

Design and Fabrication of Surface Anchored Organic Assemblies

A Thesis

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Degree of

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By

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Dedicated to

My Grandfather – the late Biswanath Roy



Indian Institute of Science Education and Research (IISER) Pune

CERTIFICATE

It is hereby certified that the work described in this thesis entitled "Design and Fabrication of Surface Anchored Organic Assemblies" towards the partial fulfilment of the BS-MS dual degree program at the Indian Institute of Science Education and Research (IISER) Pune, represents the work carried out during the academic year 2018-2019 by *Mr. Arkendu Roy*, under the supervision of Prof. Dr. Christof Wöll, Professor, Director of the Institute of Functional Interfaces at Karlsruhe Institute of Technology, Germany. The work presented here or any part of it has not included in any other thesis submitted previously for the award of any degree or diploma from any other university or institute.

Date: 2019-03-20

A handwritten signature in blue ink, appearing to read 'C. Wöll', positioned above the printed name of the research supervisor.

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Declaration:

I hereby declare that the matter embodied in the report entitled "Design and Fabrication of Surface Anchored Organic Assemblies" are the results of the work carried out by me at the Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology, under the supervision of Prof. Dr. Christof Wöll and the same has not been submitted elsewhere for any other degree. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that violation of the above will cause for disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

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Chapter - 1

Introduction

1. Introduction

1.1 Fabrication of Surface Templated Multilayer Assemblies:

Multilayer organic thin film on solid surface have been investigated for more than 80 years owing to their ease of fabrication with multicomponent molecular assemblies of tailored architectures. ^[1] Over the last few years materials science has been flourished in an interdisciplinary research field, encompassing organic, biological, polymeric component, organic-inorganic hybrid architectures, etc. with an extensive structural diversity and ease of tunability regarding potential properties. Even multilayer-composites make it possible to combine two or more properties in a single system. Moreover, understanding of molecular orientation and organization in the multi-composite assemblies is highly desirable as their properties depending on the local chemical environment. However, it is possible to consecutively deposit single molecular layer via covalent and non-covalent interactions on the planar solid surface which leads to form multilayers. Langmuir-Blodgett (LB) technique has already been well explored to fabricate multilayer nanostructured films, in which monolayers are deposited on water surface and then it has been transferred onto the solid surface. ^[2,3] The pioneering work on the synthesis of multilayer thin film of organic molecules was reported by Kuhn and et al. using LB technique ^[4]. However, this technique renders some limitations as it is hard to reliably obtain high quality thin films. ^[4] So, an alternative fabrication technique of multilayers films by consecutive adsorption though layer-by-layer (LbL) of more than one components is far more general. Traditionally, the Layer-by-layer (LbL) assembly is been constructed by immersing the substrates in the solution of desired layering materials followed by rinsing steps after each layer formation. (Figure: 1) It has been determined that LbL assembly allows the growth of homogeneous thin films, as compared to gas deposition and nucleation deposition. ^[5] Further, the subsequent studies have also shown that the parameters of LbL assemblies which can mainly cause the difference in film growth are likely the layering material's concentration, immersion time, and washing parameters. ^[6,7] Apart from immersive assembly, there are other well-established and advanced conventional LbL assembly protocols such as spin assembly, spray assembly, fluidic assembly which commonly have been used for the fabrication of thin films. ^[8]

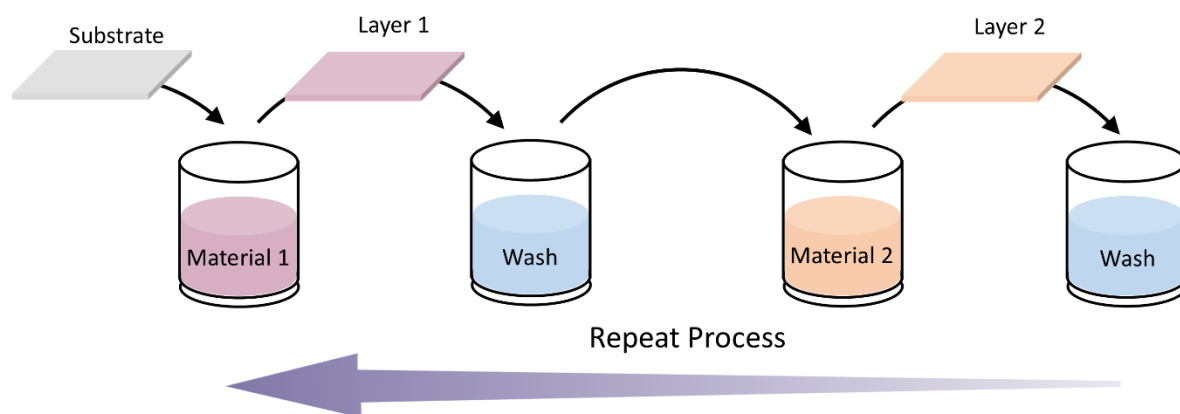


Figure: 1 Schematic illustration of immersion LbL assembly technique.

1.2. Types of Surface Multilayer Assemblies:

1.2.a LbL assembly via electrostatic interaction:

The electrostatic interaction has been the first and the most well explored assembly mechanism within Layer-by-Layer technique, this is supported by the fact that the overwhelming majority of reports in literature of LbL assemblies via electrostatic interaction. ^[9-15] The electrostatic interaction allows us to construct multilayer assemblies of oppositely charged molecules with controlled layer deposition, structure, and thickness. ^[1, 15] Since the pioneering work of Decher and et al. several reports have been published based on incorporation of polyelectrolytes or other charged building blocks to build up the multilayer films via electrostatic interactions. ^[1, 10, 11, 13] (Figure: 2A) However, this is only applicable to charged species due to the building mechanism based on the electrostatic interaction, the multilayer assemblies are less stable and robust than the one fabricated through covalent bonding.

1.2.b LbL assembly based on Coordination Bonding:

Coordination bond is a strong molecular interactions established between a metal ion and ligand, which allows the design and synthesis of novel, well ordered and controlled 1D, 2D and 3D organic-inorganic hybrid structures. The thin film materials via coordination bond can be

comprised of several materials, namely, zeolites, coordination polymers and advanced inorganic-organic hybrids, such as metal-organic frameworks (MOFs), etc. (Figure: 2B) Such materials, can have wide range of applications viz. sensing, membrane based gas separation, porous membranes, catalysis, drug delivery, optoelectronics, luminescence, etc., [16-28] can be grown by two main fabrication techniques: (a) solution based Layer-by-Layer growth method and (b) vapor based Layer-by-Layer method.

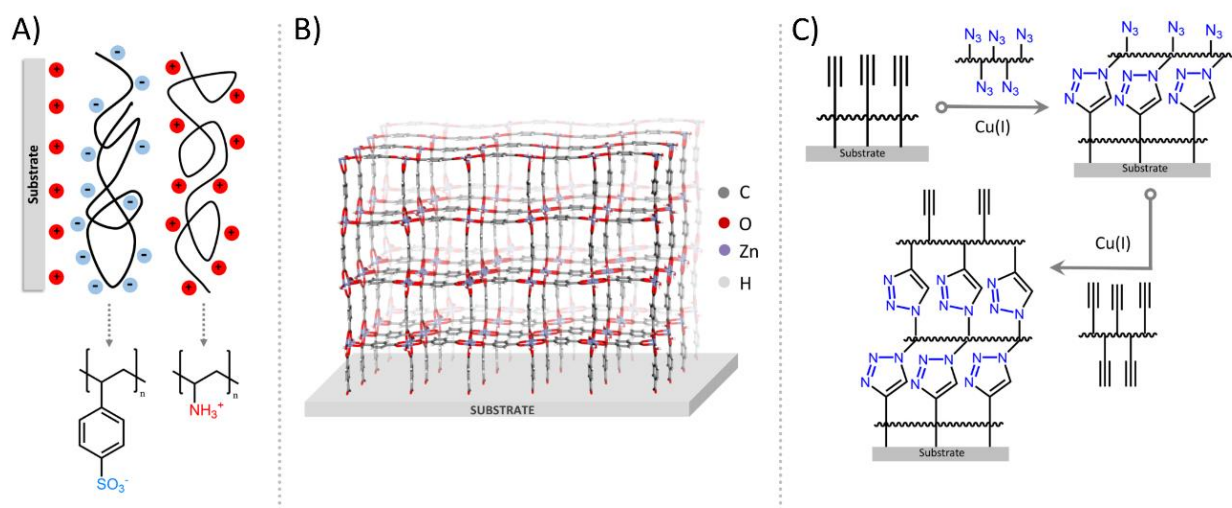


Figure: 2 (A) LBL assembly on a charged substrate consisting of oppositely charged polymer, [1] (B) Surface Metal-organic framework (SURMOF): An example of LbL assembly via coordination bonding, [28] (C) LbL assembly of polyacrylic acid multilayer films using click chemistry. [32]

1.2.c LbL assembly through Covalent Bonding:

Covalent bonds are another major construction tool to fabricate LbL films that have recently drawn attention owing to the strength and stability of the multilayer organic structures. The pioneer work of covalent LbL assembly consisting of organic polymers was reported by Crooks and et al. [29] Within few years, several approaches with diversity of materials has been reported for constructing covalent LbL assemblies using step-by-step copolymerization chemistry. [30, 31] Later on, Such and co-workers [32, 33] demonstrate a new pathway to achieve high yield, well-ordered organic LbL assemblies under mild condition, via click chemistry. (Figure: 2C) Therefore, covalent bonding is an alternative, and an efficient way to fabricate stable, and

functional multilayer LbL assembly. Therefore, these organic assemblies via strong covalent bonds can be used in various emerging fields such as biomedicine, controlled drug delivery, bio-sensing, nano-technology.

1.3 Overview of thesis / Abstract:

Herein, the work carried out in this thesis has focused on developing surface organic assemblies: (**Chapter-1**) fabrication approaches of surface aromatic di-imide polymers via step-by-step copolymerization, and (**Chapter-2**) Design and synthesis approach of 2 dimensional (2D) imine linked surface covalent organic frameworks.

(Chapter-1): A controlled on surface assembly of 1-dimensional aromatic donor-acceptor di-imide polymer chains have been grown to investigate the structure-property correlations in solid state. In an effort to facilitate the controlled incorporation of donor-acceptor moieties into a system, here layer-by-layer (LbL) fabrication technique is employed to synthesize discrete molecular layers of donor and acceptor, on top of another. Further, the organic thin films have been characterized by UV-Vis, SEM, ATR, AFM studies. Furthermore, the systems have been modified with different length of donor molecules to incorporate the π - π interactions between donor and acceptor molecules which may facilitate the charge transfer. Owing to the presence of predictable and well-organized assembly of donor-acceptor molecules, these organic thin films can be potentially useful for exhibiting suitable electronic properties.

(Chapter-2): An on surface fabrication technique of 2 dimensional (2D) imine linked Covalent Organic Framework. Herein, we have employed a bottom-up strategy for anchoring COF microcrystallites on functional substrates as thin film under ambient condition. Further, the powder COFs and the COF thin films have been characterized by XRD, ATR, FESEM, UV-Vis studies. We expect this ease of fabrication will facilitate the surface covalent organic framework thin films application for development of advanced sensors or electronic devices.

