

# DESIGN AND DEVELOPMENT OF ROBUST FLUORESCENT COFs

*A Thesis*  
*submitted to*  
*Indian Institute of Science Education and Research Pune in partial fulfillment*  
*of the requirements*  
*for the BS-MS Dual Degree Program*  
*By*  
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# Certificate

This is to certify that this dissertation entitled "***Design and Development of Robust Fluorescent COFs***" towards the partial fulfillment of the BS-MS dual degree program at the Indian Institute of Science Education and Research, Pune represents study/work carried out by **Katre Sujeet Nilkanth** at Indian Institute of Science Education and Research under the supervision of **Dr. R. Vaidhyanathan**, Associate Professor, Department of Chemistry, during the academic year 2019-2020.

Date: 01 April 2020

Date: 01 April 2020

Place: Gondiya

Place: Pune



Signature of student

Date:

Place:



Signature of supervisor

Signature of expert

# Declaration

I hereby declare that the matter embodied in the report entitled "***Design and Development of Robust Fluorescent COFs***" are the results of the work carried out by me at the Department of Chemistry, Indian Institute of Science Education and Research, Pune, under the supervision of **Dr. R. Vaidhyanathan** and the same has not been submitted elsewhere for any other degree.

Date: 01 April 2020

Date: 01 April 2020

Place: Gondiya

Place: Pune



Signature of student

Date:

Place:



Signature of supervisor

Signature of expert

## **ACKNOWLEDGEMENTS**

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## **ABSTRACT**

The incorporation of different fluorescent entities in an organic framework can be effective in generating white light emitting polymeric materials, and Covalent Organic Framework (COF) is one such compound which can be used to achieve the same. Here, we have synthesized six different Schiff-base based model compound of COFs to gain insight into steady-state emission with changing amine and aldehyde groups. After studying the model compounds, in anticipation of white light emission, we synthesized three similar Schiff-base based COFs, with the aldehyde and pyridine rich amines responsible for emission in the green and red region of the visible spectra and anthracene amine responsible for blue emission. Although we expect the COF to be a solid-state white light emitter, it turns out to show poor fluorescence because of particle aggregation-induced self-quenching. Addressing the self-quenching remains a big problem without which single-source white light-emitting materials such as COFs cannot make a windfall.

## INTRODUCTION

Fluorescent materials are an essential topic of research due to their use in light-emitting devices, bio-imaging, etc. Most of the current solid-state white light emitting (WLE) devices combine different materials to give mixed white light emission. Hence, synthesizing cheap single source solid-state white light emitting material will be a breakthrough. COFs are crystalline organic polymers [1] [2] [3] which can be used to incorporate different chemical entities in a single polymeric framework, thus giving us a periodic lattice. Recently, several COFs have been synthesized which show fluorescence [4], including a white light emitting COF synthesized from our group [5]. The Schiff base or imine-linked COF so synthesized gives white light emission in a specific solvent dispersion and also when dispersed in small quantities in a polymer film. The bottleneck remains at increasing the percentage loading in the polymer film beyond 0.32% as it shows particle aggregation-induced self-quenching [6]. The present work focuses on developing more such Schiff base COFs by getting an insight into the fluorescent properties emerging from different chemical modules, in this case, the cross-linking aldehydes and amines. To begin with, here, we have synthesized different model compounds resembling fluorescent properties of the WLE COFs made from similar molecules. Model compounds were chosen to do a preliminary analysis as they are more easily characterizable via solution as well as solid state methods (NMR, IR, X-ray diffraction etc.). The work initially focuses on these model compounds to gather insights into the responsive changes in emission spectra caused by introducing different electron-rich/deficient groups in the model compounds. For example, here as an important finding, we have observed that with increasing the number of electron-rich groups in the aldehyde and amines the emission spectra shift towards the blue region. Finally, we apply this understanding during the designed synthesis of three different COFs with tri formyl phloroglucinol as aldehyde and two different amines anticipating white light emission. These modules when combined in a polymeric framework should yield an emission covering entire visible spectrum.

## MATERIALS AND METHODS

### A. Chemicals and Instrumentation

#### **General remarks:**

Phloroglucinol, the diamines were all purchased from Sigma Aldrich; hexamine and trifluoroacetic acid (TFA) were purchased from Avra Synthesis Pvt Ltd. All other reagents were of analytical grade. All chemicals were used without any further purification.

#### **Powder X-ray diffraction:**

Powder XRDs were carried out using a full-fledged Bruker D8 Advance and Rigaku Miniflex instruments. The data analysis was performed using the Reflex module of the Materials Studio V6.0.

#### **Thermo-gravimetric analysis:**

Thermo-gravimetric analysis was carried out on NETSZCH TGA-DSC system. The TGAs were done under N<sub>2</sub> gas flow (20ml/min) (purge + protective) and samples were heated from RT to 600 °C at 5K/min.

#### **<sup>13</sup>C Solid-State Nuclear Magnetic Resonance (NMR) Spectroscopy:**

High-resolution solid-state NMR spectrum was recorded at ambient pressure on a Bruker AVANCE III spectrometer using a standard CP-TOSS pulse sequence (cross polarization with total suppression of sidebands) probe with 4 mm (outside diameter) zirconia rotors. Cross-polarization with TOSS was used to acquire <sup>13</sup>C data at 100.37 MHz. The <sup>13</sup>C ninety-degree pulse widths were 4 μs. The decoupling frequency corresponded to 72 kHz. The TOSS sample-spinning rate was 5 kHz. Recycle delays was 2s.

#### **Infra-Red Spectroscopy:**

IR spectra were obtained using a Nicolet ID5 attenuated total reflectance IR spectrometer operating at ambient temperature. The solid state IR spectra were recorded using KBr pellets as background.

#### **Field Emission-Scanning Electron Microscopy (FE-SEM):**

Electron Microscope with integral charge compensator and embedded EsB and AsB detectors. Oxford X-max instruments 80mm<sup>2</sup>. (Carl Zeiss NTS, GmbH), Imaging conditions: 2kV, WD= 2mm, 200kX, Inlens detector. For SEM images, as an initial preparation, the samples were ground thoroughly, soaked in ethanol for 30 min. and were sonicated for 2 hrs. These well-dispersed suspensions were drop casted on silicon wafer and dried under vacuum for at least 12 hrs.

#### **Adsorption study:**

Adsorption studies were carried out using a Micromeritics 3-FLEX pore and surface area analyser.

## B. Synthesis and characterization of model compounds

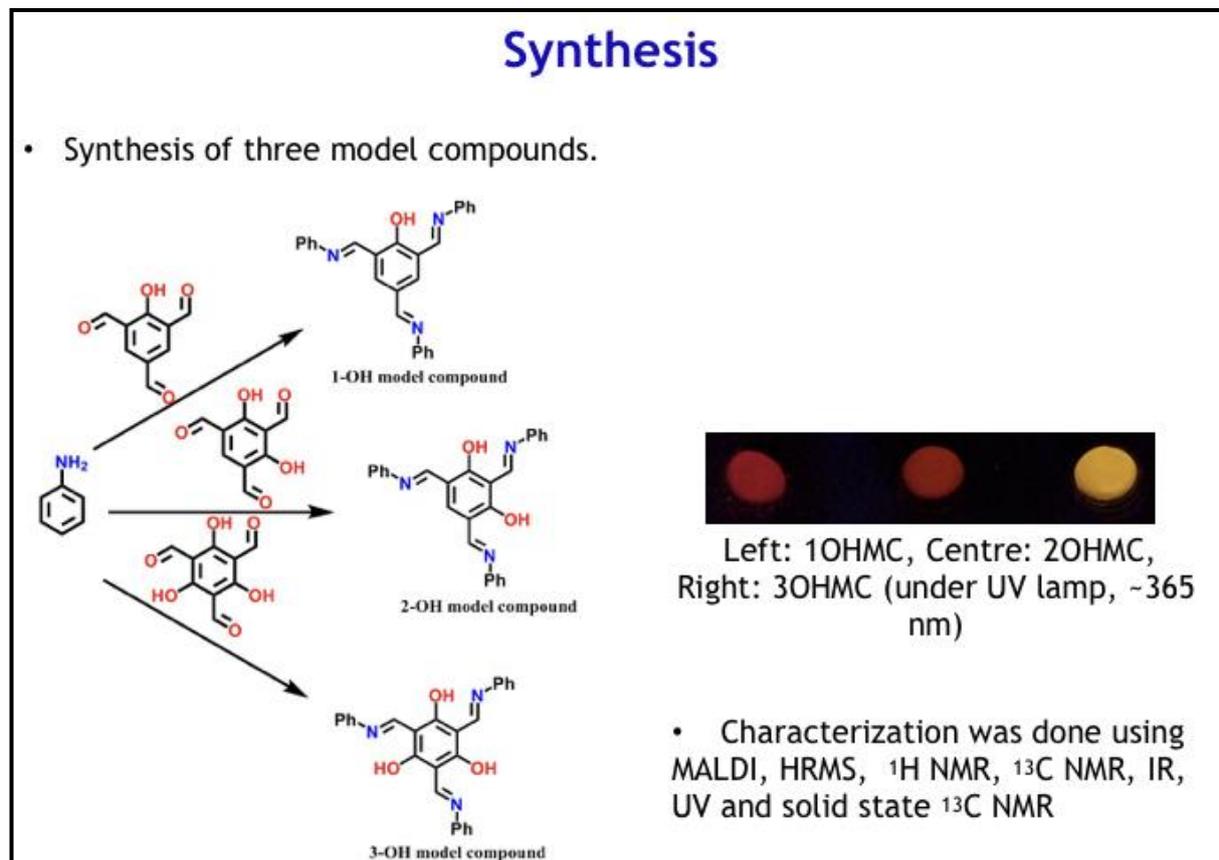


Figure 1. A schematic representation of the synthesis of model compounds with aniline in methanol under reflux condition.

