



# Defect Engineering in UiO-66 for Heterogeneous Catalysis

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# Content

English S	Summa	γxi
Nederla	ndstalig	e samenvattingxv
List of Pu	ublicatio	DNSXIX
Chanter	1 M	tions
1.1	Int	roduction
1.2	W	nere do MOFs come from?2
1.3	Re	presentative MOFs3
	1.3.1	Milestone MOFs: MOF-5 and HKUST-13
	1.3.2	Flexible and Breathing MOFs: MIL-47 and MIL-535
	1.3.3	Zeolitic Imidazolate Frameworks6
	1.3.4	Stable MOFs: MIL-101 and UiO-667
	1.3.5	MOF Glass9
1.4	Tri	cks of MOF Synthesis11
	1.4.1	Isoreticular MOFs12
	1.4.2	Multivariable MOFs13
	1.4.3	Step by Step Synthesis14
	1.4.4	Modulation14
	1.4.5	Ordered Vacancies14
	1.4.6	Metal Exchange15
	1.4.7	Linker Exchange16
	1.4.8	Sequential Linker Installation17
	1.4.9	Large Scale Computational Synthesis19
	1.4.10	) Large Scale Synthesis19
1.5	Ар	plications: catalysis19
	1.5.1	Asymmetric Catalysis20
	1.5.2	Photocatalysis21
	1.5.3	Electrocatalysis 22
Chapter 2.1	2 De Int	fect Engineering in UiO-6627 roduction27
2.2	Sy	nthesis

	2.2.1	De Novo Synthesis	
	2.2.2	Post-synthetic Treatment	
2.3	Cha	Characterization	
2.4	Application: Catalysis due to defects40		
	2.4.1	Lewis Acid Catalysis	
	2.4.2	Brønsted Acid Catalysis43	
	2.4.3	Catalysis upon Functionalized Ligand Incorporation43	
	2.4.4	Catalysis by Cluster Metalation44	
2.5	Aim	of the thesis	
Chapter 3 catalysts 3.1	3 L-pi for the Intr	roline Modulated Zirconium Metal Organic Frameworks: simple chiral aldol addition reaction53 oduction	
3.2	Exp	erimental details56	
	3.2.1	General Procedures56	
	3.2.2	Synthesis of the catalysts	
	3.2.3	General procedure for the catalytic reactions	
3.3	Res	ults and discussion58	
	3.3.1	Effect of temperature on the synthesis of L-proline modulated Zr-MOFs58	
	3.3.2	Evaluation of the modulated Zr-MOFs as catalysts in the aldol reaction 61	
3.4	Cor	clusions67	
Chapter 4 Engineering an ultra-stable 6-fold coordinated UiO-66 - The role of the hemilabile linker			
4.2	Exp	erimental Section75	
	4.2.1	Synthesis of the catalysts75	
	4.2.2	Postsynthesis treatment75	
	4.2.3	Catalytic procedure75	
	4.2.4	Computational methodology76	
4.3	Res	ults and Discussion76	
	4.3.1	PSBA as a hemilabile linker to create defects76	
	4.3.2	Post-synthetic modification with sulfuric acid and a remarkable increase in	
	stabilit	у78	

	4.3.3	Lewis and Brønsted sites, catalytic activity	82
4.4	Co	nclusions	86
Chapter 5.1	5 Co Co	Conclusions and Perspectives Conclusions	
5.2	Pei	rspectives	95
Appendix			101 101
Appendix B: Supporting information for chapter 4			111

## **English Summary**

MOFs are a class of crystalline porous materials, which are composed of metal nodes coordinated to organic linkers. These materials possess high surface areas up to 10,000 m<sup>2</sup>/g, exceeding those of other porous materials such as carbon-based materials, zeolites and silica (max ca. 1000 m<sup>2</sup>/g). The abundant clusters which can be made of by all metals from the periodic table and the number of available organic linkers to construct new MOFs is almost unlimited. These features have led to significant advances in the design and use of these materials in a wide range of applications including gas storage and separation, drug delivery, sensing, catalysis and so on. Specifically, towards their use in catalysis, MOFs offer a unique opportunity. The highly ordered structure of MOFs makes it possible to have well-defined catalytic active sites. When using these MOFs as catalysts, the observed catalytic activity is regarded as unique that provides a bridges between homogeneous and heterogeneous catalysis.

Towards these envisioned applications, MOFs need to be tailored and to be optimized their performance. Defect engineering has been used as a useful toolbox to tune properties of MOFs for the expected task-specific applications. The correlation between the defects and the chemical and physical properties has been demonstrated. For example, the mass diffusion can be increased by the introduction of missing linkers and cluster defects in addition to the presence of open metal sites to enhance the catalytic performance. From the perspective of catalysis, the incorporation of these defects into MOFs creates extra catalytic active sites, which results in either Brønsted or Lewis acid sites. Moreover, the defect vacancy can be functionalized by functionalized ligand incorporation and cluster metalation to introduce the targeted catalytic active sites.

Since the first MOF was discovered in 1995 by Yaghi and co-workers, thousands of MOFs have been reported in the last two decades. UiO-66 is one of the milestones in the field of MOFs due to its outstanding thermal, chemical and mechanical stability. The ideal structure of UiO-66 is constructed of hexanuclear  $[Zr_6O_4(OH)_4]^{12+}$  clusters with 12 BDC (BDC = 1,4-benzenedicarboxylate)organic linkers. The high degree of connectivity of the metal clusters brings a high charge density and bond polarization, resulting in an exceptional stability. The

framework is also able to tolerate the high number of defects without destruction of the original structure. So, UiO-66 is considered as a prototype in the field of MOFs and mainly in defect engineering.

In **chapter 1**, an introduction to MOFs is given. Firstly, the history of MOFs is presented, followed by the introduction of some representative MOFs. Afterwards, several ways to synthesize MOFs are presented. Finally, the use of MOFs in heterogeneous catalysis (e.g. asymmetric catalysis, photocatalysis and electrocatalysis) is discussed.

In **chapter 2**, a general overview of defect engineering in MOFs is presented. UiO-66 (Universitetet i Oslo) is chosen as an example throughout this chapter. A variety of synthetic procedures, the characterization methods for defects in UiO-66 type materials and their applications in heterogeneous catalysis are discussed in detail.

In **chapter 3**, a novel approach to incorporate active sites in Zr-MOFs, by introducing available and low cost chiral amino acids (e.g. L-proline) as modulators, is described. More specifically, three Zr-MOFs denoted as UiO-66, Zr-NDC (NDC = 2,6-Naphthalenedicarboxylate) and UiO-67 were synthesized using L-proline as a functional chiral modulator. A systematic study was conducted to explore the influence of the synthesis temperature on the amounts of L-proline in each Zr-MOF. From this study, a higher number of defects and an increased density of modulators were obtained by lowering the synthesis temperature. Meanwhile, since chirality was introduced into these frameworks, the modulated Zr-MOFs were used as chiral catalysts for asymmetric aldol addition reactions. Remarkably, the L-proline modulated Zr-MOFs showed excellent reactivity and 100% substrate conversion in the aldol reaction between benzaldehyde and cyclohexanone whereas the homogeneous L-proline catalyst only exhibited a conversion of 61%. Furthermore, a high diastereoselectivity (up to 64%) was noted and no loss of the catalytic activity was observed after 3 additional runs, demonstrating the heterogeneous nature and good stability of our catalyst.

In general, the stability compromises with the defect generation. In **chapter 4**, we employed hemilabile ligands in the structure of UiO-66 (HI-UiO-66) to introduce a high stability and high number of defects. The hemilabile ligand contains, next to the carboxylate group, an

additional relatively weaker coordinating functional group (e.g. sulfonate group). The effects of the hemilabile ligand (4-sulfobenzoic acid, PSBA) on the stability and defect engineering in UiO-66 are discussed. Furthermore, because of the inherent weak coordination mode of the hemilabile ligand, a simple post-synthetic treatment in diluted H<sub>2</sub>SO<sub>4</sub> resulted in a total of three missing BDC linkers per formula unit, which is the theoretical maximum of the missing linker defects in UiO-66 (HI-UiO-66-SO<sub>4</sub>). More importantly, this highly defective HI-UiO-66-SO<sub>4</sub> is more stable than the pristine HI-UiO-66 and UiO-66 (HI-UiO-66-SO<sub>4</sub> > HI-UiO-66 > UiO-66). Detailed modelling of this structure indicated that the combination of bent PSBA linkers, hydrogen bonding stabilization and the electrostatic attraction of the HSO<sub>4</sub><sup>-</sup> anion lead to this remarkable supplementary stabilization of highly defective UiO-66. Furthermore, the catalytic properties of the obtained materials were evaluated in the isomerization of  $\alpha$ -pinene oxide. In comparison to the pristine UiO-66 (that shows a moderate activity of 40% and low selectivity at 0.5h), HI-UiO-66-SO<sub>4</sub> showed full conversion and an enhanced selectivity in the isomerization reaction.

In conclusion, this thesis has shown that defect engineering in MOFs can tailor the properties of the materials, which creates new opportunities in catalysis. It is very important to select functionalized ligands that can be introduced into MOFs to create the defect sites. These defect sites can be considered as extra unsaturated sites that behave as either Lewis or Brønsted acid sites or functionalized to introduce the targeted catalytic active sites in MOFs. Therefore, defective MOFs provide a bridge between homogeneous and heterogeneous catalysis.

# Nederlandstalige samenvatting

Metaal organische roosters (MOFs) zijn een groep van kristallijne poreuze materialen die opgebouwd zijn uit metaal nodes die gekoppeld zijn aan organische liganden. Deze materialen bezitten interessante eigenschappen. Zo bezitten ze vaak een heel hoog oppervlak tot 10 000 m<sup>2</sup>/g, dewelke veel hoger is dan andere poreuze materialen zoals bijvoorbeeld koolstof gebaseerde materialen, zeolieten en silica (die doorgaans een oppervlak van maximum 1000 m<sup>2</sup>/g hebben). Nagenoeg alle metalen uit het periodiek system en ook een grote variëteit aan organische liganden kunnen gebruikt worden voor de synthese van nieuwe MOF structuren. Door deze inherente interessante eigenschappen hebben MOFs diverse toepassingen: adsorptie/scheiding van gassen, gecontroleerde medicijnafgifte, sensors, katalyse, enzovoort. Vooral het gebruik als heterogene katalysator is heel interessant gezien de aanwezigheid van goed gedefinieerde actieve sites op MOFs. De inherent katalytische activiteit die MOFs bezitten kan aanzien worden al een brug tussen homogene en heterogene katalyse.

Voor een specifieke toepassing moeten MOFs getuned worden zodanig dat ze een optimale prestatie kunnen leveren. Een manier van "tuning" is door het introduceren van defecte sites. In diverse rapporten is een verband aangetoond tussen de geïntroduceerde defecten en de invloed ervan op de resulterende chemische en fysische eigenschappen. Zo kan men bijvoorbeeld het massa diffusie verhogen doorheen het netwerk door het verwijderen van enkele organische liganden of het introduceren van cluster defecten. Verder kan de aanwezigheid van open metaal centra de katalytische activiteit verhogen. Vanuit het katalytisch perspectief, zal de introductie van defect sites in MOFs aanleiding geven tot extra Brønsted of Lewis zuur sites. Daarnaast kunnen de geïntroduceerde defecten gebruikt worden door gefunctionaliseerde liganden en metallische clusters om actieve sites te introduceren..

Sinds de ontwikkeling van de eerste MOF in 1995 door Yaghi et al., werden talloze andere MOF structuren gerapporteerd. Een van die MOF netwerken is de zogenaamde "UiO-66" (UiO= universiteit van Oslo). Dit materiaal werd reeds uitgebreid onderzocht omdat het een heel hoge thermische, chemische en mechanische stabiliteit bezit. De ideale structuur van

UiO-66 is opgebouwd uit 6  $[Zr_6O_4(OH)_4]^{12+}$  clusters met 12 BDC (BDC = 1,4benzenedicarboxylaat)organische liganden. De hoge bindingsgraad van de metaal clusters zorgt voor een hoge ladingsdichtheid en polarisatie van de binding, wat aanleiding geeft tot een hoge stabiliteit. Er kunnen ook defecten geïntroduceerd worden in dit netwerk zonder een destructie ervan. Vandaar dat UiO-66 wordt aanzien als prototype in het gebied van "defect engineering".

In **hoofdstuk 1**, wordt een introductie tot MOFs gegeven. Ten eerste wordt de geschiedenis en oorsprong van MOFs geïntroduceerd. Ten tweede wordt overgegaan op de verschillende synthese manieren om MOFs te maken. Tot slot wordt het gebruik van MOFs in heterogene katalyse beschreven (bijvoorbeeld hun gebruik in assymetrische katalyse, fotokatalyse en elektrokatalyse).

In **hoofdstuk 2**, wordt een overzicht gegeven over de introductie van defecten in MOFs. In dit hoofdstuk, wordt UiO-66 als voorbeeld gebruikt. De verschillende synthese routes en karakterisatie technieken om defecten in MOFs te introduceren/bestuderen worden weergegeven. Tot slot, wordt het gebruik van defect sites als actieve sites in katalyse gepresenteerd.

In **hoofdstuk 3**, wordt een nieuwe syntheseroute voorgesteld om actieve sites in Zr gebaseerde MOFs te introduceren. In dit hoofdstuk wordt gebruik gemaakt van goedkope en commercieel beschikbare chirale aminozuren (bv L-proline) als modulatoren. Meer bepaald, worden 3 Zr gebaseerde MOFs gemaakt: UiO-66, Zr-NDC (NDC = 2,6-naphthalenedicarboxylaat) en UiO-67, gebruik makend van L-proline als chirale modulator. Een systematische studie wordt uitgevoerd om de invloed van de synthese temperatuur op de hoeveelheid geïntroduceerd L-proline in elke Zr-MOF te onderzoeken. Uit deze studie bleek dat een hoger gehalte aan defecten en een hogere hoeveelheid aan modulator wordt waargenomen als men de synthese temperatuur verlaagde. De resulterende Zr-MOFs werden geëvalueerd als chirale katalysators voor de assymetrische aldol additie reactie. De L-proline Zr-MOFs bezitten een hoge reactiviteit en vertonen 100% substraat omzetting in de aldol reactie van benzaldehyde en cyclohexanone. De homogene L-proline vertoonde slechts 61% conversie. Daarnaast werd ook een hoge diastereoselectiviteit (tot 64%) bereikt en

werd geen verlies in activiteit waargenomen gedurende 3 opeenvolgende katalytische cycli. Dit toont het heterogeen karakter aan van de katalysator alsook de goede stabiliteit.

In hoofdstuk 4, wordt een "hemilabile" ligand geïntroduceerd in de UiO-66 (Hl-UiO-66) structuur om een hogere stabiliteit en een verhoogd aantal defecten te introduceren. Het "hemilabile" ligand bevat, naast een carboxylaat groep, een extra vrij zwakke functionele groep (bijvoorbeeld een sulfonaat groep). De invloed van het hemilabile ligand (4sulfobenzoic acid) op de resulterende stabiliteit en de defect engineering in UiO-66 wordt besproken in dit hoofdstuk. Omwille van de zwakke coordinatie van het hemilabile ligand, gaf een eenvoudige post-modificatie, uitgevoerd in verdund H<sub>2</sub>SO<sub>4</sub>, aanleiding tot een reductie van drie 1,4-benzene dicarboxylate (BDC) linkers per formule eenheid. Dit is het theoretische maximum aan defecten dat kan worden geïntroduceerd in UiO-66 (HI-UiO-66-SO<sub>4</sub>). Deze defect bevattende Hl-UiO-66-SO<sub>4</sub> structuur heeft bovendien ook een hogere stabiliteit dan de "pristine" Hl-UiO-66 en UiO-66 (Hl-UiO-66-SO<sub>4</sub> > Hl-UiO-66 > UiO-66). Modelering heeft aangetoond dat een combinatie van verschillende factoren (de stabilisatie door H bindingen, de elektrostratische interactie van het HSO<sub>4</sub> anion) aanleiding heeft gegeven tot deze verhoogde stabiliteit van deze defecten bevattende UiO-66. Tot slot werd de katalytische activiteit bepaald voor de isomerisatie van  $\alpha$ -pinene oxide. In vergelijking met de pristine UiO-66 (welke een 40% conversie heeft en een lage selectiviteit na 0.5h), toont de HI-UiO-66-SO<sub>4</sub> een volledige conversie en een verhoogde selectiviteit voor deze isomerisatie reactie.

In conclusie, in deze thesis wordt aangetoond dat de introductie van defecten de eigenschappen van MOFs kan beïnvloeden. Dit kan aanleiding geven tot nieuwe mogelijkheden in katalyse. Het is van belang dat men gefunctionaliseerde liganden neemt die in de MOFs geïntroduceerd kunnen worden om defecten te generen. Deze defect sites kunnen aanzien worden als niet gesatureerde sites die zich gedragen als lewis or Brønsted zuur. Dus met andere woorden, MOFs met defecten in hun structuur vormen een soort van brug tussen homogene en heterogene katalyse.

xvii

# **List of Publications**

**Feng, X**.; Jena, H. S.; Leus, K.; Wang, G.; Ouwehand, J.; Van Der Voort, P., I -proline modulated zirconium metal organic frameworks: Simple chiral catalysts for the aldol addition reaction. *J. Catal.* **2018**, *365*, 36-42.

**Feng, X**.; Jia, C.; Wang, J.; Cao, X.; Tang, P.; Yuan, W., Efficient vapor-assisted aging synthesis of functional and highly crystalline MOFs from CuO and rare earth sesquioxides/carbonates. *Green Chem.* **2015**, *17* (7), 3740-3745.

**Feng, X**.; Hajek, J; Jena, H. S.; Wang, G.; Van Speybroeck, V; Leus, K.; Van Der Voort, P., Engineering an ultra-stable UiO-66 with the highest possible number of defects, the role of the hemilabile linker(in preparation).

**Feng, X**.; Jena, H. S.; Wang, G.; Leus, K.; Van Der Voort, P., Artificial cluster defect in stable MOFs (in preparation).

Yang, J.; **Feng, X**.; Lu, G.; Li, Y.; Mao, C.; Wen, Z.; Yuan, W., NaCl as a solid solvent to assist the mechanochemical synthesis and post-synthesis of hierarchical porous MOFs with high I2 vapour uptake. *Dalton Transactions* **2018**, *47* (14), 5065-5071.

Jia, C.; Wang, J.; **Feng, X**.; Lin, Q.; Yuan, W., Efficient vapour-assisted aging and liquidassisted grinding synthesis of a microporous copper-adeninate framework. *CrystEngComm* **2014**, *16* (29), 6552-6555.

#### **Presenations on conferences**

**Feng, X.**; Hendrickx, K.; Wang, G.; Leus, K.; Van Speybroeck, V.; and Van Der Voort, P., Defect engineering of UiO-66 using 4-sulfobenzoic acid.The Netherlands' Catalysis and Chemistry conference (NCCC-XVII), March 6-8<sup>th</sup>, 2016, Noordwijkerhout, The Netherlands, Poster.

**Feng, X.**; Jena, H. S.; Leus, K.; Wang, G.; Ouwehand, J.; Van Der Voort, P., L-proline Functionalized Modulated Zr-MOFs for the aldol reaction. The 1<sup>st</sup> European Doctoral

Symposium on Metal-Organic Frameworks (docMOF-2018: A PhD-run Symposium), April 29<sup>th</sup>-May. 2<sup>nd</sup>, 2018, Burghausen, Germany, Oral presentations.

# List of Abbreviations

# Α

AA	Acetic Acid
AFM	Atomic Force Microscopy
В	
BET	Brunauer-Emmett-Teller
BDC	1,4-benzenedicarboxylate
BTC	1,3,5-benzenetricarboxylate
с	
CFM	Confocal Fluorescence Microscopy
D	
DFT	Density Functional Theory
DMF	Dimethylformamide
DMA	Dimethylacetamide
DFA	Difluoroacetic Acid
DMSO	Dimethyl Sulfoxide
DCM	Dichloromethane
E	
EA	Elemental Analyses
EDX	Energy Dispersive X-ray Spectroscopy
EPR	Electron Paramagnetic Resonance
EXAFS	Extended X-Ray Absorption Fine Structure
F	
FA	Formic Acid
FT-IR	Fourier Transform Infrared Spectroscopy
н	

HPLC	High-Performance Liquid Chromatography
н	Hemilabile
HKUST	Hong Kong University of Science and Technology
I	
IRMOFs	Isoreticular Metal Organic Frameworks
LD	Linker Dislocation
LSD	Large Scale Defects
Μ	
MOFs	Metal Organic Frameworks
MTV-MOFs	Multivariate Metal Organic Frameworks
μርΡ	Micro Contact Printing
MIL	Material Of The Institut Lavoisie
MLD	Missing Linker Defects
MCD	Missing Cluster Defects
Ν	
NMR	Nuclear Magnetic Resonance
NDC	2,6-Naphthalenedicarboxylate
Ρ	
PXRD	Powder X-Ray Diffraction
PSBA	<i>p</i> -sulfobenzoic acid potassium salt
PALS	Positron Annihilation Lifetime Spectroscopy
CPs	Coordination Polymers
PDF	Pair Distribution Function
L	
LMCT	Ligand To Metal Charge Transfer Transition
S	
SEM	Scanning Electron Microscopy
SBU	Secondary Building Unit

SALE	Solvent-assisted ligand exchange
SALI	Solvent-Assisted Ligand Incorporation
SS-MAS-NMR	Solid-State Magic Angle Spinning Nuclear Magnetic Resonance
SXRD	Single-Crystal X-Ray Diffraction
SAM	Self-Assembled Organic Monolayers
SLI	Sequential Ligand Installation
SCSC	Single-Crystal to Single-Crystal Transformation
т	
TFA	Trifluoroacetic Acid
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TOF-SIMS	Time-Of-Flight Secondary Ion Mass Spectrometry
U	
UiO	Universitetet i Oslo
V	
VASP	Vienna Ab Initio Simulation Package
VTXRD	Variable-Temperature Powder X-Ray Diffraction
x	
XPS	X-Ray Photoelectron Spectroscopy
XRF	X-Ray Fluorescence Spectroscopy
XANES	X-Ray Absorption Near-Edge Structure
Z	
ZIFs	Zeolitic Imidazolate Frameworks

# **Chapter 1** Metal Organic Frameworks

# **1.1 Introduction**

Metal–organic frameworks (MOFs), a subclass of coordination polymers (CPs), were constructed from metal ions or clusters connected with organic linkers to form extended frameworks containing permanent porous features. More than 20,000 different types of MOFs have been reported and studied within the past decades because of the tunability in geometry, size, and functionality of the components.<sup>1</sup> Generally, organic ligands include ditopic or polytopic organic carboxylates, imidazolate, phosphonates, sulfonates or N-containing ligands. They can link to almost all the metal ions of the periodic table to form robust crystalline MOF structures. The structures have a typical porosity of greater than 50% of the crystal volume and high surface area up to 10,000m<sup>2</sup>/g, exceeding those of traditional porous materials such as zeolites and carbon-based materials.<sup>1</sup> The extremely high surface area together with the diverse functionalities and tunability of the components make MOFs promising candidates for potential application in gas adsorption and separation, heterogeneous catalysis, sensing, proton conductivity, drug delivery and so forth.<sup>2</sup>

MOFs are relatively easy to crystalize and therefore these are easy to figure out their structures by single-crystal X-ray diffraction analysis (SXRD). The beautiful crystals as well as the clear structures have drawn much attention by material scientists. The eternal aspiration for material scientists is to design a target structure with specific properties and functions. The first step is to realize comprehensive understanding of the structure. The characteristics of MOF are coveted because of their topologically diverse, aesthetically pleasing and unambiguous structures, which provided us the opportunity to recognize the connections between the structures and properties.

"To understand a science, it is necessary to know its history", as said by French philosopher Auguste Comte (From "Positive Philosophy"). MOFs, as a new research field within two decades, have been rapidly developed and more than 50,000 articles have been published until March 2019 (WoS, keyword "Metal Organic Framework"). To make it easier to understand this field, historic developments of MOFs are listed underneath in chronological order and represent the breakthrough points of this research field (Figure 1.1).



**Figure 1.1** Chronology of first reports of contributions in the field of metal–organic frameworks (MOFs). (Reproduced from reference <sup>2</sup>).

# 1.2 Where do MOFs come from?

MOFs are derived from CPs and are regarded as a subclass of these. The term CP dates back to 1916.<sup>3</sup> CPs were made from a suitable combination of metal ions and organic ligands and then reassembled to form one-, two- and three- dimensional coordination networks. Initially CPs were not meant to be used as frameworks due to lack of understanding of their structure, but the development of SXRD techniques helped to determine the structure. Recently, CPs comprised with porous properties were named MOFs by Yaghi et al. in 1995.<sup>4</sup> In order to understand the background of the field, it is necessary to explore three critical concepts: (i) formation of framework structure, (ii) porosity and (iii) molecular metal–organic hybrid.