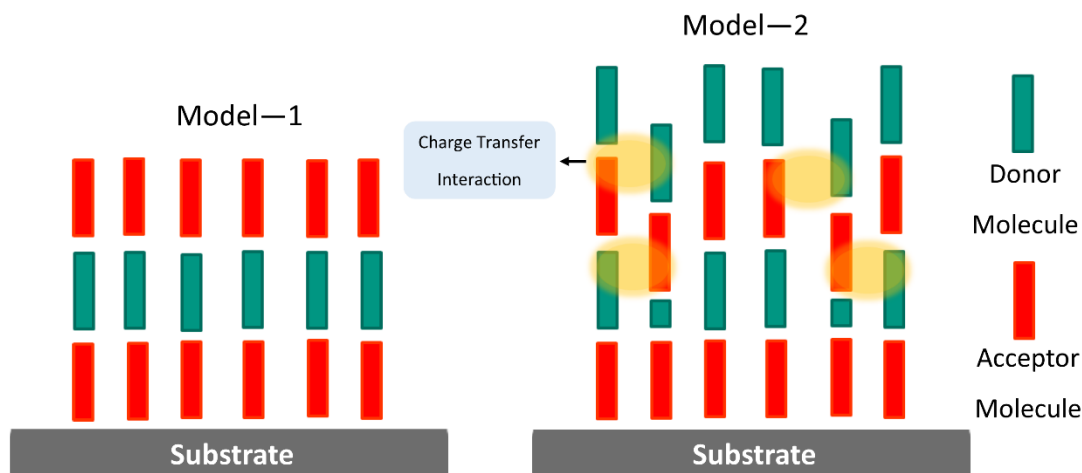
Chapter - 2

Layer-by-layer Organic Thin Films of Aromatic Di-imide Polymers

2.1 Introduction:

In recent years, the field of organic optoelectronics has dramatically expanded including the great promise and rapid advancement in various systems like organic-light-emitting-diodes (OLEDs) and organic-photovoltaic (OPV) devices. ^[1, 2] Therefore, it is highly sought after to investigate the structure-properties correlation of these systems for further improvement, optimization and controlling their optoelectronic functions. Such devices are mainly comprised of efficient charge separated states in donor – acceptor systems. Hence, changes in donor – acceptor molecules often lead to the tuning of the electronic structure of the system, which results in the formation of charge transfer (CT) complexes. ^[3] Mainly, the intermolecular interaction viz. hydrogen bonding, electrostatic, π - π interactions are used to fabricate the well-ordered donor acceptor assemblies and as well determines system's final morphologies. ^[4, 5] Further research into the ordered self-assembly of donor acceptor pairs with precise structural predictability is very active, with potential application in optoelectronic devices. ^[6]

Naphthalene diimide (NDI) is commonly incorporated in an assembly as a versatile π -conjugated electron acceptor owing to its electron-deficiency of aromatic core, high electron carrier mobility, and low lying LUMO. ^[7-9] The small π -conjugated molecules like naphthalene, biphenyl, fluorene are endowed with characteristic of donor because of their fairly delocalized π -electrons. A suitable donor – acceptor assembly is capable of giving CT complexes, by the partial or integral delocalization of electrons from donor moiety to acceptor moiety. But most of the donor acceptor assemblies are formed in liquid phase and exclusively solvent dependent in nature. ^[10-12] In an effort to facilitate the controlled incorporation of donor – acceptor moieties into a system, layer-by-layer (LBL) technique is used to synthesize discrete molecular layers of donor and acceptor on top of another (Scheme :1 Model 1). Further, in the second model the system has been modified with different length of donor molecules in the first donor layer to incorporate the dispersive interactions viz. π - π and van der Waals interactions which may facilitate the charge transfer between donor and acceptor molecules. (Scheme: 1 Model 2)



Scheme 1: Schematic models of organic thin films

2.2 Experimental Section:

Here, we have utilized a condensation reaction based layer by layer methodology between Naphthalenetetracarboxylic dianhydride (NDA) and several primary diamines to construct naphthalene diimide polymer based multilayered organic thin films of model 1&2.

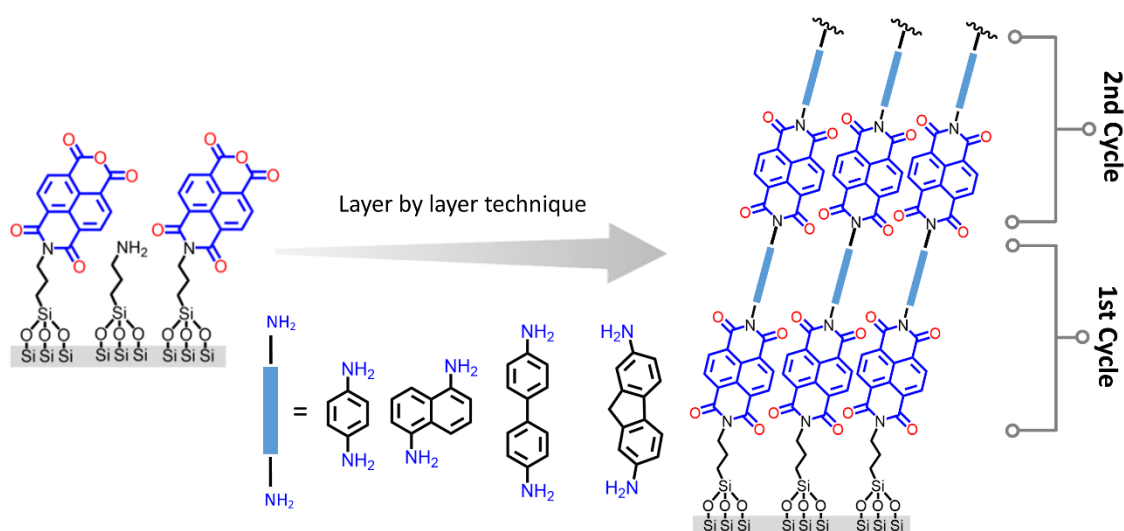
Surface Silylation of Substrates:

The amino-functionalized substrates were prepared by a post grafting strategy by a previously reported procedure.^[13] First, silicon wafers and quartz substrates were cleaned prior to the functionalization. The substrates cut into $1 \times 1 \text{ cm}^2$ pieces. Both type of substrates were cleaned by ultra-sonication in deionized water, acetone and ethanol sequentially for 20 min each. The substrates were further cleaned in ozone cleaner for 30-40 mins to expose surface hydroxyl groups. Then the cleaned substrates were dipped in 20 mM solution of aminopropyltriethoxysilane (APTES) in anhydrous toluene and kept at $100 \text{ }^\circ\text{C}$ for 24 h. The amino-functionalized products were collected and washed with EtOH for several times to remove the residual reactants, and subsequently dried under N_2 .

Multilayer fabrication of model – 1 thin films:

Multilayered organic thin film of donor and acceptor molecules were grown following the model-1 strategy and employing the imide bond formation reaction. In a typical process of *Anhydride layer* formation: Naphthalenetetracarboxylic dianhydride (NDA) (0.02 mmol) was

dissolved in 4 mL of DMF and amine functionalized substrate (APTES) were added into a Teflon vessel and heated at 155 °C for 6 h. Similarly, *Amine layer* formation: particular primary diamine (p-Phenylenediamine, Benzidine, 1,5-naphthylenediamine, 2,7-Diaminofluorene) (0.02 mmol) was dissolved in 4 mL of DMF and anhydride functionalized substrate were added into a Teflon vessel and heated at 155 °C for 6 h. After each layer formation the reaction mixture was cooled down to room temperature gradually, the functionalized substrates were collected and washed with DMF several times after each step in order to remove the residual reactants, and subsequently dried under N₂.



Scheme 2: Layer by layer growth of organic thin films.

Synthesis of model compound (C1):

NDA (1 mmol) was dissolved in 20 mL of DMF and added into a 50-mL round-bottom flask. Subsequently, aniline (2.2 mmol) was drop wise added into the reaction mixture and the solution was heated and stirred at reflux condition for 48 h. After cooling to room temperature, yellowish needle type crystals of **C1** was obtained by filtration and washed with DMF for several times in order to remove the reactants. Later the desired compound was dried under vacuum.

2.3 Result and Discussion:

Here, we have demonstrated that multilayered organic thin film can be grown using a layer by layer method on different of substrates. First, an amine functionalized substrate was synthesized and characterized by ToF-SIMS measurement which substantiate the homogenous presence of amine groups on the surface of the substrate (figure 1: A). Further, the amine functionalized substrates were used to synthesize model-1 type organic thin films with the four different diamines and the UV-Vis spectra were recorded for all the four samples after 5 cycles in order to ensure the deposition on substrates. (Figure 1: C). Furthermore, 'Figure 1: D' shows the absorbance profile of the film grown with p-Phenylenediamine and NDA on amine functionalized quartz substrate recorded after 2, 4, and 8 cycles respectively and this is evident that the NDI characteristic peak intensity gradually increases with increasing number of cycles. To substantiate the formation of imide linkage in the organic thin film, ATR spectroscopy was carried out. ATR spectra of both naphthalene dianhydride (NDA) and the model compound **C1** which shows the carbonyl stretching frequency of NDA at 1720 cm^{-1} , whereas in case of **C1** the carbonyl stretching frequency is significantly lower at 1660 cm^{-1} which is the characteristic of imide bond. ^[14] (Figure 1: E)

In addition, the aromatic CH stretching frequency in the both samples are consistent at 3087 cm^{-1} . Furthermore, ATR spectra of the organic thin film (p-Phenylenediamine and NDA) prepared by one pot synthesis technique (diamine, NDA and substrate was added in a Teflon vessel and the reaction was carried out at the same condition and concentration as LBL) and as well as layer-by-layer (LBL) method, which show the same carbonyl stretching frequency at 1662 cm^{-1} , although the aromatic CH stretching frequencies are not prominent for the thin film samples. (Figure 1: E) However, from the SEM images of this sample (p-Phenylenediamine and NDA), it is hard to comment on the morphology of the organic structures on the surface. But upon long exposure of the electron beam the SEM image shows a black rectangular spot on the sample, this would be expected from burning of the organic deposition on the sample. (Figure 1: B)

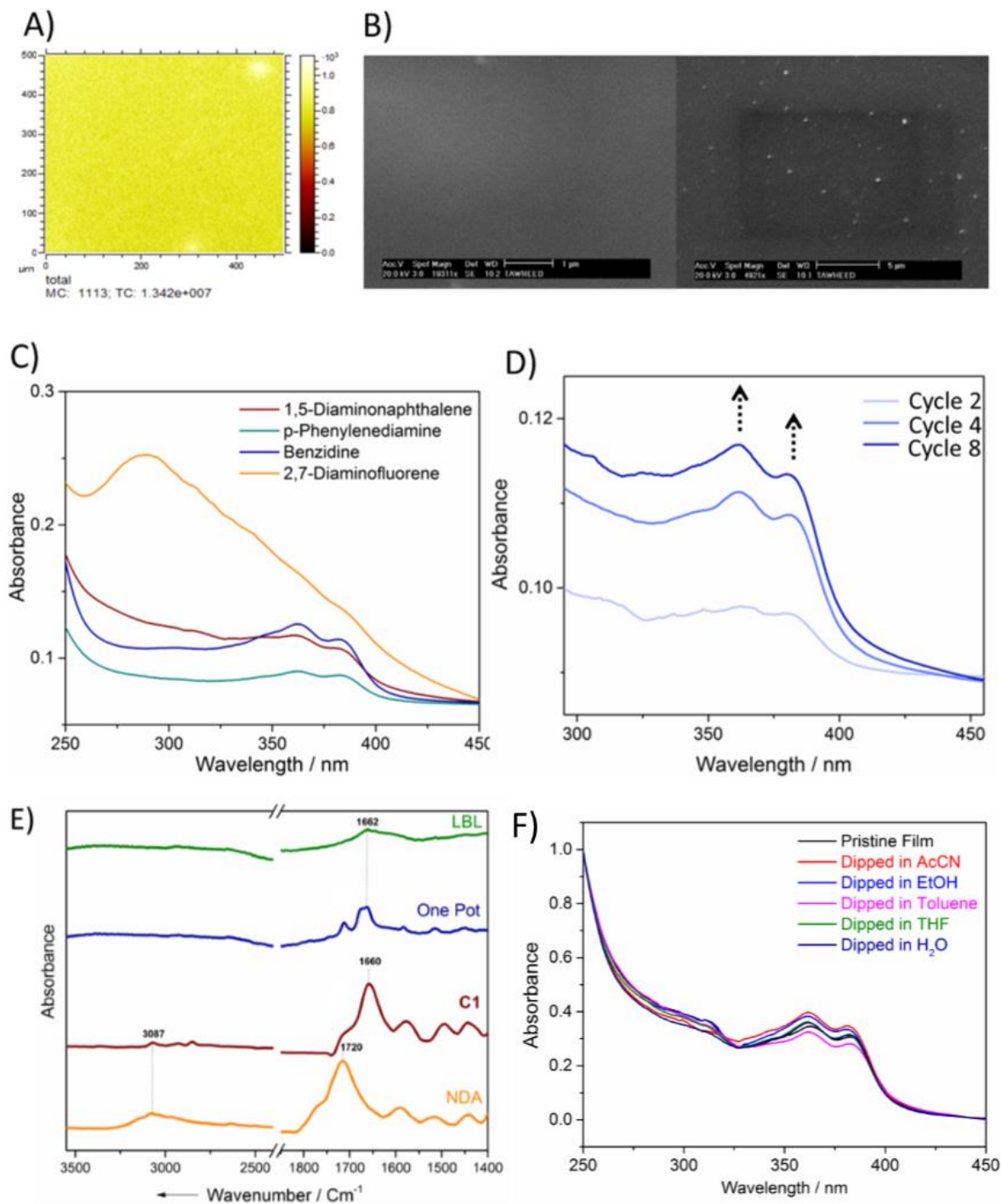
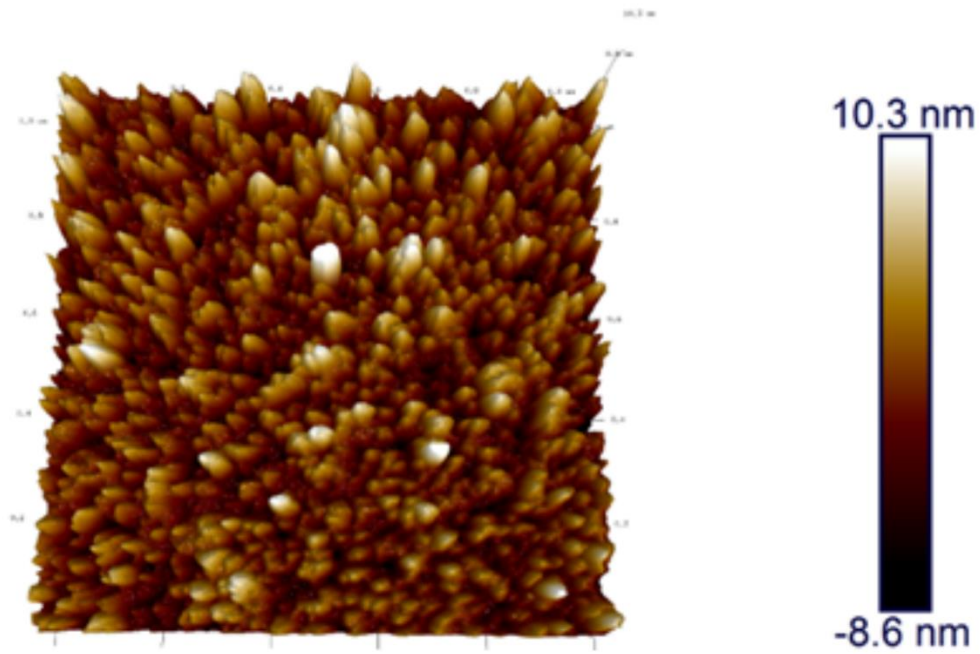


