# COVALENT TRIAZINE FRAMEWORKS AS SUPPORT FOR HETEROGENEOUS CATALYSIS

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## ENGLISH SUMMARY

Catalysis played an important role in improving our standard of living over the last century. Due to the constant environmental and economic challenges, there is an urgent need to develop a more sustainable and efficient chemical industry by establishing a more efficient application of chemical transformation. Heterogeneous catalysis, in which the catalyst and the reaction mixture are present in a different phase, often displays significant advantages over homogeneous catalysis in terms of sustainability, recyclability, robustness, and separation of catalysts. Catalysis by porous materials has been extensively used for decades and the growth rates appear to increase in scientific research due to the significant concerns regarding environmental sustainability and future energy security. Our aim in this thesis was to develop highly stable and porous Covalent Triazine Frameworks (CTFs) as scaffolds for catalytically active species in synthetic organic chemistry. CTFs have received significant attention as promising candidates to bridge the gap between homogeneous and heterogeneous catalysts due to their extraordinary stability under harsh synthesis and reaction conditions.

In Chapter 1, we presented the general introduction of porous organic frameworks (POFs) and their application in heterogeneous catalysis. POFs consist of crystalline covalent organic frameworks (COFs), and amorphous porous organic polymers (POPs) and CTFs. POFs have attracted considerable attention as platform for heterogenizing homogeneous catalysts due to their remarkable properties such as high surface area, microporosity, low density, and physicochemical stability. The versatility of POFs in heterogeneous catalysis can be achieved by introduction of the catalytic functionality via "bottom-up" synthesis or "post-functionalization" strategies.

CTFs are a subclass of POFs and are generally synthesized through the trimerization of nitriles via ionothermal conditions. CTFs exhibit high porosity with exceptional stability toward harsh environments compared to other porous organic frameworks. Because of this remarkable behavior, CTFs offer excellent potential in the development of heterogeneous catalysis. In Chapter 2, the utilization of CTFs as an efficient and highly stable support for both nanoparticles and molecular active catalysts is reviewed. This chapter also presents a general introduction to CTFs and their recent synthetic approaches.

Chapter 3 focuses on the heterogenization of a  $[Ir(OMe)(cod)]_2$  complex by postmodification of a bipyridine-based CTF (bipyCTF). Experiments and computational calculations confirm the anchoring of the Ir(I)-complex to the bipyridine moieties in the framework and indicate a similar coordination environment to that of the homogeneous counterpart. The introduction of the Ir(I)-complex to bipyCTF provides an efficient heterogeneous catalyst for C-H borylation of various aromatic compounds with the presence of B<sub>2</sub>Pin<sub>2</sub> as borylating agent. Heterogeneity test demonstrated the stability and reusability of Ir(I)@bipyCTF catalyst with excellent yield of products. A nitrogen-rich containing building blocks not only provides robust binding sites for metal complexes but also contains a Lewis basic functionality. In Chapter 4, a rigid and planar tris-bidentate ligand of 5,6,11,12,17,18-hexaazatrinaphthylene (HATN) was employed for the preparation of highly porous and nitrogen-rich CTFs. HATN-based CTF exhibited a remarkably high BET surface area of ~1700 m<sup>2</sup>/g. Post-synthetic metalation of HATN-CTF with a Cu(OAc)<sub>2</sub>.H<sub>2</sub>O complex creates an efficient heterogeneous catalyst for the Henry reaction of aromatic aldehydes and nitromethane. The high basicity of the HATN-CTF support facilitates the formation of nitronate species during the catalytic cycle, enhances the catalytic activity and produces higher yields.

In conclusion, post-functionalization with catalytic active sites have shown significant contributions to this emerging field of CTFs, particularly in organic transformations. Further examining on both their surface support features and their catalytic behavior allow for a broader insight of their development and application in the industry.

### DUTCH SUMMARY

Katalysatoren hebben de voorbije eeuw(en) een belangrijk aandeel gehad in het verbeteren van onze levensstandaard. De uitdagingen op milieu- en economisch gebied blijven echter toenemen, en daarom is er nu, meer dan ooit, nood aan de ontwikkeling van een nog efficiëntere en duurzamere chemische industrie, onder andere door een geoptimaliseerde toepassing van chemische synthese. Heterogene katalyse, waarin de katalysator en het reactiemengsel zich in een verschillende fase bevinden, kent doorgaans significante voordelen t.o.v. zijn homogene tegenhanger op gebied van duurzaamheid, recuperatie, recycleerbaarheid, en robuustheid. Dergelijke katalyse gebeurt vaak via poreuze materialen en dit al gedurende verschillende decennia. Het gebruik van poreuze materialen binnen dit domein krijgt steeds meer aandacht in wetenschappelijk onderzoek, niet geheel ongerelateerd aan de globale bezorgdheid rond milieu- en energieduurzaamheid. Het doel in deze thesis is de ontwikkeling van hoogstabiele, poreuze CTF's (Covalent Triazine Frameworks) als drager voor katalytisch actieve species in de organische synthesechemie. CTF's kennen toenemende aandacht in het onderzoek naar veelbelovende kandidaten om de kloof te dichten tussen homogene en heterogene katalyse.

Deze thesis vangt aan met een introductie in poreuze organische roosters (*porous organic frameworks*, POF's) en hun toepassingen binnen heterogene katalyse (Hoofdstuk 1). De POF materiaalklasse omvat kristallijne covalent-organische roosters (*covalent organic frameworks*, COFs) en amorfe, poreuze organische polymeren (POP's) en CTF's. POF's worden momenteel intensief bestudeerd voor hun toepassingen als platform voor het heterogeniseren van homogene katalysatoren, dankzij hun groot specifiek oppervlak, microporositeit, lage dichtheid en fysicochemische stabiliteit. Verschillende chemische functionaliteiten kunnen worden geïncorporeerd in POF's, via ofwel bottom-up strategieën (van nul opbouwen), of via post-synthese functionalizaties.

CTF's zijn een subklasse binnen de POF's en worden gesynthetiseerd door trimerizatie van nitrilen onder ionothermale condities. Deze materialen hebben een zeer hoge porositeit en kennen een uitmuntende stabiliteit onder ruwe omstandigheden, in tegenstelling tot vele andere poreuze materiaalklassen. Dankzij deze aantrekkelijke eigenschappen zijn CTF's excellente kandidaten voor het ontwikkelen van heterogene katalysatoren. In hoofstuk 2 wordt besproken op welke manier CTFs momenteel worden gebruikt als efficiënte en hoog-stabiele dragers voor zowel nanopartikels als moleculair-actieve katalyse. Er wordt eveneens een algemene introductie gegeven in CTF's en hun synthesemanieren.

Hoofdstuk 3 focust op het heterogeniseren van een  $[Ir(OMe)(cod)]_2$  complex op een bipyridine-gebaseerde COF (bipyCTF), door middel van post-modificatie. Succesvolle verankering van dit complex op de bipyridine sites in het rooster werd experimenteel en computationeel bevestigd, net als de structurele gelijkaardigheid van het verankerd

complex aan zijn homogene tegenhanger. De introductie van dergelijk Ir(I)-complex in de bipyCTF resulteert in een efficiënte heterogene katalysator voor de C-H borylatie van verschillende aromaten in aanwezigheid van B<sub>2</sub>Pin<sub>2</sub> als borylatie-agens. De katalyse werd bewezen compleet heterogeen te verlopen, waarbij de katalysator een goede stabiliteit en herbruikbaarheid bezit, en zorgt voor uitstekende productopbrengst.

Een stikstofrijke linker zorgt niet alleen voor een sterke metaal-ligand binding, maar zorgt tevens voor de aanwezigheid van een Lewis base functionaliteit. Hoofdstuk 4 bespreekt de synthese van hoog-poreuze en stikstofrijke CTF's m.b.v. rigide en planaire tris-bidentate HATN liganden (5,6,11,12,17,18-hexaazatrinaphthyleen). Deze HATN-gebaseerde CTF's vertonen een zeer hoge specifieke oppervlakte van ~1700 m<sup>2</sup>/g. Post-synthese metalering van deze CTF met Cu(OAc)<sub>2</sub>.H<sub>2</sub>O complexen resulteert in een efficiënte katalysator voor de Henry reactie van aromatische aldehyden en nitromethaan. De hoge basiciteit van de HATN-CTF drager faciliteert de formatie van nitronaat species tijdens de katalysecyclus, en verhoogt tevens de katalytische activiteit, en bijgevolg het rendement.

Als conclusie kan men stellen dat het post-functionaliseren van CTF's met katalytisch actieve sites voor een aanzienlijke toename in toepassingen voor deze materiaalklasse heeft gezorgd, voornamelijk in de chemische synthese. Het verder onderzoeken van de texturele karakteristieken en het katalytisch gedrag van CTF's kunnen leiden tot een nog dieper inzicht in hun ontwikkeling en tot een bredere toepasbaarheid in de industrie.

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## LIST OF ACRONYMS

Α						
AC	Activated Carbon					
Acac	Acetylacetonate					
В						
B <sub>2</sub> Pin <sub>2</sub>	Bis(pinacolato) diboron					
BET	Brunauer-Emmett-Teller					
bpim	2,2'-bipyrimidine					
bpy	2,2'-bipyridine					
С						
CMPs	Conjugated Microporous Polymers					
CNT	Carbon Nanotube					
COFs	Covalent Organic Frameworks					
CTFs	Covalent Triazine Frameworks					
D						
DCE	di-(4-cyanophenyl)ethyne					
DCM	Dichloromethane					
DFT	Density Functional Theory					
DMF	Dimethylformamide					
DMSO	Dimethyl sulfoxide					
DUBBLE	Dutch-Belgian Beamline					
Ε						
EA	Elemental Analysis					
EDX	Energy Dispersive X-ray Spectroscopy					
ESRF	European Synchrotron Radiation Facility					
EXAFS	Extended X-ray Absorption Fine Structure					
F						
FTIR	Fourier Transform Infrared Spectroscopy					
G						
GC	Gas Chromatography					
Н						
HAADF-STEM	High Angle Annular Dark Field-Scanning Transmission Electron Miscroscopy					
HAT	1,4,5,8,9,12-hexaazatriphenylene					
HATN	Diquinoxalino[2,3-a:2',3'-c]phenazine-2,8,15-tricarbonitrile					
HCPs	Hypercross-linked Polymers					

HMF	5-hydroxymethylfurfural
I	
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
Μ	
MOFs	Metal-Organic Frameworks
MsMOP-1	Metallosalen-based Microporous Organic Polymer
MW	Microwave
Ν	
NHC	N-heterocyclic carbene
NMR	Nuclear Magnetic Resonance
NPs	Nanoparticles
NT	Nanotube
Р	
PAFs	Porous Aromatic Frameworks
PCM	Polarizable continuum model
PCPs	Porous Coordination Polymers
phen	1,10-phenanthroline
PIMs	Polymers of Intrinsic Microporosity
РМО	Periodic Mesoporous Organosilica
PO	Propylene oxide
POFs	Porous Organic Frameworks
POPs	Porous Organic Polymers
PXRD	Powder X-ray Diffraction
S	
SEM	Scanning Electron Microscopy
Τ	
ТА	Terephthamide
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
TOF	Turn-over Frequency
TON	Turn-over Number
Χ	
XANES	X-ray Absorption Near Edge Structure
XAS	X-ray Absorption Spectroscopy
XPS	X-ray Photoelectron Spectroscopy

# 1 Introduction to Porous Organic Frameworks and their Application in Heterogeneous catalysis

### 1.1 Introduction to Porous Organic Frameworks

Porous materials have been a part of many established applications and are playing a major role in several emerging technologies such as gas storage, molecular separation, batteries, solid-state lighting, and heterogeneous catalysis.<sup>1-4</sup> Their high applicability with a tremendous performance in specific applications relies on their pore volume, pore geometry and surface nature of the pores.<sup>5</sup> Porous materials can be categorized according to the pore size and the chemical structure of building units. Depending on their pore size, these materials can be classified into microporous (pore diameter less than 2 nm), mesoporous (pore diameter between 2-50 nm), and macroporous (pore diameter greater than 50 nm).<sup>6</sup> Based on their structural and chemical composition, porous materials are distinguished as inorganic materials (zeolites, mesoporous silica), inorganic-organic hybrid materials (metal-organic frameworks), and organic porous materials (porous organic frameworks) (Figure 1.1).





**Figure 1.1.** Graphical representation of the classification of porous materials based on the structural and chemical compositions of their building units.

Inorganic porous materials are mainly based on metal oxides, such as zeolites and mesoporous silica. This group of materials possesses highly stable, abundant and cheap building units, which make them favorable in catalysis and separation for industrial applications.<sup>7</sup> However, the syntheses of these materials often require a template, from which the removal of the template can result in structural collapse and loss of porosity. Furthermore, the surface chemistry is mainly determined by the nature of the material, and thus, lack of chemical tunability and diversity limits their use to the desired application.<sup>8</sup> Metal-organic frameworks (MOFs), also known as porous coordination polymers (PCPs), have been synthesized through the reaction of a metallic node with an organic linker via a coordination bond.<sup>9</sup> MOFs exhibit distinct crystalline structures, exceptional surface areas, and an adjustable pore topology. Although MOFs have shown great potential in gas sorption and catalytic applications, the sensitivity of coordination bonds in ambient humidity and temperature limits the extraordinary properties of MOFs to be used widely.<sup>10-12</sup>

Porous organic frameworks (POFs) are an emerging class of porous materials that have received considerable research interest owing to their high potential combining the advantages of both porous materials and polymers.<sup>13</sup> In particular, POFs have attracted significant attention due to their lightweight properties, permanent porosity, flexible design and ease of functionalization.<sup>14</sup> In contrast to the inorganic and hybrid porous materials, POFs are constructed through strong covalent bonds of light elements such as carbon, hydrogen, nitrogen, oxygen or boron, and have a low density with exceptional physical and chemical stability.<sup>5, 15</sup> According to their morphology, POFs are either classified as crystalline and amorphous materials, although in many cases, precise differentiation is difficult. In general, crystalline POFs are structurally more ordered with well-defined pore structure and topologies, constructed by dynamic reversible reactions forming a thermodynamically stable material. On the contrary, amorphous POFs are constructed through irreversible covalent bonds that result in disordered and non-crystalline structures mainly formed through kinetic processes, which however display excellent stability. These POFs include covalent organic frameworks (COFs), covalent triazine frameworks (CTFs), and porous organic polymers (POPs). The design and structural features of these porous organic materials are summarized in Table 1.1.

	Covalent Organic Frameworks (COFs)	Covalent Triazine Frameworks (CTFs)	Porous Organic Polymers (POPs)	
Porosity <sup>a</sup>	Exactly defined	Controlled	Poorly controlled	
Structure	Ordered	Poorly ordered	Disordered	
Crystallinity	Crystalline	Amorphous <sup>b</sup>	Amorphous	
Cross-linking	Reversible	Irreversible	Irreversible	
Synthetic procedure <sup>c</sup>	Solvothermal	Ionothermal	C-C coupling	
Stability	Low hydrothermal stability	High thermal and chemical stability	High hydrothermal stability	

Table 1.1 Design and structural properties of COFs, CTFs and POPs

<sup>a</sup>Tunability of pore size/ distribution <sup>b</sup>except CTF-0, CTF-1, CTF-2 <sup>c</sup>Typical synthesis method

COFs, which are endowed with unique crystallinity, as well as porosity, represent an important branch of POFs that enabled atomically precise integration of organic monomers into crystalline architectures through robust covalent bonds.<sup>16</sup> COFs are synthesized through the reversible condensation reactions of organic building blocks into predictable and periodic 2D or 3D frameworks.<sup>17-18</sup> For instance, COFs can be formed either by self-condensation of boronic acids or by condensation reaction of boronic acids with diols to form boroxine rings. The first COFs (named COF-1 and COF-5), pioneered by Yaghi and co-workers in 2005, were synthesized under solvothermal conditions using a dioxane/mesitylene mixture.<sup>19</sup> COFs can be subdivided according to their covalent linkages, including boronate ester, imine, azine, hydrazone, squaraine, β-ketonamine, borazine, azodioxide, and phenazine. The triazine- based frameworks (CTF-0, CTF-1 and CTF-2) are assigned to the COF family as well. However, most of the synthesized CTFs exhibit poor crystallinity and therefore should be described as a subclass of POFs and will be discussed in more details in the next subtopic. From a synthetic perspective, COFs can also be synthesized using several different reaction conditions. including microwave-assisted solvothermal, mechanochemical, and room temperature synthesis in solution, while preserving the crystallinity of the resulting frameworks.<sup>20</sup> Although COFs exhibit highly porous crystalline materials with low density, their applications are often limited as COFs have low hydrothermal stability.<sup>16</sup> Although recently, several strategies have been implemented to improve the stability of COFs. Especially, β-ketonamine COFs have shown exceptional stability under strong acidic conditions.<sup>21</sup>

POPs are the examples of amorphous POFs. POPs are generally developed through highly cross-linking polymers and irreversible polycondensation reactions.<sup>22</sup> Depending on the choice of suitable monomers, functionality and polymerization methods, they can be prepared both as soluble or non-soluble network materials. These amorphous organic polymers can be divided into i) hypercross-linked polymers (HCPs, polymers with highly crosslinked networks and permanent nanopores synthesized by Friedel-Crafts reactions),<sup>23-24</sup> ii) polymers of intrinsic microporosity (PIMs, microporous polymers with highly rigid and contorted molecular structures assembled by a continuous chain of interlocked aromatic rings),<sup>25-26</sup> iii) conjugated microporous polymers (CMPs,  $\pi$ -conjugated polymers with permanent microporosity),<sup>27-28</sup> and iv) porous aromatic frameworks (PAFs, polymers with rigid aromatic open-network structures constructed by covalent bonds).<sup>29-31</sup>

Covalent triazine frameworks (CTFs) were first reported by Kuhn et al. in 2008 where they used the dynamic reversible reaction of aromatic nitrile trimerization to form extended porous organic frameworks.<sup>32</sup> CTFs are a distinct subclass of crystalline COFs, synthesized under ionothermal conditions where ZnCl<sub>2</sub> acts both as a catalyst and a solvent. However, due to the harsh synthesis conditions, most synthesized CTFs are carbonized resulting in amorphous characteristics. Since their inception, these triazine-based porous frameworks have become very popular due to their exceptional thermal and chemical stability in acidic and basic medium. This is a result of the strong covalent bonding paired with robust triazine linkages. The material obtains high stability by reaching thermodynamical stability under the high temperature synthesis conditions. The tremendous advantages and benefits of CTFs and their respective synthetic approaches will be discussed in more detail in the next chapter.

