STATEMENT

I hereby declare that the matter presented in this dissertation entitled "**Palladium immobilized heteroporous metal organic framework for Suzuki-Miyaura coupling reaction** " is based on the result of investigations carried out by me in the School of Chemical Sciences, Goa University under the supervision of Dr. Sandeep Kumar Dey and the same has not been submitted elsewhere for the award of degree or diploma.

Ms. Rowena Mary Almeida

CH-18-02

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CERTIFICATE

This is to certify that the dissertation entitled “**Palladium immobilized heteroporous metal organic framework for Suzuki-Miyaura coupling reaction”** is an original research work carried out by Ms. Rowena Mary Almeida under the supervision of Dr. Sandeep Kumar Dey in partial fulfilment of the requirements for the award of the degree of Master of Science in Physical Chemistry, Goa University.

Dean

School of Chemical Sciences

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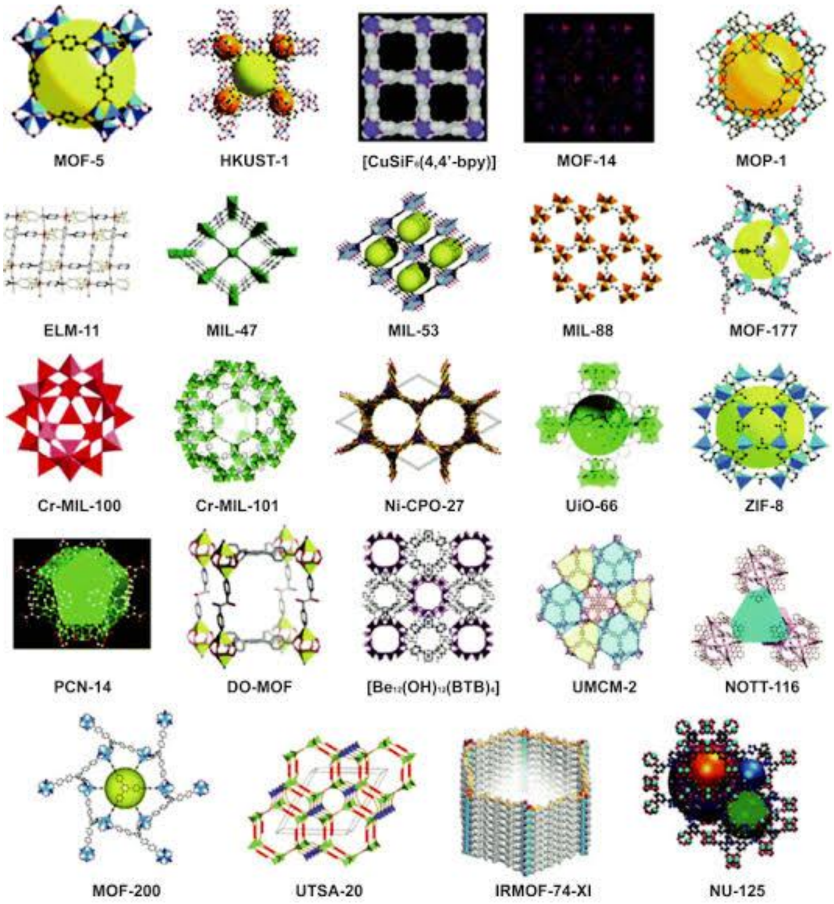
I would like to thank God above all for his blessings during this course.

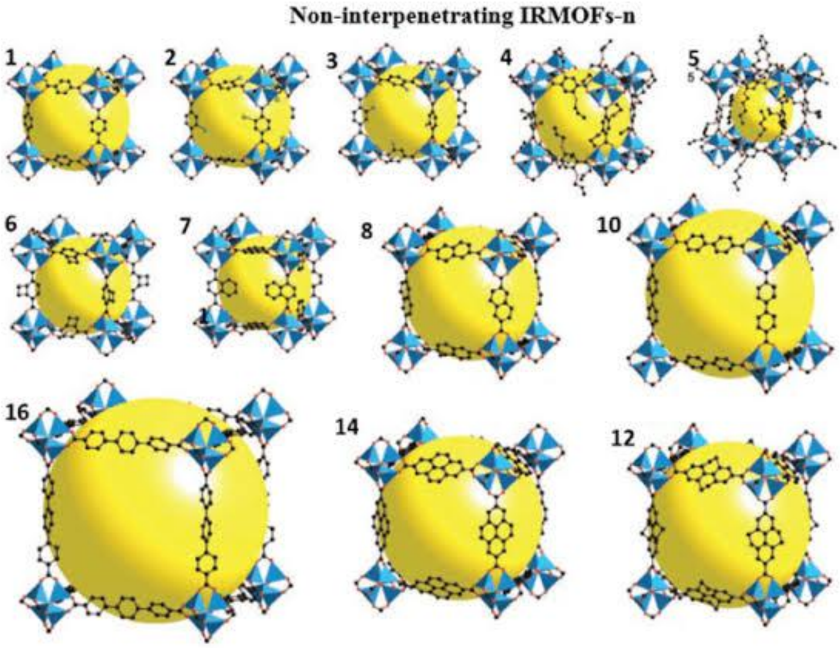
Last but not the least I would like to thank all my friends who in some way or the other helped me to complete my dissertation.

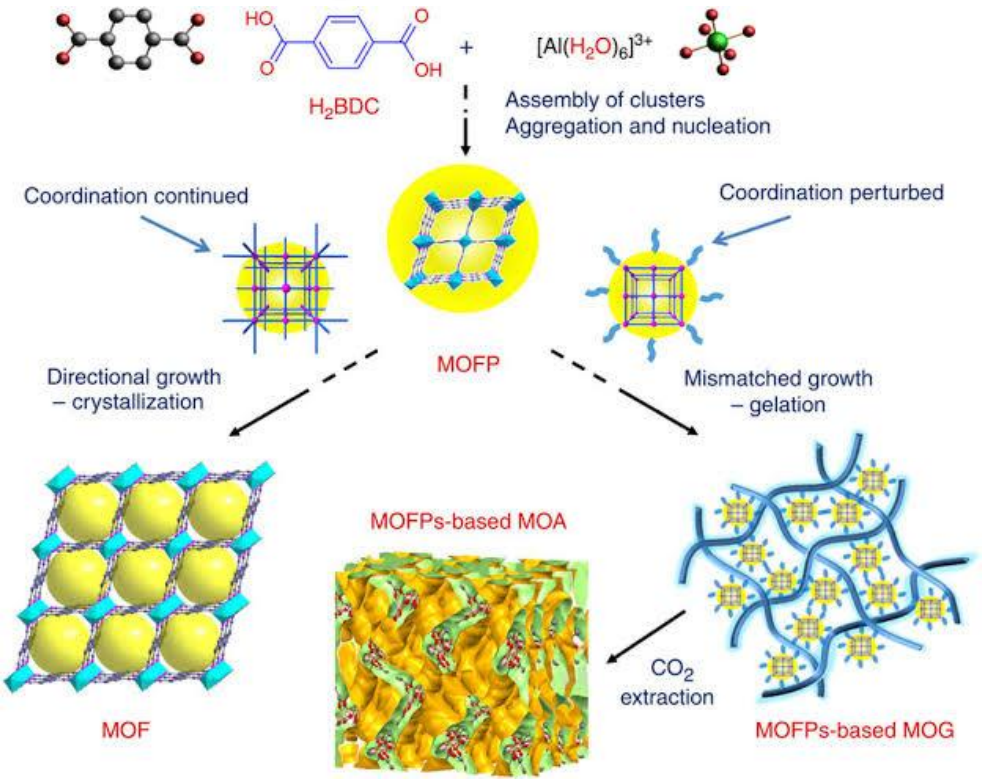
1. Introduction

Metal organic frameworks (MOFs) have emerged as an important class of crystalline materials with ultra high porosity with enormous internal surface areas. On a fundamental level, MOFs epitomize the beauty of internal structures and the power of combining organic and inorganic chemistry, two disciplines often regarded as disparate. [11]

