. The value in parenthesis is isolated yield. Reaction conditions: B₂pin₂ (76.2 mg, 0.3 mmol), arene (0.75 mmol), **COF-TPY-2-Co(AcO)**₂ (2.4 mg, 1.2 μmol), 100 °C, 48 h. For products **VI.2b-2g**: reactions performed with 7.5 mmol of arene. ^bContains 9% and 3% of 2-fluorophenyl boronic acid pinacol ester and 3-fluorophenyl boronic acid pinacol ester, respectively. ^cIsolated as alcohol after oxidation with H₂O₂. ^d**COF-TPY-1-Co(AcO)**₂ was used as catalyst.

6.2.3. Catalyst recycling

To determine recyclability, **COF-TPY-2-Co(AcO)**₂ was recovered and reused several times in the borylation of benzene. Each reaction was performed with **VI.1c** (2 mmol), B₂pin₂ (0.08 mmol) and 0.8 mol% [Co] at

100 °C over 24 h. The catalytic activity of the COF was retained after 7 cycles (79% yield), albeit with slightly lower yields each run (Figure 6.6a). Additionally, no leaching of cobalt into the solution was detected by ICP-OES (<0.005 mg/mL), and the recovered material retained its crystalline structure (Figure 6.6b). Furthermore, no changes were observed by TEM on the material before and after catalysis (Figure 6.6c-d). These results suggest that **COF-TPY-2-Co(AcO)₂** is a robust material that can be reused as a catalyst several times. Nevertheless, we suspect that the decrease in yield observed every run could be associated with material loss during the recycling process.

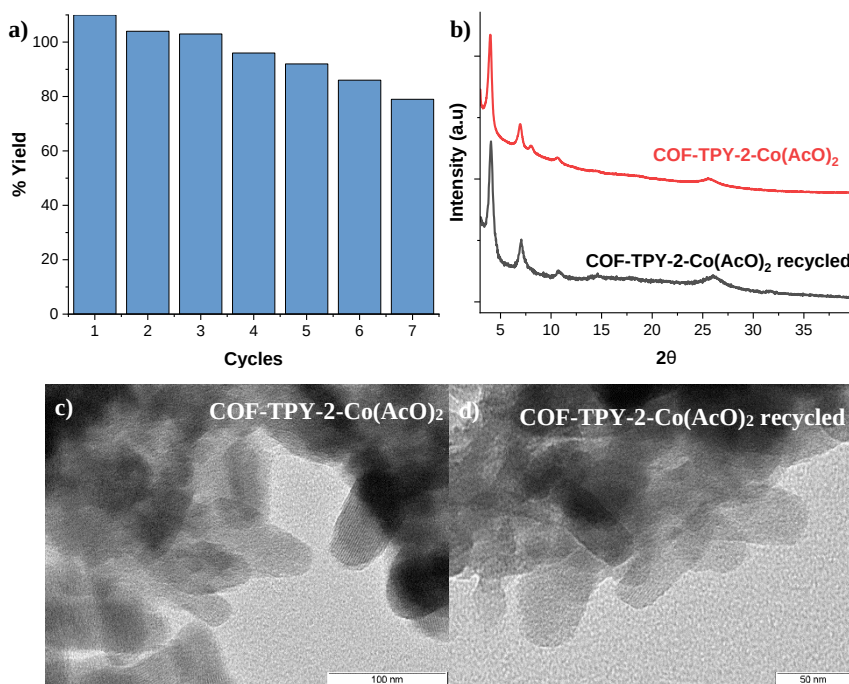
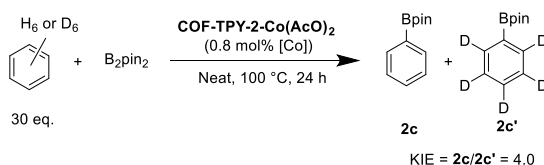


Figure 6.6. a) Yield for catalysis with recycled **COF-TPY-2-Co(AcO)₂**. b) PXRD and c-d) TEM of **COF-TPY-2-Co(AcO)₂** before and after the first reuse cycle.

6.2.4. Study of the COF-BPY-1-Co reduced species and mechanistic studies

To gain insight into the reaction mechanism, an intermolecular competition experiment was performed between C₆H₆ (**VI.1c**) and C₆D₆ (**VI.1c'**) in a 1:1 ratio (Scheme 6.3). Based on the ratio of borylated products, a KIE of 4.0 was estimated. This effect shows that the C-H bond cleavage occurs in the product-determining step.³⁸ This result is consistent with other reported cobalt catalysts.^{34,39}



Scheme 6.3. Intermolecular competition experiment

UV-vis absorption spectroscopy was used to study the catalyst activation (Figure 6.7). The spectra of **COF-TPY-1-Co(AcO)**₂ treated with B₂pin₂ in THF exhibited three broad bands centered at 522, 698, and 988 nm, which could be assigned to π to π^* and π^* to π^* transitions for the reduced tpy ligand,²⁸ although the interpretation of the results is complicated since the pristine COF presents an absorption band around 522 nm as well. Interestingly, reduction with NaBEt₃H led to the appearance of similar bands, suggesting that the Co(tpy) complex is being reduced in both cases.