Figure 1: A) TOF-SIMS measurement of amine functionalized surface and represents the homogeneous distribution of NH_4^+ groups. B) SEM Images of the organic thin film. C) UV-Vis spectra of all model-1 organic thin films. D) UV-Vis spectra at different number of cycles. E) ATR Spectra F) thin film stability in different solvents of polarity.

A)



B)

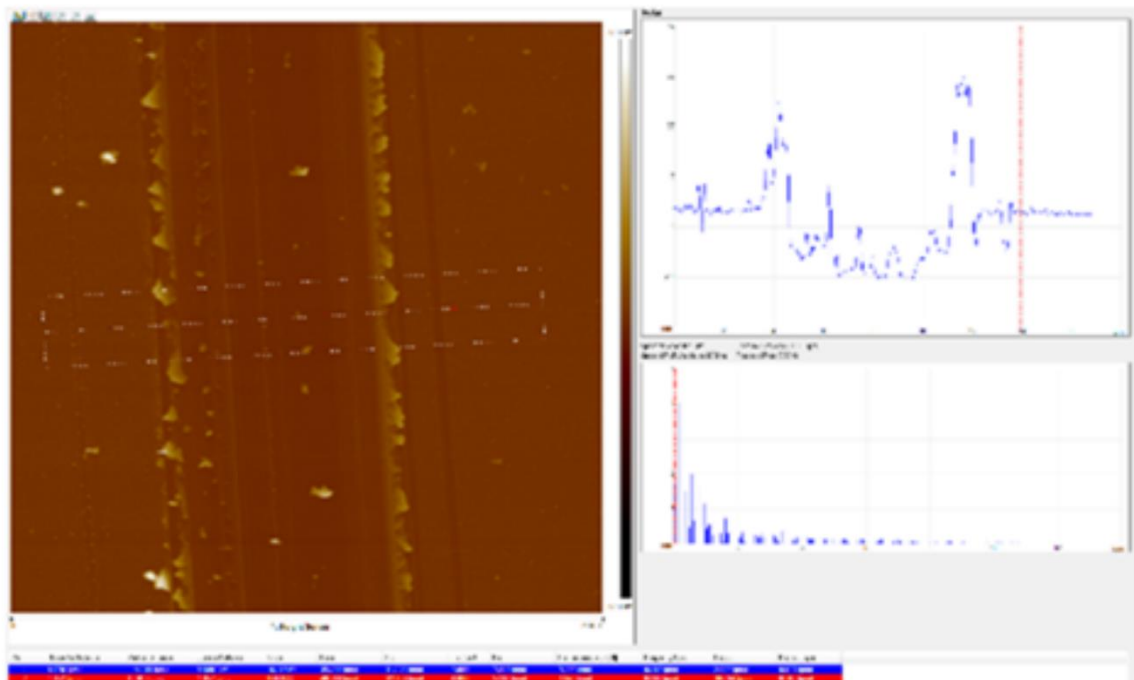


Figure 2: AFM images A) depth profile B) thickness measurement

For further understanding in the morphology of the organic structures on this sample (p-Phenylenediamine and NDA), Atomic force microscopy (AFM) measurements were carried out. Apparently, the on surface plateaus can be correlated with the 1-dimentionation organic structures which is evident from the AFM measurements. (Figure 2: A) To measure the thickness of the organic deposition, a scratch was made on the sample and the depth profile in AFM showed the height difference between scratched portion and the deposited layer on the sample is about ~14nm. Therefore, this is evident that there is organic deposition on the sample and thickness is about ~14 nm after 8 cycles. (Figure 2: B)

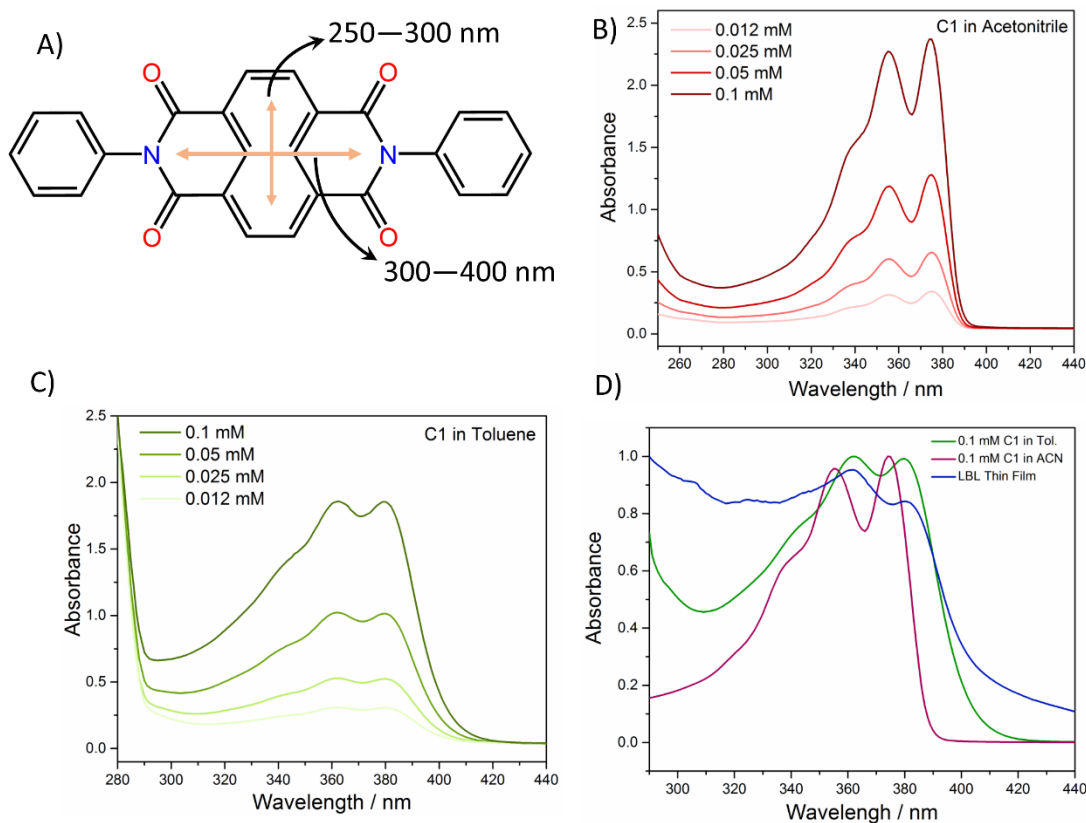


Figure 3: A) the model compound **C1** (representing the transition dipoles in the naphthalene diimide chromophore.) B) & C) UV-Vis spectra of **C1** of different concentrations in Acetonitrile and Toluene respectively. D) Comparison of NDI spectral features in different samples.

For the further understanding of the organic structure's arrangements in the thin film, a model compound **C1** was synthesized and the spectra of matrix assisted laser desorption

ionization-time of flight mass spectrometry (MALDI TOF MS) was used to confirm the formation of the product. The self-assembly process and the formation of the molecular aggregates of the compound **C1** in solution were studied using UV-Vis Spectroscopy. We choose aprotic polar (Acetonitrile) and nonpolar (Toluene) solvents, so that inter-NDI interactions differ largely. In 0.1 mM acetonitrile solution, **C1** was molecularly dissolved and the UV-Vis spectra shows prominent vibrational structures at 374, 355, and 340 nm (for A_{0-0} , A_{0-1} , A_{0-2} respectively). (Figure 3: B). The intensity ratios of the vibronics (A_{0-0} / A_{0-1}) is 1.046, which is characteristic of the monomeric nature of NDI representing allowed transition dipole moment along the long axis of NDI-core. In toluene, bathochromic shifted vibrational structures are appeared at 380, 362, and 345 nm (for A_{0-0} , A_{0-1} , A_{0-2} respectively). (Figure 3: C) Hence, in toluene we observe a change in vibronic structure and the ratio becomes ~ 0.995 (A_{0-0} / A_{0-1}). Such change in vibronics occur due to the dipole-dipole interaction among the NDI molecules. Literature shows that such change can be related to the H-type/cofacial stacking of the NDIs.^[15-17] However, the higher energy band is expected around 200-250 nm, owing to the polarization along the short axis.^[18] But it is obscure because of the solvent cut-off. In addition to that the vibrationally resolved band in absorbance spectra of the organic thin films have a close resemblance with the spectral nature and the peak positions of **C1** in aggregate state which further concludes that the NDI moieties might be arranged in dense and aggregated state in the organic thin films. (Figure 3: D)

2.3.1 Charge Transfer Interaction:

Our primary focus was to investigate the solution phase properties of the model compound-c1 (NDI) and further correlating the properties with the thin films fabricated di-imide polymers. For that, the compound-C1 (acceptor) and 1,5 Naphthalene diamine (donor), Benzidine (donor) had been chosen as the donor-acceptor pair in solution phase (in Acetonitrile) with a gradual increase of donor concentration while keeping the concentration of compound-C1 (acceptor) as constant. (Table: A). The UV absorbance spectra (Figure: 4B, 4D) depicts the increasing band for respective donors. Further, sample-5 (with BPDA and NDA, respectively) was kept under 365 nm ultra-violet (UV) lamp for 2 hours (Figure: 4C, 4E) and afterward the UV-Vis spectra substantiated the appearance of new broad band over the range of 400-520 nm, which

associated with charge transfer interaction between the NDI core (acceptor) and naphthalene (donor) (Figure: 4E).

