Design and Synthesis of Covalent Organic Framework and its Characterization

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by

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "Design synthesis of Covalent Organic Framework and its Characterization" in the partial fulfillment of the requirements for the award of the degree of MASTER OF SCIENCE and submitted in the DISCIPLINE OF CHEMISTRY, INDIAN INSTITUTE OF TECHNOLOGY INDORE is an authentic record of my own work carried out during the time period from 1st July 2018 to 1st July 2019 under the supervision of Dr. Shaikh M. Mobin, Associate Professor, IIT Indore

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

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This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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> Puja Singhvi (MSc. II year)

Dedicated to my Mother.....

ABSTRACT

Porous crystalline materials are one of the emerging and most promising branch of material chemistry, comprising of zeolites, metal organic frameworks, covalent organic frameworks and porous organic cages. The use of crystalline porous networks like **Covalent Organic Framework (COF)** have attracted enormous attention due to their porosity, tunable nature, chemical stability, long-range order, large surface area, high thermal and chemical stability, electronic interactions, charge carrier transport, efficient photocatalytic activity, tunable band gap, visible light absorbance and most important cost effectiveness etc. among widely studied porous polymers, **Covalent Amide Framework (CAF)** a type of COF with long-range order, isoreticular network structure containing strong bonds, exhibiting irreversibility of the network produced and producing locked-in disorder.

In work submitted, we have shown the synthesis of **CAF** using high pressure and hightemperature reaction conditions. Such conditions have proved their beneficiary mark on the generation of crystallinity in the amorphous locked-in network created. Further characterization shows the effect of reaction conditions utilized, and a comparative study leads to the generation of an optimized path for the above. The aforementioned material was synthesized by reaction of **melamine** with freshly prepared **trimesoyl chloride** in the presence of DMF, after which the solvent was removed and the material obtained was subjected to mechanical grinding. The material obtained subjected to different conditions of temperature and solvent amount done in an ampule sealed at low-pressure condition in the presence of liquid nitrogen to create desired isoreticular network.

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ACRONYMS

MOF	Metal Organic Framework
РОР	Porous Organic Polymer
COF	Covalent Organic Framework
DMA	Di-methyl Acetamide
CTF	Covalent Triazine framework
BET	Brunauer-Emmett-Teller
PATnT	Polyamide(1,3,5-tricarboxybenzene-
	net-1,3,5-Triazine-2,4,6-triamine)
CAF	Covalent Azine Framework
PXRD	Powder x-ray diffraction
ТМС	Trimesoyl chloride
DMF	N,N-dimethyl formamide
TEA	Triethyl amine
С	Carbon
Н	Hydrogen
Ν	Nitrogen

Chapter 1

Introduction

Past two decades have garnered the discovery and intrigued utilization of microporous materials in both academic and industrial realms, attributable to its property of exceptionally high BET surface area, a the wide range of framework composition and feasible grafting of desired functionality over the pore surface [1]. They amass huge potential in storage, separation, selective gas adsorption [2], heterogeneous catalysis [3], electrocatalytic efficiency [2], light harvesting [4], sensing of metals/ions/molecules [5], drug delivery [6] and so on. Micro- and mesoporous materials include (with pore size 2-50 nm) depending on type of network framework porous silica, zeolite, activated carbon, metal organic framework (MOF) and porous organic polymer (POP) [7].

1.1 What are POPs?

The Porous Organic Polymer is a broad spectrum term used for covalently connected polymers with linkages exhibiting high thermal and chemical stability, high specific surface area, nanometer-scale pores, and high tunability [8]. They are currently the most explored structures in the field of organic porous materials. They can be found in the form of amorphous porous aromatic frameworks (PAFs) or crystalline covalent organic framework (COFs) or as a hyper crosslinked polymer (HCPs) or in the form of conjugated microporous polymers (CMPs). Porosity is obtained by utilization of differently directionalized motifs proving porosity to the polymer with a rigid and angled structure. Generally, alkyl functionalized monomer is avoided to prevent the decrease in porosity. In case of POPs as compared to COFs, the former is found



Figure 1: Classification of POPs according to the nature of the material and dimensions of the pores [9].

to have amorphous structure due to irreversibility in the bond formation process attributable to the traditional methods of synthesis leading to the kinetically formed product. Hence, as a consequence, POPs are found to possess 3D geometry while thermodynamically stable COFs generally possess 2D geometry. Herein, we have focused on strategy in the synthesis of the covalent organic framework [9].

1.2 What are COFs?

Covalent Organic Frameworks are class of porous polymer, crystalline in constitution with the periodic skeleton. Apart from the properties they possess as mentioned above, they exhibit dynamic covalent linkage concocting the skeleton. COFs are primarily composed of light atoms, like C, H, B, N and O hence avoiding toxic metal in-route [6]. Since first reported in 2005, to up till now it has witnessed a considerable drift in composition and structure the change from boron-containing framework to imine, hydrazine, keto-enol linked frameworks has witnessed different stability under different conditions and difference in the application according to reticularity and composition [10].

