Design, Synthesis and Characterization of Hydrazone-based Covalent Organic Framework

By

Manisha Gaurav

A dissertation submitted for the partial fulfilment of a BS-MS dual degree in Science

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Certificate of Examination

This is to certify that the dissertation titled “**Design, Synthesis and Characterization of Hydrazone-based Covalent Organic Framework**” submitted by **Manisha Gaurav** (Reg. No. MS16106) for the partial fulfilment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

Dr. Raj Kumar Roy	Dr. Subhabrata Maiti	Dr. Santanu Kumar Pal
		(Supervisor)

Dated: April 30, 2021

Declaration

The work presented in this dissertation has been carried out by me under the guidance of Dr. Santanu Kumar Pal at the Indian Institute of Science Education and Research Mohali.

This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

Manisha Gaurav

(Candidate)

Dated: April 30, 2021

In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. Santanu Kumar Pal

(Supervisor)

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Manisha Gaurav

List of Figures

List of Schemes

Notation

COF	Covalent Organic Framework
MOF	Metal Organic Framework
CTF	Covalent Triazine Framework
Bth	Benzene 1,3,5-tricarbohydrazide
Tp	1,3,5- Triformylphloroglucinol
TFP	2,4,6-trimethoxybenzene 1,3,5-tricarbaldehyde
FT-IR	Fourier transform infrared spectroscopy
PXRD	Powder X- ray Diffraction
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric analysis

Contents

Chapter 1.

Chapter 2.

Abstract

Covalent Organic Frameworks (COFs) are a kind of new growing crystalline porous polymers that are building with the mixing up lighter elements (for example, B, C, N, O, and Si) via strong covalent bonds (e.g., B-O, C-N, C=N, and C=C-N double connections). Unlike other organic polymers, they show crystallinity and periodic pores. They have received much attention in the field of a porous material due to their attractive structural properties (e.g., adjustable porosity, total organic structure, large surface area, structural versatility, high chemical stability, and high modularity). It shows exciting applications like adsorption, gas storage, catalysis, sensing, optoelectric, separation, and drug delivery.

The motive of the study is to synthesize a hydrazone-based covalent organic framework (COF). A crystalline hydrazone linked Bth-Tp-COF has been designed and synthesized successfully with the Schiff-based reaction joining the monomer of triformylphloroglucinol (Tp) and Benzene 1,3,5-tricarbohydrazide (Bth) under solvothermal condition. The designed COF has a functional chelating site that can be used as a host-guest sensing application or catalysis chemistry.

The first chapter of the thesis deals with a brief introduction of COFs, design, and their applications. The second chapter contains the synthetic schemes and the experimental procedures, and basic characterizations of Bth-Tp-COF.

Chapter 1

1.1 Introduction

Porous materials include rocks and sediment (e.g., aquifers, oil and gas tank), zeolites, and biological tissues (e.g., timber, cork, and bones). Sponges are marine creatures with pores on their body surfaces. These pores sustain constant water flow across the bodies to find out the food, breathe air, and remove unwanted materials. Honeycomb is also a porous structure used by honeybees to store honey and pollen. Human skin has pores that can absorb water, radiations, etc. also acts as a porous material[1]. Material scientists utilized these natural phenomena and discovered synthetic/artificial porous materials. Porous materials are essential in many fields of science and technology. There has been a remarkable enhancement in the number of new advanced porous functional materials over the last couple of decades[2]. However, porous organic materials are mostly hydrocarbons that include pores. The pore size and the nature of the building units are two often used parameters to categorize porous materials. Based on their pore size, IUPAC categorizes these porous materials as pore diameter < 2 nm, lies from 2 to 50 nm, and > 50 nm in microporous, mesoporous, and macroporous, respectively[3]. On the other hand, the classification based on the choice of building blocks categorized into 3 main groups; (i) inorganic, which includes zeolites, porous carbon derivatives and porous metal oxides, (ii) organic-inorganic hybrid, which contains Metal-Organic Frameworks (MOFs), and (iii) organic, having porous organic polymers (POPs). The POPs include conjugated microporous polymers (CMPs), hyper-cross-linked polymers (HCPs), covalent organic frameworks (COFs), covalent triazine frameworks (CTFs). Among them, COFs and CTFs are crystalline, where CMPs are purely amorphous with a large surface area, excellent stability, and narrow pore capacity. CMPs are constructed mainly by C−C and C−H bondsor through control in the pressure in the reaction vessel. The growth of polymeric networks is generally directed by the topology diagram where the monomers with matching geometries A brief representation of discoveries of porous materials is shown in figure 1[4].

Covalent organic frameworks (COFs) are a subclass of crystalline porous material that is being focused hugely since the past decade due to their excellent crystallinity, large surface area, extraordinary thermal as well as chemical stability and diverse applications in various fields[5-7]. COFs are fully conjugated porous polymers constructed by the principles of dynamic covalent chemistry (DCC)[8]. The building blocks in COFs are directly connected by strong covalent bonds. The challenge in assembling these building blocks is to overcome the "crystallization problem" because of the presence of the strong covalent bonds that have a tendency to yield amorphous materials. During the synthesis of COFs, it is important to provide the reversible condition in a reaction that prevents the formation of disordered and amorphous products. The reversibility during the bond formation provides self-healing and error correction in the course of the crystallization process[9]. In practical, this is achieved by either using solvent combinations so that the byproducts have limited solubility are connected into polygonal backbones to construct different 2D or 3D structures and pores[10].

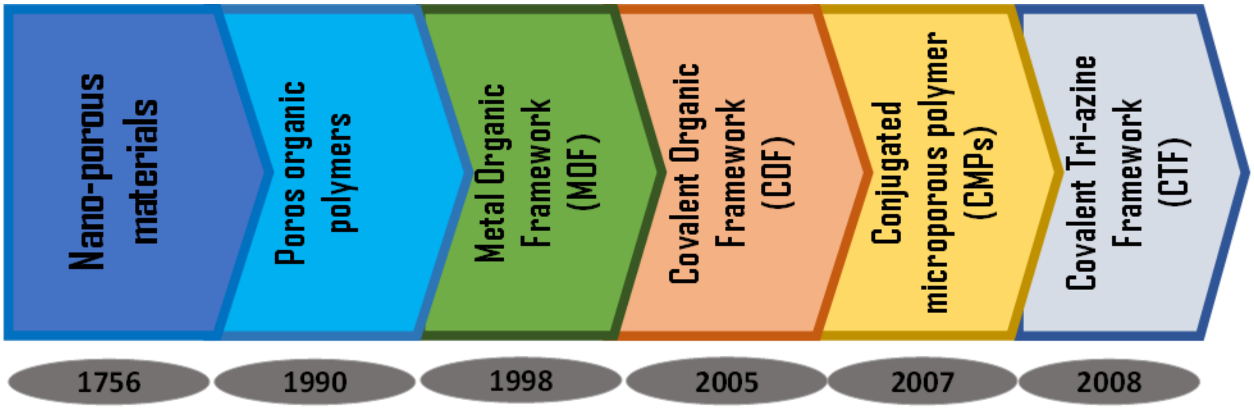

Figure 1: Discovery of porous materials.

