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par

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Abstract

Metal-organic frameworks (MOFs) have firmly established in the field of porous materials since their early discovery in the 1990s. With a plethora of applications, these materials offer endless possibilities owing to their tunable, modular nature. The vast amount of synthesized MOFs indicates an utmost interest in this topic among researchers in academia and industry. However, bulk scale uses of MOFs for gas storage, catalysis, water purification and complex separations require such MOFs to have a definite, large pore size in the nanometer range. As MOFs are modular, the production of such large pore materials requires a separate synthesis of particular building blocks called ligands. Most pathways to obtain large ligands rely on the use of palladiumcatalyzed coupling chemistry, thus incurring enormous costs and low scalability of the corresponding MOFs.

In this thesis, we explore metal-organic frameworks based on N-heterocyclic ligands. We show how the use of these heterocycles has allowed us to easily construct ligands and new MOFs with them, and we showcase various applications of these materials. In Chapter 1, we briefly overview the existing state of the art in ligand design for metal-organic frameworks and define thesis aims. In Chapter 2, we show how a new ligand forms a Cu-Sp5 MOF, which has one of the highest CO₂/N₂ adsorption selectivities in flue gas conditions reported to date. We investigate the origins of such remarkable performance via multiple characterization techniques. Chapter 3 reports a new MOF Cu-Sp5-BF4. We for the first time access N-heterocyclic carbene (NHC) adduct chemistry in a MOF via ligand post-synthetic modification. We then reveal how this process alters the dimensionality of the material and how it improves the accessibility of NHC sites for a secondstep iridium grafting. We finally shed light on iridium speciation in the final material using a combination of EXAFS and XPS methods, and how it changes upon a catalytic reaction of stilbene hydrogenation.

Chapter 4 illustrates a new approach for ligand synthesis for large pore MOFs. We show the development of a new concept in ligand design that we call LigX. Using the LigX approach, we simplify large pore MOF ligand synthesis by avoiding time- and cost-intensive Pd-based chemistry. We show the synthesis of structurally diverse MOFs using this methodology.

Keywords: metal-organic frameworks, ligand, synthesis, heterocycle

Résumé

Les structures organométalliques (MOF en anglais) se sont solidement établies dans le domaine des matériaux poreux depuis leur découverte dans les années 1990. Ces matériaux, aux nombreuses applications, offrent des possibilités presque infinies en raison de leur nature flexible et modulable. La grande quantité de différents MOF synthétisée démontre l'intérêt grandissant pour ces matériaux parmi les chercheurs universitaires et industriels. Pourtant, les utilisations à grande échelle des MOF pour le stockage de gaz, la catalyse, la purification de l'eau et les séparations complexes exigent que ces MOF aient de grands pores de taille bien définie de l'ordre du nanomètre. Puisque les MOF sont modulaires, la production de ces matériaux à grands pores nécessite la synthèse préalable de composants spécifiques nommés ligands. La plupart des méthodes de synthèse permettant d'obtenir de grands ligands reposent sur l'utilisation de la chimie de couplage catalysée par le palladium. Ceci entraine des forts coûts et une impossibilité de synthétiser ces MOF à grande échelle.

Dans cette thèse, nous explorons les structures organométalliques basées sur des ligands Nhétérocycliques. Nous montrons comment l'utilisation de ces hétérocycles nous a permis de synthétiser facilement des ligands et de nouveaux MOF. De plus, nous présentons diverses applications de ces matériaux.

Dans le chapitre 1, nous donnons un bref aperçu l'état de l'art dans la conception de ligands pour structures organométalliques; de surcroît, nous définissons les objectifs de la thèse. Dans le chapitre 2, nous montrons comment un nouveau ligand forme un MOF Cu-Sp5, qui présente l'une des sélectivités d'adsorption CO₂/N₂ les plus élevées rapportées à ce jour pour des gaz de combustion. Nous étudions les origines de ces performances notoires par le biais de multiples techniques de caractérisation. Le chapitre 3 présente un nouveau MOF Cu-Sp5-BF4. Nous décrivons pour la première fois à la chimie des adduits de carbène N-hétérocyclique (NHC) dans un MOF via une modification post-synthétique du ligand. Nous révélons ensuite comment ce processus modifie la dimensionnalité du matériau et comment il améliore l'accessibilité des sites NHC lors d'un greffage ultérieur d'iridium. Enfin, nous mettons en lumière la spéciation de l'iridium dans le matériau final en utilisant une combinaison de méthodes EXAFS et XPS; en montrant comment celle-ci change lors d'une réaction catalytique d'hydrogénation du stilbène.

Le chapitre 4 illustre une nouvelle approche dans la synthèse de ligands à grands pores pour les MOF. Nous montrons le développement d'une nouvelle stratégie dans la conception de ligand que nous appelons LigX. Grâce cette approche, nous simplifions la synthèse de ligands pour les MOF à grands pores en évitant la chimie basée sur le palladium qui est coûteuse et chronophage. Nous montrons la synthèse de MOF structurellement diversifiés en utilisant cette méthodologie.

Mots clés: structures organométalliques, ligand, synthèse, hétérocycle

Acknowledgments	
Abstract	
Résumé	5
Chapter 1. Introduction: standing on the shoulders of giants	9
1.1 Motivation	9
1.2 Metal-organic frameworks discovery	
1.3. Metal-organic framework evolution	
1.4. General notes on ligand design in metal-organic frameworks	
1.5. Ligands with N-heterocyclic backbone	
1.5.1. N-heterocyclic carbene ligands	
1.5.2. N-heterocyclic ligands based on piperazine and homopiperazine	
1.5.3. Summary	
1.6. Thesis aims and outline	
Chapter 2. Selective CO ₂ adsorption by a new metal-organic framework: synergy be metal sites and a charged imidazolinium backbone	etween open 30
2.1. Introduction:	
2.2. Results	
2.2.1. Cu-Sp5-EtOH	
2.2.2. Cu-Sp5-MeOH	
2.3. Conclusions	
Chapter 3. From 3D to 2D and back: controlling metal-organic framework dimension heterocyclic carbene chemistry	onality via N- 47
3.1. Introduction	
3.2. Results and discussion	
3.2.1. Material synthesis	
3.2.2. Methoxide treatment	52
3.2.3. Iridium modification	
3.3. Conclusions	58
3.4. Supplementary information	59
3.4.1. General notes	59
3.4.2. Synthetic protocols	61
3.4.3. Catalysis protocols	

Contents

Chapter 4. LigX methodology: a whole new world of MOF ligands	64
4.1. Diamine-based ligands	64
4.2. Piperazine-based ligands	66
4.3. DHP-based ligands	71
4.4. Linear tetracarboxylate ligands	75
4.5. MOF-74/CPO-27 based ligands	77
4.6. Triangle ligands	81
4.7. Conclusions	83
4.8. Supplementary information	84
4.8.1. General notes	84
4.8.2. General protocols	85
Chapter 5. Conclusions and future outlook	99
Chapter 6. Appendices	101
6.1. Experimental data and tables, comparison of materials for CO ₂ capture, detailed calculation description for Chapter 2	101
6.2. Experimental data and tables for Chapter 3	113
6.3. NMR and HRMS spectra of ligands and their precursors for Chapter 4	125
Bibliography	153
Curriculum vitae	164

Chapter 1. Introduction: standing on the shoulders of giants

1.1 Motivation

Humankind faces perplexing challenges in the 21st century. Mitigating global climate change, air and water pollution; increasing renewable energy production and lowering reliance on fossil fuels is on the agenda. With the CO₂ concentration in the air exceeding 420 ppm, the highest in more than 2 million years, and the sea level rising with the fastest rate in 3000 years, immediate action must be taken to prevent the acceleration of global temperature growth, according to a recent UN report on climate change.¹ With the main CO₂ emissions coming from the combustion of fossil fuels, a remedy can be found in using renewable, carbon-neutral fuel. However, since energy transitions are historically slow, a continuation of non-renewable carbon-based fuel consumption is expected for years to come before the deliverance from non-renewable, air-polluting sources, such as gas, oil and coal. Thus, the need arises to alleviate current CO₂ emissions stemming from those fuels through carbon capture and sequestration (CCS) and/or conversion. This idea is not new and it has been explored since the 1930s, nevertheless, currently, implementation of largescale carbon capture is constrained by the lack of an adequate gas separation technology.² The most mature capture technology is using liquid-amine scrubbers, such as monoethanolamine, for reversible binding of CO₂ from flue gas. However, their operation on an industrial scale is not feasible yet due to the enormous energy requirement for regeneration, which is estimated to be ~ 30 % of the total energy output of the power plant.³ The energy loss is arising from a high heat capacity of liquid scrubbers, owing to mandatory heating of solution necessary to release captured CO₂ for further treatment. It is expected that the use of solid adsorbents, with lower heat capacities, could significantly reduce the parasitic energy loss.⁴⁻⁵ Once the CO₂ is captured, the gas should either be stored and/or converted into valuable chemicals or fuels. While storage may depend on geographic and economic conditions,⁶⁻⁷ conversion of CO₂ is a promising way to re-use it as a carbon source. It has been calculated that in the case of implementation, the conversion of CO₂ for particular tasks, such as synthesis of selected fine chemicals, will produce a high added value to those products.⁸ Moreover, considering persisting development of solar cells and water electrolysers for a clean, renewable hydrogen production, the combination of hydrogen with CO₂ is expected to give a renewable carbon fuel (methanol, formic acid, hydrocarbons) which can reduce current and prevent further CO₂ emissions from mineral carbon fuels.⁹⁻¹⁰



Figure 1. A general MOF structure as exemplified by MOF-5. Empty pore spaces are represented by colored spheres. Adapted from ¹¹

To enable CCS and conversion, many materials are under consideration. Among those, metalorganic frameworks (MOFs), porous materials that consist of metal-ions or metal-ion clusters (also called secondary building units, SBUs), interlinked by organic ligands, are an especially attractive class of adsorbents that have quickly moved to the cutting edge of research due to extraordinary internal surface areas, chemical tunability, and strong and selective binding of guest molecules.¹² Through a considerate choice of the ligand and the metal, which control pore size, shape and chemical functionality, properties related to CCS, such as selectivity, capacity, and catalytic activity can be tuned.¹³ The molecular nature of the ligands within the hybrid organic/inorganic newcomers permits a modular approach to their design and allows the introduction of multifunctional properties in the MOF structure (Figure 1). Accordingly, MOFs, relative to their all-inorganic counterparts such as zeolites, offer interesting opportunities to help solve diverse environmental issues.

To achieve tunability needed for tailoring the materials for chosen applications, in MOFs, one can change the type of the SBU (metal cluster), or the organic ligand. A wide choice of metals in the

periodic table, as well as numerous ways in which the metals can form clusters, offers a certain degree of freedom when designing a MOF. The SBUs themselves are generally produced in situ from simple metal salts such as chlorides or nitrate during the MOF synthesis process. This leaves some ambiguity in structure control as the cluster geometry and connectivity depend mostly on variations in synthetic conditions rather than a pre-defined geometry of a chosen building block. While there are several research contributions dedicated to the use of pre-defined clusters for MOF construction ¹⁴⁻¹⁵, the most common MOF synthetic approaches still rely on the use of simple salts due to their low cost and easy availability.

Ligands, on the other hand, offer broader tunability for MOF design. Firstly, they benefit from a multi-century knowledge of organic chemistry, allowing one to construct virtually any molecule with a given shape and size. Further, functional groups can be easily incorporated into the ligand, providing functional properties to a resulting MOF material. Lastly, a large-sized linker is a prerequisite for the construction of MOFs with ultrahigh porosity, where the ligand size and shape dictate MOF topology and pore dimensions. This tunability, however, comes at a cost as expanded, complex linkers, in general, require a multi-step synthetic protocol with time-consuming workups. Moreover, large amounts of solvents are often consumed to produce a ligand of choice with sufficient purity.

As this thesis is dedicated to the novel ligand and MOF design, below, a brief history of MOFs and the constituent ligands designed to date is described, with a focus on ligand size and shape evolution

1.2 Metal-organic frameworks discovery

First studies on coordination polymers, i.e. materials formed by combining multi-topical ligands and metals, date back to as early as 1965.¹⁶ There, Tomic reported the differences in thermal stability of the polymers depending on ligand structure and metal valency, with polydentate ligands and tetravalent metals showing the highest stability. The structures of the materials, however, were poorly understood and the data did not suggest their porosity. Nevertheless, this study laid down the first concepts of stable MOF construction. The conceptualization of the "framework" term happened in 1989 when Hoskins and Robson for the first time crystallized a member of a MOF family, a coordination complex between Cu(I) and tetrakis-4-cyanophenylmethane.¹⁷ This 3D material featured a diamondoid structure created by combining a tetrahedral organic ligand and a

tetrahedral Cu(I) site, with BF₄⁻ ions and solvent molecules occupying the voids (Figure 2). The authors did not indicate that the removal of guest molecules was possible, although they realized the potential of such materials for exhibiting "potentially useful properties". In their future work in 1990, they synthesized several new materials with similar structures and indicated that such a class of frameworks can be used in applications of ion exchange, molecular sieving and catalysis.¹⁸ Furthermore, they suggested that such a class of materials can combine good thermal, chemical and mechanical stability.



Figure 2. Structure of $[CuC(C_6H_4-CN)_4]_n^{n+}$ framework. Reprinted (adapted) with permission from ¹⁷. Copyright (1989) American Chemical Society

A few years later, in 1995, Yaghi et.al. conceived the term "metal-organic framework", in his report of a new 3D framework structure made with Cu(I) and 4,4'-bipyridine.¹⁹ The exchange of nitrate ions in this structure with sulfate and tetrafluoroborate was shown, and the thermal stability of up to 180 °C in an inert atmosphere was demonstrated. In 1997, Kitagawa et al. synthesized several new frameworks and demonstrated that, under high pressure, gases such as CH₄, N₂ and O₂ can be reversibly adsorbed inside the pores. The breakthrough in the field happened in 1999, when Yaghi and coworkers for the first time demonstrated permanent porosity in a MOF-5 material, constructed, unlike the previous frameworks, from tetrahedral Zn₄O clusters interconnected by 1,4-benzenedicarboxylate ligands (Figure 3).²⁰ The guest solvent molecules could have been fully exchanged with chloroform and further completely removed in vacuum, resulting in a material with empty pores as indicated by SCXRD, elemental analysis, MS, TGA

and NMR. The material was thermally stable up to 300 °C, and the Langmuir surface area was estimated at 2900 m²/g, a value higher than that for the most porous crystalline zeolites at a time. This seminal manuscript laid the foundation for the era of extensive MOF research. The number of MOF publications has grown exponentially since then, as indicated by an extract from a Scopus database (Figure 4). The major milestones on this journey are outlined below.



Figure 3. Structure of MOF-5. Reprinted by permission of Springer Nature from ²⁰. Copyright



Figure 4. Number of MOF publications in Scopus database as of 23.08.2021 ("metal-organic AND framework OR MOF" search request). Inset shows the same data in logarithmic scale, indicating exponential growth

1.3. Metal-organic framework evolution

In 1999, the same year Yaghi discovered MOF-5 and demonstrated its accessible porosity, Chui et al. created a porous copper(II) trimesate, called HKUST-1.²¹ This framework had a cage structure and featured copper paddlewheel sites with terminal water coordinated to them (Figure 5). The striking feature of this framework is the ability to liberate solvent from the paddlewheel site, resulting in a high density of Lewis acidic, coordinatively unsaturated, open metal sites (OMSs) inside a porous structure.²² Such sites act as excellent spots for gas sorption and catalysis and are ubiquitously present in many frameworks synthesized during the following years.²³



Figure 5. Structure of HKUST-1 material. From ²¹. Reprinted with permission from AAAS.

A next important concept in MOF design, namely isoreticular approach, was coined by Yaghi et.al. in 2002.²⁴ There, a series of MOF within MOF-5 family was synthesized, using ligands with different functional groups and of varying lengths. All the 16 materials had similar structure and topology, derived by length expansion and/or side functional group decoration of MOF-5 (Figure 6). This for the first time demonstrated the ability to create new MOF materials using a targeted organic synthesis approach where a ligand of chosen length and function can be used to deliberately construct a MOF. With this, the well-known concept of isoreticular chemistry was born.

In 2004-2005, Férey et.al. greatly expanded the understanding of MOFs as simple combinations of metal clusters and ligands, by a combined computational and experimental approach which lead to the synthesis of mesoporous chromium (III) trimesate, MIL-100, and terephthalate, MIL-101 (MIL stands for Materials Institute Lavoisier).²⁵⁻²⁶ These materials are better understood as assemblies of supertetrahedrons formed by a trimeric chromium cluster and a corresponding carboxylate ligand (Figure 7). The development of these materials was only possible due to computational predictions that indicated the possibility of their existence and further incited experimental confirmation. Both MILs feature extra-large BET surface areas of >3100 m²/g (MIL-100) and >4500 m²/g (MIL-101), and extremely large cubic unit cells with a = 71.26 Å and 88.87 Å, respectively. The cage sizes were also unprecedented at a time, with 2.5 nm + 2.8 nm pores for MIL-100 and 2.9 nm + 3.4 nm pores for MIL-101. Further, the materials had high stability due to the strength of Cr-O bonds and their kinetic inertness.



Figure 6. Isoreticular Znbased MOFs (IRMOFs). From ²⁴. Reprinted with permission from AAAS.





Figure 7. Structures of MIL-100 and MIL-101. Adapted from ²⁵⁻²⁶ Copyright 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. Reprinted with permission from AAAS.

MIL-101

The year 2006 was marked by a discovery of a conceptually new MOFs, called zeolitic imidazolate frameworks (ZIFs), by Yaghi et al.²⁷ Going back to the roots of MOFs, N-donor ligands such as imidazolates were used instead of carboxylates. Owing to similarities in bonding angles in metal-imidazolate bonds in ZIFs and silicon-oxygen bonds in zeolites (Figure 8), a variety of zinc, cobalt and indium imidazolates were synthesized which mimicked the known zeolite structures. The resulting materials featured high thermal stability up to 550 °C, chemical stability in 100 °C 8M NaOH solution, and surface areas up to 1630 m²/g (BET). The strong resistance to hydrolysis and basic media was attributed to a hydrophobic inner surface provided by carbon-rich imidazole skeleton, as well as to an exceptional strength of bonds between imidazolates and Zn/Co.



Figure 8. Illustration of ZIF and zeolite bonding angles (~145 °). Adapted from ²⁷. Copyright (2006) National Academy of Sciences

In the next years, the development of highly stable MOFs did not stop. In 2008, Lillerud et al. for the first time reported zirconium carboxylate-based MOFs called UiO-66, UiO-67, and UiO-68.²⁸ They feature 12-connected $[Zr_6O_4(OH)_4]^{12+}$ clusters interlinked by linear dicarboxylate ligands of varying lengths (Figure 9). In these materials, the thermal stability is up to 550 °C. Interestingly, this stability is dictated not by a metal-ligand bond strength, but by a weaker benzene-carboxylate bond according to the TGA-MS investigation. Further, the UiO family of materials is highly stable in aqueous solutions of acids and bases, going in line with a strong binding between Zr and ligand.²⁹ Isoreticular chemistry allowed for large BET surface areas of 1187, 3000, and 4170 m²/g for UiO-66, UiO-67, and UiO-68 correspondingly.



Figure 9. UiO MOF series structures. Reprinted (adapted) with permission from ²⁸ Copyright (2008) American Chemical Society

Next, 2009 was marked by the development of the first crystalline titanium MOF. Férey et al. made MIL-125 material constructed from titanium cluster octamers interlinked by 1,4-benzenedicarboxylic acid (Figure 10).³⁰ The SBUs in this MOF are different from those in UiO-series Zr-based materials, but they are 12-connected as well. The BET surface area of the material reached 1550 m²/g, a value higher than that of UiO-66 constructed with Zr and the same ligand. Although the UiO and MIL-125 structures are different, Ti is lighter and more abundant than Zr, making it more attractive for future studies and large-scale applications. Further, owing to the photoactive properties of Ti(IV), this material was shown to catalyze photooxidation of benzyl alcohol to benzyl aldehyde via Ti(III) intermediate species. This paved the road for the design of porous Ti-based photocatalysts.



Figure 10. MIL-125 structure. Reprinted (adapted) with permission from ³⁰. Copyright (2009) American Chemical Society

Further, in 2009, Schröder et al. reported a series of isoreticular, copper-based NOTT-nnn materials for applications in hydrogen adsorption (Figure 11).³¹ Nine materials were prepared and characterized, amongst which NOTT-103 has achieved 77.8 mg/g (7.22 wt. %) total H₂ adsorption at 77 K and 60 bar. The exposed Cu open metal site was shown to be the strongest hydrogen adsorption site in the framework via Rietveld refinement of neutron powder diffraction data for D₂-loaded materials. Peculiarities of hydrogen interaction with ligands were highlighted as well and shown to be dependent on ligand structure and type of pockets formed inside MOF pores.

Finally, the effect of local pore metrics on strength of adsorption on Cu open metal sites was discovered and discussed.



Figure 11. Ligands employed for the construction of NOTT-nnn material series and crystal structures of the first four members of this MOF family. Reprinted (adapted) with permission from ³¹. Copyright (2009) American Chemical Society

In 2010, Long et al. for the first time synthesized a 2,2'-bipyridine-5,5'-dicarboxylate based MOF which acted as a crystalline chelating solid for guest metals such as Pd and Cu (Figure 12).³² This exemplified the ligand-induced MOF properties that allow for further applications in catalysis, separations, etc.



Figure 12. Bipyridine-dicarboxylate-based MOF with chelating sites. Reprinted (adapted) with permission from ³². Copyright (2010) American Chemical Society

In 2010-2011, Furukawa et al. brought forward the isoreticular approach concept by creating a series of MOF materials with extremely large surface areas and pore volumes.³³⁻³⁴ MOF-210 set a record of surface area within porous crystalline materials for its time, with BET and Langmuir surface areas of 6240 and 10400 m²/g, correspondingly (Figure 13). MOF-399 material, a structure isoreticular to HKUST-1, had the lowest crystal density, 0.13 g/cm³, and the largest void volume (94 %) among the materials to date, although the authors did not succeed in accessing its porosity via gas adsorption.



Figure 13. MOF-210 structure. From ³³. Reprinted with permission from AAAS.

In 2010, Snurr, Hupp et al. reported a combined computational/experimental approach for making the NU-100 material (NU stands for Northwestern University) featuring ultrahigh surface area and gas storage capacities.³⁵ This material was constructed from a large triangular hexacarboxylate linker combined with copper paddlewheel clusters (Figure 14). The use of space-efficient triple bonds allowed to minimize the mass of the linker while keeping its rigidity. NU-100 is an *rht*-topology MOF that is isoreticular to many of its analogs with smaller ligands. The measurements revealed the high BET surface area (6143 m²/g), and high storage capacities for hydrogen (164 mg/g, 70 bar, 77 K) and carbon dioxide (2315 mg/g, 40 bar, 298 K) at high pressures.



Figure 14. Structure of the ligand employed in the construction of NU-100 (top left) and crystal structure of NU-100. Reprinted by permission of Springer Nature from ³⁵. Copyright (2010) Springer Nature.

In 2012, Yaghi et al. applied the isoreticular concept to a MOF-74 framework.³⁶ This material possesses a honeycomb-like structure, a natural example of a highly stable porous scaffold. By extending its linear linkers up to 5 nm in length, the authors were able to produce stable MOFs with hexagonal pores of up to 9.8 nm size (Figure 15). This was unprecedented at a time, as this pore size regime was unattainable in MOFs before. The accessibility of the pores was shown using gas adsorption, as well as reversible uptake of large guests such as vitamin B_{12} (2.7 nm), inorganic cluster MOP-18 (3.4 nm), myoglobin (2.1×3.5×4.4 nm), and green fluorescent protein (GFP, barrel structure of 3.4×4.5 nm size).

In 2016, Kaskel et al. for the first time described negative gas adsorption (NGA) in a MOF material DUT-49.³⁷ This fundamentally new phenomenon was demonstrated to stem from a ligand-induced MOF flexibility, which appeared only at a certain pressure of adsorbate molecule, leading to a sudden change in the structure and desorption of a part of the adsorbed gas with increasing pressure (Figure 16). This seminal work laid the foundation for conceptually new applications of porous adsorbents.



Figure 15. IRMOF-74 structures. From ³⁶. Reprinted with permission from AAAS.

In 2018, a new and to the best of our knowledge current record of surface area and pore volume on porous materials was set by Kaskel et al.³⁸ A material called DUT-60 was firstly discovered *in silico* and later synthesized experimentally. Upon activation, the MOF presented a BET surface area of 7839 m²/g and pore volume of 5.02 cm^3 /g (Figure 17). The key to success in this work was not only the computational prediction but also the scrupulous experimental approach. In particular, the authors discovered that the use of simple zinc nitrate leads to the formation of other,

undesirable MOF phases, and only the pre-assembled zinc cluster in form of zinc acetate gave rise to the formation of the target material.