<u>1.3 Thermodynamics of synthesis</u>

The synthesis of COFs as perceived thermodynamically is expected to be unfavorable. While in the complete synthetic procedures often amorphous cross-linked polymers or polymers whose integrity and structure are poorly defined in accordance with the linkage of the covalent bonds is obtained. Here dynamic covalent chemistry (DCC) plays a crucial role that realizes the formation of a reversible covalent bond with error checking and proof reading leading to synthesis and reformation of stereoscopically disallowed configurations [11].

The prime importance during the synthetic procedures is the presence of reversibility in the process as this tendency promotes the crystallinity in the material due to the imbibition of the property of self-correction allowable within the reaction time scale. During reversible bond formation and extension, bonds like covalent bonds that possess high bond energy (50-110 kcal mol⁻¹) conditions for reversibility has to be harsh like high temperature

and pressure. In the reversible process the system tends to repair through back reaction and bond formation, and finally, a crystalline thermodynamic product with lowest free energy is obtained [12]. In case of lower temperature, generally, a kinetically controlled and disordered product dominates. Thus, to construct ordered covalent network solids thermodynamic reaction pathways demanding very high activation energies are preferred.



Figure 2: Schematic representation of amorphous and crystalline COF formation by irreversible and reversible reactions [13].

<u>1.4 COF structure and reticularity</u>

The conformation of building blocks rigid in nature enables the topological design of the COFs. As mentioned in Figure 3. these blocks were classified

as 2D or 3D established over the foundation of simplified symmetry notation, which points to the directional symmetry of building blocks, as mentioned in Figure 3. (2D-C2, 2D-C3, 2D-C4, and 3D-Td). The geometry of the building blocks directs the resulting COF structure. Hence, the combinations like 3D-Td + 3D-Td, 3D-Td + 2D-C2, or 3D-Td + 2D-C3 leads to the formation of 3D COFs in correspondence with different space groups crystalline in nature. In case of 2D blocks (e.g., 2D-C2 + 2D-C3, 2D-C3 + 2D-C3 or 2D-C2 + 2D-C4) selected combinations afford 2D COFs as designed topology [14]. In case of arenes, since they possess a π -aromatic system that makes them competent system to achieve rigid nature and discrete bonding direction. Their diversity allows numerous building block combinations, endowing COFs with high flexibility.



Figure 3: Combination of the building blocks with different geometries to design COFs [15].

1.5 Exclusive properties of COFs

There are properties exclusive to COF that make it a material of prime importance and promising. Few of the properties that it incorporates are:

Crystallinity: COFs reflecting their design and material tends to be ordered structures enabling characterization using diffraction techniques. The computational tools and structural studies provide powerful insight of their properties [16]. This uniformity in structure is suitable for optoelectronic devices, catalysis, and membranes [12].

Porosity: When monomers assemble into 2D and 3D networks they furnish periodic and uniform voids along with tailorable hydrophobicity, molecular functionality, and chemical affinity, where surface areas exceeding 2,500 and 4,000 m² g⁻¹ have been reported for 2D and 3D COFs, respectively [17].

Stability: Since covalent bonds lays the foundation of COF structure; hence, typically, these frameworks are stable to temperatures exceeding 300 °C and tolerant to solvents that do not interfere with their linkages or stacking. Recent developments have introduced COFs viable to hydrolysis, extreme pHs, and reductive and oxidative environments [18].

Low Density: Due to basic elemental composition as lightweight elements, COFs have shown high gravimetric performance for energy and molecular storage [12].

Modularity: COF chemistry they incorporate monomers with reduced symmetry and multiple monomer components utilized with differing lengths, that tends towards more than one bond-forming process. COFs offers a platform to design molecular assembly that has not yet been fully

exploited. In contrast, it remains difficult to predict how molecules, linear polymers, and cross-linked macromolecules arrange in the solid state [19].

<u>1.6 Synthetic methods</u>

The most crucial step determining the formation of the ordered network and regulating the thermal equilibrium during the process is reaction media and conditions, which include pressure, temperature, and presence or absence of template. In the case of reaction media generally, a mixture of solvents in the definite ratio is employed to provide solvothermal and ionothermal conditions. Other techniques employed are microwave synthesis, COF synthesis over films, etc.

1.6.1 Solvothermal synthesis

One of the most popular technique to synthesize COF, utilizes few steps to be procured to obtain desired material. A typical method like this first the Monomers and solvents are added to Pyrex tube where they are degassed via pump-freeze-thaw cycles after which the tube is sealed and is designated to the required temperature conditions following the reaction time. After the completion of the reaction, the precipitate is collected and washed with suitable solvents and later dried in vacuum rendering solid powder.