1.2. Design and Synthesis

1.2.1 Design Principle

As shown in figure 2, the topology diagram can be used to predesign the pores and structures of COFs. The topology diagram is focused on constructing unit geometry matching, and it guides the construction of a polygon structure. Polygons are made up of knot and linker units with specific configurations that give the polygon its form and proportions, as well as a distinct pore scale. The topology diagram enables numerous configurations of monomer geometries to establish COFs with various frameworks and pores, resulting in numerous orders of the structural the aspired frameworks

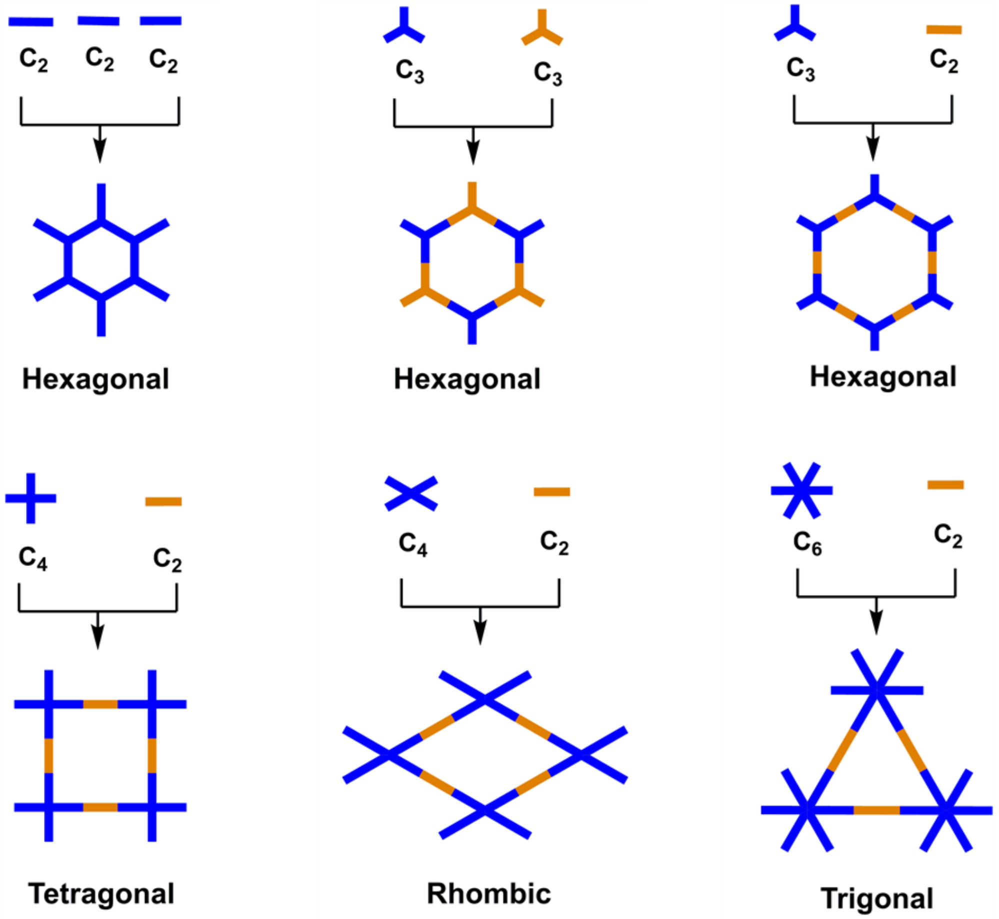

Figure 2: Topological diagrams of COFs. (Redraw from reference[12])

1.2.2 Types of linkages

In 2005, Yaghi and his co-workers[11] presented a number of different COFs that have been reported, including boroxine-linked, boronate ester-linked, imine-linked, hydrazone-linked, imide-linked, azine-linked, beta-ketoenamine-linked, triazine-linked, phenazine-linked, and sp^2-carbon linked COFs (Figure 3). Their highly crystalline structures, low density, large surface area, good chemical stability, and tunable functionalities inside the pores have furnished COF materials with unique properties and a wide range of uses, including luminescence, energy conversation, gas adsorption, catalysis, functional devices, drug delivery, and supercapacitors.

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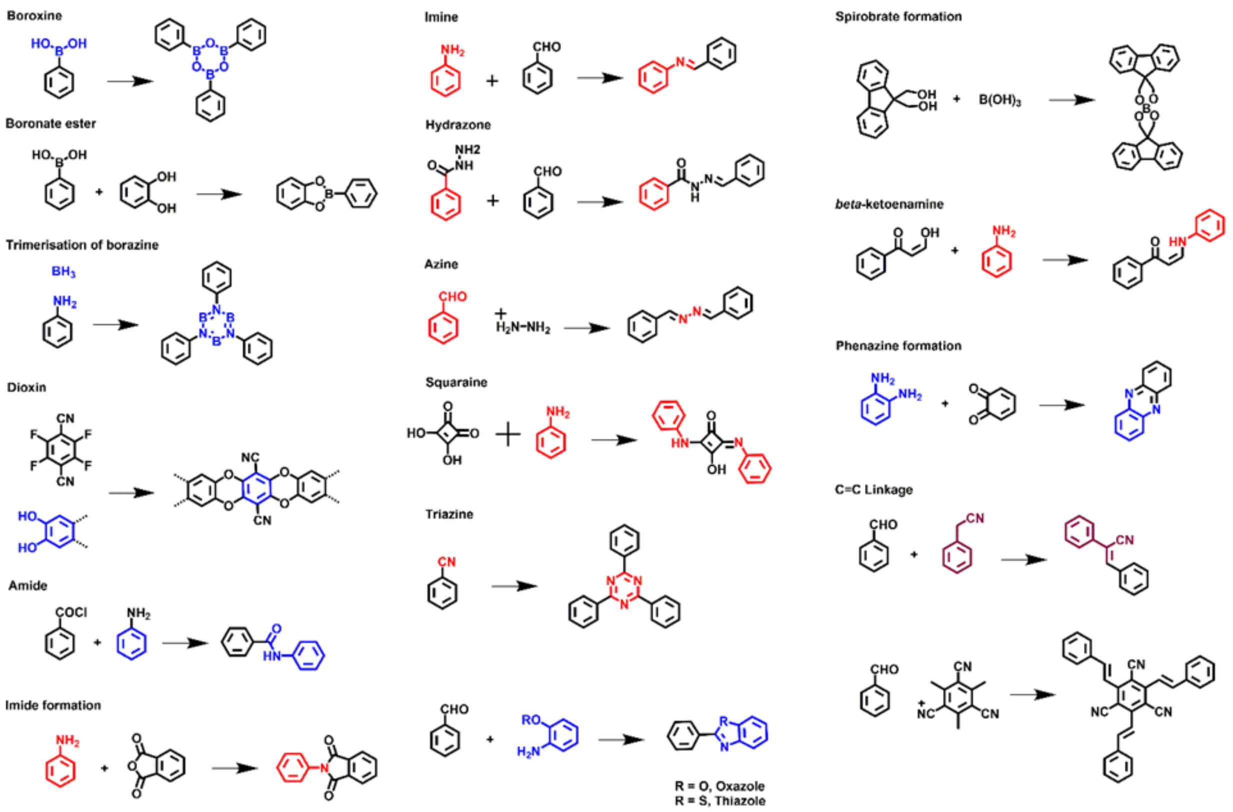


Figure 3: Different types of linkages

1.2.3 Synthetic methods

The synthesis of COFs is dependent on dynamic covalent chemistry (DCC), that aids in the formation of a well-ordered crystalline framework with excellent thermodynamic stability. Many research groups have diversified synthetic methods consisting of solvothermal, ionothermal, microwave, room temperature, and light promoted methods are majorly used methods. A brief idea about these methods is shown in figure 4.

