

Design, Synthesis, Characterization and Host-Guest Interaction Studies of Triazine based Covalent Organic Frameworks

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BS-MS Dual Degree Programme



By

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CERTIFICATE

This is to certify that this dissertation entitled "**Design, synthesis, characterization and host-guest interaction studies of triazine based covalent organic frameworks**" towards the partial fulfillment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents original research carried out by Amrit Kumar at IISER-Pune under the supervision of Dr. Sujit K. Ghosh, Assistant Professor, Department of Chemistry during the academic year 2013-2014.

Signature of student:

Date:

Signature of supervisor:

Date:

DECLARATION

I hereby declare that the matter embodied in the report entitled “**Design, synthesis, characterization and host-guest interaction studies of triazine based covalent organic frameworks**” are the results of the investigations carried out by me at the Department of Chemistry, IISER Pune, under the supervision of Dr. Sujit K. Ghosh and the same has not been submitted elsewhere for any other degree.

ACKNOWLEDGEMENT

Along with the self-effort and hard work, the success of any project depends largely on the encouragement, motivation and guidelines of many others. I take this opportunity to express my profound gratitude to the people who have been influential throughout the phase of my project.

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And last, I bow down to my mother and father to whom I am dedicating this thesis, for their moral encouragement and constant blessings...

Amrit

*Dedicated to my loving family and friends,
for their continuous support and encouragement ...*

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ABSTRACT

Four cyano-based covalent organic frameworks (COFs) were designed and synthesized successfully at room temperature in the presence of triflic acid. The starting cyano compounds differed structurally as we preferred dicyano, tricyano and tetracyano so as to find the topological difference obtained after cyclotrimerisation of the starting materials. The synthesized frameworks were characterized using PXRD and elemental analysis. Gas sorption and solvent sorption measurements were carried out to confirm the porosity of the obtained framework and excellent results were obtained for the same. High thermal stability was confirmed using TGA and display of exceptional luminescent properties along with change in properties in the presence aromatic rich solvent was confirmed by recording the UV-Vis spectra and carrying out the solid state fluorescence studies. SEM images were also recorded so as find out the structural arrangement and it revealed a highly crystalline extended network. Possession of excellent fluorescent property along with strategically designed structure is definitely going to make this material one of the most sought after in the field of optoelectronics and explosive detection.

INTRODUCTION

Attempt by human brain to mimic nature's creation, where small building blocks combine in the simplest possible fashion to form a complex structure with advanced functions led to the discovery of number of molecules. Synthesis of the molecules involved different types of connecting strategy which were aimed at exploiting the primary and secondary interactions like π - π stacking, H-bonding and covalent bonding etc. Synthesis of tropinone by Robinson signified the importance of convergent strategy which is based on covalent interaction. Covalent interactions further played a crucial role in the design and synthesis of 1D disordered macromolecules which were categorized as polymers. Nylon, Teflon, polyethylene, polystyrene etc. are some common polymers which came to be known with time. They have a number of applications and hence are used very commonly as a routine commodity. Further attempt to organize the disordered molecules gave rise to organic and inorganic porous structures. Metal organic frameworks (MOFs) and zeolites evolved as the most important and focused porous structures possessing number of functional and structural properties. MOFs came into existence by the coordinative linkage between the metal and the organic ligands whereas zeolites was based on multiple linkages of the type Si-O-Si and Si-O-Al. MOFs and zeolites exhibit specific properties such as chemo sensing, gas sorption, magnetic, heterogeneous catalysis, conduction and fluorescence properties. However silica and alumina tetrahedra being the basic building blocks for zeolites limit the number of zeolite formation and the structural variation in zeolites can only be achieved by either changing the templates or by variation in hydrothermal conditions. The advantages possessed by the porous materials and limitations of zeolites in terms of structures motivated the scientists to look for new class of materials which can overcome the structural limitations and possess properties such as crystallinity, tunable porosity, low density etc.

The first report of a completely new class of materials with desired properties called as covalent organic frameworks (COFs) was reported by Yaghi and co-workers in the year 2005.¹ He defined it as crystalline porous organic polymer and was obtained by the dehydration reactions of 1,4-benzenediboronic acid with itself. The most important aspect of the newly discovered COF was that it possessed robust covalent interactions and hence was also named as organic zeolites. Theoretically speaking all the synthetic methods leading to covalent-bond formation seemed of great interest and people started to explore each of them at great depth. However the biggest challenge that threatened the formation of COFs was maintenance of permanent porosity, structural regularity and introduction of functional moieties. As far as MOFs are concerned it is quite easy to modulate the co-ordination linkages so as to promote the self-assembly of the building blocks but the same seems to be a difficult task in the case of COFs as it has to be done in a reversible way.²

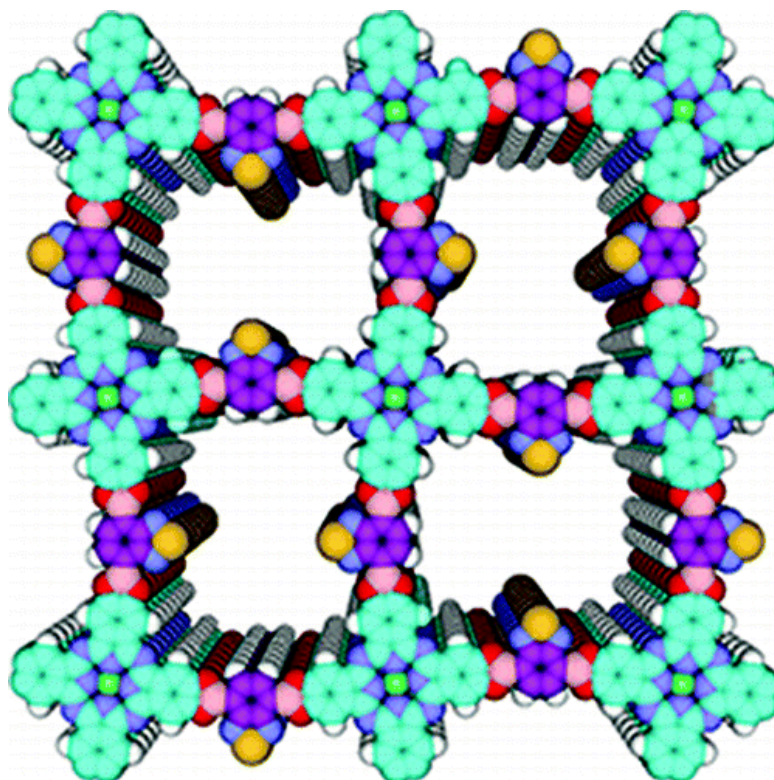


Figure 1: AA stacking of 2D (NiPc-BTDA COF) polymer sheets.

Scientists tried to deploy the ideas used in the case of MOFs and zeolites to overcome the shortcomings. The first concern regarding porosity was addressed by using a couple of strategies which were earlier used for zeolites. The first one was to use a template method,³ in which the template was removed from the as-synthesized structures to impart porosity. The other strategy was to use rigid monomers or building blocks in order to achieve permanent porosity.^{6,10} The latter one was applied in most of the cases so as to obtain permanent porous structures.

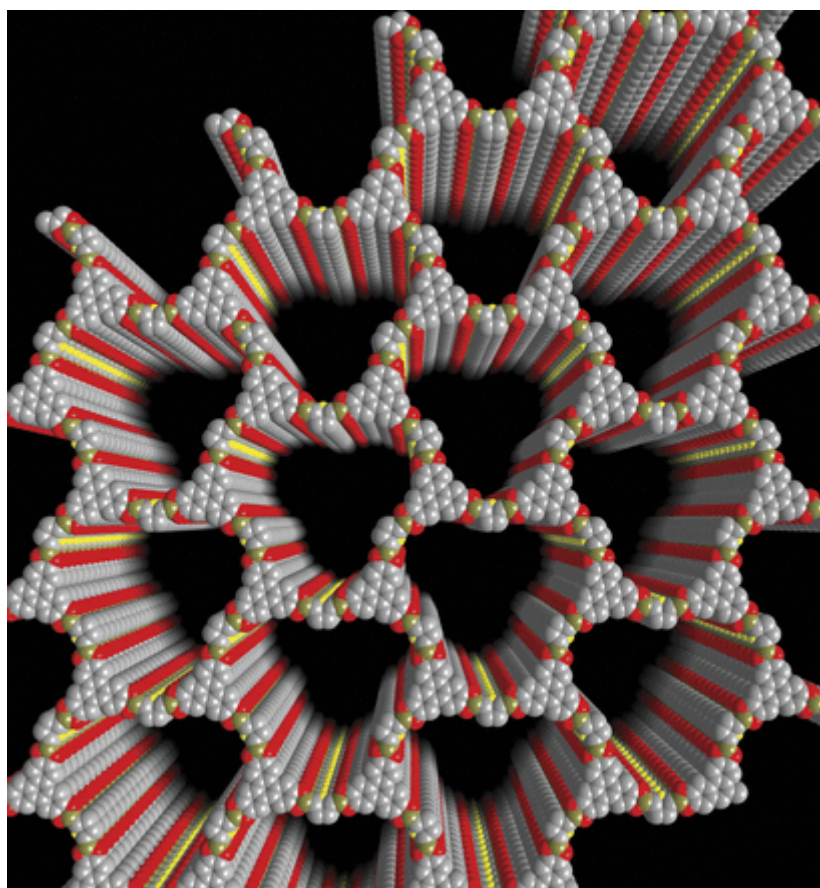
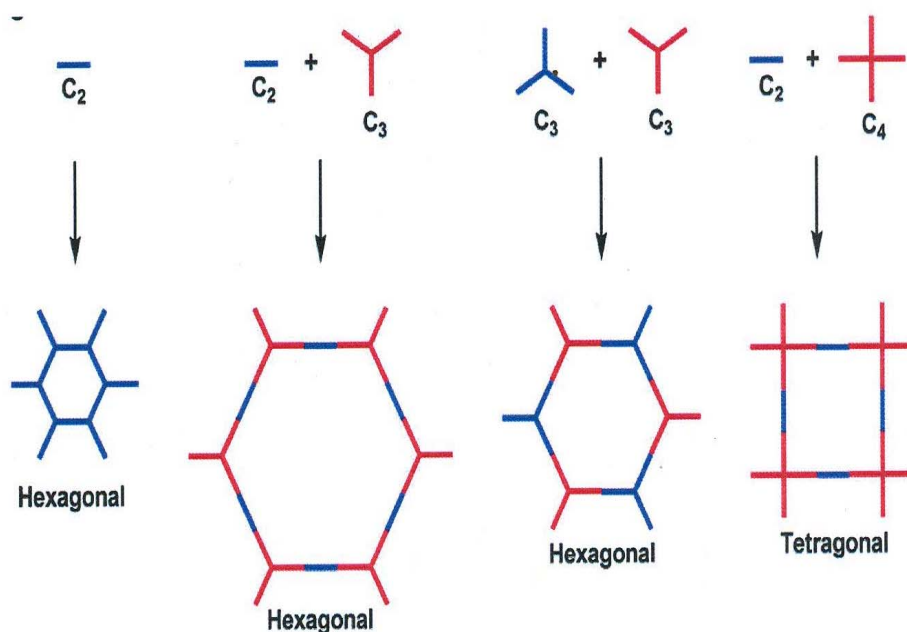


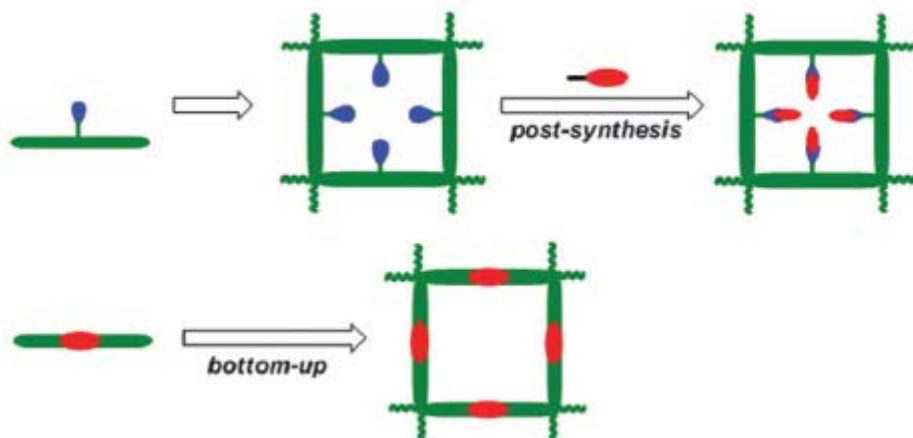
Figure 2: Packing diagram showing a porous channel view.