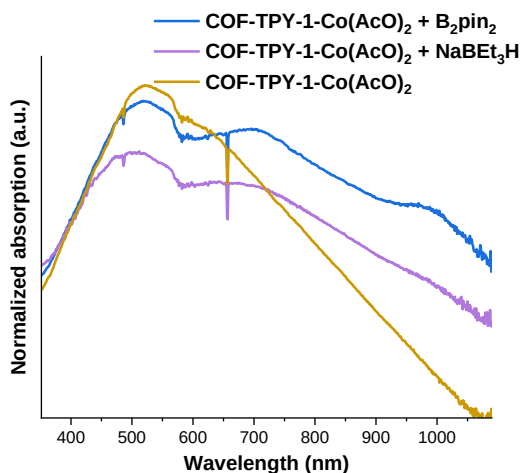
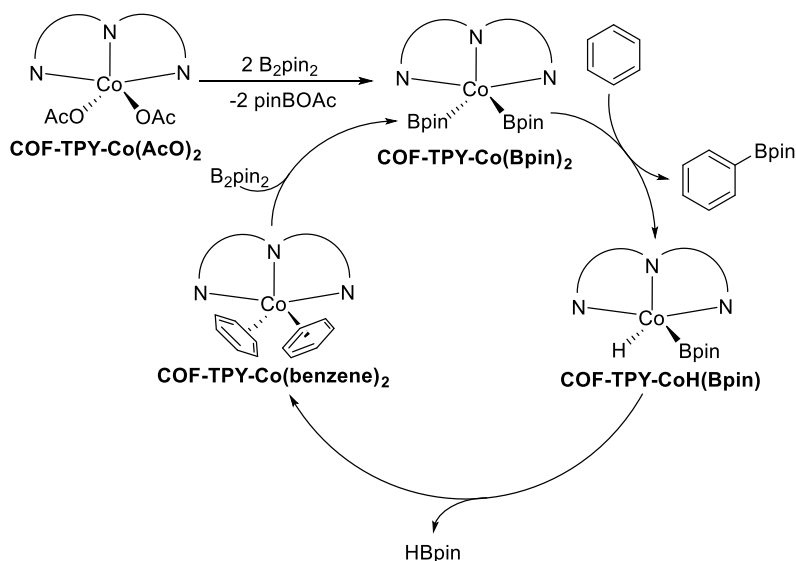


Figure 6.7. UV-vis spectrum of **COF-TPY-1-Co(AcO)₂** suspended in THF before and after treatment with NaBEt₃H (10 equiv. relative to Co) or B₂pin₂ (100 equiv. relative to Co).

We can propose a plausible borylation mechanism based on similar Co catalytic systems previously reported (Scheme 6.4).^{25,28–30} Pre-catalyst activation proceeds by reaction of B₂pin₂ with **COF-TPY-Co(AcO)₂**, generating **COF-TPY-Co(Bpin)₂**.⁴⁰ Then, the aryl boronate ester product is formed through a σ -bond metathesis of Co–Bpin and arene C–H. The resulting **COF-TPY-CoH(Bpin)** species releases HBpin by reductive elimination, followed by oxidative addition of B₂pin₂, which regenerates the catalyst.



Scheme 6.4. Proposed mechanism for COF-TPY-Co-catalyzed borylation.

6.3. Conclusions

In this chapter, we demonstrated the capacity of two new cobalt-terpyridine COFs, **COF-TPY-1-Co(AcO)₂** and **COF-TPY-2-Co(AcO)₂**, to catalyze the borylation of arenes. The catalysts could perform undirected arene C-H borylations and benzylic borylations. The arene vs benzyl selectivity on methylarenes was strongly determined by steric effects from the substrates. The materials presented high catalytic activity and stability and could be reused several times. Additionally, no additive was required to activate the catalysts. Finally, the COFs produced much higher yields compared to homogeneous analogues thanks to the isolated nature of the catalytic centers.

6.4. Experimental section

6.4.1. Materials and methods

Materials. Commercial reagents were purchased from Sigma Aldrich, Alfa Aesar, TCI Chemicals, Fluorochem or abcr and used as received without further purification. All solvents were purified by a SPS-400, Innovative Technology solvent purification system and stored under argon with activated 4 Å molecular sieves after degassing.

Nuclear magnetic resonance (NMR). NMR spectra were recorded on Bruker AV500/AV400 spectrometer using standard conditions (300 K). All ^1H chemical shifts are reported in ppm and have been internally calibrated to the residual protons of the deuterated solvent. The ^{13}C chemical shifts have been internally calibrated to the carbon atoms of the deuterated solvent. The coupling constants were measured in Hz.

Powder X-ray diffraction (PXRD). Powder X-Ray Diffraction (PXRD) PXRD measurements were made using a Siemens D5000 diffractometer (Bragg-Brentano parafocusing geometry and vertical θ - θ goniometer) fitted with a curved graphite diffracted-beam monochromator, incident and diffracted-beam Soller slits, a 0.06° receiving slit and scintillation counter as a detector. The angular 2θ diffraction range was between 2 and 40° . The data was collected with an angular step of 0.02° at 12 s per step and sample rotation. A low background Si(510) wafer was used as sample holder. $\text{Cu}_{\text{K}\alpha}$ radiation was obtained from a copper X-ray tube operated at 40 kV and 30 mA

Inductively Coupled Plasma Optical Emisión Spectrometry (ICP-OES). ICP-OES measurement was performed on the Perkin Elmer Optical Emission Spectrometer Optima 5300 DV (Scott-Chamber/Cross-Flow-Nebulizer).

Transmission electron microscopy (TEM). TEM images were collected using a JEOL 1011 Transmission Electron Microscope operating at 80 kV. Samples were dispersed in ethanol and a drop of resultant suspensions was poured on carbon coated-copper grids.

UV-vis absorption. UV-Vis measurements were carried out on a Shimadzu UV-2401PC spectrophotometer equipped with a photomultiplier tube (PMT) detector, double beam optics and D2 and W light sources.

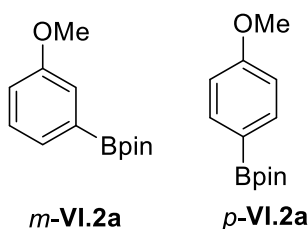
6.4.1. Catalytic experiments

General procedure for aryl borylation: Inside a glovebox, **COF-TPY-2-Co(AcO)₂** (2.4 mg, 1.2 μ mol) and B₂pin₂ (75.9 mg, 0.3 mmol) were placed on a small vial with a stirring bar. After adding the arene (0.75 mmol), the vial was sealed. After stirring for 48 hours at 100 °C, the vial was opened to air, ethyl acetate was added, and the solid was removed from the solution by filtration. NMR yields were determined by taking an aliquot of the solution and adding trimethoxybenzene as internal standard. To obtain the isolated yields, the solution was purified by silica gel column chromatography using hexane/ethyl acetate mixtures as eluent. After removing the solvent, **VI.2a-p** was obtained as the product.