Metal organic frameworks consist of two major components, a metal ion or a cluster of metal ions and an organic molecule called a linker. Transition metals are mostly used in the synthesis of MOFs. The organic units are typically di, tri, tetra and hexa-carboxylates, imidazolates, dipyridyls ligands. The choice of metal and linker has significant effects on structure and properties of MOFs. For example, metal coordination preference influences the size and shape of pores by dictating how many ligands can bind to the metal and in which orientation. For the organic linker, there are a wide variety of choices as well. Ligands with rigid backbones are often preferred, because the rigidity makes it easier to predict the network geometry in advance of synthesis, and in addition the rigidity also helps to sustain the open-pore structure after the removal of the included solvent. The linkers can be electrically neutral, anionic or cationic. MOFs offer unique structural diversity in contrast to other porous materials uniform pore structures, atomic level structural uniformity, tunable porosity, extensive varieties and flexible in network topology, geometry, dimension, and chemical functionality. This allows researchers the successful control of framework topology, porosity and functionality. Their signature property is the ultra high porosity which however imparts challenges when it comes to both constructing and working with them. In principle construction of porous coordination polymers is as simple as choosing a combination of a ligand with more than one binding site that can chelate and the metal center which has various coordination sites for the incoming ligand so as to give rise to a structure with extensive porous network. If the ligand is large enough, cavities will be left between the metal nodes and the metal ligand interactions are often strong and non-labile, such strong interactions arise as the orbital of the ligand overlaps with the appropriate orbital of the metal. In such cases product deposits in the form of amorphous powders and kinetic products of irregular structure such problems can be overcome partially by use of diffusion, solvothermal, gel permeation and crystal growth technique. It is also essential to note that the geometry of the metal ligand interactions is always not easy to predict and even if pore structure is generated there is no guarantee that the pores will be accessible to guest molecules from outside the crystals via access channels. However, there is possibility that carefully designed pores may end up being filled by interpenetration of structures instead of guest molecules. Inspite of these drawbacks, a great progress has been made specifically in designing such pore solids. Their highly ordered structures combined with exceptional surface area endow them with potential as attractive for a slew of applications ranging from hydrogen storage, gas separation, carbon capture to catalysis, sensing and light harvesting. MOFs reported to date are mostly microporous (pore size < 2nm) and mesoporous (pore size 2-20 nm). Such small pores can restrict diffusion of gases and reactive species and prevent large molecules from accessing the active metal centers with the bulk of MOFs, thus limiting their applications. To expand pore widths of MOFs, ligand extension method, which involve use of longer ligands, has been demonstrated. Mesoporous MOFs have been prepared in the presence of surfactants.







In most cases MOFs are synthesized by solvothermal or hydrothermal methods in which reactions are carried out in organic solvents or water at high temperature in closed vessels in a programmable oven. These methods require long reaction time. Microwave assisted method have been developed that allows synthesis of MOFs in few minutes. One key advantage of MOFs is the ability to integrate complex functionalities into the frameworks. Sometimes, however, installing functional groups of particular interests is hard to achieve during MOF synthesis but fortunately incorporating desired functionalities may be realized through post synthesis modification. Some of the common post synthesis modification (PSM) is by doping or by protonation. The advantage of PSM method include 1) ability to incorporate wider range of functional groups 2) ability to generate series of functionally diverse MOFs with same topology 3) ability to introduce multiple kinds of functional groups into the same framework.[1,2]

1.2 Types of coordination polymers

The introduction of molecular inorganic-organic hybrid compounds has led to the synthesis of various coordination polymers. They can be categorized into the following:

1D coordination polymers-extended along a single direction. [12]

2D coordination polymers-extended along two directions perpendicular to each other. [12]

3D coordination polymers-extended along 3D perpendicular to each other. The coordination polymers capable of retaining solvent are called as porous coordination polymers.[12]

1.3 Methods of synthesis of Metal Organic Frameworks

There are different methods of synthesis for example microwave assisted synthesis, electrochemical synthesis, mechanochemical synthesis, sonochemical synthesis, solvothermal synthesis, slow evaporation.[3]

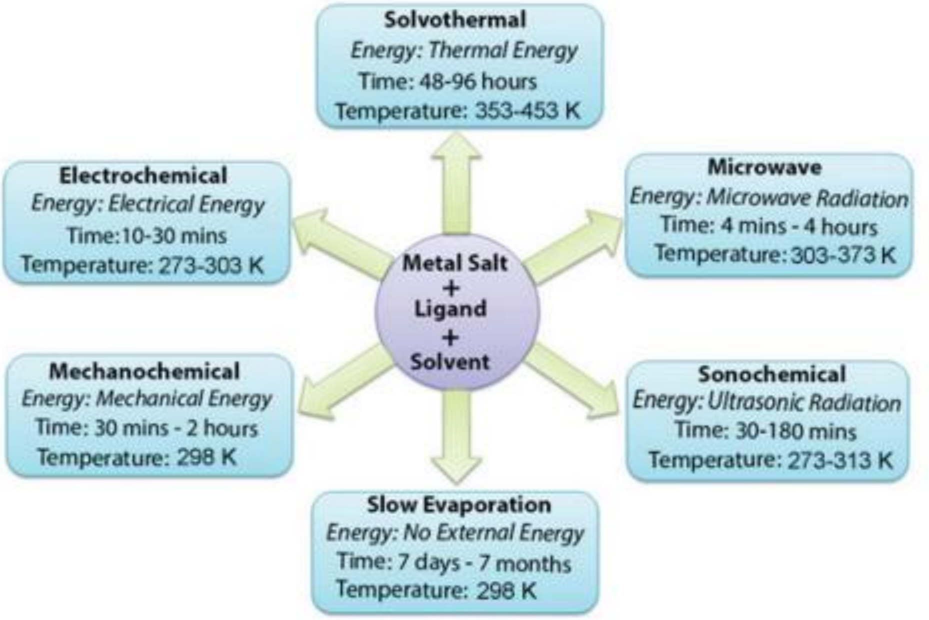


Figure: Methods of synthesis

(a) Microwave synthesis

Microwave assisted synthesis relies on the interaction of electromagnetic waves with mobile electric charges. These can be polar solvent molecules/ions in a solution or electrons or ions in a solid. Microwave assisted MOF synthesis is mainly focused on acceleration of crystallization, formation of nanoscale products, selective synthesis of polymorphs. These syntheses have been carried out at temperatures above 100°C with reaction time rarely exceeding 1 hr. In the conventional solvothermal growth process, crystals nucleate near the walls or on dust particles. That results in slow growth because there are very few seeds. In the microwave-assisted process, we observe crystals throughout the bulk of the solution because local superheating of solvent leads to hot spots that nucleate crystal growth. More seeds lead to faster growth and higher yields.[3]

(b) Electrochemical synthesis

In this technique use of metal salt is eliminated and also the method offers continuous production of MOFs crystals which is a major advantage in an industrial process. The basic principle is that the metal ions are made available through anodic dissolution in the synthesis mixture which contains organic linkers and intermediates. The main objective of electrochemical synthesis was exclusion of anions such as nitrate, perchlorate or chloride during the synthesis.[4]

(c) Solvothermal synthesis

The most commonly used method for the synthesis of porous MOFs is solvothermal process, where a metal salt and a ligand is mixed in a solvent preferably a high boiling one in a reaction vial. The most commonly used solvents are dimethylformamide, dimethylacetamide, dimethylsulfoxide, ethanol, water etc. or mixture of solvents can also be used. Solvothermal synthesis can be carried out in different temperature ranges depending on the requirement.[4]

(d) Slow evaporation method

Conventional method applied in the synthesis of MOFs. They mostly do not require external source of energy and starting materials are concentrated by slow evaporation of solvent at room temperature. The major disadvantage of this method is that it is more time consuming and this can be avoided by using mixture of solvents which increases the solubility of the reagent.