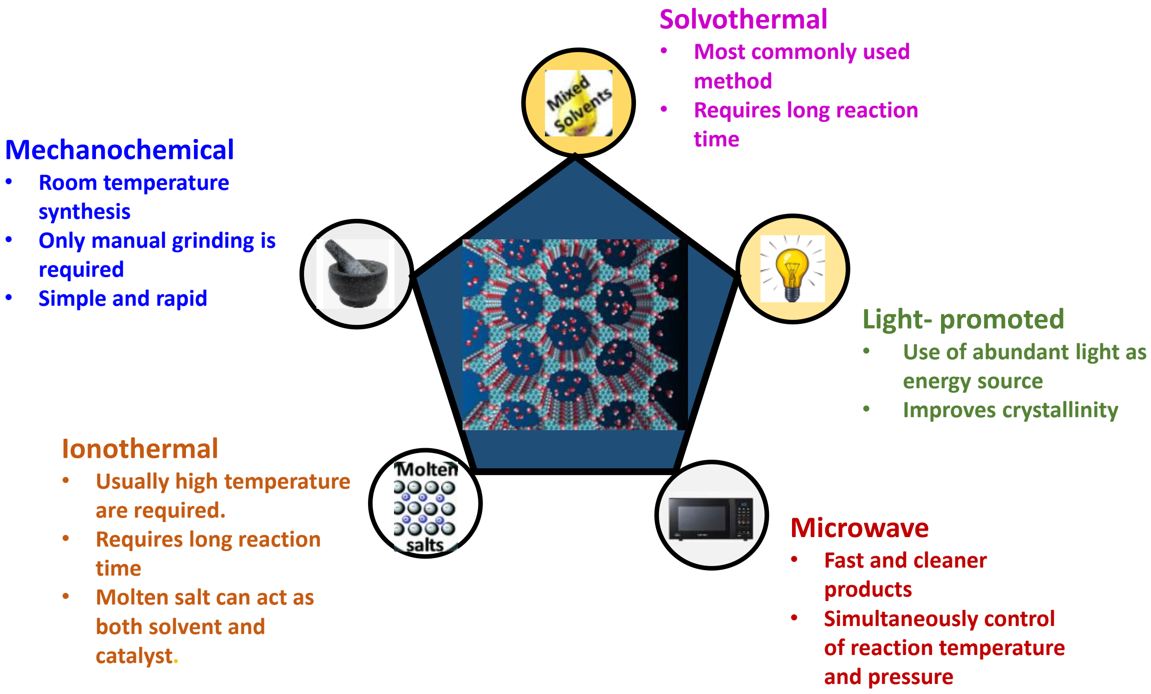


Figure 4. Synthesis methods of COFs. (Redraw from reference[15])

1.3. Applications

Covalent organic frameworks (COFs) have a unique combination of porosity and crystallinity that provide specific properties to these materials. This section briefly addresses some of the uses in the area (for example- energy conservation, catalysis, gas adsorption and storage, semiconduction, photoluminescence, photocatalysis, and drug delivery).

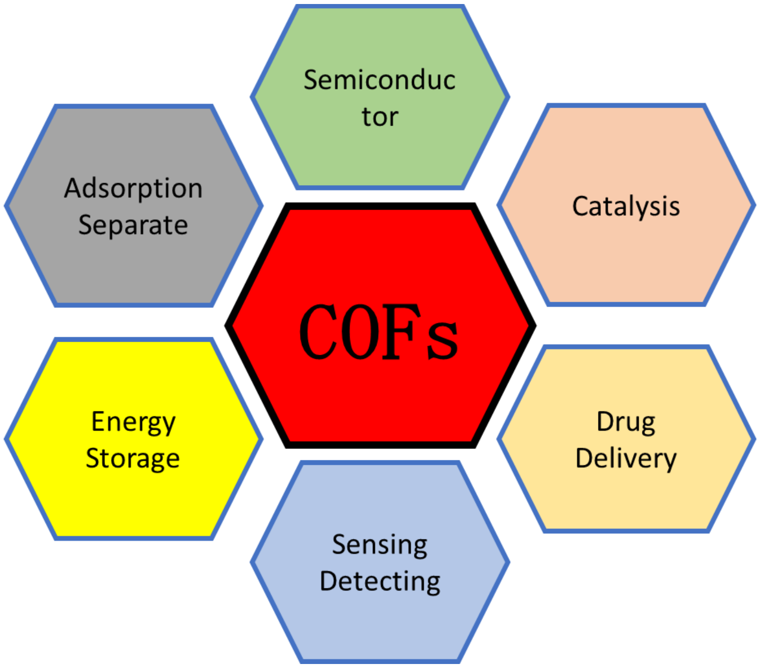


Figure 5. Application of COFs.

For the catalytic field, a well-built structure, pore structure, and pore size are the primary explanations for understanding COF catalytic sites. The design of the domain where catalytic sites is loaded is determined by the form of driven catalytic interactions. COFs provide a platform for heterogeneous catalysis activity, also as in the solvent; they are insoluble[2]. This application has been the subject of a lot of recent studies, and it can be used for electrocatalysis and photocatalysis, where it can act as metal-free catalysis by capturing metal salts/nanoparticles (NP) to provide the activity and selectivity similar to their homogeneous analogs and also for removing the organic pollutant[15].

For energy storage applications, the demand for electrochemical energy storage systems has been gradually growing in recent years. Utilizing porous structures with abundant channels, high surface area and conductivity are very important as a promising electrode material for pseudocapacitors. Remembering this, for the first time, COF (Phos-COF-1) based on phosphophine (PPh_3) has been identified for superconductors application and thus, it exhibits enormous potential for future electrochemical energy storage systems[16].

In gas separation, COFs show ideal application in gas separation technique through molecular separation membrane, but their nanopores are very wide, preventing selective gas separation by molecular sieve. Therefore, a new concept MOF-in-COF has been grown, where MOFs are supported inside a COFs layer to prepare MOF-in-COF membrane. This membrane shows magnificent performance in ultra-high H_2 permeability and separation selectivity to gas mixtures like H_2/CO_2 and H_2/CH_4[17].

Luminescent materials have a wide range of uses, including sensors, photovoltaics, bio probes, and optoelectronics. Small luminescent molecules are easily cost-effective and accessible. Compared to traditional one- or three-dimension polymer systems, the uniqueness of COFs can be logically built to generate organized π-structures with directionally predefined luminescent segment[2]. COF can also be used for sensing and detection of metal ions or small molecules. Ratiometric luminescent thermometers are a new carrier for grafting lanthanide ions (Ln^{3+}) and using these hybrid materials. Here, the LnCOF material suggests a new material for temperature sensing applications after the famous luminescent metal-organic frame thermometer[18].

The properties of COFs that influence adsorption and separation are: porosity, low densities, and large surface area, which can store and separate gases like carbon dioxide[19], methane[20], ammonia[21], and also hydrogen[20]. Due to high chemical energy density and clean combustion, hydrogen is considered an ideal alternative to traditional fossil fuels for the future. Adsorption of carbon dioxide has been intensively helpful to prevent global warming, contributing to greenhouse gas emissions and reducing industrial emissions. Methane is considered as an alternative for petroleum in automobile fuel since it is cleaner. But still, safe storage and efficiency is the main problem which is considered by COF.

For bio-related applications, the relationship between encapsulation and adsorption behaviors, COFs with nanoscale pores may be used to load and deliver medicines. In drug delivery, drugs can be delivered over time using degradable COFs based on boric acid. The chain of a molecule like Doxorubicin, Quercetin, and 5-Fluorouracil (5-FU), has contained COF as a drug delivery[22].

Chapter 2

2.1 Objective

A hydrazone-linked material is permanently porous, highly crystalline, and shows good thermal and chemical stability. Due to these characteristics, it exhibits excellent application in the field of catalysis, sensing, and host-guest chemistry.

The focus of this study is to get a [C_3+ C_3] hydrazone linked COF with narrow pore size distribution. Since the first example of hydrazone-based COF by Yaghi, a number of COFs have been reported and utilized in various applications such as catalysis, sensing, drug delivery, etc. The design of a hydrazone-based linkage for COF synthesis generally needs to be a substitution of an ethoxy group at the ortho position of linker units (e.g., 2,5-diethoxy-terephthalohydrazide (DETH)), which aids in the propagation of the two-dimensional conformation and the development of the crystalline structure. Hydrazone linkage is normally much less susceptible to hydrolysis than imine linkage. Most of the reported hydrazone COFs consist 2,5-diethoxy-terephthalohydrazide (DETH) as primary linker with substitution at ortho position, which enables specific feature for a particular application. Reported [C_3+ C_3] hydrazone COFs are limited and unexplored. With this motivation, we focused on synthesizing a [C_3+ C_3] hydrazone COF with metal chelating sites.

