Design and Synthesis of Novel N-heterocycle based Covalent Organic Framework (COF)

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Certificate of Examination

This is to certify that the dissertation titled "**Design and Synthesis of Novel N-heterocycle based Covalent Organic Framework (COF)**" submitted by **Mr. Mohamed Musthafa Iqbal** (Reg. No. MS12061) 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. Angshuman Roy Choudhury Dr. Debashis Adhikari Dr. Santanu Kumar Pal
(Supervisor)

Dated: April 19, 2017

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.

Mohamed Musthafa Iqbal
(Candidate)

Dated: April 19, 2017

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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Mohamed Musthafa Iqbal

List of Figures

List of Schemes

Abbreviations

COF	Covalent Organic Framework
MOF	Metal Organic Framework
IUPAC	International Union of Pure and Applied Chemistry
CTF	Covalent Triazine Framework
Tp	1,3,5-Triformylphloroglucinol
DAC	3,6-diaminocarbazole
DNC	3,6-dinitrocarbazole
TpAn	2,4,6-tris-[(phenylamino)methylene]cyclohexane -1,3,5-trione
FT-IR	Fourier transform infrared spectroscopy
WAXS	Wide Angle X-ray Scattering
SAXS	Small Angle X-ray Scattering
SEM	Scanning Electron Microscope
TGA	Thermogravimetric analysis
DSC	Differential scanning calorimetry
XRD	X-ray Diffraction

Contents

Abstract

Covalent organic frameworks (COFs) are a new class of porous organic polymers which is entirely made up of light elements (B, C, N, O, H). Unlike other organic polymers they show crystallinity and periodic pores. It has gained wide attraction due to its features such as the significant stability due to covalent bonding, great structural diversity due to the versatile combination of building units, large surface area, low density, tunable pore size etc. It has shown interesting applications in gas storage, adsorption, separation, optoelectricity, catalysis, and as functional devices.

In this MS project thesis, on the topic "Design and synthesis of Novel N-Heterocyclic Covalent Organic framework (COF)", we are focusing on the synthesis of COF based on imine linkage, which can act as a surface for adsorption/separation of small molecules. To use it as a substrate for catalysis or host-guest chemistry, the pores need to be functionalised. Till now there are very few reports of post-synthetically modifying the COF through substitution reactions on pore walls. As a step forward, we have introduced a carbazole moiety which can be modified through substitution reaction methods.

First chapter deals with the basic introduction of COFs, its advantages and applications. Second chapter includes the synthetic schemes we followed and the experimental procedures. In third chapter, results, conclusions and the future work that can be carried out are explained.

Chapter 1

Introduction

1.1 Basics of Covalent Organic Framework (COF)

Currently there is an urge in the chemical science to find the organic analogues of different materials in opto-electronics, solar cells, catalysis, porous materials etc. As a result there is an emerging field of a new class of materials called Covalent Organic Frameworks (COF), which is an organic analogue of porous inorganic materials known as Metal Organic Frameworks (MOF). They are two or three dimensional organic structures having periodic arrangement of linking units, which are covalently bound and have definite pore geometry. Since the first discovery of COF materials in 2005 by Yaghi and co-workers,[1] there have been tremendous advancements in the field of porous materials with exceptional porosity.

In principle the synthesis of COF is based on reticular chemistry, the geometry and dimensions of the organic building blocks and linkages determine the size and topological structures of pores in the resulting COFs. For example, a combination of C_3- symmetrical monomer and C_2- symmetrical linear monomer will give a COF with hexagonal pores. Dynamic covalent bond and reversibility of the reactants are involved in the self-reconstruction of the oligomers, till a stable framework is formed.[2] This act as an agent of error checking and proof-reading during synthesis and ensures a periodic framework structure is formed. Previous studies have proved that the introduction of heteroatoms such as oxygen, nitrogen, and boron provides crystallinity to the framework.[3]

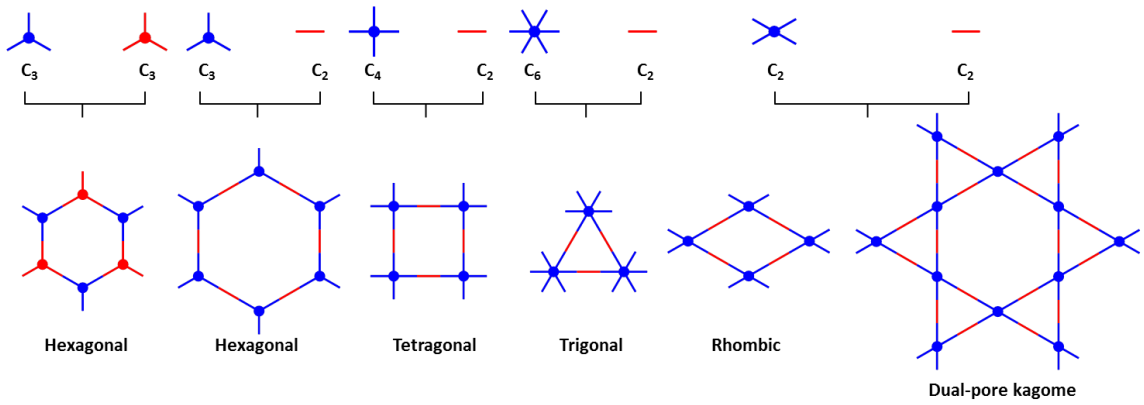


Figure 1. Different topology designs in 2D COFs

1.2 History of Nano-porous materials

According to IUPAC porous materials are classified into Microporous materials (those with pore diameter less than 2 nm), Mesoporous materials (those with pore diameter between 2 nm and 50 nm) and Macroporous materials (those with pore diameter greater than 50 nm). A large number of porous materials have been designed and synthesized since last century. One of the first nano-porous materials discovered were natural zeolites, coined by Swedish mineralogist A.F. Cronstedt in 1756. Much later Porous organic polymers like hyper crosslinked polymers (HCP), conjugated microporous polymers (CMP) etc. were discovered. Metal organic frameworks (MOF), which were the predecessor of COF were first discovered in 1998 by Yaghi and co-workers. It is made up of metal oxide nodes and organic linkers. Later COF and Covalent Triazine-based Framework (CTF) were discovered which were made up of lighter elements only.