### 1.2 General Applications of POFs

The basic features that combines all these POFs are their relatively high surface areas, tunable pore sizes, and adjustable building units that offer unprecedented possibilities to various applications including gas storage, molecular separation, heterogeneous catalysis, etc.<sup>33-36</sup> The use of POFs as potential gas capture and storage has been well-known due to their high surface area and porosity, which are essentially comparable to zeolites, activated carbons and MOFs. POFs have shown high gas storage capacities for hydrogen, carbon dioxide, methane and ammonia because of their remarkable microporosity and combined with their exceptional stability, they offer a potential for practical applications. POFs are also promising materials for adsorption of organic chemical pollutants, such as small hydrocarbons, organic vapors, organic dyes, etc. Furthermore, the conjugated based POFs, especially the CMPs, have remarkable  $\pi$ -conjugation and photo-fluorescence properties that make them attractive candidates for chemical sensing.<sup>37-38</sup> In addition to the applications described above for POFs, the most rapidly developing area for POFs is as high potential materials for heterogeneous

catalysis.<sup>39-40</sup> Compared to conventional heterogeneous catalysts, POFs based catalysts have shown high catalytic performance and efficiency. In the following sections, the discussion is mainly focused on the utilization of POFs in heterogeneous catalysis.

### 1.3 POFs for Heterogeneous Catalysis

POFs offer many advantages over both homogeneous and nonporous heterogeneous catalysts.<sup>41</sup> Their solid-state nature with designable pore walls and controllable chemical structures, high porosity, and excellent stability make them beneficial in the catalytic processes. Catalysis can be defined as a process of acceleration of a chemical reaction in the presence of a catalyst which lowers the activation energy for the reaction to proceed.<sup>42</sup> A catalyst is a substance that facilitates the transformation of reactant to a product and by itself is not part of the reaction product. Catalysis can also be described as an alternative way of obtaining the immediate product by lowering the energy barrier that is involved in the chemical reactions between molecules and wherein the catalyst remains unaltered at the end of the reaction (Figure 1.2).<sup>43</sup>



Reaction steps

**Figure 1.2** Diagram of chemical reaction steps and energy barrier with and without the presence of a catalyst (Adapted from Waclawek *et al.*<sup>43</sup>)

The catalysis process can be classified into homogeneous catalysis and heterogeneous catalysis. In a homogeneous process, the catalyst and reactants are in the same phase, while in a heterogeneous process, the catalyst is present as a solid phase and the reactants are in a gas or liquid phase. The gas-solid heterogeneous catalysis is often used in the refinery and in the bulk chemical industry, whereas, heterogeneous catalysis

in solid-liquid phase is common in the fine chemical industry, where large batch reactors are filled with an organic liquid and a solid catalyst.<sup>44</sup> Homogeneous catalysts exhibit excellent catalytic activities with high selectivity in a broad range of synthetic reactions, however, their practical applications are restricted due to recyclability and difficulty in catalyst/product separation. This in turn increases the downstream processing steps and hence the overall cost factor rises. For example, in Miyaura borylation process, typically utilizing palladium (Pd) catalysts and bis(pinacolato) diboron ( $B_2Pin_2$ ) as the boron source, <sup>45-46</sup> the resulting boronic esters are then typically hydrolyzed, in an additional step, to their corresponding boronic acids, a process that can be challenging given its reversible nature and that affords large amounts of pinacol waste.<sup>47</sup> Removal of this pinacol waste from the reaction mixture requiring laborious extraction and distillation techniques as the development of suitable crystallization processes is often plagued by oiling issue. Finally, reaction conditions need to be identified that minimize the competing dehydrogenation and homocoupling of the aryl halide starting material, which can significantly impact the overall process yield and isolated product purity.<sup>48</sup> On the other hand, a heterogeneous system allows an easy separation between product and catalyst because of the insolubility of the catalyst in the reactant and product phase. This makes the recycling and regeneration of the catalyst more feasible. Many industries tend to shift towards the heterogeneous catalyst because of their low cost and compatibility with continuous processing which is ideal for largescale production.49



Figure 1.3 Illustration of the immobilization of homogeneous active sites onto solid porous supports.

One of the strategy is to immobilize the homogeneous catalyst on an insoluble porous support to combine the advantages of both homogeneous and heterogeneous catalysis (Figure 1.3). Inorganic porous materials such as zeolites, mesoporous silica and others offer tremendous potential for the immobilization of activate homogeneous catalyst because of their ordered pore sizes, large pore spaces and relatively uniform pore surfaces. However, these materials are sensitive toward acid and base conditions.<sup>50-51</sup>

Alternatively, the solid nature of POFs makes them very attractive as promising candidates to heterogenized homogeneous catalyst.<sup>52</sup> POFs possess a number of unique features and properties for the future development of catalytic processes. POFs are composed of highly cross-linked organic building blocks and thus provides a chemically well-defined inner surface with high stability.<sup>53</sup> Their exceptional chemical stability to a wide range of harsh conditions allows the use of POFs as catalyst supports in many wet chemical environments, without suffering from the degradation of the framework or loss in their microporosity. The possibility of high degree of controlling the chemical structures and porosity is considered as the main advantage of POFs over conventional catalysts such as zeolite and porous carbons. By means of the versatility of organic chemistry, various functional moieties can also be incorporated into POFs for specific catalytic applications.<sup>40</sup> The versatility of POFs as platform for catalytic applications can be achieved via "bottom-up" synthesis and "post-functionalization" strategies (Figure 1.4).<sup>54</sup>



**Figure 1.4** Schematic representation of A) bottom-up synthesis and, B) post-functionalization strategy to introduce active catalytic sites into POFs.

The "bottom-up" or pre-synthesis method allows a direct synthesis of catalytic POFs by introducing building blocks containing active catalytic sites. Through this strategy, various catalytic sites can be introduced into the pore walls of POFs by polymerization of functionalized building units, including metal complexes (eg. metalloporphyrin and metallosalen) and metal-free type catalysts. Thus, the distribution of a high loading functional groups or catalytic sites can be achieved homogeneously through the frameworks. For example, a metallosalen-based microporous organic polymer (MsMOP-1) was synthesized by Sonogashira-Hagihara coupling reaction using salen-palladium as building unit (Figure 1.5(a)).<sup>55</sup> MsMOP-1 efficiently catalyzed carbon-carbon coupling reactions with excellent stability and recyclability. The strong interaction between the catalytically active metal and the framework prevents catalytic

site leaching, and the inherent pores provide space for the chemical transformation. Another example is a straightforward strategy for constructing chiral COFs (LZU-72 and LZU-76) directly from functionalized chiral building units.<sup>56</sup> Direct condensation reaction of chiral-pyrrolidine containing building blocks with aldehyde monomers successfully afforded chiral COFs. These COFs were structurally robust and were highly active heterogeneous organocatalysts in the asymmetric aldol reaction (Figure 1.5(b)). The straight channels within the frameworks provide efficient accessibility to the chiral-pyrrolidine sites and hence, facilitate the transport of reactants and products.



**Figure 1.5.** Schematic representation of (a) synthesis of MsMOP-1 using (i) DMAc-Net<sub>3</sub>, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, 80 °C, 72 h (Adapted from Mu et al.<sup>55</sup>) (b) direct synthesis of chiral COFs, LZU-72 and LZU-76 (Adapted from Wang *et al.*<sup>56</sup>)

Although the pre-synthetic strategy offers direct synthesis and functionalization of porous catalyst materials, one of the greatest drawback is that the functional groups contained in the building units may impede the polymerization of the organic units into extended frameworks. Thus, the post-synthetic modification has emerged as the alternative strategy for the functionalization of porous organic materials as selective heterogeneous catalysts. Post-synthetic functionalization involves the modifications of the pre-synthesized POFs with additional catalytic moieties. The modification strategies include the encapsulation of the molecular catalysts in the interior pore spaces or complexation of the active metal catalyst through the introduction of organic linkers on the pore surface, and modification of the organic ligands with organocatalytic species.

For example, the synthesis of a COF bearing a 2,2'-bipyridine ligand (COF-TpBpy) exhibits excellent chemical stability with large pore size, and open accessibility coordination sites for potential metalation.<sup>57</sup> The integration of active species ionic polymers in the channels of COF-TpBpy, followed by encapsulation of active Cu species on the COF-TpBpy walls exhibited significantly improved catalytic efficiency in the cycloaddition of epoxides with CO<sub>2</sub> to form cyclic carbonates (Figure 1.6(a)-(b)). In another example, a methoxy group containing COF (TPB-DMTP-COF) was modified into a chiral organocatalytic COF in which the chiral and catalytically active (S)-pyrrolidine sites are anchored onto the walls of the open channels (Figure 1.6(c)).<sup>58</sup> The outstanding properties of TPB-DMTP-COF are retained after the post-synthetic functionalization by maintaining its crystallinity and porosity. Overall, the metal-free modified chiral COF catalyst exhibited high activity, enantioselectivity and recyclability in the asymmetric Michael C-C formation reaction in water.



**Figure 1.6.** Schematic representation of (a) heterogeneous concerted catalysis between active sites on the porous materials and the linear polymers (b) synthesis of PPSCCOF-

TpBpy-Cu (Reproduced from Ma *et al.*<sup>57</sup>) (c) synthesis of chiral COF catalyst,  $[(S]-Py]_x$ -TPB-DMTP-COF, using condensation reaction of three-functionalized monomers followed by a click reaction (Reproduced from Jiang *et al.*<sup>58</sup>)

POFs have gained significant attention both as excellent catalysts and catalyst supports, due to their tunable structure and permanent porosity, high surface area, robust thermal and chemical stability, and ease of functionalization as active catalysts. Compared to all aforementioned examples of POFs, the so-called covalent triazine frameworks (CTFs), stand out as promising candidates to bridge the gap between homogeneous and heterogeneous catalysts due to their extraordinary stability under harsh synthesis and reaction conditions. The development of CTFs as catalytic support for organic transformations will be profoundly discussed in the next chapter.

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Covalent Triazine Frameworks as Support for Heterogeneous Catalysis

# 2 Covalent Triazine Frameworks as support for Heterogeneous catalysis

This chapter is based on the following publication:

"Development of Covalent Triazine Frameworks as Catalytic Support for Synthetic Organic Chemistry". N. Tahir, C. Krishnaraj, K. Leus, P. Van Der Voort. *Polymers* **2019**, under revision.

#### 2.1 Introduction to Covalent Triazine Frameworks (CTFs)

Covalent triazine frameworks (CTFs) represent a class of highly stable porous organic materials based on triazine linkages. CTFs are generally prepared through a simple trimerization of aromatic nitriles in the presence of a catalyst. The formation of triazine from nitrile compounds catalyzed by molten metal salts has been applied since the early 1960s.<sup>1</sup> G.H Miller (Texaco Inc.) extended this approach by introducing the potential of metal chloride as a good catalyst for the trimerization of a variety of aromatic nitriles.<sup>2</sup> This formation of thermally stable, insoluble and infusible polymeric materials occurs at elevated temperature of 410 to 550 °C. These triazine containing polymers possess rich electron deficient structures and have gained attention in supramolecular chemistry because of their strong tendency for hydrogen bonding, metal chelation and  $\pi$ - $\pi$ interactions.<sup>3</sup> In 2008, Thomas and co-workers adapted the concept and introduced the synthesis of CTFs catalyzed by ZnCl<sub>2</sub> under ionothermal reaction conditions which produces permanent porosity and crystallinity. They first reported CTF-1 with a surface area of 790  $m^2g^{-1}$  and pore volume of 0.40  $cm^3g^{-1}$  which was obtained from the trimerization of 1,4-dicyanobenzene in molten ZnCl<sub>2</sub> in a closed quartz ampule at 400  $^{\circ}$ C for 40 h (Scheme 2.1).<sup>4</sup>



**Scheme 2.1.** Trimerization of 1,4-dicyanobenzene catalyzed by  $ZnCl_2$  under ionothermal conditions for the formation of CTF-1 (Reproduced from Thomas *et al.*<sup>4</sup>).

Structurally, most of the reported CTFs are amorphous because of the harsh synthesis conditions and high stability of the triazine linkage, yet they exhibit high specific surface area and permanent porosities.<sup>5</sup> In addition, the chemical structures and functionalities of this porous material can be adjusted by varying the structure-directing monomers which are used as the building blocks. The introduction of heteroatoms or functional groups into the frameworks enhance the potential of CTFs for various applications especially gas storage, adsorption and catalysis. The utilization of CTFs for various applications have been reviewed in several reports. Jin *et al.* reported the synthesis and applications of CTFs toward the energy and environmental purposes.<sup>6</sup> Tan *et al.* reviewed the development and challenges in the synthesis and potential

applications of CTFs in gas adsorption and separation, energy storage and conversion, photocatalysis as well as heterogeneous catalysis.<sup>7</sup> In addition, our group has reported the functionalization of CTFs with nitrogen rich functionalities, (pyridine-4,2,6-triyl)-based CTF, and fluorine-containing hydrophobic CTF. The synthesized materials effectively enhanced the adsorption properties and selectivity towards CO<sub>2</sub> and H<sub>2</sub> due to stronger interaction between the gas molecules and the functionalized CTF materials.<sup>8-9</sup> Furthermore, we also demonstrated the potential of CTFs as a platform for the encapsulation of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> for implementing it as an excellent and novel adsorbent toward remediation of inorganic contamination in water.<sup>10</sup>

The presence of stoichiometric and well-defined triazine moieties in the framework makes CTFs very attractive materials as a metal scaffold, especially in heterogeneous catalysis.<sup>11</sup> They are particularly interesting owing to their high basic functionality derived from the resulting nitrogen-containing frameworks, exceptional chemical inertness, especially in acidic and basic media, and outstanding stability over a broad range of temperatures and pressure. Furthermore, their high surface area and porosity with rigid pore structures enables the facile diffusion of substrates and products during catalysis. Application of CTFs in catalysis is a rapidly developing interdisciplinary research field. A number of reviews have been reported toward the applications of triazine-based polymers in heterogeneous catalysis.<sup>12,13</sup> This chapter will present a thorough review of the recent advances in preparation and functionalization of CTFs materials for heterogeneous catalysis, and focuses on the development of CTFs as catalyst supports with an emphasis on the application in synthetic organic chemistry.

### 2.2 Design and synthetic method of CTFs

Over the last decade, several procedures for CTFs synthesis have been developed. Porous CTFs materials with desired topology and functionality can be constructed from various monomers with specific functional groups, under a suitable reaction condition. Since the first introduction of CTF-1 by Thomas et al., a number of approaches have been explored for the development of CTFs having crystallinity with long-range order which have allowed a better understanding of the material and also have been utilized for a wide variety of applications. For instance, CTFs can be prepared through the trimerization of aromatic nitriles in the presence of acid-based catalysts, polycondensation reaction of monomer containing specific functional groups, and crosscoupling reaction of triazine containing building units (Table 2.1). However, for catalytic applications, surface area and pore size, as well as stability over catalytic reaction conditions and reusability are more important criteria for the material assessment. Especially for catalytic purposes in regards to the accessibility of immobilized metal species, specific surface area and porosity play a major role especially in terms of mass transfer in the catalyst and eventually the overall catalytic activity.

Method	Monomer	Catalyst	T (°C)	t (h)	$S_{BET} (m^2 g^{-1})$	Crystallinity	Reference
Ionothermal	2,2'-bipyridine-5,5'- dicarbonitrile	ZnCl <sub>2</sub>	400	48	2509	Amorphous	[4]
Bronsted acid	4,4'-biphenyldicarbonitrile	CF <sub>3</sub> SO <sub>3</sub> H	RT	12	776	Amorphous	[20]
Amide condensation	1,4-benzenedicarboxamide	$P_2O_5$	400	/	2034	Crystalline	[21]
Low-temperature condensation	1,4-phthalaldehyde /amidine dihydrochloride	Cs <sub>2</sub> CO <sub>3</sub>	120	72	663	Amorphous	[22]
In-situ oxidation	1,4-benzenedimethanol/ terephthalamidine	Cs <sub>2</sub> CO <sub>3</sub>	100/ 180	24/ 36	599	Crystalline	[23]
Friedel-Crafts	Cyanuric chloride/ 1,3,5- triphenylbenzene	AlCl3	70	16	1452	Amorphous	[24]
Yamamoto	2,4,6-Tris-(4-bromo-phenyl)- [1,3,5]triazine	Ni(cod) <sub>2</sub>	105	12	2015	Amorphous	[27]

**Table 2.1** Summary of synthetic methods of CTFs and their respective main features
#### 2.2.1 Trimerization of aromatic nitriles

There are several pathways for the trimerization of nitrile compounds leading to a triazine unit. The most common trimerization of nitrile is conducted under ionothermal conditions in molten ZnCl<sub>2</sub> at 400 °C for 40-48 h in a closed quartz ampule.<sup>4</sup> Molten ZnCl<sub>2</sub> is a good catalyst for the trimerization reaction and a highly soluble medium reaction for the nitrile compounds. Harsh reaction conditions are applied to ensure the reversibility of cyclotrimerization reaction.<sup>14</sup> However, the high stability of the triazine linkage causes low reversibility of the polymerization process. Hence, most of the obtained CTFs have low crystallinity or show a limited long-range order to which correspond to the formation of amorphous structures. To date, only CTF-0, CTF-1 and CTF-2 have been successfully synthesized as crystalline CTFs using the ZnCl<sub>2</sub> route.<sup>4</sup>, <sup>15-16</sup> An excess amount of ZnCl<sub>2</sub> as the molten solvent as well as an increase in the synthesis temperature, results in increased specific surface area and porosity of CTFs. However, partial decomposition occurs at elevated temperature causing a loss of nitrogen, creation of structural defects and thus resulting in mainly amorphous materials. Besides, synthesis at a lower temperature below 350 °C even with extended reaction time up to 168 h leads to the formation of oligomeric products without any porosity.<sup>17</sup>

An advanced synthetic protocol involves addition of a salt template during the polymerization of CTFs to introduced mesopores into a microporous material without the loss of nitrogen content in the framework. In this approach, binary mixtures of ZnCl<sub>2</sub> with various alkali chlorides such as LiCl, NaCl, and KCl were used as a reaction medium for the trimerization of nitriles.<sup>18</sup> The synthesis was performed at 300 °C for 60 h to initiate the formation of oligomers and subsequently, the samples were heated for 450 °C for an additional 5 h for complete polymerization. Salt-templated samples exhibit significantly increased specific surface area and lead to an enormous increase of the mesopore volume up to ten times compared to the conventional method for CTF-1. However, the solubility of the used organic species in the corresponding salt melt turned out to be crucial for the generation of porous CTFs. Another approach to reduce the polymerization reaction time is by using microwave (MW)-assisted ionothermal synthesis.<sup>19</sup> ZnCl<sub>2</sub> is a good MW absorber, and high porosity CTFs were obtained easily within 10-60 min. However, fast heating rate and high reaction temperature led to carbonization and rather low nitrogen contents.

The trimerization of aromatic nitriles can also be catalyzed by CF<sub>3</sub>SO<sub>3</sub>H in CHCl<sub>3</sub> at room temperature or even within a microwave-assisted condition.<sup>20</sup> Despite mild reaction conditions that avoid the incipient carbonization of the materials, this approach cannot be applied to all functional nitriles building blocks and also the CTFs produced using this method exhibited low to moderate BET surface area compared to ionothermal synthesis route. Hence, the ZnCl<sub>2</sub> catalyzed trimerization of aromatic nitriles is the most practical approach due to their ease of synthesis and feasibility for a

variety of functional building units, which in turn can be utilized for heterogeneous catalytic application.