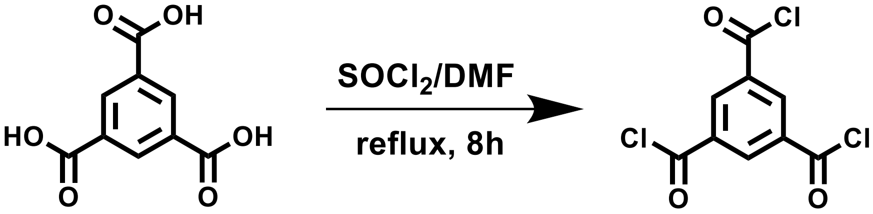
2.2 Materials and Methods

Without further purification, the solvents and chemicals were used as obtained. Thin-layer chromatography (TLC) was carried out on an aluminum sheet precoated with silica gel (Merck, Kieselgel 60, F254). Column chromatography was carried out on silica gel (60-120 and 100-200 mesh. The compound's structural properties were studied using a combination of ^{1}H NMR and ^{13}C NMR (Bruker Biospin Switzerland Avance-iii 400 MHz and 100 MHz spectrometers) and Infrared spectroscopy (Perkin Elmer Spectrum AX3). For intermediate and final compounds, infrared spectra were performed as KBr pellets. Deuterated solvents such as $CDCl_3$ and DMSO-d_6, as well as tetramethylsilane (TMS) as an internal standard, were used to record ^{1}H NMR spectra.

2.3 Synthesis of monomers and COF

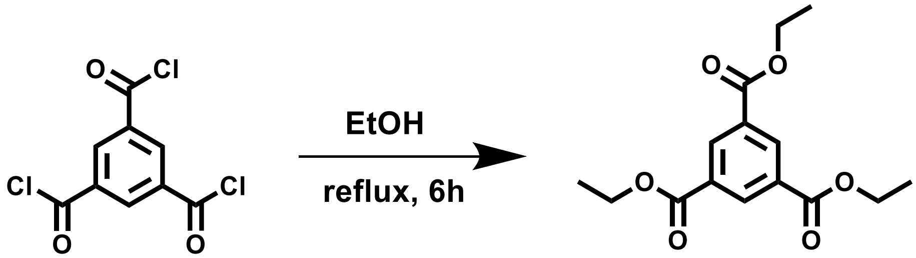
2.3.1 Synthesis of 1,3,5-Benzenetricarbonyl Trichloride:

As per literature[23], in a round bottom flask, (2 g, 0.0095 mol) 1,3,5-benzenetricarboxylic acid, 1 drop of dimethylformamide (DMF) and 5 mL of thionyl chloride ($SOCl_2$) were added. Then the reaction solution was heated under reflux for 8 hours, resulting in a clean solution. The excess $SOCl_2$ was removed under vacuum and the resulting colorless liquid benzene-1,3,5-tricarbonyl trichloride was used for the next step without any further purification.



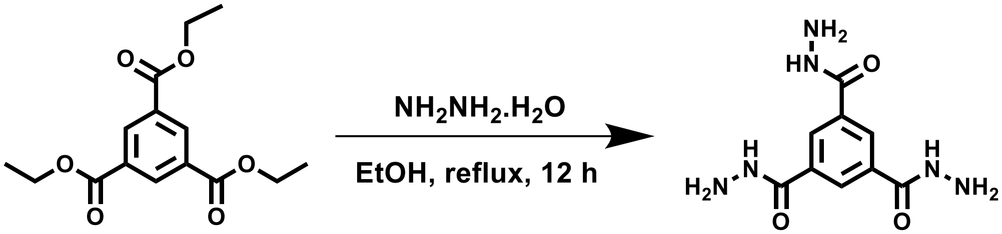
2.3.2 Synthesis of Triethyl 1,3,5-Benzenetricarboxylate:

As per literature[23], 5 mL of ethanol was 1,3,5-Benzenetricarbonyl trichloride, obtained from the previous step, this mixture was heated at 80 °C for 6 h and a solid white precipitate was formed. After cooling to RT (~1 h). The precipitate was washed in cold EtOH and then kept overnight for drying, forming triethyl benzene-1,3,5-tricarboxylate. The resulting compound used for the next step without any purification.



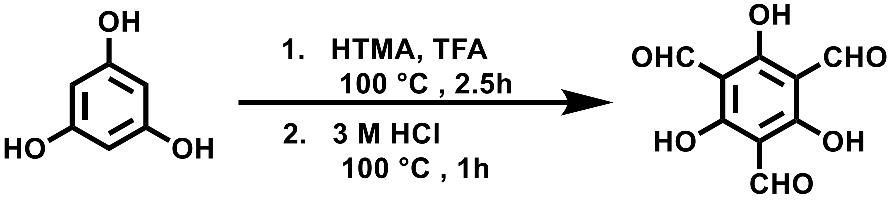
2.3.3 1,3,5-Benzenetricarboxylic Acid Trihydrazide (Bth):

As per literature[23], in a 100 mL round bottom flask, the solid (2 gm, 6.79 mmol) Triethyl 1,3,5-Benzenetricarboxylate was suspended in 50 to 80 mL of ethanol and 5 mL of hydrazine hydrate. Then the suspension was heated under reflux for 12 hours. After that, the reaction mixture was kept at room temperature for cooling. Then the mixture was filtered to collect the precipitate and washed with ethanol and water. The white solid was dried to yield the respective final product, and the yield of the product obtained was 95%. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.87 (s, 3H), 8.32 (s, 3H), 4.59 (s, 6H). ^{13}C NMR (DMSO-$d_{6,}$ 100 MHz) δ 165.47, 134.3, 128.51.



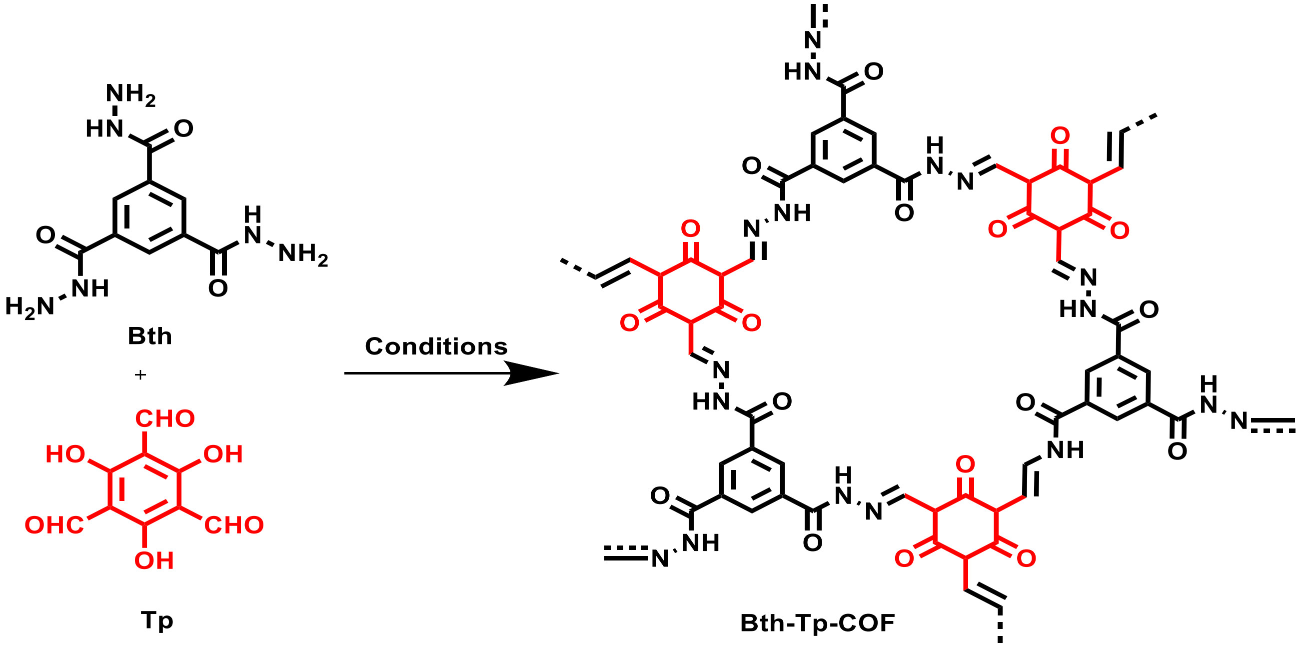
2.3.4 Synthesis of Triformylphloroglucinol (Tp):

According to literature[24], in a 250 mL round bottom flask, (3.0 g, 49 mmol) anhydrous phloroglucinol, (7.5 g, 108 mmol) hexamethylenetetramine (HMTA) and 45 mL trifluoroacetic acid (TFA) were added and refluxed for 2.5 h at 100 °C under inert atmosphere. Then by slowly adding 75 mL of HCl (3M) in a mixture and heating for 1 hour at 100 °C. Then the mixture was cool to room temperature, filtered the mixture through Celite, and extracted with DCM. Evaporate a resulting solution in a vacuum to obtain white powder product and the yield of the product was 80%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 14.1 (s, 3H), 10.0 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 192.11, 173.61, 102.89.