**a. Synthesis of 1OH Model Compound:** Synthesis of the model compound was carried out by the reaction between 2, 4, 6-triformylphenol (0.122 g, 0.69 mmol) and aniline (0.401 g, 4.305 mmol) in 75 mL methanol. The reaction mixture was kept for 24 h in reflux condition under  $\text{N}_2$  atmosphere. After 24 h red colored compound was collected by filtration, washed with methanol and dried under vacuum. Characterization was done using  $^1\text{H}$  and  $^{13}\text{C}$  NMR (Figure 2), FT-IR (Figure 3), and matrix assisted laser desorption/ionization (MALDI) (Figure A1) studies [7].

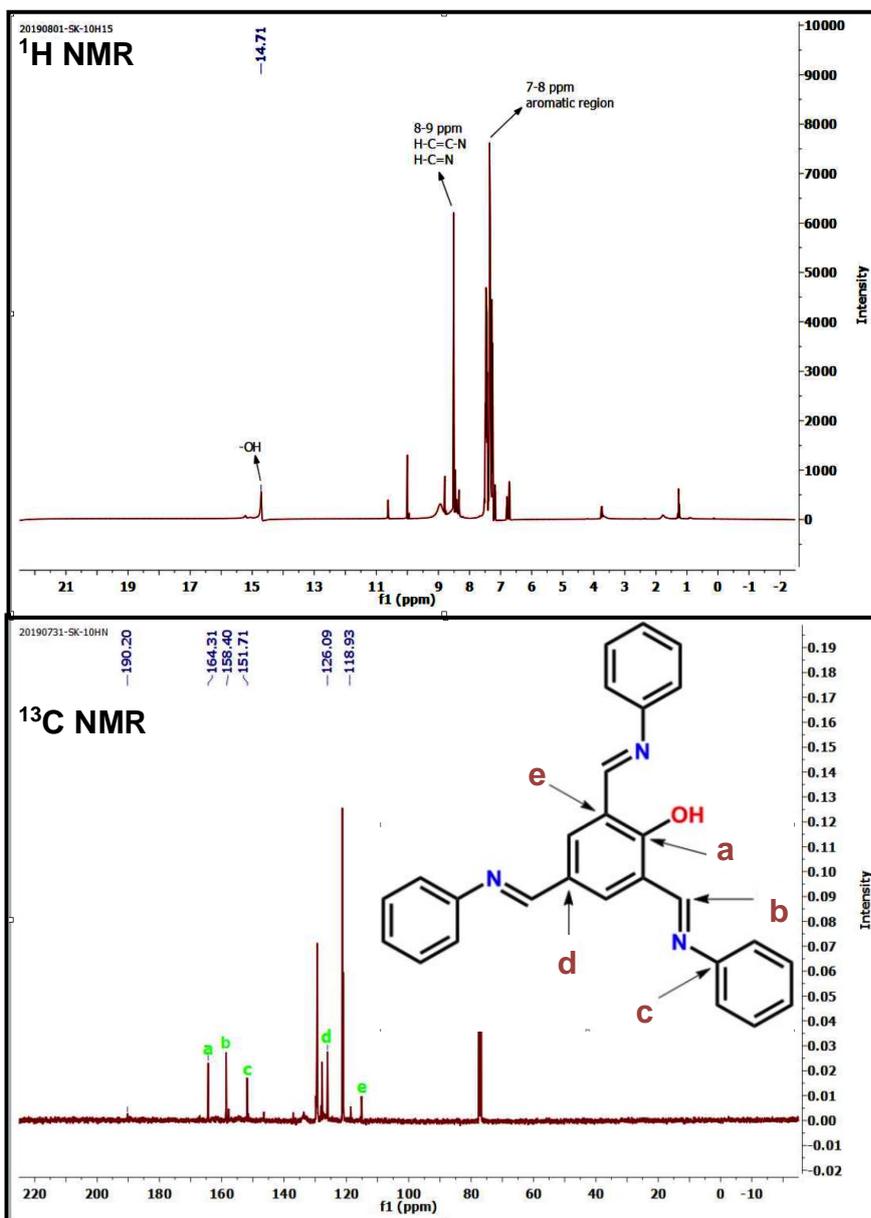


Figure 2. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR of 1OH Model Compound were recorded in Chloroform-d (CDCl<sub>3</sub>) at room temperature. Chemical shifts of <sup>13</sup>C-NMR at δ = 77 ppm is from Chloroform-d. Atoms of the Model Compound corresponding to the specific peaks are marked in the insets.

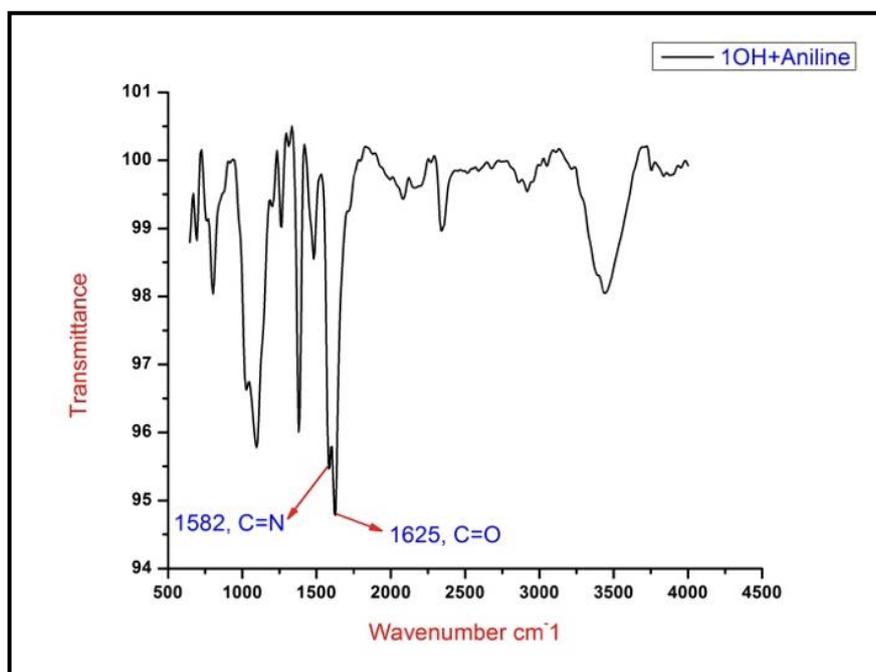


Figure 3. FT-IR spectra of 1OH Model Compound showing C=O and C=N stretching frequency.

**b. Synthesis of 2OH Model Compound:** Synthesis of the model compound was carried out by the reaction between 2, 4, 6-triformylresorcinol (0.165 g, 0.69 mmol) and aniline (0.401 g, 4.305 mmol) in 75 mL methanol. The reaction mixture was kept for 24 h in reflux condition under N<sub>2</sub> atmosphere. After 24 h orange colored compound was collected by filtration, washed with methanol and dried under vacuum. Characterization was done using <sup>13</sup>C solid state NMR (Figure 4), FT-IR (Figure 5), MALDI and high resolution mass spectroscopy (HRMS) (Figure A2) studies [7].

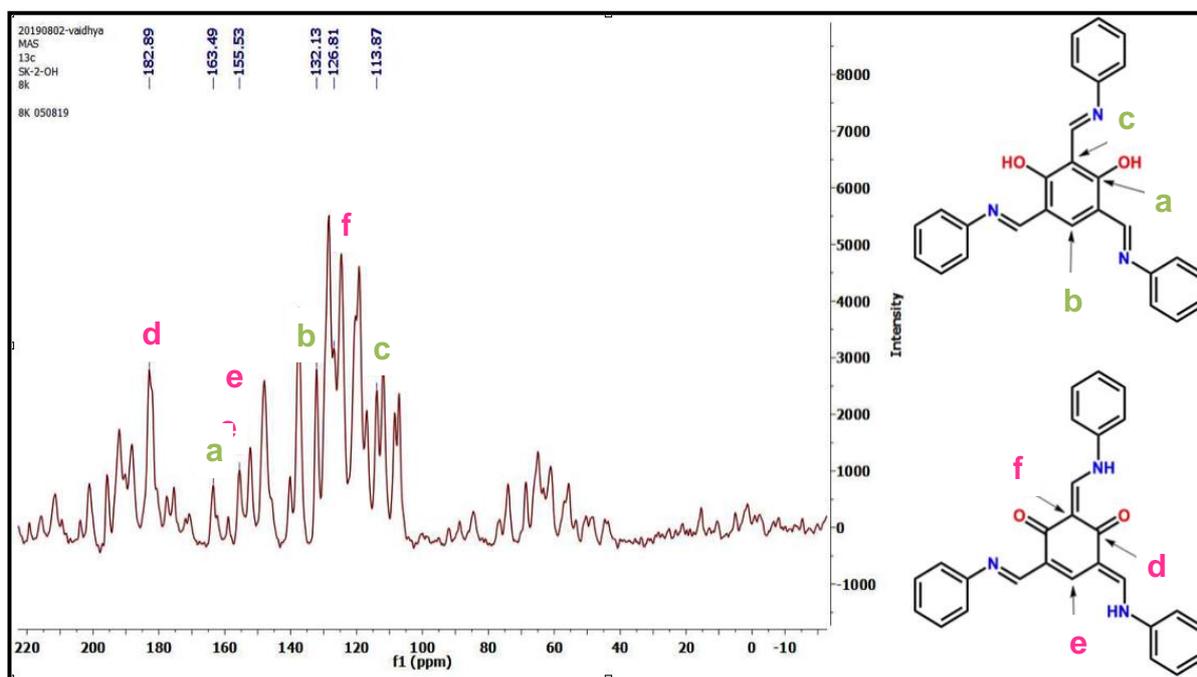


Figure 4. Solid state  $^{13}\text{C}$  NMR of 2OH Model Compound showing peaks for both keto and enol form as labelled.