The **framework** concept was established by Hofmann and Kuspert<sup>5</sup>, and later twodimensional layer-based architecture were named as Hofmann clathrates. The Prussian Blue complex, a complete three-dimensional framework, emerged in 1936.<sup>6</sup> The compounds are bridged by an inorganic anion (CN<sup>-</sup>) and are limiting the variety of the structure. The first **molecular metal–organic hybrid** materials of [Cu(adiponitrile)<sub>2</sub>]·NO<sub>3</sub> emerged in 1959.<sup>7</sup> The organic linkers allowed endless functional possibilities. However, the compounds have no porosity. **Porosity** means "the quality or state of being a porous entity, which has many small holes that allow water, air, and so on, to pass through".<sup>8</sup> The permanent porosity of the CPs was still challengeable and no widely accepted characterization model was used until 1990. IUPAC recommends low temperature isotherms using nitrogen or argon gas as a standard procedure to confirm the permanent porosity.<sup>9</sup> In 1997, porosity was views as an accessible void which demanded a stable compound without guests filling in the pores and have a gas sorption property.<sup>10-11</sup> While the reversible gas storage was carried out, MOFs have drawn extensive attention as novel porous materials for energy storage applications. Hereafter, the field made an explosive development and thousands of MOFs and related research are reported every year.

## **1.3 Representative MOFs**

MOFs have emerged as a new class of crystalline materials with ultrahigh porosity and the numbers of novel MOFs have been increasing exponentially. Because of the large number of linkers and metal nodes that can be combined, the numbers of possible MOFs are limitless. Herein, the most important MOFs are highlighted and discussed in detail.

#### 1.3.1 Milestone MOFs: MOF-5 and HKUST-1

In 1999, two milestone MOFs, **MOF-5**<sup>12</sup> and **HKUST-1**<sup>13</sup>, were discovered and symbolized a new chapter in the field of porous materials due to their robust porosity. **MOF-5** was discovered by Yaghi et al., and it has a cubic framework structure comprising octahedral  $Zn_4O$  secondary building units (SBU) that are linked by six chelating 1,4-benzenedicarboxylate (BDC<sup>2–</sup>) units (Figure 1.2, left). MOF-5 possesses a good thermal stability and maintains crystalline even after desolvation by heating up to 300 °C. N<sub>2</sub> sorption measurement shows that the Langmuir surface area and pore volume of MOF-5 can be as high as 2900 m<sup>2</sup>/g and 0.61 cm<sup>3</sup>/g, respectively. This value represented the **record surface** 

area at that moment and was higher than most of the porous materials such as zeolites and activated carbon. Additionally, for the first time, reversible sorption behavior of gases and organic vapors (N<sub>2</sub>, Ar, CO<sub>2</sub>, CHCl<sub>3</sub>, CCl<sub>4</sub>, C<sub>6</sub>H<sub>6</sub>, and C<sub>6</sub>H<sub>12</sub>) was observed in MOF-5. Another major advancement in the field of MOFs arose in the same year. HKUST-1,  $[Cu_3(BTC)_2(H_2O)_3]_n$  (BTC = benzene-1,3,5-tricarboxylate) was synthesized by Willians et al.<sup>13</sup> This material forms cubic lattice crystals that provide a three-dimensional connected network of large square-shaped channels (9 Å × 9 Å) and 40% void volumes in the solid (Figure 1.2, right). The surface area was measured by N<sub>2</sub> adsorption, showing that it has the Langmuir surface area of 917.6 m<sup>2</sup>/g and pore volume of 0.333 cm<sup>3</sup>/g. In HKUST-1 two Cu<sup>2+</sup> ions form the famous paddlewheels SBU, where each copper atom is coordinated by four oxygens from the BTC linkers and by one water molecule. The labile water molecules in the dimers copper ions has been removed by sample dehydration to obtain uncoordinated sites on Cu<sup>2+</sup> species and can be replaced by other functional groups such as pyridines. The uncoordinated copper sites are open metal sites, which display an important role for the applications such as adsorption and catalysis<sup>14</sup> and were firstly exploited by Yaghi et al in 2000.<sup>15</sup> The authors synthesized MOF-11 in which copper paddlewheels, the same as HKUST-1, are linked through 1,3,5,7-adamantanetetracarboxylate. The rigid nature of the MOFs allows the extraction of the coordinating water molecules at high temperatures. This extraction of coordinating water molecules led to uncoordinated copper sites that are open metal sites and can be utilized as catalysis and adsorption active sites.



Figure 1.2 The structure of the MOF-5 (left) and HKUST-1 (right). (Reproduced from reference <sup>12-13</sup>).

#### 1.3.2 Flexible and Breathing MOFs: MIL-47 and MIL-53

In 2002, Férey and coworkers synthesized a flexible MOF, named MIL-47<sup>16</sup>, and then followed to find a breathing MOF, named MIL-53<sup>17</sup>. MIL-47 is constructed with cornershared trans chains of VO<sub>6</sub> and the BDC linker to form 1D lozenge-based channel. The channel is flexible between the filled and evacuated phases. The channels (7.9 × 12 Å) filled with disordered terephthalic acid guest in the as-synthesized form of MIL-47. Free terephthalic acid was removed from MIL-47 upon calcination at 573K for 24h and the dimensions of channels increased to 10.5 × 11 Å. MIL-53, was synthesized using different chromium(III) salts but was found to have same topology as MIL-47. A different form of MIL-47 and MIL-53 was observed when the structure cools down at air and re-absorbs water (Figure 1.3). This form is named MIL-53lt and is considered a third phase. This transition between MIL-53ht and MIL-53lt is fully reversible. This is because the OH groups in the framework of MIL-53 exhibits hydrogen bond with solvent water molecules. MIL-47 is flexible but cannot breathe due to the lack of the OH groups. MIL-53 has also shown high breathing ability to other species such as DMF and  $H_2BDC$ , which provide the adaptability to the shape of the chemical stimulus. The flexibility of the framework exhibited the noticeable breathing effect responding to the stimulus of adsorbed compounds or temperature.



**Figure 1.3** (a) Perspective view of MIL-53-ht; (b)–(d) projection along the direction of the tunnels of (b) MIL-53-as (with some atoms of the disordered terephthalic acid in blue), (c) MIL-53-ht, and (d) MIL-53-lt with variable parameters; (e), (f) perspective views of the connection between the chromium chains and the terephthalate ions. Chromium octahedra are in green, water molecules in dark blue, OH groups in pale blue, oxygen in red and carbons in black. (Reproduced from reference<sup>18</sup>).

### 1.3.3 Zeolitic Imidazolate Frameworks

*In 2006*, Yaghi reported twelve **zeolitic imidazolate frameworks (ZIFs)** which were fabricated as crystals with imidazolate-type links (Figure 1.4).<sup>19-20</sup> In contrast to the previous metal-carboxylate MOFs, azolate ligands have the benefit of strong and directional coordination ability in bridging metal ions. The ZIF crystal structures were zeolite-type tetrahedral topologies materials and the bridging angle in the M-Im-M fragment is similar to that of Si-O-Si in zeolites. ZIF demonstrated their permanent porosity, exceptional thermal stability, and

outstanding chemical stability such as the resistance in boiling alkaline water for days and organic solvents.



**Figure 1.4** The single crystal x-ray structures of ZIF-8 (Left and Center). The net is shown as a stick diagram (Left) and as a tiling (Center). (Right) The largest cage in each ZIF is shown with  $ZnN_4$  tetrahedra in blue. H atoms are omitted for clarity. (Reproduced from reference<sup>20</sup>).

#### 1.3.4 Stable MOFs: MIL-101 and UiO-66

Férey group synthesized **MIL-101** through combined targeted chemistry and computational design.<sup>21</sup> It has a large cell volume (~702,000 Å<sup>3</sup>), two types of mesoporous cages of 29 Å and 34 Å with 12 Å and 16 Å opening windows and a Langmuir surface area of 5900±300m<sup>2</sup>/g (Figure 1.5). This solid can incorporate Keggin polyanions within the cages, which showed the potential as a nano-sized host for monodisperse nanomaterials. This is the first time the computation guided method was employed to design MOFs. The following studies demonstrated MIL-101 to be one of the most potential materials for applications in industry due to the excellent stability against moisture and other chemicals as well as their unsaturated open metal sites.



**Figure 1.5** (A and B) Ball-and-stick view and free dimensions (Å) of the pentagonal and hexagonal windows. (C and D) Ball-and-stick view of the two cages. Chromium octahedra, oxygen, fluorine and carbon atoms are in green, red, red and blue, respectively. (Reproduced from reference<sup>21</sup>).

In 2008, another famous MOF, UiO-66 was synthesized using less common metal salts zirconium (Zr) by Lillerud group.<sup>22</sup> The general formula of UiO-66 is  $[Zr_6O_4(OH)_4(BDC)_6]$  which constructs the high nuclearity SBUs with the BDC organic linkers (Figure 1.6). In the SBU, each Zr atom coordinates with eight oxygen atoms, which have four from carboxylates, and four from  $\mu_3$ -O and  $\mu_3$ -OH groups. The Zr<sub>6</sub>-octahedron SBU is alternatively connected with  $\mu_3$ -O and  $\mu_3$ -OH groups in the triangular faces and is connected with 12 other inorganic clusters through BDC ligands. The inner Zr<sub>6</sub>-cluster showed а reversible dehydration/hydration phenomenon while the connecting carboxylate did not change in the process. The framework contains two kinds of cages with 8 Å and 11 Å diameter free dimensions, which are accessible with 6 Å triangular windows. The Langmuir surface area of UiO-66 is 1187m<sup>2</sup>/g. UiO-66 shows high stability up to 500 °C in air. This enhanced stability can be assigned to the presence of high-valent metal cations creating clusters with high charge densities. The Zr<sub>6</sub>-cluster SBU formed make the MOF with good chemical stability and resistant towards elevated pressures. The isoreticular frameworks were obtained with the different length linkers.



**Figure 1.6** Formation of UiO-66. (Reproduced from reference <sup>23</sup>).

### 1.3.5 MOF Glass

*In 2015*, Bennett et al. observed the new **glass state** formation of zeolitic MOFs.<sup>24</sup> ZIF-4 showed that the melting temperature was lower than the thermal decomposition temperature by slowly heating in an inert gas (Figure 1.7). The low-density amorphous to high-density amorphous phase polymorphic transition occurred at ca. 300 °C. Subsequently, densification was observed before the material melted at ca. 575 °C. Cooling of the liquid form a glass state. The coordination bonds are coordinated in the glass state while absent in the liquid state. This glass displays a clear glass transition behavior upon reheating. A thin film with an aligned crystal orientation and a monolith crystal of the CP was fabricated via phase transition and this transition is the fundamental process for the potential application in MOFs.



**Figure 1.7** Left panel: Heat flow and mass change as a function of temperature for ZIF-4, which are measured by differential scanning calorimetry and thermogravimetric measurements, respectively. The figure shows thermal responses to phase transitions and degradation. Right panel: The isobaric heat capacity as a function of temperature, exhibiting a typical glass transition peak of ZIF-4 glass. Inset: a piece of quenched ZIF-4 glass (size: ca. 3 mm long). (Reproduced from reference<sup>25</sup>).

Though MOF glass<sup>26,27</sup> has been reported earlier, they lack descent surface properties.<sup>24</sup> Zhao et al. first synthesized a transparent **glassy MOF with a permanent porosity** by assembling viscous solutions of metal node and organic strut in modulator solvent and subsequent evaporation of a plasticizer–modulator solvent (Figure 1.8). N<sub>2</sub> adsorption isotherms showed the Ti-BPA and Ti-BPP MOF glasses have 330 m<sup>2</sup>/g and 267m<sup>2</sup>/g surface area respectively. The porosity consists of a 3D highly cross-linked nanostructure when the solvent is removed. The glass transition signature has disappeared. Bennett et al. also obtained microporous glasses from ZIFs, which reversibly adsorbed CO<sub>2</sub> molecules.<sup>27</sup> The method is based on the rapid cooling of a liquid MOF without the chemical modification.



**Figure 1.8** Photograph of monolithic MOF glass in a 10 cm diameter Petri dish, following vitrification by *m*-cresol evaporation (left);  $N_2$  adsorption isotherms (77 K) for MOF glasses (right). (Reproduced from reference<sup>26</sup>).

*In 2017*, accompanying with the extensive attention of MOF glass, the liquid state, which was obtained by melting MOFs and do not transform to MOF glass by cooling, have been studied by Gaillac et al.<sup>28</sup> The nature of the ZIF-4 melting into liquid was illustrated in combination of in situ variable temperature X-ray, ex situ neutron pair distribution function experiments, and first-principles molecular dynamics simulations. The research demonstrated that the chemical configuration, coordinative bonding, and porosity of the parent crystalline framework survive upon formation of the **MOF liquid**.

## **1.4 Tricks of MOF Synthesis**

Several synthesis methods have been developed in the last 20 years (Figure 1.9).<sup>29</sup> In addition to conventional solvothermal synthesis, microwave-assisted, electrochemical, mechanochemical, ultrasonic synthesis methods as well as high-throughput methods have been employed. Several smart strategies are listed and reviewed.



**Figure 1.9** Overview of synthesis methods, possible reaction temperatures, and final reaction products in MOF synthesis. (Reproduced from reference<sup>29</sup>).

#### 1.4.1 Isoreticular MOFs

**Isoreticular** MOFs (IRMOFs) have the same structure topology but different functionalities and different sizes of linkers. Yaghi developed this new strategy and designed a series of IRMOFs based on MOF-5.<sup>30</sup> The IRMOF series of cubic frameworks were made of the some octahedral Zn<sub>4</sub>O SBU and the different dicarboxylate with different functional groups: R<sub>2</sub>-BDC, R<sub>3</sub>-BDC, R<sub>4</sub>-BDC, R<sub>5</sub>-BDC, R<sub>6</sub>-BDC, R<sub>7</sub>-BDC, 2,6-NDC, BPDC, HPDC, PDC and TPDC (Figure 1.10). These 16 crystalline materials, characterized by SXRD, were produced with different permanent porosites and non-interpenetrating structures. In all these cases, the percentage of free volume varies from structure to structure; e.g. from 55.8% (R<sub>5</sub>-BDC) to 0.21 g cm<sup>-3</sup> (TPDC)and the free pore diameters vary from 3.8 Å to 19.1 Å. All aspects were difficult to achieve by the existing materials at that time. The isoreticular MOFs have the essential potential to be employed in several applications. For example, the IRMOF-6 has exhibited the highest adsorption uptake of methanol, which almost reached the US Department of Energy guidelines.



**Figure 1.10** Organic linkers and Single crystal X-ray structures of IRMOF-n (n = 1 through 7, 8, 10, 12, 14, and 16) labelled appropriately. (Reproduced from reference<sup>31</sup>).
## 1.4.2 Multivariable MOFs

**Multivariate MOFs** (MTV-MOFs) have multiple organic functionalities integrated within a single framework to combine many designing properties in a controlled manner and were termed by Yaghi<sup>32</sup> (Figure 1.11). Eighteen MVT-MOF-5 were made from eight distinct functionality linkers in a random fashion. The effects of the mixing lead to nonlinear properties on porosity and absorption characteristics. For example, MTV-MOF-5-EHI exhibits up to 400% better selectivity for CO<sub>2</sub> over CO in comparison with its best single linker MOF.



with eight different functionalities

**Figure 1.11** Scheme of the formation of MTV-MOF. (Reproduced from reference<sup>32</sup>).

### 1.4.3 Step by Step Synthesis

A thorough understanding of the formation process of MOFs was reported by Christof et al., which presented the stepwise formation of HKUST-1 on functionalized SAMs on Au surface using SPR spectroscopy.<sup>33</sup> The **step-by-step deposition** was formed by the metal salt and the organic linker where highly oriented growth was observed. This study shows the 3D self-assembly process and provides the evidence of the 3D long range ordering deposited MOFs. The step by step preparation provides the unique opportunity to fabricate the ordered MOF thin films. The first MOF **thin films** were also produced by Fischer's group, which employed Self-Assembled Organic Monolayers (SAMs) combined with soft lithographic techniques (Micro Contact Printing,  $\mu$ CP).<sup>34</sup> Functionalization of the surface of Au(111) was prepared with a microcontact method using 16-mercaptohexadecanoic acid and 1H,1H,2H,2H-perfluorododecane thiol, then the  $\mu$ -CP printing-patterned SAM was immersed into a supersaturated mixture of metal salts and linkers to synthesize the thin film of MOF-5. The film only grew on COOH-terminated parts on a bifunctional CF<sub>3</sub>/COOH<sup>-</sup> terminated SAM.

## 1.4.4 Modulation

**Modulation synthesis** is an important way to regulate the size and morphology of MOFs or to create the defect.<sup>35-36</sup> As a first modulator, *p*-perfluoromethylbenzoic acid, a kind of monocarboxylic acid, was used to adjust the particle size of MOF-5.<sup>37</sup> In general, the modulator compete with the organic linker to coordinate the SBU units. Because of the higher amount of the modulator, it forms bigger size crystals. Moreover, the study also showed the controlled step is the particle growth, not the nucleation in the procedure. Extensive researches on this topic are discussed in Chapter 2.

## 1.4.5 Ordered Vacancies

**Ordered vacancies**<sup>38</sup> are not easy to control in solid materials. The creation of the ordered vacancies in MOFs was successful realized by Tu et al. From MOF  $[Zn_4O(PyC)_3]$  (PyC = 4-pyrazolecarboxylate) a quarter of the metal ions and half of the ligands can be removed to create the ordered vacancy sites through the immersion in water in a single-crystal to single-

crystal (SCSC) transformation (Figure 1.12). The vacancies can be pre-coordinated by a new metal or a new linker or both together to rebuild the original structure. The bigger pores were generated with ordered vacancies and allowed the large dye molecules to enter. This was not observed in pristine MOFs to confirm the ordered vacancy.



**Figure 1.12** By elimination of PyC linkers and metal ions (blue), the single-crystal structure of  $[Zn_4O(PyC)_3]$ (a) shows vacancy sites (b). These vacancy sites can be filled gain with (functionalized) PyC (pink pyrazole ring) and metal ions (orange) (c). (Reproduced from reference<sup>38</sup>).

#### 1.4.6 Metal Exchange

*In 2009*, the Kim group were first report to the complete and reversible **exchange of the metal component** in MOFs in a SCSC fashion under mild conditions (Figure 1.13).<sup>39</sup> A novel Cd(II) MOF was prepared using solvothermal reaction with a rigid, tricarboxylate ligand. The framework constituting Cd(II) ions underwent complete and reversible exchange with Pb(II) in an aqueous solution of Pb(NO<sub>3</sub>)<sub>2</sub> at room temperature. Structural integrity was maintained, and single crystallinity was the same as in the starting MOF determined from SXRD analysis. Moreover, the Cd(II) ion could also be exchanged with the lanthanides Dy(III) or Nd(III) possessing the higher charge, which cannot be obtained from direct solvothermal MOF synthesis.



**Figure 1.13** Photographs of dative PSM of a Cd(II)-based MOF. In this example, the Cd(II) ions of the SBUs are replaced by Pb(II) ions upon crystal soaking in an aqueous solution. (Reproduced from reference  $^{39}$ ).

## 1.4.7 Linker Exchange

After successful metal ion exchange was realized by Kim group, **linker exchange** was reported by Burnett et al. using PPF-18 and PPF-20.<sup>40</sup> PPF-18 is a 2D MOF containing porphyrin-based 2D bilayer connected by N,N'-di-4-pyridylnaphthalenetetracarboxydiimide (DPNI) pillars whereas PPF-20 is a 3D porphyrin-based MOF. In both cases, a DPNI linker was successfully exchanged by a 4,4'-bipyridine (BPY) linker by simple immersing both MOFs in DEF/EtOH mixture containing BPY linker (Figure 1.14). This exchange created a template effect in the "parent" structure for the resulting "daughter" structure and the layers had no lateral movement during this process. The transformation occurred in a SCSC fashion, which was verified by single crystal and powder X-ray diffraction (PXRD) measurements of the "daughter" MOF. Moreover, using this method one can easily synthesize daughter MOFs that are difficult to obtain in conventional ways.



**Figure 1.14** Introduction of the bridging linker BPY to crystals of (a) PPF-18 and (b) PPF-20, transforming them to PPF-27 and PPF-4, respectively. Blue and pink bands represent "A" and "B" layers, respectively. The AB and ABBA topologies in PPF-18 and PPF-20 are retained in PPF-27 and PPF-4, respectively, showing a template effect. (Reproduced from reference<sup>40</sup>).

## 1.4.8 Sequential Linker Installation

Yuan et al. developed a new method, **sequential ligand installation** (SLI), to assemble multivariate MOFs (MTV-MOFs) in a controlled manner.<sup>41</sup> Different from the conventional mixed-linkers approach, the method could precisely install the positions of the distinct lengths and functional linkers (Figure 1.15). In this study, a prototype Zr-MOF, PCN-700, has an exceptional stability and 8-connected  $[Zr_6(\mu_3-O)_4(\mu_3-OH)_4(OH)_4(H_2O)_4]$  clusters which have a tunable connectivity. PCN-700 has two sizes of pockets (pocket A: 16.4 Å and pocket B: 7.0 Å), which allow to incorporate two kinds of suitable lengths linkers by replacing the terminal OH/H<sub>2</sub>O ligands with the SLI method. 1,4-benzenedicarboxylate (BDC<sup>2-</sup>) and 2',5'-dimethylterphenyl-4,4''-dicarboxylate (TPDC-Me<sub>2</sub><sup>2</sup>)<sup>-</sup> ligands were two examples based on the suitable lengths for the pocket size. Subsequently, PCN-700 crystals were soaked to solutions of H<sub>2</sub>BDC and H<sub>2</sub>TPDC-Me<sub>2</sub> in DMF at 75 °C, resulting in mixed-ligand Zr-MOFs, [Zr<sub>6</sub>( $\mu_3$ -O)<sub>6</sub>( $\mu_3$ -O)<sub>6</sub>(

OH)<sub>2</sub>(OH)<sub>4</sub>(BPDC-Me<sub>2</sub>)<sub>4</sub>(BDC)] (PCN-701) and  $[Zr_6(\mu_3-O)_6(\mu_3-OH)_2(OH)_4(BPDC-Me_2)_4(TPDC-Me_2)]$  (PCN-702), respectively. Upon exposing PCN-701 in a DMF solution of H<sub>2</sub>TPDC-Me<sub>2</sub> sequentially,  $[Zr_6(\mu_3-O)_5(\mu_3-OH)_3(OH)_2(BPDC-Me_2)_4(BDC)(TPDC-Me_2)_{0.5}]$  (PCN-703) was isolated. However, PCN-703 could not be synthesized from PCN-702 because the pocket was elongated to 8.2 Å after the incorporation of TPDC-Me<sub>2</sub><sup>2-</sup>, which is too long compared with the size of H<sub>2</sub>BDC (6.9 Å). This transformation was realized in SC to SC fashion. To extend this method, functionalized linkers of 2-amino-1,4-benzenedicarboxylate (BDC-NH<sub>2</sub><sup>2-</sup>) and 2',5'-dimethoxyterphenyl-4,4''-dicarboxylate (TPDC-(CH<sub>3</sub>O)<sub>2</sub><sup>2-</sup>) were also installed effectively into MTV-MOFs to obtain  $[Zr_6(\mu_3-O)_5(\mu_3-OH)_3(OH)_2(BPDC-Me_2)_4(BDC-NH_2)(TPDC-(CH<sub>3</sub>O)_2)_{0.5}]$  (PCN-704).



**Figure 1.15** Schematic representation for synthesis of PCN-701–703 based on the sequential ligand installation in PCN-700. (Reproduced from reference<sup>41</sup>).

## 1.4.9 Large Scale Computational Synthesis

MOFs are modular construction of metal clusters and organic linkers that self-assemble to form almost unlimited number of MOFs. Thousands of reports of novel MOFs have appeared every year and 102 building blocks were selected from the known units to form 137953 hypothetical MOF structures by computational simulation by Snurr and co-workers.<sup>42</sup> The pore-size distribution, surface area and methane-storage capacity were calculated and more than 300 MOFs have a storage capacity exceeding the world-record-holding material. Meanwhile, the structure–property relationships were revealed that the volumetric CH<sub>4</sub> adsorption has a linear relationship with the volumetric surface, while MOF with pore sizes of 4–8 Å is the best one for methanol adsorption in MOFs. The top 2% MOFs from the screening are similar with PCN-14 which has the highest methane storage at 35 bars. NOTT-107 was unknown to authors at the time of synthesis and was synthesized with different protocol by computational guide. It has a higher storage than PCN-14 in calculation but has less storage (at the higher 8 K temperature) than the experimental value of ~230 vol(STP)/ vol for PCN-14.