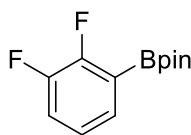
Procedure for catalyst recycling: The catalysis was set up following the general procedure. Inside a glovebox, **COF-TPY-2-Co(AcO)₂** (1.3 mg, 0.64 μ mol) and B₂pin₂ (20.2 mg, 0.08 mmol) were placed on a small vial with a stirring bar. After adding **VI.1c** (0.18 mL, 2 mmol), the vial was sealed. After stirring for 24 h at 100 °C, the vial was opened inside a glovebox and trimethoxybenzene was added as an internal standard. The solid was separated by centrifugation, and the solution was analyzed by GC

to determine the yield of **VI.2c**. Then, the catalyst was reused for subsequent reactions.

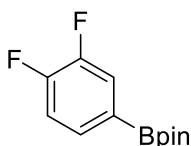
Borylation of anisol (VI.1a): The reaction was performed following the general procedure using **VI.1a** (81 mg, 0.75 mmol), B₂pin₂ (75.9 mg, 0.3 mmol) and **COF-TPY-2-Co(AcO)₂** (2.4 mg, 1.2 μmol) to produce **VI.2a** as a mixture of *meta* and *para* isomers in a 86:14 ratio. (39 mg, 0.17 mmol, 56%). ¹H NMR (400 MHz, CDCl₃) *m*-**VI.2a** δ: 7.46 – 7.40 (m, 1H), 7.36 (dd, *J* = 2.8, 1.0 Hz, 1H), 7.32 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.04 (ddd, *J* = 8.2, 2.8, 1.1 Hz, 1H), 3.86 (s, 3H), 1.38 (s, 12H). *p*-**VI.2a** δ: 7.79 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H), 1.36 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) *m*-**VI.2a** δ: 159.06, 128.95, 127.20, 118.73, 117.91, 83.83, 55.25, 24.87. *p*-**VI.2a** δ: 159.06, 136.52, 113.32, 83.55, 55.09, 24.87.



Borylation of 1,2-difluorobenzene (VI.1b): The reaction was performed following the general procedure using **VI.1b** (855 mg, 7.5 mmol), B₂pin₂ (75.9 mg, 0.3 mmol) and **COF-TPY-2-Co(AcO)₂** (2.4 mg, 1.2 μmol) to produce **VI.2b** as a mixture of 3- and 4- isomers in a 70:30 ratio. (69 mg, 0.28 mmol, 96%). A small amount of ortho and meta borylated fluorobenzene was detected in the ¹⁹F NMR, caused by defluoriation. ¹H NMR (400 MHz, CDCl₃) 3-**VI.2b** δ: 7.51 – 7.45 (m, 1H), 7.30 – 7.21 (m, 1H), 7.12 – 7.05 (m, 0H), 1.38 (s, 12H). 4-**VI.2b** δ: 7.64 – 7.57 (m, 1H), 7.57 – 7.52 (m, 1H), 7.20 – 7.12 (m, 1H), 1.35 (s, 12H). ¹⁹F NMR (376 MHz, CDCl₃) 3-**VI.2b** δ: -129.14 (d, *J* = 21.6 Hz), -139.18 (d, *J* = 21.7 Hz). 4-**VI.2b** δ: -133.99 (d, *J* = 20.7 Hz), -139.64 (d, *J* = 20.7 Hz).

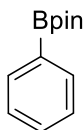


3-VI.2b



4-VI.2b

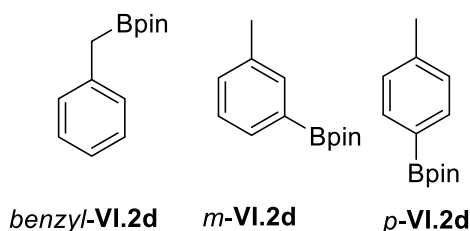
Borylation of benzene (VI.1c): The reaction was performed following the general procedure using **VI.1c** (585 mg, 7.5 mmol), B₂pin₂ (75.9 mg, 0.3 mmol) and **COF-TPY-2-Co(AcO)₂** (2.4 mg, 1.2 μmol) to produce **VI.2c**. (49 mg, 0.24 mmol, 79%). ¹H NMR (400 MHz, CDCl₃) δ: 7.86 (dt, J = 6.8, 1.5 Hz, 2H), 7.49 (d, J = 7.4 Hz, 1H), 7.44 – 7.38 (m, 2H), 1.39 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 134.77, 131.27, 127.73, 83.78, 24.90.



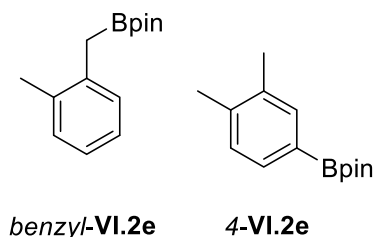
VI.2c

Borylation of toluene (VI.1d): The reaction was performed following the general procedure using **VI.1d** (690 mg, 7.5 mmol), B₂pin₂ (75.9 mg, 0.3 mmol) and **COF-TPY-2-Co(AcO)₂** (2.4 mg, 1.2 μmol) to produce **VI.2d** as a mixture of *meta*, *para* and *benzyl* isomers in a 63:21:16 ratio. (48 mg, 0.22 mmol, 73%). ¹H NMR (400 MHz, CDCl₃) *m*-**VI.2d** δ: 7.71 – 7.64 (m, 2H), 7.34 – 7.30 (m, 2H), 2.40 (s, 3H), 1.39 (s, 12H). *p*-**VI.2d** δ: 7.76 (d, J = 7.9 Hz, 2H), 7.25 – 7.21 (m, 2H), 2.41 (s, 3H), 1.38 (s, 12H). *benzyl*-**VI.2d** δ: 7.29 – 7.25 (m, 3H), 7.19 – 7.13 (m, 1H), 2.34 (s, 2H), 1.28 (s, 4H). ¹³C NMR (101 MHz, CDCl₃) *m*-**VI.2d** δ: 137.14, 135.37, 132.06, 131.82, 127.72, 83.73, 24.89, 21.29. *p*-**VI.2d** δ: 141.40, 134.85, 128.54, 83.62, 24.89, 21.74. *benzyl*-**VI.2d** δ: 137.14, 129.02, 128.27, 124.85, 83.42, 24.75.