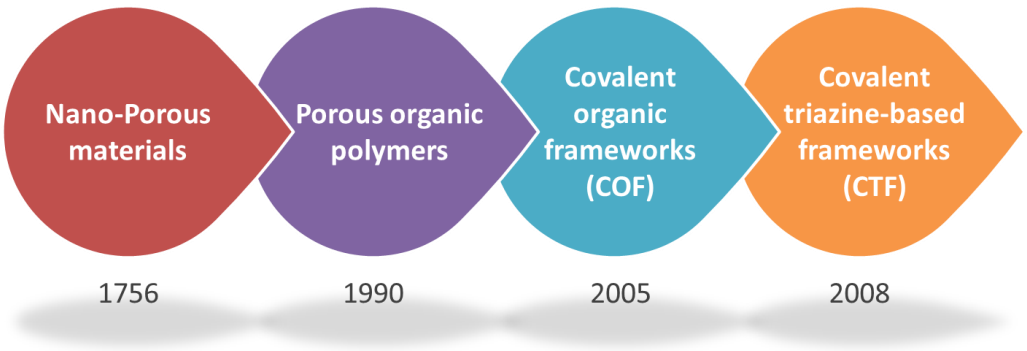


Figure 2. History of Nano-porous materials

1.3 Classification of COFs

On the basis of linking reactions used, COFs are mainly classified into *boronate ester linkage* based COF, *imine linkage* based COF, *hydrazone linkage* based COF and *triazine* based COF or CTF. On the basis of dimensionality there are two and three dimensional (2D and 3D) COFs. In 2D COFs, the monomers combine to form 2D nano-sheets which assemble on top of each other with help of weak interactions (such as π–π stacking). 3D COFs are made using tetrahedral-structured building units like adamantine[4] or tetraphenylmethane linkers.[5]

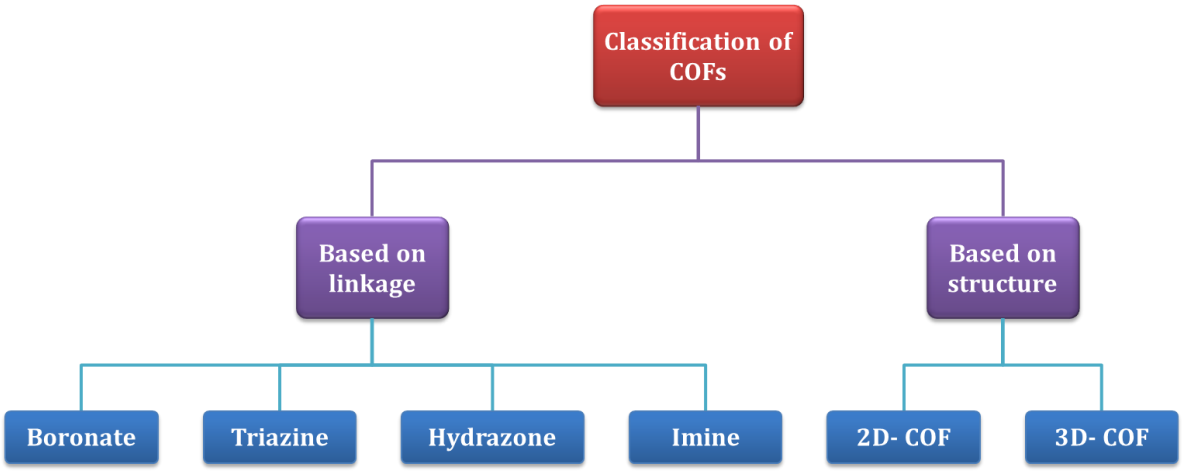


Figure 3. Classification of COFs

1.4 Synthetic methods and Linkages

COFs are crystalline porous organic polymers, but to ensure its structural regularity and porosity the chemical reactions should be reversible. This enables the COF to proof-read its structure during synthesis and self- repair any structural defects. Hence the reversibility of linkage and dynamic covalent chemistry plays a crucial role in the formation of these highly ordered frameworks.

1.4.1 Boronate anhydride and Boronate ester linkage

Boronate anhydride is formed by self-condensation of boronic acid residues. Condensation of boronic acid and catechol residues gives boronate ester linkage. These were the linkages used by Yaghi and coworkers to synthesize the first COF materials, COF-1 and COF-5.[1]

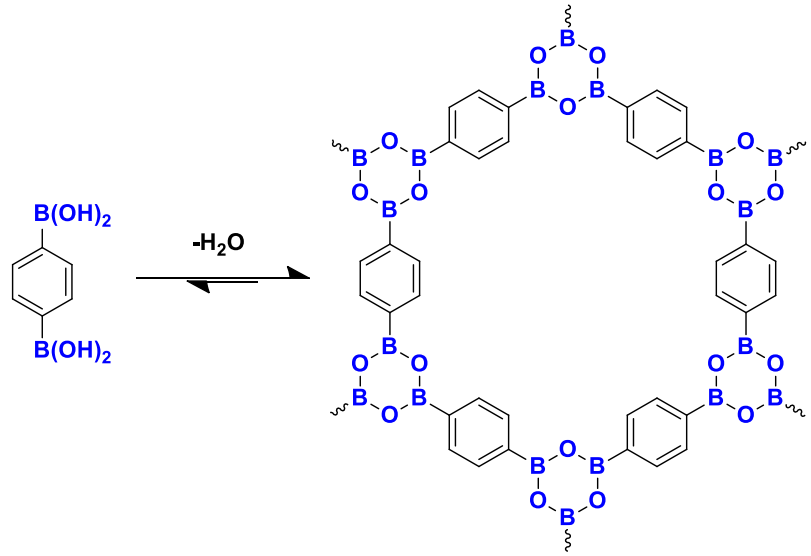


Figure 4. Self-condensation of boronic acid to synthesize COF-1

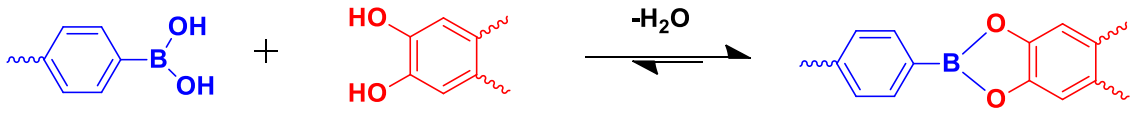


Figure 5. Boronate ester linkage formation

1.4.2 Imine (Schiff-base) linkage

This is a common linkage used to prepare COFs. There has been many report of COFs with this linkage,[6] it is mainly due to the facile reaction conditions. This is prepared by the condensation between aldehyde linkers and amino linkers. The main advantage of this linkage is that the materials prepared by this route show exceptional stability in acidic and basic medium.

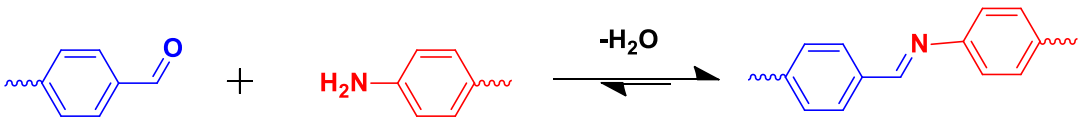


Figure 6. Imine linkage formation

1.4.3 Hydrazone linkage

Similar to imine linkage, C-N bond is also formed by condensation between hydrazine linker and aldehyde linker. Hydrazine linkers with alkoxyl groups in o–position is reported to have H-bonding, thus it will stabilize to form robust frameworks.

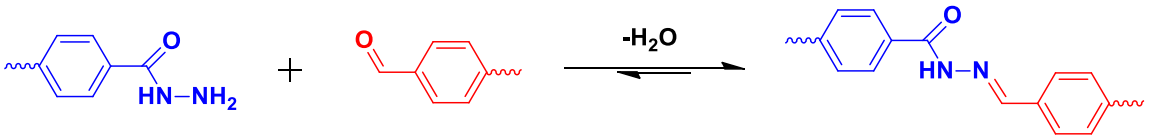


Figure 7. Hydrazone linkage formation

1.4.4 Triazine linkage

Aromatic nitrile linkers in molten $ZnCl_2$ at 400˚C, cyclotrimerize to form triazine linkage. It can also be performed at room temperature in presence of strong acid catalyst, like triflouromethylsulphonic acid. CTFs were first developed by Thomas and co-workers (CTF-1).[7] CTFs can be used as a catalytic support for metal center due to the presence of nitrogen atoms, but till now none have been reported.