## 1.4.10 Large Scale Synthesis

**Industrial synthesis** of MOFs at BASF has already been into barrel-size pilot scale, as well as an electrochemical route which is an alternative salt-free procedure without high nitrate concentrations.<sup>43</sup> One can see that conventional crystallization and precipitation manufacturing methods have been available and adapted to prepare and fabricate industrial MOFs without additional capital investment to exploit the new synthesis technology. The formed solid can be produced by filtration to harvest the final product after drying. There is no major obstacle to preform large scale synthesis of MOFs. The testing of MOFs in fields of catalysis and gas processing is exemplified as well.

## **1.5** Applications: catalysis

The potential of MOFs depends on its design of MOFs with exceptional porosity, tunable pore size, specific functional groups and/or frameworks flexibility. These characteristics

renders them remarkably attractive for a large scope of applications including, but not limited to, heterogeneous catalysis, <sup>14</sup> separation, <sup>44-45</sup> drug delivery<sup>46</sup> and sensing<sup>47</sup> (Figure 1.16). In the following, few examples where MOF firstly used as catalyst are discussed.



**Figure 1.16** MOFs are being developed in many areas ranging from energy storage, gas separation, water capture, and catalysis to biomedical applications. (Reproduced from reference<sup>2</sup>).

## 1.5.1 Asymmetric Catalysis

In 2000, Kim et al. reported the first **homochiral MOF** (POST-1), which exhibited enantioselectivity in **asymmetric catalysis.**<sup>48</sup> POST-1 was built with an enantiopure tartaric acid-derived bridging ligand and the  $Zn_3(\mu_3-O)(carboxylate)_6$  SBU. Large chiral 1D channels are constructed by six trinuclear zinc clusters and six pyridyl groups. While three of the six pyridines are coordinated by Zn(II) ions, the others are free in the channel without any

connections with the framework. The non-coordinated pyridyl groups exposed in the channel provide the opportunities to catalyze trans-esterification reactions. The authors examined the trans-esterification activity of the MOF materials in a reaction between an aromatic ester and ethanol to form ethyl acetate in carbon tetrachloride medium, which produced in 77% yield after 55 h. When the substrate was changed to racemic 1-phenyl-2-propanol, an enantiomeric excess (ee) of ~8% was observed, which was the first time to observe the asymmetric induction in porous materials (**Figure 1.17**).



**Figure 1.17** (a) Scheme for synthesis of POST-1, (b) transesterification reactions catalyzed by POST-1. (Reproduced from reference<sup>48</sup>).

## **1.5.2** Photocatalysis

*In 2004*, the **photoluminescence** properties of MOF-5 were firstly discovered and reported by Zecchina et al.<sup>49</sup> UV–Vis DRS spectra demonstrated that MOF-5 occurred at an intense emission at 525 nm, which is the result of ligand to metal charge transfer transition (LMCT). Photoluminescence spectroscopy (PL) and excitation selective Raman spectroscopy revealed that the organic part acts as a photon antenna, which can efficiently transfer the energy to the inorganic ZnO-like quantum dot part. After the photoluminescence of MOF-5 was observed,<sup>49</sup> the charge separation (electrons and holes) also was reported by Garcia et al., which opened the possibility using MOF as a **photocatalyst**.<sup>50</sup> MOF-5 is stable upon light excitation and undergoes the charge separation. While the photoinduced electron was transferred to electron acceptors methyl viologen dichloride to generate the corresponding radical cation, the hole trapped electron donors N,N,N',N'-tetramethyl-*p*-phenylenediamine to oxidize. The photodegradation of phenol in aqueous solution was examined using hydrated MOF-5 to prove the photocatalytic activity. MOF-5 showed the comparable activity with  $TiO_2$  P-25, either per mass unit or per metal of active atom. Furthermore, the shape-selective activity is possible due to the presence of a regular pore.

#### **1.5.3 Electrocatalysis**

The *p*-type semi conductivity and redox behavior were observed by Long and coworkers in a new type of MOF Cu[Ni(pdt)<sub>2</sub>] (pdt<sub>2</sub>-=pyrazine-2,3-dithiolate).<sup>51</sup> This MOF implied an optical band gap of about 2 eV and a low intrinsic conductivity being only  $1 \times 10^{-8}$  S/cm, but this is the first time it showed election transfer with porosity. The conductivity increased doping with I<sub>2</sub> vapor in the pore, which showed *p*-type semiconducting behavior. Author suggested the conduction is attributed to the framework due to the small amount of  $I_2$ required. The redox property was studied that redox couple is from the framework, not the impurities, which peak separation is closer to hexacyanoferrate particles deposited on graphite electrodes. After the electron conductivity in MOFs was studied, it was used as an electrocatalyst for the first time by Kitagawa's group.<sup>52</sup> The MOF, [(HOC<sub>2</sub>H<sub>4</sub>)<sub>2</sub>dtoaCu] ((HOC<sub>2</sub>H<sub>4</sub>)<sub>2</sub>dtoa = N,N'-bis(2-hydroxyethyl)dithiooxamidato), had a good proton conductivity around  $3.3 \times 10^{-4}$  S/m.<sup>53</sup> The catalytic activity of ethanol electrooxidation reaction (EER) using this MOF was evaluated by cyclic voltammograms. The MOF was coated with a glassy carbon electrode within 0.5 M H<sub>2</sub>SO<sub>4</sub> containing different concentrations of ethanol. Cyclic voltammetry showed two redox peaks, which 0.35 V vs. Ag/AgCl peak was ascribed to Cu<sup>I</sup>/Cu<sup>II</sup> and 0.71 V is attributed to Cu<sup>II</sup>/Cu<sup>III</sup> oxidation couple. The noble-metal-free MOF based material exhibits lower catalytic activity than Pt-based catalysts, but oxidation potential and current density is comparable with Pt-based catalysts.

In summary, MOFs have been seen an enormous growth for catalysis in last decades and will be foreseen the further development in the coming years. However, the clear guidelines for this field are expected for researchers and industry to compare catalytic performance between laboratories and investigate MOFs as catalysts for different organic reactions.

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# Chapter 2 Defect Engineering in UiO-66

## 2.1 Introduction

MOFs are chemically diverse materials and have wide applications in various fields, including chemistry, engineering, physics, biology and medicine. Apart from the perfect structures on which almost were focused in this field, it is now a clear trend which shifts the emphasis onto the defective states. This subfield is *defect engineering* in MOFs. Defect chemistry in doped semiconductors was a great success.<sup>1</sup> It is also useful in MOFs, which can tailors many properties and opens up novel opportunities to optimize and discover even new technological applications of materials.<sup>2-3</sup> With the development of the MOF field, numerous MOFs were synthesized and UiO-66 is one of the stars due to its stability. Considering the aim of this thesis, I limit the range of discussion to UiO-66. More specifically, only defect engineering in UiO-66 will be reviewed in detail.

The discovery of zirconium-based MOFs, UiO-66 , is one of several milestones in MOF chemistry.<sup>4</sup> The ideal structure constructs hexanuclear  $[Zr_6O_4(OH)_4]^{12+}$  clusters with the BDC organic linkers. The details of the properties can be found in the previous chapter about UiO-66 (Figure 1.6). Since 2008, Zr-MOFs have grown into a large family featuring their high stability while the diverse geometrical and symmetrical organic linker have been combined with the Zr node (Figure 2.1).<sup>5</sup>



**Figure 2.1** Connectivity of  $Zr_6$  nodes in zirconium-based metal–organic frameworks and the associated carboxylate molecules required to link nodes together. (Reproduced from reference<sup>6</sup>).

Due to the high charge density and bond polarization, the carboxylate-Zr bonds have a strong affinity. This is the reason that UiO-66 display outstanding stability and has none of the limitation most of MOFs have for practical application due to their weak either thermal, chemical or mechanical stability. It is thermally stable up to 500 °C and has a remarkable

chemical resistance in water, acidic or base aqueous solutions and organic solvents without suffering any significant damage<sup>4, 7-8</sup> and maintains crystalline exposing high pressure.<sup>9-10</sup> The improvement in the stability of MOFs expands extremely attractive for practical applications, including gas sorption, separation, catalysis, drug delivery and electrochemistry.<sup>5, 11</sup>

Defect engineering in MOFs release new opportunities for many applications and drawn the extensive attention about the synthesis of the defect and the development of applications.<sup>2-</sup> <sup>3</sup> UiO-66 is one of well-known MOFs due to the exceptional stability to bear the high amount of the defect. It tolerates the high concentration of these defects due to a high degree of connectivity of the metal clusters, resulting in the stability of the structure.<sup>12</sup> The first evidence of the existence of defects in MOFs was provided from thermogravimetric analysis (TGA) of UiO-66.<sup>12</sup> More specifically, the weight loss during decomposition is lower than the theoretical weight loss. Valenzano and coworkers attributed this discrepancy to the presence of missing-linker defects in the framework.<sup>12</sup> Two years later, high-resolution neutron diffraction study on UiO-66 showed direct structural evidence of the presence of missing-linker defects in UiO-66.<sup>13</sup> SXRD has given further insight on missing-linker defects on UiO-66 and UiO-67, when synthesized in similar conditions using benzoic acid as a modulator, which showed a noteworthy difference to confirm the missing linker defect.<sup>14-15</sup> The other important point defect, the missing clusters defect, was discovered combined with X-ray scattering and pair distribution function (PDF).<sup>16</sup> The weak and broad reflections come from the nano-regions with reo topology in UiO-66. It provides new insight on defect which is not randomly distributed of the missing linker and has an unequal distribution of the missing linker defect to form the cluster missing defect. In overall, two types of defect were discovered in UiO-66, (i) missing linker defects (MLD) and (ii) missing cluster defects (MCD).

These two types of defects are point defect in solid state chemistry perspective, which is similar with Schottky-type defects in ionic crystals.<sup>2</sup> The defect has been discussed broadly in Fischer's review.<sup>2</sup> Missing-linker defects are caused by the removal of an organic linker from the framework, generating defect sites on two adjacent metal clusters (Figure 2.2).<sup>13</sup> Missing-cluster defects occur when a  $[Zr_6O_4(OH)_4]^{12+}$  cluster is removed together with its total connecting twelve organic linkers, leaving twelve coordination vacancies on corresponding twelve neighboring clusters (Figure 2.2).<sup>16-17</sup> The compensated terminal

ligands on vacancies can be the modulators<sup>13</sup> which are in addition of monocarboxylic ligands during the synthesis, or water<sup>15</sup>, hydroxide<sup>18</sup>, chloride<sup>97</sup> and fluoride<sup>19</sup>.



**Figure 2.2.** Illustration depicting the structural and compositional differences between the ideal UiO-66 unit cell and those with missing cluster/missing linker defects. Trifluoroacetate ligands compensate for the defects in the examples above. (Reproduced from reference<sup>17</sup>).

The most studies about defect engineering in UiO-66 so far are summarized in Table 1 and some of these studies are discussed in detail.

Type of defect	Defect engineering	Characterizations	Applications	Ref
MLD	Modulation approach	TGA-MS	-	12
MLD	Modulation approach	High-resolution neutron	CO <sub>2</sub> adsorption	13
		scattering, N <sub>2</sub> adsorption (BET)		
MLD	Modulation approach	Synchrotron SXRD	-	14
MLD	Modulation approach	SXRD	-	15
MLD	Modulation approach,	TEM, XRD, X-ray PDF scattering,	-	16
and	Computational study	quantum chemical calculations		
MCD		18		
MLD	Modulation approach	TGA, <sup>19</sup> F NMR, FTIR (CD₃CN	Meerwein-Ponndorf-Verley	20-
		probe), $N_2$ adsorption (BET),	reduction	21
		periodic DFT, molecular		
		dynamics, nudged elastic band		
		theory, free energy diagrams		
MCD	Modulation approach	PXRD, $N_2$ adsorption (BET), TGA,	-	1/
		NMR		
MLD	Mix-linker approach	PXRD $N_2$ adsorption (BET),	-	22
		NMR, TGA, <sup>1</sup> H spin diffusion		
		NMR measurements, DFT		
MLD	Postsynthetic Ligand	NMR, N <sub>2</sub> adsorption (BET), XRD	CO <sub>2</sub> adsorption	23
	Exchange			
MLD	Modulation approach	XRD, $N_2$ adsorption (BET)	Cyclisation of acetaldehyde	24
MLD	Modulation approach	Potentiometric acid-base	Styrene oxide ring-opening	25-
		titration	reaction	26

#### Table 1. Summary on defective UiO-66.

MCD	Modulation approach	PXRD, N <sub>2</sub> adsorption (BET), TGA, NMR, FTIR and Raman, DFT	-	27
MCD	Computational study	Grand canonical Monte Carlo simulations, simulation of water and $CO_2$ isotherms	CO <sub>2</sub> adsorption	28
MCD	Modulation approach	Water adsorption measurement	Cyanosilylation of benzaldehyde	29
MLD	Functional linker	First-principles kinetic and molecular modeling calculations	Cyclization of citronellal	30
MLD	Variations of BDC: Zr ratio, Synthesis temperature	TGA-DSC, NMR, Raman spectroscopy, N <sub>2</sub> adsorption (BET)	-	31
MLD	Computational study	DFT	-	32
MLD	Microwave synthesis, Modulation approach	TGA, $N_2$ adsorption (BET), NMR, EDS	$CO_2$ and water adsorption	33
MLD	Modulation approach	N <sub>2</sub> adsorption (BET)	NH <sub>3</sub> adsorption	34
-	Modulation approach, Metalated-ligand exchange	N <sub>2</sub> adsorption (BET)	CO <sub>2</sub> adsorption	35
MLD	Modulation approach	TGA, NMR	Proton conductivity	36
MLD	Modulation approach	Extensive IR study, DFT calculation	-	37
MLD and MCD	Computational study	Simulated BET, Young modulus, CO <sub>2</sub> uptake	CO <sub>2</sub> adsorption, Mechanical stability	38
MLD	Computational study	DFT	Mechanical stability	39
-	Sulfonated functional ligand	<b>C</b> onductivity experiments, DFT calculation	Proton conductivity	40
MLD	Computational study	DFT	Photocatalysis	41
MLD	Computational study	Atomistic force field, DFT	-	42
MLD and MCD	Modulation approach,	TGA, PXRD, DFT	Negative thermal expansion	43
LD	Ball milling	<sup>13</sup> C SS-MAS-NMR, PDF	-	44
LSD	Modulation approach (long chain modulator), linker insufficiency	N <sub>2</sub> adsorption (BET)	Dye and particle uptake and catalysis	45
MLD	Modulation approach	XRD, $N_2$ adsorption (BET), TGA	Esterification of levulinic acid	46
LSD	Template approach	N <sub>2</sub> adsorption (BET), TEM	Cytochrome encapsulation	47
MLD and MCD	Post Synthetic modifications and Ligand Exchange	NMR	CO <sub>2</sub> adsorption	48
-	Thermal Modulation	Acid-base titration, N <sub>2</sub> adsorption (BET)	-	49
MLD and MCD	PostSynthetic Linker Exchange	NMR, TGA, SSNMR, DFT	-	50

MLD	Modulation approach	IR, <sup>1</sup> H NMR, TGA, N <sub>2</sub> adsorption (BET), SEM, PXRD, DFT	-	51
LSD	Microdroplet flow reaction	N <sub>2</sub> adsorption (BET), XPS	$CO_2$ and $CH_4$ adsorption	52
MLD and MCD	Computational study	DFT	Electronic structure	53
MLD	Modulation approach	NMR. IR, DFT	Ethanol Dehydration	54
-	Modulation approach	TGA, N <sub>2</sub> adsorption (BET)	Mechanical Response	55
MLD	Functional linker	EPR, DFT	Diels–Alder and C–H iodination reaction	56
MLD	Synthesis with Ionic liquid	N <sub>2</sub> adsorption (BET), TGA, EA	Meerwein-Ponndorf-Verley reaction	57
MLD	-	Acid-base titration	Degradation of Nerve Agent Simulants	58- 59
-	Modulation approach	TGA, NMR	Aldol reaction	60
-	Metalation	NMR, IR, Raman, XPS, TOF-SIMS	Oxidative dehydrogenation of cyclohexene	61
-	Metalation	XPS. STEM, XANES, DFT	Oxidation of CO	62

MLD: Missing linker defects, MCD: Missing Cluster Defects, LD: Linker dislocation, LSD: Large scale defects (mesopore).

# 2.2 Synthesis

It is still challenging to control the defect distribution and chemical nature of the defect. But some general synthetic routes to create defect in MOFs have been explored and distinguished by Fischer et al. The two main types are: (i) the "de novo" synthesis and (ii) post-synthetic treatment methods.<sup>3</sup> All main general applied procedures to create defects in MOFs are illustrated in Figure 2.3. This thesis is limited to discuss UiO-66 as an example.



**Figure 2.3** Representation of all main procedures to create defects in MOFs. (Reproduced from reference<sup>3</sup>).

#### 2.2.1 De Novo Synthesis

To date, **modulation approach** is the most common method for the formation of defective MOFs. The approach requires to add the extra-large amounts of monocarboxylic acids except the linkers during the MOF synthesis. Initially, the method tries to reduce the crystallization speed of MOFs to form higher degrees of crystallinity in the synthesis procedure. The monocarboxylic acids, so called modulators, impact the equilibrium reaction and compete with the linkers to decrease the speed of crystallization. Meanwhile, the modulator can occupy the coordination sites and form the defect in the synthesis process (Figure 2.4). Many types of monocarboxylic acids were studied, and the typical modulator is formic acid (FA), acetic acid (AA), trifluoroacetic acid (TFA) and difluoroacetic acid (DFA). It is worth noting that UiO-66 is the model system for many cases representing the carboxylate MOFs studies in this approach.



**Figure 2.4** Illustration depicting of modulated stepwise growth of the UiO-66. (Reproduced from reference<sup>24</sup>).

The highly defective UiO-66 was obtained using the modulator approach by Vermoortele et al.<sup>20</sup> The high equivalent TFA and HCl were added in synthesis process and TFA partial substituted the linker. After the treatment at high temperature, the TFA was removed and a large number of open sites were created. The highly defective UiO-66 exhibited a high active catalytic activity for some Lewis acid catalyzed reactions. Shearer et al. demonstrated the systematically influences of different modulators to create defects in UiO-66.<sup>17</sup> They showed that the predominant defect is the cluster defect and it can be altered by changing the concentration and/or acidity of the modulator systematically. The higher concentration and

higher pK<sub>a</sub> of the modulator led to more defects in synthesis. One can explain the observation with an easy logic: more acidic/concentration modulator  $\rightarrow$  higher concentration of deprotonated modulator in solution  $\rightarrow$  more monocarboxylate ligands for the linker to compete with  $\rightarrow$  increased probability of modulator remaining bound to cluster in product  $\rightarrow$  more missing cluster defects. It is obvious that TFA, owing a highest pK<sub>a</sub>, is the most effective modulator to synthesize defective UiO-66.

The **mixed linker approach** employs the different stabilites of the linkers to create the defect. De Vos group presented the defect engineering strategy using the mixed linker approach to generate the missing linker defects in UiO-66.<sup>22</sup> When mixed with trans-1,4-cyclohexane-dicarboxylate (cdc), a labile linker, in the synthesis process, this labile linker could be removed by post-synthetic thermal decomposition to create missing linker defects. The defects are homogeneous distributied because of the homogeneous distribution of the labile linker. The highest defective UiO-66 has up to 4.3 missing linkers per node while maintaining structure integrity and porosity. Zhou group also employs the different stabilities of the mixed linkers to construct the defective hierarchically UiO-66 after post-synthetic thermal treatment.<sup>63</sup> The mixed linker UiO-66 was synthesized with BDC and BDC-NH<sub>2</sub>. Due to the thermolability of the amino linker, the mesopores were generated and ultra-small nanoparticles were dispersing in the pore from the linker thermolysis process.

When the behavior of de modulator is understood, a fast crystallization process can be inspired to create the defects. **The fast crystallization methods** included microwave-assisted synthesis and a high concentration of the precursors. Other species (counter anions) present in the reaction mixture can occupy defect sites by this approach and further increase the functionality of OH groups in MOF-5 and IRMOF-3.<sup>64,65</sup>

#### 2.2.2 Post-synthetic Treatment

In contrast of de novo synthesis, post-synthetic treatments try to introduce the defect after the formation of MOFs. There are several variations which can be employed to remove the component in extreme conditions. Shearer et al. demonstrated that linker vacancies in UiO- 66 increased with **harsh washing** which is probably due to hydrolysis of linkers.<sup>31</sup> Bennett et al., reported that the metal-ligand bonds can be affected in **ball milling** which can then create defects in UiO-66, MIL-140, and MIL-140b.<sup>44</sup> Furthermore, Vermoortele et al., treated MIL-100(Fe) using a **strong acid** such as  $HClO_4$  and TFA to form additional Brønsted acid sites around the Lewis acidic open sites.<sup>66</sup>

**Solvent-assisted ligand exchange** (SALE) is the most established post-synthetic treatment method (Figure 2.5). Briefly, the approach exchanges the linkers in MOFs for modified linkers, e.g., functionalized or longer linkers, or linkers with an incorporated catalyst precursor, immersing in proper solvent. In defect engineering, the compensated ligand on the defect can exchange according to the target application without any change in the linker of the framework. The method can manipulate the functionality of the metal node. Lillerud et al. used different amino acids to replace the formate on vacant sites to increase the CO<sub>2</sub> capture ability of UiO-66.<sup>23</sup> Alexandr group studied thatthe target monocarboxylic species can easily exchange by simple suspension of the MOFs in the desired acid solution in a SALE-like fashion with monocarboxylate group attached at defective sites in UiO-66 and UiO-67.<sup>24</sup> Moreover, the MOF cannot be obtained with the mixed linker approach and can be produced by SALE, e.g., NU-125-HBTC.<sup>67-68</sup>



**Figure 2.5** Pictorial representation of SALE-like process on a UiO-66-type defective Zr-MOF. (Reproduced from reference<sup>24</sup>).

## 2.3 Characterization

The electronic and spatial properties at the defect sites in molecular-level characterization remain a challenge until this day. Therefore, it is still difficult to ascertain fundamental

correlations between the defects and properties of the defective MOFs. At present the research has primarily focused on the synthesis and properties of MOF with defects. In this part, the most useful techniques for the analysis of defective MOFs are highlighted, specifically the characterization for UiO-66.

**Thermogravimetric analysis (TGA)** is one of the most common ways to calculate the number of defects in MOFs. UiO-66 is a typical example of this method, assembled of  $[Zr_6O_4(OH)_4]$ clusters with the maximum of 12 BDC linkers. TGA was carried out in air and showed three resolvable steps of sequential weight loss. The first weight loss occurs in the region 25-150 °C and can be assigned to the removal of solvent molecules (H<sub>2</sub>O and methanol) from the pores. The second weight loss occurs in the temperature range of ca. 150-400 °C, due to the loss of structural water. The final weight loss above 400 °C can be attributed to the weight loss of the linkers or in other words to the structural degradation of the framework. The final residue was identified as ZrO<sub>2</sub>. The final weight loss displays significant differences, as the loss shows a lower than that of the ideal chemical formula  $[Zr_6O_6(bdc)_6]$  of a desolvated and dehydroxylated UiO-66. The difference is attributed to the presence of defects in the framework, which is used to quantify the missing linkers per node. From TGA, it was estimated that the inherently missing linker at each cluster is about 1 to 3 out of 12 linkers in UiO-66 (Figure 2.6).<sup>12</sup> Combined with mass spectrometry (MS), the type and quantity of incorporated guest molecules can be decided, which provides reliable information about the capping molecules on vacancies on the clusters after the creation of the defects. Meanwhile, the thermal stability of the defective MOFs decreases in comparison with their non-defective analogues.<sup>31</sup> This method includes the overall estimation of missing linkers compared to the theoretically equation but does not elucidate for the types of defects and their spatial distribution. In addition, this method can be misled by for instance inconclusive on- and offset temperatures, the formation of nonvolatile carbonaceous products, or incomplete activation procedures.<sup>12</sup>

36



**Figure 2.6** TGA curves of UiO-66 samples in different batches. For all curves, the ordinate axis was normalized to 100 for the solid residual at high temperature, corresponding to  $ZrO_2$ , gray horizontal line. In this scale, the dehydrated, desolvated UiO-66 should have a stoichiometry of  $[ZrO(CO_2)_2(C_6H_4)]$ , corresponding to a normalized weight of 235.7 (black horizontal line). The horizontal bold arrow represents the expected weight loss for an ideal UiO-66 material characterized by 12 BDC linkers per  $[Zr_6O_4(OH)_4]$  octahedron. Experimental curves, reporting a lower weight loss (see vertical arrows with the same line code) at this stage testify of the presence of framework defective: linker vacancies. (Reproduced from reference<sup>12</sup>).