CHAPTER VI: Terpyridine Covalent Organic Frameworks as efficient C-H borylation catalysts

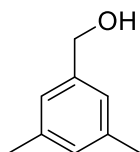


Borylation of o-xylene (VI.1e): The reaction was performed following the general procedure using **VI.1e** (795 mg, 7.5 mmol), B₂pin₂ (75.9 mg, 0.3 mmol) and **COF-TPY-2-Co(AcO)₂** (2.4 mg, 1.2 μmol) to produce **VI.2e** as a mixture of 4- and *benzyl* isomers in a 68:32 ratio. (52 mg, 0.23 mmol, 75%). ¹H NMR (400 MHz, CDCl₃) **4-VI.2e** δ: 7.65 (s, 1H), 7.61 (d, J = 8.8 Hz, 1H), 7.20 (d, J = 7.4 Hz, 1H), 2.33 (s, 3H), 2.32 (s, 3H), 1.39 (s, 12H). *benzyl-VI.2e* δ: 7.19 – 7.07 (m, 4H), 2.31 (s, 2H), 1.28 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) **4-VI.2e** δ: 140.14, 135.99, 135.87, 132.47, 129.20, 83.60, 24.88, 20.03, 19.49. *benzyl-VI.2e* δ: 137.54, 135.92, 129.80, 129.48, 125.88, 125.17, 83.37, 24.76, 20.12.



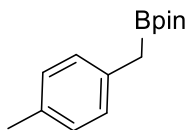
Borylation of mesitylene (VI.1f): The reaction was performed following the general procedure using **VI.1f** (900 mg, 7.5 mmol), B₂pin₂ (75.9 mg, 0.3 mmol) and **COF-TPY-2-Co(AcO)₂** (2.4 mg, 1.2 μmol) to produce **VI.2f**. To prevent excessive loss of mass during the column purification, **VI.2f** was oxidized into the corresponding alcohol **VI.3f** by dissolving it in ether followed by the addition of 2 ml NaOH (2M aqueous solution) and 2 ml H₂O₂ (30% in water). (36 mg, 0.26 mmol, 88%). ¹H NMR (400 MHz,

CDCl_3) δ 7.01 (s, 2H), 6.97 (s, 1H), 4.63 (s, 2H), 2.36 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.86, 138.17, 129.25, 124.86, 65.35, 21.27.



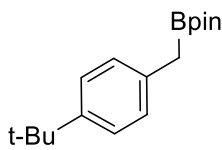
VI.3f

Borylation of p-xylene (VI.1g): The reaction was performed following the general procedure using **VI.1g** (795 mg, 7.5 mmol), B_2pin_2 (75.9 mg, 0.3 mmol) and **COF-TPY-2-Co(AcO) $_2$** (2.4 mg, 1.2 μmol) to produce **VI.2g**. (50 mg, 0.22 mmol, 72%). ^1H NMR (400 MHz, CDCl_3) δ : 7.13 – 7.05 (m, 4H), 2.32 (s, 3H), 2.28 (s, 2H), 1.26 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ : 135.38, 134.11, 128.98, 128.86, 83.36, 24.74, 20.96.



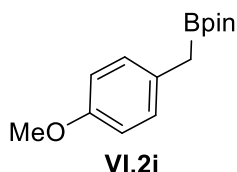
VI.2g

Borylation of 4-tert-butyltoluene (VI.1h): The reaction was performed following the general procedure using **VI.1h** (112 mg, 0.75 mmol), B_2pin_2 (75.9 mg, 0.3 mmol) and **COF-TPY-2-Co(AcO) $_2$** (2.4 mg, 1.2 μmol) to produce **VI.2h** (54 mg, 0.20 mmol, 66%). ^1H NMR (400 MHz, CDCl_3) δ : 7.31 – 7.28 (m, 2H), 7.17 – 7.14 (m, 2H), 2.30 (s, 2H), 1.33 (s, 9H), 1.28 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.45, 135.36, 128.69, 125.19, 83.36, 34.25, 31.44, 24.77.



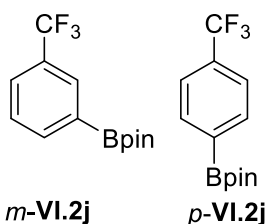
VI.2h

Borylation of 4-tert-butyltoluene (VI.1i): The reaction was performed following the general procedure using **VI.1i** (94 mg, 0.75 mmol), B₂pin₂ (75.9 mg, 0.3 mmol) and **COF-TPY-2-Co(AcO)₂** (2.4 mg, 1.2 μmol) to produce **VI.2i** (30 mg, 0.12 mmol, 40%). ¹H NMR (400 MHz, CDCl₃) δ 7.13 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.7 Hz, 2H), 3.79 (s, 3H), 2.25 (s, 2H), 1.26 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 157.13, 130.49, 129.81, 113.76, 83.35, 55.20, 24.74.