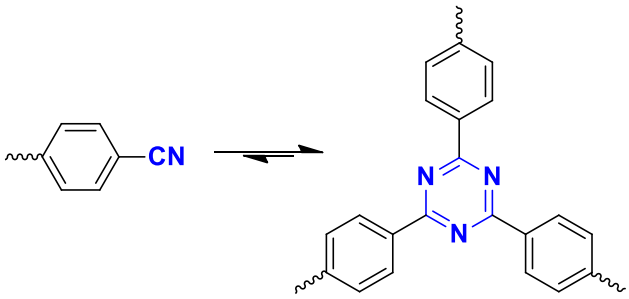


Figure 8. Triazine linkage formation

1.5 Functionalization of COFs

For performing certain specific functions like catalysis and host-guest chemistry, the pore walls of the COF can be modified. The functionalization of COF can be done in two ways. (i) Pre-synthetic modification, it is through functionalizing the molecular building units by attaching different alkyl groups or functionalities before the synthesis of COF. (ii) Post-synthetic modification, it is by modifying the pore walls after the synthesis of COF mainly click chemistry. Figure 9 shows the common reactions used for post-synthetic modification. These methods allow the incorporation of controlled amounts of different functionalities, creating modified versions of COFs with different properties.

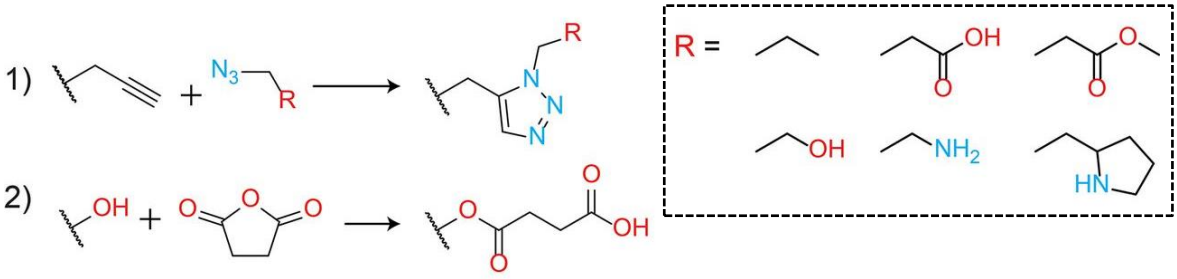


Figure 9. Common Post-synthetic modification routes

Another modification possible is by incorporation of metal ions or complexes into COFs. C-N linkages in COFs are demonstrated to coordinate with variety of metal ions. Most of the time hydroxyl groups in the building units also take part in stabilizing the coordination. Palladium(II) coordinated-COF material has been prepared by treatment of an imine based-COF with $Pd(OAc)_2$ and has been used for heterogenous catalytic application.[8]

1.6 Applications of COFs

Many COFs with variety of functionalities can be obtained using design principles described above. It has gained wide attraction due to its features such as the robust

stability due to covalent bonding, great structural diversity due to the versatile combination of building units, large surface area, low density, periodic and homogenous pores, tunable pore size, insolubility etc. In 2D COFs, continuous nano-channels are formed as a result of stacking the planar sheets. Their diameter can be varied by linkers or the favoured configuration. 2D COFs having eclipsed configuration will have wider channels while those having staggered configuration will have narrow channels.

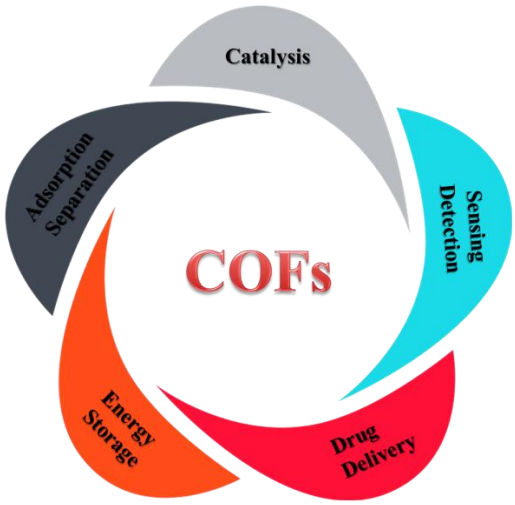


Figure 10. Selected application areas of COFs

The main application of COF is in gas adsorption and storage. It is the most studied characteristic of COFs. Their porosity, large surface area and low densities enable them to store and separate gases such as carbon dioxide,[9] methane,[10] ammonia[11] and even hydrogen.[12] Carbon dioxide capture will help to reduce the emissions and prevent global warming. Methane is considered as an alternative for petroleum in automobile fuel since it is cleaner. Due to the green combustion and high energy density, hydrogen is considered as the ideal power source of future. But the main problem faced is its efficient and safe storage, which is addressed by COF. COFs are also used for sensing and detection of small molecules, metal ions etc.[13]

For catalytic applications also, COFs have been successfully used. There are examples of base functionalised COFs which are used for Knoevenagel condensation reactions[4] and for Micheal addition reactions.[14] They are also used as a catalyst after loading with metal

centres. Pd loaded COF-LZU1, synthesized by Wang and co-workers showed very good catalytic activity in the Suzuki-Miyaura coupling reaction.[15] Water splitting reactions are also carried out with help of COF. Lotsch and co-workers synthesised hydrazone-based COFs doped with Pt which can act as hydrogen evolution catalyst from water in presence of visible light.[16] Banerjee and co-workers made COF modified with Co ions as a water oxidation electrocatalyst.[17] Carbon dioxide reduction has also been carried out using cobalt porphyrin based COF in aqueous medium.[18]

In the field of energy storage and opto-electronics also COF is a feasible candidate. Incorporating electron donors and acceptors moieties as linkers for making COFs make them suitable for organic opto-electronic devices. This donor-acceptor interface and aligned π arrays help them achieve light adsorption, electron transfer and charge separation thus they can be used for photo-induced electron transfer.[19] COFs prepared from aromatic building units and luminescent π systems like pyrene, porphyrine, perylene etc. show possible application in these fields. For light emitting applications also emmisive COFs are being developed.[20] Their π–π stacked layered structure makes them suitable for these applications. Recently, a boronate ester linked naphthalene diimide based 2D COF showed interesting application as cathode material in Li-ion batteries.[21] A new porphyrin based 2D COF was used as host materials for sulphur impregnation in Li-S batteries and thus able to improve its performance and stability.[22]

Chapter 2

Experimental Procedures

2.1 Objective

As we discussed in the first chapter, 2D COFs has a wide range of applications in the field of catalysis. Their porosity, large surface area and insolubility help them in heterogeneous catalytic application. For using the COF specific functions like catalysis and host-guest chemistry, the pore surface need to be modified. There are many reports of using pre-designed building units for pore functionalization but reports for pore surface modification post-synthesis are few. Most of the functionalization is through click chemistry using azide group.[23] The examples of COFs using substitution reactions (S_N1 or S_N2) are close to none. Bearing this in mind, in our project we have incorporated a post-synthetic modification site, which can be modified through substitution reaction methods.