2.3.5 Synthesis of Bth-Tp-COF:

In a 10 mL Schlenk tube, (10 mg, 0.039 mmol) Bth and (8.3 mg, 0.039 mmol) Tp both were added in a different proportion of solvents, given in table 1. The mixture was sonicated for 10 min until it became homogeneous. 0.1 mL (6M) of the acetic acid solution was then added to a tube. By connecting the vacuum, the tube was dipped in liquid nitrogen at 77K to freeze the mixture, and then the vacuum was applied to degas and then close the tube. Place the solid mixture in hot water to convert it into a liquid, repeat the process until it degassed. Then the mixture was allowed to heat for 72 hours at 120 °C. After that, the tube was cool to room temperature, and the precipitate was formed by filtration, washed with a different solvent like acetone, dichloromethane (DCM), 1,4-dioxane, and anhydrous tetrahydrofuran (THF), and kept for drying at 100 °C for 9 hours under vacuum to give a yellowish solid.



The synthesis of Bth-Tp-COF was carried out under solvothermal conditions. To get the crystallinity in the framework, various solvent combinations were used. All the solvent combinations are given in Table 1, and the observed PXRD patterns are given in Figure 7.

S.N.	**COMP A(mg)**	**COMP B(mg)**	**SOLVENT**	**VOL. (mL)**	**AcOH (6M) (mL)**	**RESULT**	**PXRD**
1	Bth (12mg)	Tp (10mg)	Mesitylene	0.75	0.1	Amorphous	01
			Dioxane	0.25			
2	Bth (37.5mg)	Tp (31.5mg)	DMAc	1	0.15	Crystalline	16
			DMSO	0.5			
3	Bth (10mg)	Tp (8.3mg)	DMAc	0.5	0.1	Crystalline	17
			DMSO	0.5			
4	Bth (10mg)	Tp (8.3mg)	DMAc	0.3	0.1	Moderate crystalline	18
			DMSO	0.7			
5	Bth (10mg)	Tp (8.3mg)	DMAc	0.9	0.1	Crystalline	19
			-	-			
6	Bth (10mg)	Tp (8.3mg)	DMF	1	0.1	Crystalline	20
			-	-			
7	Bth (10mg)	Tp (8.3mg)	DMF	0.7	0.1	Crystalline	21
			DMSO	0.3			
8	Bth (10mg)	Tp (8.3mg)	DMSO	1	0.1	Amorphous	12
			-	-			

Table 1. Optimization table for the synthesis of Bth-Tp-COF

2.4 Bulk Characterization of Bth-Tp-COF:

The successful formation of Bth-Tp-COF was initially characterized by FT-IR spectroscopy. Powder X-ray diffraction study used to understand the crystallinity of Bth-Tp-COF. Measurement of surface area and pore diameter were characterized by nitrogen adsorption-desorption isotherm. To observe the morphology of Bth-Tp-COF, SEM and TEM studies were carried out. Thermal stability was characterized by TGA. In this section, the observed results from these studies are discussed in detail.

2.4.1 FT-IR Spectroscopy:

The FT-IR spectra of Bth, Tp, and Bth-Tp-COF are given in Figure 6. The carbonyl stretching (C=O) frequency of Tp at 1639 cm^{-1} and amine (N-H) stretching frequency in Bth at 3302 cm^{-1} disappeared from spectra of Bth-Tp-COF. A new stretching frequency at 1550 cm^{-1} appeared in the FT-IR spectrum of Bth-Tp-COF that could be assigned as imine (C=N) stretching vibrations.

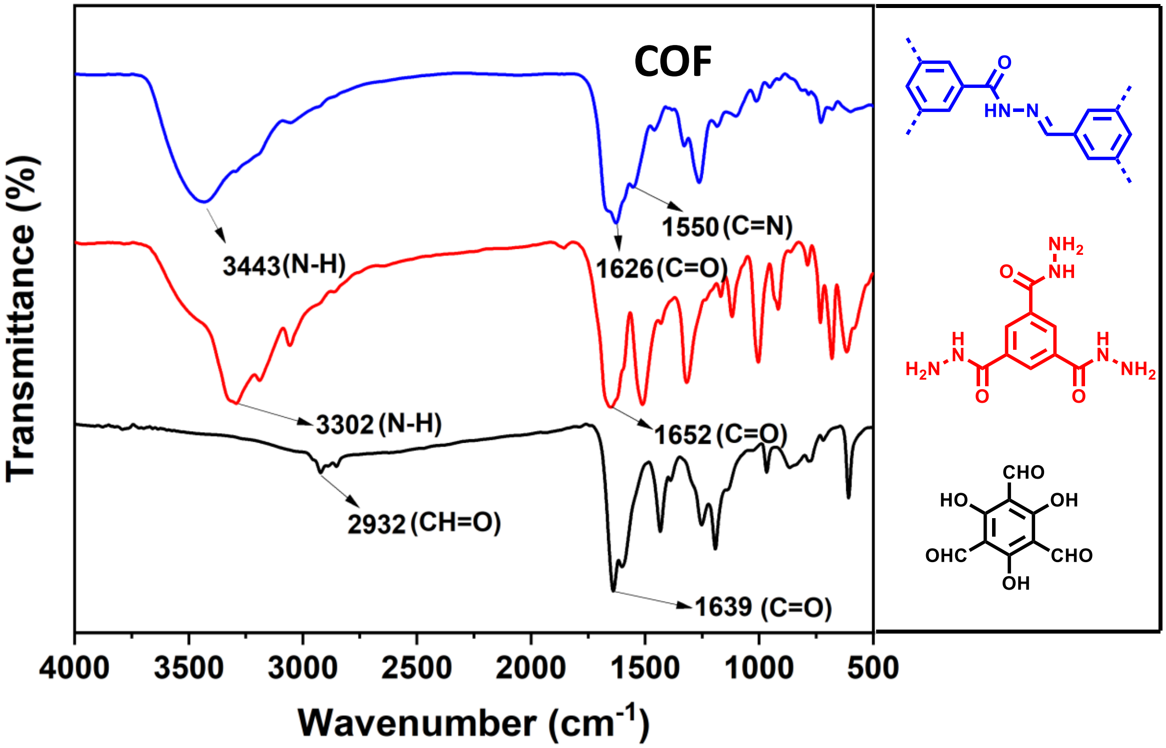


Figure 6: FT-IR spectra of Tp (black), Bth (red) and Bth-Tp-COF (blue).

2.4.2 Powder X-ray Diffraction (PXRD) pattern of Bth-Tp-COF:

The powder X-ray diffraction (PXRD) was used to analyze the crystallinity of Bth-Tp-COF. As shown in Figure 7, the first prominent peak was observed at 6.2° and an additional weak peak at 11°. Another broad peak at 23.9° was observed, which could be assigned to the π - π stacking between layers.