#### 2.2.2 Polycondensation synthesis route

The triazine-based frameworks can also be synthesized through direct condensation of aromatic amides catalyzed by phosphorus pentoxide ( $P_2O_5$ ) (Scheme 2.2).<sup>21</sup> The polymerization of amides catalyzed by  $P_2O_5$  was conducted in a degassed flame-sealed ampule at a temperature of up to 400 °C. The resulting CTFs exhibit not only high specific surface area and stability but also high crystallinity. Because of the lower sublimation temperature of amide monomers, an appropriate temperature for the synthesis of CTFs is crucial in order to ensure better structural properties of the frameworks.



**Scheme 2.2.** Schematic representation of  $P_2O_5$ -catalyzed direct condensation of terephthamide (TA) to a discrete *p*CTF-1 (Adapted from Baek *et al.*<sup>21</sup>).

Another approach is by a polycondensation reaction of aldehydes and amidines in DMSO at 120 °C in the presence of cesium carbonate (Cs<sub>2</sub>CO<sub>3</sub>) as a base (Scheme 2.3).<sup>22</sup> The condensation reaction involves a Schiff base formation followed by a Michael addition. An advanced condensation approach can be utilized for the formation of crystalline CTFs by in situ formations of aldehyde monomers through the controlled oxidation of alcohols.<sup>23</sup> The reaction takes up by slow oxidation of alcohol to aldehyde monomers in the DMSO solution, and the reaction temperatures were subsequently increased to boiling point. Reaction temperature plays a critical role in this polycondensation reaction. By performing the polymerization reaction at high temperature, the alcohol will oxidize rapidly to form an aldehyde and generates a high concentration of nuclei to form small particles, and thus only soluble oligomers or fragments were formed, while polymerization reaction at a temperature below boiling point mainly yielded a low degree of crystallinity of CTFs. Therefore, it is very crucial to keep the polymerization reaction at a lower temperature in the initial stage to control

the in-situ formation of aldehyde and then maintain a higher temperature to boiling point to enhance the polymerization rate to improve the crystallization of the CTFs.



**Scheme 2.3.** a) Mechanism of condensation reaction between aldehyde and amidine for the formation of CTFs. b-e) Representations of the CTFs from different structures of aldehyde monomers. The cycle filled with different colors represents the presence of two types of pores (Adapted from Tan *et al.*<sup>22</sup>)

#### 2.2.3 Cross-coupling of triazine-based building block

Microporous triazine-based polymers can also be derived from triazine containing building blocks through a relatively simple cross-coupling reaction such as Friedel-Crafts and Yamamoto homo-coupling. In Friedel-Crafts reaction, cyanuric chloride acts as the triazine monomer which reacts with aromatic compounds in the presence of AlCl<sub>3</sub> as Lewis acid catalyst.<sup>24-26</sup> Generally, the cross-coupling reaction is performed under reflux in dichloromethane (DCM) solution and is feasible for various aromatic components. This produced a microporous CTF with a specific surface area of up to 1668 m<sup>2</sup>g<sup>-1</sup>, and exhibited low crystallinity due to the irreversible polymerization linkage.

In a similar manner, CTFs can also be derived by Ni-catalyzed Yamamoto reaction between 2,4,6-tris-(4-bromo-phenyl)-(1,3,5-triazine) and Ni(cod)<sub>2</sub> catalyst in the presence of 2,2'-bipyridyl in dehydrated dimethylformamide (DMF) under inert conditions at 105 °C.<sup>27</sup> High hydrothermal-stability was successfully obtained for porous CTFs with a specific surface area of up to 2015  $m^2g^{-1}$  at pore volume of 1.36 cm<sup>3</sup>g<sup>-1</sup>.

#### 2.3 CTFs as support for heterogeneous catalysis

CTFs have emerged as a novel platform for high-performance heterogeneous catalysis owing to their rigid structures, thermal stability, as well as high acid-base resistivity in comparison to other porous organic frameworks. The most significant advantages of this porous material are well-defined nitrogen components in their triazine units and ease of functionalization of organic ligand as their backbone where various catalytic functions can be obtained merely by changing the active metal species. Furthermore, high specific surface area and porosity provide accessibility of active sites, and heteroatoms contribute to the stabilization of the active species.

#### 2.3.1 Support for metal nanoparticles

N-heterocyclic moieties in the CTFs materials are beneficial for improving the stability of nanoparticles, especially in the liquid phase catalytic reaction conditions. Also, the porous surface of the support can offer steric restriction to prevent the growth of metal clusters which causes agglomeration and thus deactivation of the active catalyst species. Table 2.2 summarize the functionalization of CTFs as nanoparticles support for synthetic organic chemistry.

Thomas *et al.* immobilized Pd NPs on to CTFs materials to develop an active and efficient catalyst for the oxidation of glycerol in a liquid phase reaction system.<sup>28</sup> The CTFs based support was synthesized through trimerization of 1,4-dicyanobenzene using ZnCl<sub>2</sub> at 400 °C and then heated up to 600 °C for local expansion of the network. These exhibited surface areas up to 2814 m<sup>2</sup>g<sup>-1</sup> with pore volume of 1.79 cm<sup>3</sup>g<sup>-1</sup> (Scheme 2.4). Further on, Pd NPs-supported CTF (Pd<sub>PVA</sub>/CTF) were prepared by sol immobilization technique (NaBH<sub>4</sub>/polyvinyl alcohol (PVA)) to ensure better dispersion of the small NPs on the solid support. Pd<sub>PVA</sub>/CTF was found to be highly active than Pd-supported activated carbon (Pd/AC) with better activity and selectivity toward the formation of glycerate, and high stability up to three cycles. Furthermore, Pd<sub>PVA</sub>/CTF was more resistant to deactivation which was attributed to the stabilizing effect achieved through the nitrogen functionalities present in the CTF materials.

Monomer	NP	S <sub>BET</sub> * (m <sup>2</sup> g <sup>-1</sup> )	V <sub>p</sub> <sup>*</sup> (cm <sup>3</sup> g <sup>-1</sup> )	Catalysis	TON/ TOF (h <sup>-1</sup> )	Selectivity (%)	Reference
1,4-dicyanobenzene	Pd	2490	1.56	Glycerol oxidation	-	81	[29-31]
1,4-dicyanobenzene	Pd	631	-	Hydrogenation of N-heterocycles	380.8/ 47.6	97.9	[32]
1,4-dicyanobenzene	Pd	607	-	Carbonylation of aryl iodides	-	88	[33]
1,3-dicyanobenzene	Ru	2439	1.96	Oxidation of 5-hydroxymethylfurfural	-	63.6	[34,35]
Pyridine-2,6- dicarbonitrile	Ru	1399	0.92	Hydrogenolysis of xylitol	-	80	[36]
Di(4- cyanophenyl)ethyne	Ag	409	0.3	Alkyne carboxylation	226/-	-	[37]

**Table 2.2** Functionalization of CTFs as catalytic support for metal nanoparticles

\*after nanoparticles (NP) loading



Scheme 2.4. Reaction scheme of the dynamic trimerization of 1,4-dicyanobenzene for the formation of CTF (Adapted from Thomas *et al.*<sup>28</sup>).

The preparation technique of immobilizing Pd NPs to the CTFs was observed to influence the activity and stability of Pd/CTF catalyst in this catalytic reaction. The preparation of  $Pd_{IMP}/CTF$  via impregnation method led to the confinement of the particle Pd within the pores of the CTF (Figure 2.1).<sup>29</sup> A slight decrease was observed in the activity and selectivity for the Pd<sub>IMP</sub>/CTF compared to the Pd<sub>PVA</sub>/CTF which could be attributed to the lower Pd exposure in the Pd<sub>IMP</sub>/CTF sample. Remarkably, owing to the physical confinement of Pd NPs within the CTF materials, Pd<sub>IMP</sub>/CTF showed superior durability up to nine cycles.



**Figure 2.1.** TEM images of  $Pd_{PVA}/CTF$  (left) and  $Pd_{IMP}/CTF$  (right). Insets: particle size distributions of NPs (Reproduced from Prati *et al.*<sup>29</sup>).

Prati *et al.* examined the influence of N-containing support on the catalytic activity and stability of Pd system in benzyl alcohol oxidation.<sup>30-31</sup> The Pd NPs-supported CTF (Pd/CTF), activated carbon (Pd/AC), carbon nanotubes (Pd/CNTs) and nitrogen-doped carbon nanotubes (Pd/N-CNTs) were prepared by the sol immobilization method. Indeed, a triazine-rich material CTF with the highest number of N-groups significantly increased the Pd-catalyst performance compared to AC- and CNT-based support, which

can be ascribed to the presence of N-functionalities which limit the growth of the NPs and contributes to a positive effect toward particle dispersion avoiding aggregation of NPs. Moreover, He *et al.* highlighted the enhanced catalytic activity of Pd/CTF in the hydrogenation of *N*-heterocyclic compounds compared with the traditional Pd/AC (Figure 2.2a).<sup>32</sup> They also indicated that well dispersed and uniform distribution of Pd NPs on the CTF and excellent catalytic activity were attributed to the electron-donation from the N-moieties in the CTF to the Pd NPs which exhibited strong electronic metal-support interaction. Zhang *et al.* also reported the high activity and selectivity of Pd/CTFs were prepared by the impregnation-reduction method (PdCl<sub>2</sub>/NaBH<sub>4</sub>) and they catalyzed the synthesis of  $\alpha$ -ketoamides under atmospheric pressure of CO without any specific additives, for which the typical reaction of Pd-catalyzed double carbonylation of aryl halides required additives such as amine base and high pressure of CO to drive the catalytic reaction.



**Figure 2.2.** Schematic picture of **a**) Pd/CTF catalyzed hydrogenation of *N*-heterocycles (Adapted from He *et al.*<sup>32</sup>) **b**) Pd/CTF catalyzed carbonylation of aryl iodides with amines (Adapted from Zhang *et al.*<sup>33</sup>)

Palkovits *et al.* developed Ru/CTF catalysts for the selective oxidation of 5-hydroxymethylfurfural (HMF).<sup>34-35</sup> Ru NPs were finely distributed to various CTFs using the coordination-reduction approach in which the RuCl<sub>3</sub>.xH<sub>2</sub>O precursor in ethanol solution was refluxed with CTFs materials, and then the resulting coordinated Ru-species were reduced under H<sub>2</sub> atmosphere (Scheme 2.5). The reported study showed that the enhanced catalytic performance of Ru-supported CTF was not only depending on the surface area and porosity of the prepared materials but also was based on the N-content and the inherent polarity of the catalyst. Furthermore, the CTF-based support catalysts were far more active compared to the conventional Ru/C, and Ru/Al<sub>2</sub>O<sub>3</sub> catalysts and additionally, the N-functionalities provided stabilizing effect to the Ru species, enabling easy recycling of the catalysts. Ru/CTFs were also utilized as a selective catalyst for the conversion of xylitol to glycols with up to 80% yield.<sup>36</sup> The catalytic results revealed that the increased N-content in CTF-supported Ru catalysts

suppressed the decarbonylation reactions and hence leading to the high selectivity of desired products.



Scheme 2.5. Schematic representation of the coordination and stabilization of Ru NPs onto CTF material (Adapted from Palkovits *et al.*<sup>34</sup>)

Zhang *et al.* synthesized a novel porous CTF-based on di-(4-cyanophenyl)ethyne building units (CTF-DCE) to anchor Ag species as an outstanding heterogeneous catalyst for the terminal alkyne carboxylation reactions under atmospheric pressure.<sup>37</sup> The CTF-DCE was synthesized under ionothermal strategy through a sequence of the heat-resistant oligomer formation at moderate temperature to a highly porous CTF at high temperature with a BET surface area of 1355 m<sup>2</sup>g<sup>-1</sup> and pore volume of 0.93 cm<sup>3</sup>g<sup>-1</sup> (Scheme 2.6). CTF-DCE supported-silver (CTF-DCE-Ag) was prepared by treating the CTF material with AgNO<sub>3</sub> in hot DMSO at 80 °C. FTIR, PXRD and XPS analysis confirmed the deposition of metallic Ag<sup>0</sup> on the triazine moiety of CTF-DCE. CTF-DCE-Ag exhibited over sixfold higher TON compared to the Ag@MIL-101 catalyst for CO<sub>2</sub> capture and conversion into propiolic acids under similar catalytic conditions. The CTF-DCE-Ag could be recovered and reused up to five runs without any significant decrease of activity and, thus indicated the stability and recyclability of the catalyst.



**Scheme 2.6.** Polymerization of di-(4-cyanophenyl)ethyne (DCE) under ionothermal conditions (Adapted from Zhang et al.<sup>37</sup>)

#### 2.3.2 Immobilization of molecular metal catalyst

CTFs have been targeted as catalyst supports for molecular complexes because of their potential for incorporating functional organic ligands on the pore surfaces. Their exceptional chemical inertness toward acidic and basic media, paired with their outstanding stability over a broad range of temperatures and pressures enable CTFs to be particularly interesting for sustainable development in heterogeneous catalysis. To date, the aim to design CTF materials with strong electron-donating based ligand to provides high efficiency, good selectivity, and robust stability have been targeted by several research groups. From the design of organic functionalized ligand-based CTF supported transition metal complexes to their specific catalytic applications are summarized in Table 2.3.

Nitrogen-based ligands such as pyridine and bipyridine have been widely applied as homogeneous active transition metal catalyst supports. Functionalization of strong binding sites to a framework leads to various catalytic applications through efficient and stable heterogeneous based catalysts. Nitrogen-rich microporous CTFs derived from pyridine containing building units have been reported by Thomas *et al.*, synthesized by trimerization reaction under ionothermal conditions at temperatures up to 600 °C (Scheme 2.7).<sup>14</sup> The resulting pyridine-based CTF with a specific surface area of 1061 m<sup>2</sup>g<sup>-1</sup> and pore volume of 0.93 cm<sup>3</sup>g<sup>-1</sup>, contained numerous bipyridyl moieties that are accessible and enable anchoring of a transition-metal complex.



**Scheme 2.7.** Representation synthesis of pyridine-based CTF (Reproduced from Thomas *et al.*<sup>14</sup>)

Schüth *et al.* reported the potential of pyridine-based CTF material as a solid matrix for Pt(II) complex catalyzed methane oxidation.<sup>38</sup> The platinum species were introduced to the CTF using two different routes; by in-situ reaction of CTF and the Pt(II) precursor in the catalytic reaction mixture ( $K_2$ [PtCl<sub>4</sub>]-CTF), or by pre-coordination of the Pt(II) complex to CTF (Pt-CTF).

Monomer	Metal complex	$\frac{S_{BET}}{(m^2/g)}^a$	V <sub>p</sub> <sup>a</sup> (cm <sup>3</sup> /g)	Catalysis	TON/ TOF (h <sup>-1</sup> )	Selectivity (%)	Reference
2,6-dicyanopyridine	Pt(II)	1061 <sup>b</sup>	0.93 <sup>b</sup>	Oxidation of methane	246	-	[38]
	Ir(III)	500	-	Transfer hydrogenation	-/24	78	[40]
	Ni(II)	330	0.24	Oligomerization of ethylene	252	59	[41]
	Rh(III)	836	0.37	Hydroformylation of 1-octene		62	[42]
2,6-dicyanopyridine + 4,4'- biphenyldicarbonitrile	Ir(III)	970	-	Production of hydrogen from formic acid	-/27000	-	[43]
	Ir(III)	970	-	Hydrogenation of CO2	302/ 21300	-	[44]
5,5'-dicyano-2,2'- bipyridine	Ir(III)	170.24	0.09	Hydrogenation of CO2	5000/5300	-	[47]
	Ru(III)	502	0.29	Hydrogenation of CO2	21200/ 22700	-	[48, 49]
	Ir(III) /Ru(III)	-	0.095/ 0.126	Hydrogenation of acetophenone	-	99 <sup>c</sup>	[50]
	Al(III)-Co(I)	203	0.14	Carbonylation of epoxide	-	90	[51]
	Ir(I)	494	0.27	CH borylation	64	-	[52]
1,3-bis(5-cyanopyridyl)- imidazolium bromide	Ir(III)	693 <sup>b</sup>	0.38 <sup>b</sup>	Hydrogenation of CO2	24300/ 16000	-	[53]
	Rh(I)	1651	0.79	Methanol carbonylation	-/2100	56	[54]
	Co(I)	490	0.27	Carbonylation of epoxide	-	86	[55]

**Table 2.3** Functionalization of CTFs as catalytic support for metal complexes

Bis-(imidazolium)-methane bromide	Co(I)	570	0.28	Hydroesterification of epoxides	60	93	[56]
4,4'-malonyldibenzonitrile	V(IV)	900	0.65	Mannich reaction	213	-	[57]
<sup>a</sup> after metal loading							
<sup>b</sup> before metal loading							
_							

<sup>c</sup>conversion

The catalytic reaction of both Pt-modified CTF catalysts (K<sub>2</sub>[PtCl<sub>4</sub>]-CTF and Pt-CTF) exhibited high activity and selectivity for oxidation of methane to methanol under extremely harsh reaction conditions at 215 °C in concentrated sulfuric acid (30% SO<sub>3</sub>) and high pressure of CH<sub>4</sub> (40 bar). Pt-CTF catalyst shows high stability over several runs with TON above 250. Also, K<sub>2</sub>[PtCl<sub>4</sub>]-CTF catalyst shows a deactivation after the fifth run. The platinum sites were analyzed by XPS before and after catalysis, revealing the Pt(II) to be the predominant species. It was observed that the K<sub>2</sub>[PtCl<sub>4</sub>]-CTF material possesses a lower amount of incorporated Pt species than Pt-CTF. In a followup study, the local environments of Pt sites within Pt-CTF catalyst were identified analogue of the molecular Periana catalyst, Pt(bpym)Cl<sub>2</sub> (Figure 2.3).<sup>39</sup> The analysis by EXAFS, XANES, XPS, and surface characterization methods, provided evidence for the coordination of Pt(II) to pyridinic nitrogen sites in the Pt-CTF catalyst which are similar to one of the two coordination environments in crystalline Pt(bpym)Cl<sub>2</sub>. In addition, this study provides detailed insights into the underlying molecular compositions, structures, and distribution of a heterogenized Periana catalyst on CTF materials.