The main factors affecting the growth rate, crystal nucleation, reaction rate, solubility, and the self-healing mechanism are the solvents used and temperature to which the reaction media is subjected.

(1) Solvent combinations with optimized ratios prove beneficial in balancing framework formation and crystallization. For example, in the case of synthesis of boronate esters and boroxine COFs combinations like dioxane-mesitylene, DMA-o-dichlorobenzene and methanol-THF are used while in the case of imine linked COFs dioxane-aq. Acetic acid mixture is proven worthy. Hydrazone linked COFs shows the best crystallinity when mesitylene–dioxane–aqueous acetic acid is used. Also, a fully soluble and a completely insoluble starting material renders the observer with negative results. Hence the criteria have to optimized accordingly [15].

(2) Suitable temperature ensuring the reversibility conditions and a closed environment triggering the reverse reaction in the presence of water is essential. Generally, synthesis is done between the temperature ranging from 85-120 °C.



Figure 4: Synthesis of COF by solvothermal method [20].

1.6.2 Microwave synthesis

The rapidification of the process of COF synthesis has been achieved by this process. First used by Cooper and co-workers to synthesize boronate ester linked COFs. Along with the accelerated procedure, this method allows bulk synthesis without sealed process and renders the material with better porosity [15].

1.6.3 Ionothermal synthesis

This method was first reported by Thomas and co-workers to produce CTFs by cyclotrimerization of aromatic nitrile in molten ZnCl₂ at 400 °C offering a crystalline, robust conjugated CTF. Here ZnCl₂ acts both as a catalyst and solvent

for trimerization reaction with partial reversibility. However, with extremely harsh conditions, it limits the building block availability and resulting material lacks long range order [18].

1.6.4 Mechanochemical synthesis

Another way of synthesis is via mechanical grinding of the linkers to yield COF where the starting materials are ground together with mortar and pestle. It was observed that this method rendered comparatively less crystalline material and rather had low BET surface areas. Their stability, as compared to the solvothermal reactions, were found to be nearly the same. The Figure 9. Below shows a β -ketoenamine COF using 1,3,5-triformylphloroglucinol (Tp) (0.30 mmol) and either p-phenylenediamine (Pa-1) (for TpPa-1), 2,5-dimethyl-p-phenylenediamine (Pa-2) (for TpPa-2), or benzidine (BD) (for TpBD) leading to solvent-free synthesis of COF [21].



Figure 5: Mechanochemical synthesis of the COF using mortar and pestle [21].

1.6.5 Synthesis of monolayers on metal surfaces

Another technique prevalent is the condensation of COF building blocks over metal surfaces to form monolayers. The as-synthesized examples are SCOF-1 and SCOF-2 synthesized by sublimating the starting material in molybdenum crucible on Ag (111) surface in ultra-high vacuum. The texture of the material is characterized via scanning tunneling microscopy (STM) with an observation of defect-free pores [15].

1.6.6 Synthesis of thin films

This has been one of the most interesting methods of synthesis with broad scientific interest and significant technological importance. Such a method is generally employed when the material of interest is either insoluble powder or is in the form of monolayer which renders problems in case of electrodes or similar devices. The characterization is done via grazing incidence x-ray diffraction that reveals thin film's crystallinity and alignment [22].



Figure 6: Solvothermal condensation of building blocks in the presence of a substrate-supported surface providing COF-5 as both a film on the graphene surface, as well as powder precipitated in the bottom of the reaction vessel [22].

<u>1.7 Typical linkages in COF</u>

1.7.1 Boron containing COFs

The first reactions reported like COF-102, COF-103, COF-105, and COF-108 were self-condensation reaction of boronate esters and boroxine rings and the co-condensation of boronic acids and catechols to boronate ester rings. They had the advantage of reversibility in reactions, although slight but this helped in gaining crystalline, porous frameworks. For e.g., the condensation of 1,4-benzene diboronic acid (BDBA) to form a boroxine network yielded COF-1. This framework arranges in staggered fashion, unlike other 2D COFs. Solvothermal synthesis route was most commonly used where suspensions of precursors were solubilized in mesitylene/dioxane. Later rapid microwave synthesis and purification were successfully demonstrated [23].



Figure 7: Boron oxygen linked COF [23].