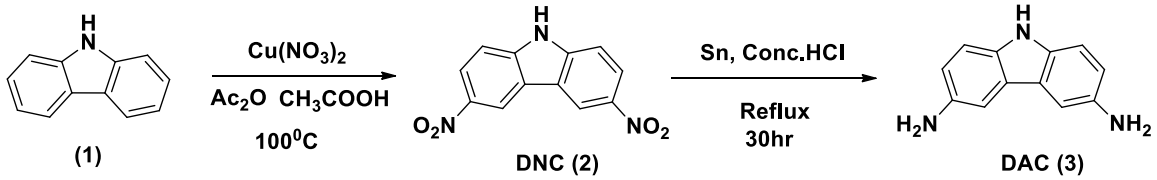
Imine-linked COFs are well studied and easy to prepare also, but the major drawback faced by them is instability due to reversibility of the linkage. They are sensitive to moisture, acidic and basic conditions. Some previous studies has proved that using 1,3,5-Triformylphloroglucinol (Tp) could enhance the chemical stability by keto-enol tautomerism and H-bonding.[24] There are previous reports of using carbazole moiety in hypercrosslinked porous polymers (HCPs) for CO_2 capture and storage.[25] There are also reports of other carbazole based polymers mainly due to its fluorescence and electron accepting properties. But till date there are no reports of using carbazole moiety as a linking unit for COFs. So our aim is to make an imine-linked COF with Triformylphloroglucinol (Tp) and 3,6-diaminocarbazole (DAC).

2.2 Materials and Methods

All the reactions were performed under N_2 atmosphere. Chemicals and solvents (AR quality) were used as received without any further purification. Column chromatographic separations were performed on silica gel (100–200 & 230-400 mesh). Thin layer chromatography (TLC) was performed on aluminium sheets pre-coated with silica gel (Merck, Kieselgel 60, F254). Structural characterization of the compounds was carried out through a combination of ^{1}H NMR and ^{13}C NMR (Bruker Biospin Switzerland Avance-iii 400 MHz and 100 MHz spectrometers respectively), Infrared spectroscopy (Perkin Elmer Spectrum AX3), and ESI-MS spectrometry (WATERS Synapt G-2-S QTOF). IR spectra were recorded in KBr pellet form for intermediate and target compounds. ^{1}H NMR spectra were recorded using deuteriated solvents like $CDCl_3$, DMSO-d_6 etc. and tetramethylsilane (TMS) as an internal standard.

2.3 Synthetic scheme of 3,6-diaminocarbazole (DAC)

The proposed synthesis of DAC is outlined in scheme 1. DNC (2) and DAC (3) were synthesized according to the reported methods[26]. The synthesis starts from nitration of carbazole (**1**) with copper(II) nitrate to give DNC (2). Reduction of DNC (2) with tin and conc.HCl gave DAC (3). The formation of the product was confirmed by ^{1}H NMR and FT-IR spectroscopy.



Scheme 1. Synthesis of 3,6-diaminocarbazole (DAC) **(3)**

2.3.1 Synthesis of 3,6-dinitrocarbazole (DNC) (2)

In a 100 mL round bottom flask, $Cu(NO_3)_2 \cdot 3H_2O$ (5.218 g, 21.6 mmol), acetic acid (14.4 mL), and acetic anhydride (21.6 mL) was taken. A homogenous mixture was prepared at

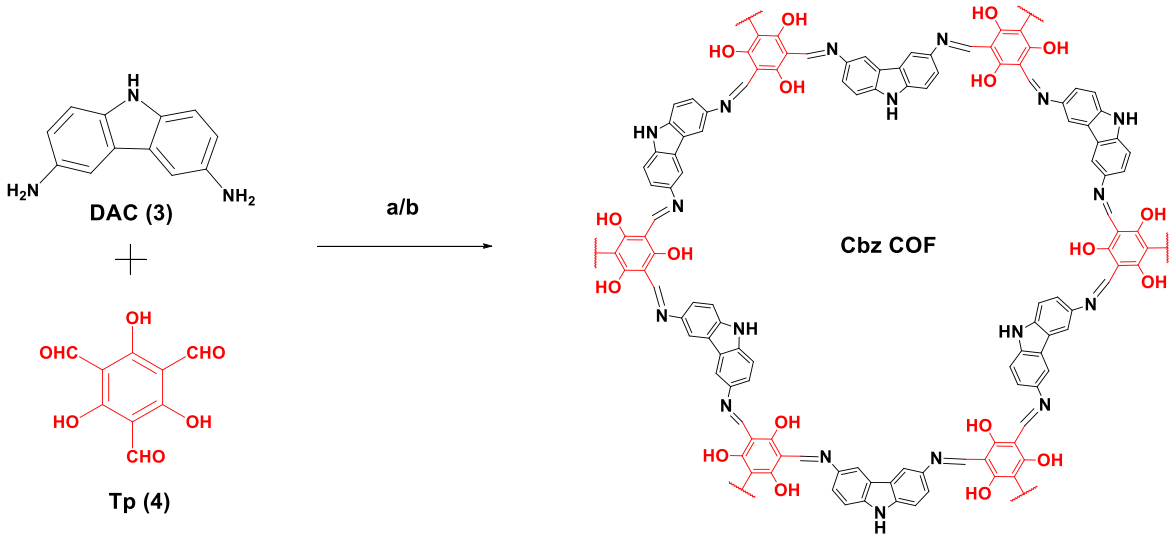
room temperature. Then carbazole **(1)** (3 g, 18 mmol) was added to this slowly in 10 mins at 15–20˚C. Then gradually the temperature was allowed rise to room temperature over a period of 30 min and then to 90-100˚C. The reaction mixture was stirred at this temperature for 30min. The mixture was diluted with additional 10 mL of acetic acid, and poured into 180 mL of distilled water with constant stirring. The precipitate was collected by filtration, and washed five times each with about 100 mL of distilled water. The wet residue was dissolved in a cold solution of 12 g of KOH, 180 mL of ethanol, and 180 mL of water. The red solution was stirred for 30 min, and filtered. The filtrate was then acidified with concentrated hydrochloric acid, and allowed to settle for 30 min. The precipitate was collected by filtration, washed several times with cold water, and dried in vacuum at 100˚C to get a fluffy yellow solid of yield 3.23 g (70%). **^{1}H NMR (400MHz, DMSO-d_6, δ ppm)**: 9.51 (s, 2H), 8.42 (d, 2H), 7.79 (d, 2H). **IR (KBr pellet, ν_{max}/cm^{-1})**: 3082, 1618, 1577, 1503.26, 1467.78, 1332.85, 1221.26, 1171.7, 868.15, 806.37

2.3.2 Synthesis of 3,6-diaminocarbazole (DAC) (3)

A 100ml 2-necked round bottom flask was charged with compound DNC **(2)** (1.5 g, 5.80mmol) and 36 mL of acetic acid. The mixture was stirred well under a nitrogen atmosphere. Then tin metal bits (6 g, ∼50 mmol), and 9 mL of concentrated hydrochloric acid were added to it. The mixture was stirred in 100˚C under nitrogen atmosphere for 30 hrs. After cooling the resulting reaction mixture, it was poured into an aqueous solution of 7.5 g of NaOH in 300 mL of water and adjusted pH to alkaline. The precipitate was filtered, washed with water to remove trace of alkali, and dried in vacuum at about 60˚C for 24 h. It was then extracted by tetrahydrofuran and then tetrahydrofuran was evaporated under vaccum. After recrystallization with ethanol grey solid of yield 1.02g (68%) was obtained. **^{1}H NMR (400MHz, DMSO-d_6, δ ppm)**: 10.12 (s, 1H), 7.07 (d, 4H), 6.69 (d, 2H), 4.57 (s,4H). **IR (KBr pellet, ν_{max}/cm^{-1})**: 3386.84, 3282.97, 3187.50, 1632.60, 1577.31, 1503.29, 1467.85, 1332.91, 1221.28, 1169.74, 868.22, 806.22, 710.36, 587.43

2.4 Synthetic scheme of Cbz-COF

Imine condensation was used for the synthesis of proposed COF. Tp **(4)** was taken as the aldehyde unit and DAC **(3)** was taken as the amine unit. The reaction was carried out in two different routes. The proposed synthesis of Cbz-COF is outlined in scheme 2.