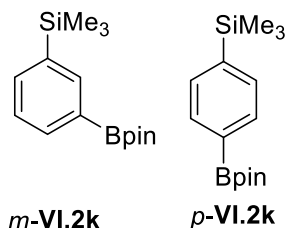


Borylation of α,α,α-Trifluorotoluene (VI.1j): The reaction was performed following the general procedure using **VI.1j** (111 mg, 0.75 mmol), B₂pin₂ (75.9 mg, 0.3 mmol) and **COF-TPY-2-Co(AcO)₂** (2.4 mg, 1.2 μmol) to produce **VI.2j** as a mixture of *meta* and *para* isomers in a 67:33 ratio. (72 mg, 0.26 mmol, 88%). ¹H NMR (400 MHz, CDCl₃) *m*-**VI.2j** δ: 8.10 (s, 1H), 8.01 (d, J = 7.4 Hz, 1H), 7.72 (d, J = 7.9 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 1.38 (s, 12H). *p*-**VI.2j** δ: 7.95 (d, J = 7.6 Hz, 2H), 7.64 (d, J = 7.6 Hz, 2H), 1.38 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) *m*-**VI.2j** δ: 138.02, 131.40, 131.36, 131.33, 131.29, 130.20, 129.88, 128.02, 127.81, 127.77, 127.74, 127.70, 125.66, 122.95, 84.27, 24.82. *p*-**VI.2j** δ: 135.02, 132.99, 130.20, 129.88, 124.31, 124.27, 122.95, 83.05, 24.51. ¹⁹F NMR (376 MHz, CDCl₃) *m*-**VI.2j** δ: -62.73. *p*-**VI.2j** δ: -63.15.

CHAPTER VI: Terpyridine Covalent Organic Frameworks as efficient C-H borylation catalysts

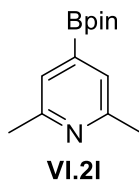


Borylation of trimethyl(phenyl)silane (VI.1k): The reaction was performed following the general procedure using **VI.1k** (114 mg, 0.75 mmol), B₂pin₂ (75.9 mg, 0.3 mmol) and **COF-TPY-2-Co(AcO)₂** (2.4 mg, 1.2 μmol) to produce **2k** as a mixture of *meta* and *para* isomers in a 72:28 ratio (63 mg, 0.23 mmol, 76%). ¹H NMR (400 MHz, CDCl₃) *m*-VI.2k δ: 8.03 (s, 1H), 7.89 – 7.84 (m, 1H), 7.68 (dt, J = 7.4, 1.4 Hz, 1H), 7.41 (td, J = 7.4, 0.8 Hz, 1H), 1.40 (s, 12H), 0.34 (s, 9H). *p*-VI.2k δ: 7.89 – 7.84 (m, 2H), 7.60 (d, J = 8.1 Hz, 2H) 1.39 (s, 12H), 0.33 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) *m*-VI.2k δ: 139.66, 139.54, 136.30, 135.37, 127.07, 83.73, 24.91, -1.00. *p*-VI.2k δ: 144.25, 133.91, 132.63, 83.75, 24.88, -1.20

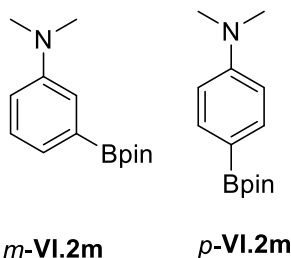


Borylation of 2,6-lutidine (VI.1l): The reaction was performed following the general procedure using **VI.1l** (84 mg, 0.75 mmol), B₂pin₂ (75.9 mg, 0.3 mmol) and **COF-TPY-2-Co(AcO)₂** (2.4 mg, 1.2 μmol) to produce **VI.2l**. The product could not be separated from the HBpin by-product by column chromatography (99% yield based on quantitative NMR with trimethoxybenzene as internal standard). ¹H NMR (400 MHz, CDCl₃) δ

7.30 (s, 2H), 2.51 (s, 6H), 1.32 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.93, 125.36, 84.34, 24.80, 23.91.

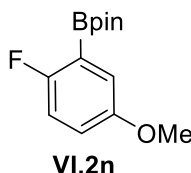


Borylation of *n,n*-dimethylaniline (VI.1m): The reaction was performed following the general procedure using **VI.1m** (91mg, 0.75 mmol), B_2pin_2 (75.9 mg, 0.3 mmol) and **COF-TPY-2-Co(AcO) $_2$** (2.4 mg, 1.2 μmol) to produce **VI.2m** as a mixture of *meta* and *para* isomers in a 75:22 ratio (43 mg, 0.17 mmol, 58%). Traces of the *ortho* isomer could also be detected. ^1H NMR (400 MHz, CDCl_3) *m*-**VI.2m** δ : 7.33 – 7.27 (m, 1H), 7.27 – 7.21 (m, 2H), 6.91 (ddd, $J = 8.2, 2.8, 1.3$ Hz, 1H), 3.00 (s, 6H), 1.39 (s, 12H). *p*-**VI.2m** δ : ^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, $J = 8.8$ Hz, 2H), 6.75 – 6.72 (m, 2H), 3.02 (s, 6H), 1.37 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) *m*-**VI.2m** δ : 150.18, 128.52, 123.28, 118.73, 115.84, 83.63, 40.80, 24.89. *p*-**VI.2m** δ : 152.59, 136.18, 111.28, 83.17, 40.13, 24.88.

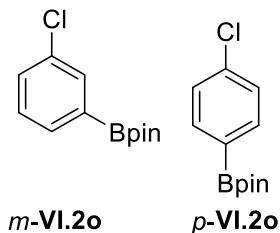


Borylation of 4-Fluoroanisole (VI.1n): The reaction was performed following the general procedure using **VI.1n** (94 mg, 0.75 mmol), B_2pin_2 (75.9 mg, 0.3 mmol) and **COF-TPY-2-Co(AcO) $_2$** (2.4 mg, 1.2 μmol) to produce **VI.2n** (59 mg, 0.23 mmol, 78%). A small amount of 2-substituted

product was detected in the ^{19}F NMR. ^1H NMR (400 MHz, CDCl_3) δ 7.24 – 7.20 (m, 1H), 6.98 – 6.96 (m, 1H), 6.95 (d, J = 1.8 Hz, 1H), 3.81 (s, 3H), 1.38 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.83, 160.41, 155.25, 155.22, 119.90, 119.82, 119.33, 119.24, 116.18, 115.92, 83.95, 55.80, 24.81.