1.7.2 Imine linkage

Imine linkages are formed by the reaction of aldehydes and amides. They have been reported to assume higher stability than boronic esters hence making it more prevalent than boronic esters. Further modification includes, inclusion of aromatic rings inculcating conjugation of the π -systems and enabling conjugation over the whole 2D layer. The first 3D COF with imine linkage was introduced by Yaghi resulted from the reaction between from tetra-(4-anilyl) methane and terephthalaldehyde (TA) in 2009. The first imine based 2D COF by Wang et al. by condensation of TFB and 1,4-phenylenediamine (PDA) cresting a planer morphology with hexagonal pores. Imine linked COFs have demonstrated higher stability in terms of vapors present and pore flexibility allowing effective gas adsorption. Uptill now the most popular strategy of COF synthesis is the imine based [24].



Figure 8: Imine linked COF [24].

1.7.3 Hydrazones and Azines

Hydrazones are synthesized via condensation of aldehydes and hydrazides. The first kind of this material was synthesized in the lab of Yaghi in 2011 which were named as COF-42 synthesized via a combination of 2,5-diethoxy terephthalohydrazide and TFB, and of COF-43 from 2,5-diethoxy terephthalohydrazide. In the synthesis of azine framework co-condensation of hydrazine is done where the nitrogen-containing hydrazine is used to establish the linkage. The interesting property of azine linkage is its utility to serve as a docking site for guest molecule, hence beneficiary in sensing. The structure modulation is another prime property associated with the azine linked COF [25].



Figure 9: Synthetic pathway of the first 3D covalent triazine framework [25].

1.7.4 Ketoenamines

Such kind of COFs, the building block consist of hydroxyl groups adjacent to the formyl groups. The mechanism of synthesis first involves formation of imine COF which undergo irreversible enol-keto tautomerization to form a ketoenamine linkage. Hence the formed ketoenamine COFs were seen to possess resistance from strong bases, hence high chemical stability. The first of this kind was reported by Banerjee et al. in 2012. The only reduction in crystallinity is due to the fact of the irreversible nature of the step in COF synthesis that inhibits the property of error correction [24].



Figure 10: Scheme for β -ketoenamine COF via enol-keto tautomerization [26].

1.8 Characterization of COFs

Characterization of COF is done primarily on the basis of solid-state NMR, which is undoubtedly the most reliable technique. Meanwhile, other techniques include FTIR, UV-vis spectroscopy, providing complementary information.

The main concern regarding this material is the characterization of atomic connectivity, structural regularity, morphology, and porosity. Unfortunately, unlike MOF single crystal cannot be grown in case of COF and hence the absence of SC-XRD data marks great difficulty in structure elucidation. The only way out is analysis of COF by powder X-ray diffraction (PXRD). The crystallinity is roughly estimated by the signal intensity. To elucidate structural information from the PXRD data, the first step is computational stimulation using software like. Material Studio (MS) programs. The Pawley method is applied to refine the obtained PXRD data to generate the unit cell lattice in the most possible manner. The well-known Rietveld method proves dysfunctional in this case, as the above is not suitable for low-resolution PXRD patterns [27]. The stimulated pattern also provides density data, which is further matched with average pore size derived from the gas absorption isotherm data. The presence of newly formed covalent bonds rendering the molecule with exclusive structural integrity and atomic connectivity is essential to characterize.

The porosity data of the material is accessed by gas (nitrogen or argon) adsorption-desorption measurements. SEM is utilized to observe morphology. Important information for the characterization and application of COF in a predictive way is done by the theoretical investigations.

1.9 Applications of COF

1.9.1 Gas adsorption

The lightweight nature of the material is the most lucrative feature in this regard, unlike other, materials it shows promise for porosity and exhibits ideal thermodynamic adsorption parameters along with minimizing cost. 2D COF topologies harness new potential applications with functional monomers and relatively large pores [15].

1.9.1 Catalysis

The monomers, post-synthetic functionalization with metal ions or incorporation of organocatalysts impart catalytic function to the material. For instance, Yaghi, and co-workers synthesized cobalt porphyrin COFs catalyzing the electrochemical reduction of CO₂ with promising activity and selectivity for H₂ formation (Figure 2, COF-366-Co). The material exhibits a turnover number (TON) of 34,000 after 24 h, with 4-fold higher activity. Structurally, COFs supports asymmetric catalysis. Another advantage is heterogenous catalysis hence can be readily used and reused for further catalysis [28].

1.9.1 Energy storage

With possession of the high surface area, they become a material of interest for electrochemical capacitors. Also, insolubility and stability allow repeated cycles. COF-based materials are expected to outperform other materials looking at the current reported materials and progress with regards to the energy and power densities achieved [29].

1.9.1 Light conversion

Due to the presence of π -orbital overlap, layered structures, and ordered heterojunctions 2D COFs have been designed for light conversion. The impressive hole mobility is observed most probably due to planarity and aromaticity. This efficiency relative to the field of organic photovoltaics needs improved control over the morphology, materials quality, and processing.



Figure 11: Few of COFs applications [30].