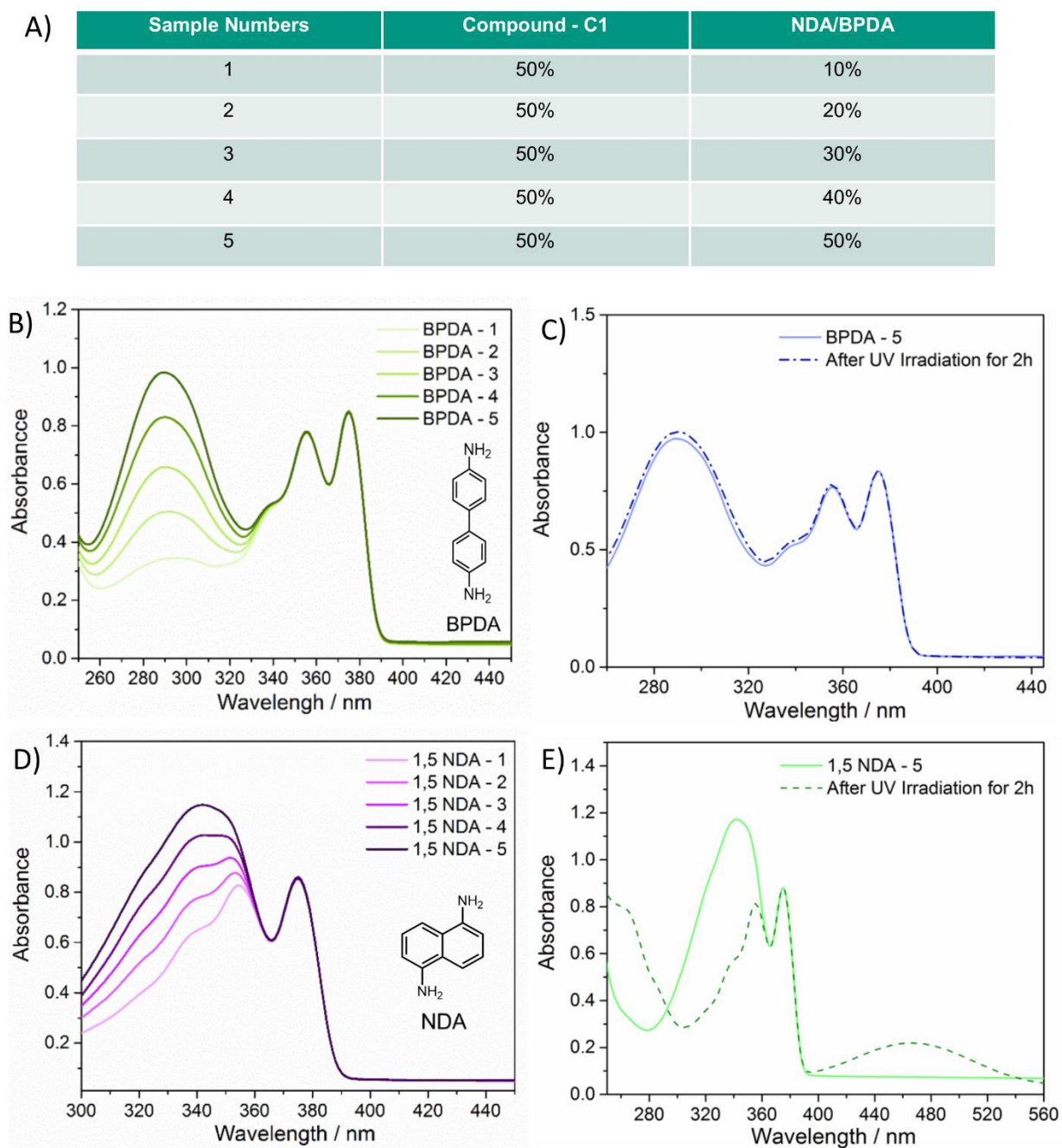


Figure: 4 (A) Table of samples at various ratios of donor acceptor concentration. (B), (D) UV-Vis spectra of donor (BPDA and NDA)-acceptor pair in solution at various concentration. (C), (E) UV-Vis spectra after UV light irradiation.

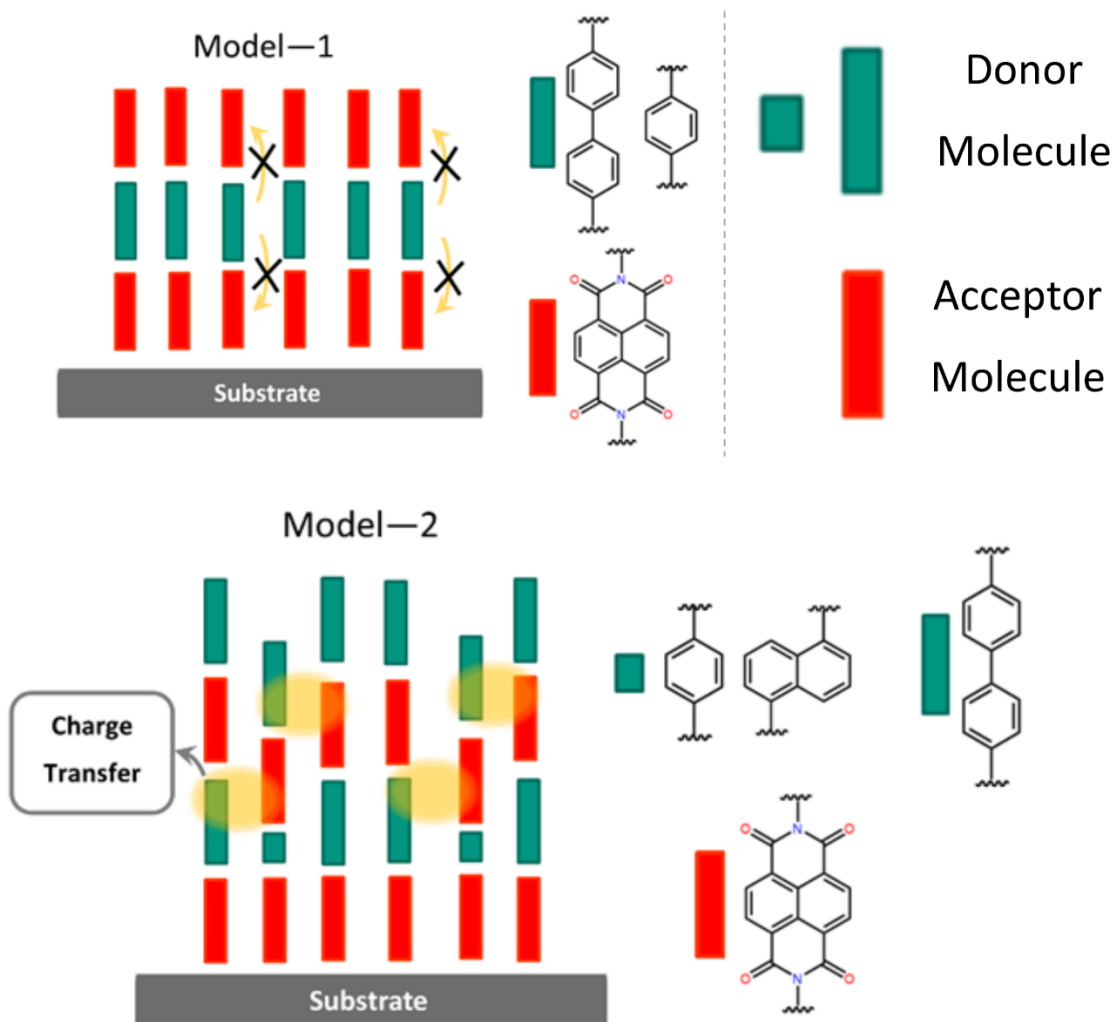


Figure: 5 Schematic Illustration of Model-1 and Model-2 thin films and the feasible charge transfer interactions between consisting donor and acceptor layers.

In addition to that, the reduction of the peak intensity at the donor band suggests the formation of the CT complex. However, such significant change was not observed in the case benzidine, owing to the lack side-by-side π stacking between NDI (Acceptor) chromophore and Benzidine (Donor).

Generally, intermolecular charge transfer (ICT) takes place in conjugated systems that associated with donor-acceptor pair connected through – conjugated bridge.^[19] Therefore, here we summarize our attempts at designing the model-1 organic thin film, which is consist of donor

(D), acceptor (A) with the alternative assemblies by the substitution through imide position of NDI. From UV-Vis spectra of the thin films, it is evident that no new charge transfer band is observed after UV irradiation (365 nm) for 6h. (Figure: 6A) This is supported by that the claims that generally the charge transfer between donor and acceptor molecules is not favorable when the connected bridge between donor (D) and acceptor (A) has the breakage in π -conjugation. Further, we have modified our strategy of model-1 and doped the first layer of the donor molecules with two different diamine length, such as 1, 5 naphthalene diamine and Benzidine (combination as figure: 5 model-2) to ensure a length mismatch in donor layer. As a result, the donor and the acceptor molecules in model-2 are expected to interact in phase to phase fashion which can make charge transfer feasible between NDI chromophores and aromatic donors.

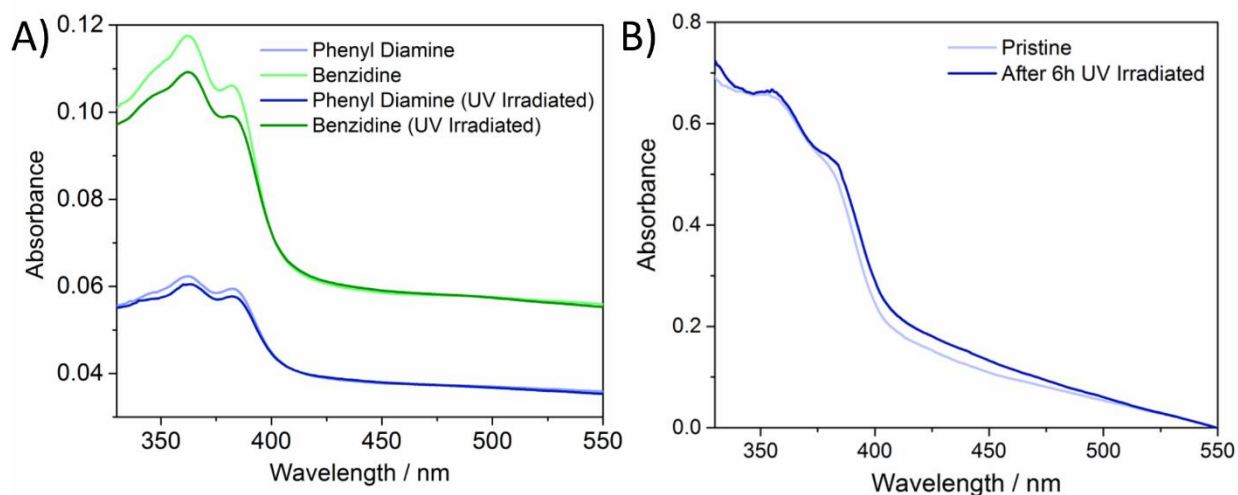


Figure 6: (A) UV-Vis Spectra of Model-1 thin films, (B) UV-Vis Spectra of Model-2 thin film.

To substantiate this fact, we have irradiated Model-2 sample (Acceptor: NDI, Donor: 1, 5 naphthalene diamine and Benzidine) for 6 hours under 365 nm UV light. The UV-Vis spectra shows the broadening of the spectra over the range of 400-500 nm with the respect to pristine thin film spectra (Figure: 2B), which substantiates the similar charge transfer interaction in Model-2 thin films as previously studied in solution phase.

2.4 Conclusion:

In conclusion, here we have demonstrated a layer by layer growth of organic multilayer thin films for studying optical properties and charge transfer between donor and acceptor chromophores. This thin films exhibits suitable electronic properties like charge transfer and as well as offers controlled incorporation of donors and acceptor into well-organized architectures. We are currently developing next-generation model-2 thin films based on these findings and checking the reproducibility of these thin films. Further, the charge transfer between the donor and acceptor in all the model-1 and model-2 thin films will be re-examined to strengthen our claims.