Figure 16. NGA effect demonstration in DUT-49. Adapted and reprinted by permission of Springer Nature from ³⁷. Copyright (2016) Springer Nature.



Figure 17. DUT-60 structure. Adapted from ³⁸. Copyright 2018 Wiley-VCH Verlag GmbH &Co. KGaA, Weinheim

1.4. General notes on ligand design in metal-organic frameworks

From the above summary of key accomplishments made in the field with regard to MOF structure design, we note that in the first years of MOF design, the attention was drawn to materials with relatively small ligands, which are generally commercially available and/or are easily synthesized. However, many of the record-breaking materials in the past few years contain larger ligands, which were tailored for specific needs. Figure 18 shows a generalized, non-exhaustive compilation of the most common symmetrical ligand types in literature (several comprehensive reviews are available on the topic of ligand design³⁹⁻⁴²). It is noted that ligands having relatively low symmetry are not covered as they mostly lead to just moderately porous structures.

A common, notable feature for larger ligands of almost all geometries is that they are constructed using oligo-aromatic units. For instance, the longest ligand in IRMOF-74 paper was synthesized in 12 steps,³⁶ most of which required the use of palladium as a catalyst, as well as column chromatography purification. This, therefore, is a major factor that complicates the further development of applications for these materials, with other factors being solvent cost, recycling, synthesis temperature, solvent/solid ratio, etc. In fact, techno-economic analyses for large-scale applications such as carbon capture and gas storage require the price of the MOF to be in the range of \$10-\$100 per kg, a value nearly unattainable with current palladium prices. ⁴³⁻⁴⁸

We further noted a lack of carboxylate ligands with N-heterocyclic backbones in the current literature.^{*} While numerous ZIFs and pyridine/pyrazolate/triazolate/tetrazolate-based MOFs are well studied, ^{41-42, 49-50}, they do not fall under the definition of ligands with an N-heterocyclic backbone. Such ligands have N-heterocyclic carbene, piperazine, and homopiperazine cores. In the following section, the current state of the art in this field is summarized and the corresponding thesis direction is outlined.

1.5. Ligands with N-heterocyclic backbone

1.5.1. N-heterocyclic carbene ligands

N-heterocyclic carbenes (NHCs) are unique ligands simultaneously bearing strong σ -donating and weak π -accepting properties. NHC studies have strongly emerged since their first isolation in 1991.⁵¹ A general structure of a typical NHC is shown in Figure 19, where the heterocyclic ring

^{*} By ligands with N-heterocyclic backbone here we mean the ligands where a C-N bond between an N-heterocycle and another part of the ligand lies in the structural core of the ligand, i.e. serves as a mean of connection for two parts of a ligand. For instance, 4,4'-bipyrdine is not considered as having N-heterocyclic backbone because it is built using a C-C bond between two N-heterocyclic rings

size, the number and heteroatom kind, and the saturation of the ring may differ.⁵² NHCs are known to form stable complexes with nearly all transition metals and many complexes exhibit superior catalytic activity for different reactions such as cross-coupling, olefin metathesis, asymmetric catalysis, and umpolung reactions.⁵³⁻⁵⁷ Importantly, NHCs exhibit excellent reactivity with CO₂ as well. They readily form stable betaine adducts which can further be used for CO₂ conversion.⁵⁸⁻⁶² Moreover, the NHC-metal complexes are also capable of CO₂ valorization such as hydrogenation or addition to epoxides/alcohols/alkynes.⁶³⁻⁶⁶



Linear

Figure 18. General symmetrical MOF ligand designs found throughout the literature



Figure 18 (continued). General symmetrical MOF ligand designs found throughout the literature



Figure 19. The general structure of an N-heterocyclic carbene. Adapted and reprinted by permission of Springer Nature from ⁵². Copyright (2014) Springer Nature.

Fusing MOFs with NHCs seems promising, as the resulting nature of hybrid materials would allow one to combine the benefits of the MOF and carbene counterparts. For instance, having NHCs inside a crystalline, well-defined structure, in combination with a distinct pore size and extra functionality like Lewis acidic open metal sites, might lead to interesting properties and performance. In addition, the use of solid support for NHCs for CO₂ capture and conversion would be beneficial because of the lower energy penalty for separation versus liquid-phase reactions, high accessible surface area, and ease of separation. There are several examples of supported NHCs or NHC-metal complexes employed for that purpose. ⁶⁷⁻⁷⁰

The field of NHC MOFs, up to date, has been studied to a certain extent. There is a brief review paper on the topic from 2016.⁷¹ Various geometries of the ligands are summarized in Figure 20. Most notably, the work of Fei et al. for the first time illustrated a free carbene inside a zirconium MOF, to produce a material that was the first catalyst capable of performing quantitative hydrogen transfer from silanes to CO₂ achieving >99 % methanol yield.⁶⁹ The same material was further modified with metal salts such as ZnCl₂ and CuCl to produce catalysts for N-methylation of amines using CO₂⁶⁸ and gold nanoclusters to produce a photocatalyst for CO₂ reduction.⁷⁰

1.5.2. N-heterocyclic ligands based on piperazine and homopiperazine

Very few ligands with piperazine and homopiperazine were reported in the literature. To the best of our knowledge, the only members of this class are illustrated in Figure 21. Two NbO-type copper-based MOFs were prepared using piperazine-based tetracarboxylate ligands, with synthesis requiring the use of metal-based catalysts and featuring low to moderate yields.⁷²⁻⁷⁵ These MOFs featured improved CH₄ storage capabilities compared to analogs that have benzene rings in place of the piperazine unit due to the saturated character of cycloaliphatic piperazine ring. Further, a homopiperazine Zn-MOF was also reported which was only moderately porous, owed to the high flexibility of the 7-membered homopiperazine ring.⁷⁶

1.5.3. Summary

Above we briefly described the main achievements in the field of ligands with N-heterocyclic backbone. Relatively few materials were made using such ligands, a fact that is likely due to either the complicated synthesis of these molecules or their non-linear geometry that could give rise to frameworks with just moderate to low porosity. It is further noted that all reported NHC MOF ligands share one feature, which includes the presence of an *unsaturated* 5-membered imidazolium ring. A difference between a saturated and unsaturated NHC ligand is illustrated in Figure 22. Based on classical, solution-based NHC chemistry, it is known that saturated NHCs possess

stronger donating power, which can be tuned by changing the ring size.⁷⁷ Thus, a simple change in bond order in the N-heterocyclic ring leads to notable changes in the carbene behavior.

Single imidazolium core



Figure 20. NHC MOF ligands reported in literature ^{68-69, 71, 78}



Figure 21. N-heterocyclic MOF ligands based on piperazine and homopiperazine reported in the literature ⁷²⁻⁷⁶



Figure 22. Illustration of differences between unsaturated and saturated NHC MOF ligands

1.6. Thesis aims and outline

Given the current state of MOFs with N-heterocyclic units in the ligand backbone, this direction seemed promising for the current thesis. We were fascinated by an uncharted territory of saturated NHC-MOF ligands owing to the interesting properties of saturated NHCs and their geometric tunability, which can give rise to new MOF structures. Further, piperazine-based linkers seemed highly attractive as due to their right geometric shape, we expected them to give rise to highly porous MOFs of known topologies. Following the discovery of the first way to access the saturated NHC MOF ligands made in our lab, in this thesis we focused on synthesizing the first MOFs from the resulting ligands, placing particular attention on CO₂ capture and NHC chemistry in the resulting MOFs. Next, as we realized that the area of MOFs constructed by piperazine-based ligands could be accessed by certain modifications in the ligand synthesis, we shifted focus on this effort later and subsequently developed a modular approach to the design of a host of new piperazine-based ligands using low-cost catalyst-free methods. The latter was also used in the synthesis of a number of new MOFs.

In particular, in Chapter 2, we show how a new saturated NHC ligand H_2 Sp5-BF₄ gives rise to a copper MOF Cu-Sp5, which has one of the highest CO₂/N₂ adsorption selectivities (15 % CO₂/85 % N₂ mixture at 1 bar at 298 K) reported to date. We shed light on reasons for such performance using a combination of SCXRD, in situ FTIR, and standard gas adsorption measurements. Chapter 3 shows that through a simple modification of the copper anion, a new copper MOF, Cu-Sp5-BF4, can be formed which features more than two times larger pore size and surface area compared to the aforementioned Cu-Sp5. We show how this change decreases the CO₂ uptake and the corresponding isosteric heat of adsorption. On the other hand, the large pore size enabled us for the first time to access the saturated N-heterocyclic carbene chemistry in this MOF, via a postsynthetic ligand modification using sodium methoxide. We reveal how this process alters the dimensionality of the material and how it improves the accessibility of NHC sites for a secondstep, iridium grafting. We finally shed light on iridium speciation in the final material using a combination of EXAFS and XPS methods, and how the speciation changes upon the model catalytic reaction of stilbene hydrogenation. Last, Chapter 4 illustrates a new approach for ligand synthesis that we discovered during our NHC-MOF work. We show the development of a new concept in ligand design, which entails the use of piperazine rings in place of benzene units that are commonly found in many MOF ligands reported to date. Using this approach, one can gain access to a host of complex MOF ligands without the need for time- and cost-intensive Pd-based chemistry. Moreover, these ligands provide us with access to a number of several structurally diverse large pore MOFs that are isoreticular to some of the most well-known MOF families reported to date such as UiO-68, NOTT-101, MOF-74/CPO-27, NU-100.

Chapter 2. Selective CO₂ adsorption by a new metal-organic framework: synergy between open metal sites and a charged imidazolinium backbone

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Statement of contribution: Development of synthetic protocol of **Cu-Sp5** MOF, full characterization and data collection for **Cu-Sp5**, data analysis and plotting, writing the manuscript.

2.1. Introduction:

Following our discussion above, herein we focused on designing a MOF material for highly selective CO₂ capture. We chose copper as the metal counterpart as it is known to form paddlewheel-based clusters that connect with carboxylate ligands to form porous and highly crystalline structures. Further, the apical paddlewheel sites, upon solvent removal, can act as Lewis acidic open metal sites that enhance CO₂ uptake properties. From a ligand perspective, Lewis base sites (NH₂, OH and derivatives) or other strongly polarizing functional groups (e.g. ion pairs, -F, -CN,-NO₂ functionalities, ion pairs, etc.).⁷⁹⁻⁸¹ can be attractive to enhance CO₂ uptake.

We thus combined two central features for a selective CO₂ capture: the presence of open metal sites and charged moieties inside a MOF, to produce a new MOF material for this application. We designed a new ligand bearing, to the best of our knowledge, a yet non-reported in MOFs charged saturated imidazolinium ring, 1,3-bis(4-carboxyphenyl)-4,5-dihydro-1H-imidazol-3-ium tetrafluoroborate (H₂Sp5-BF₄). We further present a new metal-organic framework with this ligand, [Cu(Sp5)(C2H₅OH)]NO₃ (Cu-Sp5-EtOH), and its derivative, [Cu(Sp5)(CH₃OH)]NO₃ (Cu-Sp5-MeOH), both featuring a combination of copper paddlewheel sites and ion pairs inside the structure. We report activation of the Cu-Sp5-MeOH with the formation of open metal sites inside, proved by *in situ* FTIR with CO probe, and a high CO₂/N₂ selectivity of this material values based on Ideal Adsorbed Solution Theory (IAST) calculations.

2.2. Results Ligand synthesis

To obtain the diamine compound to be converted into the target ligand, shown in Scheme 1, we performed synthesis using a recently reported procedure by our group.⁸² In the first step, a formamidine was prepared using methyl 4-aminobenzoate and triethyl orthoformate in the presence of a small amount of glacial acetic acid (0.1 eq.). During the reaction, the formed ethanol was removed by distillation pushing the equilibrium forward in favor of the product formation. The formamidine was isolated as pure solid (up to 20-25 g scales) and employed in step two without any further purification. In this step, potassium carbonate (K₂CO₃), a mild base, was used to deprotonate/activate the formamidine for the subsequent substitution of the bromines in 1,2dibromoethane, and hence promote the C-N bond formation. Subsequently, the resulting intermediate, formamide was easily converted into the diamine-carboxylic acid building block using a standard hydrolysis procedure with sodium hydroxide. In the final step, the diamine was allowed to react with triethyl orthoformate and NH4BF4 in the presence of a small amount of glacial acetic acid (0.1 eq.), giving the closed ring ligand used in this work. All reactions, shown in Scheme 1, provide products in excellent yields, 97 % for formamidine, 94 % for diamine, and 99 % for closed ring ligand with a five-membered saturated ring (H₂Sp5-BF₄). It should be noted that this is the first saturated imidazolinium ligand with carboxylic acid functionality reported to date in the literature. The high purity of the compound was confirmed by a combination of ¹H, ¹³C, ¹⁹F, ¹¹B, COSY, and HSQC NMR as well as TGA and HRMS (Figures S1-S8).



Scheme 1. Synthetic route for the preparation of the closed ring amidinium ligand with a fivemembered saturated ring ($H_2Sp5-BF_4$).

2.2.1. Cu-Sp5-EtOH

Synthesis and crystal structure. The synthesis of Cu-Sp5-EtOH proceeds smoothly under solvothermal conditions with the formation of large single crystals (> 200 µm, Figure S9). Single crystal X-ray diffraction unveiled the structure of Cu-Sp5-EtOH, which is constructed by copper paddlewheel clusters where carboxylate groups of the Sp5 ligand (Figure 23) are found in the equatorial position of the cluster and ethanol molecules in apical positions. The material crystallizes in an orthorhombic space group, *Pbca* (N \ge 61), with unit cell axes of *a* =17.705(2) Å, *b* = 9.252(1) Å, *c* =24.566(2) Å, and an overall unit cell volume of 4023.9(6) Å³. The SBU and Sp5 ligand interlink in such a way to form zigzag 2D layers with aperture sizes of 17.3 Å as indicated in Figure 24 (a), (b) and (d). In order to form the final 3D structure of Cu-Sp5-EtOH, two sets of the 2D layers are interpenetrated, as shown in Figure 24 (c), (e).

The final structure possesses triangular channels with several noteworthy features that are highlighted in Figure 24 (f). First, the C² atoms of **Sp5** ligands point directly towards each other inside the channel with an interatomic C-C distance of only 5.490(9) Å. This feature is of particular interest as imidazolinium ligands readily undergo H⁺ extraction for the formation of N-heterocyclic carbenes (NHC).⁸³ With this close distance, further metalation or modification of the NHC center may lead to double-NHC metal complexes or other interesting adducts, respectively. Next to each imidazolinium ring, there are nitrate counter anions with the shortest distance of 3.21(1) Å between the C² carbon and the O atom of the nitrate. The anions are well ordered in the structure and hence are readily observed via structure solution, even at room temperature (see ESI, Table S1, Figure S10).



Figure 23. Ball and stick model showing the structure of the copper paddlewheel building unit in **Cu-Sp5-EtOH**. Atom colors are Cu: turquoise, O: red, N: blue, C: gray, H: white.

In addition to C^2 atoms, the terminal paddlewheel sites, located below in Figure 24 (f), also point inside the channel. They are occupied by ethanol molecules, whose C-C bonds are aligned nearly parallel to the *b* axis. The distance between the two closest Cu atoms from two different 2D layers is 8.519(1) Å.

The synchrotron powder diffraction pattern of a powder sample of **Cu-Sp5-EtOH** matches perfectly with the calculated pattern obtained from the single crystal structure (Figure 25). This indicates the high phase purity of the material. Moreover, the Le Bail fit of the powder pattern obtained at 100 K shows good agreement of lattice parameters and cell volume with the single crystal data, as indicated in Table 1.

Thermal analysis and gas adsorption. The gas sorption isotherms were measured for the sample treated in vacuum at 120 °C for 15 h. For nitrogen at 77 K and 278 K, as well as for CO₂ at 195 K and 278 K, there was no sorption detected. This is no surprise as the space-filling model of **Cu-Sp5-EtOH** (Figure S11) clearly indicated limited accessibility of the channels. It is thought that the pores of the **Cu-Sp5-EtOH** are not available to additional guest molecules due to the presence of ethanol molecules that are coordinated to the Cu²⁺



Figure 24. Structural features of **Cu-Sp5-EtOH**. (a) Side view of a 2D layer formed by copper paddlewheels and **Sp5**, (b) Top view of the 2D layer, (c) View along the *b* axis of the **Cu-Sp5-EtOH** structure, where separate sets of layers are shown in red in blue, (d) Schematic representation of the top view of the 2D layer, (e) Schematic representation of view along *b* axis in **Cu-Sp5-EtOH** indicating interpenetration of 2 layer sets, (f) Close-up view of a single channel in **Cu-Sp5-EtOH**, view along *b* axis. Hydrogen atoms are omitted for clarity. Atom colors for (a), (b), (f) are Cu: turquoise, O: red, N: blue, C: gray.

ions. This is further supported by thermogravimetric analysis (TGA) which indicates no mass loss until 230 °C in air (Figure S12), while afterward, the mass decreases continuously until the completion of the sample decomposition. In a separate experiment, we heated the **Cu-Sp5-EtOH** in an inert atmosphere (nitrogen) to 230 °C and held it at that temperature for 3 h. Again, there was a continuous mass loss of more than 40 % without showing a step for the removal of the ethanol (9.6 % expected as calculated from the molecular formula of **Cu-Sp5-EtOH**), and the PXRD indicated the presence of only metallic copper as residue (Figure S13, S14). Under air, the final decomposition product was copper (II) oxide, as determined by PXRD (Figure S15). Its mass (16.3 %) is in perfect agreement with the calculated CuO content in **Cu-Sp5-EtOH** (16.5 wt. %).



Figure 25. Calculated and experimental synchrotron powder patterns for Cu-Sp5 derivatives.

Sample	Cu-Sp5-EtOH,	Cu-Sp5-EtOH,	Cu-Sp5-H ₂ O,	Cu-Sp5-MeOH,
	powder	single crystal	single crystal	powder
Space	Pbca	Pbca	Pbca	Pbca
group				
a, Å	17.775(2)	17.705(2)	16.610(4)	16.676(6)
b, Å	9.218(1)	9.2515(9)	8.957(2)	8.953(3)
c, Å	24.621(3)	24.566 (2)	25.681(6)	25.80(1)
V, Å	4034.0(8)	4023.9(6)	3821(2)	3852(3)

Table 1. Unit cell parameters determined from Le Bail fits (powder samples) and single-crystalXRD. All the datasets were obtained at 100 K

2.2.2. Cu-Sp5-MeOH

Synthesis and crystal structure. Given our inability to activate the sample containing ethanol, we tried to exchange ethanol with a more volatile solvent. Upon soaking the material in methanol at room temperature, the crystal size decreased significantly (Figure S16), yielding a crystalline powder with particle sizes that range from 10-20 μ m (Figure S17). However, soaking the starting material in methanol at 50 °C produced crystals with a relatively larger size distribution, which were more suitable for SCXRD.

The new material crystallizes in an orthorhombic space group, *Pbca* ($\mathbb{N} \le 61$), with unit cell axes of a = 16.610(4) Å, b = 8.957(2) Å, c = 25.681(6) Å, and an overall unit cell volume of 3821(2) Å³. While the structural motif of this material is the same as that of the parent structure, **Cu-Sp5-EtOH**, the interpenetrated 2D layers have shifted so that the channel shape, the unit cell dimensions, and unit cell volume have changed significantly, as illustrated in Figure 26. After methanol exchange, the lengths of the *a* and *b* axes decreased while the *c* axis elongated. This leads to an overall decrease in unit cell volume by more than 200 Å³, a change of approximately 5 %. Importantly, the chemical environment in the channel changed as well. Since the channel shrinks laterally along the *a* axis, the interatomic distance between two adjacent C² atoms decreases to 5.30(3) Å, and the Cu-Cu distance between two neighboring paddlewheel units decreases to 7.940(3) Å. Compared to parent **Cu-Sp5-EtOH**, which has well-resolved ethanol molecules at the Cu-coordination site, structural analysis of the solvent exchanged material reveals a single Q peak in close proximity to the Cu with a distance of 2.16(1) Å. As such, this excess electron density was

refined as oxygen. Additionally, a second Q peak is found inside the pore, at the distance of 2.64(2) Å from a Cu-bound oxygen atom. It was also refined as oxygen with an occupancy of 0.84(4). This distance is similar to that of the O-O distances observed for hydrogen-bonded water molecules. Due to this and the absence of additional Q peaks that would indicate the methyl groups of methanol, we attribute this excess electron density to surface-bound water. For the single crystal measurements, the operation time needed to mount crystals and carry out measurements gives rise to long air exposure. Since methanol is highly volatile, it is thought that water displaces it, leading thus to Cu-Sp5-H₂O single crystal instead of Cu-Sp5-MeOH. The high volatility of the methanol indicated that activation was now a possibility. It should be noted that while the single crystals show water, elemental analysis obtained from a powder sample of Cu-Sp5-MeOH that was stored in the sealed container under methanol shows a carbon content that is in perfect agreement with the Cu-Sp5-MeOH composition (46.16 %, calc. 46.23 %). For Cu-Sp5-H₂O on the other hand, the calculated carbon content is significantly lower, 43.53 % only. It indicates that methanol is likely adsorbed inside the crystal structure upon solvent exchange and it is only after prolonged air exposure when water displaces methanol. Further, Le Bail refinement carried out on the methanol soaked Cu-Sp5-MeOH powder sample measured at 100 K (Table 1, Figure 25) shows a slightly larger unit cell volume than the single crystal of Cu-Sp5-H₂O (see Figure 25 for powder pattern comparison), also implying the presence of methanol rather than water in the structure of Cu-Sp5-MeOH powder.



Figure 26. View of a channel in Cu-Sp5-H₂O structure
Thermal analysis, activation, X-ray diffraction and in situ FTIR. The key point of methanol exchange with the formation of **Cu-Sp5-MeOH** was to obtain a material that can be thermally activated to gain access to a structure that would be porous to small molecules like CO₂ and to impart the formation of open metal coordination sites. The TGA of **Cu-Sp5-MeOH** (Figure S18) clearly indicates a mass loss step of 7.8 % starting at 120 °C with further decomposition beginning at 230 °C. This value is in agreement with the expected mass loss of the material if one methanol is liberated from each copper atom, 6.9 %. Thus, we used the TGA results to develop an activation protocol. **Cu-Sp5-MeOH** was heated at 120 °C in vacuum for 15 h to prepare the **Cu-Sp5** for further gas sorption measurement.

To prove the crystallinity of the material after activation, we measured synchrotron powder diffraction data of the activated sample under a nitrogen atmosphere. The data show an interesting phenomenon of a structural change upon activation. As can be seen in Figure 27, the powder pattern of the activated sample features different peak positions and a lower number of peaks in general. The very first peak appears at a higher angle, $3.743 \circ (d = 9.467 \text{ Å}) \text{ vs } 2.798 \circ (d = 12.66 \text{ Å})$ for solvated **Cu-Sp5-MeOH**. This indicates a phase transition presumably due to a shift in the 2D layers following solvent removal. Importantly, this process does not significantly alter the crystal quality of **Cu-Sp5**, as high-angle diffraction data indicates the presence of Bragg reflections as high as at $2\theta = 28.8 \circ$. Moreover, upon resolvation of the activated sample in methanol for 24 h, the MOF gains the initial structure back (Figure 27), again without any apparent loss in the crystallinity. While we are currently working on the structure determination of the activated sample, we can deduce that the **Cu-Sp5-MeOH** is stable upon activation and its structure is reversibly changed during that process.

In order to further evidence the solvent removal from the pore and from the copper paddlewheel terminal site, we performed *in situ* FTIR measurements of the activated material after dosing it with the CO gas (Figure 28). This technique is a common approach for sensing accessible metal sites, not only in MOFs,^{14, 84} but also in a variety of other materials.⁸⁵ During measurement performed at 150 K, the signal of Cu-bound CO appeared at 2135 cm⁻¹. Compared to the vibration frequency of the free CO (2143 cm⁻¹), the signal is red-shifted upon CO coordination to copper, a phenomenon that is due to classical, π -backbonding interactions. Interestingly, the reported stretching frequencies of the Cu-bound CO for two structurally related MOFs, Cu-BTC (HKUST-1)^{22, 86-87} and Cu-TDPAT⁸⁸, are blue-shifted with values ranging from 2178-2174 cm⁻¹ and

unperturbed, respectively. Given that these two structures have a similar Cu-paddlewheel SBU with open Cu^{2+} sites, this indicates that the ligand field environment and local pore structure strongly influence the interaction of Cu^{2+} with CO. Similar phenomena has also been illustrated in Cu-ZSM-5 zeolite, which shows a large change in the CO stretching frequency depending on the local environment of the Cu^{2+} ion. In particular, it was found that for two copper sites, the first being inside an oxygen-lined five-membered ring window and the second located in a channel intersection in ZSM-5 structure, the associated Cu-bound CO frequencies were blue- and red-shifted with values of 2157 and 2138 cm⁻¹, respectively.⁸⁹



Figure 27. Synchrotron powder patterns for Cu-Sp5-MeOH, activated Cu-Sp5 and resolvated Cu-Sp5-MeOH



Figure 28. In situ FTIR data in the C-O bond region for activated Cu-Sp5 dosed with 0 (black), 2 (red), 5 (blue), 10 (pink) and 20 (green) Torr CO. Measured at 150 K.