The next concern was to achieve structural regularity .It seemed to be the most difficult one because even porosity did not ensure structural regularity and the same was observed by Thomas and co-workers.¹² They used rigid but twisted nitrile as building blocks in the cyclotrimerisation but still obtained amorphous porous polymer. To

overcome the problem, it was suggested that we should use rationally designed rigid building blocks and try to assemble them in a certain unique way i.e. both the shapes as well as the angles of the building blocks are equally important in order to carry out reversible covalent bond formation. For example if a linear building block is connected to another linear block we get a linear material¹⁵ but if the same linear one is connected to another blocks with an angle of 90° or 120° we get hexagon or tetragonal 2D structures as shown below.^{1,11} 3D structures can also be obtained by the reaction of a tetrahedral unit along with a linear one .¹³



The last but the most important concern in terms of application was the introduction of functional moieties. The first step in this regard was taken by Jiang and co-workers.¹⁶ They carried out the condensation reactions of the building blocks to obtain the parent material and then carried out post-synthetic modifications to introduce new functional moieties; which is one of the approaches. The other one is to design functional building blocks and then condense them to obtain the desired products.¹⁸ This is called as the bottom-up approach and is the difficult one among the two.



Scheme 1: Schematic representation showing general procedure for COF functionalization.

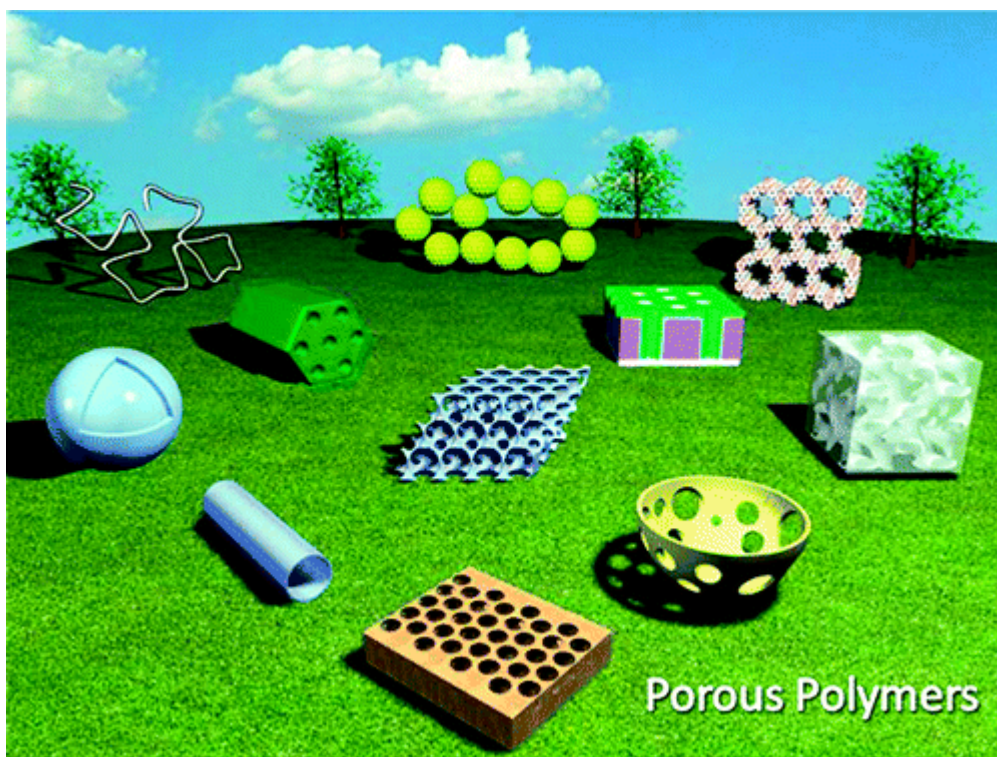
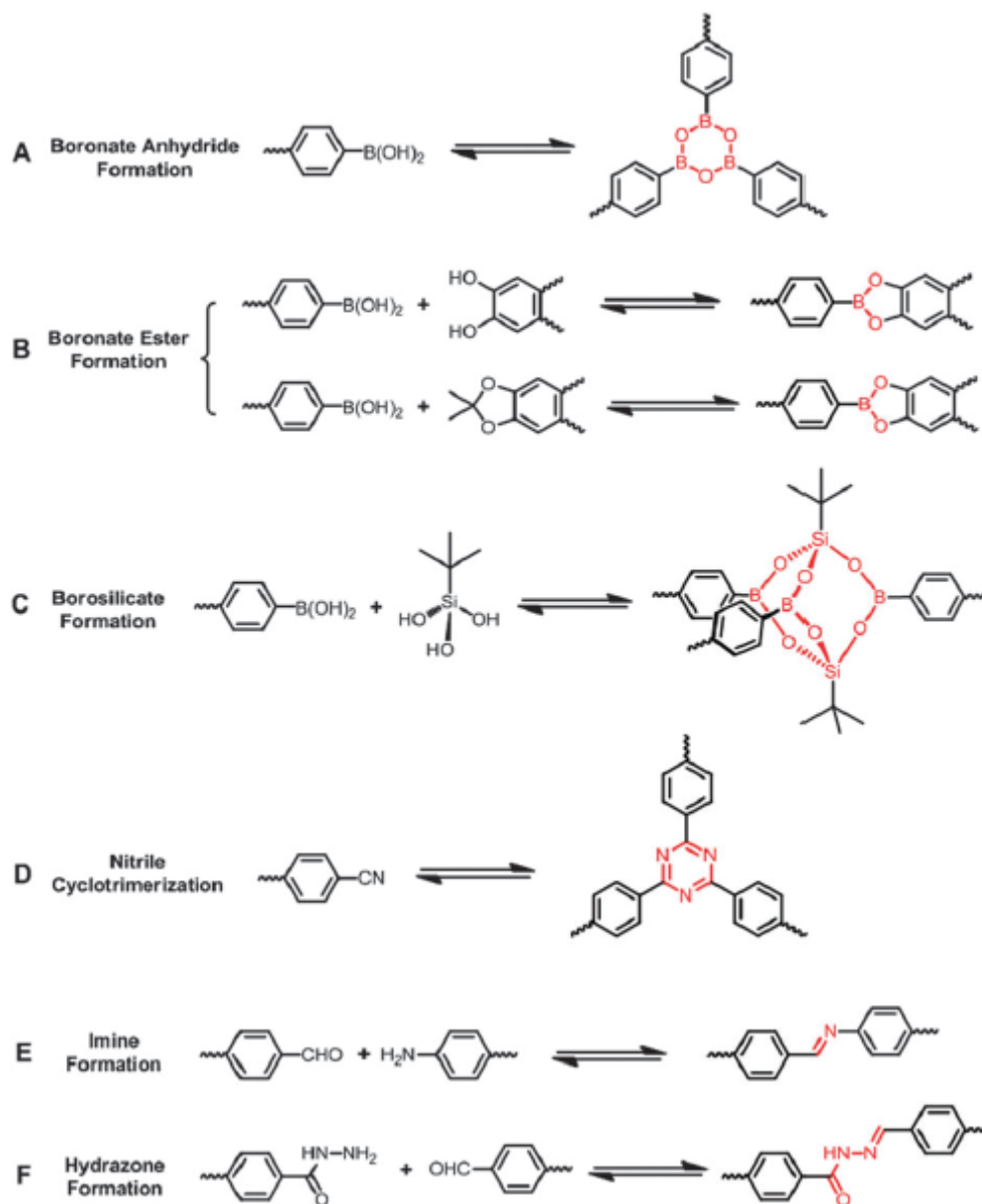


Figure 3: Different kinds of porous polymers.

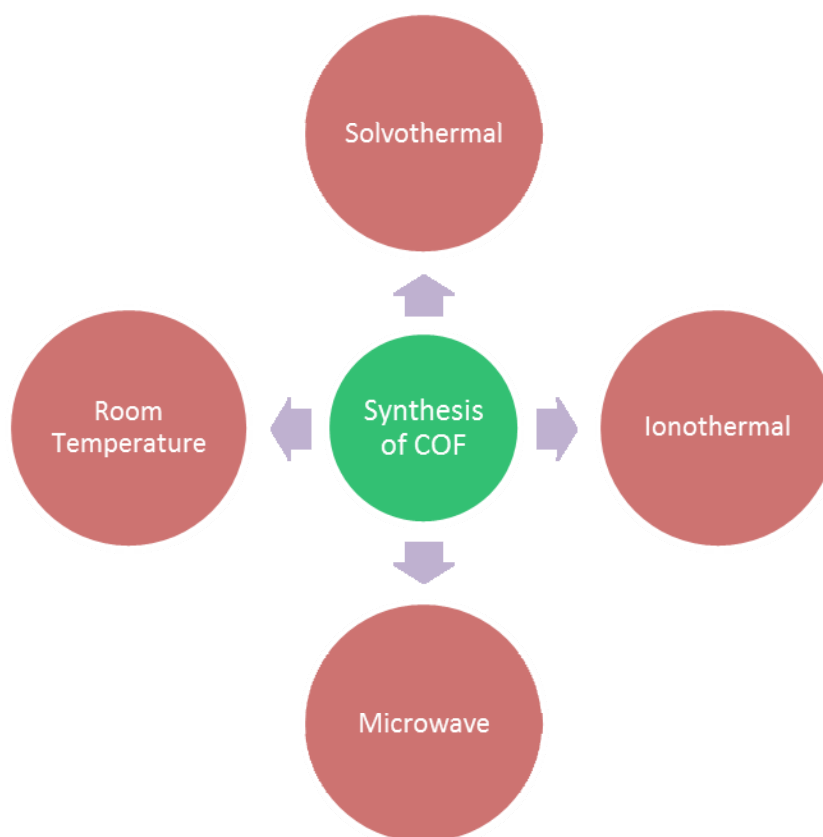
In order to obtain porous COFs, not only the design and shape of the building blocks are important, but the way they are connected and the methods used to ensure the connectivity is also equally important. Some of the important reactions used for the synthesis of the COFs are as follows:^{1,4}



Scheme 2: Schematic diagram showing different kind of linkages for making COF.

The most important one to be explored so far is the dehydration reaction of boronic acid so as to form boronate anhydride. This very reaction was used by Yaghi and co-workers to synthesize the first COF. They carried out the dehydration reaction of 1,4-benzenediboronic acid with itself to generate COF-1 and with hexahydroxytriphenylene to generate COF-5.¹

Alongwith the type of reaction it is equally vital how the reactions are the carried out because that helps us to control the pore size and the structure. Some of the methods are listed as follows:



Scheme 3: Schematic representation showing different methods for synthesis of COF

The first method to be used was the solvothermal method. It generally took 2-9 days and had to be carried out at specific pressure in sealed tube alongwith constant heating at 80-120°C. Yaghi and co-workers showed that 150mTorr was the optimal pressure to be applied in the vacuum line.¹ However it was a very tedious process and a

modification to the same was exhibited by Lavigne and co-workers.²⁰ They showed that reflux under ambient pressure can be used to obtain the desired COFs. The solvothermal method also largely depended on the choice of solvent as it governed the solubility of the reactants.²¹ Even though solvothermal method seemed to be quite important, it had its own limitations. The COFs obtained by this method was generally in the form of powders and hence had limited applications. This shortcoming was overcome by Dichtel and co-workers. He designed a solvothermal method to generate 2D COF as thin films on single layer of graphene.²² These thin films of COF have strong tendency to absorb visible light and hence can be used in solar devices.

An alternative to solvothermal method was presented by Thomas and co-workers where he used an ionothermal method to produce crystalline COFs. He carried out the cyclotrimerisation of the nitrile building blocks in the presence of ZnCl_2 at 400°C to give crystalline covalent triazine-based frameworks with high chemical and thermal stability. ZnCl_2 plays a dual role of solvent as well as catalyst and hence helps to carry out the reactions. However, the harsh conditions used in the reaction i.e. high temperature has an adverse effect on the crystallinity of the COFs obtained and also limits the number of building blocks that can be used. Hence it has limited applications.