**Figure 2.3.** a) Schematic diagram of molecular Pt-CTF catalyst having similar coordination environment to the molecular Periana catalyst (Pt(bpym)Cl<sub>2</sub>) for the oxidation of methane to methanol in concentrated sulfuric acid. b) structural model of Pt(bpym)Cl<sub>2</sub>. c) EXAFS analysis of Pt-CTF and the fitted theoretical Pt(bpym)Cl<sub>2</sub> model. d) XPS N 1s spectra of Pt-modified 2,2'-bypyrimidine ligand and e) XPS N 1s spectra of Pt-modified CTF (Reproduced from Schüth *et al.*<sup>39</sup>)

Gascon *et al.* reported the immobilization of [IrCp\*Cl<sub>2</sub>]<sub>2</sub> complex on the pyridine based CTF material as a base free catalyst for the transfer hydrogenation reaction.<sup>40</sup> The Ir(III) complex coordinated to the bipyridyl moieties within the framework, resulting in an airand moisture stable Ir@CTF catalyst. XPS analysis revealed that Ir species in the system is in the oxidation state 3+ and remained unchanged prior to and after catalysis. In an optimized reaction condition, the Ir@CTF (0.40 mol% Ir) catalyzed transfer hydrogenation of 1-octene-3-ol with a 98% conversion and 82% yield of the targeted 3octanone, in the presence of isopropanol as solvent at 120 °C under an inert atmosphere (N<sub>2</sub>, 2 bar) for 23 h, without the need for additives. In a typical catalytic reaction of allylic alcohols, an additive such as bases or hydrogen acceptors are needed to promote the reaction. Most likely, the CTF material is not just an inert support for Ir(III)Cp\* complex dispersion, but rather the presence of pyridine molecules plays an active role as co-catalysts by assisting the deprotonation and coordination of initial alcohol to the Ir center to form the initial metal enolate for the isomerization reaction. The turn-over frequency (TOF) of the Ir@CTF catalyst was 24 min<sup>-1</sup>, and they outperformed other Ir(III)-based porous material catalysts. The recyclability studies of the Ir@CTF material was performed up to six consecutive runs. However, a slight decrease of activity was observed over the first three runs, while a more pronounced decrease of activity was observed afterwards. The catalyst surface, progressively blocking the active sites.

In another catalytic application for pyridine-based CTF as catalytic support, the same group of Gascon *et al.* reported the immobilization of Ni(II) complex on the CTF which catalyzed the oligomerization of ethylene.<sup>41</sup> Ni(II) was coordinated to the support CTF material by excess impregnation of Nickel(II) bromide ethylene glycol dimethyl ether (DME\*NiBr<sub>2</sub>) under mild conditions. TEM micrographs revealed a good dispersion of Ni throughout the solid materials with no metal nanoparticles and XPS analysis indicated the preferential coordination of Ni to pyridinic N species within the CTF. The catalytic performance and active site accessibility influenced the selectivity of the catalyst in the ethylene oligomerization. The microporous Ni(II) supported pyridine-CTF catalyst showed higher selectivities to C<sub>8=</sub> than to C<sub>6=</sub>. The slower diffusion of olefins throughout the pores of the materials causes to re-adsorption of the products, thus leading to further oligomerizations.

Palkovits *et al.* reported that the porosity and polarity of CTF supported Rh(III) catalysts significantly influence the catalytic activity in hydroformylation reaction.<sup>42</sup> Rhodium(III) chloride hydrate was immobilized to various CTF materials with different porosities and surface polarities. Superior results were obtained with Rh(III) catalyst supported to the highly mesoporous and low polarity of 4,4'-dicyanobiphenyl based CTF, whilst the microporous and high surface polarity of 2,6-dicyanopyridine based CTF support showed the lowest activity. This study reports that the mesoporosity and accessibility to active site in combination with the polarity of the surface support offers high activity and selectivity for the solvent-free hydroformylation of 1-octene.

One of the great advantages of CTFs is that their solid-state properties can be adjusted by varying the starting building blocks. Gascon *et al.* designed a mesoporous CTF constructed by using a mixture of 2,6-dicyanopyridine and 4,4'-dicyanobiphenyl with the ratio of 1:2 (Scheme 2.8).<sup>43</sup> The biphenyl monomer induced the mesoporosity to the CTF and the presence of pyridine sites in the frameworks not only provided inherently basicity but also introduced bipyridine moieties that acted as metal support and in addition assited in the activation of small molecules.



**Scheme 2.8.** Synthesis of mesoporous CTF from trimerization of mix monomers using 2,6-dicyanopyridine and 4,4'-dicyanobiphenyl under ionothermal synthesis (Reproduced from Gascon *et al.*<sup>43</sup>)

To be more practical in terms of catalyst recycling, the mesoporous CTF were shaped into a spherical form, without losing their properties. The CTF-based spheres were prepared by a phase inversion method using polyimide Matrimid<sup>®</sup> as a binder (Figure 2.4).<sup>44</sup> These CTF spheres showed high thermal stability, porosity, and the possibility of coordinating metal clusters. In contrast to the powder, the spheres-based catalyst is more easily handled, and fully recycled without loss of material through at least four consecutive runs. A highly efficient organometallic complex, Ir(III) Cp\* was immobilized through coordination within the CTF spheres to render a molecular yet heterogeneous and stable catalyst, which is easy to handle and recycle in the CO<sub>2</sub> hydrogenation to formic acid. Moreover, utilization of shaped particles carries the advantage of facile catalyst recycling and improved reproducibility.

However, porosity of the CTFs could not be completely preserved upon formulation. Thus, to address this issue and the diffusion limitations derived from heterogenization, Gascon and the co-workers introduced a well-defined CTF coated on cordierite monoliths, prepared by quasi chemical vapor deposition (Figure 2.5).<sup>45</sup> These coatings are stable, easy to handle, and can be used in the same way as the parent material to coordinate metal complexes. Extensive characterization demonstrates that these coatings contain properties similar to those of the material in powder form. Monolith-supported CTF showed superior performance for the selective partial oxidation of methane to methanol, attributed to the better mass transport properties of the thin layer coated on the monolith channels compared to powder-form CTF.



**Figure 2.4.** A) SEM of cut CTF-based sphere B) Synthesis reaction of shaping CTF C) SEM image and its molecular structures of immobilized Ir complex on the CTF-based sphere D) XPS analysis of iridium species in the powder and shaped CTF catalysts (Adapted from Gascon *et al.*<sup>44</sup>)



**Figure 2.5.** (Left) Representation of coating procedure step. (Right) SEM micrograph of A) CTF powders B-E) CTF-coated monolith F) view on wall of a CTF-coated monolith (Reproduced from Gascon *et al.*<sup>45</sup>)

The presence of stoichiometric and well-defined nitrogen sites within the frameworks render the CTF as a good catalyst support and catalytically active metal ions can be anchored by strong nitrogen-metal interactions. Lotsch *et al.* developed a CTF based on the bipyridine-based building block with hierarchical microporosity and high specific surface area of up to 1100 m<sup>2</sup>g<sup>-1</sup> where the bipyridine units acts as scaffold to site-specifically coordinate the molecular metal including Co, Ni, Pt and Pd (Scheme 2.9).<sup>46</sup>



**Scheme 2.9.** Schematic representation of the synthesis of bipyridine-based CTF (bpyCTF) (Adapted from Lotsch *et al.*<sup>46</sup>)

Yoon et al. utilized the bipyridine-based CTF (bpyCTF) as support for Ir- and Rucomplexes in the hydrogenation of CO<sub>2</sub> to formate.<sup>47-49</sup> The XPS measurements revealed the complexation of both Ir and Ru ions onto bpyCTF and showed the coordination environment to be similar to that of their homogeneous counterparts. The catalysts efficiently converted CO<sub>2</sub> into formate under mild reaction conditions in the presence of triethylamine as a base and demonstrated excellent recyclability over consecutive runs. The TON and TOF was reported to outperformed conventional heterogeneous catalysts. Owing to the high stability of CTFs in acidic and basic media, they extended the study of bpyCTF as catalytic support by incorporating the Ir and Rh half-sandwich complexes as active heterogeneous catalysts for the aqueous-phase hydrogenation of carbonyl compounds (Figure 2.6).<sup>50</sup> The optimized catalytic conditions of this hydrogenation reaction for analogous homogeneous system showed the highest TOF at acidic medium reaction (pH 3.5), in which most of the MOFs and other transition metal-based oxide catalysts are unstable. Interestingly, these CTF [bpy-CTF-(Cp\*IrCl)]Cl supported heterogeneous catalysts and [bpy-CTF-(Cp\*RhCl)]Cl are demonstrated to be efficient, recyclable, and have superior activities

with a broad substrate scope. In addition, these are also industrially viable catalysts for the exclusive production of alcohols in water.



**Figure 2.6.** Structural representation of (a) homogeneous Ir- and Rh-based catalysts, and (b) CTF-supported catalysts (Adapted from Yoon *et al.*<sup>50</sup>)

High specific surface area and robust stability of bpyCTF in various catalytic conditions was further utilized by the group of Yoon et al. to immobilized bimetallic [Al(OTf)<sub>2</sub>][Co(CO)<sub>4</sub>] based catalyst onto bpyCTF for the carbonylation of propylene oxide (PO) into  $\beta$ -butyrolactone (Figure 2.7).<sup>51</sup> The catalyst was prepared by immobilization of Al(OTf)<sub>3</sub> onto bpyCTF under hydrothermal method and subsequently the OTf anions was exchanged with  $[Co(CO)_4]^2$  anion. Nitrogen adsorption measurement proved that the presence of the anions did not completely block the pores of bpyCTF, leaving possible channels for small molecules such as PO and CO to reach the active catalytic sites. XPS analysis revealed similar coordination environment of the developed heterogeneous catalyst as observed in the homogeneous catalyst. The active heterogeneous [bpy-CTF-Al(OTf)<sub>2</sub>][Co(CO)<sub>4</sub>] catalyst converted the PO to  $\beta$ butyrolactone with a high selectivity of 90%, which is comparable to those of the homogeneous catalyst. Moreover, the catalyst was readily separated from the product and repeatedly used for several runs. The selectivity was maintained, although a slight reduction of activity was also observed which may originate from partial discharge of the  $[Co(CO)_4]^-$  anion from the catalyst upon product separation.



**Figure 2.7.** Structural representation of (a) homogeneous  $[(salph)Al(THF)_2][Co(CO)_4]$ , and (b) structural features of the heterogenized catalyst  $[bpy-CTF-Al(OTf)_2][Co(CO)_4]$  (Adapted from Yoon *et al.*<sup>51</sup>)

N-heterocyclic carbene or imidazolium-based ligand possess strong  $\sigma$ -donating and poor  $\pi$ -accepting characters which can improve the electron density on central metal ions that would enhance the efficiency of transition metal complexes heterogenized catalysts. Hence, Yoon and co-workers introduced the NHC-based CTF as catalyst support and employed as an efficient heterogeneous catalyst for the CO<sub>2</sub> hydrogenation to formate (Scheme 2.10).<sup>52</sup> The Ir(III) complex was immobilized onto NHC-functionalized CTF through N^C coordination site via post-synthetic metalation strategy. Remarkably, Ir-NHC-CTF system exhibited excellent activity with better TON and TOF in comparison to the values observed for the Ir-based bpyCTF and sphereshaped Ir@CTF mentioned above for the same catalytic reactions. However, activity of the catalyst decreased over three successive runs which is attributed to the Ir leaching in every cycle.



<sup>a</sup>Reagents: (i) ZnCl<sub>2</sub>; (ii) [IrCp\*Cl<sub>2</sub>]<sub>2</sub> and Et<sub>3</sub>N.

Scheme 2.10. Schematic representation of synthesis of Ir-NHC-CTF (Adapted from Yoon *et al.*<sup>52</sup>)

These positive charged imidazolium-CTF was also employed as an exceptionally stable support for Rh-based molecular catalyst in the carbonylation of methanol.<sup>53</sup> The characterization of the catalyst system revealed that the Rh-complex was incorporated as a single-site catalyst throughout the support by ligation of the Rh complex to the abundant N-atom sites of the CTF (Figure 2.8). Rh-bpim-CTF system showed higher efficiency and long-term stability in methanol carbonylation in plug-flow reaction in gas phase compared to the Rh-bpy-CTF catalyst. The electron donation effect of the abundant N-atom sites in the CTF enhanced the nucleophilicity of central metal ion and hence increased the catalytic activity, and the strong ion-pair interaction between Rh centers and the positive charged support dramatically increased the stability.



**Figure 2.8.** Structural representation of Rh-bpim-CTF catalyst in resting state (1), and (2) the suggested structure of in situ generated active state (Adapted from Yoon *et al.*<sup>53</sup>)

In another catalytic study, the same group of Yoon *et al.* reported the potential of this charged imidazolium-based CTF to form complexes with  $[Co(CO)_4]^-$  ion by maintaining the homonuclear ion pair and efficiently catalyzed the carbonylation of

epoxide.<sup>54</sup> The imidazolium-CTF were treated with  $KCo(CO)_4$  in methanol under a CO atmosphere and subsequently a facile exchange of endogenous Cl<sup>-</sup> anions with exogenous  $[Co(CO)_4]^-$  anions occurs. XPS analysis showed that the coordination environment of Co anions present in the heterogenized catalyst were similar to that in homogeneous system and further characterization by ICP-OES, SEM and elemental analysis collectively confirmed the existence of  $[Co(CO)_4]^-$  in the frameworks. The heterogenized [imidazolium-CTF][Co(CO)\_4] catalyst exhibited a much better selectivity in comparison to its homogeneous counterpart [Bmim][Co(CO)\_4] catalyst for the production of methyl 3-hydroxybutyrate (MHB) from propylene oxide (PO) and CO. Typically, the formation of side products in this catalytic reaction were inevitable due to the nucleophilic attack of methanol on PO under the reaction conditions. Furthermore, the catalyst stability was revealed via the recycling experiments which shower that a small amount of  $[Co(CO)_4]^-$  ions leached in every successive cycle.

The leaching of metal active catalyst from the catalytic support leads to a decrease in activity and recyclability of the catalyst. Thus, Yoon and co-workers designed a bis-imidazolium-based CTF as catalytic support to enhance the stability of the  $[Co(CO)_4]^-$  ions in the catalytic process of the hydroesterification of epoxides (Figure 2.9).<sup>55</sup> The catalytic results demonstrated that the bis-imidazolium-functionalized framework introduced intramolecular dication-anion interaction within the framework and literally activated more epoxide with better selectivity and decreased the  $[Co(CO)_4]^-$  ions leaching from the CTF. This significantly increased the catalytic stability for epoxide carbonylation.

Acetylacetonate-based transition metal complexes have shown significant catalytic performance in a wide variety of organic transformation such as cross-coupling reaction, alcohol oxidation, hydroxylation, etc. Our group designed and presented CTFs functionalized with acetylacetonate (acac) group (acac-CTF) supported VO(acac)<sub>2</sub> complex which efficiently catalyzed a Mannich-type reaction (Figure 2.10).<sup>56</sup> The acac-CTF were prepared from the trimerization of 4,4'-malonyldibenzonitrile under ionothermal synthesis, obtained BET surface area of up to 1626  $m^2g^{-1}$  and showed excellent CO<sub>2</sub> and H<sub>2</sub> storage capacity and good CO<sub>2</sub>/N<sub>2</sub> selectivity. The V@acac-CTF catalyst was synthesized by post-synthetic metalation of VO(acac)<sub>2</sub> complex in toluene with the acac-CTF material. The strong metalation of vanadium ions toward O^O coordination sites in the frameworks were confirmed by FTIR, <sup>13</sup>C MAS NMR, and XPS analysis. The in-situ formation of iminium ions from tertiary amine oxides in the presence of V<sup>4+</sup> anchored on acac-CTF facilitates the potential application in modified Mannich-type reactions. The V@acac-CTF showed outstanding reactivity and reusability with a TON of 213 and for a wide substrates scope. The higher reactivity and reusability of the catalyst is attributed to the strong coordination of the vanadyl ions to the electron-donating based acetylacetonate groups in the framework.



**Figure 2.9.** A) Comparison of intramolecular stabilization of anion in [bis-imidazolium-CTF-Cl][Co(CO)<sub>4</sub>] (right) over [imidazolium-CTF][Co(CO)<sub>4</sub>] complexes (left) B) Representation of synthesis of [bis-imidazolium-CTF-Cl][Co(CO)<sub>4</sub>] (i) ZnCl<sub>2</sub>, 400 °C, 48 h (ii) KCo(CO)<sub>4</sub>, MeOH, 50 °C, 0.5 MPa of CO, 24 h (Reproduced from Yoon *et al.*<sup>55</sup>)



**Figure 2.10.** A) Schematic representation the synthesis of acac-CTF supported  $VO(acac)_2$  complex (Adapted from Van Der Voort *et al.*<sup>56</sup>)

#### 2.4 Conclusions

CTFs have attracted a great deal of attention especially in heterogeneous catalysis due to their functional diversity that allows exquisite control over the chemical nature of the specific surface areas and physical properties of the resulting networks. They offer a number of advantages over conventional porous solid catalysts such as metal-organic frameworks (MOFs) or zeolites towards selected challenges in the development and intensification of catalytic processes. CTFs can be utilized as a support for catalytically active metal nanoparticulate species wherein it can provide a stabilization effect compared to conventional porous solid supports. Additionally, the organic building units can be tailored synthetically with defined functional moieties to enable the immobilization of molecular metal complexes. Despite the tremendous potential of CTFs as catalytic support, as demonstrated in this chapter, there are still challenges which need to be addressed in order to further the application in organic synthesis and in industrial chemical production. Owing to their amorphous solid nature, their behavior in catalysis are often difficult to understand. The accessibility of active catalytic species into the frameworks is not always guaranteed, thus, the catalytic activity has always been determined by their TONs and TOFs calculated from the entire metal loading instead of accessible species. Although metal leaching is a limited issue, catalyst deactivation is still observed upon extended recycling reaction. Further insight into deactivation pathways is necessary for developing more robust catalysts with extended lifetimes. CTFs are becoming an exciting new type of porous organic support for heterogeneous catalysts owing to their well-defined nitrogen contents and high thermal and chemical stability. Although numerous catalytic reactions catalyzed by metal supported CTFs have been presented in this chapter, further development of CTFs as metal support are still highly desired, especially toward industrially relevant reaction classes, such as C-H functionalization and asymmetric catalysis.