(e) Hydrothermal synthesis

Synthesis includes mixing of reagents initially at room temperature with constant stirring and later sealing into Teflon lined stainless steel autoclaves, which can be subjected to heat over temperature range of 80°C to 200°C for maximum 2-3 days in temperature-controlled oven which is followed by gradual cooling. This method features some advantages over the other methods which include 1) high reactivity of reactants, 2) growth of good quality crystals, 3) formal metastable state possessing unique structure is made possible, 4) use of water as solvent.

1.4 Ligands used in MOF synthesis

(1) Carboxylate based metal organic frameworks

Carboxylate based metal organic frameworks have been widely studied because they can be easily designed and synthesized in low cost and can be strongly coordinated with most metal ions to offer relatively high stability. Ligands with more than one carboxyl group are used due to its structural stability such as dicarboxylic, tricarboxylic, tetracarboxylic acids.

Terephthalic and trimesic acids have emerged as low cost polycarboxylic acids with rigid structure that have been used in the synthesis of large number of MOFs. Several MOFs of cobalt, copper, nickel, aluminium have been prepared using polycarboxylic acids.[5]

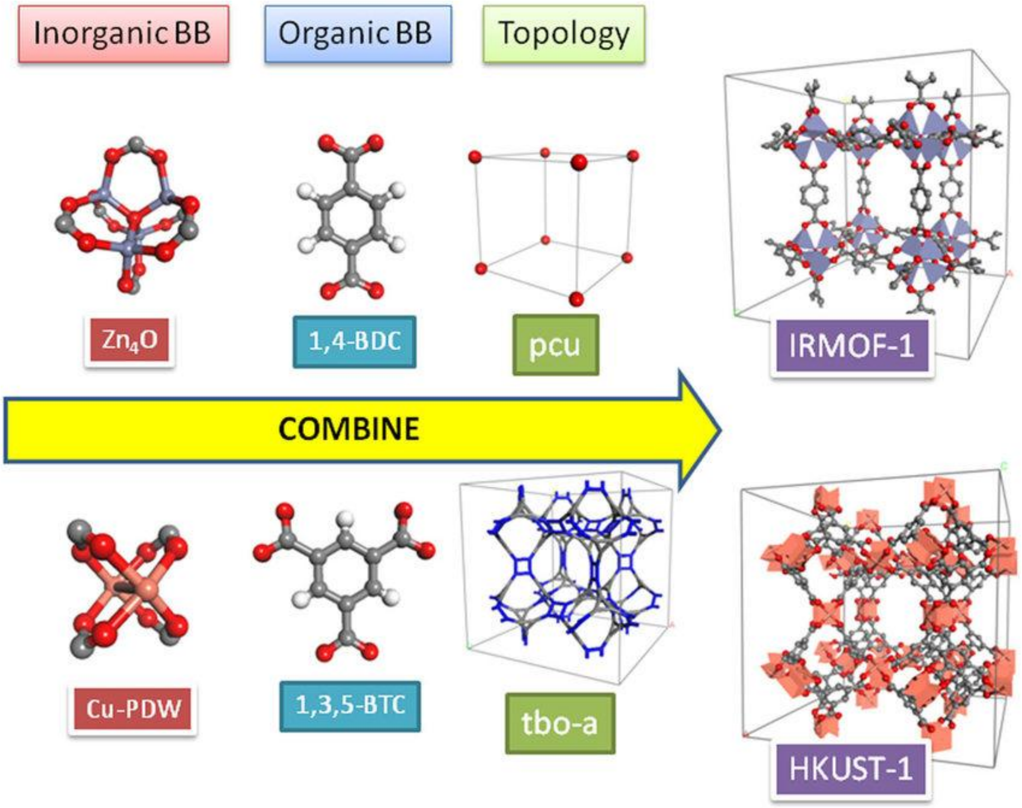


Figure 2: Terephthalic acid and trimesic acid used for the synthesis of MOFs.

(2) Imidazole ligands

Imidazole 4,5 dicarboxylic acid (H_3IDC) is a planar rigid ligand containing two nitrogen and four oxygen atoms has gained considerable attention in the past decade. The main reasons are H_3IDC can partially or fully deprotonate to generate H_2IDC^-, H_3IDC^{2-}, IDC^{3-} at different pH values and each one can employ various coordination modes to bond with the metal ion. H_3IDC is a bifunctional ligand containing imidazole ring and two carboxylate groups which allow H_3IDC to coordinate with the metal ion.[6]

(3) Tetrazoyl ligands

Recently, tetrazoyl compounds have also attracted considerable attention in the field of coordination chemistry, due to their strong coordination ability of the 4 nitrogen atoms which allow them to serve as a bridging or a multidentate ligand in coordination polymer assemblies. 1-H tetrazole (HTz) is the simplest tetrazoyl compound showing rich coordination modes.

Other ligands which can also be used are pyridine or bipyridine based.

1.5 Applications of porous Metal Organic Frameworks

Metal organic frameworks have a wide variety of applications in modern research and technology. Some of the essential applications are listed below:[7]

1) Catalysis

   Porous MOFs form a part of attractive research wherein they can be used as solid-state catalyst similar to zeolites. Porous MOFs have been widely used as heterogenous catalyst for organic reactions such as oxidation, epoxidation, Knovenagel, condensation, hydrogenation, friedel crafts alkylation. These MOFs have also been used for C-C bond formation or coupling reactions like Suzuki-Miyaura coupling, Stille coupling etc. The added advantage of using solid state catalyst is that it can be easily separated from the product by simple centrifugation and filtration and thus can be reused for other reactions.

2) Hydrogen storage

   Hydrogen is considered as possible ideal source of energy due to its large gravimetric heat of combustion however due to its low density in gaseous phase its storage at ambient temperature and pressure is difficult. Low volumetric storage density of hydrogen hinders its use as fuel therefore effective storage materials need to be explored. Hydrogen storage in porous metal organic framework is influenced by several factors such as large surface area, functionalised polar groups, open metal centres and specific weak interactions. It has been proven that MOF materials possess the required underlying characteristics to act as hydrogen uptake materials by physisorption and they can be the best option to reach the set DOE targets in near future. More than 300 MOFs have been tested so far for their hydrogen uptake capacity. Generally, MOF with open metal site provide high surface area which facilitates stronger interaction between metal ion nodes and hydrogen molecules. This is the principle reason behind high hydrogen uptake in this promising class of materials. In addition, theoretical calculations have suggested that doping MOFs with metal ions could enhance hydrogen uptake capacity.

3) Drug delivery system

   Porous MOFs have also shown immense importance in the field of medical science as a part of drug delivery system. The synthesis, characterisation and drug related studies of low toxicity bio-compatible, porous coordination polymers has shown that they have potential for medical applications. A variety of methods exist for inducing drug release, such as pH response, magnetic response, ion response, temperature response and pressure response.

4) Carbon dioxide storage in MOFs

   The rising level of CO2 is the hottest topic world wide and its consequence is considered to provide major threat towards living beings. The emission of coal, oil and natural gas due to rapid industrial development is mostly responsible for rising level of CO2 in the environment. Earlier zeolites and activated porous carbons were explored for CO2 adsorption and other classes of porous materials like MOFs have now picked up attention as potential adsorbents. Very high surface area with polar functional groups decorating the pores provide opportunities for high CO2 uptake in MOFs. [13]

5) Methane storage in MOFs.