1.10 Covalent Amide Framework

The intricate relation of COF and reversibility of bond formation is vital for possession of crystallinity in the synthesized material. The crystallinity requires positional coherence over several nanometers, unlike local bond formation. Hence it is challenging to assemble a unit with strong linkages to a well-developed crystalline material. Although the synthesis of porous material is a straightforward task, but the difference is amorphous structure is not appreciated. The desirability of crystalline material is more due to ease of conceiving the structure and hence related thermodynamic, physical and chemical aspects linked with the above.

For a covalent material to be crystalline, the primary goal is to achieve longrange positional order affected by bond length, dihedral angles within the molecular unit and angles in a single unit to avoid non-ideal conformations. Crystalline frameworks such as MOFs, COFs, and zeolites allow thermodynamic growth control due to repeated bond breaking and bond forming process that allows error checking and enhances thermodynamically controlled growth. Such reversibility in the bond formation allows removal of spatially non-ideal conformations and reformation of the bonds, thus increasing the likelihood of the crystalline structure.

In case of amide bonds, they exhibit high stability and under ambient conditions are considered practically irreversible (for hydrolysis of amides rate constant reported is of the order 10^{-11} s⁻¹), including both basic and acidic solutions and with thermal stability. The major advantage of the high throughput synthesis is the cheap and easy availability of starting materials. Amides are formed in non-equilibrium conditions by reaction of activated carboxylic acids, i.e. their acid chloride derivatives followed by their reaction with amines leading to the synthesis of amide polymer displaying

extensive structural and chemical diversity. The presence of reversible conditions is achieved under nonlabile ambient conditions but harsh enough to escalate the process. The aim of the work is thus to synthesize an amide polymer and optimize the activation process in order to gain crystallinity and porosity in the material so as to use it further in the field of electrocatalytic water splitting by conductivity measurements [31].

Here we have shown a polyamide network synthesized via typical acid chloride route. Polyamide(1,3,5-tricarboxybenzene-net-1,3,5-Triazine-2,4,6-triamine) (PATnT) which consists of trimesic acid and melamine. The reaction of trimesoyl chloride and melamine yielded as expected amorphous material. As deciphered from the literature reported, the idea of inclusion of crystallinity in the amorphous material reported above came from amorphous silica which is highly stable under ambient conditions but when exposed to harsh conditions inculcates crystallinity by forcing strong Si-O bonds to form reversibly namely strong hydrolytic environment, high temperature, and high pressures. The similar methodology is garnered by Matthew and co-workers by using harsh conditions to obtain a CAF. By using similar conditions, we have been able to achieve a ordered porous framework of CAF whose structural system and arrangement is yet to be deciphered.

1.11 Constitution of Thesis

The aim of the project was to synthesize Covalent organic framework and the characterization of the above so as to elucidate the structure, constitution, crystallinity and various other parameters like porosity, pore diameter, the stability of the material in order to find its suitability in other applications like electrocatalysis, conduction properties, catalysis, etc.

The chapters further have been divided in the following way as mentioned below:

- <u>Chapter 2:</u> This chapter includes materials, instrumentation used, and the synthesis procedure followed to synthesize CAF.
- <u>Chapter 3:</u> it includes data of the material characterized and along with conclusion deciphered from the data.
- <u>Chapter 4:</u> it concludes the described work and also looks for possible future scope and applications.

Chapter 2

Experimental Section

2.1 Chemicals and materials

The commercially available starting materials 1,3,5- trimesic acid (Sigma-Aldrich), Melamine (Sigma-Aldrich), Thionyl Chloride (Spectrochem) and dry N,N-dimethyl formamide (Spectrochem), Triethyl amine (Spectrochem) were used as received. All the chemicals were used without further purification.

2.2 Instrumentation

¹**H NMR** studies of the material synthesized were done in DMSO-*d*₆ using Fourier transform Nuclear Magnetic Resonance spectrometer, Model AVANCE III 400 Ascend Bruker BioSpin International AG, Switzerland at 400 MHz. **X-Ray diffraction patterns** of the powder material were obtained in a Rigaku SmartLab, Automated Multipurpose x-ray Diffractometer using Cu source. **Thermogravimetric analysis (TGA)** of the samples were carried out between the temperature ranges from 308 to 873 K with a temperature ramp of 10 °C/min using TGA 4000/Pyris 6, TGA thermal analyzer under N₂ flow. **Elemental analysis** was done with FLASH 2000 (The Thermo Scientific) elemental analyzer. **Fourier transform infrared spectral (FTIR)** was done by Tensor 27, BRUKER spectrometer (with MIR source, ZnSe beam splitter, and DLaTGS detector) at 25 °C. The microstructures and morphologies of the material were characterized using **Field-Emission Scanning Electron Microscope** (FE-SEM), Supra55 Zeiss. N₂ adsorption/desorption isotherm of the sample was recorded using quantachrome, Autosorb iQ2, **BET Surface Area & Pore Volume Analyzer** at 77 K. **CO₂ adsorption isotherm** of the material was recorded by using the same instrument at 177 K. Prior to both the measurement, the sample was degassed at 423 K for 24 hr. under high vacuum conditions.