Chapter - 3

Synthesis of 2D Imine-Linked Surface Covalent Organic Framework

3.1 Introduction:

Covalent organic frameworks (COFs) is an emerging class of porous materials which exhibits periodically extended covalently bound crystalline porous networks with tunable features, including thermal stability, and permanent porosity with high specific surface area. [1,2] In recent years, COFs have evolved as an important class of material due to their enormous potential as selective membranes, [3-4] gas storage, [5-6] energy-storage materials.[7-9] Understanding the bond formation chemistry reveals that for constructing an extended porous crystalline organic framework, it demands “chemically induced dynamic covalent chemistry” (DCC) [10-12] to maintain the reversibility during covalent bond formation where organic building blocks are connected to form two or three dimensional frameworks. [13] (Figure: 1) However, crystallizing of such extended polymeric frameworks often leads to framework’s structural defects because of its compositional inhomogeneity, which hinders the growth of COF crystallites and restricts them within nanometer domain range. [14-16] As a result in, COFs are insoluble and unprocessable micro-crystallites powders. Hence, the fabrication of these insoluble COF particles for the further application manifests a formidable challenge. For overcoming this issue, several other synthesis approaches including ‘bottom-up’ and ‘top-down’ approaches have been employed to grow COFs on surface. Although the ‘top-down’ strategy: exfoliation of layers from bulk crystallites is effective to get single-layered graphene, and other metal chalcogenide material. [17-18] But, it turns out that preparing surface COFs by this strategy could be practically difficult because of the unavailability of large-sized COF crystallites. On the other side, on surface ‘bottom-up’ synthesis strategy is considered to be more promising for the construction of surface COFs. [19]

COFs have been recently drawn attention as an interesting candidate for applications in organic electronics due to the successful incorporation of photoactive building blocks into the frameworks. [20-23] In addition to that, interlayer π -stacking in COFs offer a pathway for charge transport. [24, 25] Thus, charge separation between ordered donor-acceptor interpenetrated-networks can be studied. [26] Moreover, deeper understanding of charge separation between COF bilayers can open a new pave for implementing COF structures in photovoltaic devices [27-31]

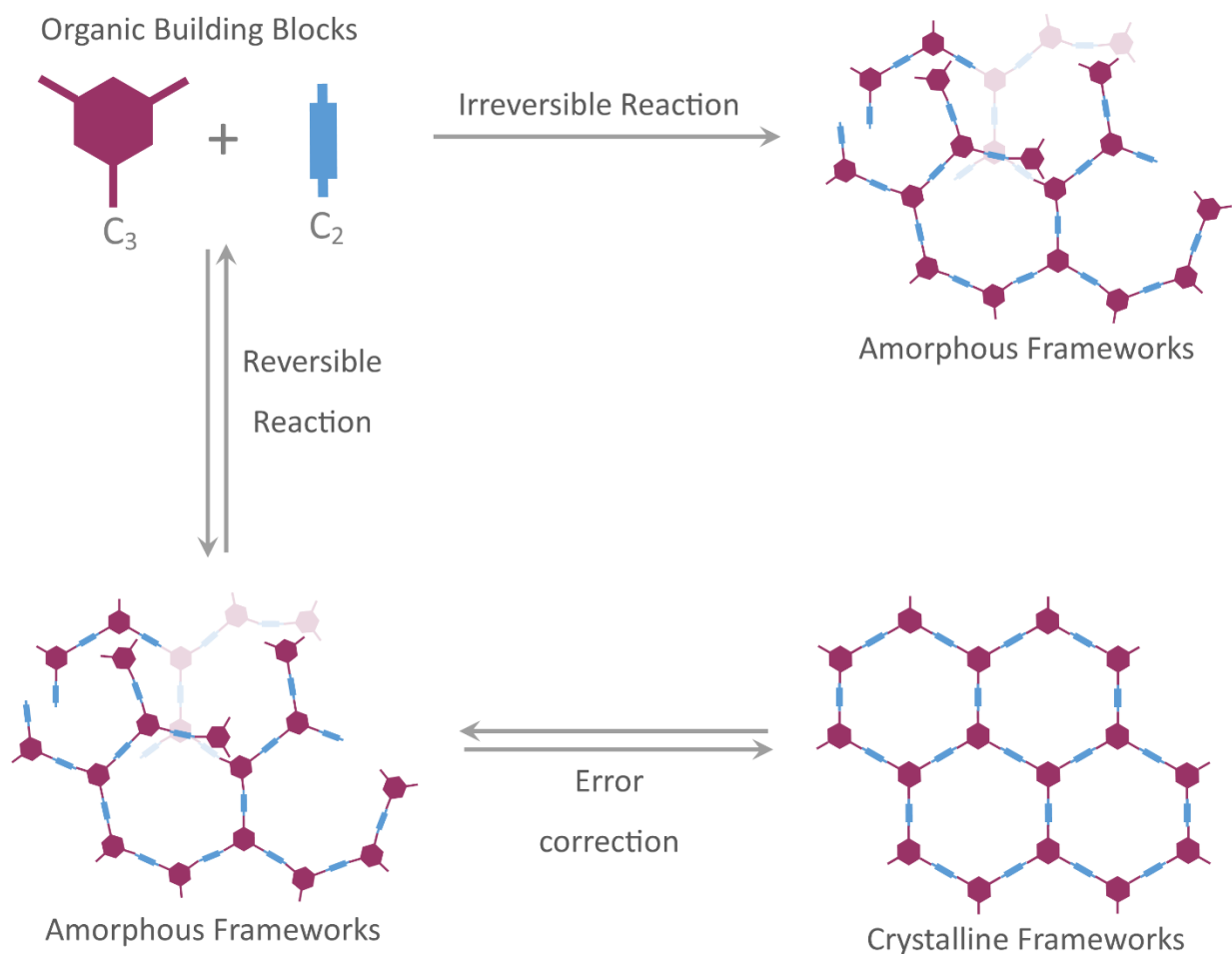


Figure: 1 Schematic representation of crystalline Covalent Organic Framework (COFs) and amorphous organic polymers, formation via reversible and irreversible reaction. ^[1, 13,]

The growth of highly oriented crystalline COF thin films on the desired substrates can provide an insight for charge migration towards the respective electrodes. Apart from the potential of Surface COFs for optoelectronic applications, their highly oriented pore channels and the position of the channels make them interesting for membrane based gas separations also. ^[32] It is therefore of great interest to synthesize a well-ordered on surface crystalline organic porous material viz. COF, and to study its physical and optoelectronic properties in the form of oriented thin films.

3.2 Experimental Section:

Materials:

4-aminobenzonitrile (M.W. = 118.14), Benzene-1,3,5-tricarboxaldehyde (BTC) (M.W. = 162.14) were purchased from Sigma Aldrich, 9,10-Anthracenedicarboxaldehyde (ADC) (M.W. = 234.25) was purchased TCI Chemicals and used without further purification.

Preparation of 2,4,6-Tris(4-aminophenyl)-s-triazine (TAPT):

TAPT was synthesized via super-acid (trifluoromethanesulfonic acid) catalyzed trimerization of 4-amino benzonitrile with the help of a previous reported protocol. ^[33] In a typical synthesis process, 4-aminobenzonitrile (0.772 g / 6.538 mmol) was added to 10 ml round bottom flask at 0 °C. Then 2 ml of trifluoromethanesulfonic acid was added drop wise for 20 min maintaining the temperature as same. Finally, the mixture was stirred for 24h at room temperature in N₂ atmosphere. After that, 50 mL distilled water was added to the mixture and followed by adding 2M NaOH solution until pH reaches to 7. With the increase in pH, the orange precipitate dissolves to give a bright yellow solution and which upon further increase in pH gives a pale yellow precipitate. Further, the precipitate was filtered and washed several times with water. The product was characterized by ¹H and ¹³C NMR. (Figure: 2) Yield: 84.4 mol %

¹H NMR (400 MHz, DMSO-D₆): $\delta_3 = 8.37$ (d, J = 8.7 Hz, 6H), $\delta_2 = 6.70$ (d, J = 8.6 Hz, 6H), $\delta_1 = 5.96$ (s, 6H)

¹³C NMR (101 MHz, DMSO-D₆): $\delta_5 = 170.1$ (s), $\delta_1 = 152.9$ (s), $\delta_3 = 130.5$ (s), $\delta_4 = 122.9$ (s), $\delta_2 = 113.2$ (s)

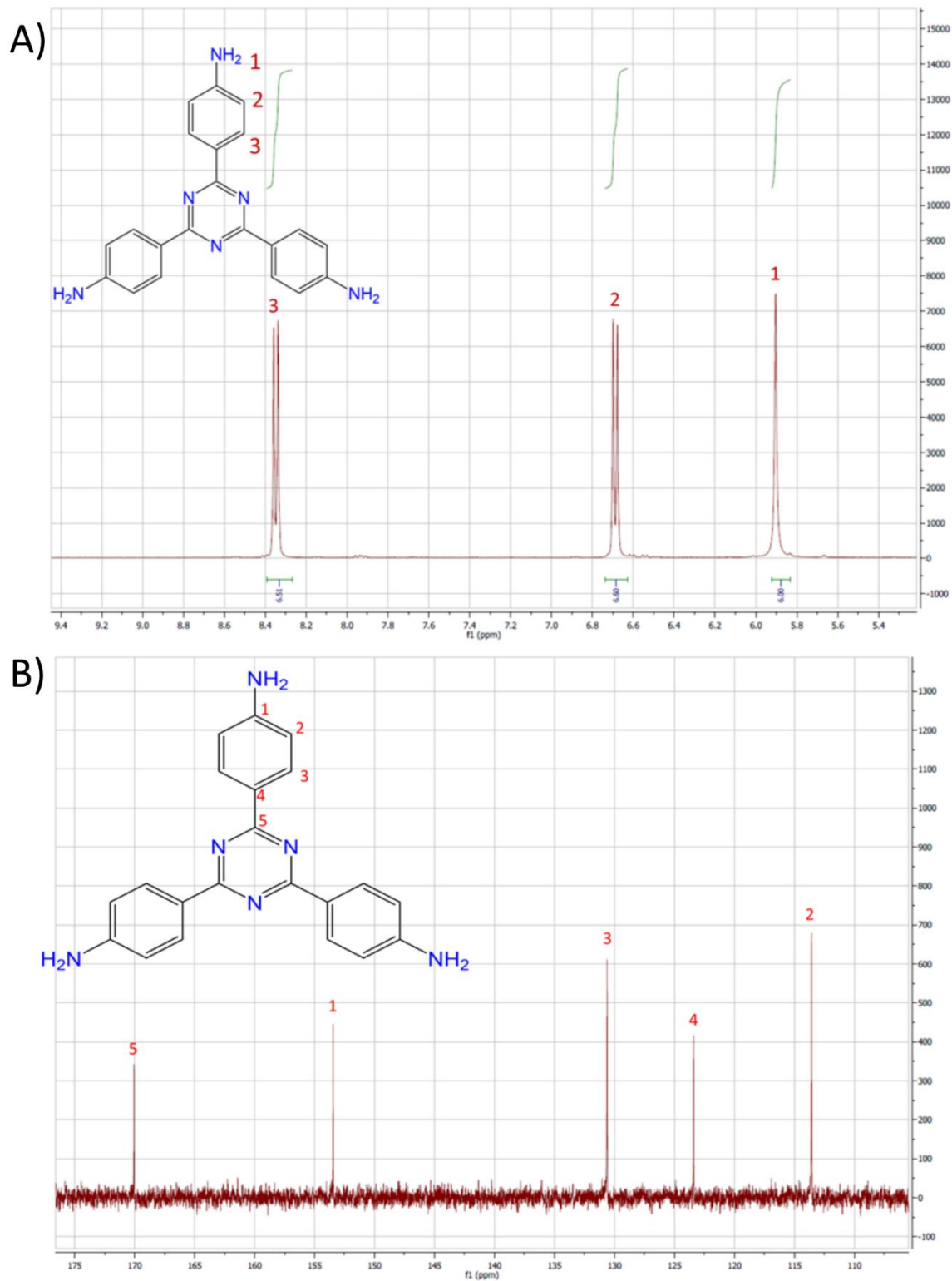
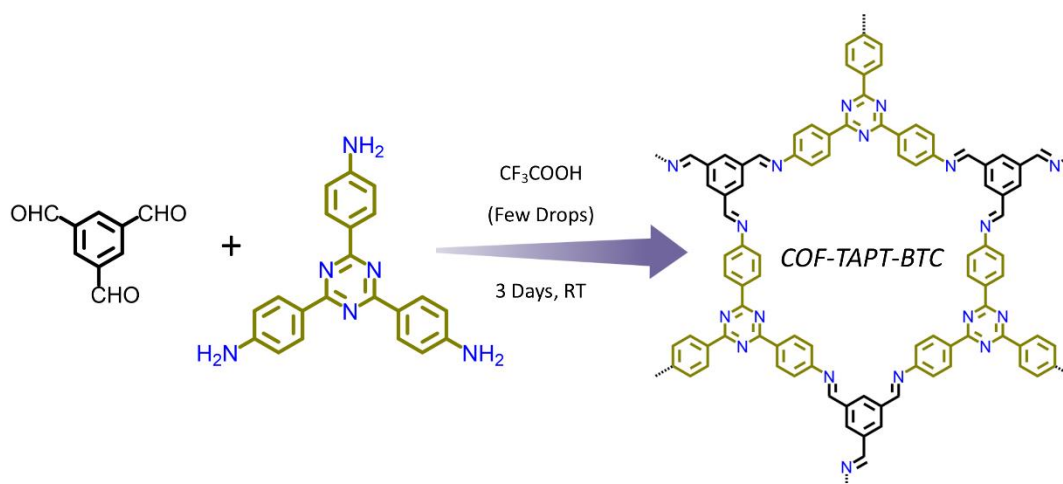


Figure: 2 A) ^1H NMR spectra of TAPT in DMSO-d_6 , B) ^{13}C NMR spectra of TAPT in DMSO-d_6 .