   Methane is the potential storage as natural gas contains about 95% methane. Methane has comparable gravimetric heat of combustion to gasoline. For methane MOFs have achieved the DOE target of 180 v/v at ambient temperature and pressure but improving further the methane storage capacity is still an active area of research. Other important hydrocarbons like benzene, toluene, xylene and linear hydrocarbons have been effectively seperated from liquid mixtures by trapping inside MOFs.[7]

6) MOFs as sensors

Use of MOFs as luminescent materials has become an important area of research due to their potential application in small molecule sensors, pH sensors, light concentrators for photovoltaic devices, antennae in photosensitive bioinorganic compounds and high technology optics. MOF materials are advantageous because of their hybrid nature which includes inorganic metal ions, organic linkers and also guest molecules. MOFs can be considered excellent solid state luminescent materials since they have structural predictability and well defined environments for chromophores in crystalline form. Lanthanide metal ions are widely used for synthesis of luminescent MOF due to their electronic transitions from d to f shell with accompanying photoemission. Naphthalene, Anthracene, pyrene, pyrelene and stilbene types of ligands are commonly used for luminescent MOF synthesis.[7]

7) MOFs as magnetic materials

Magnetism in solids is of considerable interests due to its widespread application in electromagnetism, devices and sensing. Recently researchers have introduced magnetism within MOFs through the use of paramagnetic 3d transition metal nodes along with suitable organic linkers subsequently named as MMOFS (Magnetic metal organic framework). The MOFs based on first row transition metals have contributed significantly to porous molecular magnets. The porous nature of MOFs combined with magnetic properties could find interesting application in air separation. Another important factor responsible for magnetism in MOFs is the framework structure which may involve layered geometry with shorter conjugated distance between metal clusters and organic linkers have also been used for the synthesis MMOFs, where radicals are present in the organic linker are responsible for magnetic properties. Also metal radical combined approaches have been used to synthesize a variety of MMOFs. [7]

1.6 Metal functionalized MOF for catalytic applications

Metal organic frameworks have emerged as a fruitful material for diversity of applications owing to their advantage in pore size adjustability, structural diversity and functional tailorability. Their great prospect in heterogenous catalysis has attracted continuous interest. In recent years metal organic frameworks also known as porous coordination polymers have gained enormous attention due to promising applications such as gas storage, gas and liquid separation techniques, drug delivery, magnetism, heterogenous catalysis, host for metal nanoparticles. MOFs are composed of metal ions or clusters connected through organic linkers which lead to versatile topologies and architectures. MOFs surpass classical porous materials such as zeolites or activated carbon in their permanent porosities, high surface area, tuneable pore size and topologies. Currently, MOFs are investigated as heterogenous catalyst for various organic reactions. An advantage of MOFs over related porous materials towards catalysis should be their high order and uniformity of porous network for size and shape selective catalysis. Molecular feature of MOFs enables installation of catalytic centres using predesigned molecules which can be systematically tuned by synthetic chemistry. Moreover, the active sites in MOFs have identical local environment and are separated by fixed distance from each other which can be precisely determined by single crystal X-ray crystallography. Furthermore, MOFs allow incorporation of multiple functional sites that work cooperatively in the same nanocavity to achieve activity and selectivity that cannot be obtained by physical mixture of individual components. MOFs thus provide tuneable platform in the construction of solution inaccessible catalytic species that have unusual reactivity and selectivity. Catalytic function can be implemented at the organic or inorganic component and this can be done by direct synthesis of the envisaged scaffold by post synthetic modification. Alternatively pore system of MOF can also serve as the physical space in which a catalytic species is encapsulated or as the confined space where the chemical reaction can take place. In these cases, MOF may act as simple spectator or passive medium dispersing for dispersing catalytic species but it can also participate in the catalytic reaction by stabilising transition state, orienting molecules or introducing additional active sites. Moreover, pore dimensions of many MOFs may change without breaking chemical bonds within the framework.[8]

Palladium MOFs have efficiently been employed in C-C cross-coupling reactions such as, Suzuki-Miyaura coupling, Stille coupling, Sonogashira/Heck-coupling and Hiyama coupling. The Pd catalysed Suzuki-Miayaura cross coupling reaction of aryl halides with aryl boronic acids is one of the most efficient methods in the synthesis of biaryls, triaryls etc or introduction of several substituted moieties in organic synthesis. All S-M coupling reactions are catalysed by Pd grafted MOFs employed room temperature or higher using ethanol water mixture in most cases. Several post modification Pd grafted MOFs and other Pd grafted porous materials like porous carbon and silica are also been used for S-M catalysis.[9]

2 EXPERIMENTAL METHODS AND CHARACTERISATION

2.1 Synthesis of QMOF

Isonicotinic acid and $Zn(NO_3)_3.6H_2O$ were purchased from Sigma-Aldrich. Dimethylformamide were purchased from Avra. All the reagents were of analytical grade and used without further purification.

Isonicotinic acid (0.1mmol, 0.0123g) was dissolved in 5 ml DMF in a clean dry glass vial. If needed the mixture was sonicated. To this Zinc nitrate (0.1 mmol) was added and kept in oven for solvothermal synthesis for 48 hrs at 100°C after which the white crystals were obtained in the glass vial. The crystals were analysed by single crystal and powder X-ray diffraction. These crystals were washed with methanol and dried and used to make Pd functionalized QMOF to study catalytic activity.

2.2 Structure of QMOF

A single crystal X-ray diffraction analysis was performed on the above obtained crystals and the structure was solved using ShelX. It revealed that the QMOF crystallised in hexagonal space group $P6_2$(171). Each zinc is tetrahedrally bonded to two nitrogen of isonicotinic acid and two oxygen of carboxyl group of isonicotinic acid. When extended along 3D dimensions its showed hexagonal and trigonal pores thus proving its heterogenicity. Hexagonal pores have pore size 11 A and trigonal pores of 7 A.

2.3 STRUCTURAL INFORMATION USING SINGLE CRYSTAL XRD

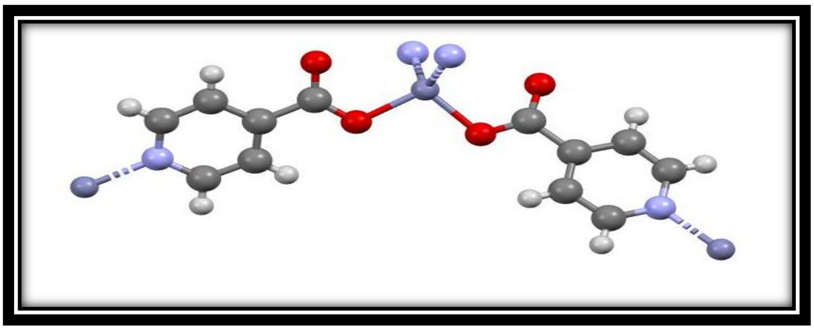


Figure 1: Asymmetric unit of Zn-isonicotinate QMOF where zinc is tetrahedrally coordinated to two carboxylate oxygen and two pyridine nitrogen donated from four isonicotinate ligands.