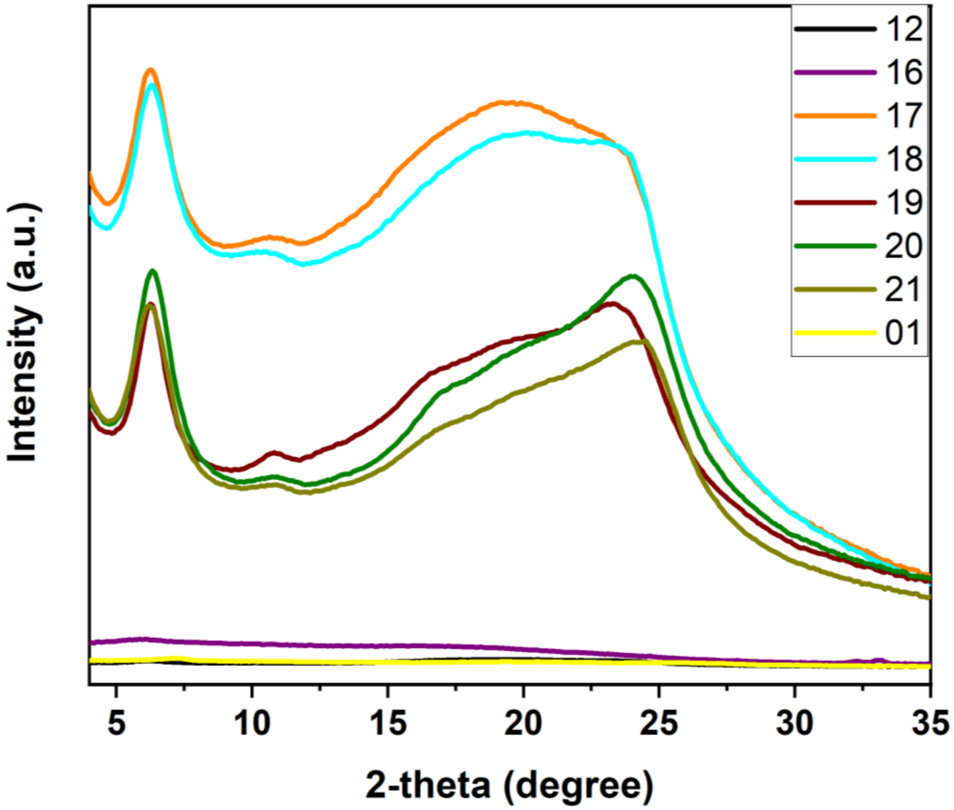


Figure 7: Experimental PXRD pattern of Bth-Tp-COF.

2.4.3 Brunauer–Emmett–Teller (BET):

The formation of micropores is clearly visible in nitrogen sorption measurements at 77 K, as shown by a standard type I adsorption isotherm. Brunauer–Emmett–Teller (BET) was calculated to be 120 m^2 g^{-1}. Non-local density functional theory (NLDFT) was used to measure the pore size distribution, which showed the prominent peak with a pore radius of 1.5 nm. (Figure 8).

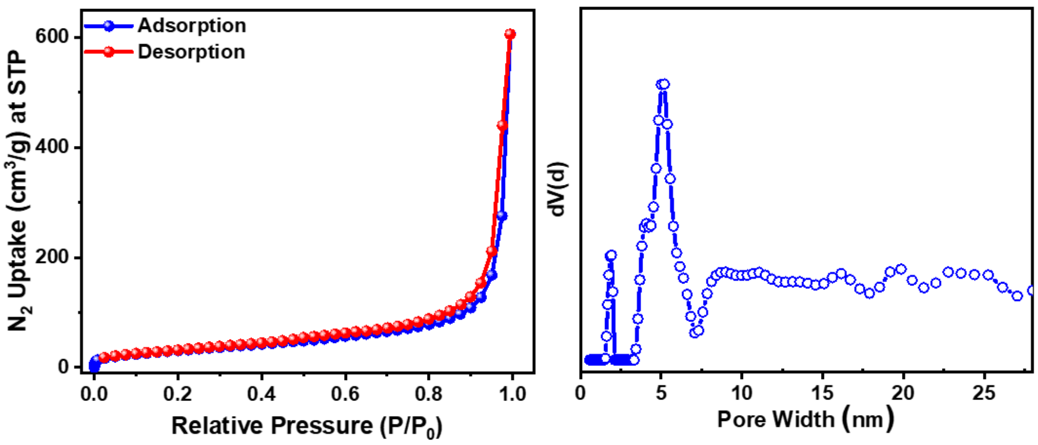


Figure 8: N_2 adsorption-desorption and pore size distribution curve of Bth-Tp-COF.

2.4.4 Thermogravimetric Analysis (TGA):

Thermogravimetric analysis (TGA) was carried out on the dry COFs samples under a nitrogen atmosphere. TGA result shows the thermostability of Bth-Tp-COF, and it displayed that the Bth-Tp-COF is stable up to 320 °C, as shown in Figure 9. COF has usual thermal stability of up to 450 °C.

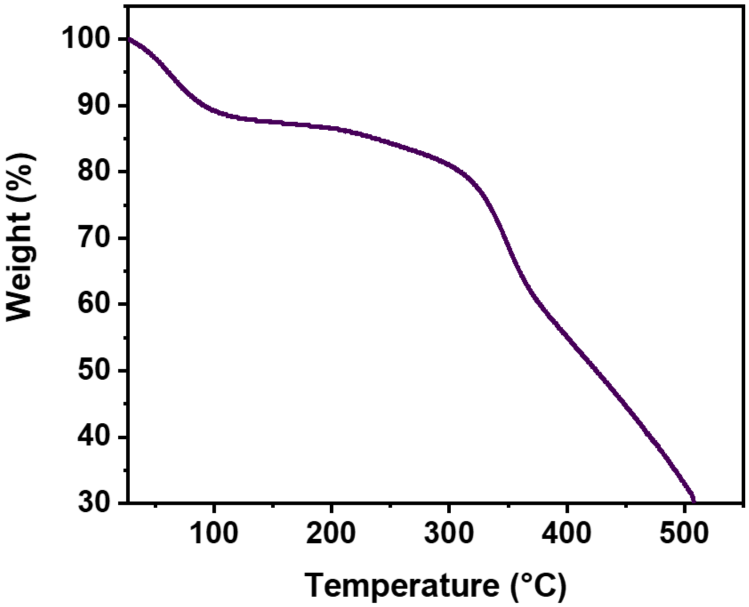


Figure 9: TGA plot of Bth-Tp-COF.

2.2.5 SEM and TEM analysis:

The morphology of the Bth-Tp-COF was determined by the Scanning Electron Microscopy (SEM) technique. As shown in figure 10, a porous, sponge-like morphology was observed. HR-TEM images revealed stacked lattice fringes with a layer distance of 0.35 nm.