Preparation of COF-TAPT-BTC:

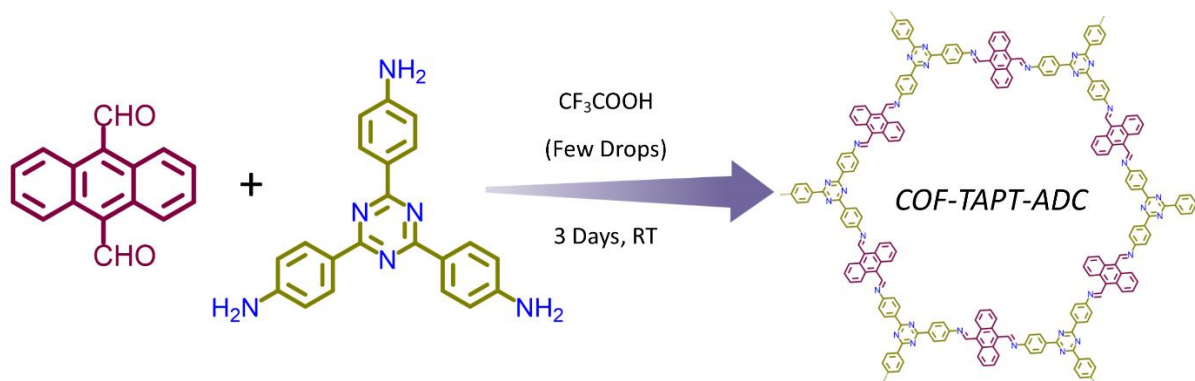
The COF-TAPT-BTC was synthesized by Schiff base condensation reaction between TAPT and Benzene-1, 3, 5-tricarboxaldehyde (BTC). In a typical reaction 16.2 mg (0.1 mmol) of TAPT was dissolved in 2mL of 1, 4 Dioxane : Mesitylene (1:1) and 100 μ L of trifluoro acetic acid and then sonicated the resultant for 15-20 min. Separately, 0.1 mmol of BTC was taken in 2mL of 1,4 Dioxane : Mesitylene (1:1) and followed by sonication for 15-20 min . Afterward, the TAPT solution was added drop wise over the period of 20 min in BTC solution and the resultant mixture was kept undisturbed for 3 days. (Scheme: 1)



Scheme: 1 Preparation of COF-TAPT-BTC.

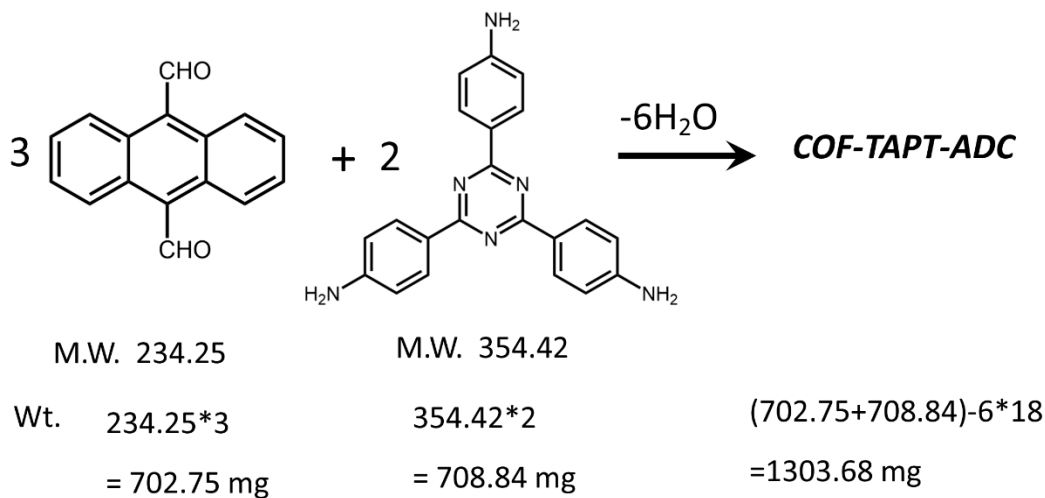
Preparation of COF-TAPT-ADC:

The COF-TAPT-BTC was synthesized by the similar condensation reaction between TAPT and 9,10-Anthracenedicarboxaldehyde (ADC). In a typical reaction 23.4 mg (0.1 mmol) of TAPT was dissolved in 2mL of 1,4 Dioxane : Mesitylene (1:1) and 100 μ L of trifluoro acetic acid and sonication for 15-20 min. Separately, 0.15 mmol of ADC was taken in 2mL of 1,4 Dioxane : Mesitylene (1:1) and followed by sonication. Afterward, the TAPT solution was added drop wise over a period of 20 min in the respective aldehyde solution and the resultant mixture was kept undisturbed for 3 days. (Scheme: 2)



Scheme: 2 Preparation of *COF-TAPT-ADC*.

Yield and Scalability:



702.75 mg of aldehyde reacts to give 1303.68 mg of *COF-TAPT-ADC* then 35 mg of aldehyde reacts to give 64.9 mg of *COF-TAPT-ADC*. (Theoretical Yield)

Experimental Yield from 35 mg of aldehyde = 28.4 mg

Yield (% wt/wt) = (28.4/64.9) * 100 = 41.2 %

Similarly, we calculated yields for other COFs. Yield of *COF-TAPT-BTC* = 37.7 %

COF thin films fabrication:

COF-TAPT-BTC thin film was prepared by *in situ* growth through a facile room temperature imine condensation method. Firstly, Quartz and Silicone substrates were functionalized by amine via reported protocol. [34] The amine functionalized substrates were cleaned by EtOH and dried under N₂. Further the functionalized substrates were placed horizontally face up in a glass vessel, which was filled with 0.02 mmol of BTC (Aldehyde) in 2 ml of Dioxane and Mesitylene solvents mixture (1:1). The reaction vessel was kept in heating oven at 80°C for the duration of 4 hours and afterward the reaction was cooled down to room temperature. Separately, 0.02 mmol of TAPT (Amine) was dissolved in 2 ml of Dioxane and Mesitylene solvents mixture (1:1) and added few drops of Trifluoroacetic Acid. The resultant mixture of amine and acid was added slowly to the reaction vessel over a period of 30 min. The system was kept at room temperature for 3 days in undisturbed condition. The thin film of COF was formed on the top of the functionalized surface and washed with dimethylformamide (DMF), Acetone and Methanol to purify the thin film. In addition to that the remaining COF powder was also collected, followed by the same washing steps.

3.3 Result and Discussion:

In this study, we have synthesized COF-TAPT-ADC and COF-TAPT-BTC at room temperature condition as given in the experimental section. The Powder X-ray diffraction (PXRD) clearly substantiates that the formation of highly crystalline COFs at room temperature. Its d-values are in the agreement with the hexagonal unit cell with $a=b=14 \text{ \AA}$, 22 \AA for COF-TAPT-BTC and COF-TAPT-ADC respectively, as expected from the planar COF 2D sheet represented in Figure: 3. The COF-TAPT-ADC shows intense peak at lower 2θ value at 3.9° , which corresponds to the reflection from 100 plane. However, in the case of COF-TAPT-BTC, the same peak gets shifted to higher 2θ value of 5.7° due to smaller pore aperture. Further, to determine the packing arrangement (eclipsed or staggered stacking), structure simulation will be carried out with Materials Studio software afterward.

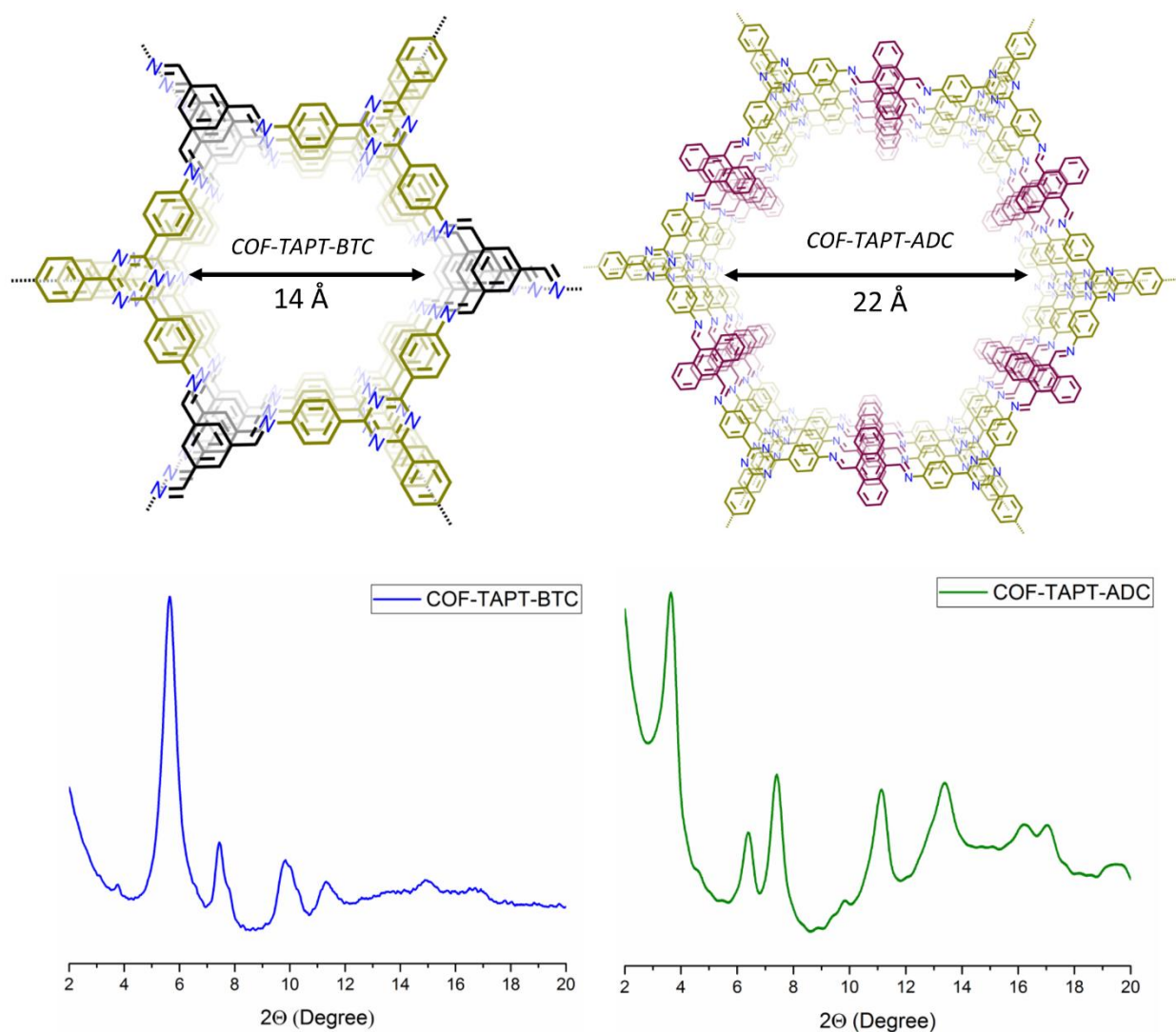


Figure: 3 Schematic representation of COF structures and their structural characterization by X-ray diffraction analysis of *COF-TAPT-BTC* (blue) and *COF-TAPT-ADC* (green)