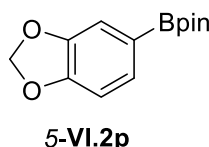
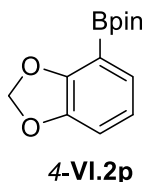


Borylation of chlorobenzene (VI.1o): The reaction was performed following the general procedure using **VI.1o** (84 mg, 0.75 mmol), B_2pin_2 (75.9 mg, 0.3 mmol) and **COF-TPY-2-Co(AcO) $_2$** (2.4 mg, 1.2 μmol) to produce **VI.2o** as a mixture of *meta* and *para* isomers. The product could not be separated from the unreacted B_2pin_2 by column chromatography (49% yield based on quantitative NMR). ^1H NMR (400 MHz, CDCl_3) *m*-**VI.2o** δ : 7.76 (dd, J = 2.4, 1.1 Hz, 1H), 7.66 (dt, J = 7.3, 1.2 Hz, 1H), 7.41 (ddd, J = 8.0, 2.3, 1.2 Hz, 1H), 7.29 (dd, J = 8.3, 7.1 Hz, 1H), 1.34 (s, 12H). *p*-**VI.2o** δ : 7.72 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) *m*-**VI.2o** δ : 134.53, 133.99, 132.64, 131.23, 129.16, 83.07, 24.82. *p*-**VI.2o** δ : 137.50, 136.11, 127.96, 84.12, 24.52.



Borylation of 1,3-benzodioxol (VI.1p): The reaction was performed following the general procedure using **VI.1p** (92 mg, 0.75 mmol), B_2pin_2

(75.9 mg, 0.3 mmol) and **COF-TPY-2-Co(AcO)₂** (2.4 mg, 1.2 μmol) to produce two separate isomers: **4-VI.2p** (43 mg, 0.17 mmol, 55%) and **5-VI.2p** (11 mg, 0.05 mmol, 18%). ¹H NMR (400 MHz, CDCl₃) **4-VI.2p** δ: 7.26 – 7.19 (m, 1H), 6.92 (dd, J = 7.7, 1.4 Hz, 1H), 6.84 (t, J = 7.7 Hz, 1H), 6.03 (s, 2H), 1.38 (s, 12H). **5-VI.2p** δ: 7.38 (dd, J = 7.7, 1.2 Hz, 1H), 7.26 (d, J = 1.1 Hz, 1H), 6.85 (dd, J = 7.8, 0.5 Hz, 1H), 5.97 (s, 2H), 1.35 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) **4-VI.2p** δ: 152.57, 146.91, 127.85, 121.07, 111.16, 100.83, 83.89, 24.83. **5-VI.2p** δ: 150.17, 147.53, 129.73, 113.95, 108.29, 100.73, 83.71, 24.84.



6.5. Bibliography

- (1) Kuhl, N.; Hopkinson, M. N.; Wencel-Delord, J.; Glorius, F. Beyond Directing Groups: Transition-Metal-Catalyzed C-H Activation of Simple Arenes. *Angew. Chemie - Int. Ed.* **2012**, 51 (41), 10236–10254.
- (2) Gandeepan, P.; Müller, T.; Zell, D.; Cera, G.; Warratz, S.; Ackermann, L. 3d Transition Metals for C–H Activation. *Chem. Rev.* **2019**, 119 (4), 2192–2452.
- (3) Gensch, T.; James, M. J.; Dalton, T.; Glorius, F. Increasing Catalyst Efficiency in C–H Activation Catalysis. *Angew. Chemie Int. Ed.* **2018**, 57 (9), 2296–2306.
- (4) Moselage, M.; Li, J.; Ackermann, L. Cobalt-Catalyzed C–H Activation. *ACS Catal.* **2016**, 6 (2), 498–525.
- (5) Santoro, S.; Kozhushkov, S. I.; Ackermann, L.; Vaccaro, L.

Heterogeneous Catalytic Approaches in C–H Activation Reactions.
Green Chem. **2016**, *18* (12), 3471–3493.

- (6) Dalton, T.; Faber, T.; Glorius, F. C-H Activation: Toward Sustainability and Applications. *ACS Cent. Sci.* **2021**, *7* (2), 245–261.
- (7) Wencel-Delord, J.; Glorius, F. C–H Bond Activation Enables the Rapid Construction and Late-Stage Diversification of Functional Molecules. *Nat. Chem.* **2013**, *5* (5), 369–375.
- (8) *Contemporary Boron Chemistry*; Davidson, M. G., Wade, K., Marder, T. B., Hughes, A. K., Eds.; Special Publications; Royal Society of Chemistry: Cambridge, 2007.
- (9) Mkhaliid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. C-H Activation for the Construction of C-B Bonds. *Chem. Rev.* **2010**, *110* (2), 890–931.
- (10) Xu, L.; Wang, G.; Zhang, S.; Wang, H.; Wang, L.; Liu, L.; Jiao, J.; Li, P. Recent Advances in Catalytic C–H Borylation Reactions. *Tetrahedron* **2017**, *73* (51), 7123–7157.
- (11) Iverson, C. N.; Smith, M. R. Stoichiometric and Catalytic B–C Bond Formation from Unactivated Hydrocarbons and Boranes. *J. Am. Chem. Soc.* **1999**, *121* (33), 7696–7697.
- (12) Ishiyama, T.; Nobuta, Y.; Hartwig, J. F.; Miyaura, N. Room Temperature Borylation of Arenes and Heteroarenes Using Stoichiometric Amounts of Pinacolborane Catalyzed by Iridium Complexes in an Inert Solvent. *Chem. Commun.* **2003**, *3* (23), 2924–2925.
- (13) Boller, T. M.; Murphy, J. M.; Hapke, M.; Ishiyama, T.; Miyaura, N.; Hartwig, J. F. Mechanism of the Mild Functionalization of Arenes by Diboron Reagents Catalyzed by Iridium Complexes.