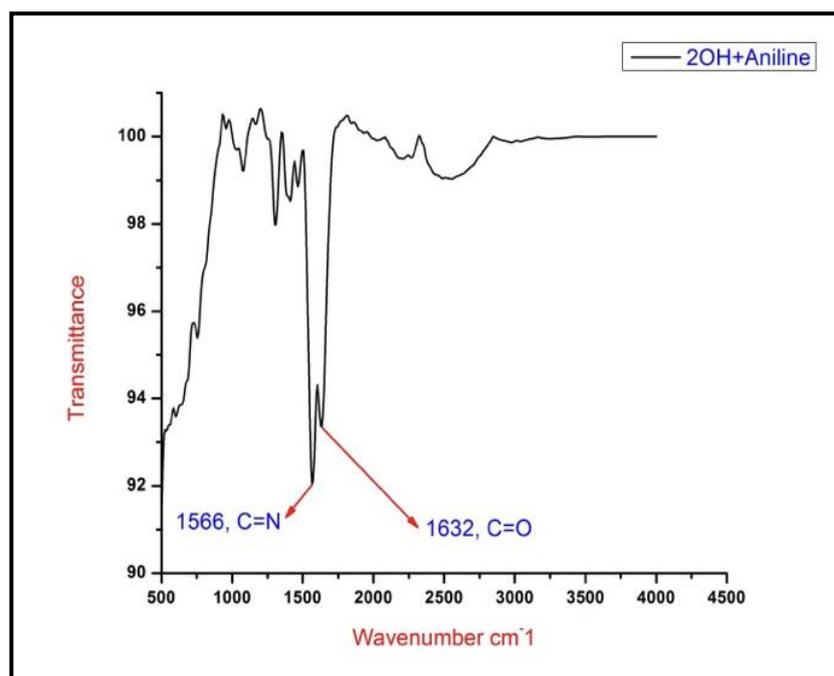


Figure 5. FT-IR spectra of 2OH Model Compound showing C=O and C=N stretching frequency.

**c. Synthesis of 3OH Model Compound:** Synthesis of the model compound was carried out by the reaction between 2, 4, 6-triformylphloroglucinol (0.171 g, 0.69 mmol) and aniline (0.401 g, 4.305 mmol) in 75 mL methanol. The reaction mixture was kept for 24 h in reflux condition under N<sub>2</sub> atmosphere. After 24 h yellow colored compound was collected by filtration, washed with methanol and dried under vacuum. Characterization was done using <sup>13</sup>C solid state NMR (Figure 6), FT-IR (Figure 7), MALDI and HRMS (Figure A3) studies [7].

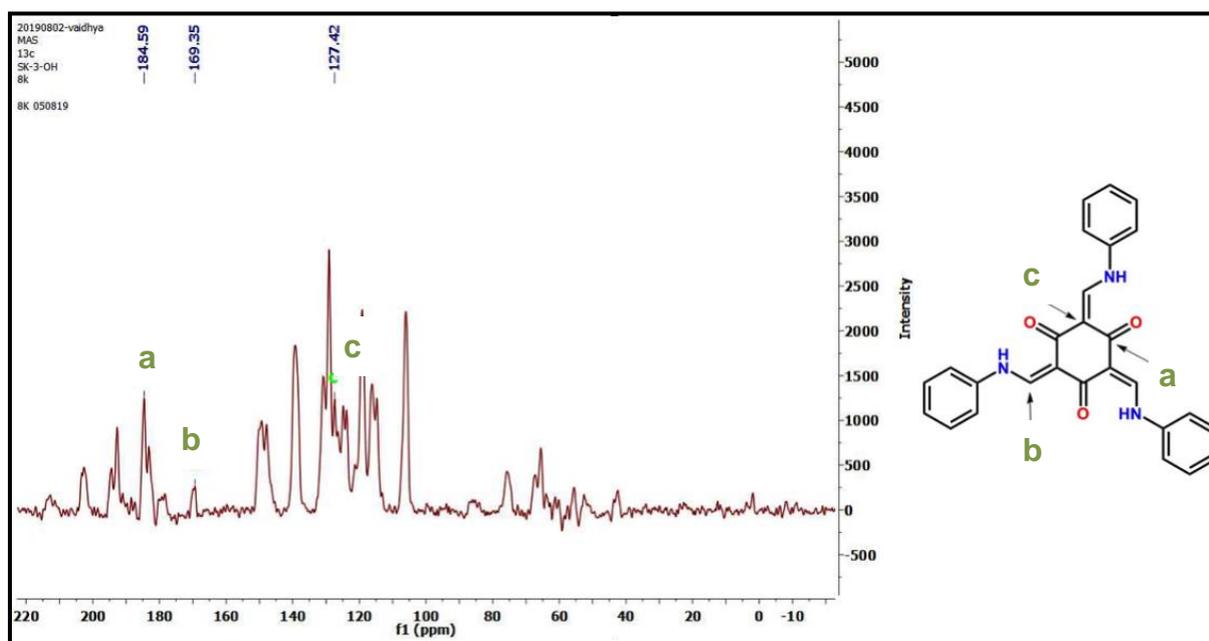


Figure 6. Solid state <sup>13</sup>C NMR of 3OH Model Compound showing presence of keto form with peaks labelled to respective carbon atoms.

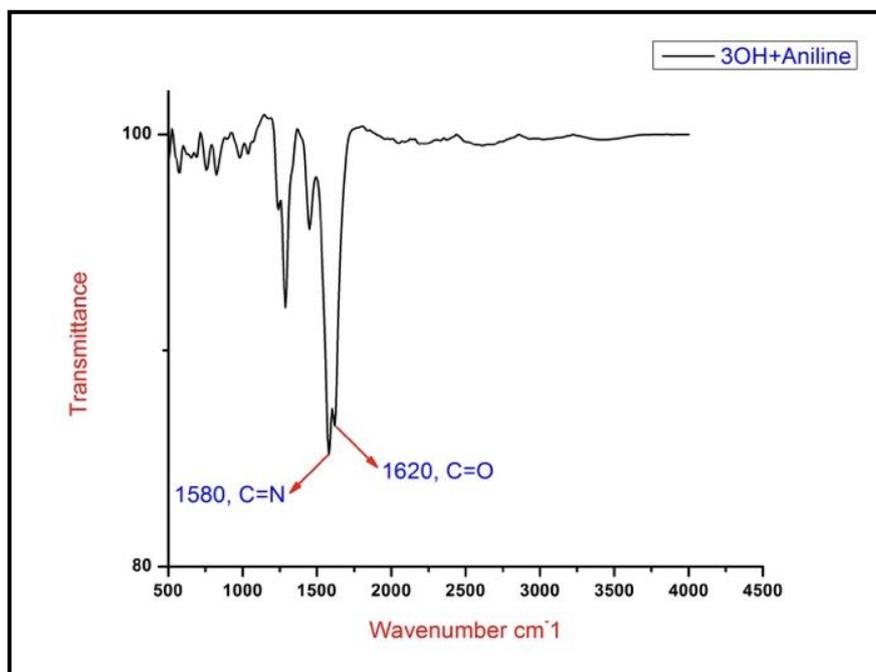


Figure 7. FT-IR spectra of 3OH Model Compound showing C=O and C=N stretching frequency.