The Fourier transform infrared (FT-IR) spectra of the *COF-TAPT-BTC* shows the characteristic stretching bonds at $1700 - 1660 \text{ cm}^{-1}$ ($-\text{C}=\text{O}$), $1507-1576 \text{ cm}^{-1}$ ($-\text{C}=\text{C}$), and 1620 cm^{-1} ($-\text{C}=\text{N}$), assigned directly in the Figure: 4. ^[35-38] Moreover, the absence of N-H at $3100-3300 \text{ cm}^{-1}$ peak in the *COF-TAPT-BTC* IR spectra, confirms that the absence of starting precursors in the synthesized COFs after washing. Moreover, in the IR spectra

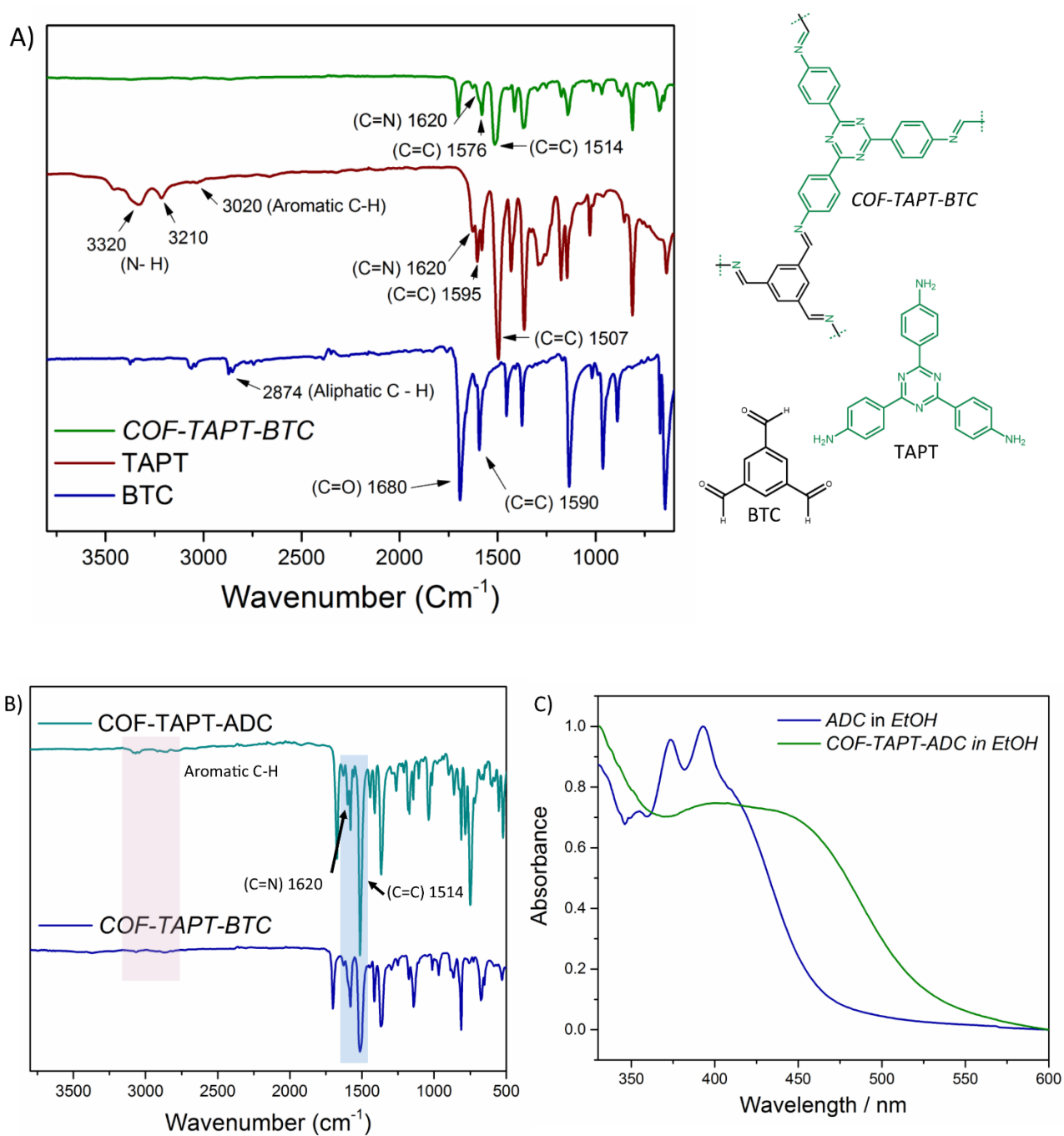


Figure: 4 A) FT-IR spectra of TAPT, BTC and COF-TAPT-BTC. B) FT-IR spectra of COF-TAPT-ADC and COF-TAPT-BTC respectively, showing the characteristic peaking from the COF structures, C) UV-Vis spectra of ADC (aldehyde building block) and COF-TAPT-ADC dispersed in EtOH.

-of *COF-TAPT-ADC* showing the characteristic peaks of the COF structure of (C=C) and (C=N) stretching at similar position as the *COF-TAPT-BTC*. (Figure: 4B) Further, 1 mg *COF-TAPT-ADC* and 1 mg of Anthracene 9, 10- dicarboxaldehyde (ADC) were dispersed in 2ml of EtOH separately to carry out UV-Vis experiment. The UV-Vis spectra of ADC reveals the characteristic absorbance band (350-450nm) from anthracene moiety. Whereas, the UV-Vis spectra of *COF-TAPT-ADC* shows a broad absorbance range from 500-350 nm, possibly the broad absorbance owing to the charge transfer interaction, arising from the charge transfer from the donor anthracene moiety to the electron deficient triazine core of the COF structure.

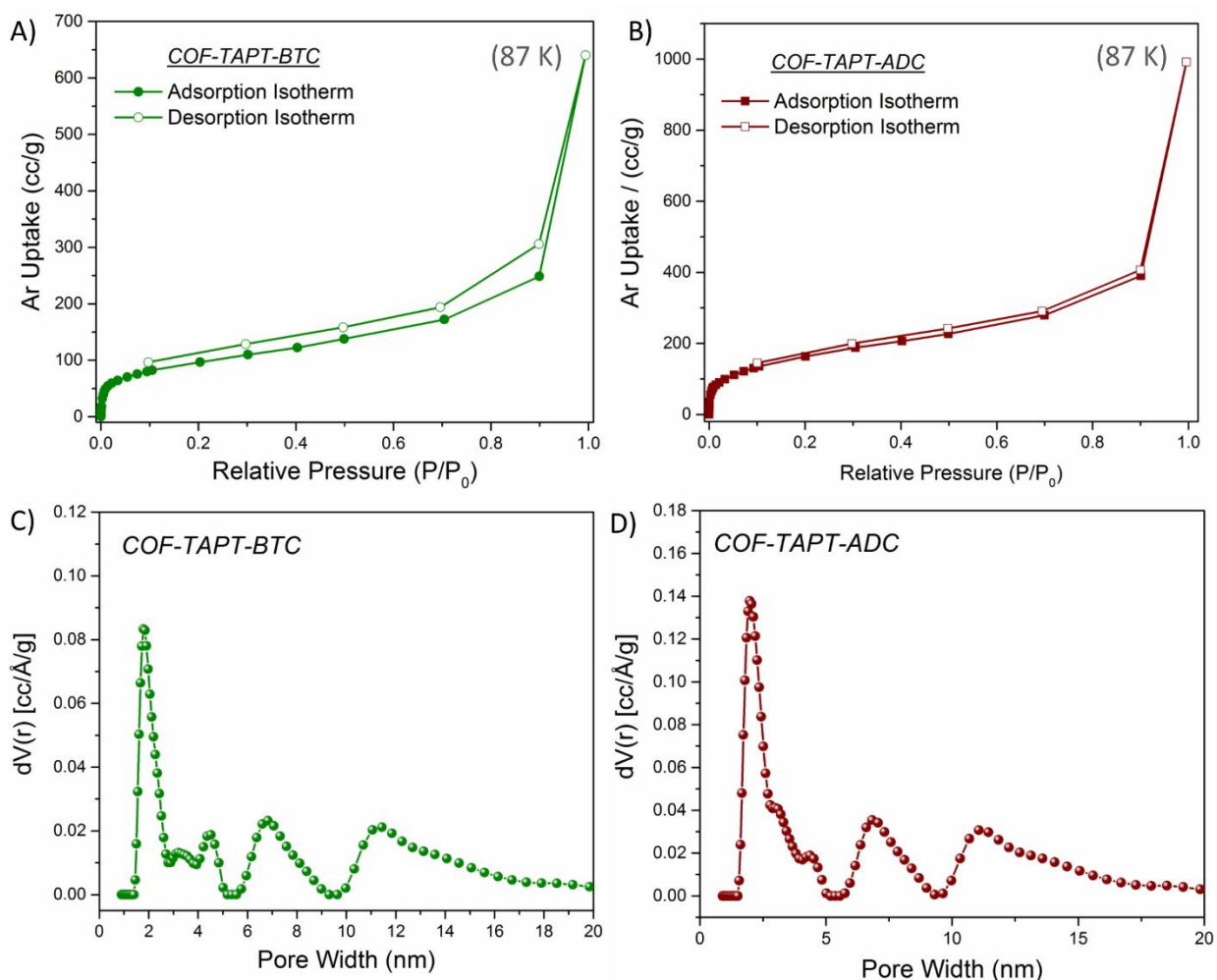


Figure: 5 A), B) Ar uptake isotherm at 87 K and C), D) Pore size distribution of *COF-TAPT-BTC* and *COF-TAPT-ADC*, respectively.

Tunability and permeability nature of COFs makes them promising and as well an ideal candidate for permeable membrane applications. Therefore, incorporating new functionality and utilizing the porosity of COF thin films is of high essence. As a preliminary step, the low temperature (87K) Ar adsorption was recorded to check the porous characteristics of the compounds. (Figure: 5) Both the compounds exhibited uptake at low pressure which increased with increasing pressure. No hysteresis was observed for the desorption profiles suggesting presence of channel pores. From the adsorption isotherms the Brunauer-Emmett-Teller (BET) surface areas were calculated to be $307 \text{ m}^2/\text{g}$ and $534 \text{ m}^2/\text{g}$ for *COF-TAPT-BTC* and *COF-TAPT-ADC* and the total pore volume are $0.63 \text{ cm}^3/\text{g}$, $0.97 \text{ cm}^3/\text{g}$, respectively. The pore size distribution of the COFs are calculated using the density function theory (NLDFT), representing the ordered pore channels of *COF-TAPT-BTC* and *COF-TAPT-ADC* with some distribution at higher pore diameters as well. Further, the X-ray diffraction (XRD) analysis of the COFs after adsorption confirms the retention of the well-ordered framework even after activation and gas adsorption. (Figure: 6) FESEM images were recorded for the two compounds to understand the morphology of the material (Figure: 7), the images revealed similar irregular tubular morphology with dimensions in the nanometer regime for both the COFs.