**Potentiometric acid–base titration** is another way to understand the nature and types of the defects in stable MOFs. As we know, potentiometric titration indicates the quantification and differentiation between distinct Brønsted sites and their  $pK_a$  values. Klet et al. introduced this method to quantify the defect sites in several water stable MOFs including UiO-66.<sup>25-26</sup> The three inflection points were displayed in the titration curves, while the only point that should be present in defect-free UiO-66, was assigned to the  $\mu_3$ -OH groups. The other two different  $pK_a$  values were determined in the occurrence of missing linker defects, which matched the acidity of metal-bound hydroxo and aqua ligands (Zr–OH<sub>2</sub>, and Zr–OH) (Figure 2.7). The prerequisite for the measurement is the stability of MOFs in acids and bases. However, potentiometric titrations results reveal several issues, such as inconsistent reproducibility and challenging data interpretation, for similar  $pK_a$  values, flat titration curves, and diffusion limitations.



**Figure 2.7** Left panel: Titration curve (red) and its first derivative (blue) from an UiO-66 sample. Right panel: Missing linker defects as reason for  $M-OH_2$  and M-OH groups. (Reproduced with permission<sup>26</sup>).

The X-ray diffraction patterns provide symmetry and lattice of the periodic arrangement. Even though PXRD can be used to identify the structure, PXRD cannot determine the minor changes of the Bragg diffraction pattern caused by defects. In contrast of the insensitivity to the lighter element of linker in PXRD, the neutron diffraction is sensitive to both organic linkers and heavy metal centers. Hence, the direct structural evidence of the presence of missing-linker defects for UiO-66 was provided by **high-resolution neutron scattering** studies.<sup>13</sup> Using the model of the ideal UiO-66, the structure was refined and the occupancy of the linkers was found to be 91.7% which was well correspondent to one linker missing per node. This was further supported by TGA analysis. Furthermore, **Single-crystal XRD** could provide valuable insight into the defect structures of systems in large single crystals. Lillerud group prepared single crystals of UiO-66 employing benzoic acid as a modulator. The crystal enables to refine the UiO-66 structure and shows an approximate 27% of missing linkers.<sup>14-15</sup> The vacancy was filled with benzoate as a compensating group.

The study by Cliffe et al. published in 2014 describes a rare example.<sup>16</sup> The weak and broad intensity at low 20 degree of PXRD pattern of hafnium-based UiO-66 [UiO-66(Hf)] revealed the existence of nanoregions in the secondary crystalline phase, which has lower symmetry than the *fcu* UiO-66 phase within the same unit cell size. Using combination of several techniques such as **anomalous X-ray scattering and PDF combined with computational modeling**, this phase increased the formation of nanoregions with *reo* topology in UiO-66, which is eight-connected on each node and the ideal formula [Hf<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(bdc)<sub>4</sub>(HCOO)<sub>4</sub>].

The defective sites were filled with formate ligands. This study extends the understanding of PXRD data of defective MOFs.

Shearer and coworkers employed **PXRD**, **BET** (N<sub>2</sub> adsorption), and **NMR** studies (after digesting) to systematically determine the defects in UiO-66.<sup>17</sup> A correlation between the amount of modulators and reo nanoregions in a defective UiO-66 was confirmed by these four quantitative defect descriptors while the effectiveness of these methods was verified simultaneously. Similarly, Atzori et al. elucidated the same correlation of benzoic acid modulation in defective UiO-66 by these methods and further identified the defect structure with vibrational spectroscopies (FTIR and Raman) combined with DFT-simulated spectra.<sup>27</sup> Noted that the scope of laboratory PXRD can only use UiO-66 derivatives because the nanoregions have only been observed in UiO-66.

**Water adsorption** measurement is another accessible and useful technique to indicate the defects in the field of defect engineering in MOFs. Snurr and co-workers simulated the water adsorption behavior of defective UiO-66 by grand canonical Monte Carlo simulations, which illustrated that MOFs have more hydrophilic defects due to the missing linker defects.<sup>28</sup> Then, the defect-induced hydrophilicity was quantitatively reflected by the Henry constant and the saturation water uptake by Dissegna et al.<sup>29</sup> Meanwhile, the amounts of the defect were also evaluated with an activity in a Lewis acid catalyzed cyanosilylation of benzaldehyde reaction.

**FTIR spectroscopy with various probe molecules** is another powerful method to indicate the nature of defects in MOFs, which is the common characterization of the acid-base properties of zeolites. The common probes for the studies on MOFs are CO and CD<sub>3</sub>CN, which have proper peak positions to distinguish the peak of the linkers.<sup>2-3</sup> The amount of Lewis acid sites on the node was indicated using this method using CD<sub>3</sub>CN probe.<sup>20</sup> The number of Lewis-acidic sites increased to 1.1 mmol/g in the TFA modulated UiO-66, which corroborated to the two defects per cluster.

Other than the above discussed characterization techniques, the following techniques are used to determine defects in other kinds of MOFs: scanning electron microscope (SEM),

transmission electron microscopy (TEM), atomic force microscopy (AFM), 3D confocal fluorescence microscopy (CFM), electron paramagnetic resonance (EPR), positron annihilation lifetime spectroscopy (PALS), extended X-ray absorption fine structure (EXAFS), and X-ray absorption near-edge structure (XANES) analyses.<sup>2-3, 69</sup>

## 2.4 Application: Catalysis due to defects

As discussed in chapter 1, MOFs are a good platform to establish structure-property relationships due to the regularly repeating crystal structures. The pores in MOFs have the same dimensions and functionalities, which make them easy to design and tailor for the target catalytic applications. Defect engineering in MOFs disrupts their interior structure and their properties are drastically altered correspondingly. This makes the field drawn extensive attention to manipulate their properties. For example: mass-transport pathways can be altered by linker and/or metal missing defects within the pores. The targeted active sites can be created for the certain catalysis upon defect engineering. Since my thesis is focusing on catalysis, herein I discussed only catalysis using UiO-66 in reference defects, however other applications can be found in some reviews.<sup>2-3, 69-71</sup>

In catalysis, defect sites can be regarded as Lewis acid when capping ligands are removed from the sites or as Brønsted acid sites when nodes are occupied by additional -OH/H<sub>2</sub>O group (Figure 2.8). The existence of defects also provides the coordination vacancy, which can be modified, including linker incorporation and cluster metalation. These two modifications offered two kinds of catalytic sites: (i) organic ligand functionalized catalytic sites and (ii) metalation catalytic sites (Figure 2.9).

40



**Figure 2.8** The Lewis acid and Brønsted acid sites around  $Zr_6$  node of UiO-66. (Reproduced from reference<sup>72</sup>).



**Figure 2.9** Schematic representations of (a) ligand incorporation, (b) 8-connected  $Zr_6$  clusters, and (c) cluster metalation. Structures of (d)  $Zr_6$  clusters after ligand incorporation, (e) 8-connected  $Zr_6$  clusters, and (f)  $Zr_6$  clusters after cluster metalation. (Reproduced from reference<sup>11</sup>).

## 2.4.1 Lewis Acid Catalysis

The presence of Lewis acid sites in UiO-66 is very important for catalytic purposes.<sup>73-74</sup> The number of Lewis acidic sites generally increases by introducing a greater number of defects, which have mainly been used for catalytic applications. De Vos and co-workers reported an approach using trifluoroacetic acid (TFA) as a modulator to create defects, which incorporates trifluoroacetate groups in defective sites as vacancy fillers (Figure 2.10).<sup>20</sup> TFA

was removed easily at 320 °C under vacuum, and thereby it forms Lewis acid sites on the clusters. These sites were validated by TGA and CD<sub>3</sub>CN chemisorption. The amounts of defects are consistent with the catalytic activity of the Lewis acid catalyzed citronellal cyclization reaction. In addition, the catalytic activity of the Lewis acid catalyzed Meerwein-Ponndorf–Verley reaction of 4-tert-butylcyclohexanone (TCH) and isopropanol are also claimed for the presence of more linker vacancies and the corresponding enlarged pore size. While almost no activity was displayed in the parent UiO-66, the defective UiO-66 yielded more than 60 % of TCH after 24 h. Hereafter a theoretical study elucidated the thermodynamic properties of defects formation and their catalytic implications.<sup>21</sup>



**Figure 2.10** Pictorial representation of the removal of TFA grafted at defective sites in UiO-66 upon heating at 320 °C and under vacuum, leading to formation of catalytically active Lewis-acidic coordinatively unsaturated sites for the cyclization of citronellal. Colour code:  $ZrO_8$  polyhedra, light blue;  $ZrO_7$  polyhedra, violet; O, red; C, grey; F, green. H atoms are omitted. (Reproduced from reference<sup>20</sup>).

The catalytic decomposition of phosphate-based nerve agents using defect UiO-66 is another example.<sup>58</sup> Subsequently, the Lewis acidic Zr<sup>IV</sup> ion as active sites were confirmed by experimental and computational method.<sup>75</sup> Further it was demonstrated that the biomimetic constructed Zr cluster coordinated to the nerve agent via the weakening of P–O bonds which make the material more susceptible to hydrolysis.<sup>59</sup> Furthermore, Dissegna et al. investigated the defects of UiO-66 as Lewis catalytic sites in the cyanosilylation of benzaldehyde.<sup>29</sup> This study used water adsorption measurements to characterize defects and correlated well with the catalytic performance.

#### 2.4.2 Brønsted Acid Catalysis

Brønsted acid sites are the main active sites for catalysis but these have not been exploited much in MOFs because of their labile nature.<sup>76</sup> UiO-66 are ideal MOF platforms for the introduction of Brønsted acidic sites due to its superior robustness. Apart from the inherent  $\mu_3$ -OH groups in the clusters as acting as weak Brønsted acids, the Brønsted acid sites can be created by the formation of defects. Whereas the single equivalent point at pH = 7.1 corresponding to pK<sub>a</sub> of 3.44 was assigned to the  $\mu_3$ -OH groups in defect-free UiO-66, three obvious inflection points were observed at pH 5.44, 7.56 and 9.51 and calculated pK<sub>a</sub> values of 3.52, 6.79 and 8.30 by potentiometric acid-base titration.<sup>26</sup> The lowest pK<sub>a</sub> matched with  $\mu_3$ -OH groups and was in agreement with the observation made for UiO-67. This displays a single equivalent point at pH=7.1 and calculated pK<sub>a</sub> of 3.44. The other two remaining pK<sub>a</sub> values were attributed to the Zr–OH<sub>2</sub> (6.79) and Zr–OH (8.30) protons present, which were the capping species at defect sites. These defects are regarded as Brønsted acid sites. The catalytic activity of this material was evaluated for the epoxide ring-opening reaction with alcohol.<sup>25</sup> The number of defects was correlated quantitatively with the catalytic activity of the material.

## 2.4.3 Catalysis upon Functionalized Ligand Incorporation

Inspired by the solvent-assisted ligand incorporation (SALI) method,<sup>77</sup> the defect sites can be modified and functionalized by the incorporation of suitable ligands in UiO-66. The vacancy creating by a defect is displaceable. Therefore, the existing ligands can easily be replaced by the targeted linker using linker incorporation method for various applications. Gutov et al. revealed that the defect sites in UiO-66 and UiO-67 can be functionalized and "healed" with a monocarboxylic species.<sup>24</sup> Subsequently, different amino acids were attached to the defect sites of UiO-66 post synthetically to enhance CO<sub>2</sub> uptake.<sup>23</sup> Motivated by this, I introduced L-proline as chiral modulator via direct modulated synthesis to obtain a simple chiral catalyst based UiO-66, which showed good reactivity and diastereoselectivity in the Aldol addition reaction. The details are described in Chapter 3.

#### 2.4.4 Catalysis by Cluster Metalation

Similar to ligand incorporation,  $Zr_6$  cluster acts as acid in cluster metalation, conjugated with metal cation as a base to introduce extra catalytic sites. The heterometals was grafted on the defective Zr-cluster which appeared as functionalized catalytic sites (Figure 2.9). Nguyen et al. demonstrated that UiO-66 metallated with a V<sup>V</sup> ion converts to VUiO-66, which exhibited higher selectivity in the vapor-phase oxidative dehydrogenation of cyclohexene to benzene under low-conversion conditions (Figure 2.11).<sup>61</sup> VUiO-66 maintained the structure after catalysis.



**Figure 2.11** Oxidative dehydrogenation of cyclohexene to benzene using V-UiO-66 as a catalyst. (Reproduced from reference<sup>6</sup>).

## 2.5 Aim of the thesis

The inherent or modification to create defects is an important strategy to incorporate active sites upon the functionalization of UiO-66 by pre-/post-synthetic methods. Apart from the Lewis and Brønsted acidic sites, the functionalized ligands can also be incorporated on defect sites and these defects create unlimited potential of UiO-66 in heterogeneous catalysis.

The modulation approach is the most common method and several typical monocarboxylic acids were used to create and tune the defects. Therefore, in chapter 3, we employed Lproline as a functional modulator to incorporate chiral active site into MOFs. A systematic study was conducted to explore the effect of the synthesis temperature on the amount of Lproline incorporated in Zr-MOFs. As chirality is introduced into these frameworks, we consequently explored their use as chiral catalysts for asymmetric reactions. In general, the stability of UiO-66 compromises with the defect generation. Introduction of hemilabile ligands in UiO-66 improved the stability with defect formation. The hemilabile ligands contain next to the carboxylate group an additional but weaker coordinating functional group (e.g. sulfonate groups). In chapter 4, synthesis, characterization and catalytic reactivity of a hemilabile UiO-66 MOF (HI-UiO-66), using BDC and 4-sulfobenzoic acid were compared with pristine UiO-66. Because of the weak coordination mode of the sulfonate group, a simple post-synthetic treatment in  $H_2SO_4$  resulted in a total of three BDC missing linkers per formula unit (HI-UiO-66-SO<sub>4</sub>), which is the theoretical maximum of missing linker defects in UiO-66. Importantly, this highly defective HI-UiO-66-SO<sub>4</sub> is more stable than HI-UiO-66 and UiO-66. Detailed modelling of this structure supported the remarkable supplementary stabilization. Furthermore, the catalytic activity of these three MOFs in isomerization of  $\alpha$ -pinene oxide (which differentiates the Brønsted and Lewis acid sites) were explored. HI-UiO-66-SO<sub>4</sub> and HI-UiO-66 showed enhanced Lewis acid catalysis and higher activity and selectivity in comparison to the pristine UiO-66. Finally, in chapter 5, important results obtained in this thesis and future developments in this field are discussed.

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# Chapter 3 L-proline Modulated Zirconium Metal Organic Frameworks: simple chiral catalysts for the aldol addition reaction



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#### Abstract

Three L-proline modulated zirconium-based MOFs denoted as UiO-66, Zr-NDC (NDC= 2,6-Naphthalenedicarboxylate) and UiO-67 were synthesized, characterized and explored as heterogeneous catalyst in diastereoselective aldol addition reactions between 4-nitrobenzaldehyde and linear/cyclic ketones. Upon L-proline modulation, chirality was introduced into these Zr-MOFs which were consequently explored as chiral catalysts for asymmetric reactions. A systematic study was conducted to look into the effect of the synthesis temperature on the modulation in each Zr-MOF. The modulated UiO-66 material synthesized at 120 °C exhibited full conversion and a good diastereoselectivity whereas the homogeneous L-proline catalyst showed only 61% conversion and a reversed diastereoselectivity. The catalyst exhibited no leaching of the catalytically active species and was reused for at least three additional cycles. The observed high catalytic activity is a result of the electron withdrawing nature of the Zr-node coordinated to L-proline.

# 3.1 Introduction

In catalysis, both homogeneous and heterogeneous catalysts have their own advantages and disadvantages. Homogeneous catalysts exhibit high catalytic activity and selectivity but are difficult to recover and reuse. Heterogeneous catalysts are easy to recover and reuse, but it is difficult to identify the active site that is responsible for the catalytic activity. Researchers are trying to bridge this gap between homogeneous and heterogeneous catalysis by designing different kinds of supports having active catalytic binding sites.<sup>1-2</sup> Among them, MOFs have shown great potential because they display many properties of an ideal heterogeneous catalyst such as crystallinity, active-site uniformity, high surface area, and permanent porosity.<sup>3-6</sup> Therefore, MOFs are intensively explored for a variety of catalytic applications,<sup>6-7</sup> including hydrogenations, oxidation reactions and asymmetric catalysis. Generally, three approaches are used to design catalytic active MOFs, (i) MOFs having unsaturated metal sites, (ii) post-synthetic modifications of linker/functional organic sites, (iii) encapsulation of transition metal complexes or metal nanoparticles into the channels/cages.<sup>6</sup> Specifically, for chiral catalysis, MOFs are integrated with chiral ligands, by either direct grafting them onto the linker or post-synthetic modification of the achiral linker. However, functionalization of MOFs by grafting or post synthetic modifications of the linkers demands complex reaction protocols, expensive multistep synthesis and several instrumental methods for their characterization.

Asymmetric aldol reactions are very important C-C coupling reactions in organic chemistry and are generally catalyzed by proline as a homogenous catalyst.<sup>8-9</sup> Recently, proline functionalized MOFs were explored for such applications.<sup>10-15</sup> For example, Kaskel et al.,<sup>10</sup> reported proline functionalized Zr-MOFs (UiO-67 and UiO-68) by pre-synthetic modification of the organic linker and achieved good diastereoselectivity after 10 days of reaction. Subsequently, the same group reported another L-proline functionalized zirconium-MOF<sup>16</sup>, denoted as DUT-67 as heterogeneous catalyst for asymmetric Michael addition reaction in which the parent monocarboxylic ligand was exchanged with L-proline after five days of treatment.

55

Nowadays, the modulation synthesis has become a common approach for defect engineering in MOFs.<sup>17</sup> Modulated MOFs to create defect sites were used in heterogeneous Brønsted<sup>18</sup> and Lewis acid<sup>19</sup> catalysis. Recently, Lillerud et al. introduced a "functionalized modulator" – a monocarboxylic acid having other functionalized groups - and exploited post-synthetic ligand exchange for CO<sub>2</sub> adsorption.<sup>20</sup> Therefore, designing functionalized modulators presents a new opportunity to create highly active and functionalized low-cost catalysts with less effort.

In this work, we synthesized three L-proline functionalized modulated Zirconium MOFs denoted as UiO-66, Zr-NDC and UiO-67 at three different synthesis temperatures and explored their catalytic activity in diastereoselective aldol addition reactions. In these Zr-MOFs, L-proline is not only used as a modulator but is also employed to introduce the chiral active site. Moreover, a systematic study was conducted to examine the influence of the temperature on the number of defects and the density of modulator present in the framework.

### 3.2 Experimental details

#### 3.2.1 General Procedures

All chemicals were purchased from Sigma Aldrich, ABCR, TCI Europe and used without further purification. X-ray powder diffraction (XRPD) patterns were collected on an ARL X'TRA X-ray diffractometer operating at 40 kV/40 mA using Cu-K $\alpha$  radiation ( $\lambda$  = 0.15418 nm) and a solid-state detector. Nitrogen adsorption experiments were carried out at 77 K using a Belsorp-mini II gas analyzer. Prior to adsorption measurements, the samples were activated under vacuum at 150 °C for 16 h to remove the adsorbed solvent. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 449 F3 Jupiter in a temperature range of 20-600 °C in air and a heating rate of 5 °C /min. For <sup>1</sup>H NMR, the samples were dissolved in a heated mixture of D<sub>2</sub>SO<sub>4</sub> and [D<sub>6</sub>] DMSO (1:6). Spectra were recorded on a Bruker 300 MHz ADVANCE spectrometer.

#### **3.2.2** Synthesis of the catalysts

The proline modulated Zr-MOFs were synthesized following the procedure of Gutov et al. and Marshall et al.<sup>21-22</sup> Briefly, ZrO<sub>2</sub>Cl<sub>2</sub>·8H<sub>2</sub>O (485 mg, 1.51 mmol), the dicarboxylic acid (251 mg, 1.51 mmol), HCl (0.625 mL, 7.55 mmol) and L-proline (866 mg, 7.55 mmol) were dissolved in 20 mL DMF in an ultrasonic bath for 30 min. The resulting mixture was placed in a Teflon-lined autoclave at 150 °C, 120 °C or 70 °C for 4 days, and successively cooled to room temperature. The solid was collected by filtration, subsequently stirred in DMF at 70 °C for 24 h followed by stirring it in methanol for 24 h to remove unreacted linker, modulator and DMF. The final purified product was dried under vacuum at 65 °C before use in catalysis.

#### **3.2.3** General procedure for the catalytic reactions

The catalysts (20 mol% regarding the amount of proline groups with respect to the 4nitrobenzaldehyde concentration) were placed in a 15 mL screwed glass vial under vacuum at 150 °C for 16 h. Afterwards, a mixture of 4-nitrobenzaldehyde (0.03 mmol/mL<sup>-1</sup>), methyl 4-nitrobenzoate (internal standard, 0.022 mmol/mL<sup>-1</sup>), acetone (50 vol.%) and a solvent (50 vol.%) were added and stirred at 20 or 45 °C for 24 h. The conversion and selectivity were determined by means of HPLC (Shimadzu LC-20AT) having a C18 column equipped with an SPD-M20A UV detector and LC-Solution software. The HPLC apparatus was operated at a column temperature of 30 °C by using a gradient method with water (0.1 % trifluoroacetic acid) and acetonitrile (HPLC grade) as solvents. In this gradient method, the volumetric percentage of acetonitrile was changed from 30 to 62 % over a period of 7 min. The chirality of the aldol products was analyzed by chiral HPLC (Chiralpak AS-H; hexane/ethanol, 90:10). Besides acetone also two other substrates were examined. For these substrates 4nitrobenzaldehyde (0.3 mmol) and cyclohexanone (3 mmol) or cyclooctanone (3 mmol) was placed in a 15 mL screwed glass vial and stirred in 1.5 mL solvent at 45 °C for 24h. The conversion and diastereoselectivity were determined using the same non-chiral column under equal conditions. Enantioselectivities were measured by chiral HPLC (LUX<sup>®</sup> 5 µm Amylose-1, 250x4.6 mm, hexane/iPrOH, 91:9). After the first run, the catalyst was removed by filtration, repeatedly washed with acetone and dried at 150 °C under vacuum before reuse in the subsequent runs.

## 3.3 Results and discussion

#### 3.3.1 Effect of temperature on the synthesis of L-proline modulated Zr-MOFs

Three zirconium based MOFs, UiO-66<sup>23</sup>, Zr-NDC<sup>24</sup> and UiO-67<sup>25</sup>, were synthesized in the presence of L-proline as modulator. Each MOF was synthesized at three different temperatures (70 °C, 120 °C and 150 °C) to explore the temperature effect on the density of defects in the resulting framework (Scheme 3.1). The experimentally obtained ratio of L-proline and linker in each Zr-MOF was calculated by means of <sup>1</sup>H NMR analysis by digesting the sample in a mixture of D<sub>2</sub>SO4 and DMSO (Figure A6-A8, Page 103). Furthermore, the number of defects was calculated using TGA analysis (Table 3.1, Figure 3.3, Figure A3-A5, see appendix A, Page 102) in accordance to Lillerud's method.<sup>26</sup> The powder X-ray diffraction patterns of the obtained L-proline modulated Zr-MOFs corresponds well with the non-modulated Zr-MOFs reported in the literature demonstrating that the crystalline structure is preserved during the modulation approach (Figure 3.1, Figure A1, Page 101). The nitrogen adsorption analysis confirmed that the porosities of these materials depend on the densities of defects and modulator as can be seen from Figure 3.2, Figure A2and Figure A3 (Page 102).



Scheme 3.1. Synthesis of UiO-66 using L-proline as modulator.

UiO-66-LP-120 and UiO-66-LP-150 (LP = L-proline) exhibited a similar Langmuir surface area, whereas the Langmuir surface area of the UiO-66-LP-70 is slightly higher (Table 3.1). As shown in Table 3.1, UiO-66-LP-120 and UiO-66-LP-150 have an equal amount of missing BDC linkers and a quasi-similar number of L-proline modulators whereas UiO-66-LP-70 has a

higher number of missing BDC linkers which results into a higher surface area. Furthermore, one can see an increase of the ratio of modulator and linker with decreasing synthesis temperature, whereas a similar trend is observed for the number of missing linkers.



Figure 3.1 PXRD pattern of the UiO-66-LP materials synthesized at 150°C, 120 °C and 70°C respectively.



**Figure 3.2** Nitrogen adsorption isotherms of the UiO-66-LP materials synthesized at 150°C, 120 °C and 70°C respectively.



Figure 3.3 TGA results of the UiO-66-LP synthesized 150 °C, 120 °C and 70°C respectively.

Similarly, a series of Zr-NDC-LP MOFs were obtained at three different temperatures. Based on the defect analysis, it was found that Zr-NDC-LP-70 has the largest number of missing NDC linkers and highest amount of defects (Table 3.1). As can be seen from Table 3.1, the number of missing linkers and ratio of modulator and linker increased with decreasing temperature which was also observed for the UiO-66-LPs materials. In contrast to the UiO-66-LP and UiO-67-LP materials which showed an increase in surface area when the synthesis temperature was decreased, the Zr-NDC-LP materials show the opposite (Figure A2, Page 101). More specifically, here a decrease in surface area was noted when the synthesis temperature was lowered. This is probably due to the fact that the modulator is preferentially introduced into the framework in comparison to the organic linker. This not only results in a reduced surface area but also in a less crystalline material (Figure A1, Page101).