Gas adsorption measurement. Upon the standard measurement of nitrogen sorption at 77 K, the activated sample **Cu-Sp5** did not exhibit significant gas uptake (Figure 29 (a), bottom). However, when CO₂ was used as a probe molecule with the measurement performed at 195 K, rapid uptake in the low-pressure region with further slow increase up to a value of 2.38 mmol/g (9.5 wt.%) at 95 kPa (Figure 29 (a), top) was observed. This indicates that the pores were indeed accessible for gas adsorption upon solvent removal. The adsorbed amount is in good agreement with the calculated CO₂ loading if each copper site adsorbs one CO₂ molecule (2.29 mmol/g, 9.2 wt. %). The surface area of the material, determined by the Langmuir model of CO₂ adsorption at 195 K, is 204 m²/g. However, the use of CO₂ as a probe molecule for surface area measurement could be associated with underestimating the surface area of the material because of strong CO₂-CO₂ interactions in the pore.⁹⁰⁻⁹² Therefore, the obtained surface area value should be treated as a lower estimate.

With a high preference for CO_2 over N_2 shown by the material at low temperatures, we were eager to investigate the gas sorption properties of **Cu-Sp5** in the ambient conditions, which are close to relevant conditions for industrial flue gas. The data were obtained at three temperatures, namely 298 K, 288 K, and 278 K to examine the thermal dependency of the isotherms and calculate isosteric heats of adsorption of both gases. As shown in Figure 29 (b), the nitrogen uptake in all

cases is much lower than that of CO_2 , proving that the material is selective for CO_2 in a range of temperatures close to ambient. The CO₂ uptake at 298 K reaches 1.30 mmol/g (5.41 wt.%), whereas at 278 K it increases up to 1.65 mmol/g (6.77 wt.%) at 1 bar. The zero-coverage isosteric heat of CO₂ adsorption, -Q_{st}, for Cu-Sp5, calculated via the Clausius–Clapeyron equation (see the ESI), is 43.1 kJ/mol. Interestingly, it stays nearly constant during the adsorption as indicated in Figure 30. This indicates the unceasing strong framework interaction with CO₂ during the adsorption process. The isosteric heat of nitrogen adsorption at zero coverage, as calculated via similar procedures, is 20.2 kJ/mol (Figure S19). This vast difference between the isosteric heats of CO₂ and N₂ clearly shows the thermodynamic preference of CO₂ interaction with the MOF interior. The trends, in turn, indicate a clear and stable thermodynamic CO₂/N₂ selectivity for Cu-Sp5 in a wide range of loadings and pressures. The observed isosteric heat of CO₂ adsorption corresponds to an upper limit of those values previously reported for MOFs featuring open metal sites as the main feature for CO₂ capture. Compared to two other structurally related MOFs that have Cupaddlewheels as SBUs including Cu-BTC and Cu-TDPAT the observed values are 25.9 and 42.2 kJ/mol, respectively. In order to quantitatively investigate the adsorption selectivity of the MOF in a CO₂/N₂ mixture, we performed Ideal Adsorbed Solution Theory (IAST) calculations using the single component isotherms. Based on the calculated data obtained via pyIAST software⁹³ (see ESI), the selectivity factor for CO₂ over nitrogen in a 15 % CO₂/85 % N₂ mixture at 1 bar is 207.1 at 298 K and 252.5 at 278 K. This value is superior to the selectivity values of many other reported MOFs,⁸⁰ exceeding ones bearing open metal sites only, even the top performers such as Mg-MOF-74 (IAST selectivity = 175 at 313 K), which features high densities of open Mg^{2+} sites (Table S2).⁹⁴

According to this, the striking selectivity of **Cu-Sp5** towards CO₂ could not be explained by the presence of open metal sites only. As a matter of fact, the other species present in **Cu-Sp5** pores are ion pairs of charged imidazolinium rings of **Sp5** and nitrate anions. It turned out that limited nitrogen uptake both at ambient temperature and 77 K was reported for several MOFs bearing charged moieties.⁹⁵⁻⁹⁸ Since both polarizability and quadrupole moment for nitrogen molecule are lower than for CO₂ (Table S3), such conditions lead to very small N₂ sorption values, which in combination with reasonable CO₂ uptake gives rise to good selectivities. Further, as kinetic diameter of N₂ molecule is ca. 10 % larger than that of CO₂ (Table S3), we cannot exclude the contribution of the sieving effect to CO₂/N₂ selectivity owing to a small pore size in **Cu-Sp5**.

Thus, **Cu-Sp5** combines the presence of both open metal sites and ion pairs inside the channel, which together participate in rendering high CO₂ selectivity to the material. Compared to MOFs bearing open metal sites only, the selectivity of the **Cu-Sp5** is much higher, whereas MOFs with only ion pairs in the pore present lower isosteric heat values (Table S2) and lower selectivities. Only one reported MOF with the charged moieties features a very high zero coverage isosteric heat of adsorption (58.1 kJ/mol), which is also caused by the presence of open metal sites, uncoordinated nitrogen atoms of tetrazolate and fluorine atoms.⁹⁶ However, while the low-pressure CO₂ uptake and isosteric heat for this material were very high, the latter quickly dropped below 40 kJ/mol after 0.75 mmol/g, and even below 30 kJ/mol after 1.0 mmol/g. In total, this gave rise to a limited IAST selectivity for 10 % CO₂/90 % N₂ gas mixture at 298 K which was only 15 at 1 bar, while **Cu-Sp5** presents almost constant high isosteric heat (43.1 kJ/mol) in the whole loading range and IAST selectivity 15 % CO₂/85 % N₂ mixture at 1 bar is 207.1.

This shows that there is a clear synergy of ion pairs and open metal sites inside the channel, which drastically enhances the CO_2 selectivity towards nitrogen in relevant conditions. For other materials, showing only one of those features, either isosteric heats or selectivity values are low. Therefore, the **Cu-Sp5** material uniquely features the combination of both properties giving rise to outstanding IAST CO_2/N_2 selectivity and high isosteric heat of adsorption, introduced by ligand design.



Figure 29. Gas adsorption isotherms for activated **Cu-Sp5**. Filled symbols represent adsorption, open symbols represent desorption. (a) Low temperature isotherms; (b) ambient temperature

isotherms



Figure 30. Isosteric heat of CO₂ adsorption for Cu-Sp5

2.3. Conclusions

A new charged imidazolinium ligand, $H_2Sp5-BF_4$, gives rise to a novel metal-organic framework, **Cu-Sp5**. The activated framework features triangular channels with imidazolinium rings interlinked by Cu-paddlewheel SBUs. Upon solvent exchange and thermal activation, the channel interior of **Cu-Sp5** becomes decorated with both open Cu²⁺ sites and ion pairs, giving rise to an exceptional CO₂/N₂ IAST selectivity that reaches 252.5 at 278 K at 0.15 bar CO₂ and 0.85 bar N₂. This study indicates that engineering charge into frameworks combined with other interesting functionalities such as open metal sites can significantly enhance the performance of materials towards important environmental challenges like post-combustion CO₂ capture.

2.4. Supplementary information

Experimental

Materials and general procedures

The reactions were carried out in air, unless stated otherwise. Acetonitrile, methanol, ethanol, dichloromethane and *n*-hexane were obtained in analytical grade from commercially available sources and were used without any further purification or drying. The reactions under water-free conditions were carried out using standard vacuum and Schlenk techniques. For these reactions, acetonitrile was distilled after refluxing with CaH₂ overnight and stored in a glove box under a nitrogen atmosphere. 4-aminobenzoic acid, ammonium tetrafluoroborate and deuterated chloroform (CDCl₃) were obtained from Acros, triethyl orthoformate, potassium carbonate (anhydrous), Cu(NO₃)₂·3H₂O (99.5 %) and deuterated dimethyl sulfoxide (dmso-d6) were obtained from ABCR, sodium hydroxide, hydrochloric acid (37 %) and 1,2-dibromoethane were obtained from Sigma-Aldrich, sulfuric acid (95-97 %) and acetic acid (glacial) were obtained from Merck and used as received without further purification.

$Synthesis \ of \ 1,3-bis(4-carboxyphenyl)-4,5-dihydro-1H-imidazol-3-ium \ tetrafluoroborate \ (H_2Sp5-BF_4)$

The synthesis of the formamidine and diamine compound on Scheme 1 was carried out using a recently reported procedure by our group.⁸² For the synthesis of closed ring ligand with a fivemembered saturated ring ($H_2Sp5-BF_4$), the diamine (1 eq.), triethyl orthoformate (1.05 eq.), glacial acetic acid (0.1 eq.) and ammonium tetrafluoroborate (1 eq.) were weighed in a round bottom Schlenk flask that was then connected to a Schlenk line and evacuated at room temperature in vacuum (0.1 Pa) for 1 h. Dry acetonitrile (approx. 15 mL solvent per 1 mmol diamine) was added and the mixture was refluxed at 120 °C for 3 days under a nitrogen atmosphere. NMR was used to watch the reaction proceed, and more triethyl orthoformate was added every 18 h (0.5 eq. each time). After complete conversion to the amidinium salt, as observed by NMR, the mixture was cooled to room temperature and acetonitrile was removed using a rotary evaporator. The remaining solid was suspended in diethyl ether (approx. 15 mL solvent per 1 mmol diamine), sonicated for 0.5 h and filtered over a G4 frit. The cake was further washed with 200 mL diethyl ether and finally with 200 mL *n*-hexane. The product was obtained as a rose-colored powder and dried at room temperature in vacuum (0.1 Pa) for 1 day. **Experimental data for H₂Sp5-BF4.** Diamine (8 g, 26.64 mmol), triethyl orthoformate (4.145 g, 27.97 mmol), glacial acetic acid (0.16 g, 2.664 mmol), ammonium tetrafluoroborate (2.793 g, 26.64 mmol); isolated yield (rose-colored powder): 10.478 g (98.8 %). ¹H NMR (400.13 MHz, DMSO-*d*₆, 298 K): δ = 13.18 (s, 2H), 10.20 (s, 1H), 8.12 (d, *J* = 8.4 Hz, 4H), 7.78 (d, *J* = 8.4 Hz, 4H), 4.82 – 4.48 (m, 4H). ¹³C NMR (100.61 MHz, DMSO-*d*₆, 298 K): δ = 166.4, 152.9, 139.4, 130.8, 129.1, 118.4, 48.4. ¹⁹F NMR (376.50 MHz, DMSO-*d*₆, 298 K): δ = -148.3. ¹¹B NMR (128.38 MHz, DMSO-*d*₆, 298 K): δ = -1.29. IR (diamond ATR): $\tilde{\nu}$ = 415 (w), 454 (s), 475 (m), 512 (s), 522 (s), 546 (s), 634 (m), 689 (s), 771 (vs), 798 (s), 846 (vs), 892 (s), 1002 (vs), 1060 (vs), 1126 (s), 1189 (vs), 1251 (vs), 1275 (vs), 1343 (m), 1427 (vs), 1518 (m), 1581 (vs), 1633 (s), 1687 (vs), 2539 (m), 2826 (m). *T*_d (TGA) = 213.6/401.1 °C. HRMS (ESI) *m/z*: [M]⁺ calcd for C₁₇H₁₅N₂O₄⁺, 311.1026; found, 311.1025.

Cu-Sp5-EtOH and Cu-Sp5-MeOH synthesis

[Cu(Sp5)(C₂H₅OH)]NO₃ (Cu-Sp5-EtOH). In a 16 mL scintillation vial, 24.2 mg of Cu(NO₃)₂·3H₂O (0.1 mmol) and 39.8 mg of H₂Sp5-BF₄ (0.1 mmol) were mixed with 10 mL of ethanol. After 10 minutes of sonication, the vial was placed in the oven and heated to 80 °C at 10 °C/h rate. The mixture was kept at 80 °C for 48 h and then cooled back to room temperature at 10 °C/h rate. Large single crystals of Cu-Sp5-EtOH were washed with a copious amount of ethanol and dried in air. Yield 47 % (22.6 mg). By changing the heating and cooling rate the crystal size can be tuned. Elemental analysis (%) calc. for C₁₉H₂₀CuN₃O₈: C, 47.35; H, 4.18; N, 8.72. Found: C, 47.78; H, 4.07; N, 8.05.

[Cu(Sp5)(CH₃OH)]NO₃ (Cu-Sp5-MeOH). In a typical experiment, 100 mg of Cu-Sp5-EtOH crystals were placed in 20 mL of methanol and soaked for 2 days either at room temperature or 50 °C. The solvent was exchanged for a fresh one each 3-6 h. Elemental analysis (%) calc. for C₁₈H₁₈CuN₃O₈: C, 46.21; H, 3.88; N, 8.98. Found: C, 46.16; H, 4.03; N, 8.13.

Cu-Sp5-MeOH activation

Cu-Sp5-MeOH was heated in vacuum (< 50 µbar) at 120 °C for 15 h. The activated sample, **Cu-Sp5**, was used to perform the gas adsorption measurements. Elemental analysis (%) calc. for C₁₇H₁₄CuN₃O₇: C, 46.85; H, 3.24; N, 9.64. Found: C, 46.40; H, 3.04; N, 8.16.

X-Ray crystallography

Laboratory single-crystal X-ray diffraction was performed at 100 K using a Bruker D8 Venture diffractometer equipped with graphite monochromator and microfocused Mo K_{α} radiation source ($\lambda = 0.71073$ Å). The data was integrated with SAINT⁹⁹ and corrected for adsorption with SADABS software.¹⁰⁰ Synchrotron single-crystal X-ray diffraction data were collected using a multipurpose PILATUS@SNBL diffractometer with PILATUS2M detector at the BM01 at European Synchrotron Radiation Facility ($\lambda = 0.67522$ Å). Single crystals were mounted on a Kapton loop and measured at 293 K. The structure solution and refinement were performed using ShelXT¹⁰¹ and ShelXL-2013¹⁰² operated through the Olex2 interface.¹⁰³ First, non-hydrogen atoms were located and refined anisotropically, then H atoms were introduced with corresponding HFIX commands and refined isotropically.

Synchrotron powder diffraction was performed at the BM02 beamline at ESRF (Grenoble, France) using monochromatic X-ray radiation ($\lambda = 0.618375$ Å) in transmission mode.

Laboratory powder X-ray diffraction was performed using Bruker D8 Discover instrument equipped with Cu K_{α} radiation source operated in Bragg-Brentano geometry. The scan step was 0.02 ° and the time per step was 1 s.

FTIR measurements

Ex situ FTIR spectrum was recorded at room temperature on a PerkinElmer FTIR/FIR spectrometer using a Diamond ATR cell with the PerkinElmer spectrum software package (a resolution of 4 cm⁻¹ was used). *In situ* FTIR data were collected using the same spectrometer. The sample for *in situ* FTIR analysis was mixed with KBr and placed into a custom-built cell with diffuse reflectance Praying MantisTM accessory. The sample was first activated by treating at 120 °C in vacuum for 15 h. Then the sample was cooled to -123 °C (150 K) and dosed with selected CO pressures using a custom-built gas manifold. The spectrum was collected at 2 cm⁻¹ resolution. All spectra were background-subtracted.

NMR measurements

Solution NMR spectra were recorded in deuterated solvents on a BRUKER AVIII HD 400 spectrometer; data are given in ppm relative to 1 % TMS solution in CDCl₃ using the solvent signals as a secondary reference (¹H, ¹³C). NMR spectra were recorded at room temperature, if not mentioned otherwise. The Bruker Topspin software package (version 3.2) was used for measuring and Mestrenova NMR software (version 11.0.1) was used for processing the spectra.

HRMS analysis

High-resolution mass spectrometry (HRMS) analysis was performed using Q Exactive HF Hybrid Quadrupole-Orbitrap mass spectrometer (Thermo Scientific, Germany) in ESI ionization mode with ionization source TriVersa NanoMate (Advion, USA) and quadrupole mass analyzer.

TGA measurements

Thermogravimetric analysis (TGA) and decomposition temperatures were determined from TGA experiments on a TGA Q500 device from TA Instruments in 100 μ l platinum pans with an empty pan of the same type as reference. To infer the decomposition temperatures, the onset points were taken into account.

Gas adsorption measurements

The CO₂ sorption isotherms were obtained using BELSORP-max system equipped with a dry iceethanol bath (195 K) or temperature-controlled circulating water bath (278 K, 288 K, 298 K). The nitrogen sorption isotherms were obtained using Micromeritics 3FLEX instrument equipped with liquid nitrogen Dewar (77 K) or temperature-controlled water bath (278 K, 288 K, 298 K).

Chapter 3. From 3D to 2D and back: controlling metal-organic framework dimensionality via N-heterocyclic carbene chemistry

3.1. Introduction

Metal-organic frameworks (MOFs), an emerging class of porous materials that consist of metal ions or metal ion clusters interlinked by organic ligands, find application in various areas of hostguest chemistry such as catalysis ¹⁰⁴ and gas separation.¹⁰⁵⁻¹⁰⁷ These frameworks are particularly attractive because they offer record internal surface areas and pore volumes, combined with a wide range of structural and chemical tunability, which stems from their highly modular nature. In fact, modifications can be readily made to each MOF building block, giving access to a plethora of porous structures that are tailored for a given application. In this regard, constructing MOFs from heterocyclic ligands that can post-synthetically form stable N-heterocyclic carbenes (NHCs) or NHC-derived species is a potentially interesting topic to explore. Such work could provide MOFs having a range of tunable reactivity for a variety of interesting catalytic applications. Moreover, with their highly crystalline structures, MOFs often offer well-defined catalytic sites. This, combined with the high tunability of the catalytically active sites themselves, would enable structure-property correlation studies and provide ways to extract mechanistic insight into various NHC-based catalytic reactions. Unfortunately, to date, the topic of MOFs containing NHCs or NHC-derived species is not yet widely studied. A few studies in the literature have demonstrated the formation of NHC-based MOFs that have been modified with metalorganic complexes or used directly for catalytic applications. 68-69, 108

To date, only unsaturated, imidazolium-based NHCs were reported in MOFs where the Nheterocyclic ring was a part of the linker backbone. The saturated imidazolium-based NHCs, on the other hand, offer more tunability and are generally stronger σ -donors compared to their unsaturated counterparts due to lack of conjugation in the NHC ring and stronger donating power of –CH₂ groups.¹⁰⁹ The reported syntheses of saturated NHCs without carboxyl groups and their corresponding metal complexes obtained from the imidazolinium salt precursors seem generally facile as the corresponding C² atom readily undergoes deprotonation in basic media.¹¹⁰ With this in mind, we designed a MOF linker **H₂Sp5-BF₄** that bears a saturated 5-membered N-heterocyclic ring and two carboxylate groups. We previously reported the formation of a microporous MOF, **Cu-Sp5**, from this ligand, which exhibits a combination of open metal sites and charged ion pairs, two structural features that lead to a remarkable CO₂/N₂ selectivity for potential gas separations.⁸², ¹¹¹ Thus in the present work, we build off our previous results and report the synthesis of a new MOF, Cu-Sp5-BF₄, that has the same linker, but possesses larger, nanometer-sized pores, which are an important prerequisite for post-synthetic NHC chemistry. We further show that the Nheterocyclic carbenes can be readily accessed in this MOF via a post-synthetic formation of NHCmethoxide adducts. Moreover, we, for the first time, demonstrate show how this post-synthetic methoxide ligand modification in the MOF leads to a change in material dimensionality with the formation of a turbostratic phase (i.e. a phase of layered material where layers have slipped out of alignment). Next, we show that after such modification, we can load more iridium a second-step post-synthetic modification, where we form NHC-iridium complexes inside the material via treatment with [Ir(cod)(OMe)]₂. To the best of our knowledge, only one previous work showed the incorporation of an NHC-iridium complex inside a MOF, using a pre-formed metallololinker.¹¹² Here, we show the post-synthetic formation of Ir-NHC complexes inside a MOF structure, and its dependence on material structure and the presence of defects. We then shed light on iridium speciation in the material using a combination of EXAFS and XPS techniques, and show iridium performance in a model reaction of stilbene hydrogenation.

3.2. Results and discussion

3.2.1. Material synthesis

Having shown the applicability of a new ligand $H_2Sp5-BF_4$ for MOF construction in our previous work¹¹¹, herein we continued our investigation of MOFs formed by this ligand. When copper (II) tetrafluoroborate was used as a copper source instead of copper (II) nitrate, new material was synthesized. Single-crystal X-ray diffraction (SCXRD) revealed that by a simple change of the copper counterion, we were able to alter the structure dramatically and prevent the interpenetration of the copper paddlewheel-ligand layers, which were interlinked in the previously reported **Cu-Sp5** MOF. This was possible due to the increased steric bulk of tetrahedral BF_4^- anion compared to a flat, triangular nitrate anion in the previous **Cu-Sp5** structure. Interestingly, this led to a change of a secondary building unit (SBU) in a newly formed **Cu-Sp5-BF4-EtOH** structure. Instead of paddlewheel SBUs, we observed an infinite bridged SBU as depicted in Figure 31.



Figure 31. Structure of Cu-Sp5-BF₄-EtOH. (a) view of SBU, L – ligand, L_d – dangling ligand
(b) view along *a* axis depicting channel front (c) view along *c* axis depicting walls of the channel and connection of SBUs with linkers. Hydrogen atoms on (b) and (c) are omitted for clarity. Atom colors: C, gray; O, red; N, blue; H, white; B, brown; F, green; Cu, turquoise

There are two crystallographically distinct copper atoms present in the SBU. Both metal ions, Cu1 and Cu2, have a square planar geometry. and are connected to two bridging carboxylates from the ligand in a *trans* orientation relative to each other, with nearly equal Cu-O bond lengths of 1.9338(1) Å for Cu1 and 1.9309(1) Å for Cu2 and. Cu1 is additionally coordinated to two ethanol molecules with Cu-O_{EtOH} bond length of 1.9254(1) Å. Cu2 on the other hand is connected to two dangling carboxylate groups (Cu-O_{Ld} 1.9705(1) Å) that are also hydrogen-bonded to the ethanol molecules on the first Cu atom (O_{EtOH}-O_{Ld} 2.5242(1) Å). The Cu1-Cu2 distance is 3.3196(3) Å. This arrangement leads to the formation of 1D rod-like SBUs that are aligned along the *a* axis. The carboxylates interconnect the copper cations within the 1D SBUs along *a* and also in a rhombic fashion within the *bc* plane forming a 3D channeled structure. The BF4⁻ anions are positioned inside these channels next to the charged imidazolinium rings (See Table S4 for refinement details). The phase purity of the material is confirmed by a full agreement between the experimental and calculated PXRD patterns (Figure S20).

Using SCXRD, ethanol molecules are clearly seen bound to the copper atoms; thus, prior to performing any further studies, efforts were made to liberate the ethanol that occupies part of the

pore space. For this, TGA experiments were first carried out, which reveal (Figure S21) a broad weight loss between 90 and 200 °C, which is believed to be attributed to ethanol existing in the pores of the material. Thus, the selected activation protocol entailed heating the material to 185 °C under vacuum for 16 hours. During this time, a color change from pale blue to dark green was observed. Interestingly, the powder pattern of the so-obtained Cu-Sp5-BF₄-A did not match the pattern obtained from the solvated parent material (Figure S22); although, the high crystallinity of the sample was retained as indicated by well-defined diffraction peaks at high 20. Angles. Further, after activation, the Cu-Sp5-BF4-A material did not revert to the structure of the parent material upon soaking in ethanol, even after 36 hour soak times (Figure S22), indicating an irreversible structural transition and further prompting a detailed examination of the material's structure. Single crystal diffraction (SCXRD) performed on activated single crystals (See Table S4 for refinement details) revealed a drastic change in the copper-containing SBU from the aforementioned 1D rod to a stack of copper paddlewheels (Figure 32, a). Inside these paddlewheels, Cu-Cu distance is 2.594(2) Å, while between the paddlewheels the Cu-Cu distance is 3.203(2) Å. On the contrary, the shortest Cu-Cu distance observed in the solvated parent structure is 3.3196(3) Å. This rearrangement of the copper ions indicates that upon the thermally driven decoordination of ethanol, the now-vacant copper coordination sites became occupied by the dangling carboxylate, which was coordinated to EtOH via hydrogen bonding in the parent material. This change in the coordination of the carboxylate thus forms the Cu paddlewheel, leading to a significant contraction of the SBU along the *a* axis. This structural change does not go unnoticed by the ligand, which buckles inside the MOF pore to adapt for changes as indicated in Figure 32, b, which shows a decrease in the Cu-Cu distance across the pore window from 33.5424(9) Å in Cu-Sp5-BF4-EtOH (Figure 31, b) to 31.562(5) Å for Cu-Sp5-BF4-A (Figure 32, b). When viewed along the c axis (Figure 31, c to 32, c), the structural transition can be illustrated as a shift from a fully interlinked 3D structure to a stacked 2D structure where a single stack unit is a ligand-thick layer as shown in the Figure S23. The process, when followed by an *in situ* synchrotron PXRD, revealed the first signs of new phase formation at 140-145 °C, in line with the weight loss observed in the TGA data and corresponding to ethanol decoordination and removal from the structure (Figure S24). Moreover, the phase purity and the high degree of crystallinity of the newly formed material, Cu-Sp5-BF4-A, is proven by a full agreement between the experimental and simulated powder patterns (Figure S25).