2.3 Synthesis of 1,3,5-trimesoyl chloride (TMC)

To 3 gram of trimesic acid add dropwise (0.5 mL/min) Thionyl chloride from the dropping funnel at 0 °C and 300 rpm so as to combat the heat evolved from the exothermic reaction inside the reaction vessel. After two hours of stirring at 0 °C and later for an hour at room temperature, the reaction vessel was placed under reflux at 80 °C in oil bath till completion. After consummation of reaction, the volatiles (HCl and SOCl₂) were removed under condition of low pressure and temperature. The generated gases (hydrogen chloride and sulfur dioxide) were vented to a caustic scrubber, and 1,3,5-trimesoyl chloride was obtained (Scheme 1.).

Scheme 1.



2.4 Synthesis of Polyamide(1,3,5-tricarboxybenzene-net-1,3,5-Triazine-2,4,6-triamine) (PATnT)

To solution of trimesoyl chloride (14.2 mM) in dry DMF (10 mL) add dropwise solution of melamine (14.2 mM) dissolved in a mixture of dry DMF (50 mL) and Triethyl amine (5 mL) at 0°C with strong stirring over the course of 1 hour under an inert atmosphere. Allow the suspension to warm at room temperature and stir overnight. Succeed the aforementioned step by quenching of reaction mix with water (500 mL at room temperature, 1200 rpm, 6h). Filter the obtained solids, wash them thrice with distilled water and dried in a heating oven at 100 °C for 3 h. and ground the obtained solid to homogenous size precipitate. The above-mentioned powder was subjected to ball mill with 4 repetitive cycles of 20 min forward, 10 min rest, 20 min backwards at 350 rpm. to obtain a grey colored fine powder. Suspend the powder in water (500 mL) overnight at room temperature, after which filter the solids and ensure pH neutrality. Dry the solids at 160 °C in the heating furnace for 6 hrs. to obtain dry grey colored powder, PATnT (2.34 gm).

2.5 Synthesis of CAF via PATnT

A borosilicate tube was charged with dry PATnT (100 mg) and water (150 μ L). The solvent was added, and the tube was sealed after evacuation at 10⁻³ mbar. The tube was placed in a heating furnace at 160 °C for 3 days, where the temperature was made to reach to 160 °C. The sealed tube was broken to obtain the reaction contents and was subjected to washing with DMF (3x12 mL), water (3x12 mL), methanol (3x12 mL) then dried by filtration yielding **CAF** as a pale violet powder (52.3 mg) (Scheme 2.).

Scheme 2.



Chapter 3

Results and discussion

CAF was synthesized under different conditions of water and temperature under low-pressure conditions in an ampule sealed at 10⁻³ mbar pressure by devitrification of PATnT. Devitrification, a process is utilizing which glassy amorphous substance changes its structure to a crystalline network. A most common example of it is silicates, i.e. compounds of silicon, oxygen, and metals which abstain from the repetitive arrangement of molecule essential for the formation of crystals [32]. When rock magma melts glass is formed, a rapid phenomenon which leads it the inclusion of irregularity. The strategy of utilizing harsher conditions like maintaining the reaction mix at high temperature for long at low pressures and allowing it to cool to it's more crystalline and ordered framework has been exploited in the synthesis of CAF just as used in devitrification of silicates.

PATnT, after synthesis was ball milled to a homogenous material and the powder dried by evacuation of above, was loaded in a borosilicate tube and sealed at very low pressure. The tube was then placed in a pressure reactor. The reactor was loaded with a small quantity of water (typically 40 mL) which is crucial for maintaining pressure balance. The water inside the sealed tube and outside the tube generates pressure, and the state of balanced pressure conditions on both side of the wall plays a crucial role in abstaining the tube from failing at high temperature and low-pressure conditions. The similar devitrification was tried to achieve using autoclave with the same amount of water and temperature, but the temperature utilized to attain reversibility makes the material susceptible to oxidation in the presence of

air. Hence, when the reaction was placed in autoclave the material, PATnT got partially degraded from a grey colored material to a water-soluble pink colored part.

The successful synthesis and devitrification were first confirmed by the presence of functional groups, i.e., stretching frequency of bonds by FT-IR, then via ¹H NMR analysis. CHN analysis confirmed the expected molar ratio of both the reactants. If a sample of dry PATnT is subjected to devitrification in a different amount of water and temperature conditions the crystallinity generated was confirmed by PXRD data analysis.