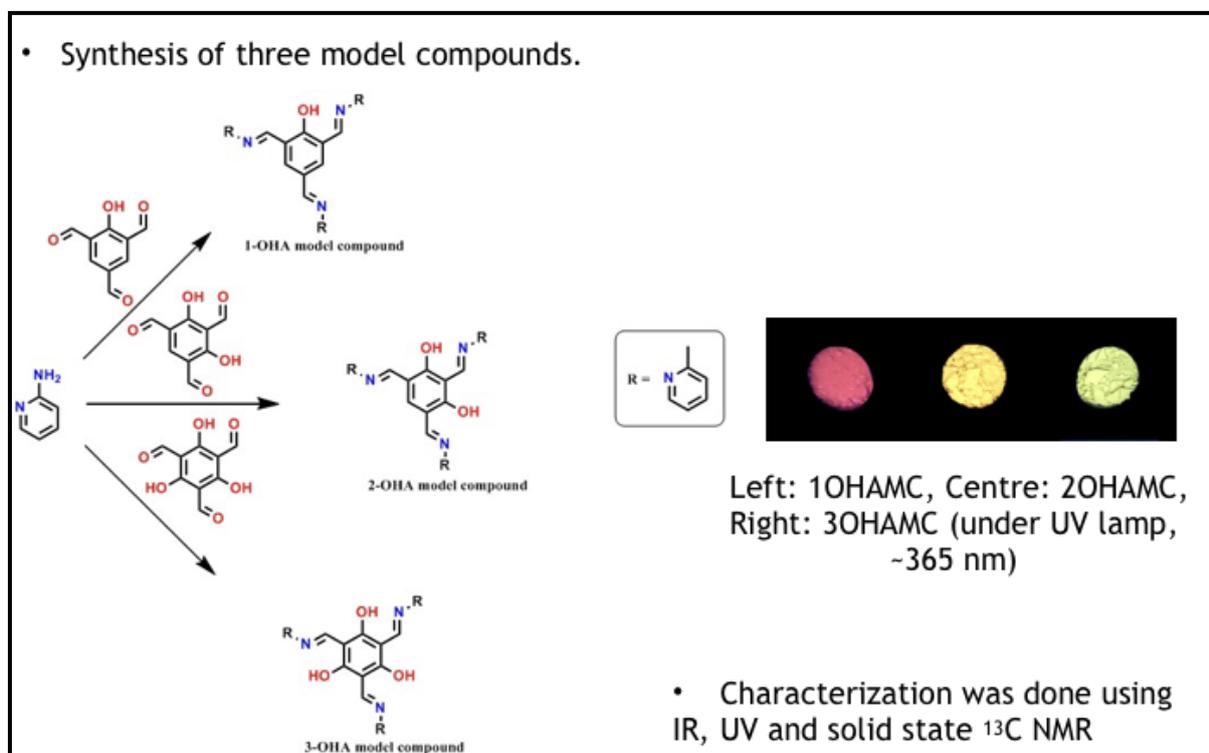
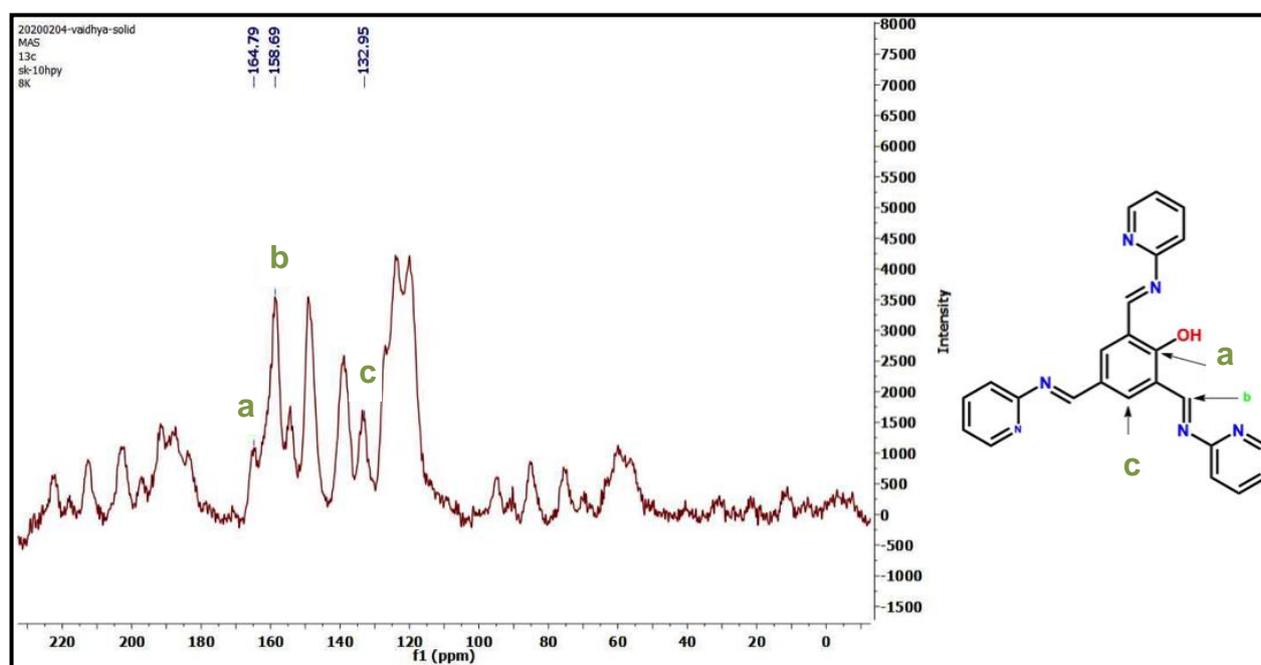


Figure 8. A schematic representation of the synthesis of model compounds with 2-aminopyridine in methanol under reflux condition.

**d. Synthesis of 1OHA Model Compound:** To a round bottom flask 2, 4, 6-triformylphenol (1 mmol, 178.14 mg) and 2-aminopyridine (6 mmol, 0.564 g) was added in 50 ml methanol. The reaction mixture was kept for 24 h in reflux condition under N<sub>2</sub> atmosphere giving off a compound soluble in methanol. After 24 hours the solvent was evaporated using rotary evaporation and compound dried under vacuum. The dried compound was dissolved in dichloromethane and leftover amine was extracted using water. The leftover dichloromethane solution was then dried using sodium sulfate and the solvent was evaporated using rotary evaporation thus finally giving us the red product. Characterization was done using <sup>13</sup>C solid state NMR (Figure 9) and FT-IR (Figure 10).



**Figure 9. Solid state <sup>13</sup>C NMR of 1OHA Model Compound showing presence of enol form with peaks labelled to respective carbon atoms.**

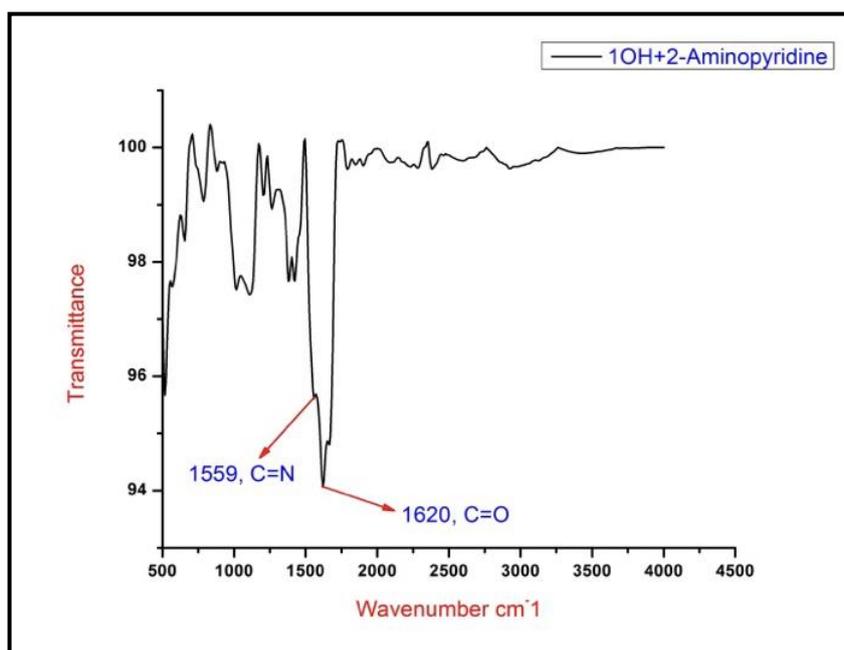


Figure 10. FT-IR spectra of 1OHA Model Compound showing C=O and C=N stretching frequency.

**e. Synthesis of 2OHA Model Compound:** To a round bottom flask 2, 4, 6-triformylresorcinol (1 mmol, 185 mg) and 2-aminopyridine (6 mmol, 0.564 g) was added in 50 ml methanol. The reaction mixture was kept for 24 h in reflux condition under N<sub>2</sub> atmosphere. After 24 h yellow colored compound was collected by filtration, washed with methanol and dried under vacuum. Characterization was done using <sup>13</sup>C solid state NMR (Figure 11) and FT-IR (Figure 12).