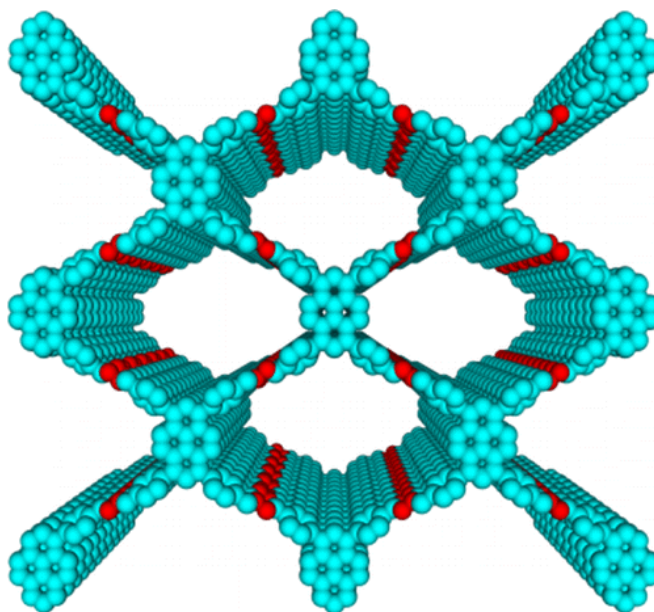


Figure 4: Perspective view of a 2D porous COF.

Cooper and co-workers tried to overcome the limitations of the earlier method and hence reported a micro-wave assisted method to synthesize COFs.^{19,23} They showed that the desired COF can be obtained in 20 minutes, much quicker as compared to the solvothermal method that generally takes 72 hours. Moreover the COF obtained had high BET surface area as compared to the ones obtained by other method.

Recently scientists have also tried to synthesize room temperature COFs and have achieved success to a certain extent. A number of imine based COFs have been synthesized at room temperature.

Once synthesized the characterization of COFs possesses a further challenge. In case of MOFs single crystals are obtained and hence can be easily characterized using single crystal x-ray diffraction but the same cannot be done in COFs because single crystals in COF is not yet reported. So the other option left is powder x-ray diffraction. The signal intensity gives us a rough estimate of the crystallinity of the COF. In order to determine the structure from the PXRD, computational simulation is required and software such as Material Studio is used.¹⁴ Pawley Refinement method is also very helpful and helps us to refine the observed PXRD pattern so as to generate the unit cell lattice. Alongwith structural regularity it is also important to determine the atomic connectivity and the same can be done using solid state NMR. Porosity and surface area can be determined using gas adsorption-desorption measurements. SEM helps us to understand the morphology of the COF materials. Alongwith the instrumental techniques, theoretical investigations have also been very helpful and it has helped us to predict and verify the characteristic properties of the synthesized COFs.^{17,24}

COFs exhibit low density, permanent porosity, and large surface area alongwith tunable functional properties. All this makes it a highly application based material and hence it finds a number of applications in the field of gas storage, catalysis, optoelectricity and adsorption. A recent report by Yaghi and co-workers mentioned that a COF named as COF-10 exhibited an exceptionally high uptake of ammonia as compared to other porous materials.¹⁸ It showed an uptake capacity of 15 mol kg⁻¹ at 298 K and 1 bar. Jiang and co-workers showed that pyrene functionalized COFs can be used for photoelectric applications. TP-COF synthesized by them showed enhanced luminescent

properties and potential to harvest photons from visible to uv region.¹³ It also displayed semi conductive characteristics due to the structural arrangement. A number of other COFs have been synthesized by different groups which can be incorporated into electronic devices so as to enhance their performance. COFs also play a critical role in the field of catalysis. Wang and co-workers synthesized a functionally modified COF named as Pd/COF-LZU1 and tested it for catalyzing Suzuki-Miyaura reaction and it showed excellent catalytic performance.¹⁷

Having talked about the development and applications of COF in the last few years, the most important thing that we observed was that most of the COFs are synthesized under harsh conditions which have an adverse effect on the crystallinity of the COF. To overcome the problem we selectively designed rigid organic building blocks with –CN functional group and tried to cyclotrimerize it at room temperature in the presence of triflic acid. Constant stirring for 3 days at room temperature yielded the required COF with desired properties. Having generated an electron donor-acceptor system in the COF we tried to analyze the luminescent properties of the COF so as to find some applications in the field of optoelectricity.

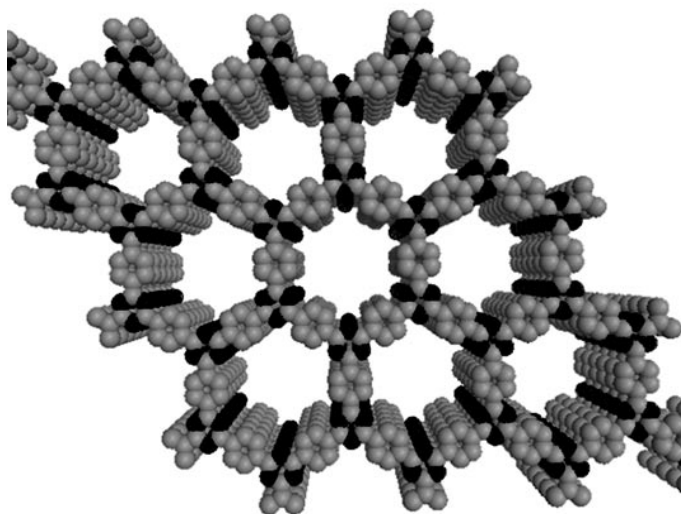
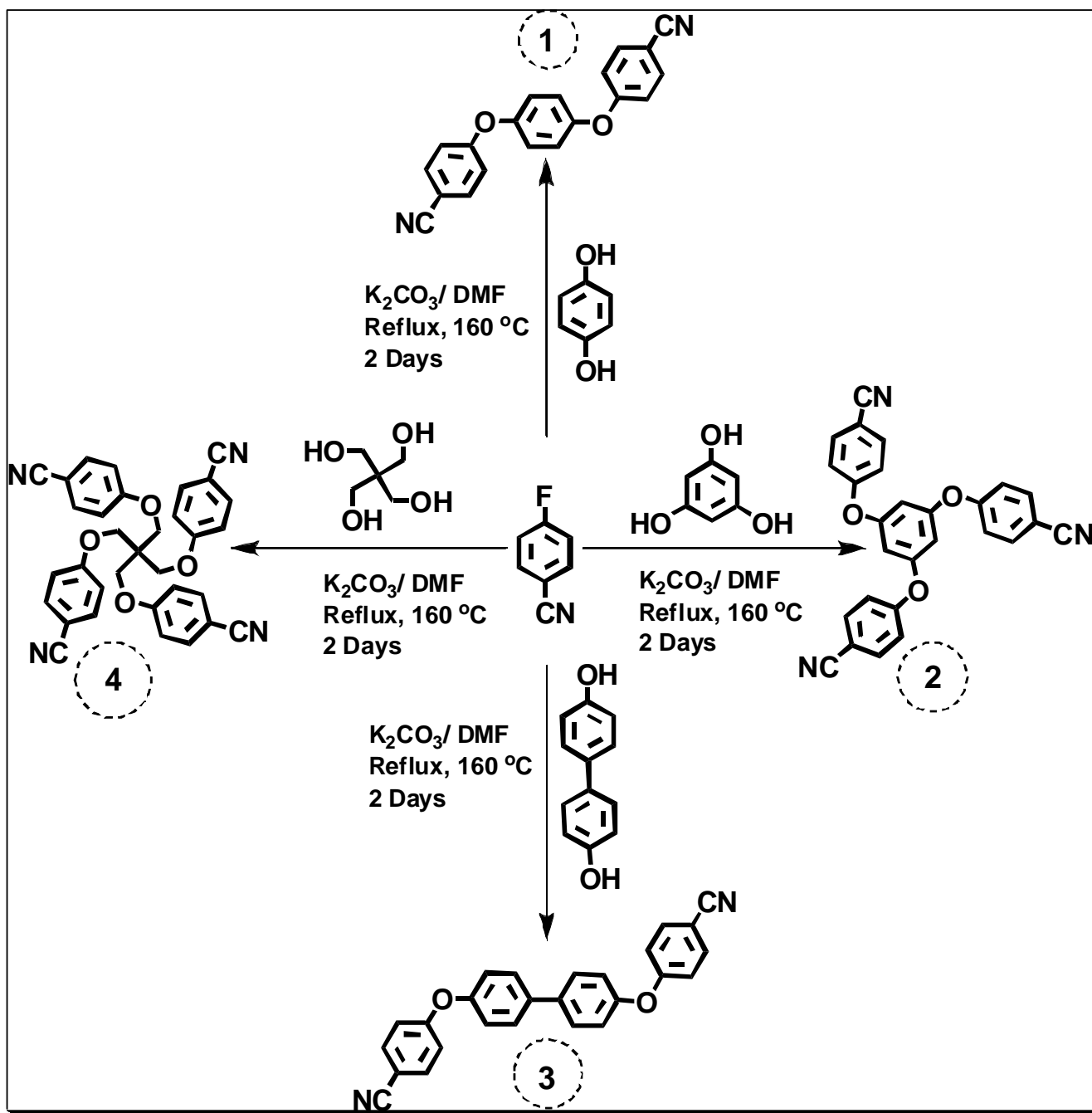


Figure5: Perspective view of a COF showing porous channel

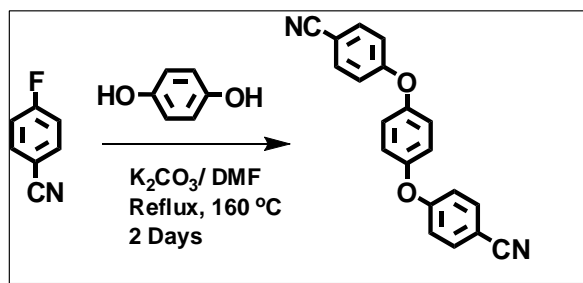
SYNTHESIS AND CHARACTERIZATION

All the reagents and solvents were commercially available and used without further purification. Powder X-ray diffraction (PXRD) patterns were measured on a Bruker D8 Advanced X-ray diffractometer at room temperature (RT) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Thermo gravimetric analyses was Recorded on Perkin-Elmer STA 6000 TGA analyzer under N₂ atmosphere with heating rate of 10° C/min. Low pressure gas and solvent sorption measurements were performed using BelSorpmax (Bel Japan). All of the gases and solvents used were of 99.999% purity. As-synthesized compounds were heated at 150 °C under vacuum for 16 hrs to get guest free compounds. Prior to adsorption measurement the guest free samples were pretreated at 150 °C under vacuum for 5 hrs using BelPrepvacll and purged with N₂ on cooling.



Scheme 4: Schematic representation of the synthesis strategy

Synthesis of Compound 1:



In a 50 mL flask, 1mmol of hydroquinone and 3mmol of K_2CO_3 were suspended in 10mL of DMF. The suspension was heated at reflux temperature for 4 hrs. Then the reaction mixture was cooled to about 60°C and 2.1 mmol of p-fluorobenzonitrile was added and heating continued at 160°C for 24 h. On cooling, the reaction mixture was poured into 500 mL of water and the precipitated solid was collected and washed with water followed by methanol. The yield of the product was 82%. The crude product was purified by recrystallization from ethanol to afford pure compound 1.

PROTON (1H) NMR :

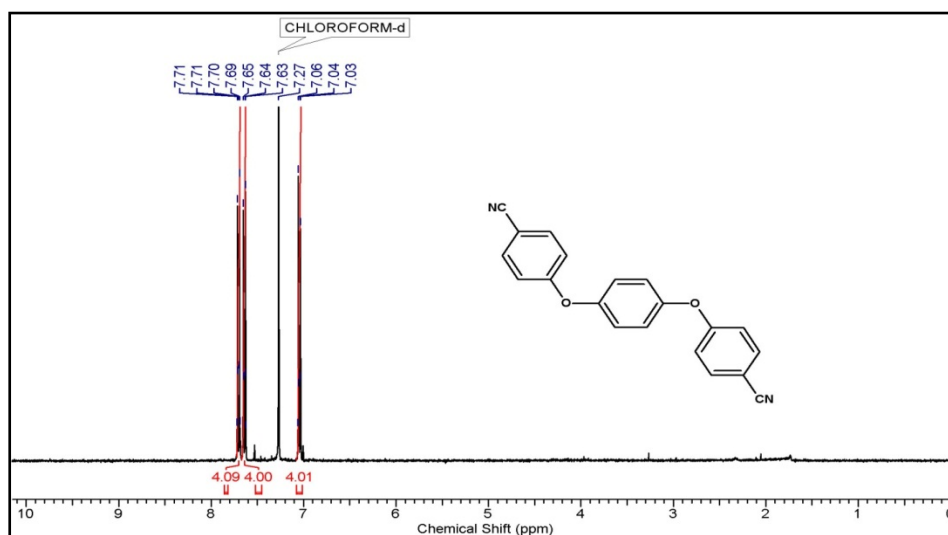
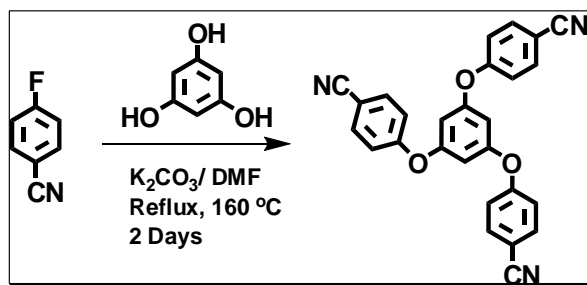


Figure6: 1H NMR of Compound 1

Synthesis of Compound 2:



In a 50 mL flask, 1mmol of phloroglucinol and 4.5mmol of K_2CO_3 were suspended in 10mL of DMF. The suspension was heated at reflux temperature for 4 hrs. Then the reaction mixture was cooled to about 60°C and 3.2 mmol of p-fluorobenzonitrile was added and heating continued at 160°C for 24 h. On cooling, the reaction mixture was poured into 500 mL of water and the precipitated solid was collected and washed with water followed by methanol. The yield of the product was 86%. The crude product was purified by recrystallization from ethanol to afford pure compound 2.