Chemical formula	$C_{12}H_8N_2O_4Zn$
Crystal system	Hexagonal
Formula weight	309.38
Space group	$P6_2$
Cell lengths	a = 15.5036(6) b = 15.5036(6) c = 6.2564(3)
Cell angles	A = β = 90, γ 120
Cell volume	1302.33
Z, Z’	Z:3 Z’:0
R-Factor (%)	6.2

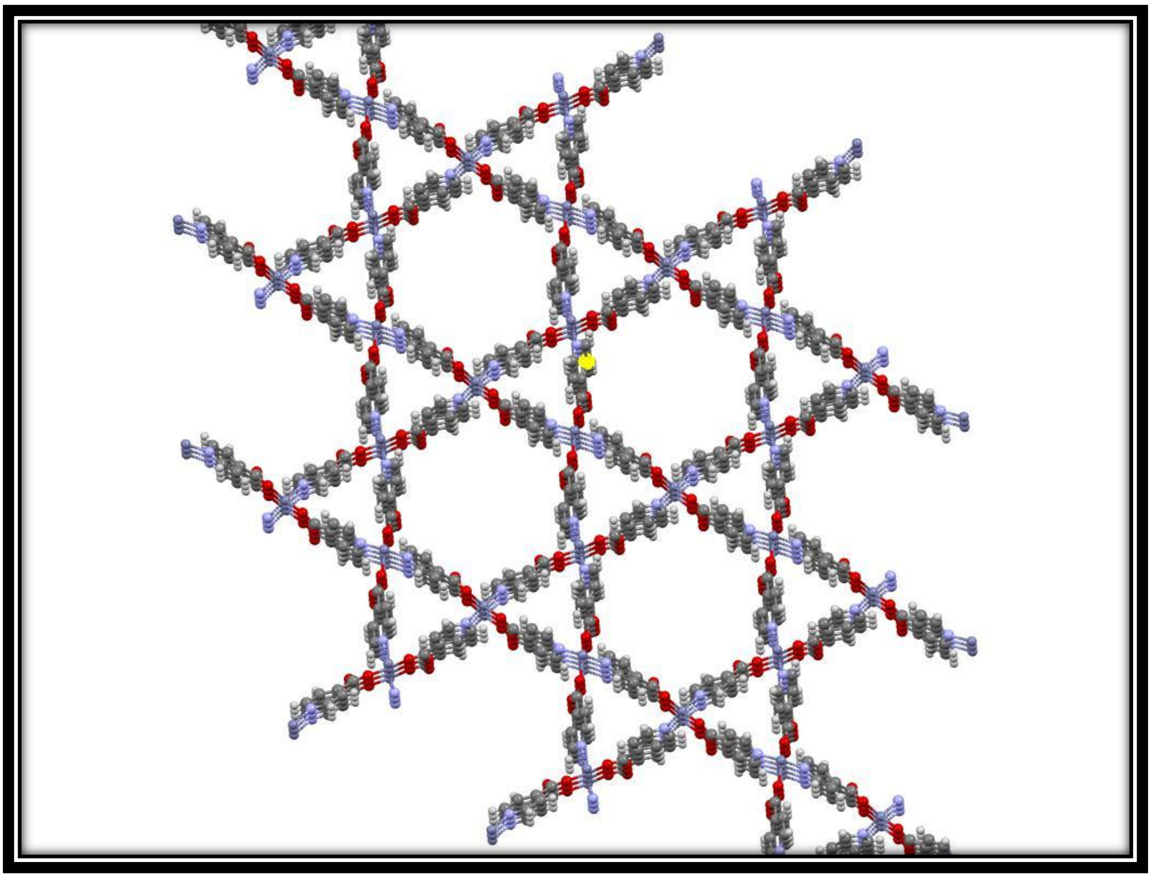
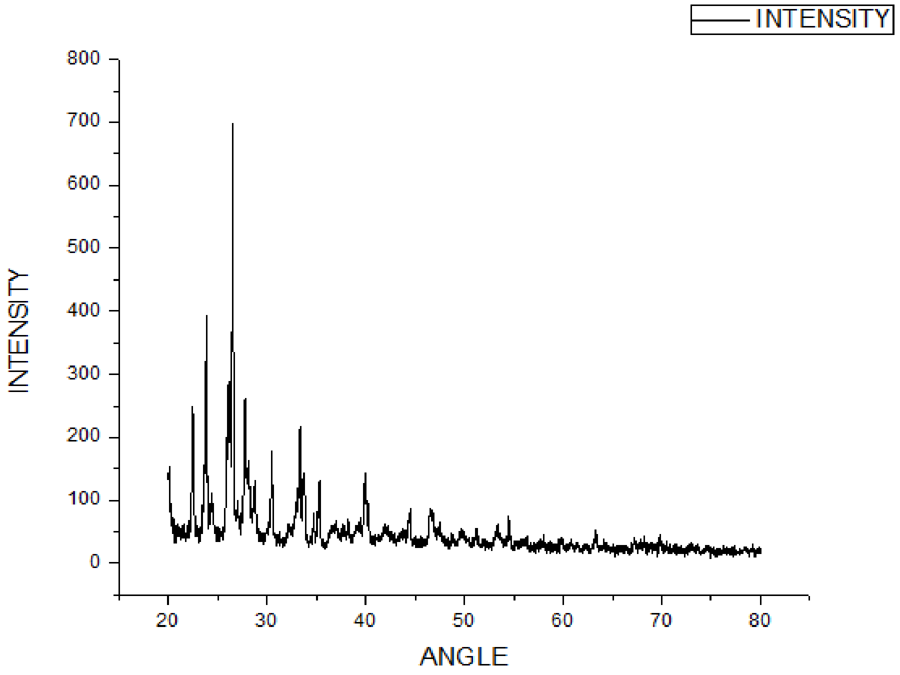
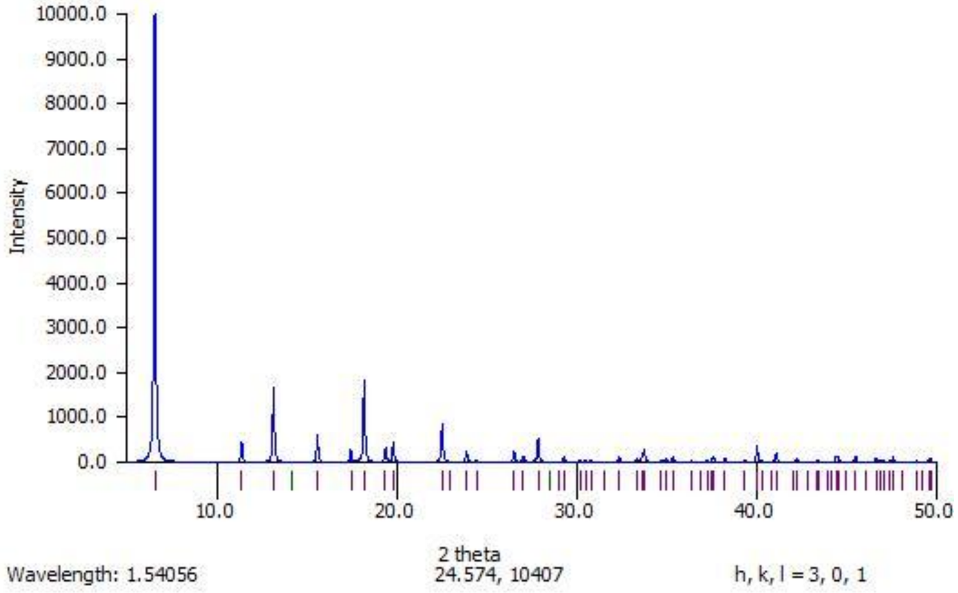


Figure 2: The above figure shows the 3D arrangement. It shows the hexagonal and triangular pores.

2.3 Powder XRD

Powder XRD was performed on the synthesised crystals.





The above PXRD plot is obtained through Mercury software.