Scheme 2. Synthesis of Cbz-COF (a) dioxane : mesitylene (1:1), acetic acid, 120˚C, 3 days – **Cbz-COF1** (b) o-DCB/n-Pentanol (1:1), acetic acid, 120˚C, 3 days – **Cbz-COF2**

2.4.1 Synthesis of Cbz-COF1

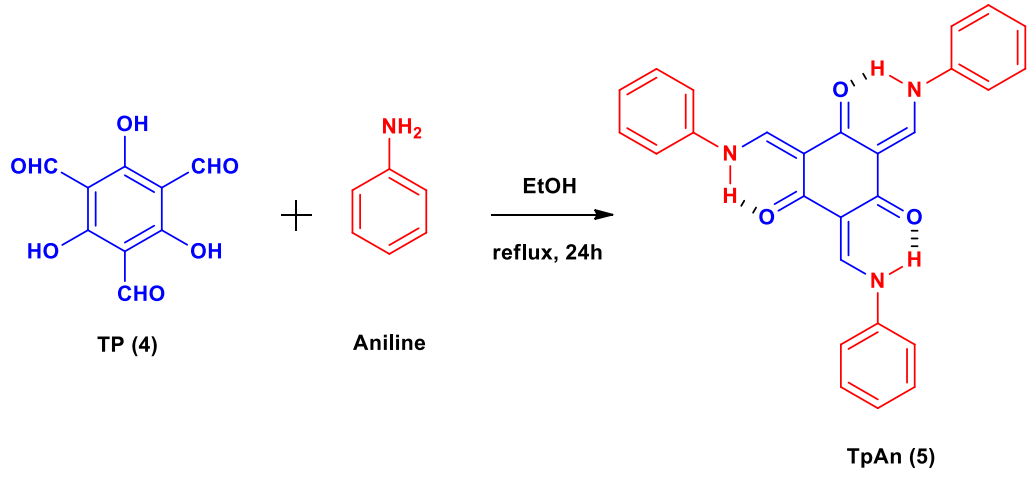
A reaction tube (10 mL) is charged with Tp (**4**) (63 mg, 0.3 mmol), DAC (**3**) (88 mg, 0.45 mmol). To the reaction mixture, 1.5 mL of mesitylene, 1.5 mL of dioxane, 0.5 mL of 3 M aqueous acetic acid was added and stirred well under nitrogen atmosphere to get a yellowish solution. To make the reaction mixture homogenous it was sonicated for 10 min. The reaction tube was closed tightly and then heated at 120˚C for 3 days. A red coloured precipitate was collected by filtration and washed with anhydrous acetone. It was then vortexed with anhydrous acetone followed by centrifugation 5-6 times and then dried at 180˚C in vaccum for 24h. A deep red coloured powder was obtained. **IR (KBr pellet, ν_{max}/cm^{-1})**: 1600, 1578, 1498.34, 1439.29, 1299.46, 1253, 994.12, 806.05

2.4.2 Synthesis of Cbz-COF2

The synthesis of Cbz-COF 2 was carried out by almost same procedure explained above. A mixture of Tp (**4**) (16.8 mg, 0.08 mmol), DAC (**3**) (23.65 mg, 0.120 mmol), *o*-Dichloro benzene (1 mL), n-pentanol (1 mL) in the presence of acetic acid catalyst (6 M, 0.1 mL) was prepared in a reaction tube (10 mL). It was stirred well in nitrogen atmosphere for 15-20 min and then sonicated to get homogenous dispersion. The reaction tube was closed tightly and then heated at 120˚C for 3 days. After the reaction precipitate was collected by filtration, centrifuged and washed with anhydrous acetone 5-6 times. It was then dried at 180˚C in vaccum for 24h. A dark coloured powder was obtained. **IR (KBr pellet, ν_{max}/cm^{-1})**: 1598.84, 1581, 1497.6, 1441.18, 1299.37, 1247.5

2.5 Synthetic scheme of TpAn (Reference compound)

To compare the FT-IR spectra of synthesized COF and to confirm the keto-enol tautomerism, a reference compound, 2,4,6-tris((phenylamino)methylene)cyclohexane-1,3,5-trione (TpAn) **(5)** was synthesised[27]. It was made from Tp (**4**) and aniline in ethanol solvent.



Scheme 3. Synthesis of TpAn **(5)**

2.5.1 Synthesis of 2,4,6-tris((phenylamino)methylene)cyclohexane-1,3,5-trione (5)

Triformylphloroglucinol (0.105 g, 0.5 mmol) and aniline (0.279 g, 3 mmol) was taken in a 100 mL round bottom flask. To this 50mL ethanol was added and refluxed for 24h. The reaction mixture was cooled to room temperature and the precipitate was collected by filtration. It was washed with ethanol and dried under vaccum to get a yellow fluffy solid of 0.174g (80%). **^{1}H NMR (400MHz, $CDCl_3$, δ ppm)**: 13.41 (d, 3H), 8.83 (d, 3H), 7.2-7.5 (m, 15H) **IR (KBr pellet, ν_{max}/cm^{-1})**: 1616.40, 1580.90, 1463.45, 1443.96, 1289.41, 1237.59, 1040.86, 984.10, 823.47, 754.45

Chapter 3

Results and Conclusion

3.1 Characterisation of COF

The synthesised COF was characterised by FT-IR spectroscopy, WAXS, SAXS etc. Surface area and pore size were measured by nitrogen adsorption- desorption isotherm. SEM images were taken to see the morphology of COF. TGA and DSC were carried out to study its thermal properties.