PROTON (^1H) NMR :

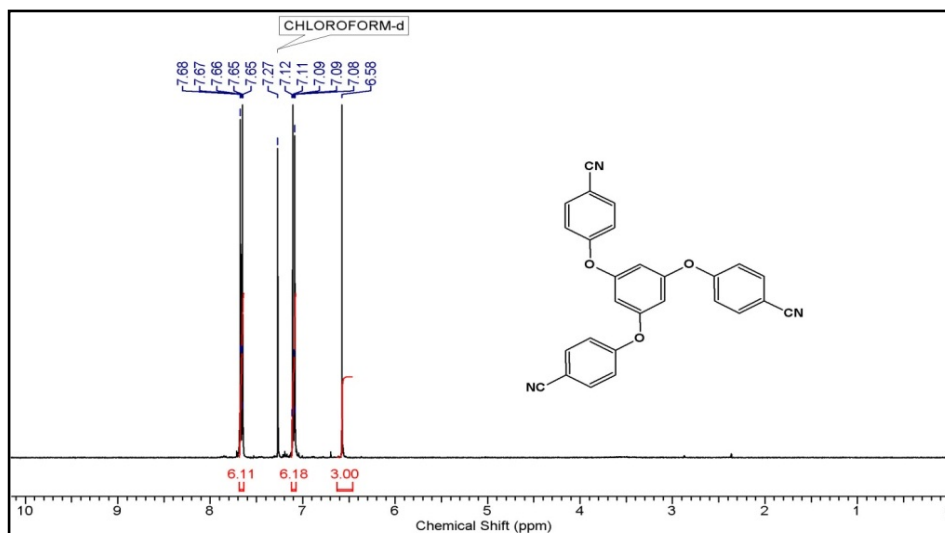
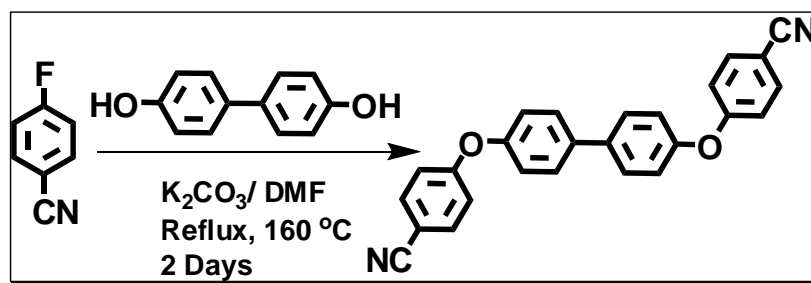


Figure7: ^1H NMR of Compound 2

Synthesis of Compound 3:



In a 50 mL flask, 1mmol of 4,4'-dihydroxybiphenyl and 3mmol of K_2CO_3 were suspended in 10mL of DMF. The suspension was heated at reflux temperature for 4 hrs. Then the reaction mixture was cooled to about 60°C and 2.1 mmol of p-fluorobenzonitrile was added and heating continued at 160°C for 24 h. On cooling, the reaction mixture was poured into 500 mL of water and the precipitated solid was collected and washed with water followed by methanol. The yield of the product was 78%. The crude product was purified by recrystallization from ethanol to afford pure compound 3.

PROTON (^1H) NMR :

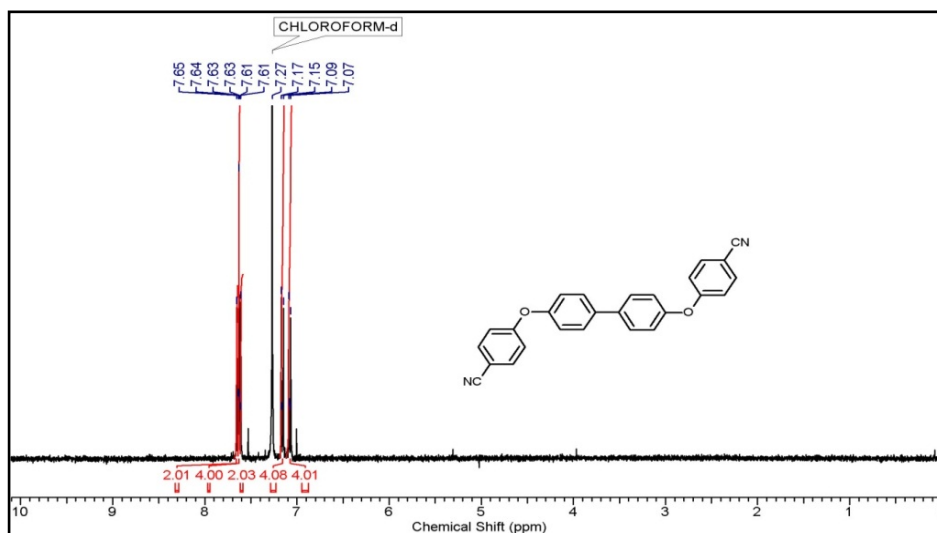
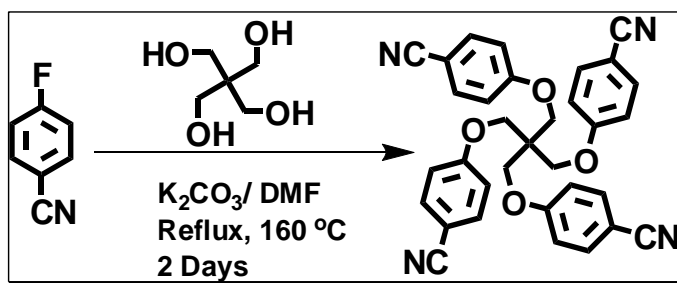


Figure 8: ^1H NMR of Compound 3

Synthesis of Compound 4:



In a 50 mL flask, 1mmol of pentaerythritol and 6mmol of K_2CO_3 were suspended in 10mL of DMF .The suspension was heated at reflux temperature for 4 hrs. Then the reaction mixture was cooled to about 60°C and 4.2 mmol of p-fluorobenzonitrile was added and heating continued at 160°C for 24 h. On cooling, the reaction mixture was poured into 500 mL of water and the precipitated solid was collected and washed with water followed by methanol. The yield of the product was 88% . The crude product was purified by recrystallization from ethanol to afford pure compound 4.

PROTON (^1H) NMR :

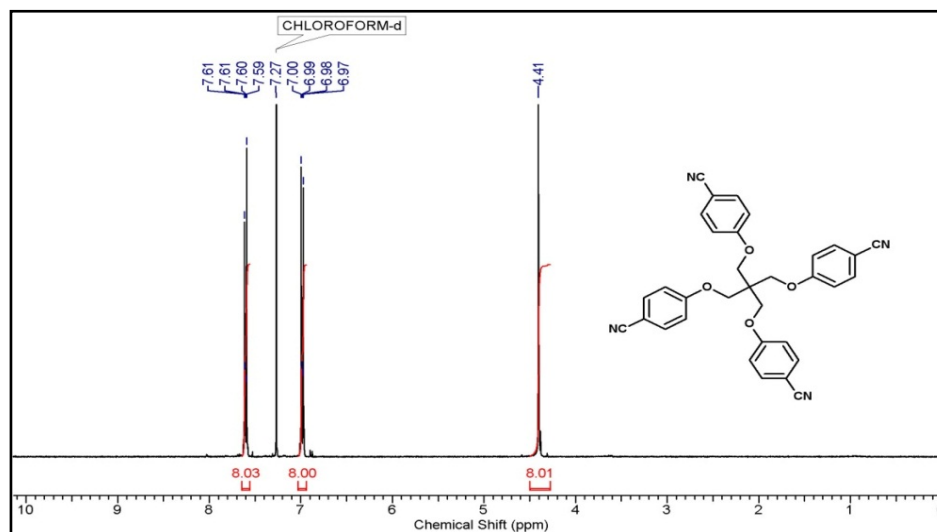
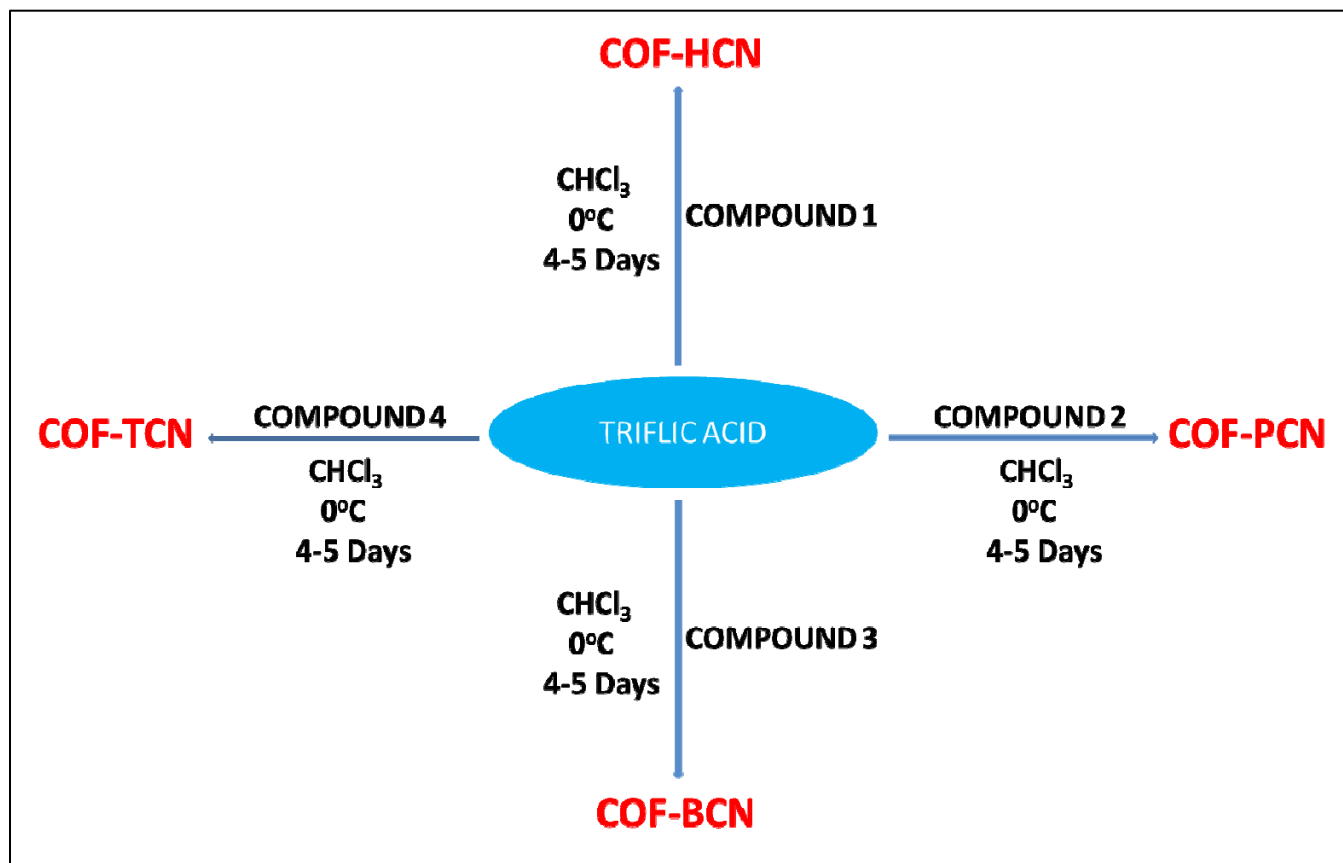


Figure 9: ^1H NMR of Compound 4



Scheme 5: Schematic representation of the synthesis of COFs

Synthesis of COF-HCN:

1 mmol of Compound 1 was dissolved in 10 mL of dry chloroform. Then 4 mmol of $\text{CF}_3\text{SO}_3\text{H}$ was added to it at 0°C . The mixture was stirred at 0°C for 10 min and then at room temperature for 5 days. The resulting solid precipitate was collected by filtration and washed with water containing a small amount of NH_4OH , excess of acetone, THF, and DCM. The solvent was removed under vacuum at 50°C to afford the materials in 75% yield. **Elemental analysis:** C, 75.27%; N, 8.92%; H, 3.81%.