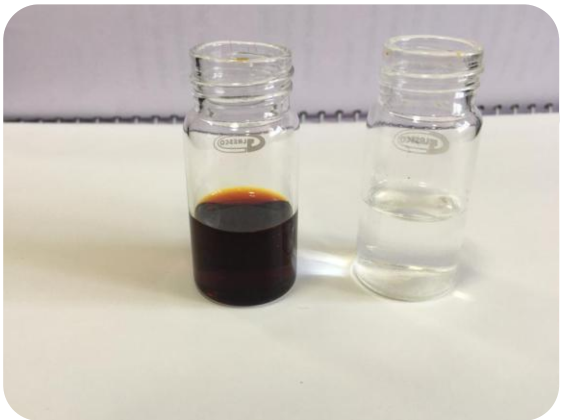
On observing both the above PXRD plots, the one obtained through the software and the one obtained through PXRD by experiment we can conclude that both the graphs show similar peaks indicating that the compound formed is QMOF.

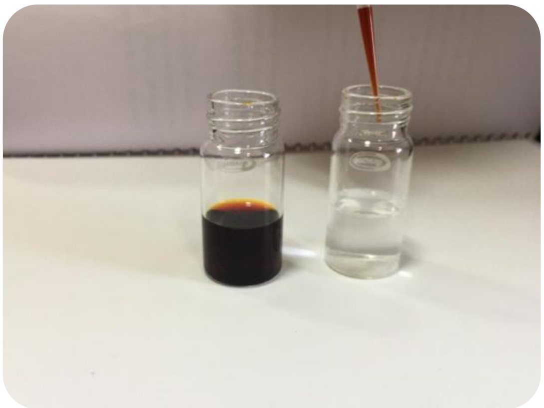
2.4 Pd-immobilized QMOF

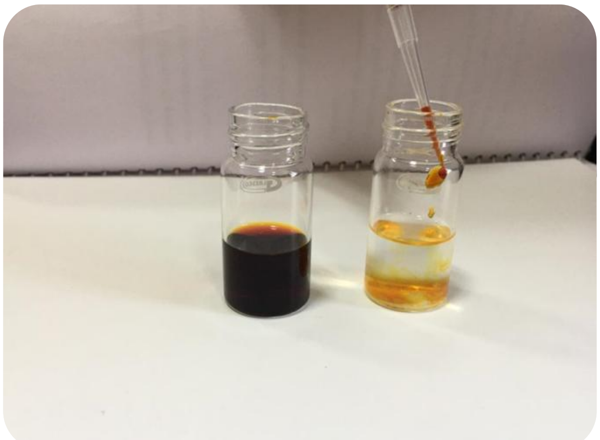
QMOF crystals obtained by solvothermal synthesis were filtered and washed with methanol and dried. To these dried crystals ethanol was added. Later dropwise $Pd(NO_3)_2$ solution was added and stirred. It was observed that QMOF readily absorbs $Pd(NO_3)_2$ forming QMOF-Pd composite. Once addition of $Pd(NO_3)_2$ solution is in excess, yellow colour was observed in the ethanol-QMOF mixture, and further addition of $Pd(NO_3)_2$ was stopped. This mixture was stirred for sometime and later filtered and dried and used for Suzuki-Miyaura cross-coupling reactions.

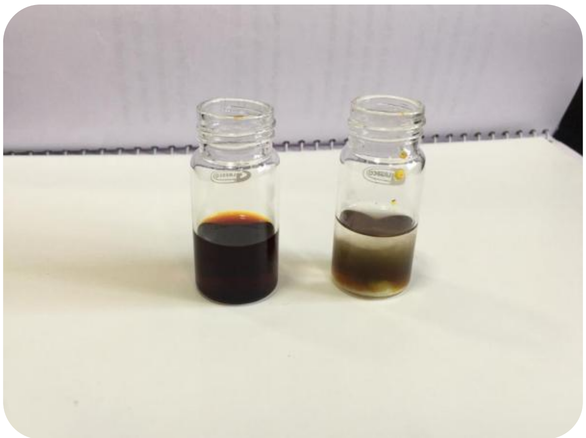
QMOF crystals after being obtained from solvothermal synthesis were subjected to doping by $Pd(NO_3)_2$ solution in ethanol. Upon performing its single crystal XRD it was observed that there was surface adsorption of Pd and that it was not incorporated into the structure.

Detailed images are shown below:









3. Pd-QMOF as heterogeneous catalyst for Suzuki-Miyaura coupling

Palladium catalysed cross coupling reactions are one of the most powerful tools for the formation of carbon-carbon bond in organic synthesis using aryl halides and aryl boronic acid. Suzuki and Stille coupling reactions have become a main stay in modern synthetic organic chemistry for preparation of biaryl compunds, polyolefins, styrenes and substituted biphenyls. Coupling products of this reactions have been applied in a variety of applications as intermediate in preparation of functional materials, natural products and bioactive compounds. All reported suzuki–miyaura coupling reactions catalysed by palladium grafted MOFs have employed temperature of 60° C or above using ethanol water mixture. Rhodium and Platinum can also be used for cross coupling reactions.[8]

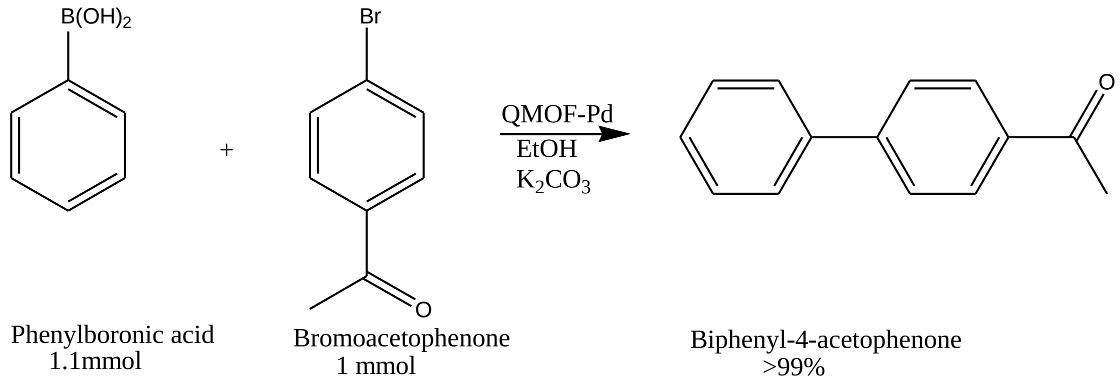
Mechanism:

1) **Oxidative addition** of palladium to halide to form organopalladium species.
2) Reaction with base gives intermediate which via **transmetallation** with boronate complex forms organopalladium species.
3) **Reductive elimination** of desired product restores the original palladium catalyst which completes the catalytic cycle.

Experimental procedure for Suzuki-Miyaura cross-coupling reactions

1) Coupling between a bromobenzene substrate and phenylboronic acid.

   The coupling was carried out in a 100 ml round bottom flask. Bromoacetophenone an aryl halide (1 mmol, 0.2 g) and phenylboronic acid (1.1mmol, 0.135g) were dissolved in 10 ml ethanol and 2 equivalents of K_2CO_3 (0.276 g) was added into it. 18.4 mg of QMOF-Pd was added as catalyst and the mixture was stirred for 1 hour at room temperature. The mixture was then filtered and the filtrate was evaporated to dryness and dissolved in DCM (compound formed readily dissolves in DCM) and filtered again. The compound thus obtained from the DCM solution was dried and characterized by H-NMR. NMR analysis showed the formation of the desired coupling product in 99 % yield.