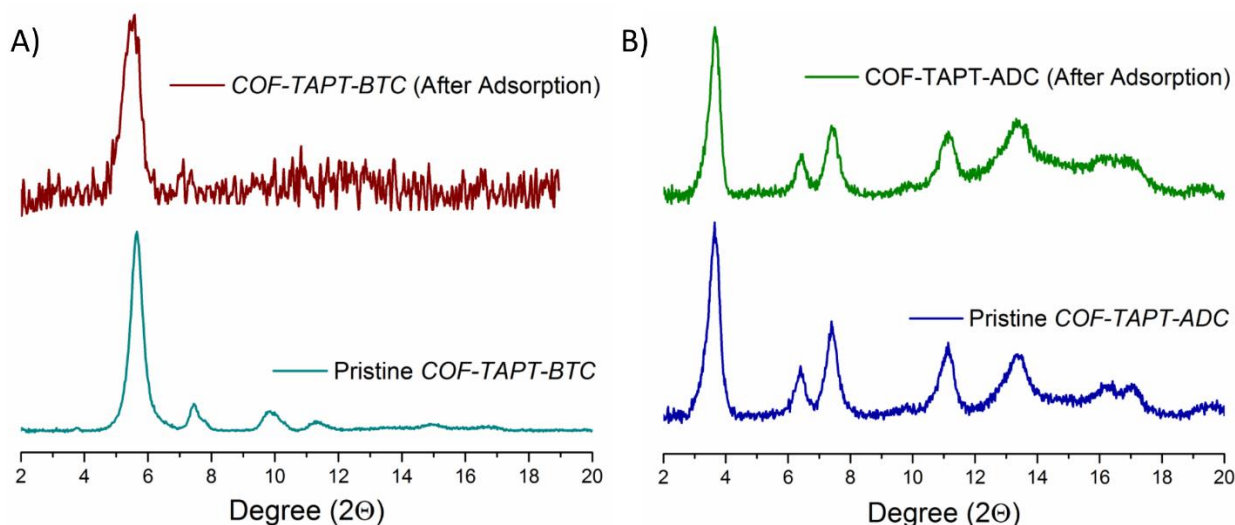


Figure: 6 X-ray diffraction (XRD) analysis after activation and adsorption-desorption process of (A) COF-TAPT-BTC and (B) COF-TAPT-ADC, respectively.

Therefore, the bulk characterization of COF powders confirms that the formation of highly crystalline COF structures at room temperature. These structures are highly porous and exhibit well-defined pore sizes. In order to study the optical or optoelectronic properties of COF nanostructures, it is essential to develop methods for COF thin films on suitable substrates.

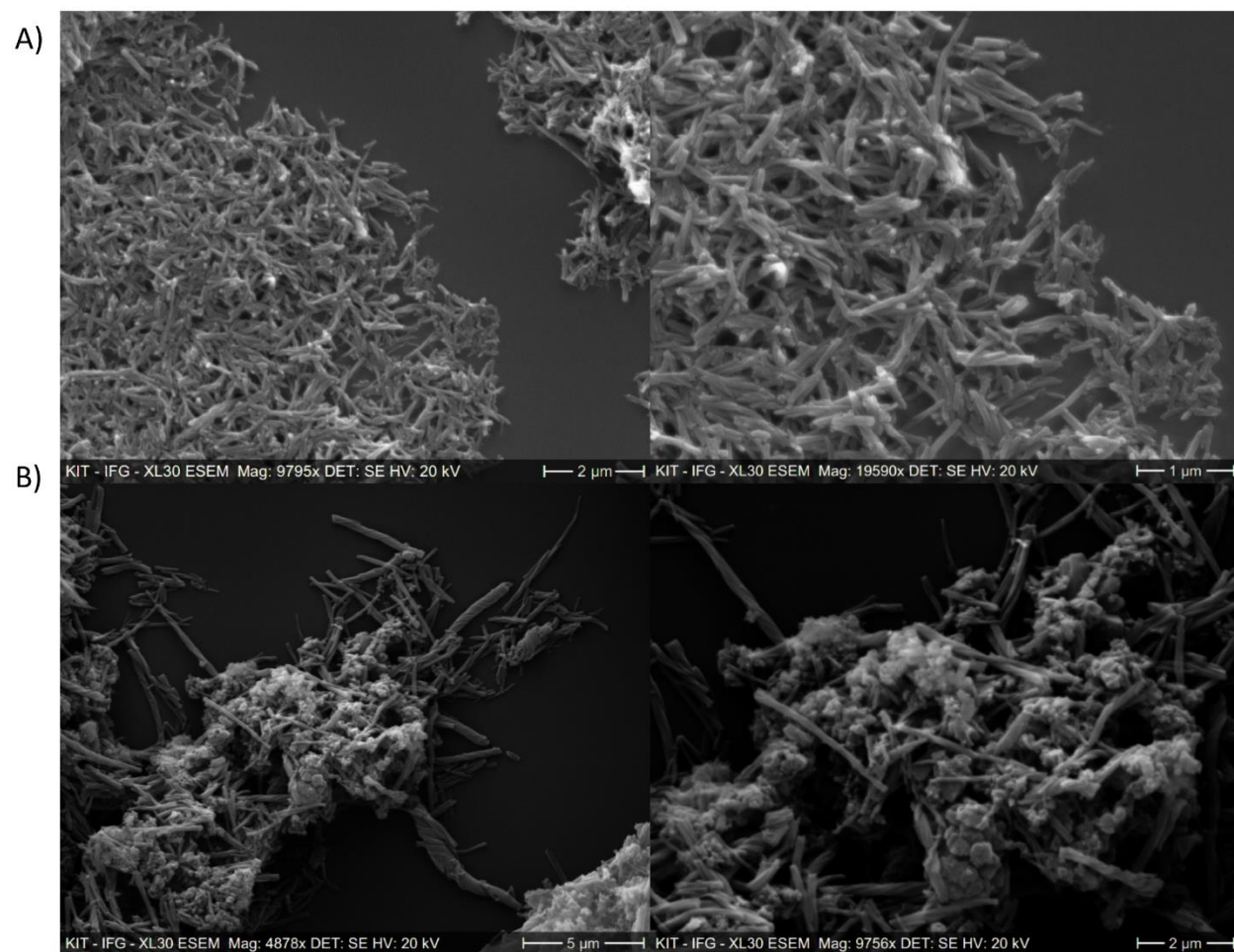


Figure: 7 SEM images showing tubular shaped of COF crystallites in nanometer dimension A) *COF-TAPT-BTC* B) *COF-TAPT-ADC*

COF Thin Film Characterization:

Here, we represent a new approach for synthesizing imine based 2D COFs on different substrates. The film of *COF-TAPT-BTC* was synthesized under similar condition at room temperature as described in the experimental section. XRD analysis was used to study the

ordered structure of the as-synthesized COF thin film. Unlike other organic thin films, these COF thin films exhibit clear peak for 100 reflection plane, confirming its crystalline nature. (Figure: 8A) FT-IR spectra of the COF-TAPT-BTC thin film exhibits the characteristic stretching band of (C=N) and (C=C) at 1620

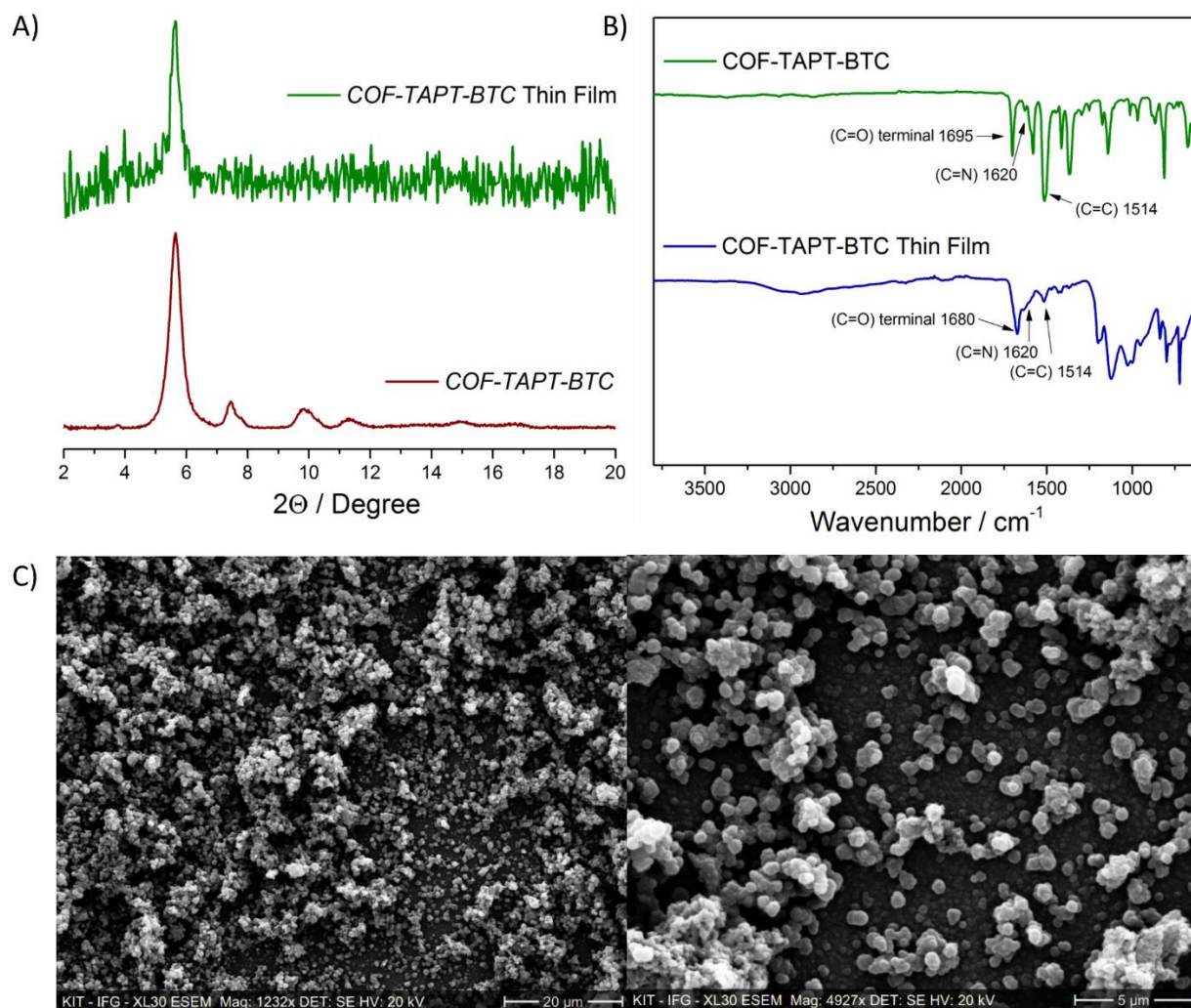


Figure: 8 A) XRD analysis of *COF-TAPT-BTC* powder and thin film, B) IR spectra of *COF-TAPT-BTC* powder and thin film, C) FESEM of *COF-TAPT-BTC* thin films showing the presence of globular on surface COF micro-crystallites.

cm^{-1} and 1514 cm^{-1} , similar as bulk COF powder. (Figure: 8B) In the next step, Field Emission Scanning Electron Microscopy (FESEM) revealed that the surface *COF-TAPT-BTC* appears as

globular agglomerates of nanometer range, which further assemble into tubular shaped micro-crystallites in the case of COF powder synthesis. (Figure: 8C)

3.4 Conclusion:

In summary, a versatile synthetic technique has been demonstrated for fabricating of COF thin films at room temperature on various substrates, which overcomes the challenges of processability of COF crystallites. We are currently developing other COF thin films on different substrates and further seeking for the applications in different areas viz. nano-filtration membrane based separation of organic molecules/dyes from solution phase or surface COF structures for optical properties. We expect that our developed method of COF thin film growth will facilitate the exploration of surface anchored COF thin film based sensors or various electronic device fabrication.

Chapter - 4

References and Future Perspective

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4.4 Future Perspective:

In a nutshell, the work carried out in this thesis demonstrates the feasibility of building Layer-by-Layer (LbL) surface anchored organic assemblies and further opt for the applications of optical properties. We expect that our newly developed organic thin films will facilitate the study of charge separation and transfer through the π -stacking. In addition to that, this work has been further emphasized with the fabrication of 2-dimensional imine linked surface anchored Covalent Organic Framework (COF) thin films which can be studied for further applications viz. size specific targeted dye, organic molecule separation. Especially, the rational approach of COF thin film

fabrication on various substrates is a take-away outcome from the present findings as this opens up a new pave for insoluble COF powders (as the COF solid powders are not easy to be applied as solid sorbent directly) for device fabrication as well as implement these materials in advanced technologies like membrane separation.

Although stability of these thin films at molecular level is one crucial aspect, the subsequent challenges include converting these materials into workable form. Hitherto, remarkable progress and development has been achieved in the area of LbL assembly, challenges and opportunities still remain open for further development of next generation multifunctional devices with superior performance for addressing several practical applications. So, it is expected that the development of organic thin films will be in line of research over the next several years.