- Intermediacy and Chemistry of Bipyridine-Ligated Iridium Trisboryl Complexes. *J. Am. Chem. Soc.* **2005**, *127* (41), 14263–14278.
- (14) Ishiyama, T.; Takagi, J.; Ishida, K.; Miyaura, N.; Anastasi, N. R.; Hartwig, J. F. Mild Iridium-Catalyzed Borylation of Arenes. High Turnover Numbers, Room Temperature Reactions, and Isolation of a Potential Intermediate. *J. Am. Chem. Soc.* **2002**, *124* (3), 390–391.
- (15) Hartwig, J. F. Borylation and Silylation of C–H Bonds: A Platform for Diverse C–H Bond Functionalizations. *Acc. Chem. Res.* **2012**, *45* (6), 864–873.
- (16) Ishiyama, T.; Ishida, K.; Takagi, J.; Miyaura, N. Palladium-Catalyzed Benzylic C-H Borylation of Alkylbenzenes with Bis(Pinacolato)Diboron or Pinacolborane. *Chem. Lett.* **2001**, *2* (11), 1082–1083.
- (17) Shimada, S.; Batsanov, A. S.; Howard, J. A. K.; Marder, T. B. Formation of Aryl- and Benzylboronate Esters by Rhodium-Catalyzed C-H Bond Functionalization with Pinacolborane. *Angew. Chemie - Int. Ed.* **2001**, *40* (11), 2168–2171.
- (18) Kawamorita, S.; Ohmiya, H.; Hara, K.; Fukuoka, A.; Sawamura, M. Directed Ortho Borylation of Functionalized Arenes Catalyzed by a Silica-Supported Compact Phosphine-Iridium System. *J. Am. Chem. Soc.* **2009**, *131* (14), 5058–5059.
- (19) Kawamorita, S.; Miyazaki, T.; Iwai, T.; Ohmiya, H.; Sawamura, M. Rh-Catalyzed Borylation of N-Adjacent C(Sp³)-H Bonds with a Silica-Supported Triarylphosphine Ligand. *J. Am. Chem. Soc.* **2012**, *134* (31), 12924–12927.
- (20) Wu, F.; Feng, Y.; Jones, C. W. Recyclable Silica-Supported Iridium Bipyridine Catalyst for Aromatic C-H Borylation. *ACS Catal.* **2014**,

- 4 (5), 1365–1375.
- (21) Maeda, K.; Motokura, K. Recent Advances in Heterogeneous Ir Complex Catalysts for Aromatic C-H Borylation. *Synth.* **2021**, 53 (18), 3227–3234.
- (22) Drake, T.; Ji, P.; Lin, W. Site Isolation in Metal-Organic Frameworks Enables Novel Transition Metal Catalysis. *Acc. Chem. Res.* **2018**, 51 (9), 2129–2138.
- (23) Manna, K.; Zhang, T.; Lin, W. Postsynthetic Metalation of Bipyridyl-Containing Metal–Organic Frameworks for Highly Efficient Catalytic Organic Transformations. *J. Am. Chem. Soc.* **2014**, 136 (18), 6566–6569.
- (24) Manna, K.; Zhang, T.; Greene, F. X.; Lin, W. Bipyridine- and Phenanthroline-Based Metal-Organic Frameworks for Highly Efficient and Tandem Catalytic Organic Transformations via Directed C-H Activation. *J. Am. Chem. Soc.* **2015**, 137 (7), 2665–2673.
- (25) Manna, K.; Ji, P.; Lin, Z.; Greene, F. X.; Urban, A.; Thacker, N. C.; Lin, W. Chemoselective Single-Site Earth-Abundant Metal Catalysts at Metal–Organic Framework Nodes. *Nat. Commun.* **2016**, 7 (1), 12610.
- (26) Zhang, T.; Manna, K.; Lin, W. Metal–Organic Frameworks Stabilize Solution-Inaccessible Cobalt Catalysts for Highly Efficient Broad-Scope Organic Transformations. *J. Am. Chem. Soc.* **2016**, 138 (9), 3241–3249.
- (27) Sawano, T.; Lin, Z.; Boures, D.; An, B.; Wang, C.; Lin, W. Metal-Organic Frameworks Stabilize Mono(Phosphine)-Metal Complexes for Broad-Scope Catalytic Reactions. *J. Am. Chem. Soc.* **2016**, 138 (31), 9783–9786.

-
- (28) Lin, Z.; Thacker, N. C.; Sawano, T.; Drake, T.; Ji, P.; Lan, G.; Cao, L.; Liu, S.; Wang, C.; Lin, W. Metal–Organic Layers Stabilize Earth-Abundant Metal–Terpyridine Diradical Complexes for Catalytic C–H Activation. *Chem. Sci.* **2018**, 9 (1), 143–151.
- (29) Newar, R.; Begum, W.; Antil, N.; Shukla, S.; Kumar, A.; Akhtar, N.; Balendra; Manna, K. Single-Site Cobalt-Catalyst Ligated with Pyridylimine-Functionalized Metal–Organic Frameworks for Arene and Benzylic Borylation. *Inorg. Chem.* **2020**, 59 (15), 10473–10481.
- (30) Newar, R.; Begum, W.; Akhtar, N.; Antil, N.; Chauhan, M.; Kumar, A.; Gupta, P.; Malik, J.; Balendra; Manna, K. Mono-Phosphine Metal-Organic Framework-Supported Cobalt Catalyst for Efficient Borylation Reactions. *Eur. J. Inorg. Chem.* **2022**, 2022 (10), 3–9.
- (31) Wu, X.; Han, X.; Liu, Y.; Liu, Y.; Cui, Y. Control Interlayer Stacking and Chemical Stability of Two-Dimensional Covalent Organic Frameworks via Steric Tuning. *J. Am. Chem. Soc.* **2018**, 140 (47), 16124–16133.
- (32) Vardhan, H.; Pan, Y.; Yang, Z.; Verma, G.; Nafady, A.; Al-Enizi, A. M.; Alotaibi, T. M.; Almaghrabi, O. A.; Ma, S. Iridium Complex Immobilization on Covalent Organic Framework for Effective C - H Borylation. *APL Mater.* **2019**, 7 (10).
- (33) Yao, W.; Fang, H.; Peng, S.; Wen, H.; Zhang, L.; Hu, A.; Huang, Z. Cobalt-Catalyzed Borylation of Aryl Halides and Pseudohalides. *Organometallics* **2016**, 35 (10), 1559–1564.
- (34) Pabst, T. P.; Chirik, P. J. Development of Cobalt Catalysts for the Meta -Selective C(Sp²)-H Borylation of Fluorinated Arenes. *J. Am. Chem. Soc.* **2022**, 144 (14), 6465–6474.
- (35) Schaefer, B. A.; Margulieux, G. W.; Small, B. L.; Chirik, P. J.