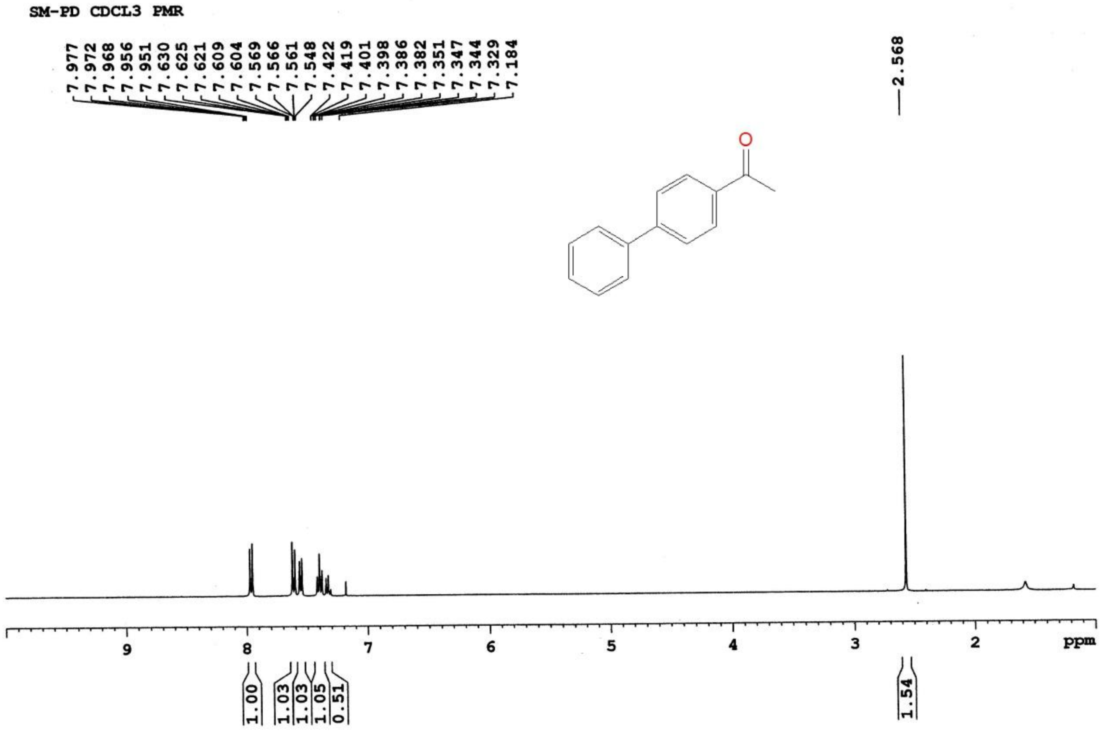


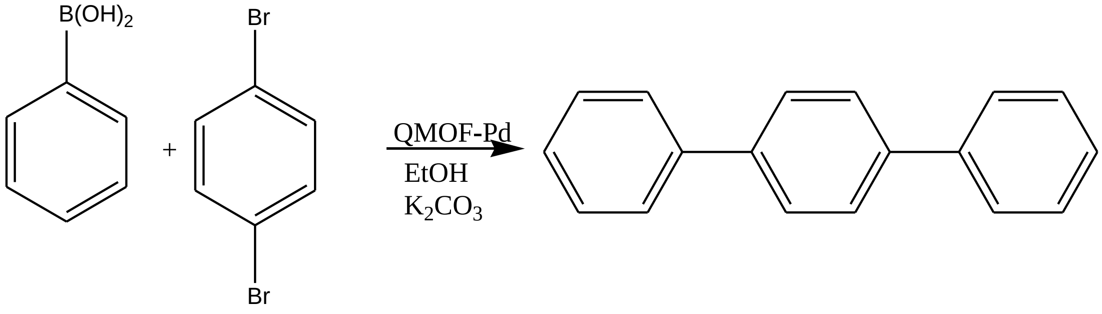
Figure 4: H-NMR spectrum (400 MHz, $CDCl_3$) of biphenyl acetophenone.

The ^{1}HNMR shows a strong peak at 2.56 ppm for methyl $-CH_3$ protons showing an integral value of 1.54, thus each proton has a value of 0.5. Peaks in the range of 7-8 ppm are for aromatic protons each having values approximately close to 0.5. Since the integral value is 4.5 for the aromatic region it's a clear indication that product formed is biphenyl acetophenone. Since there are no impurity peaks seen it is confirmed that the coupling is 99% pure.

2) Coupling between a dibromobenzene substrate and phenylboronic acid.

1,4-dibromobenzene (1 mmol, 0.235 g) and phenylboronic acid (2.2 mmol, 0.270) were dissolved in 10 ml ethanol and 2 equivalents of K_2CO_3 (0.276 g) was added into it. 18.4 mg of QMOF-Pd was added as catalyst and the mixture was stirred for 1 hour at room temperature. The mixture was then filtered and the filtrate was evaporated to dryness and dissolved in DCM (compound formed readily dissolves in DCM) and filtered again. The compound thus obtained from the DCM solution was dried and characterized by H-NMR. NMR analysis showed the formation of the desired coupling product in 92 % yield as calculated from the integral values.

Reaction scheme:



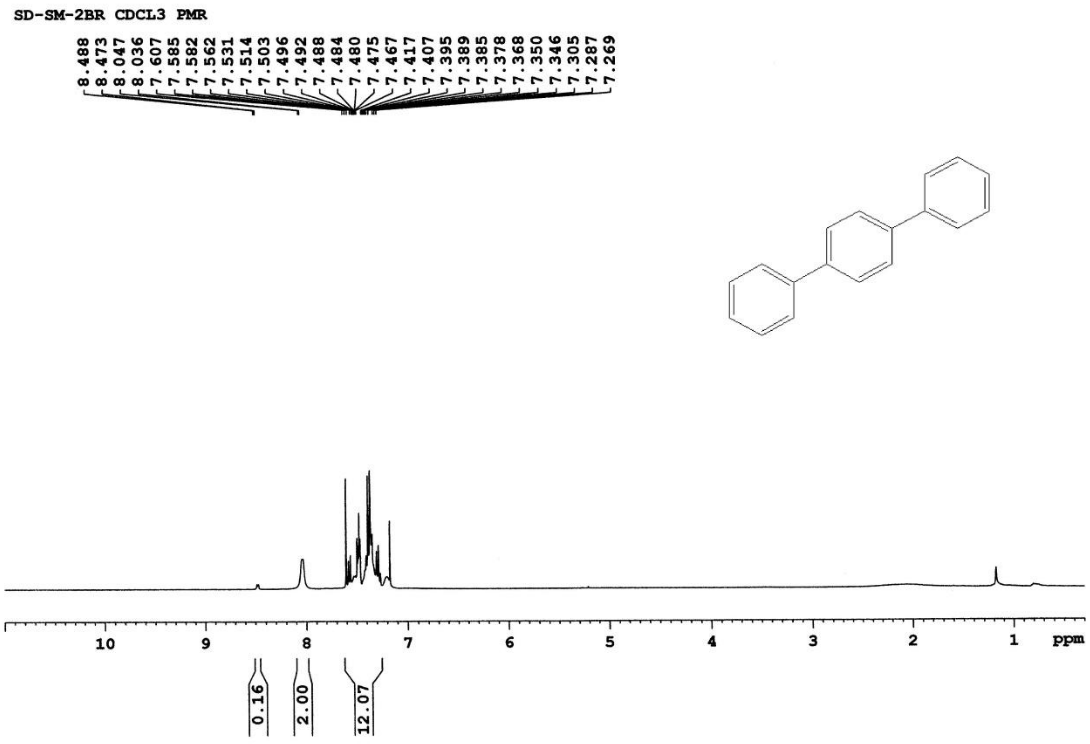
Phenylboronic acid
2.2 mmol

1,4 -dibromobenzene
1 mmol

Triphenyl
92%

Characterization of coupling product by H-NMR

The total number of protons in the 1,4-triphenyl compound is 14. Thus, ^{1}HNMR spectrum showed a peak around 8.0 ppm having integral values of 2.0 and several peaks between 7-8 ppm having integral value of 12. Peak at 8.5 ppm having integral value of 0.16 is due to unreacted 1,4-dibromobenzene. Calculating the integral values reveal that product formed is 92% pure.