Figure 32. Structure of Cu-Sp5-BF₄-A. (a) view of SBU, IL – interlayer, PW - paddlewheel
(b) view along *a* axis depicting channel front (c) view along *c* axis depicting walls of the
channel and paddlewheel SBUs. Hydrogen atoms are omitted for clarity. Atom colors: C, gray;

O, red; N, blue; H, white; B, brown; F, green; Cu, turquoise

Despite the presence of Cu paddlewheels in the new **Cu-Sp5-BF₄-A** structure, it is noted that there are no open metal coordination sites. The reason is that the apical Cu(II) sites are instead occupied by the oxygen atoms of adjacent paddlewheel units, with a Cu-O distance of 2.20(1) Å. This inaccessibility to the copper is unusual when compared to the previously reported MOF structures containing Cu-paddlewheels, such as **Cu-Sp5**, HKUST-1, or Cu-TDPAT.⁸⁸ Thus, it was further verified by *in situ* FTIR experiments using CO gas as a probe for the Lewis acidic Cu(II). In these experiments, minimal signal attributed to CO bound to an open metal site was detected upon dosing the gas up to 20 Torr at 150 K (Figure S26). When compared to the spectrum of **Cu-Sp5** assessed under similar conditions, one can see that the relative intensity of Cu-bound CO is less in **Cu-Sp5**-**BF**₄-**A**. This indicates that most of CO is unbound, unlike in **Cu-Sp5**, where there is only a negligible signal from free CO at all pressures studied. We attribute the weak signal in **Cu-Sp5**-**BF**₄-**A** to the terminal paddlewheels present at the crystal surface or on plausible defect sites that might give rise to layer misalignment in the crystal structure, and hence to a small amount of CO physisorbed to Cu(II).

Having elucidated the structure of the activated material, efforts were made to investigate its properties. Similar to **Cu-Sp5** analog, due to the presence of charged species inside the pore, nitrogen adsorption of 77 K was not conclusive for evaluating the porosity of the sample, thus, the CO₂ adsorption at 195 K was used for this characterization (Figure S27). We found that due to a lack of interpenetration, as observed for **Cu-Sp5**, the **Cu-Sp5-BF4-A** material has more than twice the surface area (544 m²/g, Langmuir) and total gas uptake (6.20 mmol/g at $p/p_0 = 0.90$) compared to the **Cu-Sp5** of (2.38 mmol/g at $p/p_0 = 0.95$) structure that has a similar composition. The new material also has a lower isosteric heat of CO₂ adsorption (-Q_{st}), 36.6 kJ/mol at zero coverage, compared to 43.1 kJ/mol for **Cu-Sp5** (Figure S28). This is attributed to the absence of accessible open metal sites in **Cu-Sp5-BF4-A**. Moreover, the smaller pore size of **Cu-Sp5** is likely to provide multiple CO₂ interactions with the internal MOF wall. This, combined with a higher charge density in the smaller pore, likely make the **Cu-Sp5** pore more favorable towards CO₂ all while more unfavorable for N₂ when compared to the larger, less polarized pore of **Cu-Sp5-BF4-A**. This was also in line with a detectable uptake of N₂ at 77 K for **Cu-Sp5-BF4-A**, (1.70 mmol/g at $p/p_0 = 0.918$) while **Cu-Sp5** has minimal uptake at all pressures.

3.2.2. Methoxide treatment

The larger pore size of the new material, **Cu-Sp5-BF4**, implied that the carbene site in the pore might potentially be accessible for post-synthetic modification. Thus, a reaction with sodium methoxide was carried out, leading to the formation of NHC adducts, as shown in Scheme 2. Such adducts are known to undergo subsequent thermal activation for the formation of free N-heterocyclic carbenes, an approach previously used in solution-based NHC chemistry.¹¹³ Thus, efforts were made to monitor the alkoxide modification by quantifying the amount of BF4⁻ ions retained in the structure via ICP of digested samples. Indeed, as the Cu:ligand ratio in the material is 1:1, a detectable decrease in the amount of boron relative to copper will indicate the extent of the modification. In fact, upon treatment of the MOF with sodium methoxide in methanol, the B:Cu ratio decreased from 1.02(3):1 in untreated **Cu-Sp5-BF4-A** to 0.22(2):1 in the newly formed material, corresponding to only 22(2) % of BF4⁻ retained in the structure. This implied the successful formation of NHC-methoxide adducts as indicated in Scheme 2, giving rise to a new material, **Cu-Sp5-OMe.** The formation of NHC-methoxide adducts was further supported by solid-state ¹³C NMR, where alongside the peaks existing in the parent structure, we observed new, broad peaks which corresponded to the methoxide adduct (Figure S29). Their relative positions

were consistent with solution-based NHC chemistry.¹¹³ The breadth of the new peaks indicate a crystallographic disorder of the methoxide-modifications, a phenomenon inciting our further investigation with the X-ray diffraction method. The presence of the residual sharp peaks corresponding to the unmodified ligand, on the other hand, indicates that a certain part of the material contains the pristine, charged ligands, which are more ordered.



Scheme 2. Schematic of NHC-methoxide modification inside Cu-Sp5-BF4-A

The powder diffraction pattern of this material showed loss of order along *a* axis, which was the stacking direction of the Cu-paddlewheels in the original crystal structure. This was determined based on the disappearance of the major *hkl* peaks where $h \neq 0$. On the contrary, peaks representing *Okl* diffraction planes were retained (Figure S30). This change is likely attributed to a decrease in the electrostatic interactions between the layers; this stems from a decrease in the amount of BF₄⁻ ions, which help hold the layers together. It is noted that when the methoxide adduct is formed, this portion of the ligand also becomes neutral releasing the BF₄⁻ anions. Further, light microscope images indicate that this modification results in a bending of the MOF particles (Figure S31), and

subsequent SEM images indicated the formation of a large number of defects such as bending and cracking of the MOF crystals, both of which are likely attributed to misalignment between the MOF layers (Figure 33). These observations are typical for turbostratic materials, such as turbostratic graphite.¹¹⁴⁻¹¹⁷ Moreover, the cracks are transversely oriented with respect to the MOF pore, alternatively, the crystallographically *a* axis, as indicated by indexing carried out during SCXRD measurements (Figure S32). Together with the loss of order along this axis, as indicated by PXRD, this supports the idea that the driving force for the formation of such defects is related to weakened interaction between layers, which gave rise to the turbostratic material **Cu-Sp5-OMe**. Owing to layer misalignment, the Langmuir surface area of this material is slightly lower than that of the parent MOF, 432 m²/g (Figure S33).



Figure 33. SEM images of Cu-Sp5-BF₄-A (a, b) and Cu-Sp5-OMe (c, d)

3.2.3. Iridium modification

Having shown accessibility to the NHC centers inside the MOF and gaining insight into how the methoxide modification at the C^2 position influences the dimensionality of the material, an effort was then made to modify the NHC centers with guest metal complexes. The [Ir(cod)(OMe)]₂ Ir(I) complex (cod stands for 1,5-cyclooctadiene, OMe stands for methoxide) was selected as it has a "self-contained", basic methoxide moiety that is also sufficient for the abstraction of the C^2 proton

from the NHC·HBF₄ precursor for the direct formation of an Ir-NHC complex.¹¹⁸ Moreover, the targeted Ir-NHC complex has interesting catalytic activity in various reactions including hydrogenation.¹¹⁹ Upon treatment of Cu-Sp5-BF₄-A with this complex in THF, we were delighted to find that the Ir-modified MOF material, denoted as Ir/Cu-Sp5-BF₄-A, contained 0.82(1) wt% Ir corresponding to 2 % of NHC sites occupied by metal. While this result indicated a successful iridium immobilization inside the MOF pores, the relatively low iridium loading in this material was disappointing. This issue likely stems from the limited accessibility of the complex to the C^2 carbon, which is owed to the 3-D porous MOF structure. This, combined with large crystal size, could limit the diffusion of the [Ir(cod)(OMe)]₂ complexes into the MOF pores decreasing the extent of the desired modification. This shortfall incited us to perform iridium modification on Cu-Sp5-OMe as well. As mentioned above, this material has 22 % of the unmodified NHC·HBF4 ligands, which could be used to append the desired Ir complex. Moreover, it was hypothesized that the targeted C^2 carbons are expected to be more accessible in **Cu-Sp5-OMe** due to the transition to the layered structure after methoxide modification, making it easier for the [Ir(cod)(OMe)]₂ complex to infiltrate the MOF. Moreover, Cu-Sp5-OMe is also turbostratic, and the resulting defects are expected to provide easier access to the C^2 sites and hence promote their modification. After Cu-Sp5-OMe was treated with the Ir complex, the modified material, denoted as Ir/Cu-**Sp5-OMe**, indeed offered an iridium content that was more than 3 times higher, 2.47(6) wt%, than the modification of Cu-Sp5-BF4-A. According to TEM images, no iridium nanoparticles were present inside the structure (Figure S34). To shed further light on the iridium speciation and coordination environment in Ir/Cu-Sp5-OMe, XPS and XAS spectroscopies were employed. XPS clearly indicated that most of the iridium has an Ir(III) oxidation state, with only a small contribution of the Ir(I) counterpart (Figure S35). As the simple formation of a metal-NHC complex does not induce oxidation state change, the presence of Ir(III) presented a discrepancy with the Ir^{+1} employed in the starting complex, $[Ir(cod)(OMe)]_2$, and hence required further explanation; thus, EXAFS was used to help unravel the and speciation inside the material. First, it was found that the Ir coordination cannot be described by a simple mono- or bis-iridium(I) NHC complex, as neither their Ir-ligand distances nor their coordination numbers were sufficiently well describing the major contribution in the radial distribution function. Further, these complexes don't explain the Ir(III) oxidation state. Air oxidation of iridium was excluded as the synthetic process was performed under a nitrogen atmosphere, and the introduction of oxygen atoms led to a

decrease in fit quality. Thus, we were delighted to find that the best fits were obtained using a cyclometalated iridium (III) complex, such as the one shown in Figure 34. In fact, the benzene rings of H₂Sp5-BF₄ ligand do not have a substituent in the position that is ortho to the nitrogen atom, thus allowing this atom to also be attacked by iridium during the grafting procedure. Further, the literature provides evidence that the conditions used for the modification with the Ir complex, namely refluxing in THF, favor the formation of the cyclometalated Ir (III) complex. In such complexes, Ir is coordinated not only to the C^2 position of the NHC, but also the C1 found on the neighboring aromatic ring.¹²⁰⁻¹²⁴ The final fit results thus indicate three types of atoms coordinated to iridium: C1 at 2.00(8) Å (Ir-benzene ring), C² at 2.06(8) Å (Ir-NHC) and O1 at 2.16(8) Å (Ir-THF), all with a coordination number of 2.6(3). The small quantity of Ir(I) complexes seen on XPS is explained by the fractional presence of Ir(I)-NHC complexes coordinated to the cod ligand, which was not refined separately and likely explain the small increase in EXAFS coordination number compared to the expected value of 2. Notably, the presence of the bis-cyclometalated complexes goes in line with an increase of crystallinity after the modification of Cu-Sp5-OMe with iridium (Figure S36), where the re-appearance of high-angle peaks can be attributed to iridium acting as a heavy atom that connects two ligands, therefore, decreasing the disorder of the turbostratic phase and providing a strong scattering density.



Figure 34. EXAFS fits for the first Ir coordination shell and plausible molecule arrangement Ir/Cu-Sp5-OMe. Atom colors: Ir, dark blue; C, grey; O, red; N, blue; H, white.

Next, HAADF-STEM was employed to visualize the iridium distribution in the material (Figure S37). The analysis revealed numerous, homogeneously distributed features with sizes up to 1 nm. While the smallest features are clearly described as single Ir atoms, the larger ones required further explanation. EXAFS data indicated no noticeable contribution from Ir-Ir scattering, thus ruling out

the formation of small Ir clusters. Further, given the layered structure of the Ir/Cu-Sp5-OMe material, the crystal is most likely observed along the *a* axis. Thus, it is thought that this feature stems from iridium atoms in subsequent layers that also scatter and, hence, give rise to a bright feature that appears to be larger in size than an individual atom. This goes in line with the increase in the density of single atom features in the darker regions of the image, where the material thickness and, therefore, the number of observed layers are much smaller.

Having firmly established the nature of the iridium grafting in the material, catalytic investigations were subsequently carried out. For this, stilbene hydrogenation using hydrogen gas in mild conditions was used as proof of heterogeneous catalytic activity (Scheme 3). The results of catalytic runs are presented in Table 2. Both Cu-Sp5-BF₄-A and Cu-Sp5-OMe were not active in the reduction even at a high pressure of 10 bar (Table 2, 1-2), indicating that iridium was indeed necessary for the reaction to happen. We further observed higher activity of Ir/Cu-Sp5-OMe vs. Ir/Cu-Sp5-BF4-A material due to the aforementioned diffusion issues and hence lower iridium loading in the latter (Table 2, 3-4). The split test indicated a true heterogeneous nature of the catalysis as no extra conversion happened after the removal of the catalyst via filtration (Figure S38). Moreover, the catalytic activity, compared to other heterogeneous Ir-NHC materials, is slightly lower, which might be linked to a bis-cyclometalated NHC nature of the active site. As observed for other Ir-NHC systems¹¹⁹, our catalyst was not recyclable and offered no conversion on the second run (Table 2, 5-6). To gain insight into the catalyst deactivation, we analyzed it with HAADF-STEM, EXAFS, and XPS. XPS spectrum indicated the presence of Ir⁰ (Figure S39), while EXAFS (Figure S40) showed a clear feature at larger R distances which correspond to Ir-Ir distances in the metallic state. HAADF-STEM images showed an uneven aggregation of iridium to nanoparticles with a size increase of up to 5 nm (Figure S41). This shows that, upon the use of the material in catalysis, iridium has reduced and aggregated to form larger particles, which are not catalytically active. Some part of iridium, however, is still coordinated to the MOF backbone as the peak at lower R in EXAFS is still present. While the exact nature of the active site is hard to determine due to change in iridium speciation over the course of the reaction, we believe these results indicate better suitability of Cu-Sp5-OMe compared to Cu-Sp5-BF₄-A for preparation of grafted metal-NHC catalysts.

#	Material	Cat. Mol %	P(H ₂), bar	Time, h	NMR yield, %
1	Cu-Sp5-BF ₄ -A	7.5 (Cu)	10	18	0
2	Cu-Sp5-OMe	7.5 (Cu)	10	18	0
3	Ir/Cu-Sp5-BF4-A	0.25	5	24	66
4	Ir/Cu-Sp5-OMe	0.25	5	24	>99
5	Ir/Cu-Sp5-BF ₄ -A*	0.25	5	24	0
6	Ir/Cu-Sp5-OMe*	0.25	5	24	0

Table 2. Catalytic test results. Yields are determined by NMR using n-octane as an internal standard

*Second catalytic run



Scheme 3. Stilbene hydrogenation reaction

3.3. Conclusions

In this work, a new metal-organic framework called **Cu-Sp5-BF**₄, which features a large channellike structure with abundant NHC·HBF₄ sites was designed. The material was post-synthetically modified for the successful formation of NHC-adducts. First, the NHC ligand was modified with methoxide adducts, leading to a change in the charge of the ligand and an overall reduction in the dimensionality of the material from a 3D porous material to a layered 2D turbostratic phase, **Cu-Sp5-OMe**. Next, both materials were modified to form an Ir-NHC adduct. Using a combination of XPS and EXAFS, it was found that this modification leads to the formation of cyclometalated Ir(III) complexes inside the MOF. It was further demonstrated that the iridium loading and hence catalytic performance in a model reaction of stilbene hydrogenation is improved if the turbostratic **Cu-Sp5-OMe** is used as the iridium support rather than the parent **Cu-Sp5-BF**₄. This observation is owed to the presence of defects in the former, which leads to easier access to the NHC functionality inside the MOF pores.

3.4. Supplementary information3.4.1. General notes

Materials:

All the commercially available chemicals were used as received without further purification. $Cu(BF_4)_2 \cdot 6H_2O(99\%)$ and n-octane (>99\%) were obtained from ABCR, $CDCl_3$ (>99.8% D) was obtained from Acros, ethanol (A15 pharmaceutical grade) was obtained from Reactolab SA, anhydrous tetrahydrofuran (THF, >99.5%) and trans-stilbene (>98.0%) were obtained from TCI, [Ir(cod)(OMe)]_2 was obtained from Sigma-Aldrich (cat. #685062), anhydrous toluene (≥99.5%), HNO₃ (69%), HCl (37%), ICP elemental standards for B and Cu were obtained from Carl Roth AG, Ir ICP elemental standard was obtained from Alfa Aesar.

X-Ray crystallography:

Laboratory single-crystal X-ray diffraction was performed at 100 K using a Bruker D8 Venture diffractometer equipped with a graphite monochromator and microfocused MoKa radiation source $(\lambda = 0.71073 \text{ Å})$. The data was integrated with SAINT⁹⁹ and corrected for adsorption with SADABS software.¹⁰⁰ Synchrotron single crystal and powder X-ray diffraction data were collected using a multipurpose PILATUS@SNBL diffractometer with PILATUS2 M detector at the BM01 at European Synchrotron Radiation Facility ($\lambda = 0.6866$ Å). Single crystals were mounted on a Kapton loop and measured at 100 K. The structure solution and refinement were performed using ShelXT¹⁰¹ and ShelXL-2013¹⁰² operated through the Olex2 interface.¹⁰³ First, non-hydrogen atoms were located and refined anisotropically, then H atoms were introduced with corresponding HFIX commands and refined isotropically. Powders were loaded in 1mm diameter glass capillaries and measured at 300 K in ambient conditions for ex situ samples. For studies of in situ material activation, the MOF sample was loaded in a capillary connected to a custom build manifold and evacuated using a turbomolecular pump. Then, a temperature ramp was applied and the material was heated to 190 °C over 90 minutes, kept at that temperature for 20 minutes, and cooled down to room temperature over 50 minutes. The sample structure evolution was followed by measuring a powder pattern each minute. The data was visualized using MEDVED software. 125

Laboratory powder X-ray diffraction was performed using Bruker D8 Discover instrument equipped with Cu K α radiation source operated in Bragg–Brentano geometry. The scan step was 0.02 ° and the time per step was 1 s.

FTIR measurements

The in situ FTIR data was collected using a PerkinElmer FTIR/FIR spectrometer. The sample was mixed with KBr and placed into a custom-built cell with diffuse reflectance Praying MantisTM accessory. The sample was first activated by heating at 185 °C in vacuum for 15 h. Then the sample was cooled to -123 °C (150 K) and dosed with selected CO pressures using a custom-built gas manifold. The spectra were collected at 1 cm⁻¹ resolution. All spectra were background-subtracted.

TGA

Thermogravimetric analysis (TGA) and decomposition temperatures were determined from TGA experiments on a TGA Q500 device from TA Instruments in 100 μ l platinum pans with an empty pan of the same type as reference.

ICP

An exact amount of ca. 10 mg, of MOF material was digested, inside a PTFE vial, in 1 mL of aqua regia (1:3 v/v HNO₃ 69 %+HCl 37 %) at 100 °C for 1h and further overnight at room temperature. The solution was diluted to 25 mL in a volumetric flask using 2 % HCl as a matrix, filtered through 0.22 μ m syringe membrane filter and analyzed via ICP-OES using Agilent 5110 instrument. The averaged element concentrations and their standard deviations were extracted using 5 chosen, most intense and non-overlapping wavelengths.

NMR

Solution NMR spectra were recorded in CDCl₃ using a BRUKER AVIII HD 400 spectrometer; chemical shift values were referenced to 1 % TMS solution in CDCl₃ using the residual solvent signals as a secondary reference. The Bruker Topspin software package (version 3.2) was used for measurements and Mestrenova software (version 12.0.0-20080) was used for processing of the spectra.

Solid-state ¹³C NMR was performed at room temperature using a 500 MHz 3.2 mm LTMAS probe at 24 kHz MAS, with an Avance III Bruker console.

Electron microscopy

SEM images were acquired on an FEI Teneo SEM instrument using an ETD detector at an accelerating voltage of 2.0 kV. Transmission electron microscopy (TEM) images were taken using the FEI Tecnai G2 Spirit Twin instrument with an accelerating voltage of 120 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging was performed on an FEI Titan Themis instrument operated in scanning mode at an accelerating voltage of 200 kV. This microscope is equipped with a high brightness X-FEG gun and four silicon drift Super-X EDX detectors.

3.4.2. Synthetic protocols

H₂Sp5-BF₄ and Cu-Sp5 were synthesized and characterized as previously described.¹¹¹

Cu-Sp5-BF₄ **large-scale synthesis**. In a 500 mL Schott bottle, 1.761 g of Cu(BF₄)₂·6H₂O (5.100 mmol) was dissolved in 167 mL of ethanol. To this solution was added 1.435 g (3.604 mmol) of finely ground H₂Sp5-BF₄ and the mixture was sonicated for 10 minutes to form a well-dispersed pale blue slurry. The bottle was transferred into a temperature-programmed oven and the following program was applied: ramp to 80 °C over 8 h, stay at 80 °C for 72 h, turn off heating, and cool naturally inside the oven. The pale blue crystals were filtered on a G3 frit and washed with ethanol until the filtrate was clear and colorless. The material was further dried in vacuum (10^{-2} mbar) to produce **Cu-Sp5-BF**₄·solvent. Anal. Calcd for Cu(C₁₇H₁₃N₂O₄)(BF₄)(C₂H₅OH)_{1.6}(H₂O)_{0.6}: C, 44.59; H, 4.41; N, 5.15. Found: C, 44.65; H, 4.41; N, 5.17.

Cu-Sp5-BF₄ single crystal synthesis. In a 8 ml vial, 10.3mg (0.03 mmol) of Cu(BF₄)₂·6H₂O was dissolved in 3 mL of ethanol. To this was added 12 mg (0.03 mmol) of finely ground H₂Sp5-BF₄. The mixture was sonicated for 10 minutes and transferred into a temperature-programmed oven and the following program was applied: ramp to 80 °C over 8 h, stay at 80 °C for 48 h, ramp to 25 °C during 8 h. The blue crystals were washed with ethanol by decantation until the supernatant was clear and colorless. The material was further dried in vacuum (10⁻² mbar) to produce **Cu-Sp5-BF**₄·**solvent**. Anal. Calcd for Cu(C₁₇H₁₃N₂O₄)(BF₄)(C₂H₅OH)_{1.6}(H₂O)_{0.7}: C, 44.44; H, 4.43; N, 5.13. Found: C, 44.52; H, 4.28; N, 4.93.

Cu-Sp5-BF₄ activation. In a 20 mL vial equipped with a septum cap, vacuum-dried pale blue **Cu-Sp5-BF**₄ solvent was placed and connected to a vacuum line via needle. The vial was heated stepwise in an oil bath (80 °C \rightarrow 120 °C \rightarrow 160 °C \rightarrow 185 °C), staying for 1 h at each intermediate temperature, and kept at 185 °C overnight. The resulting dark green crystals of **Cu-Sp5-BF**₄-A were cooled down under vacuum, dosed with N₂ from the Schlenk line, and immediately transferred to a nitrogen-filled glove box. Anal. Calcd for Cu(C₁₇H₁₃N₂O₄)(BF₄): C, 44.42; H, 2.85; N, 6.09. Found: C, 44.06; H, 2.08; N, 5.58.

Cu-Sp5-OMe synthesis. In a nitrogen-filled glovebox, 1.000 g of **Cu-Sp5-BF₄-A** (2.176 mmol) was added to a solution of 123.5 mg sodium methoxide (2.286 mmol, 1.05 eq) in 300 mL anhydrous methanol. After stirring for 24 h under nitrogen at room temperature, the mixture was allowed to stand still for 30 minutes and most of the liquid was decanted. The solid was isolated using centrifugation (3 min, 6000 rpm) and washed 3 times with 100 mL methanol. The obtained material, **Cu-Sp5-OMe**, was vacuum dried and then activated at 120 °C in vacuum overnight to produce **Cu-Sp5-OMe-A**. Anal. Calcd for Cu(C₁₇H₁₃N₂O₄)(BF₄)_{0.22}(OCH₃)_{0.78}(H₂O)_{2.4}: C, 46.49; H, 4.42; N, 6.10. Found: C, 46.15; H, 4.33; N, 6.14.