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Covalent Triazine Frameworks as Support for Heterogeneous Catalysis

# 3 Covalent Triazine Frameworks as Catalytic Support for C-H Borylation Reaction

This chapter is based on the following publication:

"Immobilization of Ir(I) complex on covalent triazine frameworks for C-H borylation reactions: A combined experiemental and computational study", N. Tahir, F. Muniz-Miranda, J. Everaert, P. Tack, T. Heugebaert, K. Leus, L. Vincze, C. V. Stevens, V. Van Speybroeck, P. Van Der Voort, *Journal of Catalysis* **2019**, 371, 135-143

#### 3.1 Introduction

Aromatic boronic acids are highly important compounds that have been used in numerous synthetic procedures.<sup>1</sup> They have been used extensively as important building blocks in a number of cross coupling reactions, including Suzuki-Miyaura and Chan-Lam, and recently, boronic acid-containing macromolecules and other related compounds have gained popularity in medicinal chemistry.<sup>2</sup> For example, the ability of boronic acids to bind with saccharides and potentially undergo an ionization transition makes the materials ideal for diabetes-related applications.<sup>3</sup> The transition metalcatalyzed C-H borylation of aromatic compounds is the most efficient and convenient synthetic strategy for the synthesis of organoboron compounds. It is a highly economical and environmentally benign process that can be carried out in the absence of a halogenated reactant.<sup>4-7</sup> Among the developed transition metal-based catalysts to date, Ir complexes containing bipyridine-based ligands have shown superior performance exhibiting excellent activity and selectivity for the aromatic C-H borylation under mild reaction conditions.<sup>8-10</sup> In recent decades, intensive research efforts have resulted into the development of Ir-based heterogeneous catalysts for C-H borylation in order to overcome the drawbacks related to homogeneous systems such as difficulties related to the recovery and reuse of the precious Ir catalysts.<sup>11</sup> Various heterogeneous-based bipyridine supports have been developed, including mesoporous silica,<sup>12-13</sup> periodic mesoporous organosilica (PMO),<sup>14-16</sup> metal-organic frameworks (MOF),<sup>17-19</sup> and organosilica-nanotubes.<sup>20</sup> These well-established heterogeneous Ir(I)based catalysts could catalyze the C-H borylation of arenes exhibiting a high activity and selectivity. However, their durability was somehow hampered and showed a rather low tolerance for the presence of functional groups. For example, the C-H borylation catalyzed by an Ir(I)-based PMO showed a significant decreased catalytic performance during recycling studies,<sup>15</sup> whereas for the Ir(I)-based MOF catalysts, the system required high reaction temperatures and long reaction times (up to 72 hours) for the C-H borylation of rigid and larger substrates.<sup>17</sup>

Within this context, covalent triazine frameworks (CTFs) have recently emerged as potential supports for heterogeneous catalysis due to their high surface area having an abundant nitrogen content.<sup>21-22</sup> Lotsch and co-workers synthesized a functionalized-CTF based on 2,2'-bipyridine building blocks.<sup>23</sup> They demonstrated that this bipyridine-based CTF (later known as bipyCTF) possess specific and strong binding sites for transition metals ions including Co, Ni, Pt, and Pd. Yoon et al. have further investigated the potential of the bipyCTF as a host matrix for metal complexes. They demonstrated that the bipyCTF-functionalized with either Ir, Rh or Ru complexes exhibited a good catalytic performance in the selective hydrogenation of carbonyl compounds.<sup>24-26</sup> In another study, they explored the incorporation of bimetallic Al-Co in the bipvCTF for the carbonylation of propylene oxide to β-butyrolactone.<sup>27</sup> In this chapter, we employed the bipyCTF as catalytic support for the anchoring of the [Ir(OMe)(cod)]<sub>2</sub> complex towards the borylation of aromatic C-H bonds. The immobilization of the Ir(I) complex onto the bipyCTF was investigated intensely both experimentally and computationally, showing a high reactivity in the C-H borylation of various arenes and heteroarenes in the presence of B<sub>2</sub>Pin<sub>2</sub> as boron reagent.

#### 3.2 Synthesis and methodology

All chemicals were purchased from commercial suppliers and used without further purification. Nitrogen adsorption analysis was conducted at 77K using an automated gas sorption system Belsorp-mini II gas analyzer. Prior to sorption measurements, the samples were dried under vacuum at 120 °C overnight to remove adsorbed water. FT-IR spectra in the region of 400-4000 cm<sup>-1</sup> were recorded on a Thermo Nicolet 6700 FT-IR spectrometer equipped with a nitrogen-cooled MCT detector and a KBr beam splitter. Elemental composition was measured on a Thermo Scientific Flash 2000 CHNS-O analyzer equipped with a TCD detector. Powder X-ray diffraction (XRPD) patterns were collected on a Thermo Scientific ARL X'Tra diffractometer, operated at 40 kV, 40 mA using Cu-K $\alpha$  radiation ( $\lambda = 1.5406$  Å). TGA measurements were performed using a Netzsch STA-449 F3 Jupiter. The samples were heated in the temperature range 30-800 °C under an air atmosphere at a heating rate of 10 °C min<sup>-1</sup>. The Ir loading was determined using an ICP-OES Optime 8000 atomic emission spectrometer. HAADF-STEM and the EDX mapping analysis was performed using JEOL JEM-2200FS High-Resolution STEM equipped with an EDX spectrometer with a spatial resolution of 0.13 nm, image lens spherical aberration corrector, electron energy loss spectrometer (filter) and an emission field gun (FEG) operating at 200 keV. X-ray Absorption Spectroscopy (XAS) measurements were performed at beamline BM26A (Dutch-Belgian beamline, DUBBLE) at the ESRF (Grenoble, France).<sup>28</sup> The conversion of the substrates was identified by a Finnigan Thermo Scientific Trace GC Ultra equipped with an FID, and the yield formation of borylated compounds was determined by means of <sup>1</sup>H NMR measurements on a Bruker Advance 300MHz spectrometer.

#### 3.2.1 Synthesis of 2,2'-bipyridine-5,5'-dicarbonitrile

The nitrile based monomer was synthesized according to a slightly adopted procedure reported by Duan et al.<sup>29</sup> In first instance, NiCl<sub>2</sub>.6H<sub>2</sub>O (0.12 g, 0.5 mmol) was dissolved in 20 mL dry DMF. The resulting mixture was heated to 40 °C and 2-bromo-5-cyanopyridine (1.83 g, 10.0 mmol), anhydrous LiCl (0.43 g, 10.0 mmol) and Zn powder (0.78 g, 12.0 mmol) were added. After raising the temperature to 50 °C, I<sub>2</sub> (20 mg) and acetic acid (20 mg) were added into the mixture and stirred for 30 minutes. Afterward, the mixture was cooled down to 0 °C before adding 1N HCl (15 mL) and stirring it for an additional 30 minutes. Hereafter, aqueous ammonia (25%) was added until the mixture at pH 11 and the resulting product was extracted with ethyl acetate (3x50 mL). The combined organic layers were washed with a 5% aqueous LiCl solution and dried over MgSO<sub>4</sub>, filtered and concentrated. 2,2'-bipyridine-5,5'-dicarbonitrile was obtained as a pale brown powder in 91% yield (0.94 g). No further purification was required for the next reaction step. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.97 (2H, dxd, J = 2.0, 0.8 Hz), 8.64 (2H, dxd, J = 8.3, 0.8 Hz), 8.14 (2H, dxd, J = 8.3, 2.1 Hz) (Figure A1). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  157.0, 152.1, 140.5, 121.7, 116.5, 110.7 (Figure A2).

# 3.2.2 Synthesis of the bipyCTF

The bipyCTF was synthesized according to the published procedure.<sup>23</sup> Typically, a glass ampoule was charged with 5,5'-dicyano-2,2'-bipyridine (100 mg, 0.48 mmol) and ZnCl<sub>2</sub> (332 mg, 2.40 mmol) in a glove box. The ampoule was flame-sealed under vacuum and heated in an oven towards 400 °C with a heating rate of 100 °C/h and held at this temperature for 48 h. After cooling down to room temperature, the resulting black solid was ground well and stirred in 250 mL of water for 4 h, filtered and washed with water, acetone and refluxed in 250 mL of 1M HCl overnight, filtered, and washed subsequently with 1M HCl (3x100 mL), H<sub>2</sub>O (3x100 mL), THF (3x100 mL), and acetone (3x100 mL). The resulting product was dried under vacuum overnight at 150 °C prior to use.

# 3.2.3 Post-synthetic metalation of bipyCTF with [Ir(OMe)(cod)]<sub>2</sub>

To obtain the Ir(I)@bipyCTF catalyst, 140 mg of bipyCTF was added to a solution of  $[Ir(OMe)(cod)]_2$  (10.0 mg, 0.015 mmol) in 30 mL anhydrous THF and the mixture was stirred at room temperature. After 24 hours, the solid was filtered and washed with THF (3x25 mL) to remove the weakly bounded Ir complex and dried under vacuum. It is important to note that all the handlings as mentioned above were done under an inert atmosphere to prevent oxidation of the Ir precursor.

## 3.2.4 Computational details

Density functional theory calculations have been performed with the Gaussian 16 suite of programs.<sup>30</sup> Structural optimizations were carried out with the M06<sup>31</sup> exchange-correlation functional, employing the LanL2DZ combined pseudopotential and basis set.<sup>32-34</sup> The M06 functional is known to yield accurate structural parameters and thermochemical energies with Ir<sup>+</sup>.<sup>35</sup> The lack of negative frequencies in relaxed geometries indicate that the optimized structures represent true energy minima. Calculations for the anchoring models shown in Figure 3.3 have been carried out including the THF solvent via the polarizable continuum model (PCM).<sup>36</sup> Calculations for the deprotonation energies have been carried out including the methanol solvent through the PCM procedure. Dispersion interactions have been modelled using the D3 version of Grimme's dispersion with Becke-Johnson damping.<sup>37</sup>

### 3.2.5 General procedure for the aromatic C-H borylation

All the catalytic tests were carried out in a 25 mL Schlenk-tube which was charged subsequently with bis(pinacolato)diboron (31.75 mg, 0.125 mmol), an arene (0.125 mmol), 3 mL of dry heptane and Ir(I)@bipyCTF (1.5 mol% Ir). The mixture was stirred at 90 °C for 8 h under a nitrogen atmosphere. At the end of the reaction, the reaction mixture was analyzed by means of GC and GC-MS using dodecane as internal standard and the product yield was determined by <sup>1</sup>H NMR using mesitylene as the internal standard.

For the recycling experiments, the catalyst was filtered, washed with heptane and dried at 120 °C under vacuum overnight. Hereafter, the catalyst was subsequently reused following the identical procedure as described above.

#### 3.3 Results and discussion

#### 3.3.1 Synthesis and characterization

The most commonly applied synthesis method to obtain CTFs is through trimerization of nitrile monomers using ZnCl<sub>2</sub> at 400 °C for 40-48 hours of reaction.<sup>38</sup> Notably, a high temperature is required to dissolve the monomers in molten ZnCl<sub>2</sub> in which Zn<sup>2+</sup> acts as a Lewis acid catalyst to promote the reversible trimerization throughout the CTF formation. However, at temperatures above 400 °C, carbonization and structural degradation of the triazine ring can occur, whereas shorter reaction times (<40 hours) result in an incomplete polymerization.<sup>39</sup> In this study, the bipyCTF was synthesized by heating the 2,2'-bipyridine-5,5'-dicarbonitrile monomer in the presence of ZnCl<sub>2</sub> at 400 °C for 48 hours, in a vacuum sealed glass ampoule (Scheme 3.1).



Scheme 3.1 Schematic representation of the synthesis of Ir(I)@bipyCTF

The Fourier Transform Infrared (FT-IR) analysis for the synthesized bipyCTF was performed to evaluate the trimerization process of the framework. The disappearing band of the –CN stretching vibration at 2240 cm<sup>-1</sup> indicates the complete polymerization of the framework (Figure A3). Elemental analysis (EA) revealed an

increase in the C/N ratio of the bipyCTF in comparison to the theoretically calculated values due to the decomposition of nitrile building blocks and the partial carbonization of the frameworks during the synthesis reaction,<sup>40</sup> which is commonly observed feature for CTFs (Table A1). Furthermore, the Powder X-ray diffraction (PXRD) measurement shows a broad diffraction peak representing the structural ordering of the bipyCTF (Figure A4).<sup>41</sup> The thermal stability of the studied bipyCTF was examined by means of Thermogravimetric analysis (TGA) demonstrating that the bipyCTF material starts to decompose at 450 °C, whereas approximately 10% of weight loss below 100 °C which can be assigned to adsorbed CO<sub>2</sub> or solvents (Figure A5). However, before the catalytic test, the samples were preheated overnight at 150 °C in vacuo, which should remove all adsorbed species.



**Figure 3.1** Nitrogen adsorption isotherms of bipyCTF (black) and Ir(I)@bipyCTF (red) measured at 77K

The Ir(I)bipyCTF was prepared by post-metalation of the synthesized bipyCTF with  $[Ir(OMe)(cod)]_2$  in THF at room temperature, as shown in Scheme 3.1. ICP-OES analysis was performed to determine the metal loading which amounts 8.26 wt% Ir (0.43 mmol g<sup>-1</sup>) (Table A2). The nitrogen adsorption isotherms of both the bipyCTF and Ir(I)bipyCTF material were subsequently recorded at 77 K to determine the porosity of the networks. As shown in Figure 3.1, both materials exhibit a typical type I isotherms which is characterized by a sharp N<sub>2</sub> uptakes at low relative pressure. The Brunauer-Emmett-Teller (BET) surface area and pore volume of the bipyCTF are calculated to be 714 m<sup>2</sup> g<sup>-1</sup> and 0.39 cm<sup>3</sup> g<sup>-1</sup>, respectively. These values decreased after the coordination of the Ir obtaining 494 m<sup>2</sup> g<sup>-1</sup> and 0.27 cm<sup>3</sup> g<sup>-1</sup> for the BET surface area and total pore volume, respectively (Table A2). To evaluate the occupancy of Ir(I) complex inside the pore system of the bipyCTF, we have calculated the theoretical occupied volume and weight based on a 0.43 mmol g<sup>-1</sup> Ir-complex loading which amounts 0.043 cm<sup>3</sup> g<sup>-1</sup> and 142 mg g<sup>-1</sup>, respectively. Starting from the pore volume of the pristine bipyCTF being

0.39 cm<sup>3</sup> g<sup>-1</sup>, and taking into account only the weight increase, the theoretical pore volume of the catalyst with all complexes on the outside would become 0.34 cm<sup>3</sup> g<sup>-1</sup>. The occupied volume by the complex amounts 0.043 cm<sup>3</sup> g<sup>-1</sup>, the theoretical pore volume considering all complexes inside the pores is then 0.29 cm<sup>3</sup> g<sup>-1</sup>, which is slightly higher than the experimental pore volume (0.27 cm<sup>3</sup> g<sup>-1</sup>), but definitely lower than 0.34 cm<sup>3</sup> g<sup>-1</sup>, which would be obtained taking only the weight increase and not any pore filling into account. These data are a good indication that most of the complexes are inside the pores. The presence of the anchored Ir in the Ir(I)@bipyCTF material was further confirmed by high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and the corresponding energy dispersive X-ray spectroscopy (EDX) mapping images (Figure A6). The main elements, namely carbon and nitrogen are well dispersed and the Ir(I) complex was uniformly distributed throughout the frameworks.

#### 3.3.2 Theoretical calculations

Density functional theory (DFT) calculations have been performed to investigate the anchoring of the Ir(I) complex onto the bipyCTFs. Various anchoring models were studied including the possibility of deprotonation of bipy with the methoxy anion ( $^{-}OCH_3$ ). This process can not a priori be ruled out because: (i) the  $^{-}OCH_3$  anion, which has strong basic properties, is present in the [Ir(OMe)(cod)]<sub>2</sub> precursors complex; (ii) the C-H ionic dissociation energies of the bipy embedded into CTF are close to the O-H ionic dissociation energy of methanol (Figure A7). In fact, regarding point (ii), an increase in the acidity of bipy was observed when it is embedded into the CTF environment. This increase has been traced back to the effect of the nearby triazine residues, as shown in Figure A7, which makes the C-H bond in bipy less covalent and more prone to deprotonation.

Various anchoring models have been considered which are shown in Figure 3.2, along with their stabilization free energy. Model 1 considers an anchoring of a  $^-$  OCH<sub>3</sub> anion to the two N atoms of bipy, whereas in models 2 and 3 the anchoring is through one N atom (of triazine in model 2, of bipy in model 3) and one deprotonated C atom of bipy, whereas methanol is basically dissociated from the Ir(I) cation. To assess the stability of the various model compounds, their relative energies have been computed in respect to their subunits (namely the triazine-bipy-triazine unit, Ir(I)-cod, and  $^-$ OCH<sub>3</sub>/methanol), according to the following equation:

 $\Delta G = G[model] - G[Ir(I)-cod] - G[OCH_3/methanol] -G[protonated/deprotonated triazine-bpy-triazine]$ 

This equation can be used because the three models have the same number of atoms overall and the same charge (namely, zero), even if their own subunits differ regarding this characteristic (for example, the methoxy anion has a negative charge and one proton fewer than methanol). The energies are reported in Figure 3.2. The  $\Delta G$  reported in the

previous equation is referred to the constituents of a specific model, whose details are reported in the Supporting Information.



**Figure 3.2** Structurally relaxed anchoring models (upper row) and their schematic formula (lower row). The stabilization energies are -444 kJ/mol (model 1), -414 kJ/mol (model 2), -439 kJ/mol (model 3)

These data show that model 1 has the highest stabilization energy; however, model 3 has a similar stabilization energy and thus cannot be ruled out in principle. Hence, two further model complexes were considered to study the possible coordination with  $B_2Pin_2$ .


**Figure 3.3** Possible intermediate Ir(III) complexes formation after treatment with B<sub>2</sub>Pin<sub>2</sub>. Optimized structures are reported in Figure S8 of the Supporting Information

In fact, after addition of  $B_2Pin_2$ , the Ir complex would be compound A.2 if no deprotonation of the bipy ring occurs ("anchoring A"), whereas it would lead to complex B.2 if bipy is really deprotonated and Ir is anchored to a C<sup>-</sup> anion ("anchoring B") (Figure 3.3). Model A.2 and B.2 involve coordination with three and two BPin units, as their precursor compounds A.1 and B.1 had three and two coordination bonds with the non-CTF ligands. Models A.2 and B.2 have the same charge but a different number of atoms, so to compare their relative stability it is not possible to just straightforwardly subtract the free energy of their constituent subunits from their own energy. In fact, to compare their relative energy we considered the following formal reaction connecting the two complexes A.2 and B.2:

 $[A.2] + [bpy syn \rightarrow anti isomerization] + [bpy ring deprotonation] - [BPin] \rightarrow [B.2]$ 

Thus, in this case we have computed the free energy difference  $\Delta G = G_{\text{products}} - G_{\text{reagents}}$  for this formal reaction as:

 $\Delta G = G_{\text{products}} - G_{\text{reagents}} = G[B.2] - G[A.2] - G[bpy \text{ syn} \rightarrow \text{anti isomerization}] - G[bpy deprotonation] + G[BPin]$ 

We found that in this case  $\Delta G = +106$  kJ/mole (see the details in the Appendix A), thus indicating that the B.2 complex (with Ir anchored to a deprotonated bipy ring) is

significantly less stable than complex A.2 (with Ir anchored to the two N atoms of bipy). As a consequence, these calculations suggest that the Ir(I) complex is indeed anchored to the CTF framework through the two N atoms of bipy and that this compound would be the actual active complex for the catalysis cycle.

#### 3.3.3 Aromatic C-H borylation catalyzed by Ir(I)@bipyCTF

The catalytic performance of the Ir(I)@bipyCTF was evaluated for the C-H borylation of arenes and heteroarenes under mild reaction conditions. Initially, the arene 1,2-dichlorobenzene (2 equiv.) was examined in the presence of B<sub>2</sub>Pin<sub>2</sub> (1 equiv.) at 70 °C for 24 h using Ir(I)@bipyCTF (1.5 mol% Ir) as catalyst in various solvents. The results are summarized in Table 3.1. No borylated products were observed when the borylation reaction was conducted in polar solvents such as THF and DMF (Table 3.1, Entry 1 and 2). However, 18% yield was obtained in heptane at 70 °C (Table 3.1, Entry 3). The obtained results are in accordance to literature demonstrating that the solvent polarity has a substantial effect on the conversion of the substrate.<sup>13, 42</sup> When the reaction temperature was increased to 90 °C, the yield significantly rose to 70% (Table 3.1, Entry 4). The amount of the boron reagent also plays a crucial role in the yield of the product.<sup>43</sup> For instance, upon increasing of one equivalent of B<sub>2</sub>Pin<sub>2</sub>, the rate of the borylation reaction increases drastically, reaching 95% yield after 8 h of reaction (Table 3.1, Entry 5).