- Evaluation of Cobalt Complexes Bearing Tridentate Pincer Ligands for Catalytic C-H Borylation. *Organometallics* **2015**, 34 (7), 1307–1320.
- (36) Léonard, N. G.; Bezdek, M. J.; Chirik, P. J. Cobalt-Catalyzed C(Sp²)–H Borylation with an Air-Stable, Readily Prepared Terpyridine Cobalt(II) Bis(Acetate) Precatalyst. *Organometallics* **2017**, 36 (1), 142–150.
- (37) Zhang, Y.; Li, J.; Yang, X.; Zhang, P.; Pang, J.; Li, B.; Zhou, H.-C. A Mesoporous NNN-Pincer-Based Metal–Organic Framework Scaffold for the Preparation of Noble-Metal-Free Catalysts. *Chem. Commun.* **2019**, 55 (14), 2023–2026.
- (38) Simmons, E. M.; Hartwig, J. F. On the Interpretation of Deuterium Kinetic Isotope Effects in C-H Bond Functionalizations by Transition-Metal Complexes. *Angew. Chemie - Int. Ed.* **2012**, 51 (13), 3066–3072.
- (39) Obligacion, J. V.; Semproni, S. P.; Pappas, I.; Chirik, P. J. Cobalt-Catalyzed C(Sp²)-H Borylation: Mechanistic Insights Inspire Catalyst Design. *J. Am. Chem. Soc.* **2016**, 138 (33), 10645–10653.
- (40) Obligacion, J. V.; Zhong, H.; Chirik, P. J. Insights into Activation of Cobalt Pre-Catalysts for C(Sp²)–H Functionalization. *Isr. J. Chem.* **2017**, 57 (10), 1032–1036.

Chapter VII:

General Conclusions

In **Chapter III**, we have immobilized a series of ligands inside the cavities of **MOF-520** crystals. The single-crystal to single-crystal transformation allowed us to detect the ligand arrangement by x-ray diffraction, revealing that the perylene ligands (**PC1**) are isolated. This result agreed with the photophysical studies performed in suspension, which suggested that **PC1** and **PC2** inside **MOF-520** behave as isolated units and do not form agglomerates.

MOF-520-PC2 was employed as a photocatalyst for the reductive coupling of aldehydes, ketones and imines, showing good efficiency but limited recyclability under batch conditions. The photocatalytic system was also employed successfully under continuous flow conditions.

Finally, a catalytic cycle was proposed based on mechanistic studies: the excited photocatalyst (PC^*) is reductively quenched by an electron donor, generating a radical anion ($PC^{\bullet-}$) capable of reducing the carbonyl substrate, which undergoes radical homocoupling to produce pinacols.

In **Chapter IV**, imine COFs containing bipyridine ligands (**COF-BPY-1** and **COF-BPY-2**), terpyridine ligands (**COF-TPY-1** and **COF-TPY-2**) or bispyridine-cyclohexyldiamine ligands (**MCP-polymer**) were synthesized and characterized, followed by incorporation of Co into the materials through post-synthetic metalation. The Co content for the COFs ranged from 8.3 to 2.9 w%.

The different choices of amine linkers in **COF-BPY-1** and **COF-BPY-2** led to the formation of a rhombic or kagome skeleton, respectively. **COF-TPY-1** and **COF-TPY-2** presented similar structures with high crystallinity and porosity. However, **MCP-polymer** could not be obtained as a crystalline material, possibly due to the flexibility of the **MCP** ligand.

In **Chapter V**, we employed **COF-BPY-1-Co** as an efficient and recyclable heterogeneous catalyst for the hydroboration of simple alkenes. The superior activity of this catalyst relative to molecular Co-bipyridine

UNIVERSITAT ROVIRA I VIRGILI
METAL-ORGANIC FRAMEWORKS AND COVALENT ORGANIC FRAMEWORKS AS SINGLE SITE CATALYSTS
FOR ORGANIC TRANSFORMATIONS
Luis Gutiérrez Victoriano

UNIVERSITAT ROVIRA I VIRGILI
METAL-ORGANIC FRAMEWORKS AND COVALENT ORGANIC FRAMEWORKS AS SINGLE SITE CATALYSTS
FOR ORGANIC TRANSFORMATIONS
Luis Gutiérrez Victoriano

UNIVERSITAT ROVIRA I VIRGILI
METAL-ORGANIC FRAMEWORKS AND COVALENT ORGANIC FRAMEWORKS AS SINGLE SITE CATALYSTS
FOR ORGANIC TRANSFORMATIONS
Luis Gutiérrez Victoriano

UNIVERSITAT ROVIRA I VIRGILI
METAL-ORGANIC FRAMEWORKS AND COVALENT ORGANIC FRAMEWORKS AS SINGLE SITE CATALYSTS
FOR ORGANIC TRANSFORMATIONS
Luis Gutiérrez Victoriano

UNIVERSITAT ROVIRA I VIRGILI
METAL-ORGANIC FRAMEWORKS AND COVALENT ORGANIC FRAMEWORKS AS SINGLE SITE CATALYSTS
FOR ORGANIC TRANSFORMATIONS
Luis Gutiérrez Victoriano



UNIVERSITAT
ROVIRA i VIRGILI