Iridium grafting procedure. In a nitrogen-filled glovebox, a solution of 252 mg $[Ir(cod)(OMe)]_2$ (0.380 mmol = 0.760 mmol Ir, 1 eq Ir) in 35 mL anhydrous THF was prepared in a 100 mL Schlenk flask. To this solution, 350 mg of either **Cu-Sp5-BF4-A** (0.760 mmol) or **Cu-Sp5-OMe-A** (0.841 mmol) was added. The Schlenk flask was connected to a reflux condenser under nitrogen and the mixture was allowed to stir for 16 h at room temperature. After this soaking step, the mixture was heated to reflux (oil bath temperature 75 °C) for 24 h. Upon cooling, the mixture was separated using a centrifuge and the solid was washed with THF until the supernatant was colorless (5x50 mL). The materials were dried in vacuum overnight and stored in a nitrogen-filled glovebox, to produce **Ir/MOF** and **Ir/MOF-OMe** accordingly.

3.4.3. Catalysis protocols

Catalytic test protocol. In a nitrogen-filled glovebox, a stock solution of 2.143 g *trans*-stilbene and 0.676 g n-octane (internal standard) in anhydrous toluene was prepared in a 25 mL volumetric flask. 2.918 mL of this solution (corresponding to 0.250 g *trans*-stilbene, 1.387 mmol) was added into a Parr pressure vessel. To this solution, an amount of catalyst corresponding to 0.25 mol% Ir (25.6 mg for **Ir/MOF-OMe**, 77.4 mg for **Ir/MOF**) was added, the vessel was sealed and removed from the glovebox and subsequently pressurized with 5 bar H₂ after 3 purges. The reaction was run at 40 °C for 24 hours. To stop the reaction, the vessel was cooled down in an ice bath and subsequently depressurized. The solid catalyst was removed using centrifugation and washed with THF 3 times. It was later dried in vacuum and stored in the glovebox for further characterization and recycle test. The liquid toluene solution was analyzed using ¹H NMR in CDCl₃ to determine the yield and the conversion.

Split test protocol. A catalytic reaction was run as described above for a period of 4 hours instead of 24 hours. Afterward, upon stopping the reaction and centrifugation, the supernatant was additionally filtered using a 0.22 μ m syringe membrane filter to ensure the removal of all the solid material. A sample of the solution was taken for ¹H NMR and the rest of it was loaded in the reactor again and the reaction was run for extra 20 hours as described above. Upon stopping the reaction, the solution was analyzed again using ¹H NMR spectroscopy.

Chapter 4. LigX methodology: a whole new world of MOF ligands

4.1. Diamine-based ligands

Being motivated by a constant necessity to produce multi-gram quantities H₂Sp5-BF₄ ligand for our studies on Cu-Sp5 and Cu-Sp5-BF4 MOFs (Chapters 2 and 3), we sought more optimal ways to produce this ligand on a large scale. The key step of this synthesis is obtaining a diamine precursor, a feat made possible by previous research done in our laboratory.⁸² Should this diamine be obtained, it is easily converted in one step to the target imidazolinium dicarboxylate ligand. The key step in the diamine synthesis relies on an electrophilic substitution on a nitrogen center. However, after thorough consideration, we realized that the reaction is not optimal (Scheme 4). Indeed, aromatic amines are deactivated to such substitutions due to conjugation of the lone pair with the benzene ring, and this deactivation is further strengthened by an electron-withdrawing group (EWG) such as carboxylate ester. Moreover, dibromoalkanes were also employed in the synthesis, which poses serious safety concerns owing to their volatility and carcinogenic nature.¹²⁶ Taking these shortfalls into account, it was hypothesized that if the type of reaction was altered from an electrophilic substitution to a nucleophilic substitution in the aromatic ring (S_NAr) the reaction might proceed more easily, eliminating some of the issues that pose limitations towards scalability. Hence, the type of synthons was changed to aliphatic amines and aromatic halides (see Scheme 4) and the ester group was altered to a stronger nitrile EWG, such as a nitrile to facilitate the substitution. In such a reaction, it is anticipated that the EWG activates the halogen for its easy displacement. Moreover, this approach does not require the use of dangerous dibromoalkanes and has fewer steps, only two, to reach the targeted diamine structure. Even more importantly, this reaction does not depend on the diamine length, and it is suitable for secondary and aromatic amines as well.

Having elucidated the potential benefits of this new approach, the next goal was to realize it experimentally using Scheme 5. The first step of the synthesis was, in fact, previously used in the pharmaceutical field to produce 6.5 g of product at a 70 % yield, $^{127-129}$, and in the title work, it was improved to produce 92.9 g of **2CH₂-diBN** with a 94 % yield. Further, hydrolysis of the nitrile in basic conditions overnight allowed the easy production of the desired H₂Sp5 diamine, alternatively referred to as 2CH₂-diCO₂H, in 83 % yield. This material was further routinely used

in our ongoing work to produce $H_2Sp5-BF_4$ according to synthesis presented in Chapter 2 on Scheme 1.



Scheme 4. Comparison of electrophilic substitution and S_NAr approaches for H₂Sp5 diamine

synthesis



Scheme 5. H₂Sp5 diamine synthesis using the new methodology

In order to demonstrate the feasibility of the approach for the synthesis of longer diamines, the ethylenediamine was simply replaced with longer constituents, allowing the synthesis of the corresponding ligands with 3, 4, 6, and 12 methylene bridges between nitrogen atoms combined with high to excellent yields (Scheme 6). It is clear from this success that the synthesis indeed does not depend on diamine length unlike the previous approach based on dibromoalkanes, where ligand could only be produced with 4 or fewer CH₂ groups.



Scheme 6. Synthesis of longer diamine-based ligands

After reaching the first goal, which was a simplified production of H₂Sp5 diamine for the NHC ligand synthesis, other potential applications for such linear diamines were considered. While it was envisioned that these molecules might be deployed as surfactants or biologically active intermediates, it was promptly decided that these ligands by themselves do not attract a tremendous amount of interest for MOF construction, a decision that stems from their high flexibility. Indeed, the literature provides evidence that oxygen-bridged analogs of the as-prepared diamines give rise to low porosity and stability of the corresponding MOF materials due to a high degree of flexibility in the corresponding linkers.¹³⁰⁻¹³¹ However, upon further assessment, it was realized that instead of flexible primary diamines, more rigid secondary diamines, such as piperazine (Scheme 7), could be deployed. Indeed, piperazine moieties are more rigid than alkyldiamines due to their cyclic nature. Further, aryl-substituted piperazines benefit from additional conformation stabilization due to the steric bulk of benzene rings and conjugation effects associated with the nitrogen lone pair. ¹³²⁻¹³³



Scheme 7. Comparison of ethylenediamine and piperazine as building blocks for MOF ligands

4.2. Piperazine-based ligands

Having understood the potential of the piperazine-based ligands for MOF construction, the focus of the thesis changed towards their synthesis. Similar to the synthesis of the **2CH₂-diBN** diamine, the synthesis of the simplest piperazine-based dinitrile **Pip-diBN** proceeded smoothly with a remarkable 98 % yield. The second hydrolysis step also went well giving the final dicarboxylate, **Pip-diCO₂H**, (with a 98 % yield (Scheme 8). Inspired by the ease of the ligand synthesis, we subsequently turned to screen the reaction conditions necessary for MOF formation. Bearing in mind that the **Pip-diCO₂H** has a strong resemblance to the p-Terphenyl-4,4"-dicarboxylic acid (H₂tpdc) ligand used in the synthesis of a highly porous and stable zirconium-based UiO-68,²⁸ it was hypothesized that a structurally related material would form. However, despite many trials, the targeted Zr-MOF could not be obtained. Thus, it was hypothesized that this lack of success

could stem from the extremely low solubility of the **Pip-diCO₂H** ligand in common solvents such as DMF, DMA, NMP and DMSO. In fact, we were unable to characterize **Pip-diCO₂H** using NMR in DMSO-d6 due to its extremely low solubility and we had to use NaOD/D₂O mixture instead. It is noted that such a problem is not uncommon in the MOF field. For instance, Yaghi et al. previously reported the synthesis of an IRMOF-74 series of MOFs having ligands with up to 11 benzene rings. In this work, they functionalized the benzene rings on the ligands with methyl and/or hexyl side chains in order to improve their solubility, and hence, allow for the formation of the desired MOFs using standard solvothermal approaches.³⁶ Thus, a similar strategy was used in our work. The standard piperazine unit was substituted with *trans*-2,5-dimethylpiperazine as the starting material, in hopes that the methyl functionality would help alleviate the ligand solubility issues. We were delighted to find that this reaction proceeded as planned using similar reaction conditions, with the production of 46.70 g of the **Dimepip-diBN** intermediate in a 74 % yield (Scheme 9). We immediately found that this molecule was noticeably more soluble in DMSO compared to its unsubstituted analog, as we easily prepared a DMSO-d6 solution for NMR characterization. Moreover, the ligand was crystallized from DMSO to visualize its structure and better understand the effect of adding of methyl groups onto the piperazine backbone.



Scheme 8. **Pip-diCO₂H** synthesis using the new methodology

As seen on Figure 35, the methyl groups strongly influence the crystal packing in the structure of **Dimepip-diBN** compared to **pip-diBN**.¹³⁴ In the structure of the unsubstituted analog, the neighboring molecules of the dinitrile are situated with a distance of 3.69 Å between the planes of the benzene rings (Figure 35, a-c). Further, these molecules are nearly aligned, stacking almost directly on top of one another, thus maximizing the van der Waals interaction between them.

However, this is not the case for **Dimepip-diBN**; the two methyl groups on the piperazine core prevent such close packing. In fact, the distance between adjacent molecules is significantly larger (5.07 Å) and most importantly the molecules can't fully overlap due to the steric bulk of the methyl groups that point above and below the molecular plane (Figure 35, d-f). Owed to the weaker intermolecular interaction in the substituted structure, the solubility of the **Dimepip-diBN** is increased, which is an important prerequisite for MOF construction.



Scheme 9. Dimepip-diCO₂H synthesis using the new methodology



Figure 35. Extracts from crystal structure of **pip-diBN**¹³⁴ (a-c) and **Dimepip-diBN** (d-f). (a), (d) Packing of molecules. Hydrogen atoms are omitted for clarity; (b), (e) Side view of two molecules; (c), (f) Front view of two molecules in **pip-diBN and Dimepip-diBN**, respectively. The distance illustrated is the interplanar distance between two benzene rings of two molecule. Atom colors: C, gray; N, blue; H, white

The subsequent hydrolysis of **Dimepip-diBN** using standard conditions gave rise to the **Dimepip-diCO₂H** in 87 % yield (Scheme 9). This dicarboxylic acid was also notably more soluble in DMSO during NMR measurements, indicating the successful improvement of the ligand design.

Having isolated and characterized **Dimepip-diCO₂H**, the synthesis of the related Zr-based MOF was subsequently attempted. Unfortunately, the conditions reported for related benzene-ring analogs did not produce materials crystalline and stable enough for further characterization.^{28, 112, 135} However, after numerous reactions, the proper conditions to crystallize the UiO-68 analog were elucidated with the **Dimepip-diCO₂H**, using L-proline as the modulator.¹³⁶⁻¹³⁷ After fine-tuning the synthetic protocols as well as the MOF activation conditions, the first highly porous piperazine based MOF, **Zr-dimepip**, was realized with a BET surface area of 3100 m²/g (cf. theoretical 3317 m²/g for dimethyl-tpdc UiO-68 analog called PCN-56 ¹³⁸) which, as expected, is an isoreticular analog to UiO-68/PCN-56 as indicated by powder X-ray diffraction (Figure 36). The material also is stable after activation and sitting in air for 36 hours, as evidenced by the high-angle diffraction data.



Figure 36. (a) PXRD patterns of activated Zr-dimepip after BET measurement and 18 and 36 h thereafter, compared to a calculated pattern of PCN-56. The region between 10 ° and 120 ° is scaled up 20x for PCN-56 pattern to allow for better visualization. (b) Nitrogen adsorption isotherm of Zr-dimepip measured at 77 K.

Being motivated by this success, the modular nature of the new synthetic approach was exploited to produce several new ligands and related MOF materials. For this, various nitro- and halogen-

decorated building blocks were selected for the production of 4 new ditopic ligands. It is noted, that for some of these ligands, a different hydrolysis method was employed; the method included heating the intermediates in sulfuric acid, which better tolerates the halogen- and nitro- functional groups on the ligand backbone. The ligands were further employed for MOF construction, to produce highly crystalline and porous materials (for **Zr-di(3-NO₂)dimepip**, the BET area is equal to 2300 m²/g) as indicated on Figures 37, 38.



Figure 37. (a) Structures of new ligands and microscope images of corresponding Zr-MOFs. Scale bar 100 μm. (b) PXRD of the newly synthesized MOFs



Figure 38. Nitrogen adsorption isotherm of Zr-di(3-NO₂)dimepip measured at 77K.

Single crystals of the MOF, **Zr-di**(2-F)**dimepip**, were isolated and were of a quality that is sufficient for structure determination via SCXRD. Perfectly matching the expectations, it was determined that crystals exhibited the classical UiO-based structure with 12-connected $[Zr_6O_4(OH)_4]^{12+}$ clusters bridged by the as-prepared ligands (Figure 39) with the maximum pore dimension, dictated by the size of the ligand up to 25.8 Å.



Figure 39. SCXRD structure of **Zr-di**(**2-F**)**dimepip**. Hydrogen atoms, fluorine atoms and methyl groups of the ligand are omitted for clarity. Atom colors: C, gray; N, blue; O, red; Zr, turquoise.

4.3. DHP-based ligands

To demonstrate the broader applicability of this new approach to ligand design, hereinafter referred as to LigX, an aromatic amine, including dihydrophenazine (DHP), was selected to construct MOF ligands. Due to the low nucleophilicity of the aromatic amines, the synthetic procedures had to be modified slightly; in short, this time a stronger base, such as potassium *tert*-butoxide, was required to produce the dinitrile precursors, an approach known for other aromatic amines.¹³⁹ After the alteration, the synthesis proceeded smoothly with 95 % yield, and the subsequent hydrolysis step afforded the final **DHP-diCO₂H** in 95 % yield as well (Scheme 10). It must be noted that the synthesis of this ligand was reported before, but it was done using Pd-catalyzed coupling and featured significantly lower yields.¹⁴⁰ The new approach, developed in this thesis, relies on inexpensive starting materials and does not require any transition metal catalysts. Similar to that

report, low solubility of this ligand prevented us from characterizing it via NMR; however, the ligand could instead be recrystallized from hot DMSO to obtain large single crystals suitable for diffraction measurements. As expected, the ligand has a linear arrangement and the carboxylate groups are almost orthogonal to the central DHP core with a 75.6 ° angle between them (Figure 40).



Scheme 10. Synthetic pathway to dihydrophenazine-based ligands



Figure 40. Structure of **DHP-diCO₂H** as found by SCXRD. Atom colors: C, gray; N, blue; O, red; H, white.

Having isolated **DHP-diCO₂H**, a new zirconium MOF was synthesized. The so-obtained **Zr-DHP** formed as large single crystals again suitable for structure determination. A similar UiO-type structure was found, with a 25.4 Å pore size, which is just marginally smaller than those observed in the aforementioned piperazine-based analog (Figure 41).


Figure 41. Microscope image of Zr-DHP crystals and their structure based on SCXRD data. Scale bar 100 µm. Hydrogen atoms are omitted for clarity. Atom colors: C, gray; N, blue; O, red; Zr, turquoise.

After having elucidated the structure of **Zr-DHP**, the material was solvent exchanged with hexane and activated at 40 ° C for 16 hours, however even such mild treatment led to a non-porous material. Interestingly, the powder pattern of the activated material did not indicate amorphization but instead showed that the peaks of the activated MOF shifted significantly to the right, indicating that it possesses a smaller unit cell comparable to the size of UiO-67 unit cell, an isoreticular MOF material with only two benzene rings between the carboxylates (Figure 42, center).¹⁴¹ This observation indicates the flexibility of the DHP ligand inside the MOF structure. Upon a close examination of the literature, it was determined that diarylsubstituted dihydrophenazines are indeed susceptible to buckling and loss of rigidity if the aryl substituent does not bear a functional group in ortho-position to the nitrogen atom.¹⁴² Thus, efforts were made to modify the DHP ligand, to minimize its flexibility, which is a plausible explanation for the lack of porosity in the resulting MOFs. To test the hypothesis and to produce a more stable MOF material, a tetramethylsubstituted ligand analog, tetra(3,5,3',5'-Me)DHP-diCO₂H (Figure 43, a), was synthesized using a similar synthetic pathway. Moreover, the corresponding MOF, Zr-tetra(3,5,3',5'-Me)DHP, showed an identical structure to the solvated Zr-DHP after activation, as evidenced by PXRD (Figure 43, b). Further, post activation, the BET surface area of this material was found to be approximately $1800 \text{ m}^2/\text{g}$ (Figure 43, c), indicating that indeed the stabilization of the flexible DHP ligand, through the introduction of methyl groups that sterically hinder the ligand rotation, can successfully lead to the production of a porous Zr-MOF.



Figure 42. Center: PXRD of Zr-DHP before and after activation in comparison to its calculated PXRD (bottom) and UiO-67 calculated PXRD (top).¹⁴¹ Sides: illustration of ligand buckling

inside the Zr-DHP structure upon activation



Figure 43. (a) Structure of tetra(3,5,3',5'-Me)DHP-diCO₂H ligand(b) PXRD of Zrtetra(3,5,3',5'-Me)DHP after activation compared to calculated PXRD of Zr-DHP.(c) Nitrogen adsorption isotherm of Zr-tetra(3,5,3',5'-Me)DHP measured at 77K.

4.4. Linear tetracarboxylate ligands

Having shown the formation of a series of MOFs having structures similar to UiO-68, it was necessary to understand the limits of LigX methodology through the synthesis of other ligand geometries; for instance, there is an interest in tetracarboxylate ligands that have been employed in the construction of MOFs having the NbO-type structure. Such MOFs are highly interesting for applications in gas storage and their all-benzene ring analogs have been extensively studied for that purpose.⁷²⁻⁷⁵ By a simple change of the nitrile building block from 4-fluorobenzonitrile to 5-fluoroisophthalonitrile (Scheme 11), the production of the corresponding tetranitrile **pip-tetraBN** (89 % yield) was made and subsequently converted to the tetracarboxylate ligand **pip-tetraCO₂H** (81 % yield).



Scheme 11. Synthetic pathway to the tetracarboxylate ligands

Given that this exact ligand was reported once before, it was important to exploit the tunability of the LigX approach for the synthesis of two new ligands, namely **dimepip-tetraCO₂H** (Figure 44, left) and **DHP-tetraCO₂H** (Figure 45, left), using different amine precursors. In addition to the successful synthesis of the targeted ligands, it was demonstrated that the ligands afford an isoreticular series of copper MOFs having crystal sizes large enough for structure determination (Figures 44, 45). Further, the purity of the materials was proven by PXRD (Figure 46, a). Upon activation, the **Cu-tetra-dimepip** framework was found to have a BET surface area of 2289 m²/g (Figure 46, b). This is comparable to the reported BET surface area of its isostructural analog with no methyl groups, NJU-Bai-19⁷², 2803 m²/g, taking into account the occupation of pore space with methyl groups and their slight negative gravimetric influence. However, the **Cu-tetra-DHP** showed relatively low porosity with a BET surface area of 320 m²/g. This is attributed to a

structural transformation due to the flexibility of the DHP-based ligands, as discussed earlier in the case of the **Zr-DHP** MOF.



Figure 44. Left to right: Structure of dimepip-tetraCO₂H, Microscope image of Cu-tetradimepip crystal, two types of pores in the Cu-tetra-dimepip structure based on SCXRD data. Crystal size 61×71×86 µm. Scale bar 100 µm. Hydrogen atoms are omitted for clarity. Atom colors: C, gray; N, blue; O, red; Cu, turquoise.



Figure 45. Left to right: Structure of DHP-tetraCO₂H, microscope image of Cu-tetra-DHP crystals, two types of pores in the Cu-tetra-DHP structure based on SCXRD data. Scale bar 100 μm. Hydrogen atoms are omitted for clarity. Atom colors: C, gray; N, blue; O, red; Cu, turquoise.



Figure 46. (a) PXRD of **Cu-tetra-dimepip** and **Cu-tetra-DHP** compared to their calculated PXRDs. (b) Nitrogen adsorption isotherms of **Cu-tetra-dimepip** and **Cu-tetra-DHP** measured at 77K.

4.5. MOF-74/CPO-27 based ligands

Having shown a potential for incorporation of side groups such as NO₂, halogens, or methyl inside the ligands synthesized using the LigX methodology, there was interest to introduce OH groups in the *ortho*-position to carboxylate group. Such an arrangement would lead to ligands, which can be used for the construction of MOF-74/CPO-27 analogs, a family of highly stable and porous MOF materials suitable for a host of applications.^{36, 143-144} However, to obtain such structures we must design an appropriate synthetic pathway. As attractive as it may seem, an OH-functionalized benzonitrile cannot be used directly in the synthesis, as in basic conditions, it will become deprotonated to the phenoxide moiety, which is more nucleophilic than amines; thus, undesired side reactions will occur. One viable strategy to explore includes protecting the OH group on the ligand, through the formation of a methyl ether or carboxylic ester, which can be deprotected at a later stage. However, there was limited availability of the desired blocks and also such an approach would require the need for an extra deprotection step in the case of the methyl ether. Thus, after a close inspection of the literature, evidence was found that halogen groups, such as fluorine found in the ortho-position to the -CN group can be converted to -OH via treatment with sodium/potassium acetate/hydroxide.¹⁴⁵⁻¹⁴⁸ Thus, a strategy was devised based on this finding. First, a piperazine-based molecule having pendant fluorines next to -CNs, di(2-F)pip-diBN, was

constructed, and next, the fluorines were converted to hydroxides with the formation of **di**(2-**OH**)**pip-diBN**. Last, the nitrile groups were hydrolyzed to obtain the desired ligand **di**(2-**OH**)**pip-diCO₂H** (Scheme 12). The first step proceeded smoothly but with a moderate 65 % yield, likely due to the competitive formation of the *ortho*-aminosubstituted benzonitrile byproducts as the nitrile group activates both ortho- and para-positions for nucleophilic substitution. These byproducts, however, are easy to remove as they are less symmetric and therefore more soluble than the targeted dinitrile molecule. Thus, after a simple wash with ethanol and acetone, a clean intermediate is obtained. In the second step, the use of solid NaOH afforded the complete removal of the fluorine from the structure and hence the formation of the desired dihydroxy intermediate. This success is attributed to the use of a dipolar aprotic solvent, such as dimethylacetamide (DMA), which strongly solvates the alkali metal cation while leaving anions such as the hydroxide free for the chemical reaction to proceed.¹⁴⁹ The hydrolysis carried out during the last step, following the standard procedure, afforded the final **di**(2-**OH**)**pip-diCO₂H** ligand in 90 % yield and on a 15 g scale.



Scheme 12. Synthetic pathway to di(2-OH)pip-diCO₂H

For the synthesis of isoreticular MOF-74 analogs, to our surprise, no solvothermal reactions carried out in dimethylformamide (DMF)-based solvent mixtures yielded a crystalline product using various metals, such as Mg(II), Co(II), Ni(II). This was unexpected as these conditions were used to obtain a host of large pore MOF-74 analogs with various metals in previous studies.^{36, 150} Thus, other reaction protocols were explored; the particular focus was placed on the synthetic procedures used in the first MOF-74/CPO-27 reports for the analogs constructed by 2,5-dihydroxyterepthalic acid, H4dobdc, a ligand having a single benzene ring and that leads to the production of the smallest pore analog. For instance, one of the previously reported approaches employs a THF/H₂O mixture

at a high temperature in a Teflon-lined autoclave to produce the MOFs,^{143, 151} while another one uses an aqueous solution of zinc acetate and NaOH-deportonated ligand in water to precipitate the MOF nanoparticles.¹⁵²⁻¹⁵³ After tweaking the aforementioned procedures, both conditions were found to lead to the desired crystalline products using metal salts containing Co(II), Ni(II), and Zn(II). The PXRDs of these materials are shown in Figure 47, a. It is noted that there is a relatively good match between the experimental patterns when compared to the simulated pattern of the Mg-IRMOF-74-III, which has a ligand containing three benzene units; thus, this confirms the formation of the desired structure. TEM microscopy (Figure 47, b-d) indicates that the crystals have a sub-micron size and the typical rod shape as expected for MOF-74 analogs. Moreover, for **Zn-di(2-OH)pip**, the mesoporous channels inside the structure can be observed via TEM, similar to previous reports on mesoporous MOF-74 based materials.^{36, 154}

The BET surface area measurements revealed porosity, but with moderate values of 400 m²/g for Zn-based material and 230 and 110 m²/g for Ni- and Co-MOFs, correspondingly (Figure 48, a). This is much lower than 2440 m²/g reported for Mg-IRMOF-74-III, and cannot just be explained by the use of heavier metals. To better understand the problem, TGA analysis was performed (Figure 48, b). Through a calculation, used to determine the actual and expected percentage of residual metal oxide remaining after material decomposition, it was determined that the experimental values were much lower than expected. This might indicate significant amounts of residual ligand present in the MOF pores. Thus, it was hypothesized that the **di(2-OH)pip-diCO₂H** ligand might not have been fully removed during MOF washes, which included water, methanol, and acetone, a phenomenon that could easily decrease the surface area of the materials. Further, it must be noted that the quality of the MOF-74 based materials is known to be activation protocol-dependent¹⁵³, and other problems previously reported for IRMOF-74 analogs include a partial collapse of the material during activation¹⁵⁴ as well as an intergrowth of the crystalline phases.¹⁵⁵ Thus, at the moment, work is ongoing to optimize the synthetic and post-synthetic protocols in order to obtain materials with surface areas that are closer to the theoretical values.