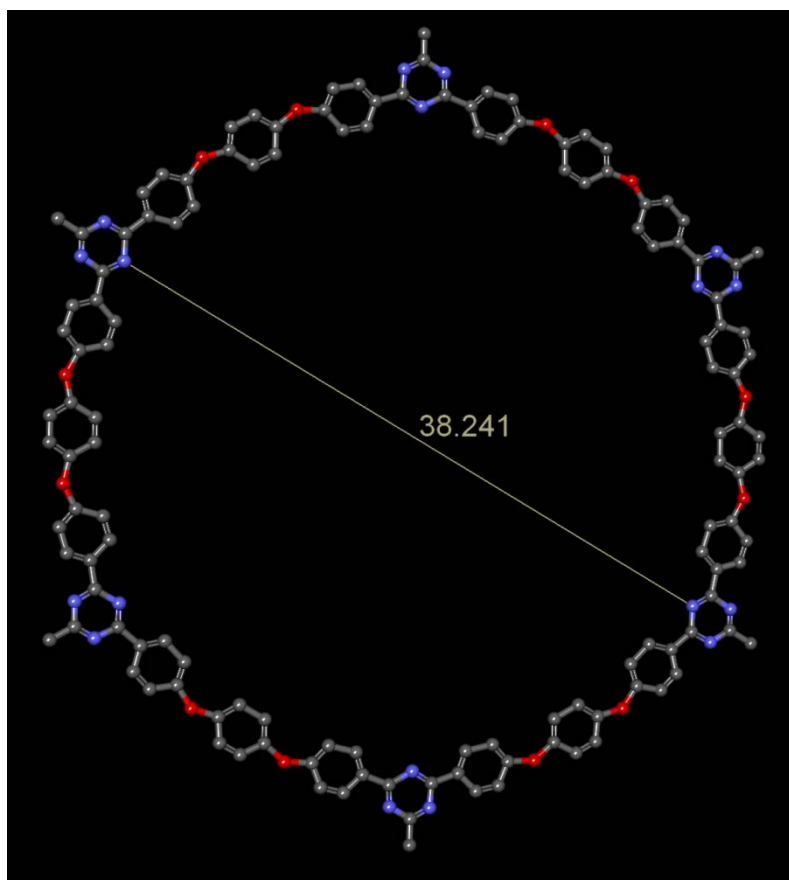


Figure 10: Predicted single pore of HCN-COF showing a pore diameter of 38.24 \AA

Synthesis of COF-PCN:

1 mmol of Compound 2 was dissolved in 10 mL of dry chloroform. Then 6 mmol of $\text{CF}_3\text{SO}_3\text{H}$ was added to it at 0°C . The mixture was stirred at 0°C for 10 min and then at room temperature for 5 days. The resulting solid precipitate was collected by filtration and washed with water containing a small amount of NH_4OH , excess of acetone, THF, and DCM. The solvent was removed under vacuum at 50°C to afford the materials in 79% yield. **Elemental analysis:** C, 71.9%; N, 8.74%; H, 3.95%.

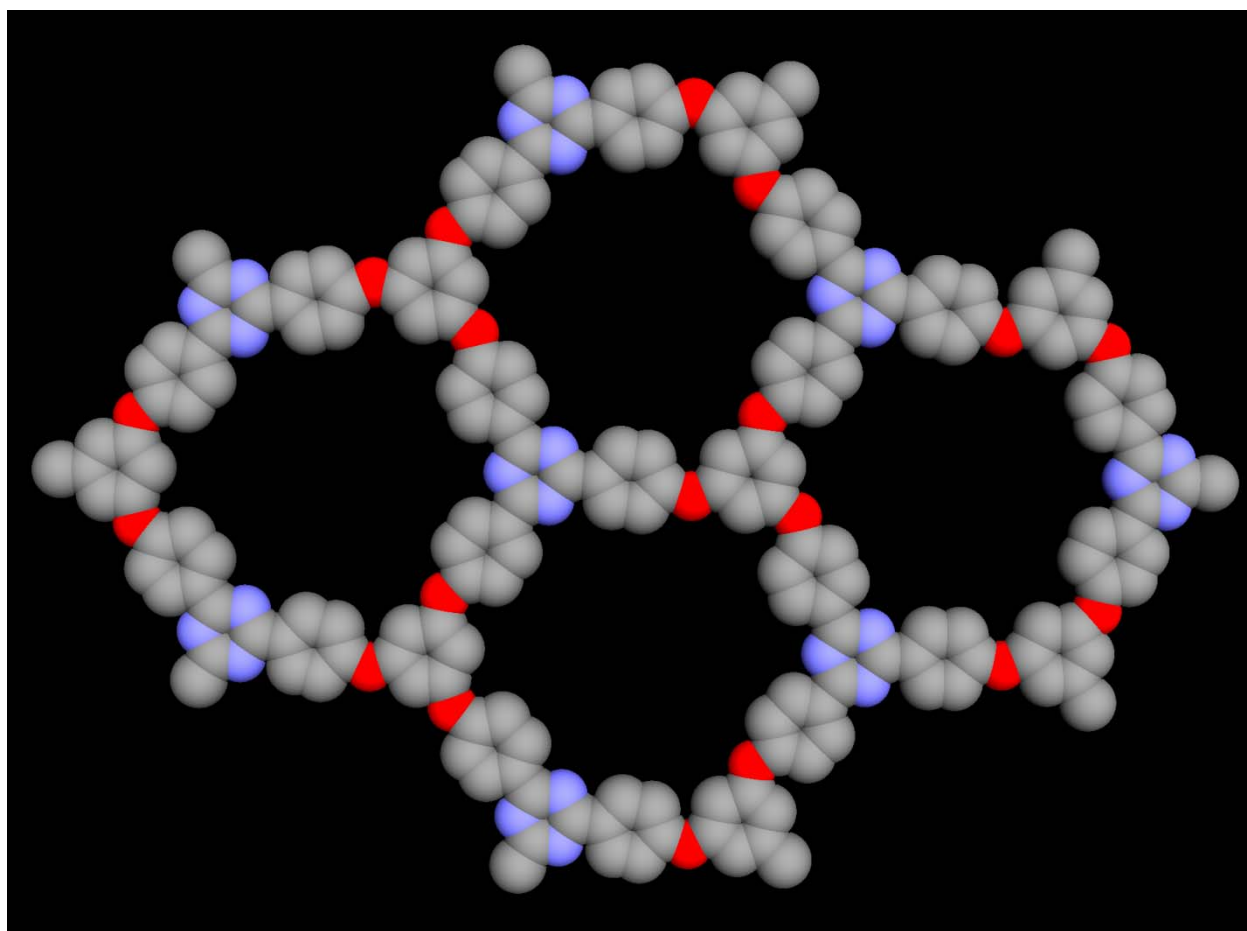


Figure 11: Predicted 2D planar structure of PCN-COF showing porosity

Synthesis of COF-BCN:

1 mmol of Compound 3 was dissolved in 10 mL of dry chloroform. Then 4 mmol of $\text{CF}_3\text{SO}_3\text{H}$ was added to it at 0°C . The mixture was stirred at 0°C for 10 min and then at room temperature for 5 days. The resulting solid precipitate was collected by filtration and washed with water containing a small amount of NH_4OH , excess of acetone, THF, and DCM. The solvent was removed under vacuum at 50°C to afford the materials in 73% yield. **Elemental analysis:** C, 79.27%; N, 6.92%; H, 3.61%.

Synthesis of COF-TCN:

1 mmol of Compound 4 was dissolved in 10 mL of dry chloroform. Then 8 mmol of $\text{CF}_3\text{SO}_3\text{H}$ was added to it at 0°C . The mixture was stirred at 0°C for 10 min and then at room temperature for 5 days. The resulting solid precipitate was collected by filtration and washed with water containing a small amount of NH_4OH , excess of acetone, THF, and DCM. The solvent was removed under vacuum at 50°C to afford the materials in 84% yield. **Elemental analysis:** C, 72.08%; N, 9.23%; H, 4.24%.

RESULTS AND DISCUSSION

Powder X-Ray Diffraction (PXRD):

To fully understand the structure of the synthesized COFs, we carried out powder X-ray diffraction (PXRD) analysis, and gas sorption experiments. The PXRD pattern of PCN-COF displayed a main peak at 4.68 which is typically due to the 100 diffraction, together with minor peaks at 15.6 and 27.2 which is possibly due to, 210, and 001 diffraction, respectively (as shown in Figure 12). The compound TCN-COF showed comparatively less crystallinity as compared to PCN-COF as shown in Figure 12.

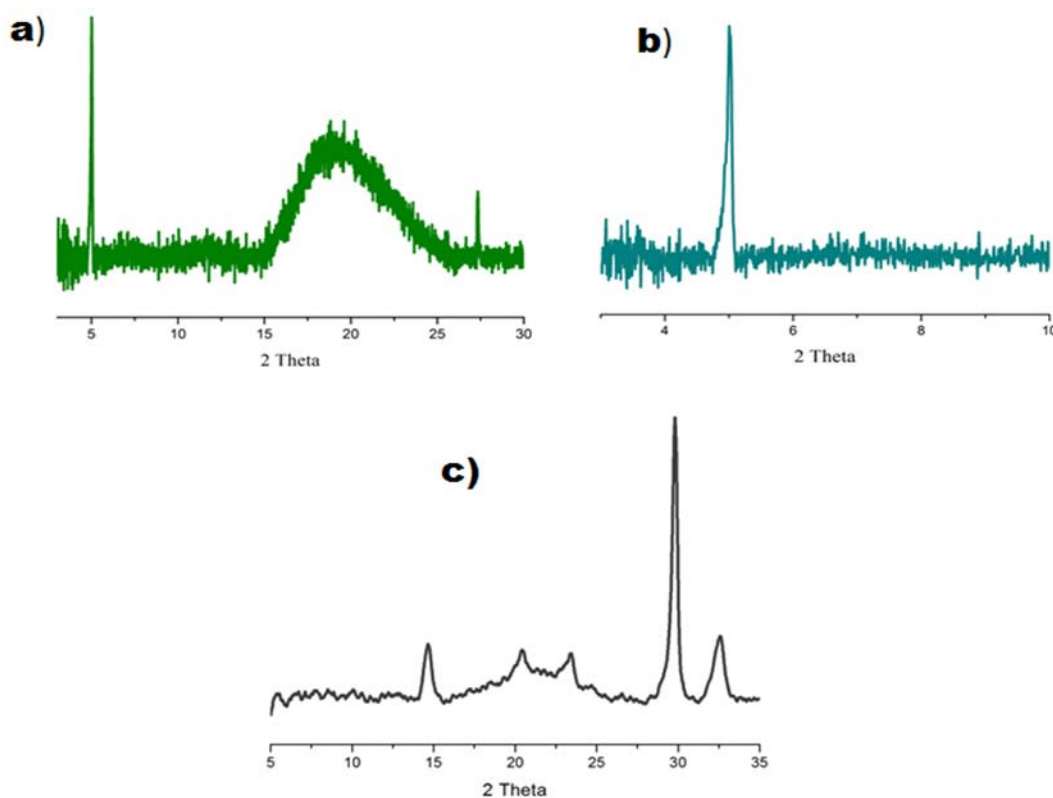


Figure 12: PXRD pattern of a) PCN COF for $2\theta = 5$ to 30° and b) zoomed view showing low angle peak at 4.68° typical for porous organic framework. c) PXRD pattern of TCN-COF

TGA Analysis:

Thermogravimetric analysis of PCN-COF revealed that the compound is thermally stable up to $\sim 530^{\circ}\text{C}$ with an initial loss of about 17% due to trapped solvent guest molecules within the framework. The exceptional stability of triazine based COFs are mainly because of the regularly ordered networks of the COF compounds. TCN on the other hand showed a thermal stability of about $\sim 350^{\circ}\text{C}$ with an initial loss of about 10% because of solvent molecules (shown in Figure 13)