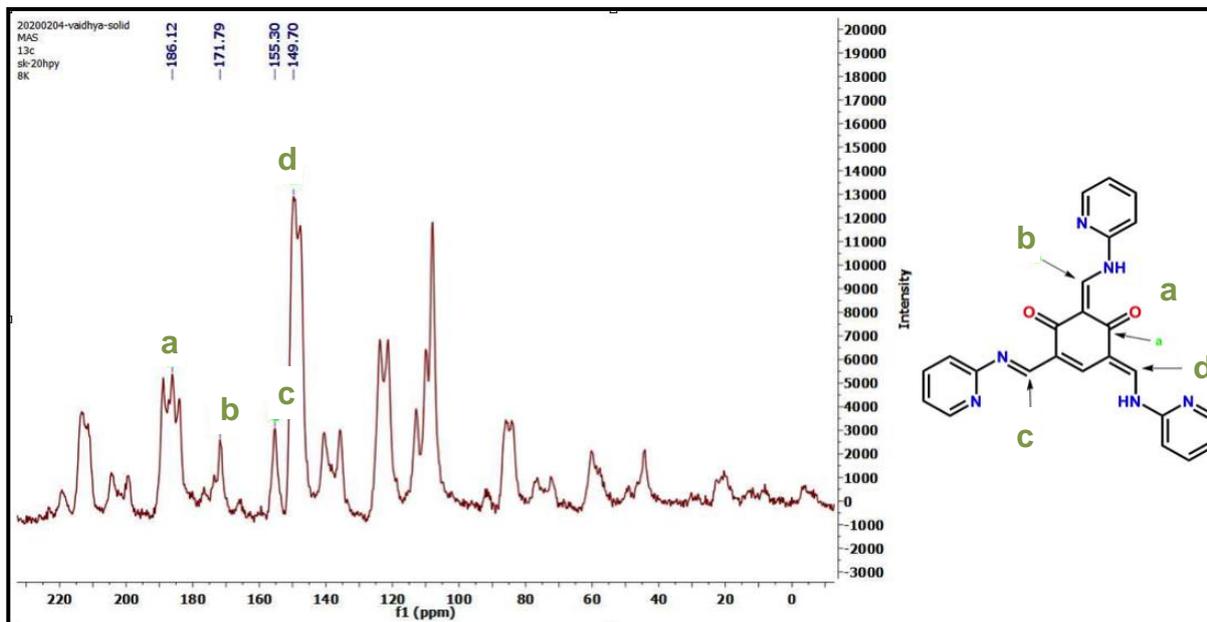


Figure 11. Solid state  $^{13}\text{C}$  NMR of 2OHA Model Compound showing presence of keto form with peaks labelled to respective carbon atoms.

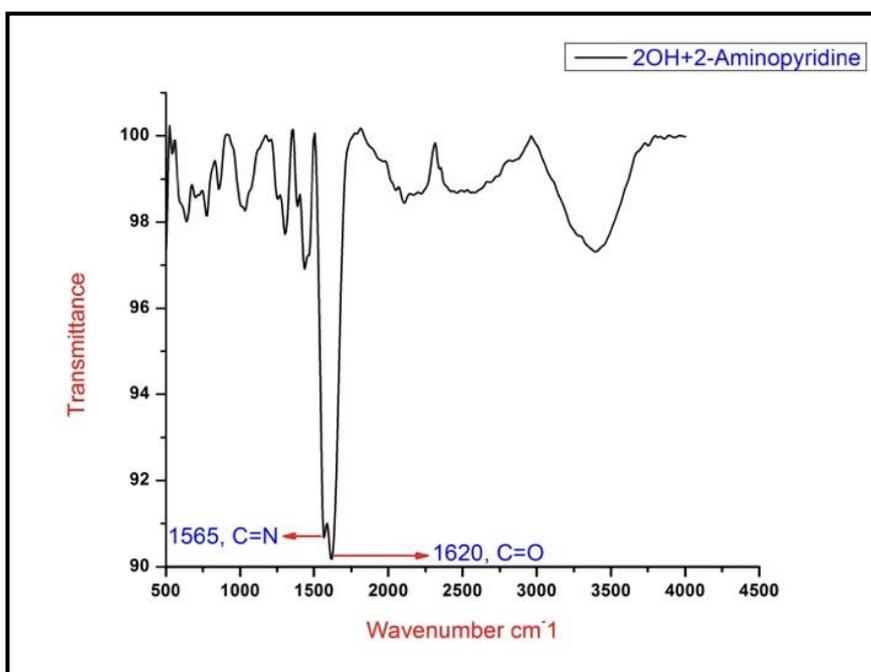
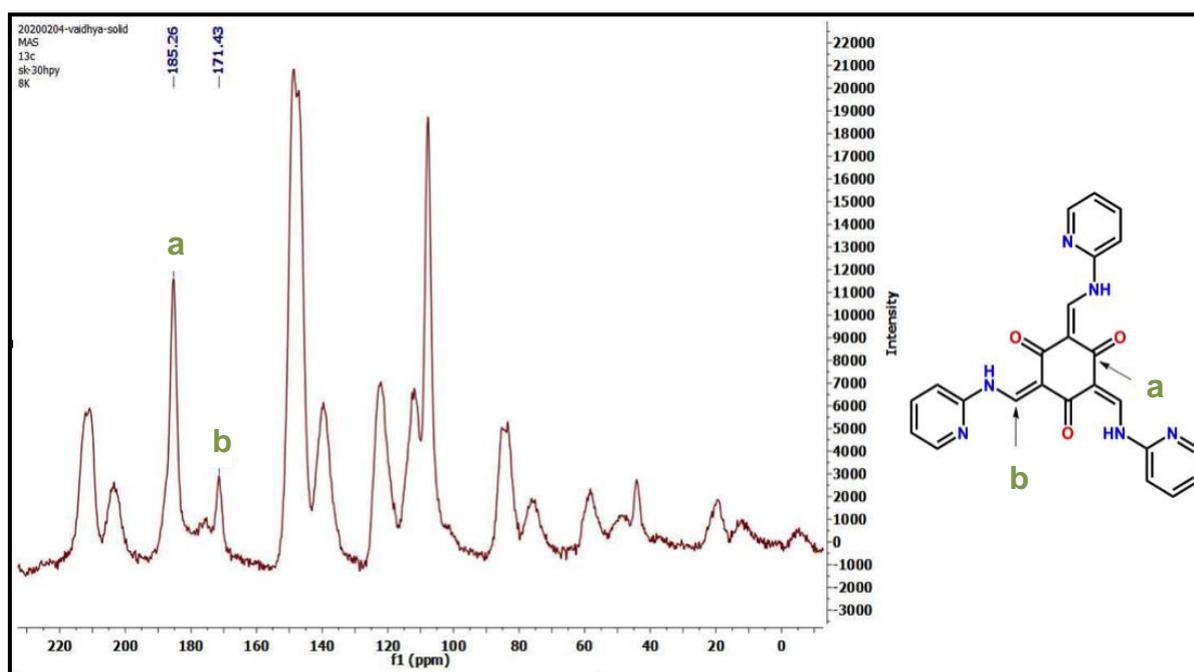


Figure 12. FT-IR spectra of 2OHA Model Compound showing C=O and C=N stretching frequency.

**f. Synthesis of 3OHA Model Compound:** To a round bottom flask 2, 4, 6-triformylphloroglucinol (1 mmol, 192 mg) and 2-aminopyridine (6 mmol, 0.564 g) was added in 50 ml methanol. The reaction mixture was kept for 24 h in reflux condition under N<sub>2</sub> atmosphere. After 24 h yellow colored compound was collected by filtration, washed with methanol and dried under vacuum. Characterization was done using <sup>13</sup>C solid state NMR (Figure 13), FT-IR (Figure 14), and HRMS (Figure A4) studies [8].



**Figure 13. Solid state <sup>13</sup>C NMR of 3OHA Model Compound showing presence of keto form with peaks labelled to respective carbon atoms.**

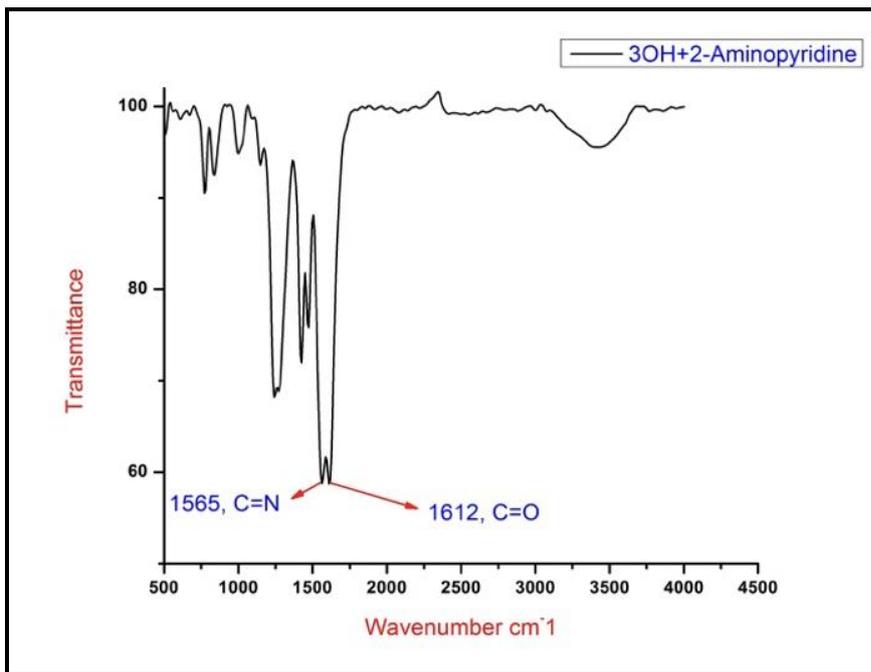
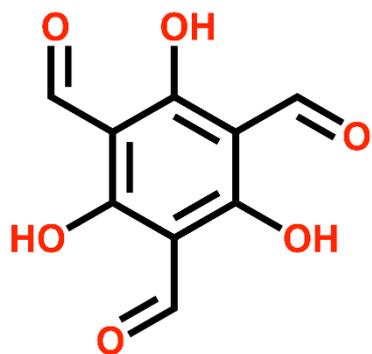


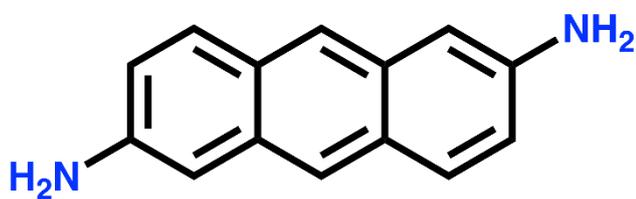
Figure 14. FT-IR spectra of 3OHA Model Compound showing C=O and C=N stretching frequency.