	150 °C			120 °C			70 °C		
Zr-MOFs	S <sub>Langmuir</sub> (m <sup>2</sup> g <sup>-1</sup> )	Mod/L <sup>a</sup>	Number of MLD (per formula unit) <sup>b</sup>	S <sub>Langmuir</sub> (m <sup>2</sup> g <sup>-1</sup> )	Mod/L <sup>a</sup>	Number of MLD (per formula unit ) <sup>b</sup>	S <sub>Langmuir</sub> (m <sup>2</sup> g <sup>-1</sup> )	Mod/L <sup>a</sup>	Number of MLD (per formula unit) <sup>b</sup>
UiO-66-LP	1572	0.77	2	1567	0.82	2	1850	0.85	2.7
Zr-NDC-LP	1625	0.51	1.5	1050	0.67	2.3	900	0.94	3

Table 3.1 Structural properties of the three Zr-MOFs and the obtained number of defects at various synthesis temperatures.

<sup>a</sup>defined as Mod/L (mol/mol) by NMR; <sup>b</sup>calculated by TGA according to Lillerud's work.<sup>26</sup>

1806

(meso)

1607

(meso)

0.51

0.8

UiO-67-LP

0.57

1

2800

0

0

For the synthesized UiO-67-LP MOFs, structural changes were noticed along the entire temperature range from low to high (Table 3.1). Although, this set of materials was synthesized similarly to UiO-66-LP and Zr-NDC-LP. UiO-67-LP-70 was found to be microporous in nature whereas UiO-67-LP-120 and UiO-67-LP-150 have hierarchical pores (Figure A3, Page102). From the PXRD analysis, all three UiO-67-LPs maintained the original UiO-67 structure and the observed shoulder peak coming off of the main peak in the case of both UiO-67-LP-150 and UiO-67-LP-120 suggests structural changes from microporous to mesoporous (Figure A1, Page101). The decrease in surface area at higher temperature is due to the competition of L-proline with H<sub>2</sub>BPDC linkers that form mesopores by linking micropores and replacing the linker. A similar trend is observed in terms of the ratio of modulator to linker and the number of missing linkers, except the UiO-67-LP-70. From the <sup>1</sup>H NMR and TGA analysis (Table 3.1, Figure A5, Figure A8, Page 103), it was found that, in contrast to the UiO-66-LP and the Zr-NDC-LP MOFs, UiO-67-LP-70 has no defects present in the structure. A similar observation was noted in the reported modulated UiO-67 MOF.<sup>21</sup> From both observations one can conclude that 70 °C is the best temperature to obtain an ideal crystalline UiO-67 MOF structure probably because the linker has low solubility at the temperature.

Based on these observations, one can conclude that the use of modulators at lower synthesis temperatures have competitive advantages in comparison to the organic linker. So, in general, more defects and relative high densities of modulators were obtained at low synthesis temperature.

#### 3.3.2 Evaluation of the modulated Zr-MOFs as catalysts in the aldol reaction

In general, defects in Zr-MOFs appear either when linkers *or* Zr clusters *or* both are missing in the framework. This causes an open coordination site around each SBU. These open sites can be occupied by the modulator or by decomposed products of the solvent used in the reactions (basically decomposed DMF). However, due to charge compensation and its coordination ability, the modulator has a higher coordination probability than the others. At a low temperature, the modulator is more likely to coordinate on the zirconium metal node and has a better chance to behave as Brønsted and Lewis acid catalysts. Several studies already demonstrated that a modulator is a compensating/capping ligand coordinated to the metal node which was confirmed through ion exchange.<sup>21, 27</sup> Based on this knowledge, we introduced L-proline to create an active chiral site for asymmetric aldol reactions.

The catalytic activity of L-proline modulated Zr-MOFs were explored in the aldol reaction between 4-nitrobenzaldehyde and acetone at room temperature. Table 3.2 shows the catalytic performance of the L-proline modulated Zr-MOFs in this reaction. As expected, two aldol products, the  $\beta$ -hydroxy carbonyl compound (1) and  $\alpha$ ,  $\beta$ -unsaturated carbonyl compound (2) were obtained. Amongst the several modulated Zr-MOFs, the UiO-66-LP materials exhibit the best catalytic activity (Table 3.2). The UiO-66-LP-70 has the highest number of defects but has the lowest reactivity. UiO-66-LP-120 and UiO-66-LP-150 have a similar reactivity with high conversion and selectivity for 1. To verify the reason for this difference in catalytic reactivity, all the catalysts were characterized by means of PXRD and nitrogen adsorption after the catalytic reaction. As can be seen from Figure A9, the UiO-66-LP-150 and UiO-66-LP-120 material remained intact after this reaction. However, the UiO-66-LP-70 lost its structure and surface area. This is probably due to the fact that the latter material has the largest number of defects and missing linkers. <sup>19, 26, 28</sup> Also the Zr-NDC and UiO-67 showed little stability during the catalysis which might be due to the defects present in the structure (Figure A10-A12, Page 105).<sup>29</sup> The UiO-67-LP-70 that is stable and does not contain L-proline in its structure also showed a very low conversion.

Upon changing the solvent, it was found that in acetone the UiO-66-LP-120 shows the highest conversion (Table A2, Page106). Although a better selectivity is observed in pure water, the conversion is quite low. Complete conversion was obtained in pure acetone after 24 h with a selectivity of 89%. A few drops of water inhibited the formation of the dehydration product with a selectivity of 99% for **1** but the conversion itself was decreased to 89%. This is because acetone can facilitate the transport of substrates and products in the framework more efficiently and stabilizes the reaction intermediates via H-bonding interaction.

62

$O_2 N \xrightarrow{CHO} O_2 N \xrightarrow{CHO} O_2 N \xrightarrow{CHO} O_2 N \xrightarrow{O} O_2 O_2 N \xrightarrow{O} O_2 O_2 O_2 O_2 O_2 O_2 O_2 O_2 O_2 O_2$						
Catalyst	T(°C)	t(h)	Conversion (%)	Selectivity <sup>a</sup> (%)		
L-proline	20	24	99	87		
UiO-66-LP-150	20	24	60	96		
UiO-66-LP-120	20	24	62	96		
UiO-66-LP-70	20	24	4	75		
Zr-NDC-LP-150	20	24	8	89		
Zr-NDC-LP-120	20	24	3	70		
Zr-NDC-LP-70	20	24	2	70		
UiO-67-LP-150	20	24	6	83		
UiO-67-LP-120	20	24	3	85		
UiO-67-LP-70	20	24	3	79		

Table 3.2 Catalytic studies for the aldol addition of 4-nitrobenzaldehyde and acetone using Zr basedMOF catalysts.

Reaction conditions: 20 °C, 0.3 mmol of 4-nitrobenzaldehyde, 10 mL acetone, 20 mol % catalyst (related to the proline amount in the material); <sup>a</sup>towards aldol product 1.

After screening the aldol reaction with L-proline modulated Zr-MOFs, it was confirmed that UiO-66-LP-120 and UiO-66-LP-150 have the best catalytic activity. Therefore, the reaction protocol using UiO-66-LP-120 was extended to asymmetric aldol reactions using 4-nitrobenzaldehyde and cyclohexanone as substrate. Theoretically, four different aldol products including two *syn* and two *anti* can be expected from this reaction. Therefore, two pairs of diastereoisomers: *syn* and *anti*-products were analyzed by HPLC analysis. During the solvent screening, it was found that DCM offered the best substrate conversion whereas methanol gave the highest diastereoselectivity (de<sub>syn</sub> = 64) (Table 3.3).Notably, the obtained diastereoselectivity is opposite to that observed using the homogenous L-proline as catalyst.<sup>8</sup>

$O_{2}N \xrightarrow{O} O_{2}N \xrightarrow{O} O_{2$						
Solvent	t(h)	Conversion (%)	dr (syn:anti)	de <sub>syn</sub> (%)	TOF (S <sup>-1</sup> ) <sup>a</sup>	
L-proline DMSO	24(72)	53(61)	50:50(42:58)	0(-16)	0.0013	
Hexane	24	70	60:40	20	-	
chloroform	24	94	66:34	32	-	
DCM	24	100	68:32	36	0.00056	
DMSO	24	22	77:23	54	-	
Methanol	24	95	82:18	64	0.00046	

Table 3.3 Solvent screening for diastereoselective aldol Reaction.

Reaction conditions: 45 °C, 0.3 mmol of 4-nitrobenzaldehyde, 3 mmol cyclohexanone, 1.5 mL solvent, 20 mol % catalyst (related to the proline amount in the material). <sup>a</sup>TOF calculated at 30 min.

The use of a polar solvent is the best medium to achieve optimum reactivity because it facilitates substrate/product transport and stabilizes the enamine intermediates by H-bonding interaction. Penhoat et al. studied the strong influence of Lewis acid with L-proline in an aldol reaction and envisaged the formation of a catalytic active complex based on Zn<sup>2+</sup> coordinated with proline.<sup>30</sup> We assume that the good catalytic performance of the modulated Zr-MOF materials presented in this study can be assigned to the beneficial formation of the L-proline intermediate state which is produced due to the electron withdrawing nature of the Zr node (Figure 3.4). Furthermore, to explore the influence of the pore confinement, cyclooctanone was used as substrate. This substrate was chosen because it has a larger kinetic diameter than the pore size of UiO-66. The catalytic activity of UiO-66-LP-120 using cyclooctanone as substrate was low in comparison to that of using cyclohexanone as substrate. This activity could be assigned to the active sites that are located on the outer surface of the catalyst.



Figure 3.4 Proposed mechanism of aldol reaction using UiO-66-LP-120.

Additionally, the catalyst's reusability was explored by recovering the catalyst from the reaction mixture and reusing it in three additional cycles (Figure 3.5b, Figure A13, Page 107). During these successive cycles, a slight decrease in the conversion was noticed while the diastereoselectivity remained the same. From the PXRD measurements of the recovered catalyst, it was confirmed that UiO-66-LP-120 retained its structural framework even after three reaction cycles (Figure A14-A15, Page108). This ruled out the possibility of the framework's decomposition. Nitrogen adsorption analysis of the recovered catalyst showed only a marginal decrease in the porosity suggesting a slight pore blocking or blocking of the catalytic site (Figure A14-A15, Page108).



**Figure 3.5** (a) Hot filtration experiment and (b) recycling experiments using UiO-66-LP-120 and cyclohexanone as substrate.

To further verify the leaching of proline, a hot filtration test was performed after 3 h of reaction. As shown in Figure 3.5a, the catalytic reaction did not proceed even after 48 h. This ruled out the leaching of proline species during the catalysis. This result further supports that the decrease in catalytic activity during the additional runs might be due to pore blocking of the active site around the SBU.

In addition, a comparison was made between our proline modulated Zr-MOFs and the ones reported in literature (see Table A4, Page 107). Although it is hard to give a fair comparison because different reaction conditions were used, one can see from this table that the modulated Zr-MOFs presented in this study displayed the highest catalytic activity in comparison to the reported proline functionalized MOFs at present<sup>10-15</sup>. The UiO-66-LP-120 material used in this study exhibited approximately full conversion after 24 hours of reaction time for the substrate cyclohexanone whereas the best performing catalyst reported in

literature, denoted as UiO-68-NHPro, exhibited full conversion after 10 days of reaction having a similar diastereoselectivity as our best performing catalyst. Furthermore, in comparison to the homogeneous counterpart which only exhibited a conversion of 61% using cyclohexanone as substrate, the L-proline modulated Zr-MOFs showed a complete conversion (Figure A16, Page 109).

# 3.4 Conclusions

In summary, three Zr-MOFs were synthesized using L-proline as a modulator. The resulting Zr-MOFs were used as heterogeneous catalysts in a diastereoselective aldol addition reaction. The results presented in this work demonstrate that a modulator offers a competitive advantage over the linker during the MOF construction at low synthesis temperature as more defects and high densities of modulators were obtained at low temperature. Upon L-proline modulation, a chiral active site was introduced into the Zr node making it a chiral catalyst for asymmetric reaction. The modulated Zr-MOFs showed high catalytic activity and good diastereoselectivity in aldol reaction in a short reaction time. The facile and inexpensive synthesis of modulated MOFs with proper functionalized groups on the modulator is a fascinating field of research which directly bridges homogenous and heterogeneous catalysis.

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# Chapter 4 Engineering an ultra-stable 6-fold coordinated UiO-66 - The role of the hemilabile linker



The results of this chapter are under revision in J. Am. Chem. Soc.:

Feng, X.; Hajek, J; Jena, H. S.; Wang, G.; Van Speybroeck, V; Leus, K.; Van Der Voort, P., Engineering an ultra-stable UiO-66 with the highest possible number of defects, the role of the hemilabile linker.

#### ABSTRACT

The stability of Metal-Organic Frameworks (MOFs) typically decreases with defect generation, limiting the number of defects that can be created in e.g. UiO-66 and hampering catalytic and other applications. Engineering stable MOFs with an optimal number of defects remains a challenge. Herein, we used a hemilabile (HI) linker to create up to 6 defects per cluster in UiO-66 and explored the remarkable stability and catalytic application using experimental and modelling studies. We have synthesized hemilabile UiO-66 (HI-UiO-66) materials using terephthalic acid as linker and 4-sulfobenzoic acid as hemila-bile linker. The 4-sulfobenzoic acid acts not only as a modulator to create defects, but also as a co-ligand to strengthen the stability of the resulting defective framework. Furthermore, upon a postsynthetic treatment in H<sub>2</sub>SO<sub>4</sub> taking advantage of the weak coordination ability of hemilabile ligands, the number of defects increases to the theoretical maximum of three missing BDC linkers, leaving the Zr-nodes 6-fold coordinated. Remarkably, the thermal stability of the materials further increases upon this treatment. Periodic Density Functional Theory calculations confirm that the hemilabile ligand strengthens this highly defective structure by several interactions. Finally, the catalytic activity of the obtained materials is evaluated in the acid-catalyzed isomerization of  $\alpha$ -pinene oxide. This reaction is particularly sensitive to the ratio of Brønsted and Lewis acid sites in the catalyst. In comparison to the pristine UiO-66, which mainly possesses Brønsted acid sites, the HI-UiO-66 and the post-synthetically treated HI-UiO-66 structures exhibited a higher Lewis acidity and an enhanced activity and selectivity. The result made the acidity of defects understood.

# 4.1 Introduction

UiO-66 is a prototypical MOF in defect engineering due to its high stability. <sup>1-4</sup> The most common approach of defect engineering is the modulation synthesis approach, in which a large amount of monocarboxylic acid is employed. These monocarboxylic acid modulators have a mono coordination mode to manipulate the synthesis process and to create the defects.<sup>3, 5-7</sup> In catalysis, the defective UiO-66 (using trifluoroacetic acid as modulator) has already shown to have a high reactivity in the Meerwein reduction of 4-tert-butylcyclohexanone with isopropanol.<sup>8</sup> In the previous chapter, we have used L-proline as a chiral modulator for the synthesis of UiO-type of MOF structures which showed an excellent reactivity in the diastereoselective aldol reaction.<sup>9</sup> Nevertheless, in all cases, the thermal stability of the framework is reduced upon the generation of defects<sup>3, 10-11</sup> and the amounts of defect were limited. Atzori et al. demonstrated that the maximum number of defects is 4.4 per cluster using benzoic acid in UiO-66.<sup>12</sup> Bueken et al. showed that 4.3 missing linkers per cluster is the maximum, because UiO-66 was no longer structurally stable when more defects were attempted.<sup>13</sup>

Apart from monocarboxylic acid modulators, *hemilabile* ligands, having next to the carboxylate group an additional but weaker coordinating functional group (e.g. sulfonate groups), can be used in the synthesis of carboxylic based MOFs (Figure 4.1). The concept on the use of hemilabile ligands, introduced by Morris et al., is based on a multidentate ligand that contains donor groups that have different binding properties in solution-state coordination complexes.<sup>14</sup> For example, the hemilabile MOF, denoted as Cu-SIP-3, prepared by Xiao et al. showed an ultra-selective low pressure nitric oxide adsorption upon the reversible phase transformation induced by the change in the coordination of sulfonate group when the water is removed.<sup>15</sup> McHugh et al. also demonstrated that a copper paddlewheel MOF exhibited good hydrolytic stability due to the presence of a hemilabile linker.<sup>16</sup> However, until now hemilabile linkers have only been used to explore the selective gas adsorption, separation, dielectric and other physical properties of MOFs.<sup>14, 17-18</sup>

Herein, we report the synthesis and characterization of hemilabile UiO-66 (HI-UiO-66) materials using BDC and 4-sulfobenzoic acid in a 1:1 ratio to explore the defect and stability properties (Figure 4.1). Because of the inherent weak coordination mode of the sulfonate group, a simple post-synthetic treatment in H<sub>2</sub>SO<sub>4</sub> was carried out, which resulted in a total of three BDC missing linkers per formula unit (HI-UiO-66-SO<sub>4</sub>). This is the theoretical limit to still maintain a three-dimensional UiO-66 network.<sup>3, 13</sup> Importantly, the thermal stability of the three MOFs follow the order UiO-66 < HI-UiO-66 < HI-UiO-66-SO<sub>4</sub>, which confirms that the material with the highest number of defects is also the most stable one. Furthermore, the catalytic properties of the obtained materials were evaluated in the isomerization of  $\alpha$ -pinene oxide. In comparison to the pristine UiO-66, which showed a moderate activity of 40% and low selectivity at 0.5h, full conversion and an enhanced selectivity is observed for the HI-UiO-66-SO<sub>4</sub> materials.



**Figure 4.1** Schematic representation of the UiO-66 and HI-UiO-66 materials with possible configurations of the bricks that give rise to coordinatively unsaturated Zr sites.

### 4.2 Experimental Section

#### 4.2.1 Synthesis of the catalysts

The synthesis procedure is based on a modified procedure of Biswas et al.<sup>19</sup>  $ZrO_2Cl_2 \cdot 8H_2O$  (1 g, 3.1 mmol), terephthalic acid (H<sub>2</sub>BDC) (515 mg, 3.1 mmol) and 4-sulfobenzoic acid potassium salt (745 mg, 3.1 mmol) were dissolved in a mixture of formic acid (12 mL, 310 mmol) and DMA (30 mL) in an ultrasonic bath for 30 min. The resulting mixture was placed in a Teflon-lined autoclave at 150 °C for 24 h, and subsequently cooled to room temperature. The solid was collected by filtration and washed with DMF and methanol, subsequently stirred in DMF at 70 °C (24 h) and methanol under ambient conditions (24 h) to remove unreacted linker, modulator and DMF. The final purified product was dried under vacuum at 65 °C.

#### 4.2.2 Postsynthesis treatment

HI-UiO-66  $H_2SO_4/K_2SO_4/HCI/H_2O$ : 150 mg catalyst was treated in 20 mL  $H_2SO_4(0.1 \text{ M H}^+)$ , HCl (0.1 M  $H^+$ ),  $K_2SO_4$  (0.05 M) or  $H_2O$ . The suspension of the solid was kept under stirring for 24h at room temperature. The resulting solid was filtered off and thoroughly washed multiple times with water until neutral pH was obtained and consequently stirred with methanol for 24h. The precipitate was filtered and dried under vacuum at 65 °C.

#### 4.2.3 Catalytic procedure

In a typical catalytic test, 50 mg catalyst (pre-activated for 16h at 150°C under vacuum) was suspended in 5 mL toluene (anhydrous) in a 25mL round bottom flask. Hereafter, 130 mg  $\alpha$ -pinene oxide (0.86 mmol) and 146 mg dodecane (0.86 mmol) as an internal standard were added. This mixture was magnetically stirred at 70°C. Aliquots were taken from the reaction mixture by syringe at indicated time intervals, filtered with a nylon filter to remove catalyst particles and diluted with toluene. The products were separated by GC and identified by GC-MS. During a recycling experiment, the catalyst was separated by filtration, washed with

toluene and methanol and dried under vacuum at 150 °C and then reused. For the filtration tests, the catalyst was filtered off and the supernatant was reacted further in another vial.

#### 4.2.4 Computational methodology

All calculations on the 2-bricks unit cell of studied UiO-66 type materials were performed using the periodic Vienna Ab Initio Simulation Package (VASP code) with density functional theory (DFT) method to represent the crystal environment.<sup>20-24</sup> We applied the projector augmented wave (PAW) approach<sup>25</sup> and the Brillouin zone was sampled by the  $\Gamma$ -point at PBE level of theory<sup>26</sup> including Grimme-D3 dispersion corrections.<sup>27-28</sup> The kinetic energy cutoff for the plane waves was 700 eV, and the convergence threshold for the electronic self-consistent field (SCF) calculations was set to 10<sup>-5</sup>eV, moreover a Gaussian smearing of 0.025 eV was included to improve convergence.

# 4.3 Results and Discussion

#### 4.3.1 PSBA as a hemilabile linker to create defects

The UiO-66 materials were synthesized according to a slightly modified procedure published elsewhere.<sup>19</sup> For the hemilabile UiO-66 (HI-UiO-66), we used a 1:1 ratio of *p*-sulfobenzoic acid potassium salt (PSBA) and BDC. The molar ratios of PSBA and terephthalic acid were mixed in N, N-dimethylacetamide (DMA) with the addition of 100 equivalents of formic acid. Subsequently, the metal salt was added, and the mixtures were sonicated and heated for 24h at 150 °C. The resulting solids were collected through filtration and thoroughly washed with DMF and methanol before drying under vacuum.

NMR studies (Figure B1, See appendix B, Page 113) were performed to verify the incorporation of PSBA and to determine the experimental molar ratio of PSBA and BDC in the obtained frameworks (see Table 4.1). Moreover, from these NMR results it was observed that the molar ratio PSBA/BDC in the structure was maintained even after heating the sample up to 400 °C for 24h (Figure B1, Page 113). This is in contrast to the results observed for monocarboxylic acids based modulators for which a lower decoordination temperature

(325°C for trifluoroacetate)<sup>8</sup> was obtained or in other words, this suggests that the hemilabile linkers coordinated with both the carboxylate side and the sulfonate side, stabilized the structure.

The IR spectra show the characteristic bands at 1035 and 1008 cm<sup>-1</sup> that can be assigned to the asymmetric and symmetric stretching frequencies of S=O respectively with a slight redshift due to the coordination with the Zr-nodes (Figure B2, Page 113). The same applies for the peak at 740 cm<sup>-1</sup>, slightly shifted from 760 cm<sup>-1</sup>, attributed to the S-O stretching vibration. These results confirm the coordination of both the carboxylic acid groups of BDC and the sulfonate group of PSBA to Zr(IV).

Sample	Initial PSBA:BDC <sup>[a]</sup>	Observed PSBA:BDC <sup>[b]</sup>	Number of missing linkers (per Zr <sub>6</sub> formula unit) <sup>[c]</sup>	S <sub>Langmiur</sub> (m <sup>2</sup> g <sup>-1</sup> )	V <sub>m</sub> (cm <sup>3</sup> (STP)g <sup>-1</sup> )
UiO-66	-	-	1.74	1451	333
HI-UiO-66	1:1	0.20:1	2.20	1588	364
HI-UiO-66-SO <sub>4</sub>	-	0.11:1	3.08	928	213

Table 4.1 Composition and properties of the UiO-66, Hl-UiO-66 and Hl-UiO-66-SO<sub>4</sub> materials.

<sup>[a]</sup>theoretical ratio of PSBA and BDC; <sup>[b]</sup>experimentally obtained ratio determined by means of NMR; <sup>[c]</sup>number of defects based on TGA and NMR results as described by Shearer et al.<sup>3</sup>

The crystallinity of the obtained solids was verified by means of PXRD (Figure 4.2a). An obvious broad diffraction in the 20 range between 3 and 7° was observed in the HI-UiO-66 materials, which originates from the cluster defects.<sup>3, 29</sup> To calculate the number of defects, we performed thermogravimetric analysis (TGA), which is one of the most general and efficient methods to study defects in MOFs as the number of defects can be calculated based on the weight loss(Figure 4.2b).<sup>2-3, 11, 30</sup> As can be seen from Table 4.1, HI-UiO-66 contains 2.20 defects. This number is significantly higher than the number of defects present in the pristine UiO-66 using only BDC as organic linker. This indicates that the PSBA does not only act as a bidentate linker, but also as a modular to create extra defects.

As shown in Figure B8, the nitrogen uptake (and porosity) of the sample increased after introduced PSBA in UiO-66, which is due to missing cluster defects. The result was consistent with previous studies.<sup>2-3</sup> SEM showed that HI-UiO-66 has larger size than UiO-66 (Figure B4, Page 114) The EDS mapping of HI-UiO-66 confirmed that the S species are uniformly

distributed inside MOFs (Figure B5, Page 115), confirming that PSBA are homogeneously distributed over the materials.