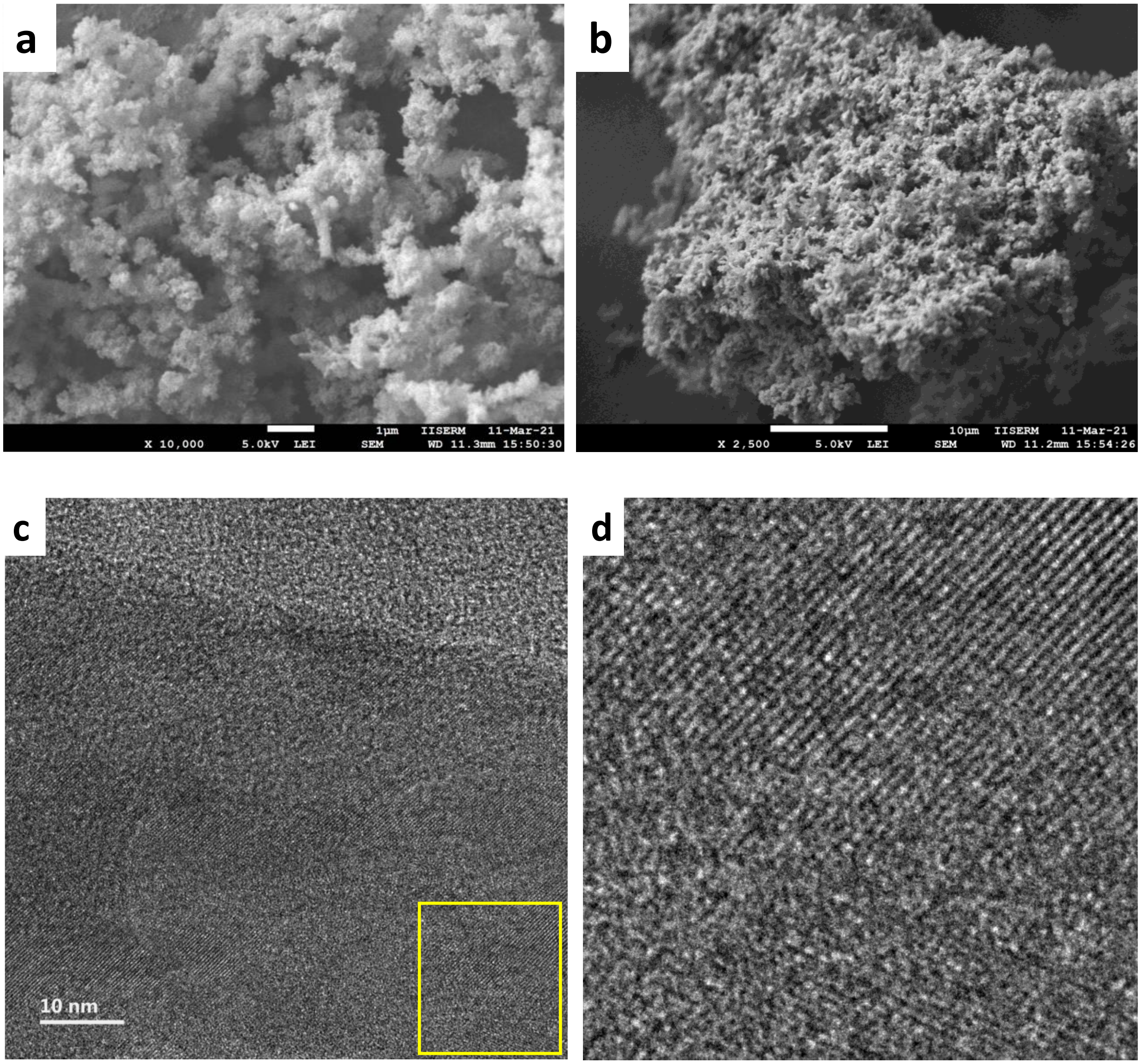


Figure 10: SEM (a,b) and TEM images (c,d) of Bth-Tp-COF.

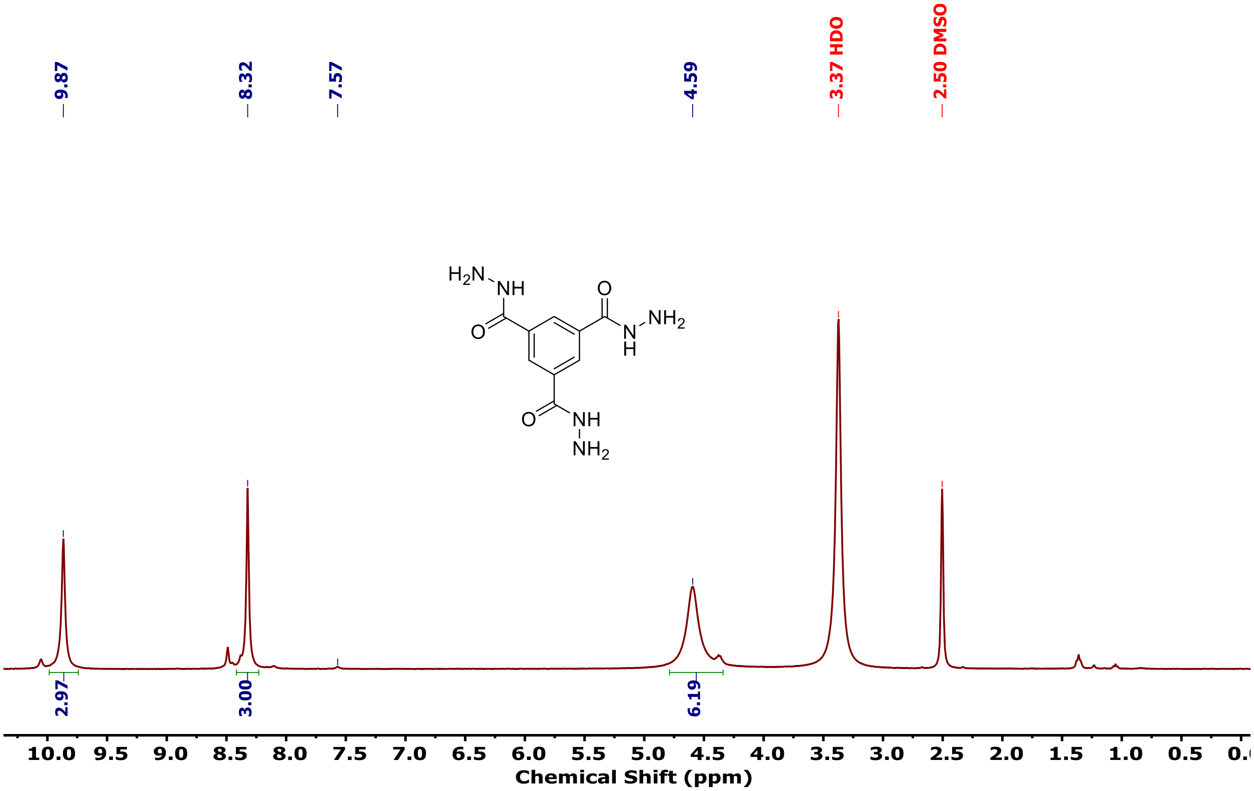
3. Conclusion

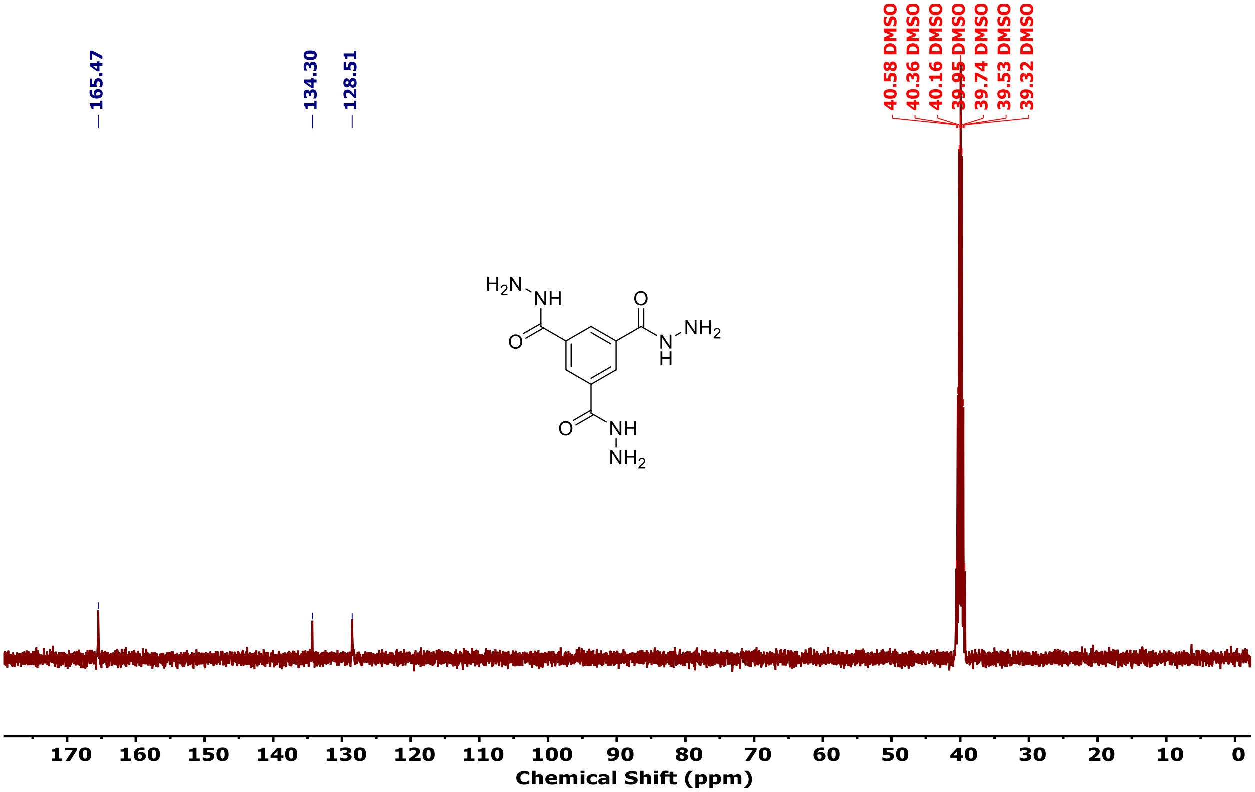
In this thesis, we have successfully synthesized a [C_3 + C_3] hydrazone-based Bth-Tp-COF. The synthesized Bth-Tp-COF is crystalline and possesses a BET surface area of up to 120 m^2g^{-1}. Bth-Tp-COF is thermally stable up to 320 °C, analyzed from TGA. SEM and TEM studies revealed the morphology and internal structure of Bth-Tp-COF. Both studies confirmed the successful synthesis of the Bth-Tp-COF.