3.1.1 FT-IR spectra

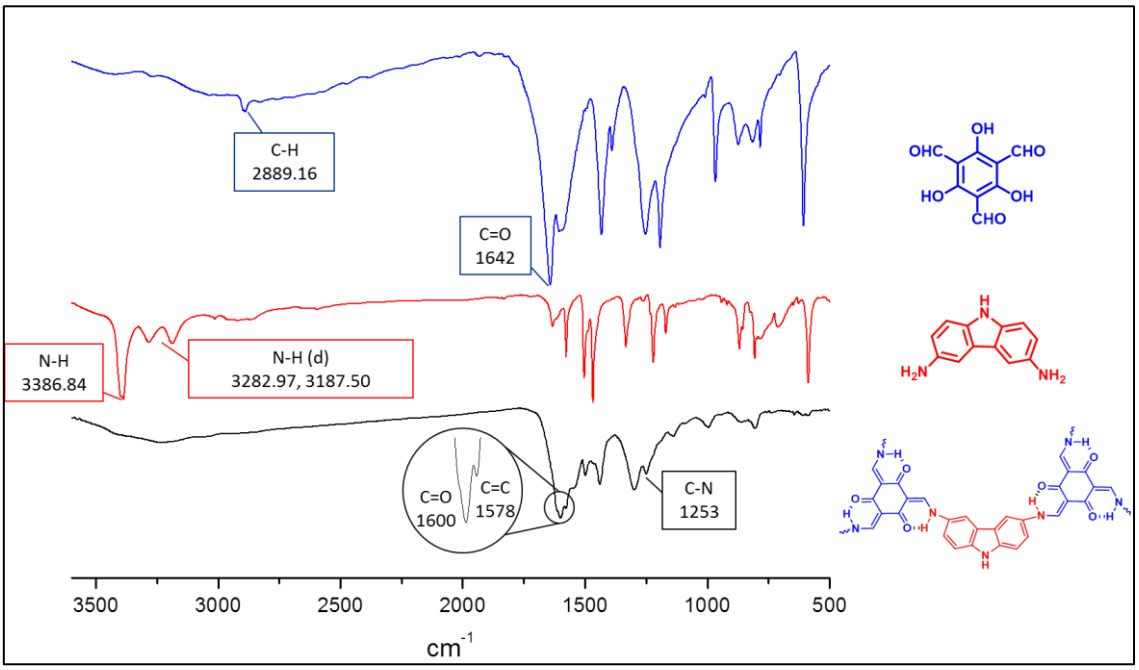


Figure 11. FT-IR spectra of Tp (blue), DAC (red) and Cbz-COF1 (black)

Both the COFs showed almost same FT-IR spectra. From the FT-IR spectra of Cbz-COF, the N-H stretching bands of DAC and the aldehyde C-H stretching band of Tp were missing. This indicates complete consumption of the reactants. Interestingly, the hydroxyl (-OH) or imine (C=N) functional groups were also absent. This shows the compound is not in the enol form. However there was a strong peak at 1600 cm^{-1} arising from C=O stretching and a C=C stretching band at 1578 cm^{-1} , which shows the compound is in keto form. Due to the strong intramolecular hydrogen bonding and extended conjugation in the structure, there is a decreased value of C=O at 1600 cm^{-1} and peak broadening caused merging of C=O and C=C peaks.

From the FT-IR spectra it was clear that Cbz-COF exhibited keto-enol tautomerism and that keto form was more stable. The basicity of imine nitrogen (C=N) is responsible for the conversion of of COF from enol to keto form. Since this is tri-substituted, the basicity of three imine nitrogen have the upper hand over aromaticity, so only keto form is observed.

To confirm the IR spectra of COF, it was compared with FT-IR spectrum of the reference compound 2,4,6-tris-[(phenylamino)methylene] cyclohexane -1,3,5-trione (TpAn).

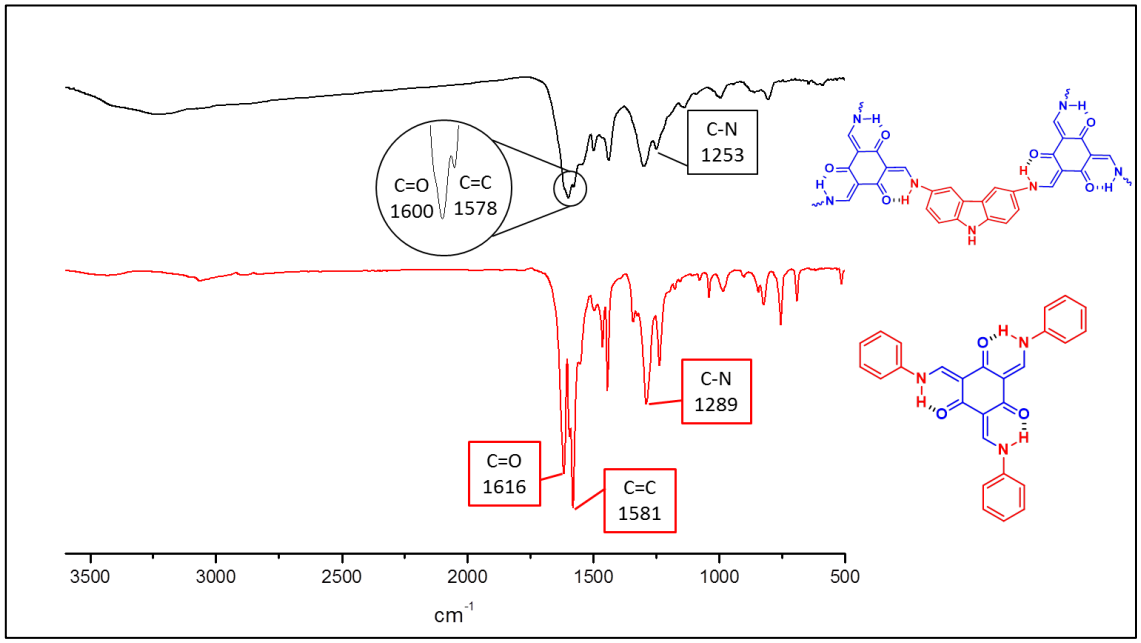
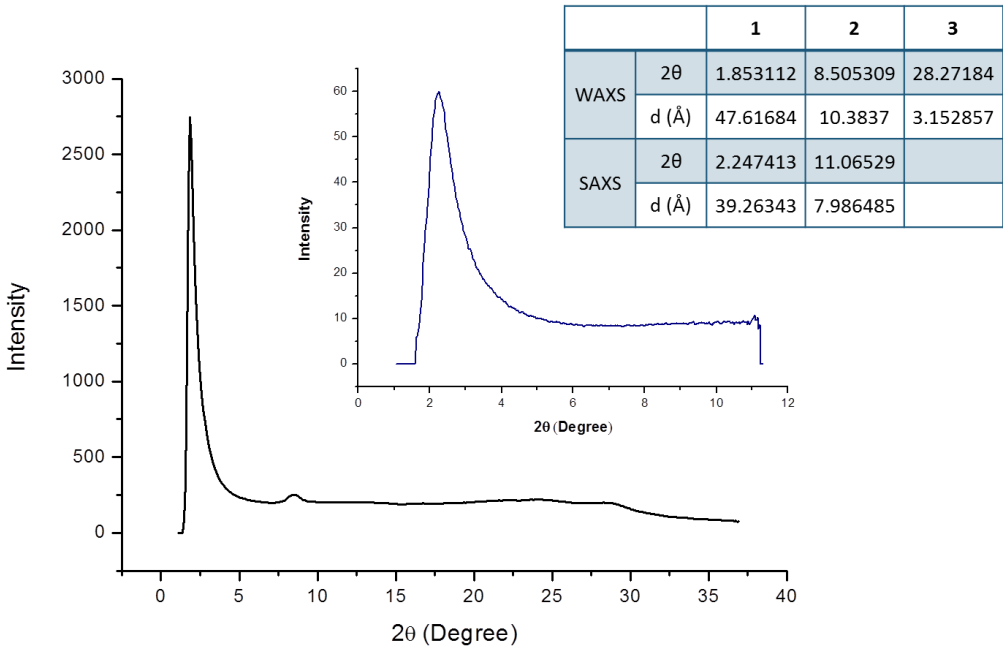