### C. Synthesis of COFs

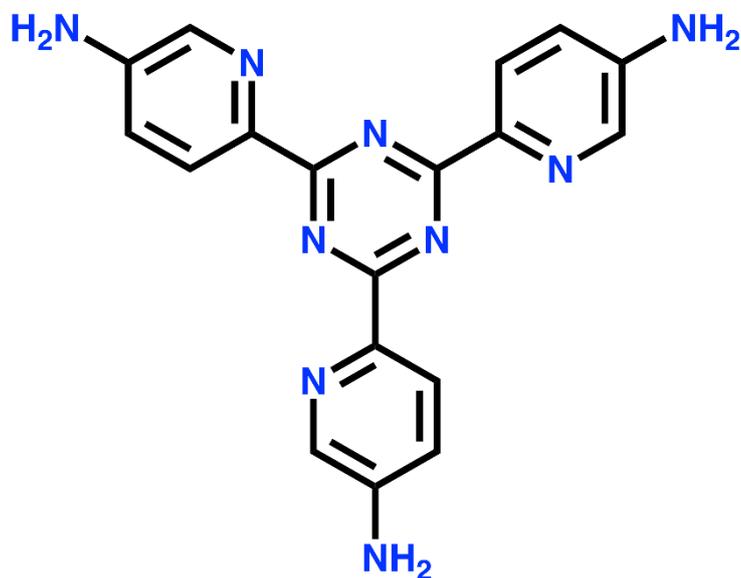
Three different COFs were synthesized using 2, 4, 6-Triformylphloroglucinol as aldehyde and 2, 6-Diaminoanthracene and 5,5',5''-(1, 3, 5-triazine-2, 4, 6-triyl)tris(pyridin-2-amine) (Pyridine group rich ligand - PYC ligand) as amines. While synthesizing three different COFs the ratio of these two amines was varied.



2, 4, 6-Triformylphloroglucinol



2, 6-Diaminoanthracene



5,5',5''-(1, 3, 5-triazine-2, 4, 6-triyl)tris(pyridin-2-amine) (Pyridine group rich ligand - PYC ligand)

**a. Synthesis of 25:75 COF with Diaminoanthracene and PYC ligand in ratio 1:3**

: 2,4,6-triformyl Phloroglucinol (65mg, 0.3mmol), 2, 6-Diaminoanthracene (23.42mg, 0.225mmol) and 5,5',5''-(1,3,5-triazine-2,4,6-triyl)tris(pyridin-2-amine (53.5mg, 0.15mmol) were weighed into a Pyrex tube and were dissolved in dioxane (3.0 mL) and mesitylene (3.0 mL) and stirred until a yellow color was observed. Following this, 1 mL of stock acetic acid was added. Then the Pyrex tube was flash frozen in a liquid nitrogen bath and sealed. The Pyrex tube along with its contents was placed in an oven at 120°C for 5 days and gradually cooled to room temperature over 12 hrs. This yielded brown colored solid which was washed with hot DMF, dioxane, methanol (MeOH), acetone and tetrahydrofuran (THF).

**b. Synthesis of 50:50 COF with Diaminoanthracene and PYC ligand in ratio 1:1**

: 2,4,6-triformyl Phloroglucinol (65mg, 0.3mmol), 2, 6-Diaminoanthracene (46.85mg, 0.112mmol) and 5,5',5''-(1,3,5-triazine-2,4,6-triyl)tris(pyridin-2-amine (80.25mg, 0.225mmol) were weighed into a Pyrex tube and were dissolved in dioxane (3.0 mL) and mesitylene (3.0 mL) and stirred until a yellow color was observed. Following this, 1 mL of stock acetic acid was added. Then the Pyrex tube was flash frozen in a liquid nitrogen bath and sealed. The Pyrex tube along with its contents was placed in an oven at 120°C for 5 days and gradually cooled to room temperature over 12 hrs. This yielded brown colored solid which was washed with hot DMF, dioxane, MeOH, acetone and THF.

**c. Synthesis of 75:25 COF with Diaminoanthracene and PYC ligand in ratio 3:1**

: 2,4,6-triformyl Phloroglucinol (65mg, 0.3mmol), 2, 6-Diaminoanthracene (70.275mg, 0.3375mmol) and 5,5',5''-(1,3,5-triazine-2,4,6-triyl)tris(pyridin-2-amine (26.75mg, 0.075mmol) were weighed into a Pyrex tube and were dissolved in dioxane (3.0 mL) and mesitylene (3.0 mL) and stirred until a yellow color was observed. Following this, 1 mL of stock acetic acid was added. Then the Pyrex tube was flash frozen in a liquid nitrogen bath and sealed. The Pyrex tube along with its contents was placed in an oven at 120°C for 5 days and gradually cooled to room temperature over 12 hrs. This yielded brown colored solid which was washed with hot DMF, dioxane, MeOH, acetone and THF.

## RESULTS

### A. UV-Vis absorption spectra of model compounds

The UV-Vis spectra (Figure 15) of all three model compounds in DMSO show a sharp absorption peak near 430 nm, which is a peak for n- $\pi^*$  absorption of a Schiff base [9]. Also, the solid-state UV-Vis absorption spectra (Figure 16) shows lesser absorption in the red region of visible spectrum as we increase the number of -OH groups in the aldehyde of model compounds, which in part explains the color of different model compounds.

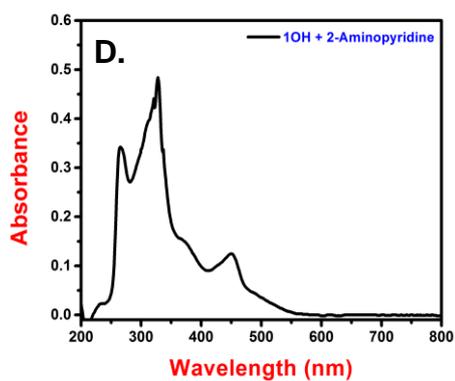
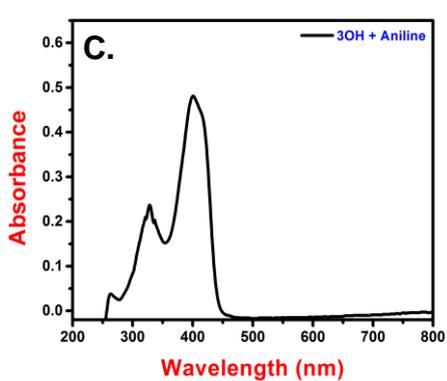
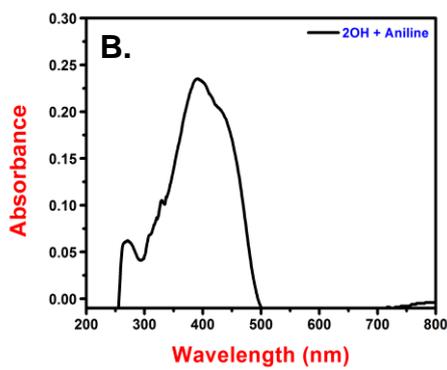
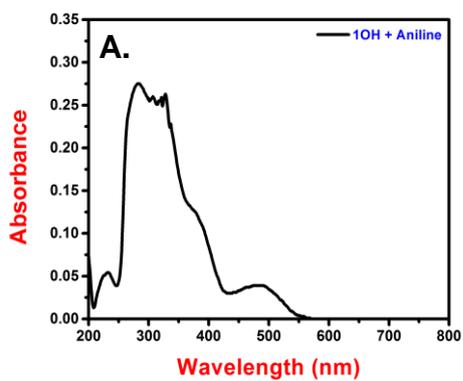
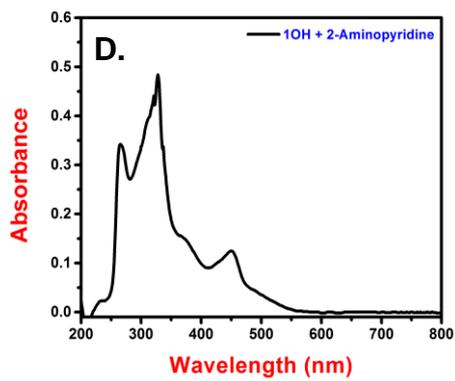
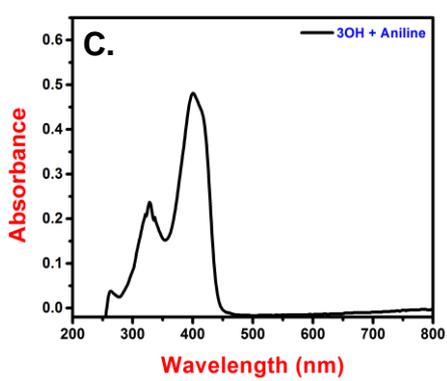
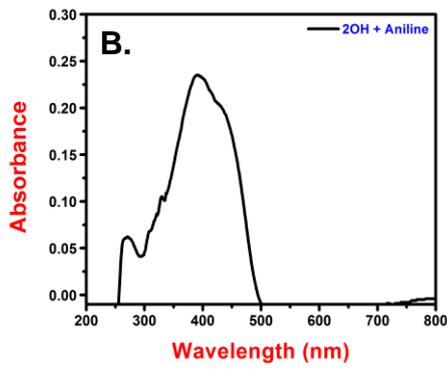
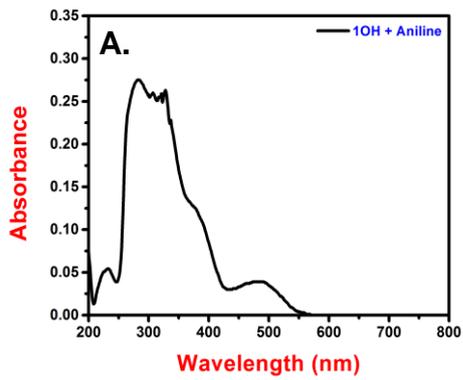