As Bth-Tp-COF possesses an excellent site to coordinate with the metals, this COF can be utilized for sensing or doping a metal. As Bth-Tp-COF has a functional chelating site, which can be exhibit fluorescence in an aqueous medium that can use as a turn-off or turn-on fluorescence sensor for some metal ions.

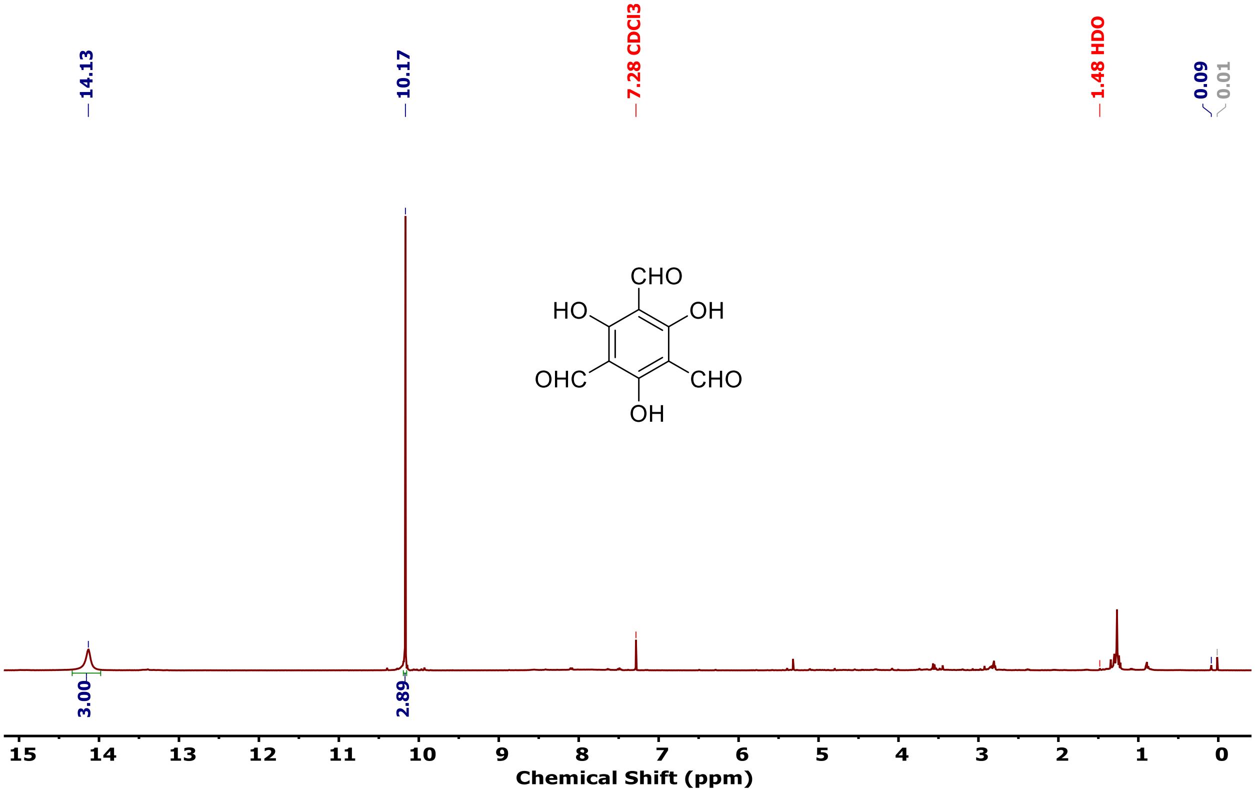
Appendices

3.1 Nuclear Magnetic Resonance (NMR)

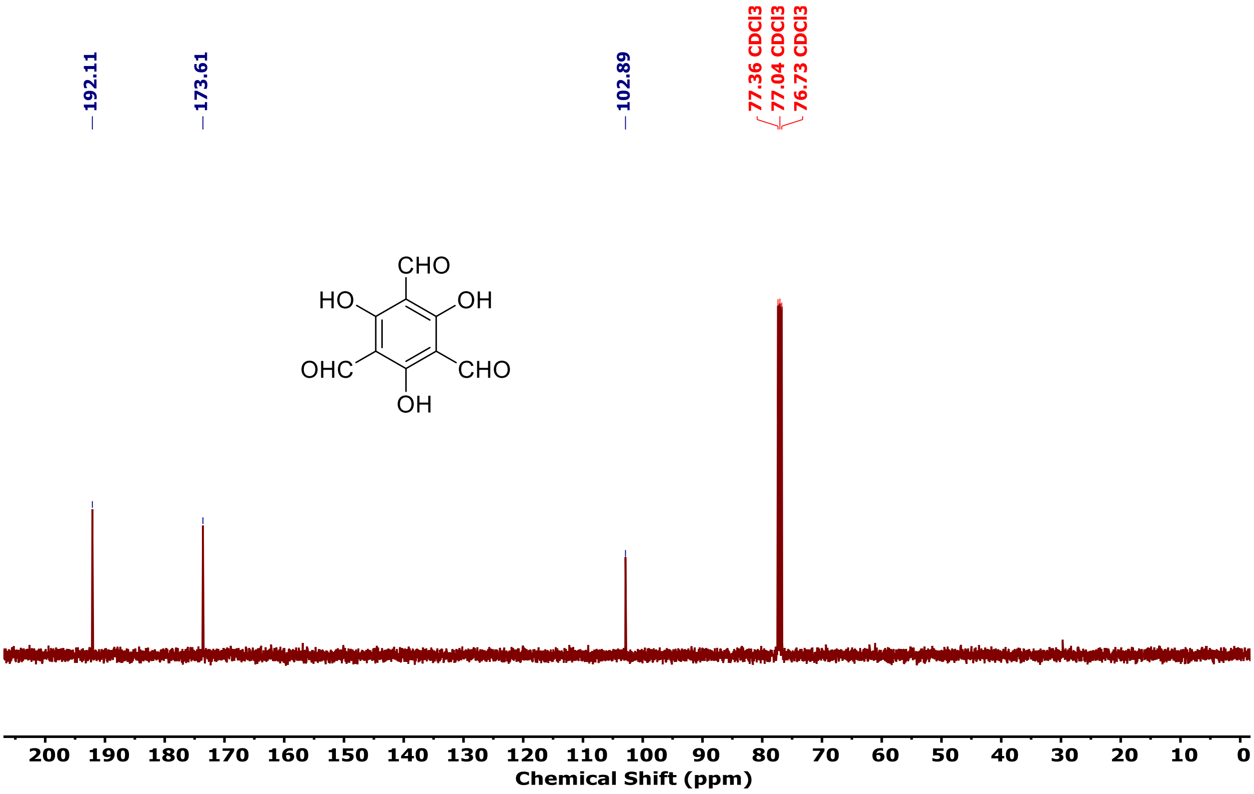




165.47
134.30
128.51
40.58 DMSO
40.36 DMSO
40.16 DMSO
39.95 DMSO
39.74 DMSO
39.53 DMSO
39.32 DMSO
H_2N
NH
O
O
N
NH_2
H
O
NH
NH_2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)



14.13
10.17
7.28 CDCl3
1.48 HDO
0.09
0.01
CHO
HO
OH
OHC
CHO
OH
3.00
2.89
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


192.11
173.61
102.89
77.36 CDCl3
77.04 CDCl3
76.73 CDCl3
CHO
HO
OH
OHC
CHO
OH
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)

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