Figure 12. FT-IR spectra of Cbz-COF1 (black) and TpAn (red)

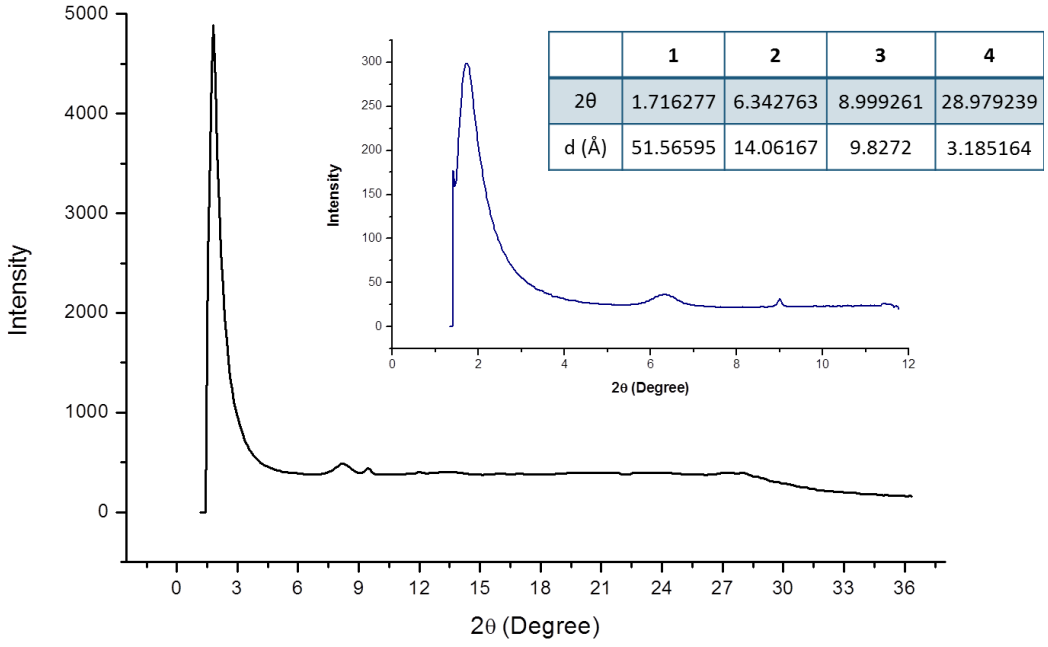
3.1.2 Wide Angle X-ray Scattering (WAXS) and Small Angle X-ray Scattering (SAXS)

An intensity versus 2θ (degree) graph was plotted from the 2D X-ray diffraction pattern of Cbz-COF1 (Figure 11) and Cbz-COF2 (Figure 12), corresponding d-values were also calculated. Cbz-COF2 was found more crystalline and a promising candidate for further studies. The XRD peak at 2θ= 28.27˚ in Cbz-COF1 and 2θ= 28.97˚ in Cbz-COF2 corresponds to an interplanar distance of 3.1 Å, which shows typical van der Waals interaction between the aromatic layers. For this COF there are two kinds of configuration possible, Eclipsed and staggered. In order to elucidate the structure of these COFs and to calculate the unit cell parameters, possible 2-D models can be made using Density Functional Tight-Binding method. The experimental XRD patterns can be compared with the simulated patterns of the stacking models.



		1	2	3
WAXS	2θ	1.853112	8.505309	28.27184
	d (Å)	47.61684	10.3837	3.152857
SAXS	2θ	2.247413	11.06529	
	d (Å)	39.26343	7.986485	

Figure 13. WAXS (black) and SAXS (blue) data of Cbz-COF1.



	1	2	3	4
2θ	1.716277	6.342763	8.999261	28.979239
d (Å)	51.56595	14.06167	9.8272	3.185164

Figure 14. WAXS (black) and SAXS (blue) data of Cbz-COF2.

3.1.3 SEM images

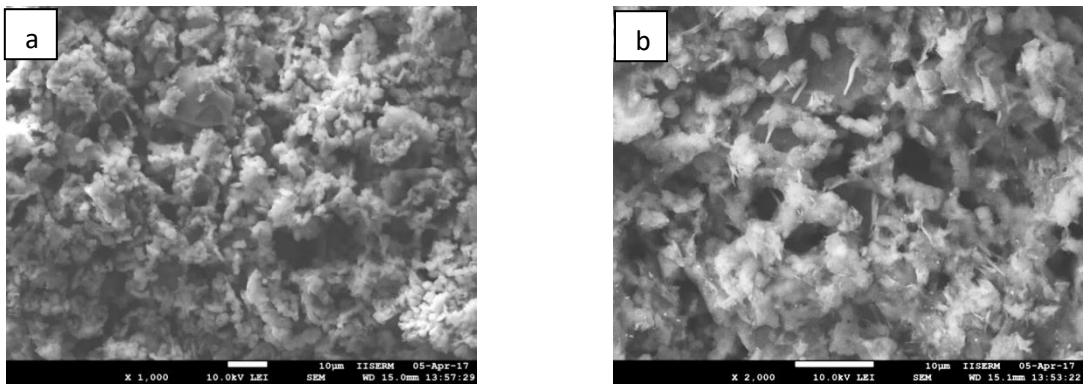


Figure 15. SEM Images of Cbz-COF2 at a) 1000x b) 2000x

Scanning Electron Microscope (SEM) images show a rough textured surface, which can be seen in case of porous materials.

3.1.4 Surface area and pore size measurements

The porosity and surface area of COF was assessed by nitrogen adsorption- desorption isotherm. The nitrogen sorption measurements carried out at 77K shows that the surface area was 207.985 m^2/g (pore volume 0.902 cc/g). The Brunauer–Emmett–Teller (BET) surface area was calculated to be 223.059 m^2/g.

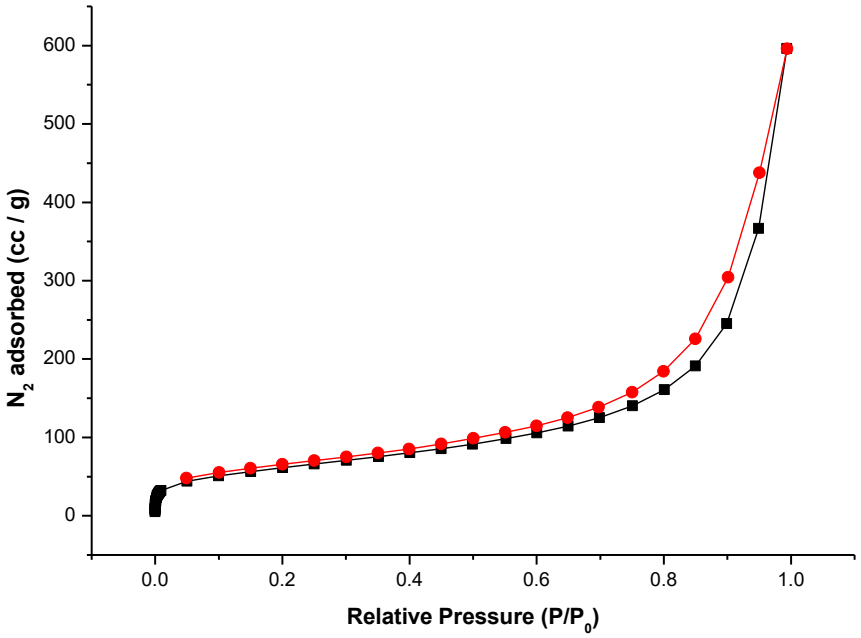


Figure 16. Nitrogen adsorption–desorption isotherm of Cbz-COF2

This nitrogen sorption profile matches with type IV isotherm having typical H3 hysteresis loop, which is characteristic of mesoporous materials. This was supported by the pore size distribution of Cbz-COF, calculated on the basis of Barrett–Joyner–Halenda (BJH) model. The average pore size was around 4.779 nm. (Figure 17)