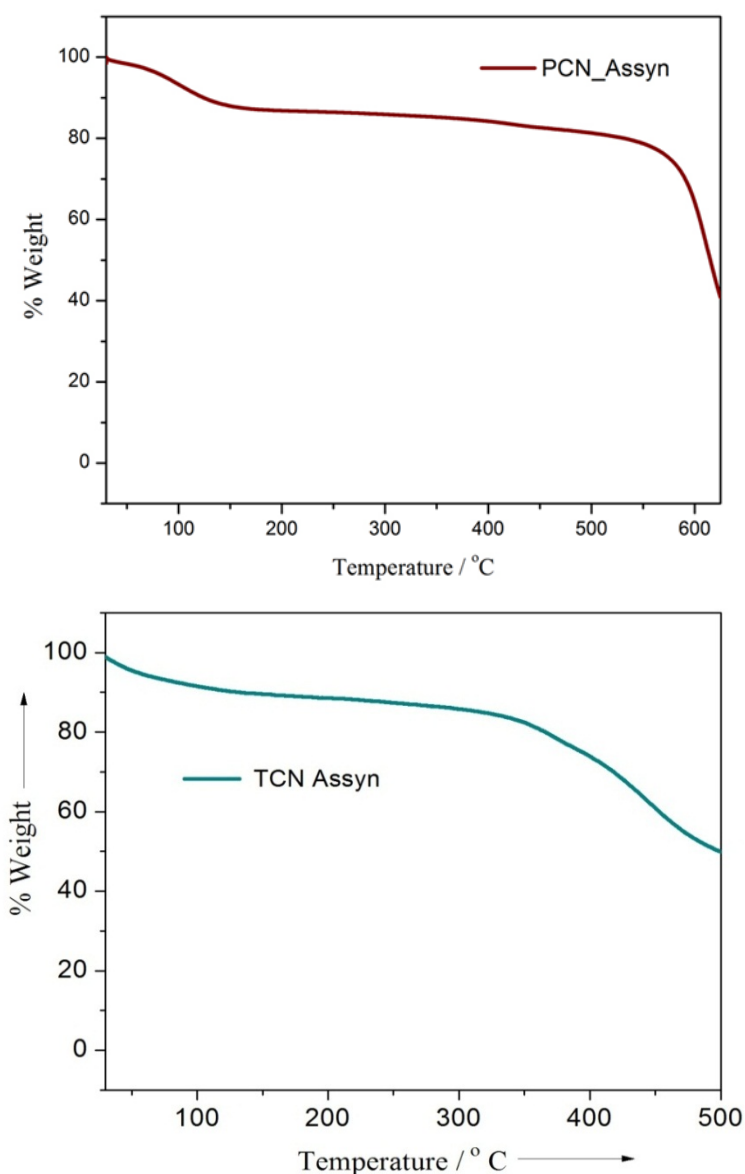


Figure 13: TGA pattern of a) PCN-COF and b) TCN-COF assynthesized.

IR RESULTS:

In the FT-IR spectrum of the PCN-COF we can clearly see that the carbonitrile band at 2246 cm^{-1} has completely disappeared which is indicative of the fact that the starting PCN-Cyano has been consumed completely. Moreover formation of new bands at 1520 and 1330 cm^{-1} indicates the aromatic C-N stretching and breathing modes which are due to formation of new triazine core in the product. Similar observation was observed for other COFs also. In case of HCN-COF the band at 2238 cm^{-1} disappeared and new bands at 1540 and 1305 cm^{-1} was observed. As far as TCN-COF was concerned we saw the disappearance of the band at 2320 cm^{-1} gradually over a period of 24 hours and formation of new bands at 1515 and 1310 cm^{-1} . Similar observation for the BCN-COF was also observed. Band at 2330 cm^{-1} disappeared and new band at 1545 and 1318 cm^{-1} was observed. (shown in Figure14)

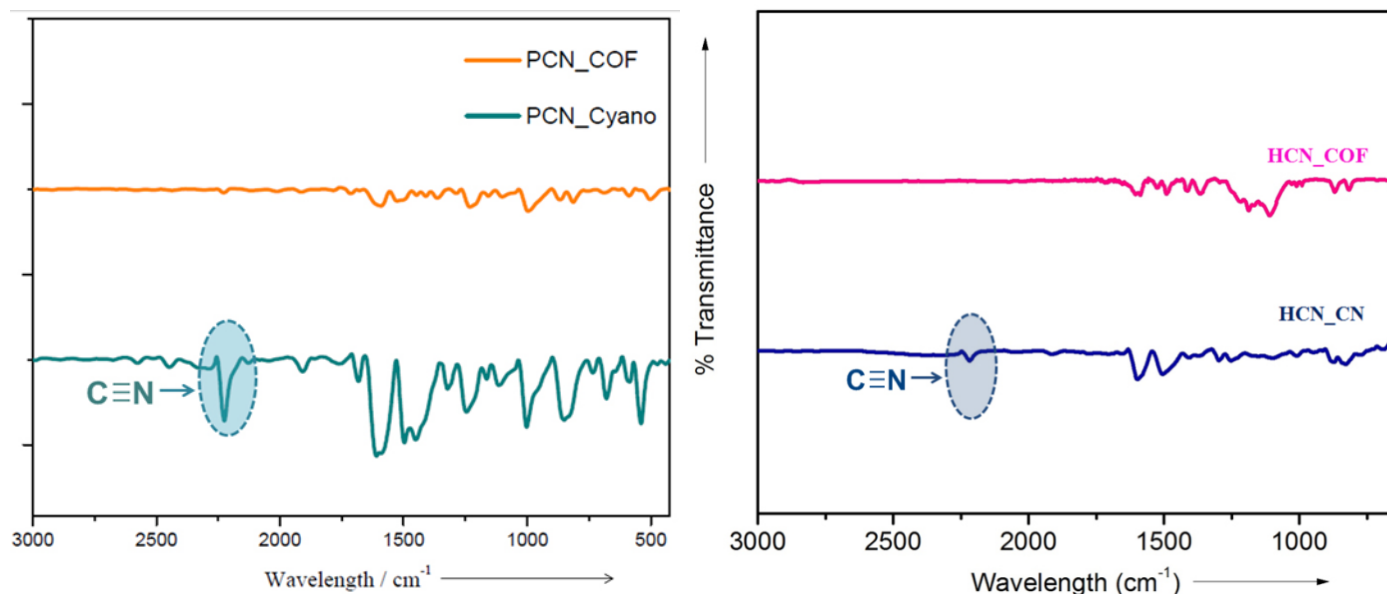


Figure 14: IR spectra for the synthesized COFs.

UV VISIBLE STUDIES:

UV Visible studies were carried out for all the COF compounds along with the starting cyano compounds. UV Visible studies reveal that all the COF compounds show a prominent red shift with respect to the cyano compounds. This is in agreement with the polymerization reaction which results in increase in the conjugation of the ordered network. PCN-COF exhibited a red shift of 20cm^{-1} as compared to the corresponding cyano compound. Similar observation was also observed for the TCN-COF. It showed a shift of 22 cm^{-1} as compared to the starting cyano. BCN-COF and HCN-COF also exhibited similar properties showing a shift of 74 and 55 cm^{-1} respectively. (shown in figure 15).

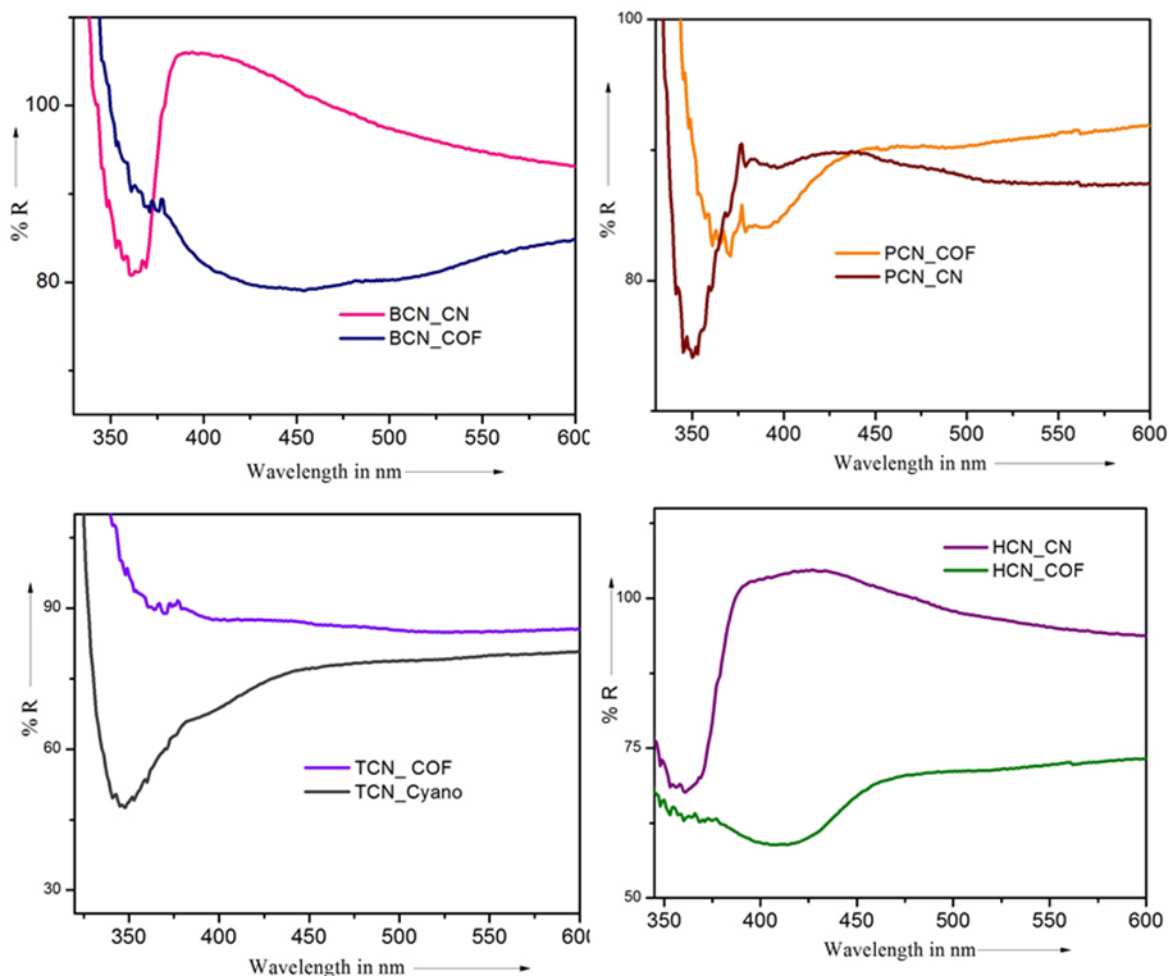


Figure 15: UV-VIS spectra of BCN, PCN, TCN and HCN COFs at room temperature.