Figure 15. UV-Vis absorption spectra of model compounds in DMSO: (A) 1OH Model Compound (B) 2OH Model Compound (C) 3OH Model Compound (D) 1OHA Model Compound (E) 2OHA Model Compound (F) 3OHA Model Compound.

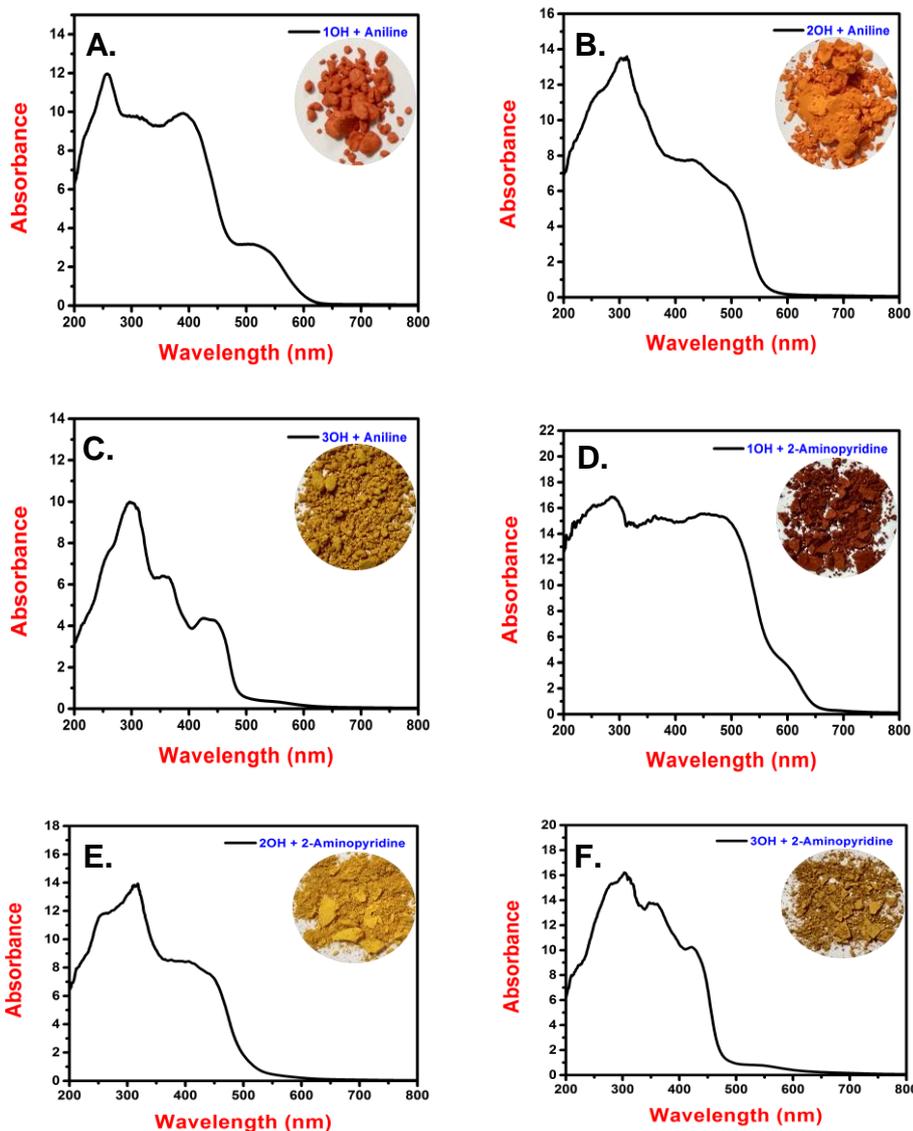


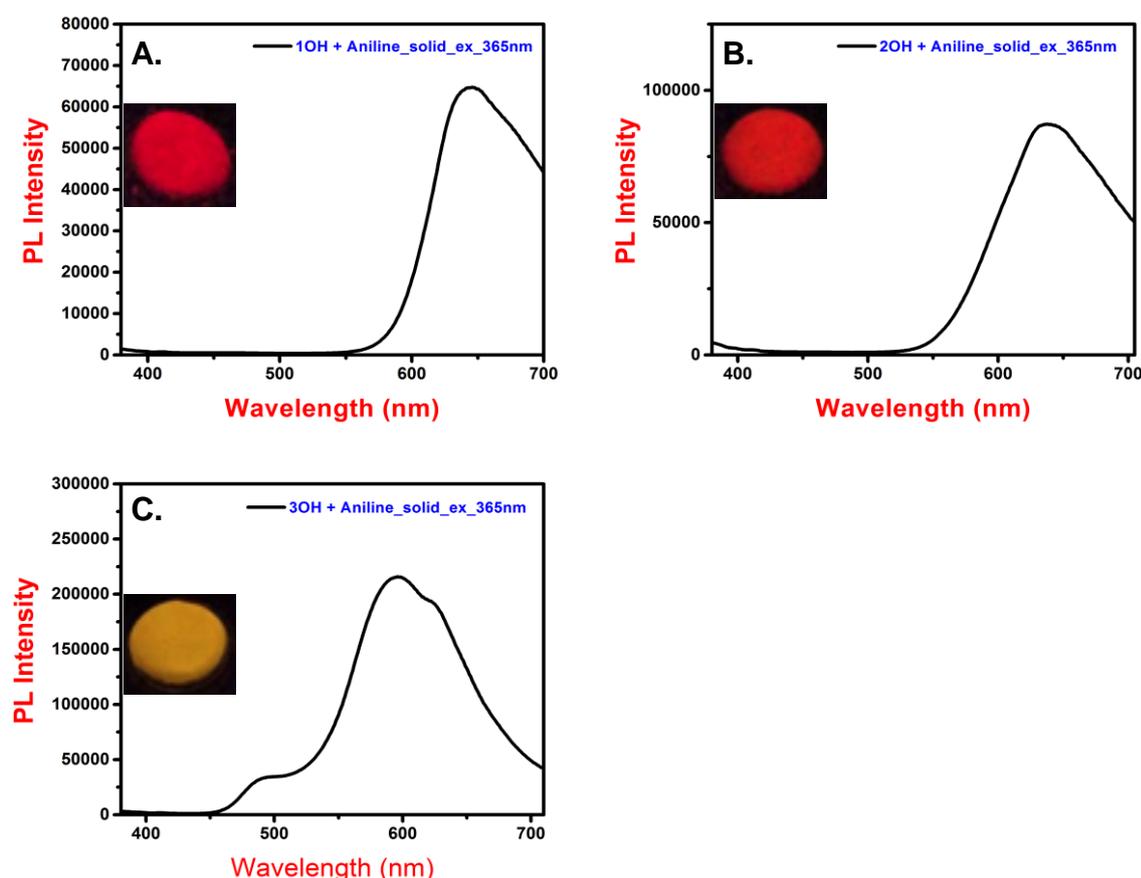
Figure 16. Solid state UV-Vis absorption spectra of model compounds along with a picture of respective model compounds under normal light: (A) 1OH Model Compound (B) 2OH Model Compound (C) 3OH Model Compound (D) 1OHA Model Compound (E) 2OHA Model Compound (F) 3OHA Model Compound.

## B. Steady state emission spectra of model compounds

### B1. Aniline based model compounds

From the solid-state emission spectra (Figure 17) of the model compounds made from aniline as an amine, we observe a blue shift in the emission as we increase the

number of hydroxyl groups or electron-rich groups in the aldehyde. The emission spectra's of the compounds made using aniline, cover the red and green region of the visible spectrum but lack the blue component, which is a must for a white light-emitting compound. From our observation of the effect of increasing electron-rich groups on blue region emission in our model compounds, we replaced aniline with



electron-rich amine group 2-aminopyridine in anticipation of getting white light emission.

Figure 17. Solid state emission spectra of model compounds upon excitation at 365nm along with a picture under UV lamp: (A) 1OH Model Compound, (B) 2OH Model Compound, (C) 3OH Model Compound.