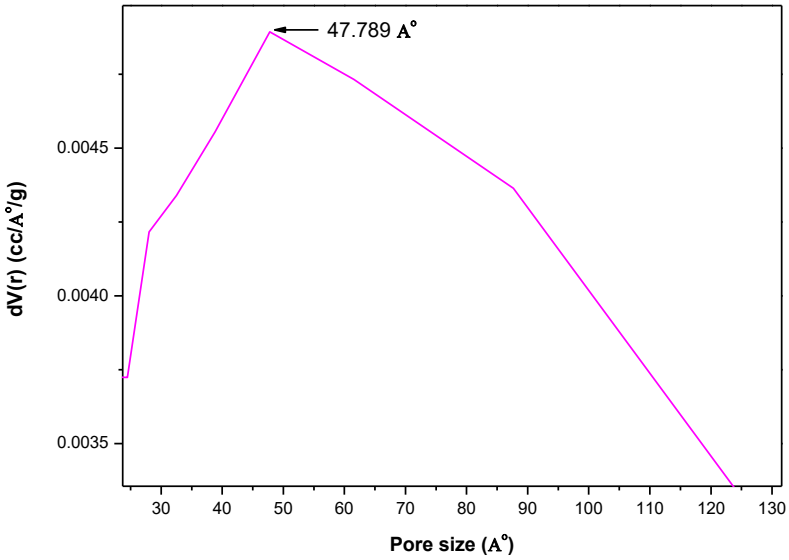


Figure 17. Pore size distribution curve of Cbz-COF2

3.1.5 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) of Cbz-COF was performed to determine its thermal stability. The sample was heated from 30-500˚C at a rate of 10 ˚C/min. TGA revealed that the COF was stable under N_2 upto 300 °C.

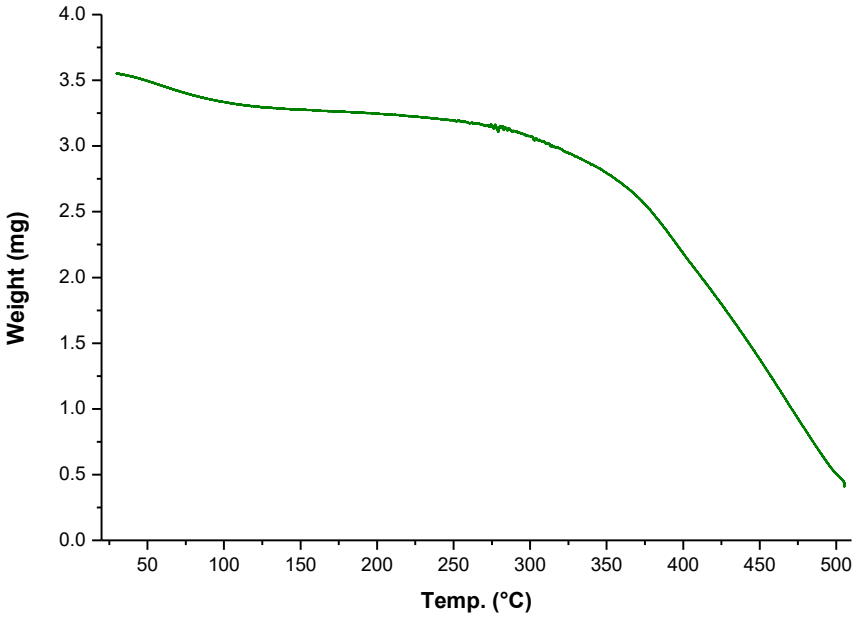


Figure 18. TGA curve of Cbz-COF2

3.1.6 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was done for Cbz-COF to check whether there is any transition in stacking or other physical changes. Scanning was done between 20-250˚C at a rate of 10 ˚C/min. No peaks were observed, which means that there were no physical changes happening in this range and our COF is stable.

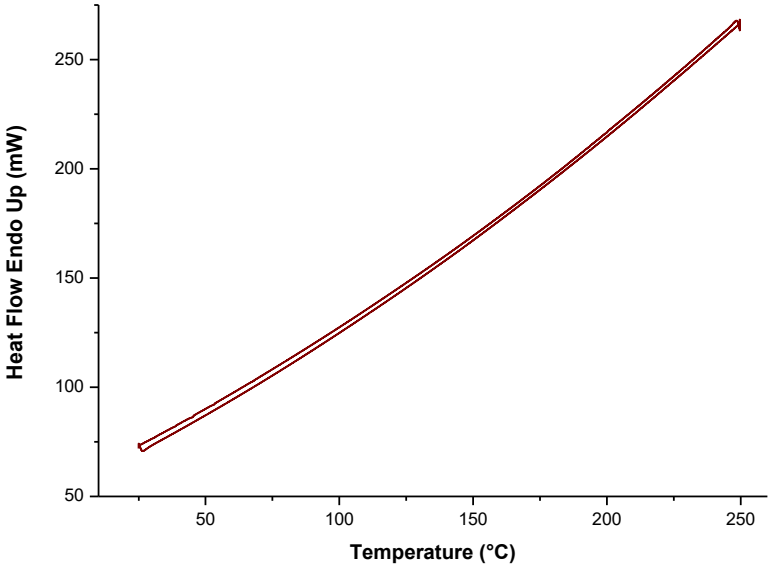


Figure 19. DSC curve of Cbz-COF2

3.2 Conclusion

Herein, we have synthesised the first example of the porous, crystalline carbazole based imine-linked 2D-COF, which is a viable candidate for post-synthetic substitution reactions. It can be utilised for catalysis, host-guest chemistry etc. The proposed COF was synthesised from Triformylphloroglucinol (Tp) and 3,6-diaminocarbazole (DAC). From the FT-IR spectra it was clear that the COF exists in keto form. The 2D-nanosheets of COF are stacked with an interlayer distance of 3.1 Å. The surface area of the synthesised COF was 207.985 m^2/g and its pore size was 4.779 nm. By comparing the pore size measurements and optimised 3D model of COF we can say that it is having an eclipsed configuration. This can be further confirmed by comparing XRD pattern with simulated patterns.

3.3 Future objectives

The surface area of the proposed COF can be enhanced by careful solvent screening and varying the solvent ratios. Investigate suitable applications of this COF in the field of catalysis, after post synthetic modification.

We are also working on a COF having pyridine units, which can coordinate with transition metal ions and to study its possible applications in the field of organic catalysis and photocatalytic reactions.

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