3.1 Analysis of PATnT and CAF by FT-IR

The FT-IR analysis of the material shows a peak in the desired region. The starting materials, Trimesic acid contained O-H group whose peak would have been observed as a broad one in the region between 3000 to 2500 cm⁻¹ whose absence have clearly indicated the residual absence from the final material. In case of melamine the absence of two N-H peak of a primary amine in the CAF levels out the presence of above.

The major expected peaks of N-H stretch and C=O stretch in the region of 3300-2800cm⁻¹ and 1690-1630 cm⁻¹. Other peaks observed are mentioned in table crucial for structural elucidation. The major conclusion drawn was from the two peaks od N-H stretch seen in PATnT FT-IR spectrum as compared to a single peak in CAF spectrum. This supports the ¹H NMR finding of the presence of salt over amide and its removal after devitrification.



Figure 13: FT-IR spectra of PATnT

 Table 22: FT-IR value of PATnT

Peak Centre	Assignment
3389	N-H Stretch
3236	N-H Stretch
2856	C-H Stretch
2600	C-H Stretch
1710	C=O Stretch (amide)
1666	C=N Stretch
1543	N-H Bend
1437	C-N Bend
1365	C-N Bend
1276	C-N Bend



Figure 14: FT-IR spectra of CAF

Table 13: FT-IR values of CAF

Peak Centre	Assignment
3396	N-H Stretch
3232	C-H Stretch
3107	C-H Stretch
2943	C-H Stretch
1708	C=O Stretch (amide)
1658	C=N Stretch
1537	N-H Bend
1435	C-N Bend
1387	C-N Bend
1280	C-N Bend



Figure 14: (a) Single unit of the assynthesized CAF, (b) Chem draw 3-D stimulation of the single unit shown in (a), (c) Multiple units of the same material shown drawn as a chem draw image, (d) 3-D stimulation of chem draw object (c) showing expected spatial orientation of the framework





Figure 15: NMR data of PATnT and CAF

The analysis of both the sample was done by solubilising the material in DMSO- d_6 where it showed partial solubility.¹H-NMR confirmed the successful synthesis of PATnT. The ¹H-NMR of PATnT showed distinct peaks corresponding to the expected structure exhibiting singlet of amide proton at δ 9.94 ppm and the aromatic protons of 1,3,5-benzenetricarbonyl trichloride group were observed as a singlet at δ 7.91 ppm. Along with the expected peaks of the functional moieties, a broad peak at δ 6.52 ppm indicated the possible presence of salt associated with the triazine moiety in

melamine. The further analysis of CAF under similar solvent conditions showed the second spectrum, where singlet of amide proton at δ 8.71 ppm and the aromatic protons of 1,3,5-benzenetricarbonyl trichloride group was observed as a singlet at δ 6.43 ppm. The results pointed towards the removal of salt from CAF, which was the prime reason for shifting of the ¹H peaks downfield in PATnT. Similar results were also deduced from FT-IR analysis.

3.3 Analysis of PATnT and CAF by CHN

The CHN analysis compares the experimental and theoretical data of PATnT and CAF.

Sample	e Measured (wt.%)		Calculated (wt.%)			
	С	Н	Ν	С	Н	Ν
PATnT	36.6561	3.9853	27.1795	36.9	1.5	21.5
CAF	37.4122	3.88	22.3813	36.9	1.5	21.5

Table 3: CHN analysis of PATnT and CAF



3.4 Analysis of the temperature dependent stability of PATnT

Figure 16: TGA data of PATnT

Thermal Gravimetric Analysis of the material showed loss of 11.54% of the mass uptill the temperature of 300 °C that shows the removal of any trapped solvent. Above 300 °C we observed a dip of more 47.97% which showed the degradation of the material above the ascribed temperature, which indicated a good thermal stability of material below 300 °C.

3.5 Analysis of PXRD data of PATnT and CAF

After sealing the PATnT material and subjecting to further processing the obtained dry powder of CAF was confirmed using PXRD. The PXRD pattern of the resultant solid showed a marked difference than its starting material, in terms of both peak intensity and area covered. The above two

graphs show a clear distinction in crystallinity of material and hence confirm the process of devitrification, developing long-range order in CAF.



Figure 17: Comparative analysis of crystallinity using PXRD data of PATnT and CAF

3.6 Analysis of PXRD data of PATnT devitrified at various temperatures

The material PATnT was devitrified at different conditions of temperature sealed with an equal water content of 100 μ L in each. The PXRD and yield for all the samples were recorded in order to optimize the process. It was observed that while the yield remained approximately similar except in the vial at 200 °C the crystallinity was obtained maximally at 180 °C. Hence it was concluded to put further reactions at 180 °C, and the further characterization was also done accordingly.