# 4.3.2 Post-synthetic modification with sulfuric acid and a remarkable increase in stability

In general, sulfonates have weaker coordination strength than carboxylates. Therefore, it is comparatively easier to replace the weaker coordinating ligands by a stronger one. In this regard, HI-UiO-66 was immersed in an acid solution to try to remove the PSBA linker. TGA measurements indicated that after immersing the samples in an H<sub>2</sub>SO<sub>4</sub> solution, the number of defects increased (Figure 4.2b). The number of defects was calculated and was found maximal for HI-UiO-66-SO<sub>4</sub> (6 defects per cluster). The untreated HI-UiO-66 sample had 4.40 defects. In general 6 defects per cluster is considered the theoretical maximum to still maintain a stable 3D UiO-66 framework. <sup>3, 13</sup> That means 6 defects per cluster or three defects per formula unit is the highest possible number of defects that can be achieved in UiO-66. A higher number of defects results in a collapse of the structure. As shown in Table 4.1 and in Figure B3, this observation is accompanied with a reduction in the amount of PSBA and BDC. The amount of PSBA that was removed during the acid treatment was higher in proportion to the amount of BDC linker that was removed upon the treatment. (50% and 13%, respectively) This is due to the hemilabile nature of the PSBA in comparison to the BDC organic linker. Notably, although the number of defects increased after the post-synthetic treatment, the crystalline structure is still preserved (Figure B7, Page 116). Nevertheless, the Langmuir surface area of HI-UiO-66 decreased after the treatment in the H<sub>2</sub>SO<sub>4</sub> solution (Figure B8, Page 116).HI-UiO-66-SO<sub>4</sub> has 6 missing linker per cluster, which corresponds to 6fold structure with more defects than the 8-fold reo UiO-66. The reo UiO-66 is a structure that possesses ordered missing clusters.<sup>29</sup> HI-UiO-66-SO<sub>4</sub> has a higher amounts of defects, forming large scale (mesoporous) vacancies. This is confirmed by the pore size distribution of HI-UiO-66-SO<sub>4</sub>(Figure B8, Page 116). Moreover, the EDS mapping of HI-UiO-66-SO<sub>4</sub> also confirmed that S species are uniformly distributed inside MOFs (Figure B6, Page 115).



**Figure 4.2** a) PXRD pattern of the pristine UiO-66 and the HI-UiO-66 samples. The inset shows the overlap of PXRD patterns from 3 to 7° and b) TGA results obtained of UiO-66, HI-UiO-66 and HI-UiO-66 washed with  $H_2SO_4$  solution.

To clarify the effect of the counter ion, the samples were immersed in  $K_2SO_4$ , a HCl solution and  $H_2O$ . In the pristine UiO-66, slightly more defects were introduced after immersing the material in a HCl solution (1.83 defect sites per  $Zr_6$  unit) and the highest number of defects was obtained when using  $H_2SO_4$  (2.33 defect sites per  $Zr_6$  unit, Figure B9, Page 116). However, the higher number of defects in HI-UiO-66 was observed only after the treatment with  $H_2SO_4$  (Figure B10, Page 117). 0.4 sulfate group per formula unit were incorporated in the structure (Table B1, Page 118). This demonstrates clearly that  $H_2SO_4$  plays a key role in increasing the number of defects. Furthermore, this observation corresponds to the work of Reinsch et al., where Zr-MOFs with more defects were obtained only in presence of sulfate ion.<sup>31</sup> However, thermal stability tests of the post-modified material gave surprising results. TGA experiments show that the thermal stability further increases from UiO-66, HI-UiO-66 to HI-UiO-66-SO<sub>4</sub>. To confirm the result, the VTXRD was performed. As can be seen from Figure B12, these VTXRD results correspond very well to the results obtained from the TGA measurements. A higher thermal stability was observed with increasing numbers of defects which resulted in the following order: UiO-66 ( $450^{\circ}$ C) < HI-UiO-66 ( $480^{\circ}$ C) < HI-UiO-66-SO<sub>4</sub> (515°C). Compared with HI-UiO-66 and UiO-66, the sulfonate group of hemilabile ligands makes the HI-UiO-66-SO<sub>4</sub> more stable in spite of the high amount of defects. The results corresponds to the work of Muesmann *et al.* concluding that Cu(BDS) (BDS = *p*-benzenedidulfonate) showed higher stability than Cu(BDC).<sup>32</sup> The enhanced stability of HI-UiO-66-SO<sub>4</sub> suggests that the sulphate groups play an important role in the stabilization of this defective structure. The phenomenon also was observed in pristine UiO-66 (Figure B9, Page 116).

In order to obtain a better insight into the structural stability of the modified material, periodic density functional theory (DFT) calculations were carried out on the UiO-66 and HI-UiO-66 materials. For UiO-66, the calculations were performed on the two bricks structure with isolated missing linker defects denoted as type 6 in the work of Rogge et al.<sup>33</sup> Each defect site was capped with one -OH as was indicated by IR studies (Figure B11, Page 117). The HI-UiO-66 was constructed accordingly by substituting one out of ten BDC linkers in the defective cluster with a PSBA linker (Figure 4.3, top). The stability of the materials was calculated based on the difference in electronic energy, following the equation:  $\Delta E = (E_{HI-UIO-})$  $_{66}$  +  $E_{BDC}$ ) - ( $E_{UiO-66}$  +  $E_{PSBA}$ ). The difference in electronic energy between the HI-UiO-66 with one PSBA linker and the pristine UiO-66 indicates that the modified material is around 20 kJ/mol more stable than UiO-66. Even though the bond between the sulfonic group and Zr atoms is expected to be weaker, the sulfonic group is stabilized by additional hydrogen bonding interactions with the  $\mu_3$ -OH group and one of the three oxygen atoms from the linker (Figure 4.3, top). The H-O distance has "moderate strength", according to the classification of the hydrogen bond of Steiner et al., as it is situated in the range of 1.5 - 2.2 Å.<sup>34-35</sup> This additional interaction slightly alters the position of the modified linker. The PSBA linker is bent and therefore the interaction of sulfonic group with Zr is weaker which is also seen by the longer Zr-O bond distance compared to the BDC linker. To further understand the hemilabile nature of the HI-UiO-66 material, the stability of the PSBA linker protonated by H<sub>2</sub>SO<sub>4</sub> was investigated. In the acidic solution the PSBA linker can be attacked and protonated either on the sulfonic or carboxyl group which results in the creation of defective site with two adjacent Zr atoms. Experimental observations indicate that during the postsynthetic treatment with H<sub>2</sub>SO<sub>4</sub> defects creation occurs on the sulfonic acid group side due to its weaker coordination to the Zr metal center. Once the linker is protonated by the acid it is in the dangling, metastable state and the HSO<sub>4</sub><sup>-</sup> anion adsorbs on the coordinatively unsaturated Zr centers (Figure 4.3 bottom). The dangling linker is always stabilized by hydrogen bond interaction of moderate strength with the neighboring  $\mu_3$ -OH group. The stability of the material with dangling, protonated PSBA linker was calculated by the following expression:  $\Delta E = (E_{HI-UiO-66-H_2SO_4}) - (E_{HI-UiO-66} + E_{H_2SO_4})$ , in which  $E_{HI-UiO-66-H_2SO_4}$  stands for either protonated carboxyl or sulfonate group of PSBA. The electronic structure calculations show that the protonated sulfonic group with adsorbed HSO<sub>4</sub><sup>-</sup> anion is around 23 kJ/mol more stable than the protonated carboxyl group. This indicates that upon postsynthetic treatment the defects creation is initiated by the cleavage of Zr-sulfonic acid group bond. The sulfonic group is a weaker base than the carboxyl group and therefore it is the best leaving group. These calculations confirmed that the creation of defects in HI-UiO-66 occurs preferentially by removal of PSBA linkers.





**Figure 4.3 Top:** Representation of the UiO-66 with one missing liner defect and HI-UiO-66 with one missing linker defect and one PSBA linker. **Bottom:** Creation of defects in HI-UiO-66 upon post-synthetic treatment with  $H_2SO_4$ . Representation of an energy optimized HI-UiO-66-SO<sub>4</sub> structure in which the PSBA linker is in the dangling state due to the protonation of a) carboxyl and b) sulfonic group while the  $HSO_4^-$  is adsorbed on the defective site.

#### 4.3.3 Lewis and Brønsted sites, catalytic activity

 $\alpha$ -Pinene oxide is a very sensible substrate which rearranges easily under the influence of a Lewis or Brønsted acid-based catalyst. One of the formed products during the Lewis-acid-catalyzed rearrangement of  $\alpha$ -pinene oxide is campholenic aldehyde (CA), an intermediate in the production of sandalwood fragrance and santalol.<sup>36-37</sup> The other major products produced during this acid-catalyzed isomerization are summarized in Scheme 4.1. The

selectivity during the isomerization of  $\alpha$ -pinene depends highly on the type of acid sites present in the reaction medium. This makes the reaction a powerful probe to determine the type of acid sites present in the catalysts.<sup>38</sup> Brønsted acids behave differently than Lewis acids for the formation of CA. More specifically, a high selectivity towards CA (up to 85%) was obtained using catalysts with Lewis acid sites, whereas for the Brønsted acid catalyzed reaction this selectivity is lower than 55% and a significant amount of trans-carveol is formed.<sup>38</sup>



**Scheme 4.1** Formation of different products during the isomerization of  $\alpha$ -pinene oxide.

The catalytic activity of HI-UiO-66 was examined for the isomerization of  $\alpha$ -pinene oxide in toluene at a reaction temperature of 70 °C. Prior to the catalytic tests, the materials were activated under vacuum at 150°C for 16 h. As can be seen from Figure 4.4, the pristine UiO-66 exhibited a conversion of  $\alpha$ -pinene oxide of 54% after a reaction time of 3h, whereas for HI-UiO-66, full conversion was obtained under the same reaction conditions. Remarkably, for the HI-UiO-66 and HI-UiO-66-SO<sub>4</sub>, 85% and 99% conversion was achieved respectively within only 30 min of reaction time (Figure 4.4). Therefore, the catalytic activity follows the order: HI-UiO-66-SO<sub>4</sub> > HI-UiO-66 > UiO-66, suggesting that the number of defects influences the isomerization reactions. The MOF with the highest number of defects showed an excellent conversion of  $\alpha$ -pinene oxide or in other words, the higher the number of defects, the faster the isomerization process.



Figure 4.4 Conversion vs. time for the isomerization of  $\alpha$ -pinene oxide over UiO-66 and HI-UiO-66 and HI-UiO-66-SO<sub>4</sub>.

As can be seen from Figure 4.5, the HI-UiO-66 and HI-UiO-66-SO<sub>4</sub> exhibit a higher selectivity (>55%) to CA than the pristine UiO-66 material (47%). The observed reactivity of HI-UiO-66 and HI-UiO-66-SO<sub>4</sub> are comparable to that of other Lewis acid based catalysts (such as Cu-BTC) while the reactivity of UiO-66 is comparable to that of Brønsted acid catalysts such as Dowex 50Wx4-100.<sup>36</sup> Recent discoveries about UiO-66 have shown that after defect engineering the material possesses not only Lewis acid sites but also significant number of Brønsted sites which reveal dynamic acidity.<sup>39-41</sup> This property of the Brønsted sites in UiO-66 plays a crucial role especially in the reactions where proton rearrangement can occur.<sup>42-44</sup> To understand the selectivity in these three Zr-MOFs, it is necessary to know the nature of the active sites, whether they reveal Lewis or Brønsted acidity. Yang et al. showed that one defect site in UiO-66 results in one Lewis and one Brønsted acidic site, which was confirmed by IR (Figure B11, Page 117).<sup>45-47</sup> The  $\mu_3$ -OH also acts as a Brønsted acid site. UiO-66 showed domain Brønsted acidity, because of the high ratio of Brønsted and Lewis sites (3.3, (1.74 Zr-OH + 4  $\mu_3$ -OH)/1.74 Zr-OH). Upon increasing the number of defects, the amount of Lewis acid sites increases, so the ratio of Lewis sites and Brønsted sites increases due to the constant concentration of  $\mu_3$ -OH (0.35 > 0.30 (1/3.3), 2.2 Zr-OH/(2.2 Zr-OH + 4  $\mu_3$ -OH)), resulting in the enhanced selectivity to CA. This results in a higher contribution of the activity of the Lewis sites compared to the Brønsted sites (high selectivity with the low amounts of Lewis sites), which is consistent with the previous report of Alaerts et al.<sup>36</sup> Since HI-UiO-66-
SO<sub>4</sub> has the highest number of defects, and the highest ratio of Lewis sites and Brønsted sites (0.43 > 0.35 > 0.30, 3 Zr-OH/(3 Zr-OH + 4  $\mu_3$ -OH)), it has the highest selectivity towards CA in comparison to the other two catalysts.



**Figure 4.5** Product selectivity for the isomerization of  $\alpha$ -pinene oxide at 100% conversion over UiO-66 and HI-UiO-66 washed with H<sub>2</sub>SO<sub>4</sub> solution. The dotted line indicates the selectivity of 55%.

To further compare the reactivity of these Zr-MOF materials with the other heterogeneous MOF based catalysts and zeolites, the reactivity and selectivity of some published catalysts are summarized in Table 4.2. From this table, HI-UiO-66-SO<sub>4</sub> shows the best activity and selectivity in comparison to the other reported MOF catalysts. In comparison to Cu<sub>3</sub>(BTC)<sub>2</sub>, which only has Lewis acid sites, a higher catalytic activity but a lower selectivity was obtained however, this catalyst is not stable and cannot be recycled. Compared to the best homogeneous Lewis-acid catalyst (ZnBr<sub>2</sub>),<sup>48</sup> the HI-UiO-66-SO<sub>4</sub> exhibits a similar selectivity but with a higher TON value.

Ent	Catalyst	Conv. (%) (h)	Selec	Selectivity (%)			Ref
ry			CA	Isopincamphone	trans-carveol		
1	UiO-66	54(3)	47	2	28	7.3	This
2	HI-UiO-66	99(3)	59	4	24	13.6	work
3	HI-UiO-66-SO <sub>4</sub>	99(0.5)/85(0.05)	71	2	18	18.0	
4	ZnBr <sub>2</sub>	93(0.05)	73	15	-	3.6	
5	UiO-66	100	45	-	-		49
6	Zr(Ti)-NDC <sup>b</sup>	88 (24)	58	20	-	-	50
7	Cu <sub>3</sub> (BTC) <sub>2</sub> <sup>b</sup>	73 (24)	82	3.5	-	-	50
8	Cu <sub>3</sub> (BTC) <sub>2</sub> <sup>c</sup>	70 (40)	80	-	-	-	36
9	MIL100(Fe) <sup>b</sup>	62 (24)	48	10	-	-	50
10	MIL100(Fe) <sup>d</sup>	22 (6)	45	40	-	-	51
11	MCM-41(Si/Al = 15) <sup>b</sup>	94 (21)	60	-	-	-	50

Table 4.2 Isomerization of α-pinene oxide using various MOF based catalysts.<sup>a</sup>

<sup>a</sup> Reaction condition: 50 mg cat, a-pinene oxide (0.86 mmol, 130 mg), 70 °C in toluene; <sup>b</sup>5 mg cat, apinene oxide (0.13 mmol, 20 mg), 70 °C in 1,2-dichloroethane; <sup>c</sup>reactions were carried out at room temperature with 0.1 g of a-pinene oxide in 5 mL of solvent added to 0.1 g of  $Cu_3(BTC)_2$ ; <sup>d</sup>0.5 mL of apinene oxide, 50 mg catalyst activated at 150 °C for 2 h under vacuum before use, 70 °C without solvent; <sup>e</sup>estimated by conversion at 3 min.

Furthermore, a hot filtration test after 3 min of reaction revealed that after the removal of the catalyst no further conversion was noted, confirming the heterogeneous nature of the catalyst (Figure B14, Page 119). Nevertheless, during the recycling experiments, the activity and selectivity decreased slightly during each run (Figure B15, Page 119). This decrease might be due to the blocking of the pores during the consecutive runs, as the surface area slightly decreased during each run (Figure B17, Page 120). PXRD measurements showed that the structure remained intact (Figure B16, Page 120).

#### 4.4 Conclusions

In summary, ultra-stable Zr-MOFs with a high number of defects using a hemilabile linker (PSBA) have been developed. PSBA not only acts as a modulator for the MOF synthesis to increase the number of defects but also as co-ligand to stabilize the defective structure. Due to the hemilability of PSBA, a simple post-synthetic treatment with  $H_2SO_4$  further enhanced the stability and the number of defects sites in HI-UiO-66. HI-UiO-66-SO<sub>4</sub> showed the

optimum number of defects (while maintaining structural integrity) and showed the highest reactivity for the acid-catalyzed isomerization of  $\alpha$ -pinene oxide with a high selectivity for campholenic aldehyde. Additionally, it was found that the increase in the number of defects increases the Lewis acid characteristics and hence favor the campholenic aldehyde formation. Importantly, the catalytic activity outperforms the best homogenous catalyst. Therefore, the use of a hemilabile linker, either as mixed linker or as the isolated linker, will be interesting in defect engineering of MOFs. Due to the different possibilities in coordination of the two different groups in a hemilabile linker, defects can be generated and hence the stability can be affected. Meanwhile, the easy post-synthetic treatment can be useful to adapt and adjust the final structure of the pristine materials for potential applications.

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# **Chapter 5** Conclusions and Perspectives

### 5.1 Conclusions

MOFs possess highly ordered crystalline structures resulting in frameworks with pores of the same size, shape and functionalities. These characteristics facilitate the establishment of the relation between structures and properties. Defect chemistry breaks the orderliness and has an influence on the resulting properties, changing the possible practical applications. For example, the mass diffusion and transport can be altered by introducing defects. In addition to this, extra active sites are generated upon the introduction of defects which might enhance the catalytic performance, and have an influence on the magnetic, electronic and optical properties.

The modulation approach is the most common examined method for the formation of defective MOFs. In this approach large amounts of monocarboxylic acids (=modulators) are added besides the employed organic linkers. Many types of monocarboxylic acids have been studied. Among all the examined modulators, formic acid (FA), acetic acid (AA), trifluoro acetic acid (TFA) and difluoro acetic acid (DFA) have been extensively employed. In chapter 3, the influence of the synthesis temperature on the modulation synthesis of three Zr based MOFs, denoted as UiO-66, Zr-NDC and UiO-67, is investigated. The results exhibit that the modulator displays a better modulation action at low synthesis temperature or in other words more defects and a higher density of modulator are introduced at low synthesis temperatures. In comparison to the typically employed modulators, L-proline was chosen in this work as a functionalized modulator, having a chiral site. Chirality was introduced into these Zr-MOFs, to explore them as chiral catalysts for asymmetric reactions. The modulated UiO-66 framework was examined in the reaction of benzaldehyde with acetone. A high catalytic activity was observed for the UiO-66 framework with TOFs up to half the TOF of the homogenous L-proline's TOF and a higher selectivity than the L-proline homogenous catalyst (99% vs 83%). For the reaction of benzaldehyde with cyclohexanone a higher catalytic

activity (100% conversion after 24h) was obtained in comparison to the reported proline presynthetic Zr-MOFs (97% conversion after 10 d). In comparison to the catalytic performance of the homogenous L-proline, our modulated material achieves complete conversion while for the homogenous catalyst an equilibrium is observed at 61% conversion. In addition to this a high but reversed diastereoselectivity (up to 64%) was obtained for our heterogeneous catalyst, in comparison to the homogenous catalyst, using methanol as solvent. The high catalytic activity of the modulated UiO-66 is the result of the electron withdrawing nature of the Zr-node coordinated to L-proline. The other two MOFs exhibit a low catalytic activity due to their instability caused upon the generation of defects.

Defect formation usually results in a decreased stability of the framework. In general, more defects will be introduced into the framework upon the addition of more equivalents of modulator. However this will result into a low yield with a limit of the amounts of defects of framework (2.2 missing linkers per formula unit). The 3D UiO-66 framework can generally have up to 3 missing linkers per formula unit. In chapter 4, the role of hemilabile ligands in the defect engineering in the UiO-66 framework was explored. Apart from monocarboxylic acid modulators, hemilabile ligands contain, next to the carboxylate group, an additional but relatively much weaker coordinating functional group (e.g. sulfonate groups). In this work, 4sulfobenzoic acid was employed as a hemilabile linker in the UiO-66 synthesis to create defects which was accompanied by an unusual increase in its stability. The produced material, denoted as HI-UiO-66, exhibits a high number of defects accompanied by an increase in its stability. Due to the presence of the hemilabile linker, a simple post-synthetic procedure was carried out which resulted in an increase in the number of missing linkers up to the theoretical maximum of three while also an increase it the stability of the framework was obtained. The thermal stability was confirmed by DFT calculations. DFT calculations showed that a combination of bent linkers, hydrogen bonding stabilization and the electrostatic attraction of the HSO<sub>4</sub> anion leads to this remarkable stabilization. In addition to this, we explored the catalytic activity of the UiO-66 framework in the isomerization of  $\alpha$ pinene oxide, to differentiate the Brønsted and Lewis acid sites. In the pristine UiO-66, Brønsted acid sites are predominantly present, resulting in a low activity and selectivity. The

defective UiO-66 structures exhibited an enhanced Lewis acid catalytic activity and a much higher selectivity, in comparison to its homogeneous counterpart.

In conclusion, it was shown throughout this work that by either using functionalized modulators or by introducing hemilabile ligands into Zr-MOFs, this had a huge effect on the structural, physical and catalytic properties.

### 5.2 Perspectives

Since their discovery in 1999, a huge variety of new MOF structures have been developed, which have been examined for their gas adsorption sorption properties besides many other applications. Compared to other porous materials, MOFs have shown outstanding results in many fields of application. For example, MOFs exhibit the highest storage capacity for gases such as methane,<sup>1-7</sup> are the best performers for the selective separation of carbon dioxide from water<sup>8-12</sup> and for the harvesting of water from air.<sup>13-17</sup> To enhance the performance of the materials, the framework's backbone structure has been designed and functionalized to exhibit a permanent porosity and long-range order. The future of reticular chemistry applied in MOFs lies in the domain of controlling the spatial arrangement of functional units and metal ions in multivariable systems.<sup>18</sup> Upon the introduction of multiple functionalities, the various chemical/physical properties can cooperate. If in future the framework could be characterized more accurately and properly, a better control can be obtained on the multiple functionalizations' present in the backbone of the framework. MOFs will provide a rich platform offering a complex, diverse and controllable environment for task-specific applications, which cannot be achieved by the current state of the art materials. MOFs are not only regarded as potential candidates for their use in the conventional industry. But they are also seen as multifunctional host materials for applications that need the use of multiple functions and control of material morphology. Possible future applications will be their use in biosensors, actuators, gas/ion transporters and so on.

Defect engineering in MOFs offers great opportunities for tailoring their application-oriented properties. The defect formation and the initial understanding of the nature of the defects have been examined a lot during the last decade, but still a lot of questions to be answered <sup>19-20</sup> Furthermore, the numbers of defective MOFs that have been studied are rather rare. This is due to the fact that many MOFs don't allow much diversity or in other words in these frameworks the active sites can only be unlocked upon a careful engineering of the defects in the future. In future, it will be of paramount importance to allow **a controlled introduction of defects and to have a thorough understanding on the nature of defects present within the framework**. In addition to this, the development of characterization techniques is required to unambiguously investigate the defect distribution and types of defects to establish the nature and distribution and/or correlation of defects. Combining theoretical modeling with experimental characterization methods can be relevant to obtain a better understanding on the engineering of the defects. The most investigated MOF so far, and probably also in the near future, for this purpose is the UiO-66 framework, which is seen as the prototypical MOF. If one can have a control on the removal of clusters to form well-defined big pores, it will offer many possibilities in many applications. For example, the *reo* UiO-66, the ideal structure with ordered missing clusters in *fcu* UiO-66, is known but is still not obtained.

Focusing on catalysis, a number of advantages can be foreseen derived from the formation of defects. For example, defects can reduce the diffusion limitations to allow a better accessibility to the active sites and the scope can be extended to larger substrates and products. So far defective MOFs have been used mostly as Lewis acid sites in several acid assisted catalytic reactions. Defective MOFs can also display Brønsted acid sites when the defects are compensated by –OH. However, only very few papers have been reported so far on using Brønsted sites for specific catalytic reactions. Furthermore, one can use specific modified defect sites for targeted catalytic reactions. As a matter of fact, functional groups such as chiral amino acid sites on L-proline<sup>21</sup> and metal active sites such as V<sup>V</sup> anchored on defective sites<sup>22</sup> were introduced on defective MOFs for targeted reaction. The accessibilities of defects offer a new position to graft the specific catalytic sites for the targeted catalysis. For examples, the organocatalysts can be incorporated on defect sited for asymmetric reactions.

In summary, MOFs show outstanding potential for a number of applications in several technological fields on a laboratory scale. Nonetheless, the field will need to break the

laboratory boundaries to foresee there industrial implementation. The time is high to prove that MOFs can compete with today's industrial materials and to establish their technological and industrial importance in our modern lifestyle.