Solid State Fluorescence studies:

Since PCN compound was highly luminescent and showed a relatively high uptake of benzene which is an electron rich guest, solid state luminescence studies were carried out with electron rich guests like benzene, toluene, o-xylene, p-xylene, mesitylene, chlorobenzene and m-cresol. In a typical experiment about 15mg of the desolvated PCN-COF compound was exposed to vapors of the corresponding electron rich analytes. After about 3-4 days solid state luminescence was taken of the vapor exposed samples. The emission spectrum show two humps in the spectrum which can be attributed to the two transitions viz. $\pi^*-\pi$ which results from the electronic transition from the electron rich benzene moieties to the electron deficient triazine rings and also $\pi^*-\pi$ transition from oxygen to the electron deficient triazine rings. Both these emission in the parent compound i.e. PCN-COF undergoes a red shift when exposed to the electron rich analytes which is a result of electronic interactions of the analytes with the COF compound.(shown in Figure16)

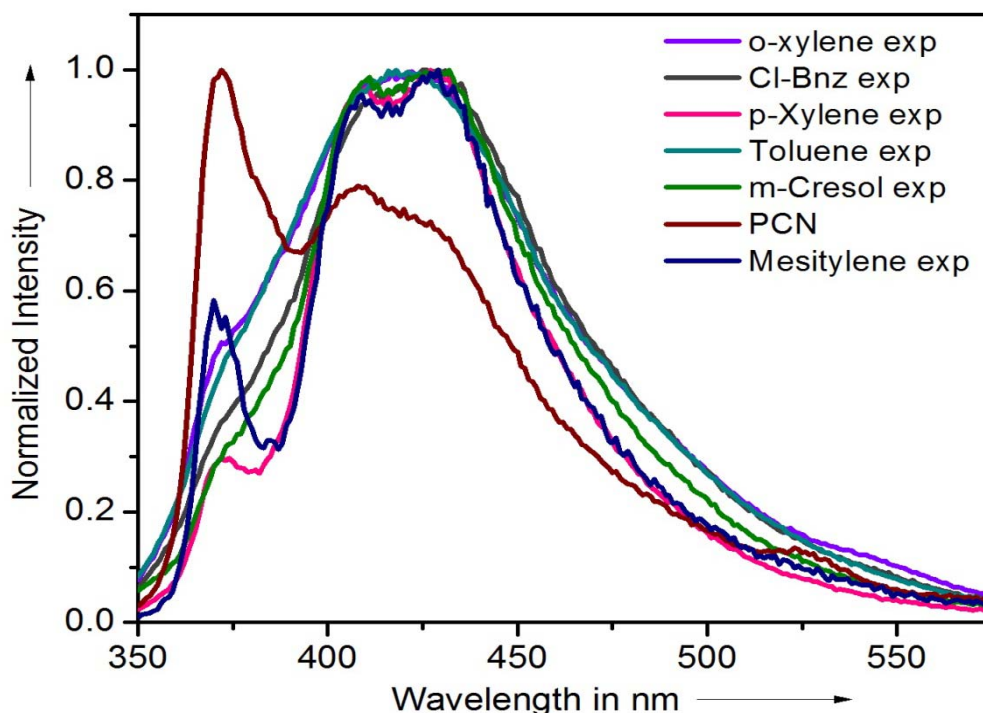


Figure 16: Solid state luminescence spectra of PCN and various aromatic solvent exposed samples.

Gas Sorption Studies:

COFs have been touted as ideal materials for gas storage applications because they are composed of light elements linked by strong covalent bonds to form highly porous materials with high surface areas. The storage capabilities of COFs for gases, such as hydrogen, methane, and carbon dioxide, have been widely investigated. In this regard, CO₂ adsorption of PCN-COF was done at 195K. Before adsorption the compound PCN-COF was activated by heating at 150 °C under vacuum. The adsorption curve shows a typical Type 1 uptake of CO₂ of about 221mL/g which infers that the compound is microporous in nature. This relatively high amount of CO₂ uptake can be attributed to the quadrupolar interaction of carbon dioxide with the lone pairs of oxygen. Further studies on calculating the BET surface area is under progress.

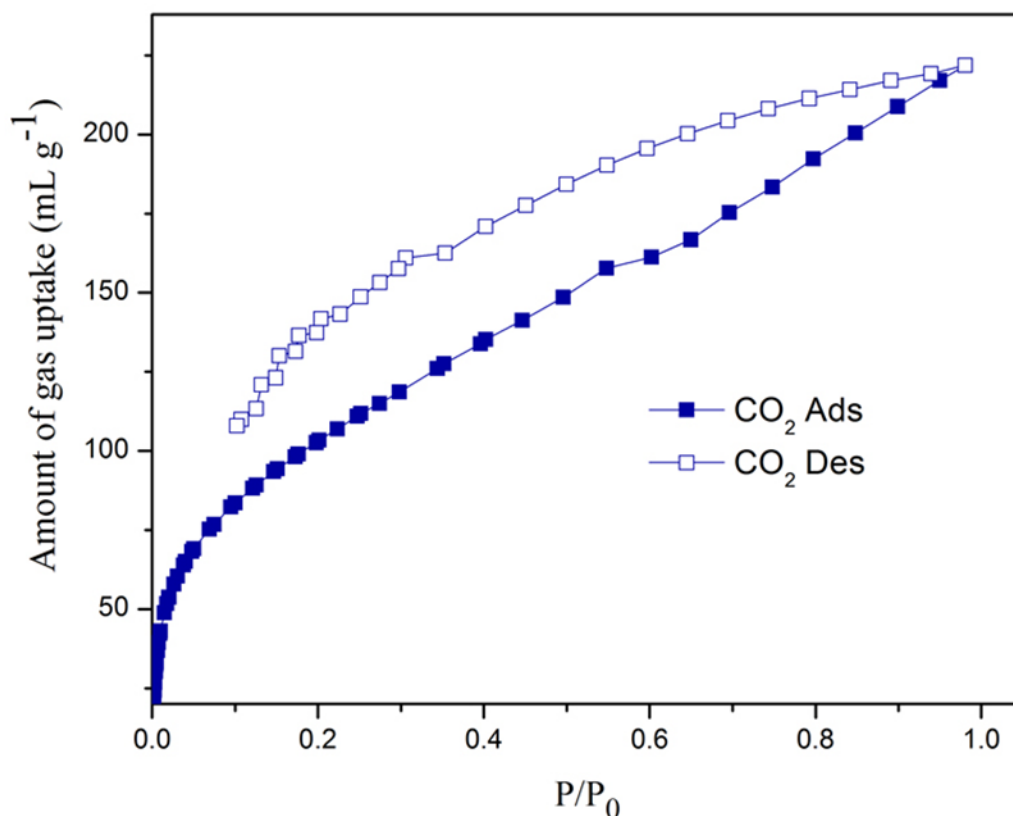


Figure17: Carbon dioxide adsorption isotherm of PCN-COF at 195K.

Solvent Sorption:

Solvent sorption studies were done with compounds PCN and TCN. For this two solvents were chosen, 1) Benzene and 2) 1-Butanol. Prior to measurements both the compounds were pretreated at 150 °C under vacuum. Benzene sorption for compound PCN-COF showed a very high uptake amount ~ 278 mL/g whereas for TCN-COF also showed a high uptake amount of 140 mL/g which is a direct result of interaction of electron deficient pore surface of the respective COF compounds with electron rich benzene molecules.

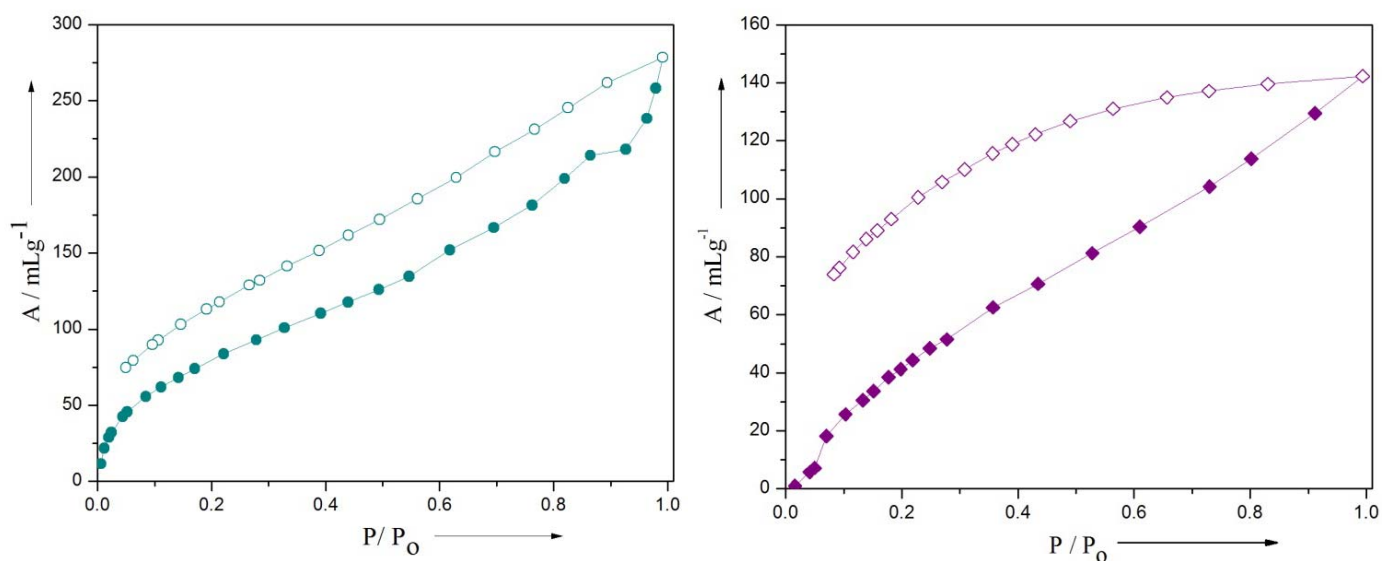


Figure 18: Benzene and 1-butanol measurement of PCN-COF at 298K

For TCN-COF Benzene and 1-Butanol measurement were carried out at 298K. The adsorption profile showed relatively lesser amount uptake of benzene and butanol. This can be attributed to the fact that because the central core of TCN-COF is aliphatic, the interaction with benzene and other aromatic solvent is quite less as compared to PCN-COF. Hence the uptake amount is less. Also because of comparatively more flexible part in the framework the pore size is also less as compared to PCN-COF, hence the uptake amount of 1-Butanol is less. (shown in Figure 19)

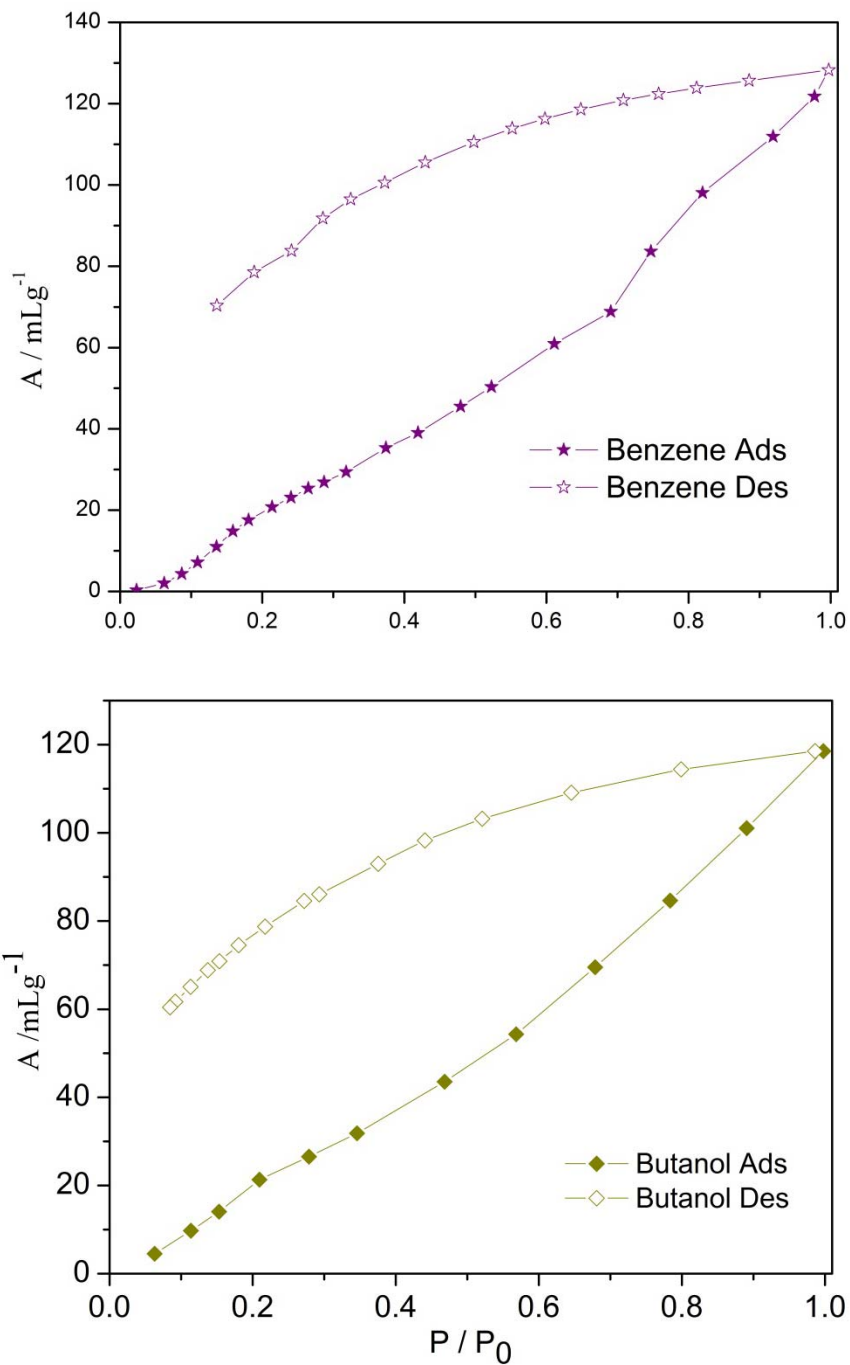


Figure 19: Benzene and 1-butanol measurement of TCN-COF at 298K.