Figure 18: PXRD patterns of devitrification of PATnT at variable temperature

Table 4: Yield of CAF obtained after devitrification of

PA	Tn	Т

Devitrification Temperature	Yield (for 100 mg substance taken)
120°C	69.8%
140°C	62.6%
160°C	66.6%
180°C	60.4%
200°C	40%

3.7 Analysis of PXRD data of PATnT devitrified at various temperatures

After obtaining optimized temperature for the devitrification process, the tubes were sealed with variable water content, and hence the PXRD was recorded. The tubes were sealed according to the protocol mentioned in the experimental section with devitrification running for 3 days at 180 °C temperature for 100 mg of PATnT taken in each tube. There was observed the considerable change from 0 and 25 μ L to 50 and 75 μ L water was added. However, the most profound change was observed in the tube sealed with 100 μ L of water. Hence, we could conclude at 180 °C and equivalent microlitre of water added to PATnT material yields the most crystalline CAF with good yield.



Figure 19: Comparison of the appearance of the reaction tubes with variable water content before and after the devitrification process



Figure 20: PXRD patterns of devitrification of PATnT variable water content

3.8 SEM analysis

The morphology and microstructure of PATnT composites were examined by SEM. The SEM image of PATnT showed an irregular directionally fine fibrous filaments. FESEM images, as shown in Figure 20. in which irregularly shaped particles were observed. However, these particles appear to form aggregates with irregular flower-shaped structures.



Figure 21: SEM images of PATnT showing irregular flower shape morphology

3.9 BET analysis

The architectural stability and porosity of PATnT and CAF were confirmed and compared by measuring the N₂ gas adsorption of the guest-free material. A sample of as-synthesized PATnT and CAF were evacuated with a dynamic 10⁻⁵ Torr vacuum pressure and heated to 150 °C for 24 hours to remove all the guest molecules residing in the pore. This sample was further utilized for measurement of the N₂ isotherm at 77 K from 0 to 1 bar, which showed a very sharp uptake at P/Po at 1 bar (Figure 22 and 23). The Brunauer-Emmett-Teller (BET) model was applied to the isotherm to calculate the apparent surface area of 27.449 m²/g of CAF and 3.269 m²/g of PATnT; the pore volume V_p = 0.417 cc/g of CAF at P/Po of 1 bar V_p = 0.013 cc/g of PATnT at P/Po of 1 bar. At higher pressures, a sharp increase in the isotherm occurs. The graph shows reversible Type III isotherm convex to the P/Po axis over the entire range. This kind of isotherms is obtained when the interactions between the adsorbate and adsorbent are weak. The respective BJH pore size distribution curves are shown in Figure 23 and 24 where pore radius of PATnT is 16.99 (Å) and CAF is 17.04 (Å)



Figure 22: Gas adsorption isotherm of PATnT:N₂ at 77 K temperature and 1 atm pressure.



Figure 23: Gas adsorption isotherm of CAF:N₂ at 77 K temperature and 1 atm pressure.



Figure 24: Pore size distribution of PATnT



Figure 25: Pore size distribution of CAF

Chapter 4

Conclusions and Scope for Future Work

Overall, the prospect of designing a new Covalent amide framework was possible by reaction of Trimesoyl chloride and melamine resulting in formation of PATnT, which was further devitrified into CAF by sealing the obtained PATnT with different content of water and proceedings done at varied temperature to obtain an optimized reaction condition. The formation of product was verified by FT-IR and by ¹H-NMR analysis, which on comparison showed the changes the former and devitrified product possessed. TGA was utilized to obtain degradation temperature that the material PATnT can withstand such that a condition below its resistance point is used. Devitrification process inculcates crystallinity by providing harsh conditions for reformation of amide bonds. The intensity of inculcated crystallinity was measured using PXRD data whose peak gave a clear idea of the above. The BET data clearly showed sharp increase in volume of gas adsorbed when compared to CAF from its precursor PATnT. Hence we can conclude the successful synthesis of CAF and the optimization of reaction to obtain material in maximum yield with high crystallinity.

In the future ventures the most important data associated with it is ¹⁵N and ¹³C cross polarization (CP) magic angle spinning (MAS) NMR, Indexing and Pawleys Refinement of PXRD data to obtain the structural information of the material. The solid-state NMR data will unequivocally show the amide bond network and structural integrity can be roughly predicted by the shifts in NMR. The first step is using indexing tools to determine cell parameters and crystal systems done by indexing the experimental powder diffraction pattern. After which powder refinement is done using Pawley method and is later refined by Rietveld method. The refined data is at last

matched with the experimental one. Hence the further aim is to find structure and lattice parameters of the material for future applications.

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