	CI		ⓐbipyCTF		BPin
Entry	DCB:B <sub>2</sub> Pin <sub>2</sub> <sup>b</sup>	Solvent	T (°C)	Time (h)	Yield (%) <sup>c</sup>
1	1:0.5	THF	70	24	0
2	1:0.5	DMF	70	24	0
3	1:0.5	Heptane	70	24	18
4	1:0.5	Heptane	90	24	70
5	1:1	Heptane	90	8	95

Table 3.1 Ir(I)@bipyCTF catalyzed C-H borylation of 1,2-dichlorobenzene<sup>a</sup>

<sup>a</sup>Reaction conditions: Ir(I)@bipyCTF (1.5 mol% Ir), 1,2-dichlorobenzene, B<sub>2</sub>Pin<sub>2</sub>, dodecane (1 mmol) <sup>b</sup>Substrate to boron reagent mol ratio. <sup>c</sup>Yield was determined by <sup>1</sup>H NMR

Several control experiments were performed. The borylation of 1,2-dichlorobenzene catalyzed by  $[Ir(OMe)(cod)]_2$  and bipyCTF, separately, were carried out under the

optimized reaction conditions (Table 3.2, Entry 2 and 3). Apparently, no catalytic activity was observed in both control experiments. In another control test, the bipyCTF and the [Ir(OMe)(cod)]<sub>2</sub> were added together resulting in a poor yield of only 10% after an extended reaction time of 24 h (Table 3.2, Entry 4). This demonstrates that the Ir(I) complex can catalyze the C-H borylation reaction in the presence of a bipy-based support. Nevertheless, only when the Ir(I) complex is anchored onto the bipyCTF, a high product yield of 95% was obtained after 8 hours of reaction (Table 3.2, Entry 1). Additionally, the Ir(I)@bipyCTF catalyst exhibited an initial slower reactivity compared to its homogeneous analog, as can be seen in the kinetic profiles for both catalysts (see Figure 3.4).

Entry	Catalyst	Yield (%) <sup>b</sup>	TON
1	Ir(I)@bipyCTF	95	64
2	[Ir(OMe)(cod)] <sub>2</sub>	0	0
3	bipyCTF	0	0
4	[Ir(OMe)(cod)] <sub>2</sub> + bipyCTF	10 <sup>c</sup>	8

**Table 3.2** Control experiments C-H borylation of 1,2-dichlorobenzene<sup>a</sup>

<sup>a</sup>Reaction conditions: Ir(I)@bipyCTF (1.5 mol% Ir), 1,2-dichlorobenzene (1 equiv.),  $B_2Pin_2$  (1 equiv.), 90 °C, heptane, 8 h. <sup>b</sup>Yield was determined by <sup>1</sup>H NMR. <sup>c</sup>Yield obtained after 24 h of reaction.



**Figure 3.4** Kinetic profiles for the C-H borylation of 1,2-dichlorobenzene catalyzed by Ir(I)@bipyCTF and its homogeneous counterpart

We extended the scope of substrates using various arenes and heteroarenes having electron-withdrawing and electron-donating groups under the optimized catalytic reaction conditions. In general, the Ir(I)@bipyCTF was able to catalyze the C-H borylation of various substrates and afforded good to excellent yield of the corresponding borylated products, as summarized in Table 3.3. The obtained results were in accordance with the literature, demonstrating that the Ir catalyst favors the conversion of electron-poor arenes in the C-H borylation.44-45 For example, it can be seen that for the borylation of 3- bromobenzotrifluoride, a higher catalytic activity was observed in comparison to 3-(trifluoromethyl)anisole using similar reaction conditions, for which a yield of 78% and 56%, respectively was obtained (Table 3.3, Entry 2 and 3). Moreover, the regioselectivity of the borylation of arenes was controlled by the steric effects, which means that the C-H boryation occurs at the least sterically accessible C-H position of the arene. On the other hand, the borylation of the heteroarenes is mainly determined by electronic effects which preferentially takes place at the C-H bond  $\alpha$ -to the heteroatom.<sup>46</sup> As can be seen from Table 3.2 (Entry 4 and 5), the borylation of indole and pyrrole, gives 92% and 84% of the respective borylated products.

A hot filtration test was conducted to verify the heterogeneous nature of the catalytic process. After the removal of the catalyst by means of filtration, the catalyst-free reaction solution was stirred for an additional 8 h (Figure A9). No catalytic activity was observed in the absence of the catalyst, which subsequently demonstrates the heterogeneity of the Ir(I)@bipyCTF catalyst in nature. As for the recycling tests, after the first cycle, the catalyst was recovered by filtration, washed thoroughly with heptane and dried under vacuum. The performance of the recycled catalyst in the borylation of 1,2-dichlorobenzene up to five successive runs is shown in Figure 3.5. Only a slight loss of product yield was observed during the sequential tests. This loss in product yield is probably due to the loss of some catalyst during the recovery process. The ICP-OES analysis was performed after the first catalytic run showed the presence of 8.09 wt% amount of Ir suggesting no significant leaching of the catalyst during the course of the reaction.



Figure 3.5 Reusability of the Ir(I)@bipyCTF catalyst for C-H borylation of 1,2-dichlorobenzene

	R II Hepta	$\begin{array}{c} @bipyCTF \\ \hline B_2Pin_2 \\ ane, 90 \ ^{\circ}C, 8h \end{array} \qquad $	BPin
Entry	Substrate	Product	Yield (%) <sup>b</sup>
1	CI CI	CI BPin	95
2	F <sub>3</sub> C	F <sub>3</sub> C BPin	78
3	F <sub>3</sub> C	F <sub>3</sub> C BPin	56
4		BPin H	92
5		N BPin	84

Table 3.3 C-H borylation of arenes and heteroarenes catalyzed by Ir(I)@bipyCTF<sup>a</sup>

<sup>a</sup>Reaction conditions: Ir(I)@bipyCTF (1.5 mol% Ir), arene (1 equiv.), B<sub>2</sub>Pin<sub>2</sub> (1 equiv.), 90 °C, heptane, 8h. <sup>b</sup>Yield was determined by <sup>1</sup>H NMR

In addition, a comparison has been made between our Ir(I)@bipyCTF catalyst to the other reported heterogeneous Ir(I)-based catalysts (Table 3.4). Although a one-on-one comparison with the PMO-based support catalyst by Inagaki et al. <sup>15</sup> and the MOF-based support variant by Lin et al. <sup>17</sup> is not straightforward, due to different operating conditions, we can conclude that the Ir(I)@bipyCTF is a highly efficient catalyst.

Catalyst	Reaction conditions	TON/ TOF (h <sup>-1</sup> )	Yield (%)	Ref.
Ir(I)@bipyCTF	1.5 mol% Ir/ 90 °C/ heptane/ 8 h	64/15.2	95	This study
Ir(cod)-BPy <sub>0.3</sub> -NT	1.5 mol% Ir/ 80 °C/ 12 h	64/nr	97	[20]
Ir-Bpy-PMO	0.75 mol% Ir/ 80 °C/ cyclohexane/ 12 h	34*/8	92	[15,16]
bpy-UiO-Ir	3.0 mol% Ir/ 115 °C/ heptane/ 72 h	nr	93	[17,19]
Ir-bpy-SBA-15	1.5 mol% Ir/ 70 °C/ hexane/ 48 h	136/6.5	95	[13]

 
 Table 3.4 Heterogeneous Ir-based catalysts catalyzed C-H borylation of 1,2dichlorobenzene

\*TON was calculated for using benzene as substrate; NT= nanotube; nr = not reported

An Ir-L<sub>3</sub> edge XANES investigation of the Ir(I) (a) bipyCTF catalyst before and after a catalytic run was carried out to elucidate the coordination environment of the Ir center in the catalytic system. The measurement displays a clear increase in the white line intensity (11.22 keV) for the sample after catalysis (Figure A10). This white line corresponds to a  $2p \rightarrow 5d$  electron transition. As the white line intensity increases, the 5d electron density decreases, denoting a shift from Ir(I) to Ir(III). This occasion can be explained by the catalytic reaction mechanism proposed by Hartwig and Miyaura's (Scheme 3.2).<sup>44</sup> During the catalytic reaction, an Ir(III) complex is formed by the reaction of an Ir(I) complex with B<sub>2</sub>pin<sub>2</sub>. As the reaction progresses, the active intermediate Ir(III) complex will regenerate by the consumption of B<sub>2</sub>pin<sub>2</sub>, explaining the increase in white line intensity. In-situ XANES experiments were also performed to monitor the change in Ir state as the catalytic reaction progresses (Figure A11). A gradual increase in white line intensity can be perceived, corresponding to a gradual increase in the presence of Ir(III)@bipyCTF. These results are in agreement with the theoretical aforementioned earlier in this study stating that the Ir oxidation state changes due to a decrease in B<sub>2</sub>Pin<sub>2</sub> as the reaction progresses.



Scheme 3.2 A proposed plausible mechanism for C-H borylation of arene catalyzed by  $Ir(I)@bipyCTF^{44}$ 

#### 3.4 Conclusions

The straightforward post-synthetic metalation of bipyCTF with  $[Ir(OMe)(cod)]_2$  afforded a robust and efficient heterogeneous system for borylation of aromatic C-H bonds. Ir(I)@bipyCTF exhibited excellent catalytic activity for borylation of arenes and heteroarenes using B<sub>2</sub>Pin<sub>2</sub> as the borylating agent. The DFT calculations gave strong evidence for Ir(I)@bipyCTF anchoring and elucidated its local geometry, while XAS analysis confirmed the change of the Ir oxidation state in the catalyst which has a similar environment to that of the homogeneous counterpart. The heterogeneity test revealed the stability and reusability of the developed heterogeneous-based bipyCTF catalyst for at least five cycles without significant loss of activity. More importantly, the catalyst performs effectively under mild reaction conditions and tolerance to functional groups which showed a similar trend to the typical homogeneous iridium-based catalysts and displayed better performances than the reported iridium-based heterogeneous catalysts.

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Covalent Triazine Frameworks as Support for Heterogeneous Catalysis

# 4 HIGH-NITROGEN CONTAINING COVALENT TRIAZINE FRAMEWORKS AS BASIC CATALYTIC SUPPORT

This chapter is based on the following publication:

"High-nitrogen containing covalent triazine frameworks as basic catalytic support for the Cu-catalyzed Henry reaction", N. Tahir, G. Wang, I. Onyshchenko, N. De Geyter, K. Leus, R. Morent, P. Van Der Voort. *Journal of Catalysis* **2019**, 375, 242-248.

#### 4.1 Introduction

The exploration of new building blocks for the synthesis of Covalent Triazine Frameworks (CTFs) is important to achieve a further advancement of functional porous materials for challenging applications.<sup>1</sup> Due to the high versatility of CTFs, there has been a growing interest in the development of new functional building blocks.<sup>2</sup> CTFs featuring well-defined N-sites, for example, pyridine-based<sup>3-5</sup> or bipyridine-based<sup>6-10</sup> CTFs, provide strong nitrogen-metal interactions resulting in an outstanding metalsupport for various catalytic applications. Furthermore, their high surface area and tunable chemical functionality are a great benefit for the enhanced adsorption and activation of the reactants.<sup>11</sup> Hexaazatrinaphthylene (HATN) has been extensively used as a scaffold for the fabrication of supramolecular building blocks.<sup>12</sup> The HATN monomer is an extended  $\pi$ -conjugated aromatic ring system of 1,4,5,8,9,12hexaazatriphenylene (HAT), so it is rigid, planar, and an electron-deficient  $\pi$ -system.<sup>13-</sup> <sup>14</sup> They can be prepared by a simple condensation reaction of readily available low-cost chemicals. Because of their outstanding structural and fundamental characteristic features, they have been widely explored not only as a basic scaffold for various applications including photochemistry,<sup>15-17</sup> n-type semiconductors,<sup>18</sup> and electronic devices<sup>19-21</sup> but also as a building block in macromolecular and supramolecular systems.<sup>22-24</sup> Despite the existence of Lewis base sites in the HATN-based porous networks, the HATN-CTFs have only been scarcely explored for the anchoring of metal complexes onto the frameworks. McKeown and co-workers synthesized HATN-based nanoporous networks which were afterwards post-modified with palladium(II)chloride. A high Pd loading in the networks was observed which appeared to be useful as a heterogeneous catalyst.<sup>25</sup> Following this, Wang and co-workers polymerized HATN using AlCl<sub>3</sub> via an ionothermal reaction. The resulting 2D extended nanosheet of microporous graphene polymers (aza-MGP-Al) demonstrated to perform well in the anhydrous proton conduction and in the catalytic cycloaddition of CO<sub>2</sub> with epoxides.<sup>26</sup>

In this chapter, we focus on the potential use of the HATN-CTF as a stable and porous platform for heterogeneous catalysis. The HATN-CTF was utilized as a catalyst support of Cu(OAc)<sub>2</sub>.H<sub>2</sub>O for the Henry reaction of aromatic aldehvdes and nitromethane. The Henry reaction which is also referred to as the nitro-aldol reaction is a classic C-C bond formation reaction in organic chemistry.<sup>27</sup> Essentially, this reaction describes the coupling of a nucleophilic nitro alkane with an electrophilic aldehyde or ketone to produce a highly synthetically useful  $\beta$ -nitro alcohol, which are extensively used reaction intermediates in pharmaceuticals, natural product synthesis and in biocatalytic applications.<sup>28</sup> The synthetic utility of the Henry reaction is based on the versatility of the nitro alcohols, which can be easily converted to intermediates such as nitroalkenes,  $\alpha$ -nitro ketones, and  $\beta$ -amino alcohols.<sup>29-31</sup> These converted products are important precursors of biologically active compounds. Many of these uses have been exemplified in the synthesis of various pharmaceuticals including the HIV protease inhibitors.<sup>32</sup> the antifungal agents efinaconazole and albaconazole.<sup>33</sup> and precursor to the synthesis of methamphetamine, namely phenyl-2-propanone (P2P) and ephedrine/ pseudoephedrine.<sup>34</sup>

### 4.2 Synthesis and methodology

All the chemicals were obtained from commercial sources and were used without further purifications. The Fourier Transform Infrared (FT-IR) spectra were recorded in the region of 800-4000 cm<sup>-1</sup> on a Thermo Nicolet 6700 FT-IR spectrometer equipped with a nitrogen-cooled MCT detector and a KBr beam splitter. Powder X-ray diffraction (PXRD) patterns were collected on a Thermo Scientific ARL X'Tra diffractometer, operated at 40 kV, 30 mA using Cu-K $\alpha$  radiation ( $\lambda = 1.5406$  Å). Elemental analysis (C, H, N, O) were performed on a Thermo Scientific Flash 2000 CHNS-O analyzer equipped with a TCD detector. XPS measurements were carried out on a PHI 5000 Versaprobe II spectrometer equipped with a monochromatic  $Al-K_{\alpha}$  X-ray source (hv = 1486.6 eV) with a beam diameter of 50 µm and operating at 50.9 W. All the survey spectra were recorded at 187.85 eV pass energy and all detailed spectra were obtained at 23.5 eV pass energy with a hemispherical analyzer set at 45° of the sample normal while the pressure in the main chamber was kept below  $1 \times 10^{-6}$ . Multipak (v 9.6.1) software was used for all spectra analysis. After peak fitting the C1s envelope, all spectra were shifted so that the unfactionalized aliphatic C1s component occurs at 285.0 eV binding energy. The metal loading was determined by an ICP-OES Optime 8000 atomic emission spectrometer. Nitrogen adsorption analysis were conducted at 77K on a Belsorp-mini II gas analyzer. All the samples were dried under vacuum at 150 °C for 3h prior measurements. Thermogravimetric analysis (TGA) was performed on a Netzsch STA-449 F3 Jupiter. The sample was heated in a temperature range of 25-800 °C under an air atmosphere at a heating rate of 5 °C/min. The <sup>1</sup>H NMR analysis were performed on a NMR Bruker Advance 300MHz spectrometer using mesitylene as internal standard.

## 4.2.1 Synthesis of Diquinoxalino[2,3-a:2',3'-c]phenazine-2,8,14-tri carbonitrile (HATN)

In a schlenk flask equipped with a stirring bar, hexaketocyclohexane octahydrate (312 mg, 1 mmol) and 3,4- diaminobenzonitrile (532.6 mg, 4 mmol) was added into a dehydrogenated acetic acid (60 mL), which was purged with argon and refluxed for 40h under argon. After cooling down to room temperature, the mixture was poured into water, filtered and washed thoroughly with water to remove the excess of acid and the greenish yellow solid of HATN was collected. The HATN product was then dried under vacuum. No additional purification steps were required (Yield, 82%). <sup>1</sup>H NMR (300 MHz, DMSO  $d_6$ ):  $\delta = 9.28-9.30$  (3H, Ar-H), 8.78-8.82 (3H, Ar-H), 8.48-8.52 (3H, Ar-H).

### 4.2.2 Synthesis of HATN-based CTF

In a typical CTF synthesis, a glass ampoule was charged with HATN (275.4 mg, 0.6 mmol) and anhydrous  $ZnCl_2$  (817.7 mg, 6 mmol) in a glovebox. The ampoule was flame-sealed under vacuum and heated in an oven at 400 °C for 48 h. After cooling down to room temperature, the crude material was ground well, stirred in water for 3 h

and filtered. The resulting solid was subsequently stirred in 1M HCl and THF for overnight, filtered and washed with water and acetone. The black material was dried at 150 °C under vacuum overnight prior to analysis.

### 4.2.3 Post-synthetic metalation of HATN-CTF with Cu(OAc)<sub>2</sub>.H<sub>2</sub>O

The as synthesized HATN-CTF (100 mg) was added to a solution of  $Cu(OAc)_2.H_2O$  (20.0 mg, 0.1 mmol) in 30 mL absolute ethanol and stirred at room temperature for 4 h, filtered and washed with copious amount of ethanol. Finally, the obtained material (named as Cu(@HATN-CTF)) was dried at 90 °C under vacuum prior to use.

### 4.2.4 Synthesis of silica-supported Cu(OAc)<sub>2</sub>.H<sub>2</sub>O

1 g of silica gel (Davisil Grade 635, pore size 60 Å, Sigma-Aldrich) was added to a solution of  $Cu(OAc)_2.H_2O$  (200 mg, 1 mmol) in 10 mL toluene and was allowed to refluxed for 2 h. After cooling down to room temperature, the mixture was filtered, washed with cold toluene, and dried in vacuo at 120 °C prior to analysis.