SEM IMAGES:

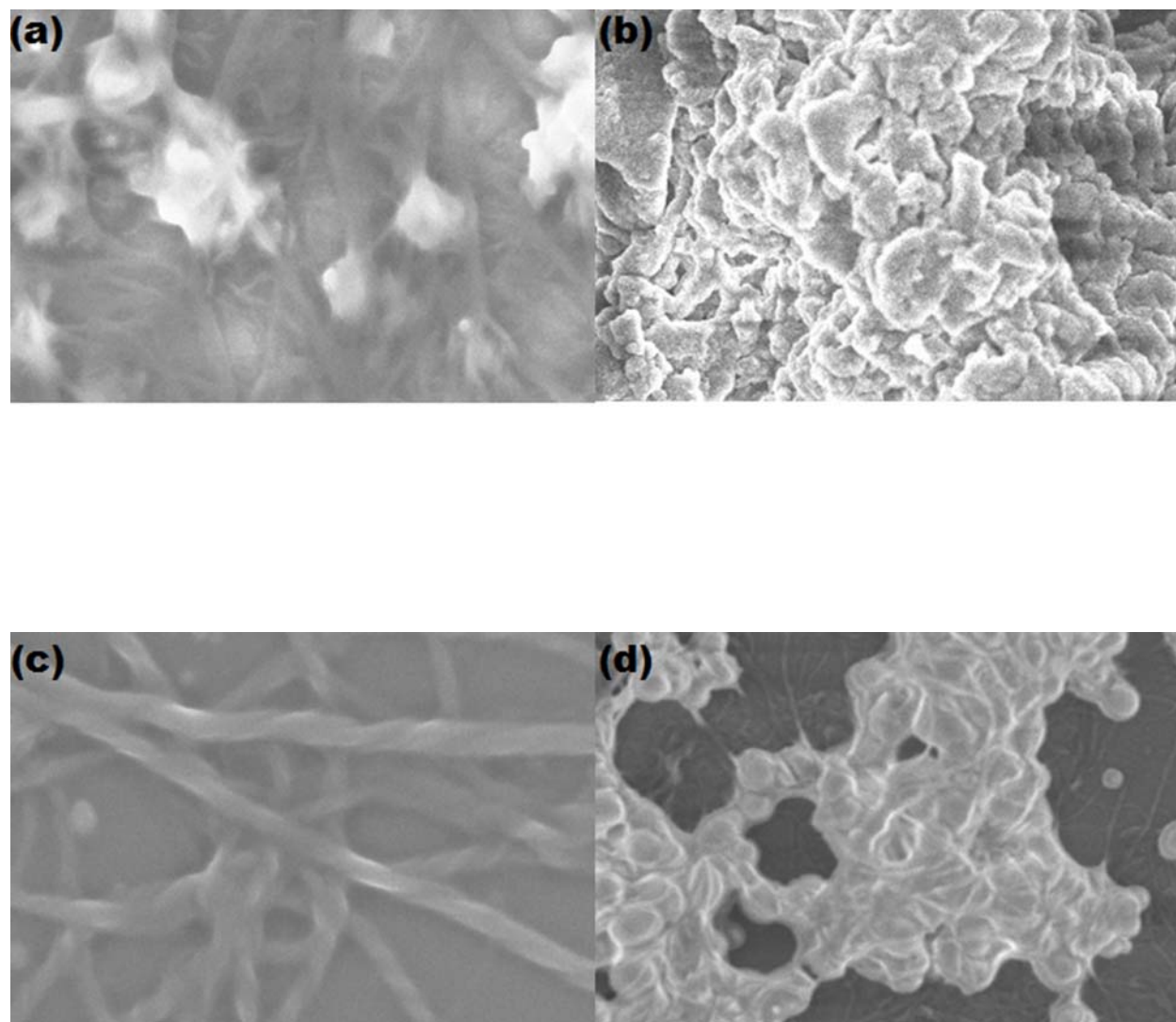


Figure 20: SEM images of HCN and BCN COFs showing fibrous network and crystalline nature respectively.

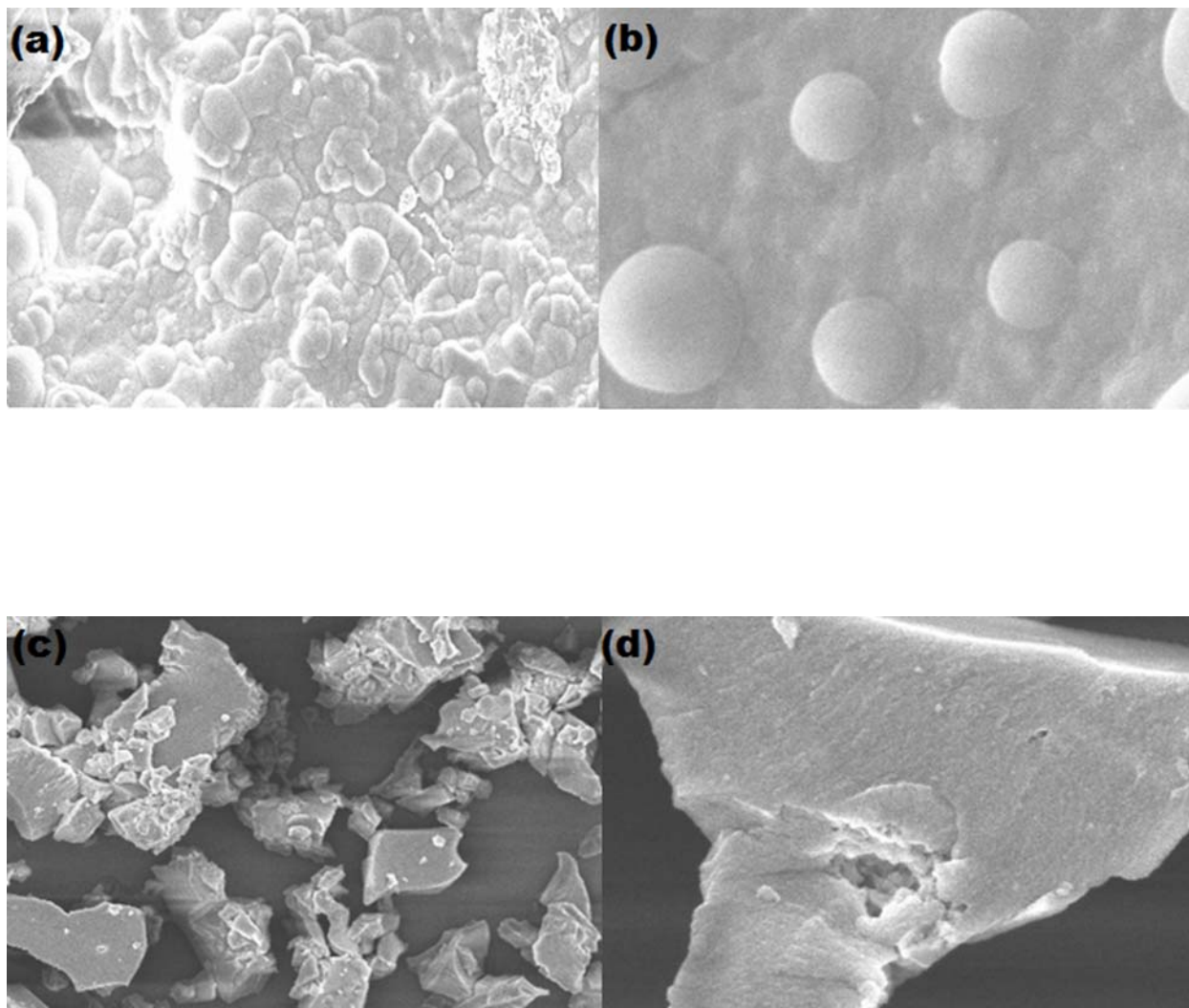
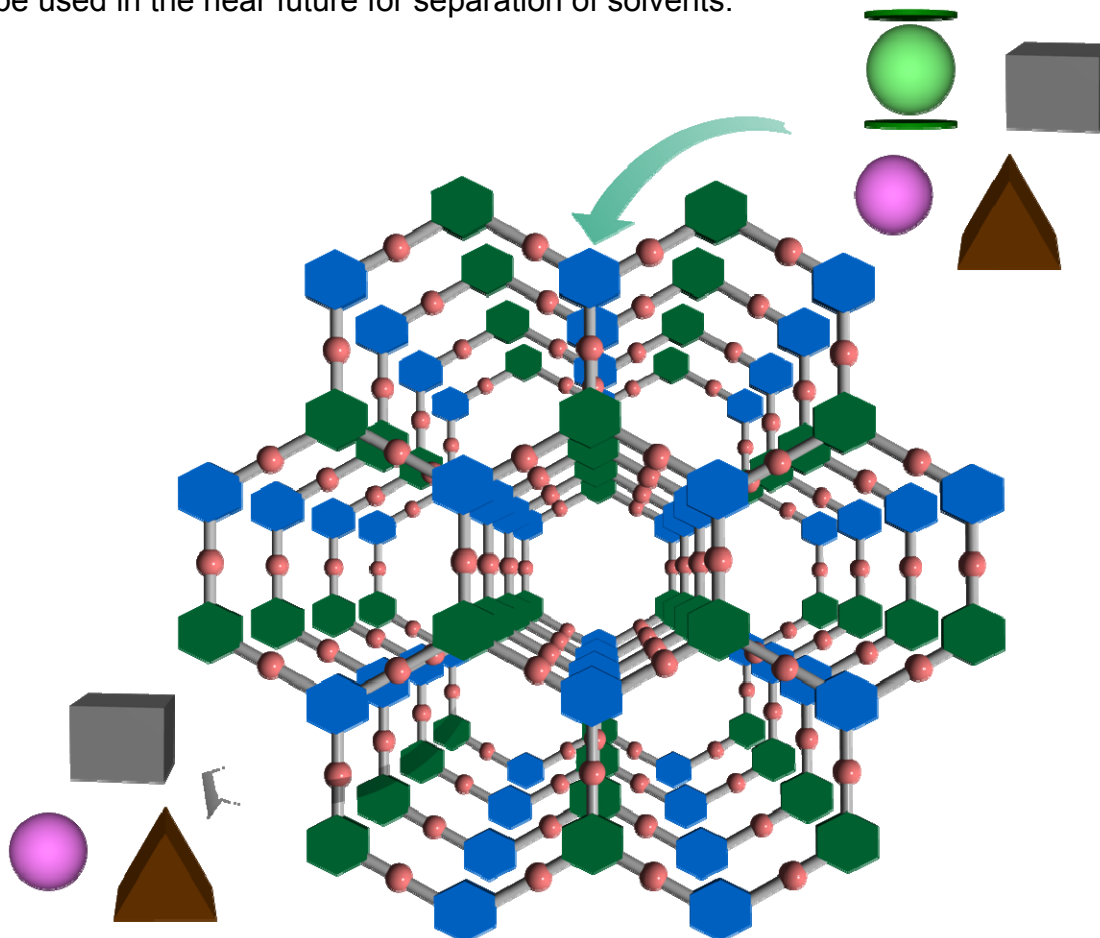


Figure 21: SEM images of PCN and TCN COFs showing ordered 2D network.

CONCLUSION

Unlike the dark colored materials obtained via high temperature method, the facile room temperature synthesis using triflic acid yielded a highly fluorescent and free flowing COF with excellent absorbance and photoluminescence property depending on the starting cyano compound. Room temperature synthesis also provided improved crystallinity which was confirmed by the PXRD spectra and SEM images. Intake of neutral gases like CO₂ confirmed porosity whereas absorption of aromatic rich solvent like benzene, xylene signified the importance of the material indicating the fact that it can be used in the near future for separation of solvents.



Scheme 6: Schematic showing aromatic guest inclusion (shown in green) in PCN-COF.

Display of excellent fluorescent property along with prominent red shift when dipped in different solvent also unleashed the potential of the synthesized COFs in the field of explosive detection. Exhibition of unique topological feature is testimonial to the fact that the COFs can find direct application in the field of optoelectricity where we need finely carved membrane so as to fine tune the electronic properties of the devices. Possession of permanent porosity, crystallinity alongwith excellent optoelectronic properties and room temperature facilitated synthesis is definitely going to make these materials the most sought after in the coming future.

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