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# Appendix

## **Appendix A: Supporting information for chapter 3**

The supplementary detailed catalysis results and data analysis results including PXRD, TGA, dissolution <sup>1</sup>H NMR and nitrogen adsorption.



Figure A1 PXRD pattern of UiO-66-LP, Zr-NDC-LP and UiO-67-LP synthesized at 150°C, 120 °C and 70°C.



**Figure A2** Nitrogen adsorption isotherms of the Zr-NDC-LP materials synthesized at 150 °C, 120 °C and 70°C.



**Figure A3** Nitrogen adsorption isotherms of the UiO-67-LP materials synthesized at 150 °C, 120 °C and 70°C.



Figure A4 TGA results obtained for the Zr-NDC-LP materials synthesized at 150 °C, 120 °C and 70°C.



Figure A5 TGA results obtained for the UiO-67-LP materials synthesized at 150 °C, 120 °C and 70°C.



Figure A6 <sup>1</sup>H NMR profiles of digested UiO-66-LP synthesized (a) 150 °C; (b) 120 °C and (c) 70 °C.



Figure A7 <sup>1</sup>H NMR profiles of digested Zr-NDC-LP synthesized at(a) 150 °C; (b) 120 °C and (c) 70 °C.



**Figure A8** <sup>1</sup>H NMR profiles of digested UiO-67-LP synthesized at(a) 150 °C; (b) 120 °C and (d) 70 °C.

Table A1 Catalytic studies for aldol addition of 4-nitrobenzaldehyde and acetone with Zr-MOFs catalysts.

$O_{2}N \xrightarrow{\text{CHO}} O_{2}N \xrightarrow{\text{CHO}} O_{2}N \xrightarrow{\text{OH}} O_{2}N \text$								
Catalyst	T(°C)	t(h)	Conversion (%)	Selectivity <sup>a</sup> (%)	ee (%)			
L-proline	20	24	99	87	62.4			
UiO-66-LP-150	20	24	60	96	5.3			
UiO-66-LP-120	20	24	62	96	5.4			
UiO-66-LP-70	20	24	4	75	17.6			
Zr-NDC-LP-150	20	24	8	89	n.d.			
Zr-NDC-LP-120	20	24	3	70	n.d.			
Zr-NDC-LP-70	20	24	2	70	n.d.			
UiO-67-LP-150	20	24	6	83	n.d.			
UiO-67-LP-120	20	24	3	85	n.d.			
UiO-67-LP-70	20	24	3	79	n.d.			

Reaction conditions: 0.3 mmol of 4-nitrobenzaldehyde, 10 mL acetone, 20 mol % catalyst (related to

the proline amount in the material); <sup>a</sup>Toward aldol product 1.



**Figure A9** PXRD pattern (left) and nitrogen adsorption isotherms (rignt) of all UiO-66-LP materials obtained before and after catalysis at room temperature.



**Figure A10** PXRD pattern (left) and nitrogen adsorption isotherms (right) of all Zr-NDC-LP materials obtained before and after catalysis at room temperature.



**Figure A11** PXRD pattern (left) and nitrogen adsorption isotherms (right) of Zr-NDC-LP-150 materials immersed in acetone for 5d.



**Figure A12** PXRD pattern (left)and nitrogen adsorption isotherms (right) of UiO-67-LP obtained before and after catalysis at room temperature.

Table A2 Solvent Screening for the Aldol Reaction between 4-nitrobenzaldehyde and acetone in the presence of UiO-66-LP-120.



Solvent	T(°C)	t(h)	Conversion (%)	Selectivity <sup>a</sup> (%)	ee (%)
hexane	45	24	100	66	13.3
chloroform	45	24	97	51	14.9
acetone	45	24	100	89	6.7
DMSO	45	24	26	90	5.3
Methanol	45	24	64	79	4.9
water	45	24	9	99	1.1
acetone+1%water	45	24	89	99	5

<sup>a</sup>Toward aldol product 1.

Table A3 Solvent Screening for the Aldol Reaction between 4-nitrobenzaldehyde and cyclohexanone inthe presence of UiO-66-LP-120.

O <sub>2</sub> N H <sub>+</sub>	o	UiO-66-L	P-120 (20 mol%) ────► O <sub>2</sub> N <sup>✓</sup>	OH O	+	OH O	
Solvent	T(°C)	t(h)	Conversion (%)	dr (syn:anti)	de <sub>syn</sub> (%)	ee(syn)	ee (anti)
L-proline DMSO	45	24 (72)	53 (61)	50:50 (42:58)	0 -16	n.d. 11:89	n.d. 47:53
chloroform	45 45	24	94	66:34	32	50:50	52:45
DCM	45	24	100	68:32	36	49:50	52:48
DMSO	45	24	22	77:23	54	50:50	53:47
Methanol	45	24	95	82:18	64	50:50	52:48

Catalyst	Substituents at ketone	Time (h)	Solvent	Conv (%)	Select <sup>a</sup> (%)	de <sub>syn</sub> (%)	TOF (S <sup>-1</sup> ) <sup>b</sup>
UiO-66-LP-120	acetone	24	acetone	100	85	-	0.0013
UiO-66-LP-120	acetone	24	Acetone	85	99	-	-
			+1% H <sub>2</sub> O				
L-proline	acetone	1	DMSO	100	83	-	0.0026
UiO-66-LP-120	cyclohexanone	24	DCM	100	-	36	0.0005
							6
UiO-66-LP-120	cyclohexanone	24	methanol	95	-	64	
L-proline	cyclohexanone	72	DMSO	61	-	-16	0.0013
				(equilibrium)			
UiO-66-LP-120	cyclooctanone	24	DCM	18	-	-	-
L-proline	cyclooctanone	24	DMSO	57(almost	-	-	-
				equilibrium)			

Table A4 Catalytic studies for the aldol reaction with UiO-66-LP-120.

<sup>a</sup>Toward aldol product 1; <sup>b</sup>TOF calculated at 30 min.



**Figure A13** Hot filtration experiment (left) and recycling experiments (right) using UiO-66-LP-120 as catalyst and acetone as substrate.



**Figure A14** PXRD pattern (left), nitrogen adsorption isotherms (right) of the UiO-66-LP-120 material obtained before and after 3 catalytic cycles using acetone as substrate.



**Figure A15** PXRD pattern (top, left), nitrogen adsorption isotherms (top, right) and <sup>1</sup>H NMR profiles (bottom left) of UiO-66-LP-120 material obtained after 3 catalytic cycles using cyclohexanone as substrate.

En tr y	Catalyst	Substrate	Tem p.	Conversion	Time	Selectivity (1)	Catalyst content	dr (syn:ant i)	de <sub>sy</sub> n	ref
1	UiO-68- NHPro	cyclohexanone	40	97	10d	-	20%	88:12	76	1
2	DUT-32- NHPro	cyclohexanone	rt	-	-	-	20%	-	-	2
3	Al-MIL-101- NH-Pro	acetone	45	95(yield)	7d	-	15%	-	-	3
4	IRMOF-Pro	acetone	rt	-	40h	-	100%	-	-	4
5	IRMOF-Pro	cyclopentanon e	rt	-	30h	-	100%	1:3	50	4
6	Cd-TBT	cyclohexanone	25	97	10d	-	5%	-	-	5
7	IRMOF-3- Pr(OP)	acetone	60	41	72h	28	-	-	-	6
8	UiO-66-lp- 120	acetone	45	100	24h	99	20%	-	-	this wor k
9	UiO-66-lp- 120	cyclohexanone	45	95	24h		20%	82:18:0 0	64	this wor k

Table A5 Comparison of the UiO-66-LP-120 catalyst with other proline functionalized MOFs catalysts in the aldol reaction.



**Figure A16** Conversion as a function of time for the aldol reaction of the homogeneous L-proline and the UiO-66-LP-120 material using cyclohexanone as substrate.

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## **Appendix B: Supporting information for chapter 4**

The Supplementary detailed catalysis results and data analysis results including PXRD, VTXRD, TGA, dissolution/<sup>1</sup>H NMR, nitrogen adsorption IR, catalysis results and the modeling data.

#### **General Procedures**

All chemicals were purchased from Sigma Aldrich, ABCR or TCI Europe and used without further purification. PXRD patterns were collected on an ARL X'TRA X-ray diffractometer operating at 40kV/40mA using Cu-K<sub> $\alpha$ </sub> radiation ( $\lambda$ =0.15418 nm) and a solid-state detector. Nitrogen adsorption experiments were carried out at 77 K using a Belsorp-mini II gas analyzer. Prior to absorption measurements, the samples were activated under vacuum at 150°C for 12 h to remove adsorbed solvent. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) measurements were recorded on a Nicolet 6700 spectrometer (Thermo Scientific) in a KBr matrix, at 120 °C under vacuum. X-ray fluorescence (XRF) spectroscopy measurements were performed using an energy-dispersive Rigaku NexCG spectrometer equipped with a silicon drift detector. Thermogravimetric analysis was performed on a Netzsch STA 449 F3 Jupiter with a temperature range of 20 - 800 °C in air with a heating rate of 2 °C /min. For <sup>1</sup>H NMR, samples were dissolved in a heated mixture of D<sub>2</sub>SO<sub>4</sub> and [D<sub>6</sub>]-DMSO (1:6). Spectra were recorded on a Bruker 300 MHz AVANCE spectrometer. An ultra-fast GC equipped with a flame ionization detector (FID) and a 5% diphenyl/95% polydimethylsiloxane column, with 10 m length and 0.10 mm internal diameter was used to follow the conversions of the products during the catalytic tests. Helium was used as carrier gas and the flow rate was programmed as 0.6 mL/min. The reaction products were identified with a TRACE GC×GC (Thermo, Interscience), coupled to a TEMPUS TOF-MS detector (Thermo, Interscience). The first column consists of a dimethyl polysiloxane package and has a length of 50 m, with an internal diameter of 0.25 mm, whereas the second column has a length of 2 m with an internal diameter of 0.15 mm. The package of the latter is a 50% phenyl polysilphenylene-siloxane. VTXRD measurements were carried out on a Bruker D8 Discover XRD system equipped with a Cu X-ray source ( $\lambda = 1.5406$ Å) and a linear X-ray detector. The samples were put on a Si sample cup on a sample heating stage. During VTXRD measurements, the samples were heated from room temperature to 600°C at a heating rate of 5°C/min in air.





**Figure B1** <sup>1</sup>H NMR profiles of digested HI-UiO-66 after being heated for 24 hours at (a) 150°C, (b) 300°C, (c) 400 °C.



Figure B2 FT-IR spectra of UiO-66 and HI-UiO-66 samples.



8.10 8.08 8.06 8.04 8.02 8.00 7.98 7.96 7.94 7.92 7.90 7.88 7.86 7.84 7.82 7.80 7.78 7.76 7.74 7.72 7.70 7.68 7.66 7.64 7.62 7.60

**Figure B3** <sup>1</sup>H NMR profiles of digested HI-UiO-66-SO<sub>4</sub>.



Figure B4 SEM images of (a) UiO-66, (b) HI-UiO-66 and (c) HI-UiO-66.



Figure B5 EDS-mapping analysis of HI-UiO-66.



Figure B6 EDS-mapping analysis of HI-UiO-66-SO<sub>4</sub>.



Figure B7 PXRD pattern of HI-UiO-66 and HI-UiO-66 washed with H<sub>2</sub>SO<sub>4</sub> solution.



Figure B8 Nitrogen adsorption isotherms obtained on UiO-66 and HI-UiO-66 and HI-UiO-66 washed with  $H_2SO_4$  solution at 77 K.



Figure B9 TGA results obtained on UiO-66 after washing different solutions.



Figure B10 TGA results obtained on HI-UiO-66 after washing different solution.



Figure B11 FT-IR spectra of UiO-66 HI-UiO-66 and HI-UiO-66-SO<sub>4</sub> after activated 150  $^\circ$ C.



**Scheme B1** Topology Change on Missing Linker Site of UiO-66 Nodes with the Initial Ligands on the As-Synthesized Sample.

According to Yang et al., the compensated ligands on the defect sites were exchanged by MeOH when the samples were stirred in MeOH for 24h.<sup>1</sup> In this process–OMe groups were introduced to balance the charge and the compensated ligands were exchanged into –OH from H<sub>2</sub>O. (The samples were stored under ambient conditions). In the end the coordination state was confirmed by IR analysis. The vibration at 3674 cm<sup>-1</sup> and 3780 cm<sup>-1</sup> correspond to  $\mu_3$ -OH and Zr-OH respectively and are comparable with the results reported by Yang et al.

Sample	formula	Calcd		Found			
		С	Н	S	С	Н	S
UiO-66	Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>4</sub> (BDC) <sub>4.26</sub> (OH) <sub>3.48</sub>	28.67	1.96	-	28.65	1.95	-
HI-UiO-66	Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>4</sub> (BDC) <sub>3.17</sub> (PSBA) <sub>0.62</sub> (OH) <sub>4.40</sub>	25.53	1.70	1.44	25.92	1.71	1.45
HI-UiO-66-	Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>4</sub> (BDC) <sub>2.63</sub> (PSBA) <sub>0.29</sub> (OH) <sub>5.36</sub> (SO <sub>4</sub> ) <sub>0.4</sub>	21.34	1.63	1.70	21.36	1.70	1.72
SO <sub>4</sub>							

Table B1 Element analysis of UiO-66, HI-UiO-66 and HI-UiO-66-SO<sub>4</sub>.



Figure B12 Results of the VTXRD measurement of (a) UiO-66, (b) HI-UiO-66 and (c) HI-UiO-66-SO<sub>4</sub>.



Figure B13 The intensity change of the main peak (6.5°-8°) in VTXRD.



Figure B14 Hot filtration experiment for HI-UiO-66-SO<sub>4</sub>.



Figure B15 Recycling experiments with for HI-UiO-66-SO<sub>4</sub>.



Figure B16 PXRD pattern of HI-UiO-66-SO<sub>4</sub> before and after reaction runs.



Figure B17 Nitrogen adsorption isotherms obtained on HI-UiO-66-SO<sub>4</sub> before and after reaction runs.



**Figure B18** PRXD pattern of the UiO-66, HI-UiO-66 and HI-UiO-66-SO<sub>4</sub> materials after the treatment with HCl (pH=1), and NaOH (pH=13) for 24h.
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Coordinates of the structures:

Unit cell parameters:

1.00538983003059

14.7440413799761423 -0.0002575548663194 -0.0266394274068111

 $0.0061443348774756 \hspace{0.1cm} 20.8097587016210248 \hspace{0.1cm} 0.0003236637937236$ 

-0.0234962230977906 0.0018826970219523 14.7450700531007222

UiO-66

216

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Zr 0.01909771545884 8.69444314684356 7.41716660352983
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Zr 1.92538146542737 11.15602286977146 9.22433084792379
Zr 9.18487759244836 0.72943306830028 13.05514071060557

0 7.42144659909392 20.23250498447471 12.83596215686678 0 4.97354820983658 2.72873717654985 2.58585786555186 0 2.32707995247247 13.24264082444146 10.04916037965424 O 2.17961114856642 12.49347952041530 7.39445206489403 0 5.96850971030754 18.07061671460337 13.46240429669034 O 3.48576157006817 0.64220312240776 13.71080780159898 0 3.53239737539859 0.65922482866413 1.15488359392653 0 11.33447787638877 0.67148167833058 13.68143379066526 0 11.37977721498032 0.64870255592694 1.12601942508850 O 4.92194169583510 2.64061307080984 12.26439909389650 0 6.04062368564453 4.26563014698080 13.38737115151292 O 1.38856237589454 7.52727353642999 8.73589490135014 0 2.59463194072716 9.09690733291518 9.84492470625451 O 9.45001923223102 2.12861590656355 0.00173242804892 0 9.98983702884216 19.66157125686058 12.34216196558391 0 9.93681255343395 2.64237249524205 2.58129731362227 0 8.80501523137193 4.26501081315150 1.46818332186406 0 0.06884794133572 12.24813820946522 8.85292695474831 0 7.45566374244689 20.22283676974745 1.99847104760564 O 2.59709649075440 13.06352063899328 4.85619611671522 O 1.51289942346984 10.13335423430727 7.40917361104584 0 1.40375877338096 14.67738358571277 5.91370487037986 O 13.33878173469061 7.69879934287670 8.81183088636504 O 8.91919558908296 18.06735756683307 1.35813038304553 0 7.44922810831343 1.75059775149122 1.47623286524898 0 4.84916441998408 19.69321586866693 12.34025641863274 0 1.37756295408594 14.81819549525745 8.72629348264883 0 12.28170218925779 13.07736444536393 9.97618905134936 0 6.28787466837370 0.77874661989488 10.90629809616527 O 1.07009803111105 11.27921040618920 3.51012671380711 0 6.03349650503903 18.05072480481815 1.34319716917249

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C 11.07809203115259 4.63469032974240 10.39969241667739 C 3.61178796141824 14.93873717512422 11.20128295874922 C 9.52718613641497 18.21019688625653 12.42247471265636 C 3.15748840606124 17.65077457376842 10.70268645307011 C 2.68200836035288 15.32886023586822 10.22527897988963 C 14,75774126870708 11.14637562567249 13,15368218726236 C 10.75472440057771 14.81412172319962 11.23149255214536 C 2.79775271289635 5.51861419767618 4.55402864897205 C 10.19256691477023 15.87322038361590 2.44737277411628 C 12.25094444074344 8.01402348610812 9.22374280519418 C 10.31278264860959 5.01235138444813 11.50410783712645 C 11.34541405890306 17.63574693122192 3.65380599811134 C 2.12550554088166 14.10868666235601 4.81624639474927 C 11.64953361577861 5.62915815642840 9.61678753740467 C 12.08001855131921 16.68218374326964 4.34963437433910 C 4.09690825010061 7.18226892849723 3.36512250082163 C 7.23915785574857 0.59994259587953 4.30457386552627 C 3.21008721024715 17.51700380822399 3.60003182801259 C 10.03157128992912 6.05506593077131 2.59468829936541 C 9.58206909641571 18.26525521182509 1.98540778993058 C 11.96180712214538 16.53852179490477 10.03252047218702 C 11.14804810970996 4.32490669381295 3.87481957352443 C 14.68533631267042 11.07912423595207 2.61906480240065 C 3.10690378778119 6.86664903510517 4.30651705344601 C 1.13431990224899 11.04020239566630 0.45492204998450 C 10.61386157565852 7.33829980615938 11.00126452325635 C 10.22483111202929 4.69846589688009 2.88730006092640 C 7.25188465977322 0.64461020136275 8.61065683828004 C 10.39257693638513 17.23669441072224 2.70394073434347 H 11.24162542247636 3.57913455426344 10.18864548256920 H 12.28931293890142 5.37823225454167 8.77241579224121

H 5.51220957385405 6.40093757905881 1.92688653764942 H 11.45073347622495 18.57347170006071 10.55614096564407 H 2.99704120014682 18.71333194430878 10.52615045420828 H 14.72279718680086 9.03838737845976 9.93175499866627 H 1.11219051991565 0.38993732675686 1.93833311864741 H 13.42560936366093 0.38020749531791 1.93961653318576 H 13.37065433237014 0.38488116132205 12.47358221882809 H 1.05754847325722 0.39492943891904 12.47025896062907 H 5.34316697152882 6.34352295453577 12.41669471310917 H 4.08124960850839 8.08657999524359 11.12298741295266 H 1.89467279419608 5.00382603695662 9.08734652340849 H 3.16026869332385 3.25934226290011 10.38222823440103 12.70755194327563 16.81168223306286 9.28707985018215 н H 5.09597418133251 0.68978186713312 5.95925097246247 1.72788003902234 16.97653465531367 9.22362351892463 н 2.06736933517752 10.95965421689750 13.35328514605701 н н 9.31089164006901 15.51833817428422 12.68030995242763 H 12.59840383694857 11.34254471334759 0.92627276604789 н 3.20906828596784 3.45904811152138 4.03873797100734 H 1.79298375709296 16.76229817227229 5.04884677761696 H 7.22902122906238 19.46719238245571 11.83152544336661 H 12.59750513225160 5.01958948865654 5.32438480754447 H 11.28651547860588 3.26581434248912 4.08863901131831 H 12.81545752768817 16.97498578324419 5.09807541532977 H 3.96482433443007 13.77585307184167 2.85820157398829 H 2.02902451982487 5.28528615339625 5.28863410941103 H 9.31444697192374 6.32816691154387 1.82209067477255 H 10.78286605690421 13.85571065199650 2.96440889423943 H 9.38691339756190 0.61822466155296 5.94383456543205 H 9.42291247043297 6.60590061740874 12.65526916008060 H 14.73272708426495 9.02522176192468 4.35157784223312

H 9.39666916612349 0.61538124818296 8.45578116355073 H 12.61940993612239 11.36275054087586 13.23667646024470 H 10.45929650224890 8.39359606938570 11.22092189691671 H 10.56749463248406 13.75665545523766 11.41347192875201 H 4.33568971869746 8.22869238388490 3.17853663667139 H 2.04764646275929 10.95485278414257 1.04194876566857 H 9.44843393275345 15.58072089402886 1.70794822107550 H 5.18419129522363 15.58356411335979 1.60737310163911 H 10.62177483717598 8.08205965039292 3.05557879698684 H 3.77538989239288 13.87523242648891 11.36897696766136 H 3.01315530228876 18.56997735937498 3.79559512739634 H 11.49127412117912 18.69918451738520 3.83629441408358 H 7.26362154703513 19.46821962272601 2.57323263367878 H 5.05027417403178 15.61202856911251 12.66892449569166 H 5.10589964399170 0.68857772561247 8.47067000469815 H 4.43836720686205 2.49278677658946 14.61362393022286 H 10.02190924426506 2.45520005197294 14.66482514707539 H 4.32199943555417 10.29029332225007 9.03829258281453 H 2.87749324772422 12.85806041986148 7.14904684262161 H 10.31657241278922 10.31138081931737 5.28380442252805 H 11.78204971310261 12.89309046306446 7.13496188706432

HI-UiO-66-H<sub>2</sub>SO<sub>4</sub> protonated carboxyl group

## 224

Zr 7.26079228581571 3.20909917394141 14.73175203297426
Zr 14.69230618649720 13.73913187866264 7.13601297941408
Zr 7.17700685417334 19.11823972093032 14.60889667618492
Zr 5.46903105266855 0.71146044917797 1.60772046133006
Zr 12.83020721017890 11.13459113005537 5.36121550752804
Zr 14.71022376244920 8.72175131072496 7.23591995082864
Zr 13.09298451540232 11.31032155766300 8.94523207588425

Zr 5.47411637163006 0.77974003090809 12.88287352508885 Zr 1.53334548531762 11.20310027026627 5.42647911822565 Zr 9.00959268080020 0.64004238141255 1.62496936770054 Zr 1.77873184173642 11.19409403611967 9.00481900069070 Zr 9.01553166319606 0.69214875985324 12.92640954687129 S 10.13029959691476 3.97075384405616 13.06818959737768 S 11.61916148619012 8.24831438706515 8.99403430232513 O 11.71990543520959 9.66531566952890 9.50214446572418 0 10.78994317621305 8.40678347762341 7.59681610190041 O 12.94991178988732 7.72400468193753 8.61686501886820 0 10.82239834529624 7.39745832315097 9.84788004132669 0 14.44024053934140 8.46524811965310 13.76817167003354 0 0.19376680107976 8.37239073886702 11.58446861295810 O 11.00630035896835 3.68314212079200 14.23121732749031 0 10.02163960660083 2.82585500713973 12.11671188068087 O 8.76320779046834 4.46019224945126 13.46339972578739 0 7.22747755453732 20.26705087810091 12.63832233778535 0 4.78987230593188 2.71930018369376 2.43104045113584 0 2.20226338477120 13.32225249261649 9.74460265491065 0 5.71708891247882 18.13899147673898 13.21837431175504 0 3.29572781728178 0.73047800181676 13.51254282715304 O 3.34319607860295 0.71046531838646 0.95596254653247 O 11.12769855834219 0.56920854906126 13.55835279158621 O 11.18624174590585 0.56185454901179 0.99931532968452 0 4.79016325063732 2.72926701501933 12.12976356236073 0 5.96411836260482 4.32996678963049 13.22933695526374 0 1.17462471772404 7.54121751086157 8.60300947866127 0 2.43011659005723 9.13380398078458 9.61473180487710 0 9.18662552298905 2.02716182129705 14.72945522701111 0 9.77290166731451 19.64667644722157 12.15946553588217 0 9.79093714296713 2.54627335728817 2.47330288372912