### 4.2.5 Preparation of [Cu(OAc)<sub>2</sub>@bipy] and [Cu(OAc)<sub>2</sub>@phen]

A solution of 2,2'-bipyridine (424,8 mg, 2.72 mmol) in 10 mL DMF was added to a stirred solution of  $Cu(OAc)_2$ .H<sub>2</sub>O (814.6 mg, 4.08 mmol) in 20 mL DMF. The mixture was allowed to stir for 5 h at room temperature, and then filtered and washed with diethyl ether. The solid product was dried in vacuo at 120 °C for overnight yielded a pale blue powder of [Cu(OAc)\_2@bipy].

The same procedure was applied by using 1,10-phenanthroline for the preparation of [Cu(OAc)<sub>2</sub>@phen].

## 4.2.6 General procedure for the Henry reaction catalyzed by Cu@HATN-CTF

In a typical procedure, a 25 mL Schlenk-tube was charged subsequently with an aldehyde (1 mmol), nitromethane (0.54 ml, 10 mmol), Cu@HATN-CTF (35 mg, 3 mol% of Cu), 2 mL of absolute ethanol and stirred at 70 °C for 12 h. After cooling down to room temperature, the mixture was filtered and the solvents were removed in vacuo. The crude product was dissolved in CDCl<sub>3</sub> and analyzed by <sup>1</sup>H NMR to determine the yield of  $\beta$ -nitroalcohol using mesitylene as an internal standard.

For the recycling experiments, the catalyst was filtered, washed with ethanol and dried at 80 °C under vacuum. Hereafter, the catalyst was subsequently reused following the identical procedure as described above.

#### 4.3 Results and Discussion

#### 4.3.1 Synthesis and characterization

The synthetic strategy for the preparation of the Cu complex functionalized HATNbased CTF is outlined in Scheme 4.1. The diquinoxalino[2,3-a:2',3'-*c*]phenazine-2,8,14-tricarbonitrile, denoted as HATN (1), was prepared by a condensation reaction of hexaketocyclohexane with 4-cyanophenylenediamine in acetic acid under reflux and in the absence of air for 40 h.<sup>35</sup> After thoroughly washing with water to remove the excess of acid, a greenish yellow solid was recovered in a high yield (82%) and characterized by <sup>1</sup>H NMR (Figure B1).

The synthesis of the HATN-based CTF (2) was carried out under ionothermal conditions. Monomer 1 was allowed to polymerize in the presence of  $ZnCl_2$  in a sealed ampule at 400 °C for 48 h. The successful formation of the HATN-CTF material was evaluated by means of Fourier transform infrared spectroscopy (FT-IR) analysis. The disappearance of the intense –CN stretching vibrations at 2240 cm<sup>-1</sup> for the HATN-based CTF material indicates the complete trimerization of the cyano groups of monomer 1 (Figure B2).<sup>36</sup>



Scheme 4.1 Schematic representation of the synthesis of 3, Cu@HATN-CTF

The elemental composition of the synthesized HATN-CTF, determined by Elemental Analysis (EA), revealed lower C, H, and N values in the resulting framework **2** in comparison to the theoretical expected values (Table B1). This difference is likely due to residual water present in the networks as the HATN units have the tendency to form hydrates and interact with water via hydrogen bonding.<sup>25, 37</sup> In addition, it is important

to note that the high synthesis temperature results in 4.9 wt% of reduction in nitrogen content and 3.5 wt% increase of carbon due to a partial decomposition of the nitrile groups and carbonization of the frameworks. This results in an increased C/N ratio compared with theoretical values, which is a common feature observed for CTFs.<sup>38</sup> The powder X-ray diffraction (PXRD) pattern of **2** shows a broad diffraction peak can be assigned to the non-structural ordering of the CTFs (Figure B3). Moreover, the framework **2** exhibits a remarkable thermal stability and only starts to decompose above 450 °C, as examined by thermogravimetric analysis (TGA) (Figure B4).



**Figure 4.1** The nitrogen adsorption isotherms of the HATN-CTF and the Cu@HATN-CTF material

Nitrogen sorption analysis was performed to examine the porosity of the HATN-CTF. As shown in Figure 4.1 (black curve), the HATN-CTF materials present a typical type I isotherm with a steep rise of the N<sub>2</sub> uptakes at low relative pressure (P/P<sub>0</sub> < 0.05), implying the microporous nature of the CTF. The Brunauer-Emmet-Teller (BET) surface area for HATN-CTF is 1684 m<sup>2</sup>g<sup>-1</sup> (Table B2). It is noteworthy that the presented CTF material exhibits a higher BET surface area in comparison to the reported nanoporous network polymers that incorporated HAT and derivatives as the rigid functional building blocks (Table B3).

After post-modification of the framework **2** with  $Cu(OAc)_2.H_2O$  in ethanol at room temperature to obtain Cu@HATN-CTF (**3**), both the BET surface area and the pore volume were decreased to 1301 m<sup>2</sup>g<sup>-1</sup> and 0.51 cm<sup>3</sup>g<sup>-1</sup>, respectively. The Cu loading in the catalyst **3** was determined by ICP-OES measurements and amounts 5.5 wt% (Table B2). The high angle angular dark field scanning transmission electron microscopy (HAADF-STEM) and the corresponding energy dispersive X-ray spectroscopy (EDX) mapping images show a uniform distribution of the Cu complex throughout the HATN-CTF framework with no apparent agglomeration (Figure B5). This result can be supported by the absence of diffraction peaks in the PXRD pattern related to the Cu nanoparticles (Figure B3). However, a significant decrease in the thermal stability of the CTF was observed after the post-modification with the Cu-complex (Figure B4).



**Figure 4.2** XPS high-resolution narrow scan of Cu2p in Cu(OAc)<sub>2</sub> (above) and catalyst **3**, Cu@HATN-CTF (below).

XPS measurements were conducted to obtain insight into the anchoring of the Cu complex onto the HATN-CTF framework. The surface elemental composition of material **2** demonstrated the presence of carbon (285.0 eV), oxygen (532.5 eV), and nitrogen (399.4 eV). Also, copper (933.1 eV) was detected on the surface of Cu@HATN-CTF catalyst. Furthermore, high-resolution narrow scans for Cu2p in the Cu(OAc)<sub>2</sub> and Cu@HATN-CTF were analyzed to obtain information on the electronic state of the Cu atoms. Figure 4.2 shows the deconvolution results of these spectra. One can see that no peaks corresponding to metallic Cu were detected on both samples indicating that atoms were isolated from each other. Moreover, the high-resolution Cu2p peak in the Cu(OAc)<sub>2</sub> showed the spectra form that matches the one for CuO with main peaks at 934.9 eV and 954.7 eV corresponding to Cu2p<sub>3/2</sub> and Cu2p<sub>1/2</sub>

photoelectron transitions respectively which are representative for Cu in +2 oxidation state.<sup>39</sup> Additionally, a shake-up satellite at higher apparent binding energy than the main core level is a characteristic feature of all Cu(II) compounds and is the best indicator of the presence of this oxidation state. However, the binding energies of these transitions obtained for catalyst **3** are 933.2 eV and 953.0 eV, respectively. The latter can be distinguished as signals from Cu(I) state. Hence, these results indicate the electronic modifications of Cu(II) as a main component (more than 76%) of Cu(OAc)<sub>2</sub> into Cu(I) (more than 88%) in the final catalyst **3** after anchoring on the HATN-CTF.

As this result was very surprising, we decided to create some other Cu(II)based catalysts. We grafted the Cu(OAc)<sub>2</sub>.H<sub>2</sub>O on a silica gel support and created also two Cu(II)-complexes by reacting the Cu(OAc)<sub>2</sub>.H<sub>2</sub>O with phenanthroline and bipyridine. Figure 4.3 shows an overlay of Cu2p spectra for Cu(OAc)<sub>2</sub>@SiO<sub>2</sub>, Cu(OAc)2@phenanthroline (Cu(OAc)<sub>2</sub>@phen), and Cu(OAc)<sub>2</sub>@bipyridine (Cu(OAc)<sub>2</sub>@bipy). The Cu2p spectrum for Cu(OAc)<sub>2</sub>@bipy has the most features from Cu(II) structure which engages approximately 79% from all detected copper. However, Cu(OAc)<sub>2</sub>@phen has a well-recognizable shoulder peak around 932 eV which proves the presence of Cu(I) component (around 39%). Cu(OAc)<sub>2</sub>@bipy also has a similar spectrum shape but it is less obvious for this sample. The maximum of the  $Cu2p_{3/2}$  is shifted to a lower binding energy for the Cu(OAc)<sub>2</sub>@silica sample since this spectrum contains compound at 933.6 eV binding energy which corresponds to CuSi (about 38%).<sup>40</sup> We believe that the observation of Cu(I) species, is mainly due to the high vacuum that is used in XPS measurement, which is known to reduce transition metal ions, such as V(V) and Cu(II).<sup>41-43</sup> We also measured the bulk Cu(OAc)<sub>2</sub> and observed 76.2% of Cu(II) and 23.8% of Cu(I). This compound is also reduced, but to a lesser extend than the highly dispersed Cu-sites on the HATN-CTF. Detailed information and XPS spectra for each sample can be found in the Appendix B.



**Figure 4.3** Cu2p spectra for Cu(OAc)<sub>2</sub>+ silica, Cu(OAc)<sub>2</sub>@phenanthroline (Cu(OAc)<sub>2</sub>+ phen), and Cu(OAc)<sub>2</sub>@bipyridine (Cu(OAc)<sub>2</sub>+ bpy).

## 4.3.2 Evaluation of the catalytic performance of the Cu@HATN-CTF in the Henry reaction

The Henry reaction or nitro-aldol reaction is a powerful and versatile method for a C-C coupling reaction between aldehydes and alkyl-nitro compounds to produce  $\beta$ -nitro alcohols, which are of great interest for the synthetic chemistry.<sup>28</sup> The transition metal catalyzed Henry reaction is the most attractive and powerful method for the synthesis of pure nitro alcohol compounds ensuring a high control on the selectivity and activity under mild reaction conditions.<sup>44</sup> Among the examined transition metal-based catalysts, e.g., Zn,<sup>45-46</sup> Pd,<sup>47</sup> Cr,<sup>48</sup> Co,<sup>49</sup> Cd,<sup>50</sup> and Mn,<sup>51</sup> the Cu-catalyzed Henry reaction has emerged as a promising catalyst because of its non-toxic nature and low-cost.<sup>52-53</sup> Moreover, the activity and selectivity of the Henry reaction can be tailored by varying the supports of the Cu catalysts.<sup>54</sup> In general, the Henry reaction involves the addition of a nitronate ion, which can be generated upon the deprotonation of a nitroalkane with an external base, to a carbonyl compound.<sup>28</sup> According to the reaction mechanism proposed by Downey et al.<sup>54</sup> the weak Lewis acidic metal complex bearing a moderate basic charged counter anion would facilitate the generation of nitronate species. As can be seen from Table 4.1, the homogeneously dissolved Cu(OAc)<sub>2</sub>.H<sub>2</sub>O complex can catalyze the Henry reaction of *p*-nitrobenzaldehyde with nitromethane, but only 28% yield was obtained under the aforementioned optimized reaction conditions (Table 4.1, Entry 1).

**Table 4.1** Control experiments of the Henry reaction of *p*-nitrobenzaldehyde and nitromethane catalyzed by  $Cu(OAc)_2.H_2O^a$ 

	$R \xrightarrow{II} H \xrightarrow{3 \text{ mol}\% \text{ Cu cat.}}_{\text{CH}_3\text{NO}_2} R \xrightarrow{II}_{\text{U}}$ EtOH, 70 °C, 12h	
Entry	Catalyst	Yield $(\%)^b$
1	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	28
2	Blank	0
3	HATN-CTF	0
4	$Cu(OAc)_2.H_2O + HATN-CTF$	19
5	Cu@HATN-CTF	94
6	$Cu(OAc)_2.H_2O + 1,10$ -phenanthroline	95

<sup>*a*</sup>Reaction conditions: 3 mol% Cu catalyst, p-nitrobenzaldehyde (1 mmol), nitromethane (10 mmol), 2 mL ethanol, 70 °C, 12 h. <sup>*b*</sup>Determined by <sup>1</sup>H NMR analysis

The intrinsic nature of the Cu(OAc)<sub>2</sub>.H<sub>2</sub>O complex comprises a basic anion to carry out the nitro-aldol process, where the acetate ion acts as a weak base for the deprotonation of nitromethane.<sup>54-55</sup> However, the desired product yield cannot be significantly improved even after prolonged reaction time, which is similar to the reported studies.<sup>55-</sup> <sup>56</sup> In addition, no detectable product was obtained in the absence of the Cu catalyst, and in the presence of only the HATN-CTF (Table 4.1, Entry 2 and 3), and a physical mixture of Cu(OAc)<sub>2</sub>.H<sub>2</sub>O and HATN-CTF produced a very low yield as well (Table 4.1, Entry 4). The heterogeneous catalyst on the other hand (Cu(OAc)<sub>2</sub>.H<sub>2</sub>O grafted onto HATN-CTF with the same amount of Cu-sites as in the other cases) yielded 94% of the end product (Table 4.1, Entry 5). This catalyst is therefore much more active than its homogeneous counterpart.<sup>57-58</sup> The reason for the increased activity lies in the geometry of the complex. Cu(OAc)<sub>2</sub>.H<sub>2</sub>O occurs always as a dimer (see Figure 4.4(a)), having the typical paddle-wheel structure of Cu-oxo-sites. Upon grafting, the complex loses its dimer-configuration and appears as a monomer that is highly approachable (Figure 4.4(b)). In order to confirm this hypotheses, we have synthesized the 1,10phenanthroline complex of Cu(II), which has a similar configuration as the grafted complex (Figure 4.4(c)).<sup>59</sup> This catalyst also yielded 95% of end product, using the same conditions as the heterogeneous catalyst (Table 4.1, Entry 6). Following the mechanism proposed by Downey et al.,<sup>54</sup> the  $Cu(OAc)_2(a)$  phen catalyst formed here is very proficient in the Henry reaction (see Scheme 4. 2).



**Figure 4.4** Paddlewheel structure of (a)[Cu(OAc)<sub>2</sub>.H<sub>2</sub>O]<sub>2</sub>, (b) Cu@HATN-CTF, and (c) Cu(OAc)<sub>2</sub>@phen



Scheme 4.2 A probable mechanism for the Henry reaction.<sup>54, 60</sup>

The high yield for the  $\beta$ -nitro alcohol prompted us to investigate a series of substituted aromatic aldehydes for Henry reaction with nitromethane. The corresponding  $\beta$ -nitro alcohol was obtained in moderate to excellent yields ranging from 34% to 95% (Table 4.2). From this study, it can be observed that the substituent of the aromatic aldehydes has a pronounced effect on the product yield. More specifically, the aromatic aldehydes bearing electron-withdrawing groups exhibit a higher activity than those having electron-donating groups. For example, *p*-nitrobenzaldehyde afforded a yield of 94% in comparison to *p*-methoxybenzaldehyde for which only a 34% of yield was observed towards the  $\beta$ -nitro alcohol under similar reaction conditions (Table 4.2, Entry 1 and 4). The presence of the withdrawing group on the aromatic aldehydes enhances the electrophilic nature, which favor the Henry reaction and resultantly afford higher yields.<sup>61-62</sup>

Entry	Aldehyde	Product	Yield $(\%)^b$
1	O <sub>2</sub> N H	OH NO <sub>2</sub>	94 (± 2.08 <sup>c</sup> )
2	O H	OH NO <sub>2</sub>	68
3	ОН	OH NO <sub>2</sub>	60
4	MeO H	OH NO <sub>2</sub> MeO	34
5	CI H	OH NO <sub>2</sub>	83
6	F H	OH NO <sub>2</sub>	85
7	O H N	OH NO <sub>2</sub>	82
8	НО	OH NO <sub>2</sub>	50
9			60

**Table 4.2** The Henry reaction of aromatic aldehydes and nitromethane catalyzed by  $3^{a}$ 

<sup>*a*</sup>Reaction conditions: 3 mol% catalyst, aldehyde (1 mmol), nitromethane (1 mmol), 2 mL EtOH, 70 °C,12 h. <sup>*b*</sup>Determined by <sup>1</sup>H NMR analysis <sup>*c*</sup>Standard deviation

Catalyst	Reaction conditions	Yield (%)	TON / TOF( <sup>h-1</sup> )	Ref.
Cu@HATN-CTF	3 mol% cat./ EtOH/ 70 °C/ 12h	94	63/22.3	This study
CCOF-TpTab-Cu	20 mol% cat. / mesitylene/ DIEA/ -10 °C/ 48h	90	-	[63]
[Cu <sub>3</sub> (pdtc)L <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> .2DMF.10H <sub>2</sub> O	10 mol% cat./ solvent free/ 70 °C/ 36h	85	-	[55]
Cu-BTC H-MOFs	10 mol% cat./ solvent free/ 70 °C/ 24h	45	-	[64]
$[Cu_2(L)(H_2O)_2].(3DMF)(4H_2O)]_n$	5 mol% cat./ solvent free/ 50 °C/ 48h	89	-	[62]
$[Cu(L)_2]_n.4n(DMF).n(H_2O)$	3 mol%/ H <sub>2</sub> O/ 70 °C/ 48h	90	30/ -	[65]
$[Cu_4(HL_{ala})_2(H_2O)_4(MeO)_4]n$	3 mol%/ MeOH/ 70 °C/ 24h	95	32/ -	[66]

**Table 4.3** The Henry reaction catalyzed by reported heterogeneous Cu-based porous frameworks catalysts

From the presented results, it can be seen that the catalyst **3** efficiently catalyzes the Henry reaction with excellent yields in the absence of an external base, which is usually required to accelerate the Henry reaction.<sup>47, 63</sup> The strong basic properties of HATN-CTF in catalyst **3** makes the Cu ion more acidic, which results in a better activation of the coordinated aldehyde towards the attack of nitronate ions. Moreover, the turn-over number (TON) and turn-over frequency (TOF) of the catalyst under the optimized catalytic conditions are 63 and 22.3 h<sup>-1</sup>, respectively, outperforming most of the reported Cu-based porous polymers for the Henry reaction (Table 4.3).



**Figure 4.5** Hot filtration experiment of Cu@HATN-CTF for the Henry reaction of *p*-nitrobenzaldehyde with nitromethane

A hot filtration test was carried out to examine the heterogeneous nature of the catalyst **3**. As can be seen from Figure 4.5, no further reaction occurred upon removal of the catalyst, which clearly demonstrate the heterogeneous nature of our catalyst. In addition, the catalyst **3** was recovered by filtration and subsequently used in eight successive cycles without a significant reduction in the catalytic performance (Figure 4.6). The ICP-OES analysis of the catalyst after catalysis showed the presence of a 5.39 wt% amount of Cu suggesting no significant leaching during the course of the reaction.