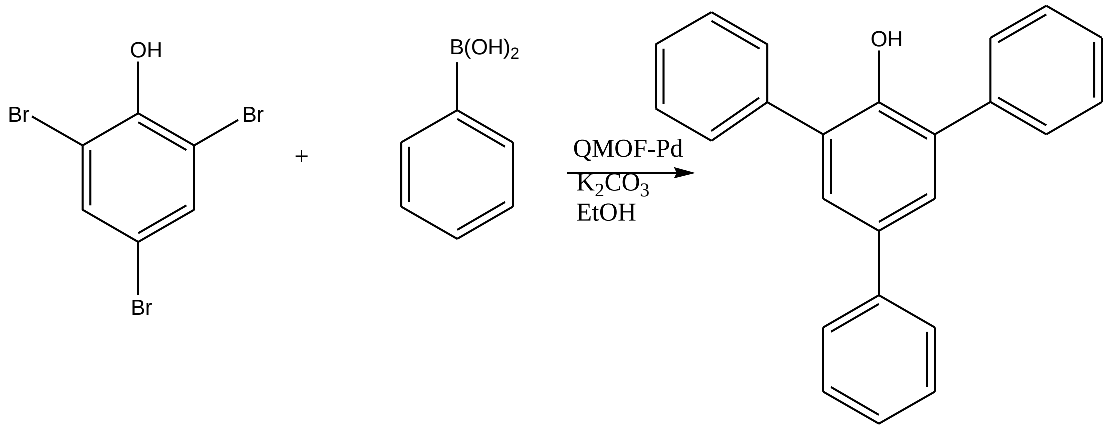


^{1}HNMR 400 MHz, $CDCl_3$

3) Coupling between a tribromobenzene substrate and phenylboronic acid.

   2,4,6-tribromophenol (1 mmol, 0.235 g) and phenylboronic acid (2.2 mmol, 0.270) were dissolved in 10 ml ethanol and 2 equivalents of K_2CO_3 (0.276 g) was added into it. 18.4 mg of QMOF-Pd was added as catalyst and the mixture was stirred for 2 hours at room temperature. The mixture was then filtered and the filtrate was evaporated to dryness. Upon adding DCM it was observed that the mixture was not soluble in DCM indicating that coupling reaction was not complete.

Reaction scheme:



2,4,6-tribromophenol
1mmol

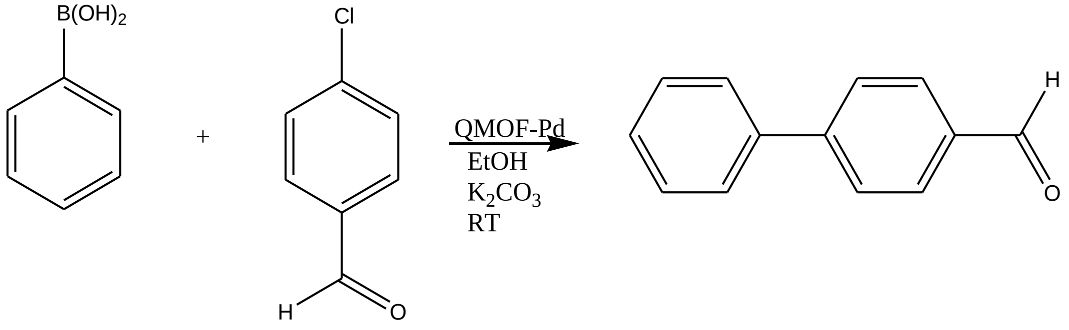
Phenylboronic acid
3.3 mmol

Tetraphenylhydroxide

4) Coupling between chlorobenzene substrate and phenyl boronic acid

The coupling reaction was carried out using p-chlorobenzaldehyde (1mmol, 0.140 g) and phenylboronic acid (1.1mmol 0.135 g) in presence of 2 equivalents of K_2CO_3 and 20 mg of QMOF-Pd as catalyst, all added into 10 ml of ethanol. This mixture was stirred at room temperature for 3 hour and it was observed that product was not formed as the compound obtained was insoluble in DCM indicating reaction did not proceed at all.

Reaction scheme:



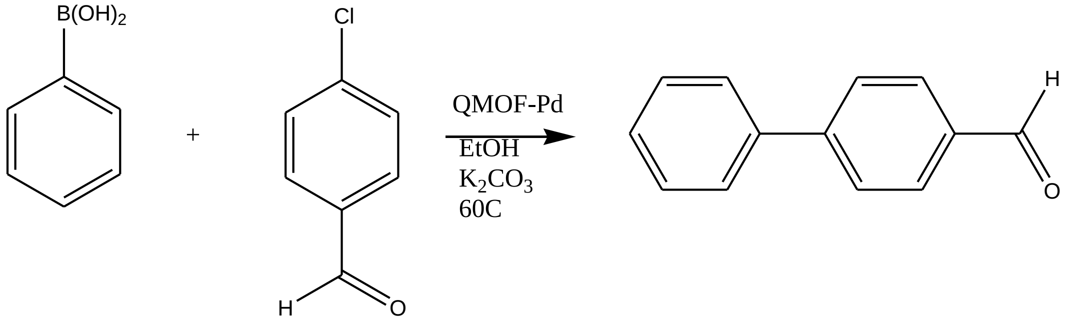
Phenylboronic acid
1.1 mmol

p-chlorobenzaldehyde
1 mmol

Biphenyl-4-carboxaldehyde

The coupling reaction between p-chlorobenzaldehyde (1mmol, 0.140 g) and phenylboronic acid (1.1mmol 0.135 g) in presence of K_2CO_3 and QMOF-Pd was carried out at 60 °C under reflux for 3 hours. However, during the reaction it was observed that palladium leached out from the catalyst and the solution turned black. No product was observed to be formed in this reaction as well.

Reaction scheme:



Phenylboronic acid
1.1 mmol

p-chlorobenzaldehyde
1 mmol

Biphenyl4-carboxaldehyde

4. Conclusion

QMOF was synthesized using solvothermal method using isonicotinic acid and zinc nitrate in N,N-dimethylformamide. This was characterized using single crystal XRD and PXRD. It was observed that this MOF had porous hexagonal structure with space group $P6_2$(171). Crystal structure revealed that QMOF had shape of star with hexagonal and triangular pores with significant porosity. QMOF nanocrystals were made using $Pd(NO_3)_2.2H_2O$. These nanocrystals were used for suzuki-miyaura cross coupling reactions which proved to be very functional in forming C-C bond to form biphenyls, triphenyls, tetraphenyls etc. Reaction with monobromo and dibromosubstituent gave desired biphenyl and triphenyl with 99% and 92% purity. It was observed that tribromosubstituent did not give desired tetraphenyl as the product formed was not soluble in DCM. When the reaction was carried out using monochlorosubstituent it was observed that it did not form biphenyl upon suzuki reaction as the product formed was not soluble in DCM. It was observed when the reaction with monochlorosubstituent was repeated at higher temperature palladium leached out from the QMOF nanocrystals giving a black precipitate.

We also tried adding $Pd(NO_3)_2.2H_2O$ to QMOF and upon taking single crystal XRD it was noted that Pd was not incorporated in the QMOF but there was only surface adsorption.

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