Figure 47. a) PXRD of **Co**, **Ni-**, **Zn-di**(**2-OH**)**pip** in comparison with a calculated PXRD of Mg-IRMOF-74-III. b), c), d) TEM images of **Zn**, **Ni-**, **Co-di**(**2-OH**)**pip** correspondingly



Figure 48. a) Nitrogen adsorption isotherms of Co, Ni-, Zn-di(2-OH)pip measured at 77K. b) TGA curves of Co, Ni-, Zn-di(2-OH)pip measured on air. Dashed lines indicate a theoretical value that corresponds to a guest-free MOF formula.

4.6. Triangle ligands

So far, we developed three different linear ligand designs, which include the piperazine- and DHPbased building blocks. Given the ease of the reactions thus far, we inquired if other ligand geometries are accessible using the LigX methodology. In theory, one electron-withdrawing group in a benzene ring activates three positions for S_NAr reaction: two *ortho-* and one *para-*. Thus, using a trifluorobenzene activated with a strong withdrawing group such as nitro should lead to trimeric piperazine moieties that can be used for the design of tritopic and hexatopic ligands. This strategy is exemplified in Scheme 13. For instance, choosing a dicarboxylate-decorated, monosubstituted piperazine building block would subsequently give rise to highly desirable hexacarboxylate-based ligands. Such ligands, combined with copper, give rise to the well-known *rht*-topology series of MOFs. These materials feature high stability, large pore size, and outstanding properties with regard to CO₂ capture, gas storage and separations.^{35, 156-158}



Scheme 13. Retrosynthetic approach for triangle ligands

To realize this strategy, the required dicarboxylate precursor was first synthesized. In fact, it is possible to build a piperazine ring around an aromatic amine group¹⁵⁹, and therefore, this approach was employed to build a piperazine precursor **5-pip-diCO₂Me·HCl** starting from the available dimethyl 5-aminoisophthalate. A simple protocol and minimal workup afforded the HCl salt of the corresponding piperazine in 81 % yield and at a 63 g scale. To our delight, this salt can be directly used for the next synthetic step as it is deprotonated *in situ* by K₂CO₃ to produce the free amine species which participate in the S_NAr synthesis. The subsequent hydrolysis afforded the triangle hexacarboxylate ligand **hexa-NO₂** in 80 % yield (Scheme 14). The purity and structure of the ligand **hexa-NO₂** are confirmed by a combination of ¹H, ¹³C, COSY, and HSQC NMR as well as ESI-MS in a negative mode.



Scheme 14. Synthetic pathway to hexa-NO₂ ligand

As soon as the **hexa-NO**₂ was obtained for the first time, the subsequent MOF synthesis quickly followed. Using this ligand, we sought a copper-based MOF having a similar structure type as NOTT-112 (Figure 49). ¹⁵⁸ After several attempts, large yellow-green single crystals of the new **Cu-hexa-NO**₂ material were acquired, and the resulting powder pattern well matched the calculated pattern of NOTT-112 (Figure 50, a). Upon activation, the measured BET surface area was 1990 m²/g (Figure 50, b), a value lower than that of NOTT-112 (3800 m²/g) We attribute our lower values to the non-optimal activation protocol, as materials with such large pore sizes require milder procedures such as supercritical CO₂ activation to achieve the ultimate porosity. Work is ongoing in this direction.



Figure 49. NOTT-112 ligand and structure. Reproduced from ¹⁵⁸ with permission from the Royal Society of Chemistry.



Figure 50. (a) PXRD of **Cu-hexa-NO**₂ compared to calculated PXRD of NOTT-112. 12.5-60 ° region in the calculated pattern is multiplied x10 for better visualization. Inset: microscope image of **Cu-hexa-NO**₂ crystals. Scale bar 100 μ m (b) Nitrogen adsorption isotherm of **Cu-hexa-NO**₂ measured at 77K.

4.7. Conclusions

In this chapter, we show that a fundamental examination of routine synthetic protocols has led to the development of a new concept in ligand synthesis that is used for the design of a host of new large pore MOFs. The new synthetic procedure, referred to as LigX, proceeds easily, is catalyst-free, and has provided the high-yield synthesis of 14 piperazine-based organic ligands to date that can be used for the construction of a structurally diverse group of MOFs. To date, nine new structurally robust MOFs were constructed from the resulting piperazine ligands after they were combined with a variety of metal salts. Moreover, it is demonstrated that the targeted piperazine-based MOFs, developed in this study, have structure types that are similar to some of the most prominent MOF families reported in the field. Thus, in the future, it is thought that the LigX method can be easily extended to a number of other ligands and hence used as a potential platform for the future design of large pore MOFs. It is thought, given the ease of the synthesis, its potential scalability, and the reduction in time and cost for the synthesis of piperazine-based ligands (when compared to their all benzene counterparts), this chemistry could provide much easier access to

large pore MOFs and hence open doors for their use in a variety of applications in host-guest chemistry.

4.8. Supplementary information 4.8.1. General notes Materials:

All the commercially available chemicals and solvents were used as received without further purification. Most of the halogenated benzonitriles were purchased from Fluorochem and/or Apollo. 5,10-dihydrophenazine (DHP) was prepared using a published procedure.¹⁶⁰ Any water used in the protocols was distilled.

X-Ray crystallography:

Laboratory single-crystal X-ray diffraction was performed using a Rigaku Supernova diffractometer, equipped with dual-wavelength micro-source and CCD camera, using a CuK α radiation source. ($\lambda = 1.54184$ Å). The data was collected, integrated and analyzed using CrysalisPRO software.¹⁶¹ Synchrotron single-crystal diffraction data was collected using a multipurpose PILATUS@SNBL diffractometer with PILATUS 2M detector at the BM01 at European Synchrotron Radiation Facility ($\lambda = 0.73074$ Å). Single crystals were mounted on a Kapton loop and measured using a one-axis goniometer. The structure solution and refinement were performed using ShelXT¹⁰¹ and ShelXL-2013¹⁰² operated through the Olex2 interface.¹⁰³ First, non-hydrogen atoms were located and refined anisotropically, then H atoms were introduced with corresponding HFIX commands and refined isotropically. Laboratory powder X-ray diffraction was performed using Bruker D8 Discover instrument equipped with Cu K α radiation source operated in Bragg–Brentano geometry. The scan step was 0.02 ° and the time per step was 1 s.

TGA

Thermogravimetric analysis (TGA) was performed on a TGA Q500 device from TA Instruments in 100 μ l platinum pans with an empty pan of the same type as a reference.

NMR

NMR spectra were recorded in DMSO-d6, D₂O and a mixture of TFA/CDCl₃ using a BRUKER AVIII HD 400 spectrometer; chemical shift values were referenced to TMS using the residual

solvent signals as a secondary reference for DMSO and D₂O, and TMS added directly in the samples for TFA/CDCl₃ solvent system. The Bruker Topspin software package (version 3.2) was used for measurements and Mestrenova software (version 12.0.0-20080) was used for processing the spectra.

Gas adsorption

Nitrogen adsorption isotherms at 77K were measured using BELSORP MAX II instrument. The samples were activated using a BELPREP VAC III instrument following a sample-specific protocol.

Mass spectroscopy

HRMS was performed using LTQ Orbitrap ELITE ETD (Thermo Fisher) instrument in ESI mode.

4.8.2. General protocols

General protocol for aliphatic dinitrile synthesis (GP-1):

To alkyldiamine (25 mmol, 1 eq), 4-fluorobenzonitrile (55 mmol, 6.661 g, 2.2 eq) and potassium carbonate (50 mmol, 6.910 g, 2 eq) anhydrous N,N-dimethylacetamide (DMA) (25 mL, 1 mL per mmol diamine) was added. The mixture was refluxed under N₂ atmosphere for 16 h. The solvent was removed using vacuum distillation, and the resulting solid was sonicated with water and then copiously washed with water and ethanol and air-dried over at least 16 h.



2CH₂-diBN. Ethylenediamine (375 mmol, 22.55 g), 4-fluorobenzonitrile (825 mmol, 99.90 g, 2.2 eq), potassium carbonate (750 mmol, 103.65 g, 2 eq) anhydrous DMA (375 mL) were reacted

according to the **GP-1**. Off-white solid, 92.85 g (94 %). ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.45 (d, 4H), 6.80 (m, 2H), 6.66 (d, 4H), 3.36 (m, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 152.07, 133.42, 120.61, 111.87, 95.80, 41.13.

NC CN 3CH₂-diBN. 1,3-propanediamine (25 mmol, 1.853 g), 4fluorobenzonitrile (55 mmol, 6.661 g, 2.2 eq), potassium carbonate (50 mmol, 6.910 g, 2 eq) anhydrous DMA (25 mL) were reacted according to the **GP-1**. Off-white solid, 5.020 g (73 %). ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.44 (d, 4H), 6.73 (t, 2H), 6.63 (d, 4H), 3.16 (q, 4H), 1.81 (p, 2H).



4CH₂-diBN. 1,4-butanediamine (25 mmol, 2.203 g), 4fluorobenzonitrile (55 mmol, 6.661 g, 2.2 eq), potassium carbonate (50 mmol, 6.910 g, 2 eq) anhydrous DMA (25 mL) were reacted

according to the **GP-1**. Off-white solid, 6.237 g (86 %). ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.65 (d, 4H), 6.55 (d, 4H), 6.36 (d, 2H), 3.09 (q, 4H), 1.64 (m, 4H).



6CH₂-diBN. 1,6-hexanediamine (25 mmol, 2.905 g), 4fluorobenzonitrile (55 mmol, 6.661 g, 2.2 eq), potassium carbonate (50 mmol, 6.910 g, 2 eq) anhydrous DMA (25 mL)

were reacted according to the **GP-1**. Off-white solid, 6.782 g (85 %).¹H NMR (400 MHz, DMSO*d*₆) δ 7.42 (d, 4H), 6.60 (d, 6H), 3.05 (t, 4H), 1.54 (p, 4H), 1.38 (m, 4H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 152.30, 133.34, 120.72, 111.62, 95.20, 42.05, 28.31, 26.34.



12CH₂-diBN. 1,12-dodecanediamine (25 mmol, 5.00 g), 4-fluorobenzonitrile (55 mmol, 6.661 g, 2.2 eq), potassium carbonate (50 mmol, 6.910 g, 2 eq)

anhydrous DMA (25 mL) were reacted according to the **GP-1**. Off-white solid, 9.099 g (90 %).¹H NMR (400 MHz, DMSO-*d*₆) δ 7.42 (d, 4H), 6.64 (t, 2H), 6.60 (d, 4H), 3.04 (q, 4H), 1.52 (m, 4H), 1.27 (m, 16H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 152.30, 133.32, 120.71, 111.59, 95.15, 42.08, 29.01, 28.98, 28.80, 28.31, 26.53.

General protocol for piperazine-based di/tetranitrile synthesis (GP-2)

To a mixture of solid piperazine (30 mmoles, 1 eq), 4-halobenzonitrile (66 mmoles, 2.2 eq) and potassium carbonate (10.4 g, 75 mmoles, 2.5 eq.), anhydrous N,N-dimethylacetamide (30 mL) was added. The mixture was refluxed under N₂ atmosphere for 24 h. The solvent was removed using vacuum distillation, and the resulting solid was sonicated with water and then copiously washed with water and ethanol and air-dried over at least 16 h. Reaction equivalents, solvent, time and temperature are the same unless otherwise stated.

Pip-diBN. Piperazine (25 mmol, 2.153 g), 4-fluorobenzonitrile (55 mmol, 6.661 g, 2.2 eq), potassium carbonate (50 mmol, 6.910 g, 2 eq), anhydrous DMA (25 mL) were reacted according to the **GP-2**. Off-white crystalline solid, 7.094 g (98 %). Poorly soluble in DMA, DMF, DMSO. ¹H NMR (400 MHz, DMSO- d_6) δ 7.61 (d, 4H), 7.04 (d, 4H), 3.52 (s, 8H).



(S)-mepip-diBN. (S)-(+)-2-methylpiperazine (30 mmol, 3.005 g), 4-fluorobenzonitrile (90 mmol, 10.90 g, 3 eq), potassium carbonate (90 mmol, 12.438 g, 3 eq), anhydrous DMA (30 mL) were reacted according to the **GP-2** for 48 h. Off-white solid, 5.275 g (58 %). ¹H NMR (400 MHz, DMSO- d_6) δ 7.59 (d, 4H), 6.99 (m, 4H), 4.24 (qt, 1H), 3.83 (m, 2H), 3.72 (dt, 1H), 3.37 (m, 2H), 3.19 (ddd, 1H), 1.11 (d, 3H).

Dimepip-diBN *trans*-2,5-dimethylpiperazine (22.8 g, 200 mmol, 1eq), 4fluorobenzonitrile (72.67 g, 600 mmol, 3 eq), potassium carbonate (82.9 g, 600 mmol, 3 eq), anhydrous DMF (100 mL) were firstly heated to 140 °C for 36 h, and then refluxed according to the **GP-2** for extra 96 h. Pale yellow solid, 46.70 g (74 %). ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.59 (d, 4H), 7.02 (d, 4H), 4.28 (m br, 2H), 3.64 (d, 2H), 3.43 (d, 2H), 1.09 (d, 6H).



di(2-F)-pip-diBN. Piperazine (0.8614 g, 10 mmol, 1eq), 2,4-difluorobenzonitrile (3.060 g, 22 mmoles, 2.2 eq), potassium carbonate (4.146 g, 30 mmoles, 3 eq), anhydrous DMA (5 mL) were reacted at 160 °C according to **GP-2**. Off-white solid, 2.382 g (74 %). ¹H NMR (400 MHz, TFA+Chloroform-*d*) δ 7.80 (m, 2H), 7.28 (m, 4H), 4.01 (s, 8H). ¹³C NMR (101 MHz, TFA+Chloroform-*d*) δ 165.83 (d), 151.27 (d), 136.71, 119.92, 115.70 (d), 113.66, 107.56 (d), 51.41.



di(2-F)-dimepip-diBN *trans*-2,5-dimethylpiperazine (20.55 g, 180 mmol, 1eq), 2,4-difluorobenzonitrile (75.11 g, 540 mmol, 3 eq), potassium carbonate (74.63 g, 540 mmol, 3 eq), anhydrous DMF (75 mL) were reacted according to the **GP-2** for 18 h. Pale yellow solid, 44.28 g (70 %). ¹H NMR (400 MHz, DMSO- d_6) δ 7.60 (t, 2H), 6.99 (dd, 2H), 6.88 (dd, 2H), 4.29 (tq, 2H), 3.70 (dd, 2H), 3.46 (dd, 2H), 1.11 (d, 6H).



di(3-NO₂)-pip-diBN. Piperazine (0.431 g, 5 mmol, 1eq), 4-chloro-3-nitrobenzonitrile (2.738 g, 15 mmoles, 3 eq), potassium carbonate (2.073 g, 15 mmoles, 3 eq), anhydrous DMF (5 mL) were reacted at 100 °C according to **GP-2** for 15 h. Bright yellow solid, 1.011 g (53 %). ¹H NMR (400 MHz, DMSO- d_6) δ 8.36 (d, 2H), 7.91 (dd, 2H), 7.34 (d, 2H), 3.44 (s, 8H).

di(3-NO₂)-dimepip-diBN. *trans*-2,5-dimethylpiperazine (0.571 g, 5 mmol, 1eq), 4chloro-3-nitrobenzonitrile (2.738 g, 15 mmoles, 3 eq), potassium carbonate (2.073 g, 15 mmoles, 3 eq), anhydrous DMF (5 mL) were reacted at 100 °C according to **GP-2** for 15 h, and additionally washed with acetone before drying. Bright orange solid, 1.275 g (63 %).¹H NMR (400 MHz, TFA+Chloroform-*d*) δ 8.52 (s, 2H), 8.23 (d, 2H), 8.03 (d, 2H), 4.24 (s, 2H), 3.96 (m, 2H), 3.62 (m, 2H), 1.18 (d, 6H). ¹³C NMR (101 MHz, TFA+Chloroform-*d*) δ 145.59, 142.53, 139.95, 131.19, 127.29, 115.09, 113.52, 60.82, 59.85, 15.36.



pip-tetraBN. piperazine (0.861 g, 10 mmol, 1eq), 5-fluoroisophthalonitrile (3.215 g, 22 mmoles, 2.2 eq), potassium carbonate (3.455 g, 25 mmoles, 2.5 eq), anhydrous DMA (10 mL) were reacted at 120 °C according to **GP-2** for 20 h. Off-white solid, 3.012 g (89 %). ¹H NMR (400 MHz, DMSO- d_6) δ 7.78 (s, 4H), 7.70 (s, 2H), 3.48 (s,

8H).



Dimepip-tetraBN. *trans*-2,5-dimethylpiperazine (1.142 g, 10 mmol, 1eq), 5-fluoroisophthalonitrile (3.215 g, 22 mmoles, 2.2 eq), potassium carbonate (3.455 g, 25 mmoles, 2.5 eq), anhydrous DMA (10 mL) were reacted at 120 °C according to **GP-2** for 20 h. Off-white solid, 2.622 g (72 %).

General protocol for dihydrophenazine-based ligand synthesis (GP-3).

In a Schlenk flask inside nitrogen-filled glovebox, 5,10-dihydrophenazine (DHP, 500 mg, 2.72 mmol, 1eq) was dissolved in 5 mL anhydrous DMSO with a formation of a brown-orange solution. Under stirring, solid potassium *tert*-butoxide (KO'Bu,763 mg, 6.8 mmol, 2.5 eq) was added and a dark red solution formed. To this solution, solid fluorobenzonitrile (7.07 mmol, 2.6 eq) was added while stirring. The capped flask was removed from the glovebox and promptly connected to a reflux condenser under N₂, taking utmost care to avoid air exposure. The mixture was then heated for 5-17.5 h at 90 °C. After this, the reaction was cooled down to room temperature and poured into 100 mL of water under vigorous stirring, and brine was added if emulsion formation was observed. The precipitated solid was filtered using a filter paper and washed with water until neutral pH and ethanol until colorless filtrate, and then dried in vacuum to obtain the product.



DHP-diBN. DHP (2.058 g, 11.2 mmol), DMSO (19.5 mL), KO^tBu (3.141 g, 28 mmol), 4-fluorobenzonitrile (3.526 g, 29.1 mmol), were reacted according to the **GP-3** for 5 h. Brown-orange powder, 4.100 g (95 %). ¹H NMR (400 MHz, DMSO- d_6) δ 8.09 (d, 4H), 7.61 (d, 4H), 6.53 (dt, 4H), 5.90 (dt, 4H).



Tetra(**3**,**5**,**3**',**5**'-**Me**)**DHP-diBN.** DHP (1.658 g, 9 mmol), DMSO (17 mL), KO^tBu (2.524 g, 22.5 mmol), 4-fluoro-3,5-dimethylbenzonitrile (3.500 g, 23.5 mmol), were reacted according to the **GP-3** for 17.5 h. Yellow powder, 1.517 g (38 %).¹H NMR (400 MHz, DMSO-*d*₆) δ 7.89 (s, 4H), 6.30 (dt, 4H), 5.32 (dt, 4H), 2.32 (s, 12H).



DHP-tetraBN. DHP (2.000 g, 11.0 mmol), DMSO (20 mL), KO^tBu (3.079 g, 27.4 mmol), 5-fluoroisophthalonitrile (4.170 g, 28.5 mmoles), were reacted according to the **GP-3** for 14.5 h. Brown powder, 4.130 g (86.6 %). ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.62 (t, 2H), 8.40 (d, 4H), 6.50 (dt, 4H), 5.86 (dt, 4H).

Protocol for F to OH group substitution:



di(**2-OH**)**pip-diBN.** In a round bottom flask, solid **di**(**2-F**)-**pip-diBN** (10.0 g, 31.3 mmol, 1eq), solid NaOH (10.00 g, 250 mmol, 8 eq) and anhydrous DMA (63 mL) were refluxed for 18 hours under nitrogen atmosphere. The solvent was then removed using vacuum distillation. Water (700 mL) was added and the mixture was vigorously stirred

to dissolve most of the material. A small amount of solid impurity was removed via filtration and the solution was acidified with aqueous 37 % HCl (~25 mL) until pH ~1-2. The precipitated product was filtered, washed with water until neutral pH and air-dried. Brown solid, 8.935 g (89 %). ¹H NMR (400 MHz, DMSO- d_6) δ 10.66 (s, 2H), 7.36 (d, 2H), 6.51 (dd, 2H), 6.37 (d, 2H), 3.42 (s, 8H).

Synthesis of monosubstituted piperazine from aromatic amine:



5-pip-diCO₂Me·HCl Dimethyl 5-aminoisopthalate (54.1 g, 259 mmol), bis(2-chloroethyl)amine hydrochloride (44 g, 246 mmoles, 1 eq.) and p-toluenesulfonic acid monohydrate (2.12 g, 11.2 mmoles, 4.5 mol%) were refluxed in xylenes (450 mL) in a 1L round bottom flask. After 23 h, the reaction was cooled down to room

temperature. The solid was filtered on a glass frit using vacuum and washed copiously with acetone to give a powder, which was vacuum dried overnight. White powder, 62.7 g (81 %). ¹H NMR (400 MHz, DMSO- d_6) δ 9.57 (s, 2H), 7.93 (s, 1H), 7.72 (s, 2H), 3.87 (s, 6H), 3.51 (m, 4H), 3.21 (m, 4H).

General protocol for base-catalyzed nitrile hydrolysis (GP-4):

1.00 g of dinitrile was mixed with 5 mL 50 % aqueous solution of NaOH or KOH, 5 mL of propylene glycol (PG) or 2-methoxyethanol (MC), and, if noted, 5 mL of water. The mixture was heated to reflux (200 °C for PG, 135 °C for MC) for 16 h in a PTFE or PFA round bottom flask. Upon cooling down to room temperature, the mixture was diluted 5 times with water and further acidified using 37 % HCl until pH ~1-2. The obtained precipitate was filtered on a paper filter,

washed with water until pH 6-7, and further three times with ethanol until the filtrate became colorless. The product was vacuum dried overnight.



2CH₂-diCO₂H (H₂Sp5 diamine). 2CH₂-diBN (10.0 g, 38.12 mmol), 25 mL NaOH 50 %, 25 mL PG, 25 mL H₂O. White solid, 9.506 g (83 %). ¹H NMR (400 MHz, DMSO-*d***₆) δ 12.02 (s, 2H), 7.68 (d, 4H), 6.60 (d, 4H),**

6.51 (m, 2H), 3.30 (m, 4H).



3CH₂-diCO₂H. 3CH₂-diBN (1.00 g, 3.62 mmol), 5 mL KOH 50 %, 5 mL MC. White solid, 0.800 g (70 %). ¹H NMR (400 MHz, DMSO-*d*₆) δ

11.98 (s, 2H), 7.66 (d, 4H), 6.58 (d, 4H), 6.48 (s, 2H), 3.17 (m, 4H), 1.83 (p, 2H).



4CH₂-diCO₂H. 4CH₂-diBN (1.00 g, 3.44 mmol), 5 mL KOH 50 %, 5 mL MC. White solid, 1.115 g (99 %).¹H NMR (400 MHz, DMSO-*d*₆) δ 11.96 (s, 2H), 7.66 (d, 4H), 6.56 (d, 4H), 6.44 (m, 2H), 3.09 (m, 4H),

1.64 (m, 4H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 167.56, 152.65, 131.16, 116.71, 110.70, 42.09, 26.14.



6CH₂-diCO₂H. 6CH₂-diBN (1.05 g, 3.29 mmol), 5 mL KOH 50 %, 5 mL MC. Off-white solid, 1.070 g (91 %).¹H NMR (400 MHz, DMSO-*d*₆) δ 11.96 (s, 2H), 7.66 (d, 4H), 6.55 (d, 4H), 6.39 (s, 2H), 3.05 (t, 4H), 1.55 (p, 4H), 1.39 (m, 4H).¹³C NMR (101 MHz, DMSO-

*d*₆) δ 167.58, 152.71, 131.19, 116.58, 110.69, 42.32, 28.54, 26.49.