0 8.62882120901624 4.18160795469519 1.41925669894182 0 14.77132234366905 12.31350912576452 8.60202741334614 O 7.22058842793050 20.18621816971488 1.80715890821974 O 2.45349115827378 13.04722481776774 4.60208588783951 0 1.36321597312997 10.14608394894765 7.21392557984349 0 1.22680414329681 14.64969601260358 5.63873188783653 0 8.64638626448636 18.00671438583890 1.14982101459063 0 7.24448659857252 1.72607426675984 1.34994474175522 0 4.64285883877061 19.79077543871354 12.09422371721993 0 1.21754138137403 14.87222750260521 8.41734621217091 0 12.12763659996173 13.14727489022378 9.69265948290634 0 6.15993208759571 0.88132415356129 10.74753076163146 0 0.98557519993090 11.22402701275271 3.26342223572616 O 5.77951500812019 18.05836121981967 1.08109848403359 0 5.74825889415356 20.63054449662770 14.63691229110030 O 12.20163907530597 9.05752290115950 4.74829939863984 0 13.33372743198097 14.80346054511216 5.80710692888510 0 7.27391204379537 1.79910016385864 13.20363239539704 0 8.60514598061246 18.03277391143132 13.24510337070726 0 12.59078527777998 12.53703388576569 7.17420342222960 0 9.77020129251034 19.60842302708738 2.29958332720578 0 5.25403166128160 2.15974824784228 14.67535040768484 O 13.54164857882180 11.17270133917068 3.20971397404534 O 5.95842411412599 4.29822711040688 1.29501669877354 O 12.38865708909570 13.19369014464208 4.52059998096169 0 14.70215629901047 9.75415061752973 5.20465836569585 0 13.31032102102403 14.76252619181469 8.63030633269224 0 6.08307282574787 0.71872815467085 3.77896567453269 0 13.23033668495077 10.16396849886430 7.19697366995990 0 14.66238295802226 9.79233707326654 9.22738444571539 0 8.35157552648519 0.68918237504171 3.77274512891551

0 1.08427945989492 11.34108787882262 11.12222492842814 O 4.64585899876675 19.64223794741445 2.24726685838214 0 8.67228723889538 20.53443004236642 14.64689104836486 O 13.64345558080364 11.43386827029187 11.09560766889533 0 2.60605571551338 9.34209437393711 4.85779018412038 0 13.39232392103747 7.51658240388447 5.91135070073379 0 8.43004511630217 0.87975850156269 10.76928758240775 0 14.68234194728965 12.23997287429696 5.72663216099383 0 1.41745332388606 7.70825575493177 5.89293120703527 O 10.83507849067066 11.22951618566993 5.49701274170337 O 3.77909332959447 11.30601196689449 8.97578376013404 0 2.08272234310922 12.47994599468764 7.14446224775290 C 14.25646447798949 8.05796088822373 12.49545898197151 C 13.07379514708713 7.18089021446395 12.36425551175568 C 13.14818894138854 6.05332176957542 11.53783611165537 C 12.13182576953476 5.10267658448812 11.57969362372470 C 11.02990567475506 5.34087041784515 12.40054808186020 C 11.92148884389581 7.44585118884229 13.11560846697873 C 10.87810484042407 6.53409643250790 13.11468061149568 C 2.53397081506623 16.68114506685255 4.30703982330829 C 4.39176447022527 16.00705093840264 2.33049735247429 C 4.30101890057248 16.17232430006045 11.86696829565166 C 0.55873459899002 0.60402406003082 1.04451879873470 C 13.99125246306871 0.57492296854163 1.05715999754431 C 1.20578698712736 0.64069176866527 14.65140679171560 C 2.70497187010621 0.69261584780725 14.64255363301128 C 13.91822990910084 0.60995679936886 13.45996833785874 C 0.48614443280943 0.63887818757315 13.44674276460600 C 13.22138449671862 0.58095179177969 14.67754678564701 C 11.72166401513955 0.56785287668603 14.69186076511608 C 4.56940758069036 6.34598437725980 11.80510858283128

C 3.83701660499791 7.29062875087348 11.09445886525343 C 4.33072648378586 4.97958416797170 11.60603188060122 C 5.09536518423624 3.94700865430457 12.37639694978272 C 2.61577714643198 5.52167836948604 9.97704801576446 C 3.34750337431655 4.57565522373181 10.68790686383552 C 2.85725343604601 6.88774392375013 10.17309981274676 C 2.09495448856541 7.92639880147799 9.41056466814732 C 10.28463372430904 17.37670393973791 11.68866889684742 C 11.93407852477894 5.42790765074409 4.65538405211787 C 13.54735772459670 11.58984338016043 0.43333204331141 C 14,72802513162566 11.39178191690315 1.16211623117959 C 13.53480409756729 11.65550530114664 13.86822212282300 C 12.49234257367717 7.86032141200924 5.06577307571162 C 1.97468348441887 14.51217075356036 9.39822651534475 C 12.43643408815121 14.37695062298427 9.46949617858708 C 4.76669223269622 6.36070350891205 2.75416358193549 C 7.29786425763177 0.90890657983203 10.17082276647840 C 5.11489742047937 3.92758242790706 2.18190020582972 C 10.02453639078445 16.01490178802051 11.90350819470920 C 4.14089998717868 17.35411696592845 2.63166500356379 C 8.48803629720154 0.91566430649031 7.94111926652875 C 3.45326254458125 4.68795475707348 3.91346099115782 C 11.72121844026520 6.78360921795479 4.36853472478960 C 11.27077076741506 17.75043636960250 10.76226631709228 C 2.33204739676909 8.10528083127949 5.10612103455483 C 11.70070310672561 15.41897145371824 10.25491447787313 C 7.23942739438725 0.84684618226446 5.86087588433893 C 6.04078273723657 0.89101357967061 6.58900531431641 C 14.77567067312416 11.43600005278197 11.68940527274308 C 3.72762252964414 15.00160974584594 3.02375129127775 C 6.06625730824007 0.93395569956078 7.97971176633024

C 10.77230441684105 7.14602437039046 3.39937685028312 C 10.84943676423895 15.03808397322122 3.15310654935598 C 4.90272243333882 18.43336279767917 1.93080189726318 C 11.81513924187910 15.43811862307061 4.08921974979954 C 9.50650740528425 3.77106675053952 2.24842716929175 C 8.46248088630270 0.87347615461480 6.54960605721908 C 4.07439030134707 17.53391453608213 11.61936624342496 C 2.80343342721697 15.33351513480175 4.02429840662562 C 2.43191366775833 16.94816719833332 9.93582538299002 C 12.57074994088154 14.39835382144737 4.85102491550163 C 1.11882565660982 11.36358660331134 13.91706098449855 C 4.86176875427619 18.56164410958326 12.36854702297383 C 4.43877375026268 5.01281554414490 2.96994089996798 C 3.60385643169310 15.20774265313182 11.15239969417542 C 9.50165185092906 18.42640262688191 12.42440362727681 C 3.12867809013210 17.91619264798063 10.65519386400857 C 2.66997738290313 15.58785357683909 10.17657407365987 C 14.75211026175531 11.51630586956478 13.18630429186984 C 10.72746777898389 15.04467117396444 11.19476560219508 C 2.79548570223143 5.69266471970994 4.61431128122637 C 10.10971115763985 15.99153478136873 2.46419443100804 C 11.30420555658272 17.75369782098446 3.63070724891005 C 2.11072091633984 14.26816908357030 4.80666284857209 C 12.04036537786079 16.80059813405360 4.32335606527330 C 4.10759846633147 7.36794472767021 3.45554179823301 C 7.22161243332777 0.75182260677435 4.36169967818001 C 3.19994517213951 17.68546614158975 3.61599802508810 C 10.05145784197405 6.16945899565831 2.72495927198595 C 9.52586308234772 18.39239148359795 1.99033733264201 C 11.97165615351839 16.78070958649604 10.05114551242352 C 11.21317063349356 4.44873908349406 3.97605950221500

C 14.68327591562774 11.25879852204464 2.65588382615150 C 3.10847834826189 7.04306308704048 4.38581739332663 C 1.13030861747156 11.30189858966448 0.48389729341704 C 10.26892161866614 4.81305370710261 3.00509204123554 C 7.28951445004374 0.93386041830658 8.66944694714095 C 10.33133311250948 17.35501389051219 2.70185675769411 H 10.00419136995051 7.83596256597471 7.69462069025221 H 12.21548781680009 4.16393511486561 11.03415458193227 H 14.03205192665976 5.90138174782438 10.91897080604040 H 9.99586413724617 6.68733772873019 13.73352423908894 H 11.86880876459747 8.34530647994045 13.72708967644965 H 5.53822074970119 6.60204946053324 2.02399795907924 H 11.47043582494611 18.80995716086182 10.60729023702827 H 2.95891857508124 18.97744104852317 10.47765025125046 H 14.68129041475431 9.22803795228823 10.03555203860870 H 0.35587561537037 9.11285276194814 13.78066993798755 H 1.12618523180163 0.60384952452563 1.97409381167496 H 13.44026387968458 0.55428257503934 1.99646629855253 н 13.34973858372982 0.61447841698669 12.53099568351079 H 1.03655427640768 0.66303261588557 12.50689681140802 H 5.33363670155693 6.64869326992990 12.52010315854079 H 4.00876396024501 8.35570367247489 11.24187966454660 H 1.85458221210192 5.21832092876270 9.25885627469500 H 3.17104062635314 3.51079887805288 10.54456971430516 H 12.73377616327563 17.06144619709486 9.32537034790870 H 5.09619121390147 0.88136997610884 6.04636889442233 H 1.70269381874515 17.23084420258408 9.17708846422027 H 2.05957543443937 11.27658385670576 13.37380509296409 H 9.26167371890627 15.73420053380483 12.62865264244043 H 12.60567470182349 11.67548005892870 0.97435646053656 H 3.20857561422825 3.63928724031336 4.07716587099612

H 1.80720465448469 16.92028223587778 5.08150681995231 H 7.22124598517515 19.73248180704598 11.83116748052909 H 12.67113994935832 5.15863819981833 5.41125053991053 H 11.37255365679976 3.39099082629026 4.18165711013691 H 12.79238578862436 17.09344712836326 5.05478588779244 H 3.91746474513724 13.95124362427537 2.80731967146636 H 2.01966433664085 5.45151217001197 5.33914745011721 H 9.31583297006582 6.43691445650171 1.96785753529621 H 10.68576500660938 13.97294409219175 2.99531768357459 H 9.38727575824833 0.85077186544960 5.97470216200832 H 14.72165183910163 9.17108645579277 4.43199523050475 H 9.43330013496209 0.92639529501165 8.48259015283150 H 12.62254501534928 11.78466499941759 13.28725626046802 Н 10.52797139223214 13.98590100375794 11.35337712130379 H 4.34968992805656 8.41628224877145 3.28366545707491 H 2.04270470829197 11.17098122821069 1.06460065144387 H 9.34903895553846 15.70007980142663 1.74107181965465 H 5.11846962787682 15.76873381722843 1.55529455363140 н 10.62012277916778 8.20302624078776 3.18577750077931 H 3.77634531946171 14.14581249887892 11.32040968503246 H 3.01287595847115 18.73640231126214 3.83173818101138 H 11.46370024230699 18.81766778556440 3.79865241017094 H 7.21908729484476 19.62246674708868 2.59418592886524 H 5.03686730564174 15.89019700272423 12.61853560148293 H 5.14144725629207 0.95652633650976 8.55424358835841 H 4.47152929303329 2.72984222917574 14.66990816523935 H 10.02757301364958 2.55923179592445 14.80115157553420 H 11.77371063707927 13.05931470098837 7.15379158766055 H 10.34754896193355 10.39615656120835 5.58216077269129 H 4.27969413135396 10.48928157360041 9.12029837346294 H 2.88540731245148 13.02354101313616 7.16467056630379

HI-UiO-66-H<sub>2</sub>SO<sub>4</sub> protonated sulfonate group

## 224

Zr 7.18280374970988 3.28404960144741 14.69510390765740 Zr 14.66482496022935 13.79618819205529 7.26204815011840 Zr 7.20370062616261 19.19688012268371 14.70835263419378 Zr 5.46078402076132 0.79051727737911 1.64508332716523 Zr 12.76651350456910 11.25172248438262 5.46242335453235 Zr 14.65321307933359 8.77695284419509 7.26764509617915 Zr 13.05258535941345 11.31978009950380 9.04684799248646 Zr 5.43084120674626 0.77124573501384 12.92677741364661 Zr 1.46666289588677 11.28436255282995 5.49243333126121 Zr 9.01966251844837 0.80523634299183 1.62984735864484 Zr 1.75983252568855 11.23673934112147 9.06084372783368 Zr 8.98106454289824 0.75657623401092 12.93121034563229 S 12.72012963557608 4.85024745948561 14.69526766555514 S 9.18413018343779 4.08088228041414 11.96615558492575 0 8.51525110252884 4.47373019230611 13.23399222777085 0 9.77015213208674 2.70651755954743 12.03837270203997 0 7.91450832252895 3.97316604258726 10.95372554612170 0 10.10731349280697 5.05453932100831 11.43515566320028 0 12.07291541787792 9.46244505560210 9.77312441519893 0 13.18086827345365 7.80161353667862 8.69837159524961 0 12.84608514839657 5.92060690237106 1.07462984354867 0 13.96932957824724 4.12836652404007 14.68318395336616 0 11.50901287711864 4.12994191793922 0.00759751875610 0 7.21144011784168 20.28008108497731 12.71558631690982 0 4.75441874169049 2.79642505355757 2.44085502670576 143

0 2.15268672488099 13.31792881894051 9.87882101011330 0 5.74948906809778 18.13002870348431 13.34871142790127 0 3.27320972156498 0.73135183637049 13.56830783957773 0 3.32035852708834 0.73065674115754 1.01163582102180 0 11.11258595934369 0.70954586906279 13.55598353099071 0 11.15966856299083 0.75391834583275 0.99724397123991 4.73152947104723 2.69810746685674 12.10762422562079 0 5.81757521398008 4.32456752725639 13.25678401163832 0 1.20548712709764 7.60102020626784 8.57889837234946 O 2.43213697401075 9.16557717880455 9.67072237417142 0 9.18954919576023 2.23142295437741 14.65780830532205 0 9.77977384313591 19.69683134379285 12.23433491477550 0 9.69324579061373 2.74493214858381 2.44495538264572 0 8.57188890834070 4.36654909139975 1.31827782466831 0 14.72284612751089 12.33496453127410 8.69589364326802 0 7.24893640907088 20.31115428357304 1.86697672549796 O 2.40355638914706 13.13788647076546 4.69861496724122 0 1.33411507351898 10.20397856838283 7.25198812744668 0 1.20943954564422 14.74670114102302 5.76515361687875 0 8.71528090917918 18.16117517400830 1.24316756365600 0 7.23592627616667 1.83198128003252 1.33271054914004 0 4.63487558973317 19.75505192781440 12.22313443431984 O 1.19426388038699 14.89816597219707 8.56853952167893 O 12.10063213978131 13.15390430069074 9.83515483849665 0 6.07894804421876 0.80075353107372 10.76607436033184 O 0.88881906414050 11.33035894489825 3.36215757595026 0 5.83487021753694 18.12768009640720 1.22198145959271 0 5.73839529517336 20.66918309571631 14.70535718566376 O 12.07058294456939 9.18944994071006 4.85077338999844 0 13.31081395321916 14.91205994614525 5.96406380519675 0 7.21037983429577 1.82066044670529 13.21552112168646 144

0 8.63331168265954 18.10113858044894 13.36757594381401 0 12.52545727986091 12.59762042482701 7.29235767787378 0 9.82876296117254 19.79113318344199 2.36235965766970 0 5.20244052728920 2.19131639287123 14.69722931768570 0 13.44748740568134 11.26637568904887 3.30475781503646 0 5.89017871527349 4.38048136464942 1.28204170960803 12.37010155633980 13.33777223562329 4.63510610325349 Ο O 14.60885576876101 9.84438415894687 5.26632027560658 0 13.29105018788943 14.77052338300123 8.77821864418683 O 6.09300645436095 0.86254924964232 3.78973288260989 0 13.18322312887058 10.23718384744158 7.28053367102309 0 14.72664337868880 9.86368715851737 9.26922013848633 0 8.36337969496537 0.85935462818770 3.79646224420857 O 1.09980375323881 11.24775638840099 11.22579069889315 0 4.67968832818373 19.72220680420721 2.35098202827763 O 8.67228565753280 20.67209222550969 14.69810396836293 0 13.66459548470203 11.41159932743940 11.17463369324916 0 2.49921385024473 9.40926117160041 4.85459960455228 0 13.25927495025862 7.60869852450820 5.96633295494083 0 8.34869042286385 0.78564613291722 10.77129309773663 0 14.62592415357853 12.32913456684551 5.82596905738306 O 1.30059067356960 7.76851353842638 5.86643807035547 O 2.00559647221127 12.56519506192869 7.23618925777852 O 3.75717164617938 11.35669985554656 8.95571404837116 0 10.76868604368001 11.38334815167851 5.56826307678250 C 12.56209387812595 8.27185623012190 9.70393373975783 C 12.51352368509564 7.41532252710414 10.93228480201288 C 13.27216380275087 6.23557819361562 10.96045611023058 C 13.35501525523556 5.47629629703602 12.12222381077489 C 12.65425939213774 5.89803415102427 13.25418916830033 C 11.82936798190799 7.82994608467026 12.08375493304234

C 11.88624892108995 7.06554637578157 13.24513483672803 C 2.54860193592239 16.77831713690749 4.43330410779026 C 4.41817340429377 16.08495248262767 2.47666355098746 C 4.29737056984221 16.13640041018331 12.02084394686149 C 0.52184891906726 0.72241259936559 1.08179767782626 C 13.95476701468752 0.72442021558164 1.07875408241890 C 1.18177859101078 0.70237237033302 14.69672007896853 C 2.68043262713331 0.71744844529758 14.69931630508155 C 13.90827556468892 0.68052248888981 13.48135109463533 C 0.47559488726388 0.67898675404104 13.48361292307909 C 13.19912798940225 0.70588951641534 14.69150421175815 C 11.70135458685331 0.72410109081005 14.69068751486469 C 4.56357005137219 6.31156368014185 11.76387255610960 C 3.86450552656176 7.27725369984383 11.05248363460684 C 4.28766519372773 4.95385917060796 11.55688675291971 C 5.00698526025883 3.91980655033493 12.35941395893504 C 2.61906981351560 5.54068525465895 9.90315785823447 C 3.31852158858043 4.57272490442376 10.61679451631456 C 2.88309871012877 6.89950763388238 10.12326713390232 C 2.12090671107540 7.96231004383325 9.39822493755463 C 10.29249519413235 17.41773934826408 11.80647816459800 C 11.73803489807646 5.57569134649369 4.71395194883067 C 13.47598787787149 11.48077442076899 0.49632942187825 C 14.64979705785329 11.34948132731007 1.25163547812539 C 13.49164596675277 11.49468800739765 13.93237276414620 C 12.36722078681848 7.98583518214877 5.13250677585228 C 1.94465025815879 14.51648022441685 9.54508078533295 C 12.41652866933184 14.38322782608397 9.61573427174825 C 4.64522933539394 6.44279732451101 2.70836106052481 C 7.21324535137167 0.82595844262779 10.18513140410619 C 5.05222246290024 4.00860619947662 2.17263386475950 146

C 10.04236742759263 16.06089642088807 12.06044949882919 C 4.17750807090641 17.43626559214026 2.76786371525978 C 8.43176281377244 0.83634637686403 7.97934650824036 C 3.38621310259274 4.75924804009395 3.90833089574251 C 11.59825547138330 6.93190665872243 4.39457201504808 C 11.25889531649848 17.77410271758331 10.85383400370383 C 2.22156585952076 8.17159400250936 5.08615338458045 C 11.68985604133697 15.43361934468735 10.39682547323216 C 7.22478352305972 0.91522475038475 5.87871091917332 C 6.01419539420128 0.98426687542839 6.58434995555276 C -0.03895598073820 11.34872015220088 11.78828762095859 C 3.73417659021605 15.08683502242861 3.16338892860619 C 6.01166832596339 0.97179098570900 7.97587263180091 C 10.72974086363944 7.31721990573733 3.36125186363703 C 10.89132033504536 15.21003977418809 3.25443227902043 C 4.94562330327792 18.50891949914712 2.05759113520194 C 11.84382856504427 15.59617152470983 4.20983486108835 C 9.41366601209540 3.96016319305539 2.18339571654638 C 8.43397468224904 0.85060000595567 6.58765396292629 C 4.08435393009858 17.49957399993101 11.77158613597866 C 2.80113353877408 15.42591051563574 4.15392789869345 C 2.43305709131384 16.93388568434632 10.09116245908929 C 12.56506496268305 14.53504887223257 4.98258209013517 C 1.07933714861855 11.24370058799902 14.03823116020288 C 4.87630807785543 18.53214459997092 12.50834036225900 C 4.35220305708117 5.09072948746920 2.94700337920988 C 3.58663123605497 15.17929569365185 11.30701173747352 C 9.51779731271623 18.48188700815355 12.52764384137839 C 3.14124082458876 17.89192169155234 10.80934461840583 C 2.65637419056258 15.57187370723556 10.33210433252570 C 14.72909931772318 11.36816396760422 13.28267041110241 C 10.73566632221103 15.07688174048484 11.36154439770034 C 2.71786778236913 5.75950136247896 4.60622351731699 C 10.17167010349945 16.17140389171338 2.55576060576779 C 11.36430409806320 17.92020081816073 3.73930224311589 C 2.08455762580920 14.36287893342260 4.92445112875010 C 12.07971228189293 16.95762113993781 4.44522580084902 C 3.97671944293725 7.44553293995307 3.40778412388427 C 7.22878111058173 0.88469768886857 4.37764636148748 C 3.23014479301514 17.77537834380398 3.74462967003286 C 10.01435247439092 6.35719064982872 2.65039137988029 C 9.59417127035851 18.56776504583113 2.07605861390435 C 11.95213665297163 16.79121601574754 10.15576919736946 C 11.02225827270895 4.61453307291507 4.00554511547065 C 14.59018503169624 11.31945845035261 2.74557517404201 C 3.00020502015043 7.11338721992435 4.35927681648598 C 1.06496174484123 11.23645568890078 0.60228396313987 C 10.15890084322206 4.99711175068065 2.96837917277910 C 7.21952589032034 0.88768867271685 8.68491918248832 C 10.39799196681855 17.53380797533744 2.79811996565227 H 8.26328762297283 3.75306501088232 10.06797203043815 H 13.96125712356877 4.57270851206703 12.16231623509724 H 13.81576463060369 5.93921849926899 10.06484705393556 H 11.35059888492519 7.38196300114473 14.13888079399173 H 11.26219609337892 8.75921416779270 12.05809652621359 H 5.39908823296872 6.69134162761406 1.96239641969657 H 11.45006321858373 18.83054786215476 10.67066150562809 H 2.98312613168282 18.95497706558837 10.63322249093781 H 14.77509209577604 9.33079832281990 10.07636747304916 H 11.98109623597226 5.94199800063008 1.54721451730698 H 1.07871416368733 0.74313993846183 2.01749238887374 H 13.39351958172888 0.74953704304873 2.01162711029808

H 13.35034338046360 0.66711973492587 12.54598394719670 H 1.03708254513730 0.66131785113510 12.55045821738545 H 5.32565291454037 6.58837984763789 12.49071161304203 H 4.05761067605049 8.33717828402500 11.20989665196416 H 1.86070133968257 5.26214203697812 9.17218166487306 H 3.12282323346104 3.51195264151152 10.46600812895154 H 12.70041201197982 17.05691884046357 9.41031481378884 H 5.08223766254544 1.04004930653040 6.02302736005563 H 1.70621670791183 17.22400068716977 9.33347244547893 2.03209147835980 11.14935596778733 13.51874868636408 н H 9.29387878714001 15.79550373036679 12.80584834425205 H 12.52390999796790 11.57718067810379 1.01699370539232 3.16545738197006 3.70826572535846 4.08995108512310 н 1.81697809987444 17.02746092662913 5.20039852066947 Н H 7.20905489292592 19.71916671983109 11.92657738781406 H 12.41603073098680 5.29277485789120 5.51830882216988 н 11.12409303258929 3.55506678933023 4.23516551499356 12.82330863423503 17.24456684244628 5.18786537303567 н н 3.91524865883640 14.03489564215902 2.94710783611272 1.95895548291396 5.51020438065443 5.34617048785775 Н H 9.33396723708584 6.63749660390051 1.84647171327626 H 10.72032846748470 14.14704619081515 3.09017148373179 H 9.36717316973965 0.79927915591403 6.02817836077076 H 14.63544270901009 9.27933594427683 4.48057915361788 H 9.36359334337141 0.76960235750423 8.54005988046735 H 12.59182886567061 11.60176903963379 13.32847635626973 H 10.54332527138695 14.02103312665074 11.54758426078663 H 4.19567161811726 8.49586008862044 3.21857509804728 H 1.96641231509754 11.14036246608419 1.20552157584399 H 9.41957315571388 15.88591018168273 1.82159824264758 H 5.15062008069009 15.83566372947809 1.71029602966266

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