**Figure 4.6** Recycling experiments of the Cu@HATN-CTF catalyst for the Henry reaction of *p*-nitrobenzaldehyde with nitromethane under the optimized reaction conditions

#### **4.4 Conclusions**

The nitrogen-rich hexaazatrinaphthylene-based covalent triazine framework (HATN-CTF) was successfully synthesized and functionalized with Cu(OAc)<sub>2</sub>.H<sub>2</sub>O to be utilized as a heterogeneous catalyst in the Henry reaction of aromatic aldehydes and nitromethane. XPS analysis observed the presence of both Cu(I) and Cu(II) in the Cu@HATN-CTF material. The Cu@HATN-CTF catalyst exhibits an excellent catalytic performance in the Henry reaction with a high stability and recyclability. Overall, the results demonstrate the potential use of the HATN-CTF material as catalyst support providing a high loading of accessible active sites.

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# 5 Conclusions and Outlook

Covalent triazine frameworks (CTFs) are nitrogen containing organic frameworks having a well-defined pore structure and controllable surface chemistry. These materials possess excellent properties and have gained extensive attention for various applications, including gas storage and sorption, molecular separation, and heterogeneous catalysis. In this dissertation, we present the use of CTFs as a promising platform for the deployment of heterogeneous catalysts. The main interesting features of CTFs compared to other porous organic frameworks are their extraordinary thermal stability as well as high acid-base resistance which allow applications under a broad range of conditions. Secondly, they exhibit a high surface area and porosity. High surface areas have always been the fascinating characteristic of porous materials that provides open space to accommodate guest molecules. For catalytic applications, surface area and pore size play a significant role in terms of mass transfer and eventually the overall catalytic activity. The most significant advantages of CTFs are the well-defined nitrogen components in their triazine units and ease of functionalization of the organic ligand so that various catalytic functions can be obtained merely by changing the active metal species. In this context, introducing a N-heterocyclic based organic ligand such as 2,2'bipyridine and 1,10-phenanthroline into the framework provides robust binding sites for metal complexes. In this thesis, we employed the bipyridine-based CTF (bipyCTF) for the anchoring of an Ir(I)-complex towards the development of a highly stable and efficient catalyst for the C-H borylation of aromatic compounds. We also designed a nitrogen-rich CTF, denoted as hexaazatrinaphthylene-based CTF (HATN-CTF), to be used as a basic catalytic support for Cu-catalyzed Henry reaction.

In the first presented work, the synthesized Ir(I)@bipyCTF catalyst exhibited excellent catalytic activity for C-H borylation of arenes and heteroarenes in the presence of B<sub>2</sub>Pin<sub>2</sub> as a boron source. This catalyst also exhibits high stability and reusability for at least five cycles without significant loss of activity. Physical characterizations combined with density functional theory (DFT) calculations elucidated the local geometry of the immobilized Ir(I)-complex onto the bipyridine moieties in the framework. A similar coordination environment in comparison to its homogeneous counterpart was observed. More importantly, this Ir(I)@bipyCTF also showed a similar catalytic trend as the homogeneous Ir-based catalyst and exhibited a better performance than the conventional Ir-based heterogeneous catalysts. In the second work, we synthesized and functionalized the nitrogen-rich HATN-CTF with a Cu(OAc)<sub>2</sub>.H<sub>2</sub>O complex and used it for the Henry reaction of aromatic aldehydes and nitromethane. Characterization of the catalyst by XPS analysis showed the presence of Cu species in the Cu@HATN-CTF material. This study demonstrated the potential of the HATN-CTF to function as a Lewis basic material for the immobilization of Cu-complexes that enhanced the catalytic activity and resulted in higher yields.

CTFs offer a number of advantages in comparison to conventional porous solid catalysts such as metal-organic frameworks (MOFs) or zeolites for the challenges we are facing nowadays in the intensification of catalytic processes. While the applications highlighted in this thesis demonstrate the tremendous potential of this emerging field, there are still several challenges that need to be addressed in order to move it from an academic curiosity to a widely applicable tool for organic synthesis and chemical production. The synthesis of CTFs often require harsh reaction conditions, resulting in porous materials with an amorphous character. This makes the use of standard spectroscopic techniques for the characterization of their structural and chemical properties extremely challenging. Hence, extensive characterization methods are required, for example, XAS, XPS, and solid-state NMR to provide more valuable details on the structural properties and the guest molecules located within the framework of these materials.

Towards the future implementation of these materials, it would be useful to develop computational models that can provide insights into the structural design and functionalization. The combination of new synthetic approaches and computational modeling have resulted already in interesting contributions to the chemistry of CTFs having well-defined pore structures and controlled dispersion of a variety of functional groups. Despite the simple conceptual idea of heterogeneous organometallic catalysts, there are significant differences in the catalytic activity and distribution of the catalytic species between metal-based CTFs and the analogous homogeneous counterparts. In general, a better understanding of the catalytic process using metal-based CTF catalysts as well as the differences and potential advantages compared to the analogous homogeneous systems is needed. In this regard, it is also essential to be able to distinguish the formation of discrete metal-ligand-CTF complexes versus much less defined catalysts in which the metal ions are randomly distributed at different types of ligand sites on a CTF support. These points could be addressed during the elucidation of the reaction mechanism and by a thorough characterization of the metal-based CTF catalysts. From an industrial point of view, significant advantages in heterogeneous catalytic systems are required. A straightforward comparison can be made based on the TON and TOF numbers of several heterogeneous catalysts in comparison to the corresponding homogeneous catalyst. For the large-scale production of bulk chemicals, continuous-flow reactors are typically preferred over batch reactors. Due to the immobilized nature of the metal complexes in the CTF materials, they could be wellsuited for such an application. However, the number of reports are still scarce.

Covalent Triazine Frameworks as Support for Heterogeneous Catalysis
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# 6 Appendices

## Appendix A: Supporting Information for Chapter 3

## Characterization data

**Table A1.** Comparison of the experimental and theoretical elemental composition of bipyCTF

	Elemental Analysis (%)			
	С	Η	Ν	C/N
calc.	67.34	2.59	30.22	2.23
bipyCTF	65.27	3.01	22.53	2.90

Table A2.	Physical parameters of bipyCTF and Ir(I)@bipyCTF

CTF	Ir loading (wt%)	Specific Surface area (m <sup>2</sup> /g)	BET (m <sup>2</sup> /g)	Total pore volume (cm <sup>3</sup> /g)
BipyCTF	-	1100	714	0.39
Ir(I)@bipyCTF	8.26	747	494	0.27

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**Figure A1.** <sup>1</sup>H NMR spectrum of 2,2'-bipyridine-5,5'-dicarbonitrile



Figure A2. <sup>13</sup>C NMR spectrum of 2,2'-bipyridine-5,5'-dicarbonitrile



Figure A3. FT-IR spectra of 2,2'-bipyridine-5,5'-dicarbonitrile and bipyCTF



Figure A4. X-Ray powder diffraction pattern of the bipyCTF



**Figure A5.** TGA curve of the studied bipyCTF measured at a heating of 5 K/min under an air flow



**Figure A6**. HAADF-STEM and corresponding EDX mapping images of carbon (blue), nitrogen (green), and iridium (red) for the sample of Ir(I)@bipyCTF material

### **Bipyridine dissociation**

Density functional theory (DFT) calculations have been performed to assess the possibility of 2,2'-bipyridine (bipy) to be deprotonated in conditions similar to those found in the Ir(I) anchoring environment, which contains  $-OCH_3$ . The computed deprotonation energies of bipy lie in the interval between -1648 kJ/mole and -1690 kJ/mole, with respect to a computed value of -1628 kJ/mole of methanol. The range of values for bipy is due to the specific proton dissociation and the syn / anti conformations of the molecule. Instead, when bipy is embedded into a structure used to mimic the CTF, the deprotonation energies range between -1545 and -1584 kJ/mole, as shown in more detail in Figure A7.



**Figure A7.** Deprotonation energies of bipy embedded into part of the CTF, in kJ/mol. Both syn and anti conformers are reported.

Hirshfeld partial charges show that in bipy the average C-H charge separation is  $\Delta q \approx 0.2 |e|$ , with |e| being the proton charge.<sup>1</sup> Instead, in the structures shown in Figure A7, the average C-H charge separation is  $\Delta q \approx 0.4 |e|$ , thus suggesting that the increased  $\Delta q$  value makes the C-H bond more ionic (i.e. less covalent) and less stable, which in turn allows an easier deprotonation. This is in agreement with the lower deprotonation energies.

#### **Anchoring models geometries**

In Table A3 some selected inter-atomic distances of Ir(I) are reported in Å for the three models after geometry relaxation.

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distances /Å	1	2	3
Ir N	2.22	2.12	2.13
Ir C (COD)	2.13	2.18	2.17
Ir C (bpy)	>3	2.04	2.06
Ir 0	2.06	2.59	2.47

**Table A3.** Interatomic distances in Å for the models reported in Figure 3.3

Since in model 1 the aromatic rings of bipy are not deprotonated, the Ir...C(bipy) distance is larger than 3 Å. It has to be pinpointed that in models 2 and 3 the Ir...O<sub>methanol</sub> distance is rather large (>2.5 Å), whereas the Ir...O<sub>methoxy</sub> distance in model 1 is reasonably smaller ( $\leq 2.1$  Å), as expected due to the increased electrostatic attraction between two charged species.

## Data regarding the stabilization energies

For the stabilization energies of models 1, 2, and 3, the free energy difference can be computed as;

 $\Delta G = G[model] - G[Ir(I)-cod] - G[OCH_3/methanol] - G[protonated/ deprotonated triazine-bipy-triazine]$ 

With,

G[model 1] = -1583.925185 Hartree

G[model 2] = -1583.425999 Hartree

G[model 3] = -1583.424025 Hartree

G[Ir(I)-cod] = -416.106448 Hartree

G[methanol] = -115.612492 Hartree

 $G[^{-}OCH_{3}] = -115.086518$  Hartree

G[syn triazine-bipy-triazine] = -1052.562982 Hartree

G[deprotonated syn triazine-bipy-triazine] = -1052.011444 Hartree

G[deprotonated anti triazine-bipy-triazine] = 1052.061754 Hartree

So we obtain

 $\Delta G(\text{model 1})=$  -0.169237 Hartree,  $\Delta G(\text{model 2})=$  -0.157772 Hartree,  $\Delta G(\text{model 3})=$  -0.166971 Hartree.

For the formal reaction between the [A.2] and [B.2] compounds

 $[A.2] + [bpy syn \rightarrow anti isomerization] + [bpy ring deprotonation] - [BPin] \rightarrow [B.2]$ 

we have the free energy difference  $\Delta G$  computed as in the following

 $\Delta G = G[B.2] - G[A.2] - G[bpy syn \rightarrow anti isomerization] - G[bpy deprotonation] + G[BPin]$ 

With,

G[B.2] = -1977.762176 Hartree G[A.2] = -2388.678711 Hartree  $G[bipy syn \rightarrow anti \text{ isomerization}] = -0.05031 \text{ Hartree}$  G[bipy deprotonation] = 0.215502 Hartree G[BPin] = -410.710839 HartreeSo we obtain

 $\Delta G = +0.040504$  Hartree = +106 kJ/mole



Figure A8. Possible intermediate Ir(III) complexes formation after treatment with  $B_2Pin_2$  and their optimized structures in square brackets on the right



Figure A9. Hot filtration experiment of Ir(I)@bipyCTF (red dotted line)

#### X-ray Absorption Spectroscopy (XAS) Analysis

XAS experiments were performed at the BM26A DUBBLE CRG beamline at the ESRF (Grenoble, France), utilizing a 0.4 T bending magnet. A narrow energy bandwith of dE/E of approximately  $10^{-4}$  was selected using a Si(111) monochromator, over the Ir L<sub>3</sub> edge (E<sub>0</sub>: 11.215 keV). The monochromator energy was calibrated using a metallic Pt foil and scanning over the L<sub>3</sub> edge (E<sub>0</sub>: 11.564 keV). A X-ray beam spot size of  $3 \times 0.5$  mm<sup>2</sup> at the sample position was used. The incident beam flux was monitored using a gas ionisation chamber, filled with 10% Ar and 90% He at 1 bar, resulting in approximately 9% absorption around the Ir L<sub>3</sub> edge. A second ionisation chamber was used for transmission mode experiments, filled with 60% Ar and 40% He, resulting in approximately 50% X-ray absorption at these energies.

An in-situ reaction cell, consisting of an inert Teflon canister, closed off by two  $25\mu$ m Kapton windows, was heated by a heat gun positioned at approximately 5 cm distance from the sample container. The heat gun temperature was set at 90 °C, resulting in a sample temperature of 70 °C. Beam induced changes were checked for by performing a series of fast, repetitive XANES scans over the reference materials. As no change in XANES profile was monitored as a function of measurement time, it was concluded no beam induced effects were monitored.

X-ray absorption near edge spectroscopy (XANES) was performed according to the following energy range: 11.115 keV to 11.172 keV in 3eV steps, 11.175 keV to 11.1918 keV in gradually decreasing steps from 3 to 1 eV, 11.193 keV to 11.238 keV in 1 eV steps and from 11.2399 keV to 11.365 in 0.05 Å<sup>-1</sup> steps, using an acquisition time of 1 s/step (approximately 2 minutes/scan). XANES data were normalised by pre-edge subtraction and normalising the edge step to 1 at an energy  $E_0+50$  eV. In-situ spectra

were compared to the spectra obtained from a reference sample before catalysis (BC) and after catalysis (AC) by means of linear combination analysis.

Extended X-ray absorption spectroscopy fine structure (EXAFS) measurements were performed using an energy range as described for the XANES experiments, except that the last energy range was measured up to wavenumber k 14. Several scans were performed, depending on the sample composition, to improve data quality. EXAFS data were processed using the Viper data processing program, and fit in R-space (Real + Imaginary, R 1-2Å) using theoretical amplitudes and phases as calculated by FEFF7.<sup>2-3</sup>



**Figure A10**. Ir-L<sub>3</sub> edge XANES spectra of the Ir(I)bipyCTF before and after catalytic run (1.5 mol% Ir, 1,2-dichlorobenzene, heptane, 90 °C, 8 h)



**Figure A11**. In-situ Ir  $L_3$ -edge XANES white line intensity as a function of reaction time during the catalysis

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10.0 9.8 9.6 9.4 9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 fl (ppm)

Figure B1. <sup>1</sup>H NMR spectra of HATN



Figure B2. FT-IR spectra of HATN precursor and HATN-based CTF



Figure B3. Powder X-ray diffraction patterns of HATN-CTF and Cu@HATN-CTF



**Figure B4.** TGA curves of HATN-CTF and Cu@HATN-CTF measured at a heating rate of 5 K/min under an air flow



**Figure B5.** HAADF-STEM images and corresponding EDX mapping images of carbon (blue), copper (red), and nitrogen (green) of the Cu@HATN-CTF material



Figure B6. XPS high-resolution narrow scan of Cu2p in Cu(OAc)<sub>2</sub>@SiO<sub>2</sub>



Figure B7. XPS high-resolution narrow scan of C1s in Cu(OAc)<sub>2</sub>@phen.



Figure B8. XPS high-resolution narrow scan of Cu2p in Cu(OAc)<sub>2</sub>@phen.



Figure B9. XPS high-resolution narrow scan of N1s in Cu(OAc)<sub>2</sub>@phen.



Figure B10. XPS high-resolution narrow scan of C1s in Cu(OAc)<sub>2</sub>@bipy.



Figure B11. XPS high-resolution narrow scan of Cu2p in Cu(OAc)<sub>2</sub>@bipy.



Figure B12. XPS high-resolution narrow scan of N1s in Cu(OAc)<sub>2</sub>@bipy.



**Figure B13.** O KLL spectra for all tested samples. In both samples with silica and Cu+silica, oxygen is mainly present in SiO<sub>2</sub> structure which results similar spectra. The main source of oxygen for both Cu(OAc)<sub>2</sub>+phen and Cu(OAc)<sub>2</sub>+bipy is Cu(OAc)<sub>2</sub> complex which explains the similarity in these two spectra.

Sample .		Elemental a	analysis (%)	
	С	Н	Ν	C/N
Ana. Calculated	68.03	3.11	28.85	2.36
HATN-CTF	53.23	3.41	17.75	3.00

Table B1. Elemental composition of calculated and experimental values of HATN-CTF

 Table B2. Physical parameters of the HATN-CTF and Cu@HATN-CTF material

	Metal loading	S <sub>BET</sub>	$V_p$
Samples	(mmol/g)	(m <sup>2</sup> /g)	(cm <sup>3</sup> /g)
HATN-CTF	0	1684	0.79
Cu@HATN-CTF	0.87 (5.5 wt%)	1301	0.51

Polymer	$S_{BET}$ (m <sup>2</sup> /g)	$V_p (\mathrm{cm}^3/\mathrm{g})$	Ref.
HATN-CTF	1684	0.79	This study
HAT-based HOF (CPHAT)	1288	-	S1
HATN-based POP (HATNPF)	384	0.27	S2
HATN-CMP	616	0.63	<b>S</b> 3
Aza-MGP-Al	1530	0.68	S4
HOTT-HATN	527	0.58	S5
HATN-based network	775	<u>_</u>	86
polymer	115		50

 Table B3. BET surface area and total pore volume of reported HAT-based porous

 organic polymers

 Table B4.
 Elemental composition of both HATN-CTF and Cu@HATN-CTF

 determined by XPS

Sample	Elemental composition (%)			
	С	Ν	0	Cu
HATN-CTF	91.64 ± 0.37	$7.75 \pm 0.55$	$0.61 \pm 0.35$	-
Cu@HATN-CTF	88.77 ± 0.19	8.76 ± 0.36	$1.05 \pm 0.27$	$1.42 \pm 0.11$

**Table B5.** Optimization of the Henry reaction of p-nitrobenzaldehyde withnitromethane catalyzed by Cu@HATN-CTF<sup>a</sup>

Aldehyde:CH <sub>3</sub> NO <sub>2</sub>				
ratio	Amount of catalyst	Solvent	<i>T</i> (°C)	Yield (%) <sup>b</sup>
1:10	1 mol%	EtOH	70	85
1:10	3 mol%	EtOH	70	94
1:10	5 mol%	EtOH	70	91
1:10	10 mol%	EtOH	70	80
1:10	3 mol%	dH <sub>2</sub> O	70	33
1:10	3 mol%	THF	70	37
1:10	3 mol%	CH3CN	70	22
1:10	3 mol%	Isopropanol	70	62
neat	3 mol%	neat	70	38
1:1	3 mol%	EtOH	70	62
1:5	3 mol%	EtOH	70	88
1:10	3 mol%	EtOH	RT	29
1:10	3 mol%	EtOH	50	55
1:10	3 mol%	EtOH	90	87
1:10	CuCl <sub>2</sub> @HATN-CTF (3 mol% Cu)	EtOH	70	0

<sup>*a*</sup>Reaction conditions: Cu@HATN-CTF (3 mol%), *p*-nitrobenzaldehyde (1 mmol), nitromethane (10 mmol), and solvent (2.0 mL) were stirred for 12 h. <sup>*b*</sup>Yield was determined by <sup>1</sup>H NMR analysis

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