12CH₂-diCO₂H. 12CH₂-diBN (1.00 g, 2.48 mmol), 5 mL KOH 50 %, 5 mL MC. White solid, 1.010 g (92 %). ¹H NMR (400 MHz, DMSO- d_6) δ 11.95 (s, 2H), 7.65 (d, 4H), 6.54 (d, 4H), 6.39 (m, 2H), 3.03 (m, 4H), 1.52 (m, 4H), 1.27 (m, 16H).

pip-diCO₂H. pip-diBN (5.00 g, 17.34 mmol), 25 mL NaOH 50 %, 25 mL PG. Off-white solid, 5.659 g (98 %).¹H NMR (400 MHz, NaOD/D₂O) δ 7.73 (d, 4H), 6.89 (d, 4H), 3.11 (s, 8H).¹³C NMR (101 MHz, NaOD/D₂O) δ 175.14, 152.58, 130.52, 128.00, 115.87, 48.14.

(**S**)-**mepip-diCO₂H.** (**S**)-**mepip-diBN** (0.666 g, 2.205 mmol), 3.3 mL NaOH 50 %, 3.3 mL PG. Pale yellow solid, 0.618 g (77 %). ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.28 (s, 2H), 7.80 (d, 4H), 6.93 (dd, 4H), 4.23 (dt, 1H), 3.84 (dd, 1H), 3.78 (d, 1H), 3.67 (dt, 1H), 3.28 (m, 2H), 3.10 (ddd, 1H), 1.11 (d, 3H).

dimepip-diCO₂H. dimepip-diBN (7.500 g, 23.7 mmol), 35 mL NaOH 50 %, 35 mL PG. Off-white solid, 7.267 g (87 %).¹H NMR (400 MHz, DMSO-*d*₆) δ 12.23 (s, 2H), 7.79 (d, 4H), 6.96 (d, 4H), 4.28 (m, 2H), 3.60 (dd, 2H), 3.41 (dd, 2H), 1.10 (d, 6H). ¹³C NMR (101 MHz, DMSO) δ 167.30, 152.99, 131.07, 118.62, 112.84, 48.76, 45.41, 40.15, 39.94, 39.73, 39.52, 39.31, 39.10, 38.90, 12.91.

DHP-diCO₂H. DHP-diBN (3.00 g, 7.77 mmol), 15 mL NaOH 50 %, 15 mL PG. Brown solid, 3.111 g (95 %).



Tetra(3,5,3',5'-Me)DHP-diCO₂H. Tetra(3,5,3',5'-Me)DHP-diBN (0.500 g, 1.135 mmol), 2.5 mL NaOH 50 %, 2.5 mL PG. Yellow solid, 0.485 g (89 %).



di(2-OH)pip-diCO₂H. di(2-OH)pip-diBN (14.8 g, 46.3 mmol), 75 mL NaOH 50 %, 75 mL PG. Brown solid, 13.6 g (82 %). ¹H NMR (400 MHz, TFA+Chloroform-*d*) δ 8.15 (d, 2H), 7.10 (d, 2H), 7.03 (dd, 2H), 4.11 (s, 8H). ¹³C NMR (101 MHz, TFA+Chloroform-*d*) δ 175.06, 163.92, 150.28, 135.16, 111.43 (d), 108.78, 52.08. HRMS (ESI, negative mode): obs. 357.10960, calc. 357.10921[M-H]⁻

General protocol for acid-catalyzed nitrile hydrolysis (GP-5)

In a round bottom flask, to 1.5 mL H₂O, 1.5 mL 98 % H₂SO₄ was added under stirring at room temperature. To this, 1 mmol of dinitrile (or 0.5 mmol of tetranitrile) was added as a solid. The mixture was heated to 130 °C for 16 h on air under a reflux condenser. Upon cooling down to room temperature, the mixture was carefully diluted 5 times with water and further 50 % NaOH solution was added until pH ~3. The obtained precipitate was filtered on a paper filter, washed with water until pH 6-7, and further three times with ethanol until the filtrate became colorless. The product was vacuum dried overnight. The exact ratios of the components might vary and are specified for each compound below.



di(2-F)**dimepip-di**CO₂H. **di**(2-F)**dimepip-di**BN (2.818 g, 8 mmol), H₂O (6.4 mL), H₂SO₄ (18.1 mL). White solid, 1.557 g (50 %).¹H NMR (400 MHz, DMSO-*d*₆) δ 12.46 (s, 2H), 7.72 (t, 2H), 6.76 (m, 4H), 4.25 (tq, 2H), 3.62 (dd, 2H), 3.41 (dd, 2H), 1.10 (d, 6H).



di(3-NO₂)dimepip-diCO₂H. di(3-NO₂)dimepip-diBN (1.500 g, 3.69 mmol), H₂O (11 mL), H₂SO₄ (11 mL). Orange solid, 1.640 g (88 %).¹H NMR (400 MHz, TFA+Chloroform-*d*) δ 8.88 (d, 2H), 8.64 (dt, 2H), 8.04 (d, 2H), 4.27 (tq, 2H), 3.96 (dd, 2H), 3.68 (dd, 2H), 1.18 (d, 6H). ¹³C NMR (101 MHz, TFA+Chloroform-*d*) δ 169.59, 145.84, 141.99, 138.06, 132.10, 128.71, 126.65, 62.22, 60.38, 15.47.



di(**3-NO**₂)**pip-diCO**₂**H. di**(**3-NO**₂)**pip-diBN** (3.026 g, 8 mmol), H₂O (12 mL), H₂SO₄ (12 mL). Orange solid, 2.820 g (85 %).¹H NMR (400 MHz, TFA+Chloroform-*d*) δ 9.03 (d, 2H), 8.65 (dd, 2H), 7.97 (d, 2H), 4.11 (s, 8H). ¹³C NMR (101 MHz, TFA+Chloroform-*d*) δ 170.63, 144.97, 143.20, 139.27, 130.96, 130.79, 55.43.



pip-tetraCO₂H. pip-tetraBN (1.692 g, 5 mmol), H₂O (15 mL), H₂SO₄ (15 mL). White solid, 1.679 g (81 %). ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.18 (s, 4H), 7.94 (d, 2H), 7.73 (d, 4H), 3.41 (s, 8H).



DHP-tetraCO₂H. DHP-tetraBN (2.172 g, 5 mmol), H₂O (15 mL), H₂SO₄ (15 mL). Green-brown solid, 2.140 g (84 %). ¹H NMR (400 MHz, NaOD/D₂O) δ 8.32 (t, 2H), 7.85 (d, 4H), 6.20 (dd, 4H), 5.57 (dd, 4H). ¹³C NMR (NaOD/D₂O) δ 173.82, 139.89, 139.66, 135.98, 134.09, 128.96, 121.38, 112.94.

dimepip-tetraCO₂H. dimepip-tetraBN (0.285 g, 0.78 mmol), H₂O (3 mL), H₂SO₄ (3 mL). White solid, 0.264 g (77 %).¹H NMR (400 MHz, DMSO-*d*₆) δ 13.18 (m, 4H), 7.88 (s, 2H), 7.67 (s, 4H), 4.32 (m, 2H), 3.46 (m, 4H), 1.08 (d, 6H). ¹H NMR (400 MHz, TFA+CDCl₃) δ 7.99 (d, 4H), 7.95 (s, 2H), 4.19 (tq, 2H), 3.79 (dd, 2H), 3.66 (dd, 2H), 1.25 (d, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 147.64, 133.27, 129.99, 115.76, 115.52, 56.81, 56.39, 14.84.

Triangle ligand synthesis



Hexa-NO₂. In a nitrogen-filled glovebox, in a 250 mL 2-neck round bottom flask to a solid mixture of **5-pip-diCO**₂**Me**·**HCl** (9.44 g, 30 mmol, 6 eq) and potassium carbonate (8.29 g, 60 mmol, 12 eq), anhydrous DMA (50 mL) was added. To this slurry, under stirring, 1,3,5-trifluoro-2-nitrobenzene (585 μ L, 0.885 g, 5 mmol, 1 eq) was added. The mixture was connected to a reflux condenser under N₂

and heated to 125 °C for 92.5 h. The solvent was removed using vacuum distillation, and the residue was fully dissolved in 150 mL water. This solution was transferred to an HDPE bottle, and 50 % solution of sodium hydroxide (23.8 mL, 450 mmol, 120 eq) was added. After 20 h stirring at room temperature, the mixture had clear dark red color and contained no solid inside. The solution was neutralized with 50 mL 37 % HCl under vigorous overhead stirring and then filtered through a paper filter. The precipitate was then washed copiously with water and acetone, and

further air-dried to obtain the product as a brown-orange solid, 3.544 g (82 %). ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.94 (m, 3H), 7.70 (m, 6H), 6.67 (s, 2H), 3.50 (br, 6H), 3.39 (br, 6H), 3.31 (br, 6H), 3.13 (br, 6H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 206.54, 167.10, 152.52, 146.40, 135.94, 132.28 (d), 120.42, 119.53 (d), 103.30, 52.09, 48.44, 47.69, 47.09. HRMS (ESI, negative mode): obs. 866.26387, calc. 866.26454 [M-H]⁻

General protocol for Zr-based MOF single crystal growth

A zirconium chloride stock solution was prepared from 233 mg ZrCl₄ (1 mmol), 11.1 mL DMF and 88 μ L of 37 % HCl, it was sonicated 5 minutes and left aside. In a 8-mL vial, solid ligand (0.05 mmol) and modulator, either L-proline or 4-nitrobenzoic acid (0.25 mmol) were mixed. To this, 0.555 mL DMF was added and the mixture was sonicated for 5 minutes. Then, 0.555 mL of Zr stock solution was added and the mixture was sonicated again for 5 minutes. Afterwards, the capped vial was placed in a pre-heated oven at 100 °C for 48 hours. The vial was allowed to cool down naturally inside the oven.

Zr-dimepip. Dimepip-diCO₂H (17.7 mg), L-proline (28.8 mg). Colorless octahedral crystals.

Zr-(S)-mepip. (S)-mepip-diCO₂H (17.0 mg), L-proline (28.8 mg). Colorless octahedral crystals. **Zr-di(2-F)-dimepip.** Di-(2F)-dimepip-diCO₂H (19.5 mg), L-proline (28.8 mg). Colorless octahedral crystals suitable for synchrotron SCXRD.

Zr-di(3-NO₂)-dimepip. Di-(3-NO₂)-dimepip-diCO₂H (22.2 mg), 4-nitrobenzoic acid (41.8 mg). Yellow octahedral crystals.

Zr-di(3-NO₂)-pip. Di-(3-NO₂)-pip-diCO₂H (20.8 mg), L-proline (28.8 mg). Yellow octahedral crystals.

Zr-DHP. DHP-diCO₂H (21.1 mg), 4-nitrobenzoic acid (41.8 mg). Orange truncated octahedral crystals.

General protocol for Zr MOF synthesis for adsorption measurements

A zirconium chloride stock solution was prepared from 582 mg ZrCl_4 (2.5 mmol), 27.76 mL DMF and 222 μ L of 37 % HCl, it was sonicated 5 minutes and left aside. In a 100 mL Schott bottle, solid

ligand (0.625 mmol, 1 eq) and, if noted, modulator, either L-proline or 4-nitrobenzoic acid (3.125 mmol, 5eq) were mixed. To this, 6.94 mL DMF was added and the mixture was sonicated for 5 minutes. Then, 6.94 mL of Zr stock solution was added and the mixture was sonicated again for 5 minutes. Afterward, the closed bottle was placed in a pre-heated oven at 100 °C for 48 hours. The bottle was allowed to cool down naturally inside the oven. The sample was recovered from the bottle and washed with fresh DMF 3 times using a centrifuge, including a soaking step in fresh DMF for at least 20 minutes each time. Materials were kept under DMF prior to activation.

Activation protocol using DCM/hexanes Soxhlet (AP-1)

The DMF-exchanged MOFs were placed in Whatman® cellulose Soxhlet thimbles, and the thimbles were soaked in dichloromethane (DCM) for 20 minutes. This was repeated three times with fresh DCM, after which the thimbles were loaded in a Soxhlet extractor and extracted with DCM for 18 hours. Then, the thimbles were placed in hexanes and soaked for 20 minutes. This was also repeated three times with fresh hexanes and then the thimbles were loaded into a Soxhlet extractor and extracted with hexanes for 18 hours. Then, the thimbles for 18 hours. Then, the thimbles were placed in hexanes and soaked for 20 minutes. This was also repeated three times with fresh hexanes and then the thimbles were loaded into a Soxhlet extractor and extracted with hexanes for 18 hours. Then, the fully exchanged MOFs were transferred under hexanes in 20 mL vials equipped with septum caps. The liquid hexanes were removed by blowing an Ar gas flow for 2-3 hours. The pre-dried samples were transferred in a nitrogen-filled glovebox and loaded in adsorption tubes, and finally activated at 40 °C in vacuum for 16 hours before the adsorption measurements.

Activation protocol using acetone Soxhlet (AP-2)

A DMF-exchanged MOF sample was washed with acetone 3 times using a centrifuge including a soaking step in fresh acetone for at least 20 minutes each time. The sample was loaded into a Soxhlet thimble under acetone and extracted with acetone for 18 hours. Afterward, the sample was vacuum dried at room temperature, loaded into an adsorption tube and activated at 40 °C in vacuum for 16 h before the adsorption measurements.

Zr-dimepip. **Dimepip-diCO₂H** (222 mg), L-proline (359.8 mg). Colorless octahedral crystals, ~200 mg (~70 %). **AP-1**.

Zr-di(3-NO₂)-dimepip. Di-(3-NO₂)-dimepip-diCO₂H (278 mg). No modulator. Yellow powder, ~250 mg (~72 %). **AP-1**.

Zr-DHP. DHP-diCO₂H (264 mg), L-proline (359.8 mg). Orange octahedral crystals, ~220 mg (~66 %). **AP-1.**

Zr-Tetra(3,5,3',5'-Me)**DHP.** Tetra(3,5,3',5'-Me)**DHP-diCO**₂**H** (299 mg). No modulator. Yellow-orange powder, ~240 mg (~65 %). **AP-2.**

Synthesis of Cu-based MOFs and MOF-74/CPO-27 analogues

Cu-tetra-dimepip. A stock solution was prepared by combining 811 mg Cu(NO₃)₂·3H₂O, 32 mL DMF and 16 mL H₂O. In a 100 mL Schott bottle, to 106.2 mg of **dimepip-tetraCO₂H** (0.240 mmol) 16 mL of this stock solution was added, followed by 360 μ L of 50 % HBF₄. The capped bottle containing a transparent solution was placed in an oven and subjected to the following temperature program: heating to 75 °C at 1 °C/min, hold 24 h at 75 °C, cooling down to 25 °C at 0.1 °C/min. The sample was recovered from the bottle and washed with fresh DMF 3 times using a centrifuge, including a soaking step in fresh DMF for at least 20 minutes each time. The same washing was repeated with acetone, and then the sample was vacuum dried and activated at 100 °C in vacuum for 12h before adsorption measurements. Yield ~100 mg (~74 %).

Cu-DHP. A stock solution was prepared by combining 2.4345 g of Cu(NO₃)₂·3H₂O, 96 mL DMF, 48 mL H₂O and 2.160 mL 50 % HBF₄. In a 16 mL vial, to 40.8 mg of **DHP-tetraCO₂H** (0.08 mmol), 4 mL of the stock solution was added. This was repeated for a total of 6 vials. The capped vials containing transparent solutions were placed in an oven and subjected to the following temperature program: heating to 75 °C at 1 °C/min, hold 24 h at 75 °C, cooling down to 25 °C at 0.1 °C/min. The samples were recovered from the vials, combined and washed with fresh DMF 3 times using a centrifuge, including a soaking step in fresh DMF for at least 20 minutes each time. The same washing was repeated with acetone, and then the sample was vacuum dried and activated at 100 °C in vacuum for 12h before adsorption measurements. Yield ~200 mg (66 %).

Cu-hexa-NO₂. A stock solution was prepared by combining 679.5mg of Cu(NO₃)₂·3H₂O, 50 mL DMF and 25 mL H₂O. 283.12 mg **hexa-NO₂** (162.6 mg, 0.187 mmol) was placed in a 250 mL

Schott bottle. To this, 31.25 mL of the stock solution was added, followed by 937.5 μ L 50 % HBF4. The mixture was sonicated for 10 minutes. The capped bottle containing a transparent solution was placed in an oven and subjected to the following temperature program: heating to 75 °C at 1 °C/min, hold 24 h at 75 °C, cooling down to 25 °C at 0.1 °C/min. The solid was recovered from the bottle and washed with fresh DMF 3 times using a centrifuge, including a soaking step in fresh DMF for at least 20 minutes each time, and further activated using **AP-1**. Green-brown solid under DMF, black solid after activation, 90 mg (45 %).

Synthesis of MOF-74/CPO-27 analogues

Zn-di(2-OH)pip. di(2-OH)pip-diCO₂H (179 mg, 0.5 mmol, 1 eq) was dissolved in 6.62 mL of H₂O with addition of 126 mg of 50 % NaOH solution (63 mg, 1.58 mmol, 3.15 eq). This solution was kept stirring at 1500 rpm in a 40 mL glass vial. $Zn(OAc)_2 \cdot 2H_2O$ (247 mg, 1.13 mmol, 2.25 eq) is dissolved separately in 6.62 mL of H₂O. Zinc solution was added dropwise to the ligand solution under stirring, and the formation of a precipitate was observed. The mixture was kept stirring for 20 hours at room temperature, and then it was subjected to centrifugation. The supernatant was discarded and the solid was washed with fresh water 3 times using a centrifuge, including a soaking step in fresh water for at least 20 minutes each time. The same was repeated with methanol and then acetone. Finally, the sample was vacuum dried at room temperature, loaded into an adsorption tube, and activated at 130 °C in vacuum during 16 hours.

Co- and **Ni-di(2-OH)pip.** Co(OAc)₂·4H₂O or Ni(OAc)₂·4H₂O (93.3 mg, 0.375 mmol, 2 eq) was dissolved in 2.5 mL H₂O in a 20 mL Teflon liner of a stainless steel autoclave. **di(2-OH)pip-diCO₂H** (67.2mg, 0.188 mmol, 1 eq) was dispersed in 2.5 mL THF using ultrasound. The THF slurry of the ligand was carefully layered on the aqueous metal solution and the mixture was sealed inside the autoclave. The autoclaves were heated in an oven at 110 °C for 3 days and cooled down to room temperature naturally inside the oven. The solid products were separated using centrifugation and washed with fresh water 3 times using a centrifuge, including a soaking step in fresh water for at least 20 minutes each time. The same was repeated with methanol and then acetone. Finally, the samples were vacuum dried at room temperature, loaded into adsorption tubes, and activated at 130 °C in vacuum during 16 hours.

Chapter 5. Conclusions and future outlook

In this thesis, we focused on investigating MOFs based on new N-heterocyclic ligands. We studied how ligand structure and function influence the properties of the final materials, paying detailed attention to understanding the underlying chemical processes. After exploring the general MOF and ligand design concepts in Chapter 1, in Chapter 2, we show how a new saturated NHC ligand **H₂Sp5-BF₄** gives rise to a copper MOF **Cu-Sp5**. We illustrate that due to a combination of open metal sites and charged species present inside the pore, the material obtains one of the highest CO₂/N₂ adsorption selectivities in flue gas conditions reported to date. We shed light on detailed material structure and performance using SCXRD, *in situ* FTIR, and gas adsorption measurements. Future works in this direction can be performed optimizing the pore shape and geometry, as well as charge distribution, to obtain even higher selectivities coupled with the stability and cyclability of the material.

Chapter 3 reports how by a simple change of copper salt anion during **Cu-Sp5** synthesis, a new copper MOF Cu-Sp5-BF₄ can be formed. We show that this MOF features more than two times larger pore size and surface area compared to **Cu-Sp5**, owing to the bulk of BF₄⁻ anion that prevents interpenetration and leads to a different, more porous structure. We further for the first time access N-heterocyclic carbene chemistry in this MOF via ligand post-synthetic modification using sodium methoxide, with the formation of methoxide adducts and removal of BF4⁻ from the pore. We then reveal how this process alters the dimensionality of the material with a formation of a new turbostratic phase. Next, we illustrate how this structural transformation improves the accessibility of NHC sites for a second-step iridium grafting with the formation of cyclometalated iridium complexes. We study iridium speciation in detail using EXAFS and XPS methods, and we show how it evolves during the catalytic reaction of stilbene hydrogenation. We believe next studies on this topic can focus on varying the nature of anion in the pore and appending different transition metal complexes on NHC sites for a plethora of catalytic applications. Further, it seems promising to completely exfoliate the layered Cu-Sp5-BF₄ structure with the formation of ligandthin 2D MOF layers with NHC functionality, for applications such as gas-phase catalysis or membrane separations.

Chapter 4 illustrates a new approach for ligand synthesis that we discovered during our NHC-MOF work. We show the development of a new concept in ligand design that we call LigX, by

substitution of benzene rings with piperazine rings. Using the LigX approach, we simplify mesoporous MOF ligand synthesis by avoiding time- and cost-intensive Pd-based chemistry. We show facile and high-yield synthesis of 14 organic ligands for the construction of various types of metal-organic frameworks. We further show accessible porosity for nine new MOFs built with these ligands and zirconium, zinc, cobalt, nickel, and copper. We see vast potential in this methodology as the possible combinations of piperazine and nitrile blocks are enormous, thus giving rise to easy synthesis of a host of new ligands for MOF construction from various families. Further, new and longer piperazine-based blocks can be designed to produce even larger ligands that can form MOFs with pores in multi-nanometer size. As all of these ligand syntheses are easily scalable and don't require precious metals, we envision a commercial interest in the materials and we will submit a patent application based on our developments in the near future. We firmly believe LigX methodology will change the approach on how the mesoporous MOF ligands are designed and will facilitate their studies and development in the years to come.

Chapter 6. Appendices

6.1. Experimental data and tables, comparison of materials for CO₂ capture, detailed calculation description for Chapter 2



Figure S1. ¹H NMR spectrum of the ligand H₂Sp5-BF₄.



Figure S2. ¹³C NMR spectrum of the ligand H₂Sp5-BF₄.



Figure S3. ¹⁹F NMR spectrum of the ligand H₂Sp5-BF₄.



Figure S4. ¹¹B NMR spectrum of the ligand H₂Sp5-BF₄.

102

19F



Figure S5. ¹H-¹³C HSQC NMR spectrum of the ligand H₂Sp5-BF₄.



Figure S6. ^{1}H - ^{1}H COSY NMR spectrum of the ligand $H_{2}Sp5$ -BF₄.







Figure S8. Theoretical (below) and experimental (above) HRMS spectra of the ligand $H_2Sp5-BF_4$.



Figure S9.Light microscope image of Cu-Sp5 single crystals. Scale bar (in red): 200 μ m

	Cu-Sp5-EtOH	Cu-Sp5-EtOH	Cu-Sp5-MeOH
Formula	C19H19CuN3O8	$C_{19}H_{19}CuN_3O_8$	C17H13CuN3O8.88
Molecular weight	480.91	480.91	464.84
T, K	100(2)	293(2)	100(2)
λ, Å	0.71073	0.67522	0.71073
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	Pbca	Pbca	Pbca
a, Å	17.7049(15)	17.8332(4)	16.610(4)
b, Å	9.2515(9)	9.26780(10)	8.957(2)
c, Å	24.5663(19)	24.5582(2)	25.681(6)
α, °	90	90	90
β, °	90	90	90
γ, °	90	90	90
$V, Å^3$	4023.9(6)	4058.84(11)	3820.7(15)
Z	8	8	8
$D_{calc}, g/cm^3$	1.588	1.571	1.616
μ, mm ⁻¹	1.14	0.99	1.20
Absorption correction	Multi-scan	Multi-scan	Multi-scan
F 000	1976	1968	1888
θ range for data collection,	2.3–23.3	1.6-25.5	2.7-24.9
0			
index ranges	$-19 \le h \le 19$	$-13 \le h \le 13$	$-15 \le h \le 15$
	$-10 \le k \le 10$	$-11 \le k \le 11$	$-8 \le k \le 8$
	$-27 \le k \le 27$	$-30 \le k \le 30$	$-23 \le k \le 23$
Reflections collected	23222	17084	23016

Table S1. Crystallographic data for Cu-Sp5-EtOH and Cu-Sp5-MeOH

Independent reflections (R _{int})	2890 (0.100)	3204 (0.020)	1494 (0.149)
reflections with $I > 2\sigma(I)$	2188	3014	1142
data/restraints/parameters	2890/19/284	3204/4/284	1494/0/212
S	1.06	1.08	1.20
R [($F^2 > 2\sigma(F^2)$]	$R_1 = 0.065$	$R_1 = 0.069$	$R_1 = 0.087$
	$wR_2 = 0.1494$	$wR_2 = 0.192$	$wR_2 = 0.183$
R (all data)	$R_1 = 0.091$	$R_1 = 0.071$	$R_1 = 0.118$
	$wR_2 = 0.163$	$wR_2 = 0.195$	$wR_2 = 0.202$
weighting Scheme [*] , x/y	0.0556/24.6838	0.1107/8.3969	0/73.2275
largest diff. peak and hole, $e/Å^3$	1.08 and -0.63	0.83 and -0.73	0.52 and -0.38

* $w = 1/[\sigma^2(F_0^2) + (xP)^2 + yP]$, where $P = (F_0^2 + 2F_c^2)/3$



Figure S10. A thermal ellipsoid plot of the asymmetric unit of **Cu-Sp5** structure obtained at 293 K. Nitrate anion is clearly positioned. Hydrogen atoms are omitted for clarity.



Figure S11.The space-filling model of **Cu-Sp5-EtOH** structure. View along *b* axis. Highlighted is a single channel in the structure.



Figure S12. TGA curve for Cu-Sp5 in air. Heating rate: 5 °C/min.



Figure S13. TGA curve for Cu-Sp5 in a nitrogen atmosphere with the following program: 5 °C/min until 230 °C, hold at 230 °C. The abscissa represents time in minutes.



Figure S14. Powder pattern of the final product after Cu-Sp5 treatment at 230 °C in a nitrogen atmosphere. The feature below 10 ° is due to the sample holder specifics.



Figure S15. Powder pattern of the final product after **Cu-Sp5** thermal decomposition in air. The broad peaks arise from the sample holder, while all the narrow peaks correspond to the copper (II) oxide.


Figure S16. Light microscope images indicating the change in crystal size of **Cu-Sp5** upon methanol soaking



Figure S17. Light microscope image of $\mbox{Cu-Sp5-MeOH}.$ Scale bar (in red): 20 μm



Figure S18. TGA curve for Cu-Sp5-MeOH in air. Heating rate: 5 °C/min.

Isosteric heat of adsorption calculation

The calculation was performed via a custom-written Matlab script. Isotherms for a particular gas were fitted using double-site Langmuir model. Then, for each loading point, the pressure was extracted from the fits and the isosteric heat of adsorption was calculated via Clausius-Clapeyron equation:

$$-Q_{st} = R \frac{\partial lnP}{\partial \left(\frac{1}{T}\right)}$$

Where $\frac{\partial \ln P}{\partial \left(\frac{1}{T}\right)}$ was extracted from a linear fit of lnP vs. 1/T.

IAST calculations

The calculations were performed using pyIAST software⁹³. Each isotherm was fitted with a double-site Langmuir model and the IAST calculation was performed for 15 % CO₂/ 85 % N_2 mixture at 1 bar.



Figure S19. Isosteric heat of N₂ adsorption for Cu-Sp5-MeOH.

MOF	Functional sites ^e	BET	mmol/g(wt	Sf	Т	-Q _{st}	Refer
		(m ² /g)	%)at 0.15			(kJ/	ence
			bar (CO ₂)			mol)	
	0.147	1000	5.87			10	80
Mg-MOF-74	OMS	1800	(25.83)	44.4	303	42	80
Ni-MOF-74	OMS	1312	3.84 (16.9)	30	298	42	80
CuBTTri	OMS	1770	0.69 (3.08)	18.4	298	24	80
en-CuBTTri	OMS/LBS	345	0.51 (2.24)	42.5	298	86.7	80
CG-9	OMS + GO	1532	2.09(9.2)	31.3	273	_	80
$[NH_2(CH_3)_2][Zn_3(bta)(btc)_2]^a$	OMS	697	1.37(6.03)	84.9	273	_	80
FeBTT	OMS	2010	1.19(5.24)	16.9	298	_	80
$[NH_2(CH_3)_2]_2[Cd_3(bta)(btc)_2]_2$	OMS	508	1.14(5.02)	23	273	_	80
Cu-btc	OMS	1400	1.04(4.56)	34.4	293	25.9	80
PCN-88	OMS	3308	0.69(3.04)	29.8	296	27	80
MIL-101	OMS	3125.4	0.32(1.41)	11.43	298	44	80
				15(IAS			96
$[(CH_3)_2NH_2]_2[Tb_6(\mu^3 - \mu)]$	OMS + 10n pairs + E + N + OH	1000	1 25(5 (1)	1,10	200	50 1	
$[Zn_3L_2(HCOO)_1][(CH_3)_2NH_2]$	$\mathbf{F} + \mathbf{N} + \mathbf{OH}$	1220	1.35(3.01)	$%CO_2)$ 24	298	38.1	97
1.5·xDMF ^c	Ion pairs	569.5	1.12(4.70)	(IAST)	273	_	
[Zn ₂ (L)(bpb) ₂](NO ₃)(DMF) ₃ (*						98
$H_2O)_4^d$	Ion pairs	425	0.89(3.77)	181	273	23.5	
				207 (LAST)			Thia
Cu Sp5 MoOH	OMS ion pairs	204	0.64(2.73)	(IAST) 80	208	13 1	1 fils work
Cu-Sp3-MCOII		204	0.04(2.73)	253	290	-13.1	WUIK
				(IAST)			This
Cu-Sp5-MeOH	OMS + ion pairs	204	1.10(4.60)	80	278	43.1	work

Table S2. Overview of metal-organic frameworks for CO2 separation

^a bta = benzotriazolate, btc = 1,3,5-benzenetricarboxylate

^b $H_2FTZB = 2$ -fluoro-4-(1H-tetrazol-5- yl)benzoic acid

^c $H_3L = 9-(4-\text{carboxy-phenyl})-9H-\text{carbazole}-3,6-\text{dicarboxylic acid}$

^d $H_4L^+Cl^- = 1,3$ -Bis(3,5-dicarboxyphenyl)imidazolium chloride, bpb = 1,4-bis(4-pyridyl)benzene

e OMS = open metal site, LBS = Lewis basic site, GO = graphene oxide, F = fluorine atoms, N = uncoordinated tetrazole atoms, OH = hydroxy ions

^f Unless otherwise mentioned, $S = [q(CO_2)/q(N_2)]:[p(CO_2)/p(N_2)]$ where q are loadings for $p(CO_2) = 0.15$ bar, $p(N_2) = 0.85$ bar from single component isotherm data

Table 55. Thysicoenemical properties of CO2 and N2 molecules					
Molecule	Normal boiling point (K)	Kinetic diameter, Å	Quadrupole moment, 10^{-27} esu ⁻¹ cm ⁻¹	Dipole moment, 10^{-27} esu ⁻¹	Polarizability, 10 ⁻²⁵ cm ³
CO ₂	194.65*	3.3	43.0	0	29.1
N ₂	77.35	3.64	15.2	0	17.4
* 11'					

Table S3. Physicochemical properties of CO₂ and N₂ molecules⁹⁴

*sublimes

6.2. Experimental data and tables for Chapter 3

Material	Cu-Sp5-BF4-EtOH	Cu-Sp5-BF ₄ -A
Empirical formula	$C_{19}H_{14}BCuF_{4}N_{2}O_{5}$	C17H13BCuF4N2O4
Formula weight	500.67	459.64
Temperature/K	100(2)	99.99
Crystal system	monoclinic	monoclinic
Space group	P21/n	P21/c
a/Å	6.6391(5)	14.932(3)
b/Å	33.5424(9)	31.562(5)
c/Å	11.4021(9)	14.861(3)
$\alpha/^{\circ}$	90	90
β/°	106.155(8)	98.450(6)
γ/°	90	90
Volume/Å ³	2438.9(3)	6928(2)
Z	4	12
$\rho_{calc}g/cm^3$	1.364	1.322
μ/mm^{-1}	0.873	0.999
F(000)	1008.0	2772.0
Crystal size/mm ³	0.15 imes 0.03 imes 0.03	0.1 imes 0.02 imes 0.02
Radiation	synchrotron ($\lambda = 0.6866$)	MoKα ($\lambda = 0.71073$)
2Θ range for data collection.	^{/°} 3.78 to 65.1	1.29 to 46.848
Index ranges	$-6 \le h \le 6, -51 \le k \le 51, -17 \le l \le 17$	$7 - 16 \le h \le 16, -35 \le k \le 35, -15 \le l \le 16$
Reflections collected	22331	79663
Independent reflections	5858 [$R_{int} = 0.2689, R_{sigma} = 0.1810$	9973 [R _{int} = 0.1906, R _{sigma} = 0.1227]
Data/restraints/parameters	5858/3/345	9973/459/495
Goodness-of-fit on F ²	1.047	1.488
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0779, wR_2 = 0.2260$	$R_1 = 0.1261, wR_2 = 0.3637$
Final R indexes [all data]	$R_1 = 0.0882, wR_2 = 0.2403$	$R_1 = 0.2099, wR_2 = 0.4251$
Largest diff. peak/hole / e Å	-3 1.65/-1.54	1.86/-1.51

Table S4. Crystallographic data for Cu-Sp5-BF4-EtOH and Cu-Sp5-BF4-A



Figure S20. PXRD data for Cu-Sp5-BF4-EtOH



Figure S21. TGA curve for Cu-Sp5-BF4-EtOH (air, 5 °C/min)



Figure S22. Comparison of PXRD patterns for Cu-Sp5-BF4-EtOH and Cu-Sp5-BF4-A



Figure S23. Structural evolution during **Cu-Sp5-BF4-EtOH** activation as viewed along *c* axis. Note the change from an infinitely interlinked structure via rod SBU to a stacked paddlewheelbased layer structure. The number of Cu atoms along *a* axis is the same in both pictures. Hydrogen atoms are omitted for clarity



Figure S24. In situ PXRD data for Cu-Sp5-BF₄ activation



Figure S25. Synchrotron PXRD data for Cu-Sp5-BF₄-A



Figure S26. In situ DRIFTS spectra of (a) ${\bf Cu-Sp5-BF_4.A}$ and (b) ${\bf Cu-Sp5}$ upon CO dosage at 150 K



Figure S27. Gas adsorption isotherms (CO₂, 195 K and N₂, 77 K) for **Cu-Sp5-BF₄-A.** Closed symbols represent adsorption, open symbols represent desorption



Figure S28. (a) Gas adsorption isotherms of CO₂ (top) and N₂ (bottom) for **Cu-Sp5-BF_{4-A}** at 283 K, 298 K, and 313 K (b) Isosteric heat of adsorption of CO₂ for **Cu-Sp5-BF_{4-A}**



Figure S29. Solid-state ¹³C MAS of Cu-Sp5-BF₄-A (bottom) and Cu-Sp5-OMe (top)



Figure S30. PXRD of Cu-Sp5-OMe and Cu-Sp5-BF4-A



Figure S31. Light microscope image of **Cu-Sp5-OMe** particles



Figure S32. A photo of **Cu-Sp5-BF**₄ crystal mounted on the goniometer, after unit cell indexing and crystal orientation determination



Figure S33. Gas adsorption isotherms of Cu-Sp5-OMe and Cu-Sp5-BF4-A



Figure S34. TEM images of Ir/Cu-Sp5-OMe



Figure S35. XPS spectrum of Ir/Cu-Sp5-OMe

EXAFS fitting details for Ir/Cu-Sp5-OMe before catalysis:

Amplitude reduction factor (S_0^2) was refined from iridium foil and set to 0.70059.

Goodness of fit parameters:

7882647

R-factor : 0.0184169

Guess parameters:

CN	= 2.62190069 # +/- 0.32231375	[2.62230]
enot	= 9.01793387 #+/- 1.38944859	[9.00967]
delr	= 0.07917294 #+/- 0.07671292	[0.07825]
SS	= 0.00393344 #+/- 0.00205075	[0.00390]
delr1	= -0.07807711 # +/- 0.07752226	[-0.07711]



Figure S36. PXRD of Ir/Cu-Sp5-OMe compared to those of Cu-Sp5-OMe and Cu-Sp5-BF₄-A



Figure S37. HAADF-STEM images of Ir/Cu-Sp5-OMe



Figure S38. Split test results for Ir/Cu-Sp5-BF4 (Ir/MOF) and Ir/Cu-Sp5-OMe (Ir/MOF-OMe)



Figure S40. (a) Real space EXAFS spectra of Ir/Cu-Sp5-OMe before and after catalysis (b)

0.2

0.0

Real space EXAFS spectrum of iridium foil.



Figure S41. HAADF-STEM images of Ir/Cu-Sp5-OMe sample after catalytic cycle

0.0





210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fi(ppm)

Figure S43. ¹³C NMR spectrum of **2CH₂-diBN**



Figure S45. ¹H NMR spectrum of **4CH₂-diBN**



Figure S47. ¹³C NMR spectrum of **6CH₂-diBN**



Figure S48. ¹H NMR spectrum of **12CH₂-diBN**



Figure S49. ¹H NMR spectrum of **2CH₂-diCO₂H**



Figure S50. ¹H NMR spectrum of **3CH₂-diCO₂H**



Figure S51. ¹H NMR spectrum of **4CH₂-diCO₂H**



Figure S53. ¹H NMR spectrum of **6CH₂-diCO₂H**



Figure S54. ¹³C NMR spectrum of **6CH₂-diCO₂H**



Figure S55. ¹H NMR spectrum of **12CH₂-diCO₂H**



Figure S56. ¹H NMR spectrum of **pip-diBN**



Figure S57. ¹H NMR spectrum of (S)-mepip-diBN



Figure S58. ¹H NMR spectrum of **dimepip-diBN**



Figure S59. ¹H NMR spectrum of **di(2-F)pip-diBN**



Figure S61. ¹H NMR spectrum of **di(2-F)dimepip-diBN**



Figure S62. ¹H NMR spectrum of di(3-NO₂)pip-diBN



Figure S63. ¹H NMR spectrum of di(3-NO₂)dimepip-diBN



Figure S64. ¹³C NMR spectrum of di(3-NO₂)dimepip-diBN



Figure S65. ¹H NMR spectrum of **pip-tetraBN**



Figure S66. ¹H NMR spectrum of **dimepip-tetraBN**



Figure S67. ¹³C NMR spectrum of **dimepip-tetraBN**



Figure S68. ¹H NMR spectrum of **DHP-diBN**



Figure S69. ¹H NMR spectrum of Tetra(3,5,3',5'-Me)DHP-diBN



Figure S70. ¹H NMR spectrum of **DHP-tetraBN**



Figure S71. ¹H NMR spectrum of **di(2-OH)pip-diBN**



Figure S73. ¹H NMR spectrum of **pip-diCO₂H**



Figure S74. ¹³C NMR spectrum of **pip-diCO₂H**



Figure S75. ¹H NMR spectrum of (S)-mepip-diCO₂H



Figure S76. ¹H NMR spectrum of **dimepip-diCO₂H**



Figure S77. ¹³C NMR spectrum of **dimepip-diCO₂H**



Figure S78. ¹H NMR spectrum of di-(2-F)-dimepip-diCO₂H



Figure S79. ¹H NMR spectrum of **pip-tetraCO₂H**



Figure S80. ¹H NMR spectrum of **dimepip-tetraCO₂H**






Figure S82. ¹³C NMR spectrum of **DHP-tetraCO₂H**



Figure S83. ¹H NMR spectrum of di-(3-NO₂)pip-diCO₂H



Figure S84. ¹³C NMR spectrum of **di-(3-NO₂)pip-diCO₂H**



Figure S85. ¹H NMR spectrum of di-(3-NO₂)dimepip-diCO₂H



Figure S86. ¹³C NMR spectrum of di-(3-NO₂)dimepip-diCO₂H



Figure S87. ¹H NMR spectrum of **di-(2-OH)pip-diCO₂H**



Figure S88. ¹³C NMR spectrum of di-(2-OH)pip-diCO₂H



Figure S89. ¹H NMR spectrum of hexa-NO₂



Figure S90. ¹³C NMR spectrum of hexa-NO₂



Figure S91. ¹H-¹³C edited HSQC spectrum of hexa-NO₂



Figure S92. ESI-HRMS (negative mode) spectrum of hexa-NO₂



Figure S93. ESI-HRMS (negative mode) spectrum of di-(2-OH)pip-diCO₂H

Name	Dimepip-diBN	DHP-diCO ₂ H	Zr-(2-F)-dimepip
Empirical formula	$C_{20}H_{20}N_4$	$C_{34}H_{42}N_2O_8S_4$	$C_{120}H_{84}F_{10}N_{12}O_{32}Zr_6$
Formula weight	316.40	734.93	2946.77
Temperature/K	140.00(10)	140.00(10)	293(2)
Crystal system	monoclinic	triclinic	cubic
Space group	$P2_{1}/c$	P-1	Fm-3m
a/Å	9.8480(2)	7.7166(3)	32.8315(3)
b/Å	12.1022(3)	8.9901(2)	32.8315(3)
c/Å	7.1084(2)	14.0706(5)	32.8315(3)
a/°	90	78.744(2)	90
β/°	104.901(2)	75.080(3)	90
$\gamma/^{\circ}$	90	75.423(2)	90
Volume/Å ³	818.71(4)	903.93(5)	35389.3(10)
Z	2	1	4
$\rho_{calc}g/cm^3$	1.283	1.350	0.553
μ/mm^{-1}	0.611	2.848	0.219
F(000)	336.0	388.0	5902.0
Crystal size/mm ³	$0.150\times0.100\times0.070$	$0.347 \times 0.202 \times 0.07$	$0.05 \times 0.05 \times 0.05$
Radiation	CuKa ($\lambda = 1.54184$)	CuKa ($\lambda = 1.54184$)	synchrotron ($\lambda = 0.73074$)
2Θ range for data collection/	9.292 to 151.368	6.566 to 152.25	3.608 to 52.436
Index ranges	$-12 \le h \le 11, -14 \le k \le 15, -7 \le 1 \le 8$	$\begin{array}{l} -9 \leq h \leq 9, -11 \leq k \leq \\ 7, -17 \leq l \leq 17 \end{array}$	$\begin{array}{l} -39 \leq h \leq 39, -39 \leq k \\ \leq 39, -28 \leq l \leq 28 \end{array}$
Reflections collected	7598	8413	27320
Independent reflections	$1694 \ [R_{int} = 0.0205, R_{sigma} = 0.0155]$	$3720 [R_{int} = 0.0202, R_{sigma} = 0.0238]$	$1625 [R_{int} = 0.2254, R_{sigma} = 0.0964]$
Data/restraints/parameters	1694/0/110	3720/0/223	1625/44/60
Goodness-of-fit on F ²	1.062	1.028	0.989
Final R indexes [I>= 2σ (I)]	$\begin{array}{l} R_1 = 0.0349, wR_2 = \\ 0.0926 \end{array}$	$R_1 = 0.0338, wR_2 = 0.0883$	$R_1 = 0.0678, wR_2 = 0.1811$
Final R indexes [all data]	$R_1 = 0.0375, wR_2 = 0.0946$	$R_1 = 0.0368, wR_2 = 0.0903$	$R_1 = 0.0864, wR_2 = 0.1901$
Largest diff. peak/hole / e Å ⁻³	0.23/-0.19	0.35/-0.28	0.94/-0.91

Table S5. Crystallographic data for ligands and MOFs

Name	Zr-DHP	Cu-tetra-dimepip	Cu-tetra-DHP
Empirical formula	C78H48N6O16Zr 3	$C_{22}H_6Cu_2N_2O_8$	C14H7CuNO5
Formula weight	3197.76	553.37	332.75
Temperature/K	293(2)	140.01(10)	140.00(10)
Crystal system	cubic	trigonal	trigonal
Space group	Fm-3m	R-3m	R-3m
a/Å	32.5636(2)	18.7045(2)	18.6305(7)
b/Å	32.5636(2)	18.7045(2)	18.6305(7)
c/Å	32.5636(2)	37.8061(4)	37.8246(12)
$\alpha/^{\circ}$	90	90	90
β/°	90	90	90
$\gamma/^{\circ}$	90	120	120
Volume/Å ³	34530.0(6)	11454.7(3)	11369.8(9)
Z	8	9	18
$\rho_{calc}g/cm^3$	1.230	0.722	0.875
μ/mm^{-1}	0.448	1.234	1.334
F(000)	12896.0	2466.0	3006.0
Crystal size/mm ³	0.1 imes 0.1 imes 0.1	$0.086 \times 0.071 \times 0.061$	$0.160 \times 0.150 \times 0.070$
Radiation	synchrotron (λ = 0.73074)	$CuK\alpha$ ($\lambda = 1.54184$)	$CuK\alpha$ ($\lambda = 1.54184$)
2Θ range for data collection/°	3.638 to 52.394	5.936 to 145.614	7.01 to 145.27
Index ranges	$\begin{array}{l} -38 \leq h \leq 38, - \\ 38 \leq k \leq 38, -32 \\ \leq l \leq 32 \end{array}$	$h \le 21, -23 \le h \le 21, -23 \le k \le 21, -33 \le 1 \le 46$	$\begin{array}{l} -22 \leq h \leq 21, -23 \leq k \leq 19, -43 \\ \leq 1 \leq 46 \end{array}$
Reflections collected	33286	19249	18896
Independent reflections	$1614 [R_{int} = 0.0970, R_{sigma} = 0.0337]$	2739 [$R_{int} = 0.0285$, $R_{sigma} = 0.0156$]	2746 [$R_{int} = 0.1192$, $R_{sigma} = 0.0506$]
Data/restraints/parameters	1614/0/45	2739/0/87	2746/12/133
Goodness-of-fit on F ²	1.152	1.085	1.367
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0604,$ $wR_2 = 0.1934$	$R_1 = 0.0594, wR_2 = 0.1669$	$R_1 = 0.1141, wR_2 = 0.3186$
Final R indexes [all data]	$R_1 = 0.0680,$ $wR_2 = 0.1993$	$R_1 = 0.0628, wR_2 = 0.1722$	$R_1 = 0.1230, wR_2 = 0.3357$
Largest diff. peak/hole / e Å- 3	0.94/-0.73	0.78/-0.79	1.27/-0.83

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Work experience

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Doctoral assistant

EPFL Valais Wallis, Sion, Switzerland

- Conceived and managed 4 projects in organic synthesis, crystallography and catalysis
- Invented and implemented new, rapid and scalable methods for organic synthesis of porous material precursors with high potential of commercialization
- Lead a team of 4 people during a 5-month innovation project
- Supervised 2 interns, teaching assistant on Coordination Chemistry course
- Developed, improved and coordinated laboratory safety practices as group's safety representative (CoSEC)
- Managed laboratory supply chain, coordinated installation of a new laboratory with a CHF 100K budget
- Implemented, managed and delegated weekly laboratory maintenance activities
- Wrote and published 7 scientific papers in high-impact research journals

05.2015

Intern

ETH Zurich, Zurich, Switzerland

- Collected and analysed data for an ongoing research on luminescent lead halide perovskite nanoparticles
- Contributed to a scientific paper in a high-impact journal

2014-2016

Research Associate

Nikolaev Institute of Inorganic Chemistry, Novosibirsk, Russia

- Pitched a startup project based on research results, shortlisted in top 10 out of 25 projects
- Developed protocols for acid stability testing of metallic alloys
- Studied X-ray and synchrotron-based techniques of material characterization

2012-2014 Research Engineer

Nikolaev Institute of Inorganic Chemistry, Novosibirsk, Russia

- Developed methodologies for synthesis of metallic alloys via double complex salt decomposition
- Studied mechanisms of metallic alloy formation
- Published two scientific papers

Education

2017 – 2021	PhD candidate in Chemistry, EPFL Valais Wallis	
	Sion, Switzerland	
2009 – 2014	Diploma in Chemistry (<i>summa cum laude</i>), Novosibirsk State University	
	Novosibirsk, Russia	

Skills

- Innovation-oriented problem solving and critical thinking
- Management and leadership skills:
 - Project and time management
 - Reliable team player and project leader
 - Strong communication and organizational skills
 - Negotiation and dealing with conflict
- Research: NMR, HRMS, SEM, TEM, PXRD, SCXRD, TGA, FTIR, BET, gas sorption, chemical synthesis, strong safety background
- IT: MS Office, EndNote, Origin, ChemDraw, MestreNova, Origin, Python, TOPAS5, Vesta, Mercury, ConQuest, Photoshop, GIMP, Inkscape
- Scientific writing, literature search, advanced database search (SciFinder, Reaxys, CSD, ICSD, PDF+).

Languages

English (fluent)
 Russian (native)
 French (basic)
 German (elementary)

Transferable skills

- Innosuisse Science2market Business Concept Training (02-06.2021):
 - Pitch training
 - Market analysis and value proposition
 - IP protection
 - Introduction to accounting and financing
 - Product development + go to market strategy
 - Financial planning

Awards

2020	Chemistry Travel Award by SCNAT and Swiss Chemical Society
2019	Swiss Society for Crystallography Travel Grant
2014	The best diploma defense certificate on the State Examination board session
2012	Absolute winner of the 3 rd International Natural Sciences Tournament, Saint Petersburg, Russia (Team challenge)
2012	British Petroleum Scholarship

Interests

Hi-fi music	 Astronomy 	Birdwatching	 Hiking
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