## B2. 2-Aminopyridine based model compounds

Replacing aniline with 2-aminoanthracene leads to enhanced emission in the blue region of visible spectrum as can be seen for 1OHA and 2OHA model compounds as compared to 1OH and 2OH model compounds respectively, also 3OHA model compound shows a shift in peak to the blue region as it can be seen from the given

figure (Figure 18) but still lacks the emission in the blue region. Replacing aniline does enhance the quality of emission spectrum, but the blue emission is still elusive.

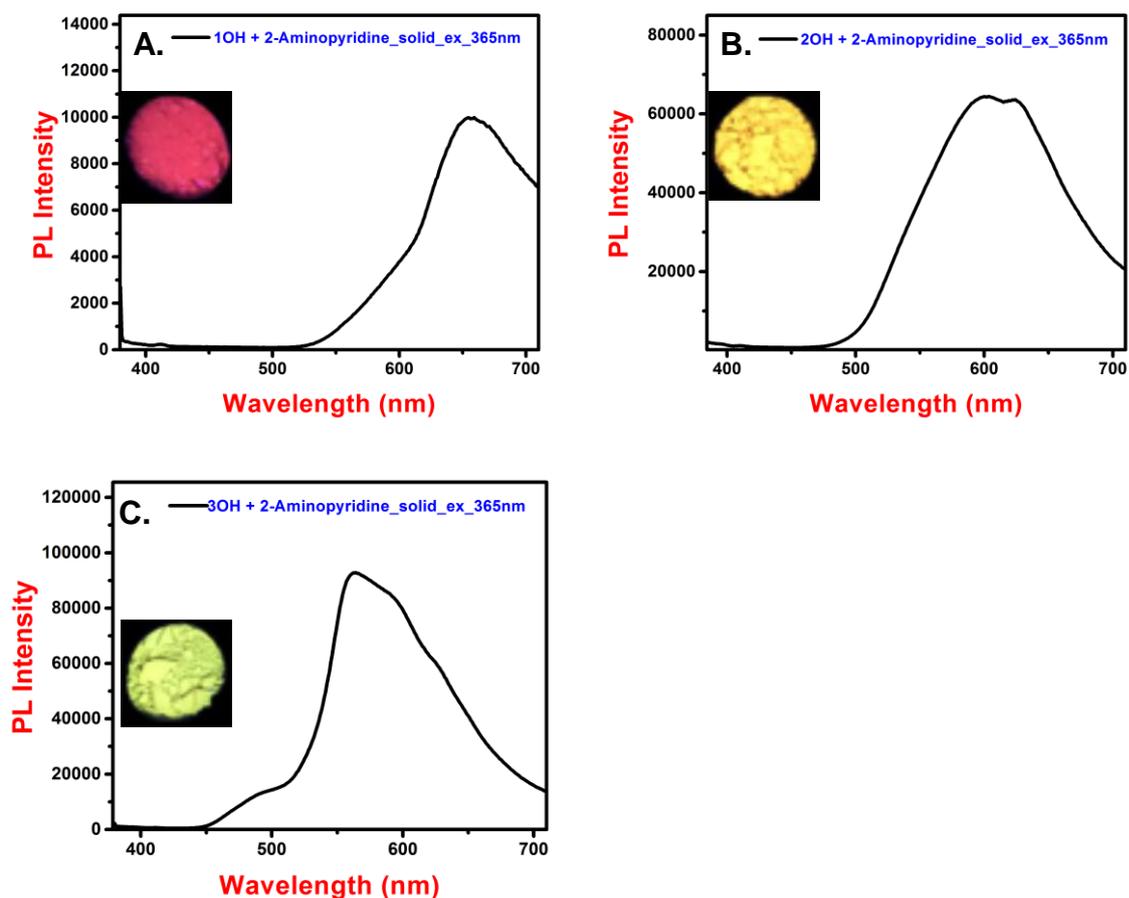


Figure 18. Solid state emission spectra of model compounds upon excitation at 365nm along with a picture under UV lamp: (A) 1OHA Model Compound, (B) 2OHA Model Compound, (C) 3OHA Model Compound.

### C. Flexible and fluorescent polymer films

To show better processability of our compounds, we made flexible fluorescent films. The polymer, poly methyl methacrylate (PMMA) and the respective compounds were sonicated in DMF. The PMMA gel was made after heating the mixture at 120<sup>o</sup> C and was coated on the glass slide to make films. This rendered flexible films, which show fluorescence (Figure 19) similar to that of powder form of respective model compounds.

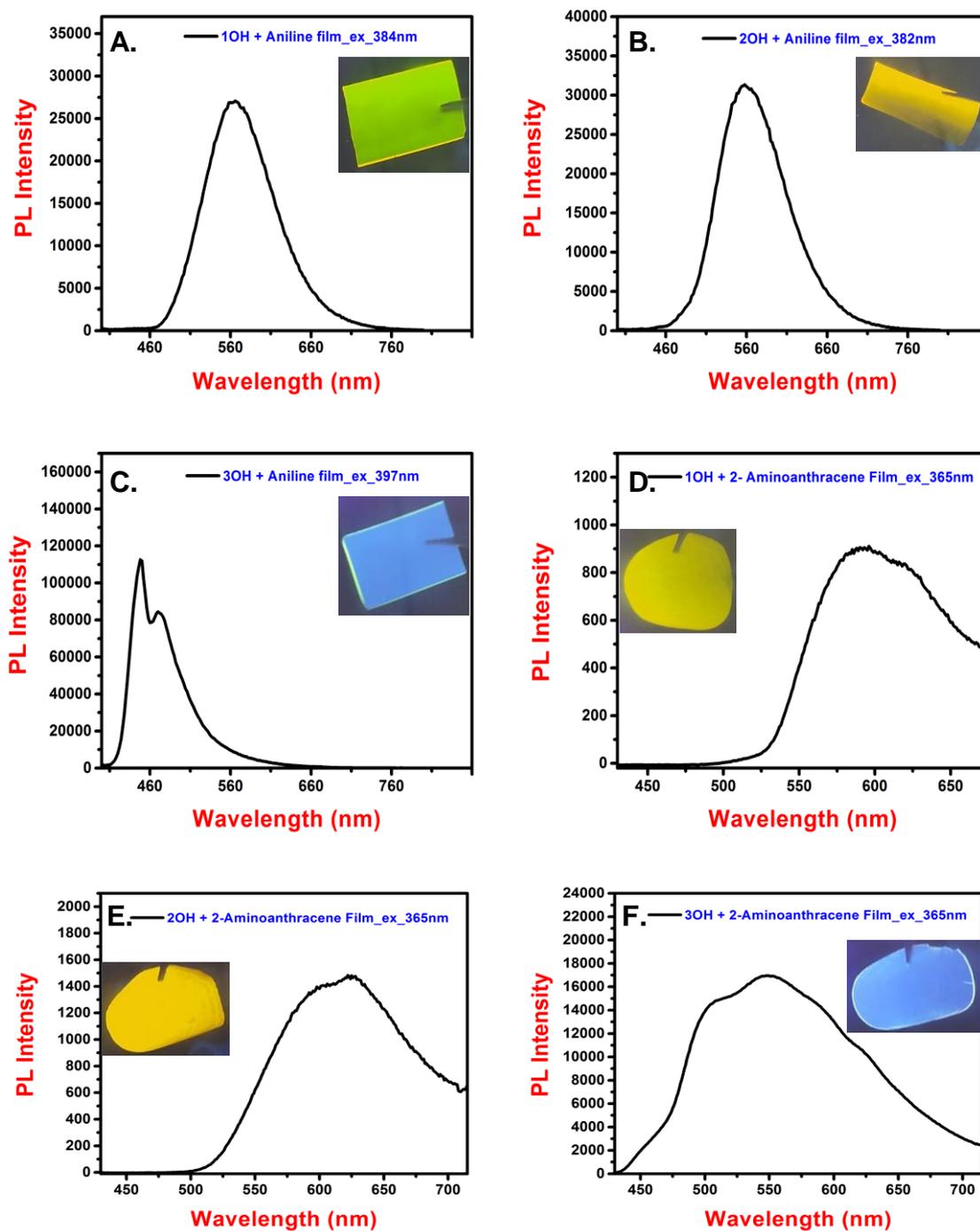


Figure 19. Solid state emission spectra of PMMA films of model compounds upon excitation along with picture under UV lamp; (A) 1OH Model Compound, (B) 2OH Model Compound, (C) 3OH Model Compound, (D) 1OHA Model Compound, (E) 2OHA Model Compound and (F) 3OHA Model Compound.

## D. Synthesis of COFs

On our way to synthesize a solid-state white light-emitting compound, the lack of blue light emission from the same is an impediment. Adding a chemical entity to our compound with the help of a chemical bond, which inherently shows blue light fluorescence could help. One such blue light fluorescent compound is anthracene diamine[9]. Hence, combining an amine which shows blue fluorescence with the compound which covers the rest of the fluorescent spectra to a great extent could help. Amongst the model compounds synthesized so far, the 3OHA Model Compound seems to be the most promising as it shows broadest emission spectra excluding the blue region, hence, using triformylphloroglucinol as an aldehyde and pyridine group as an amine is important.

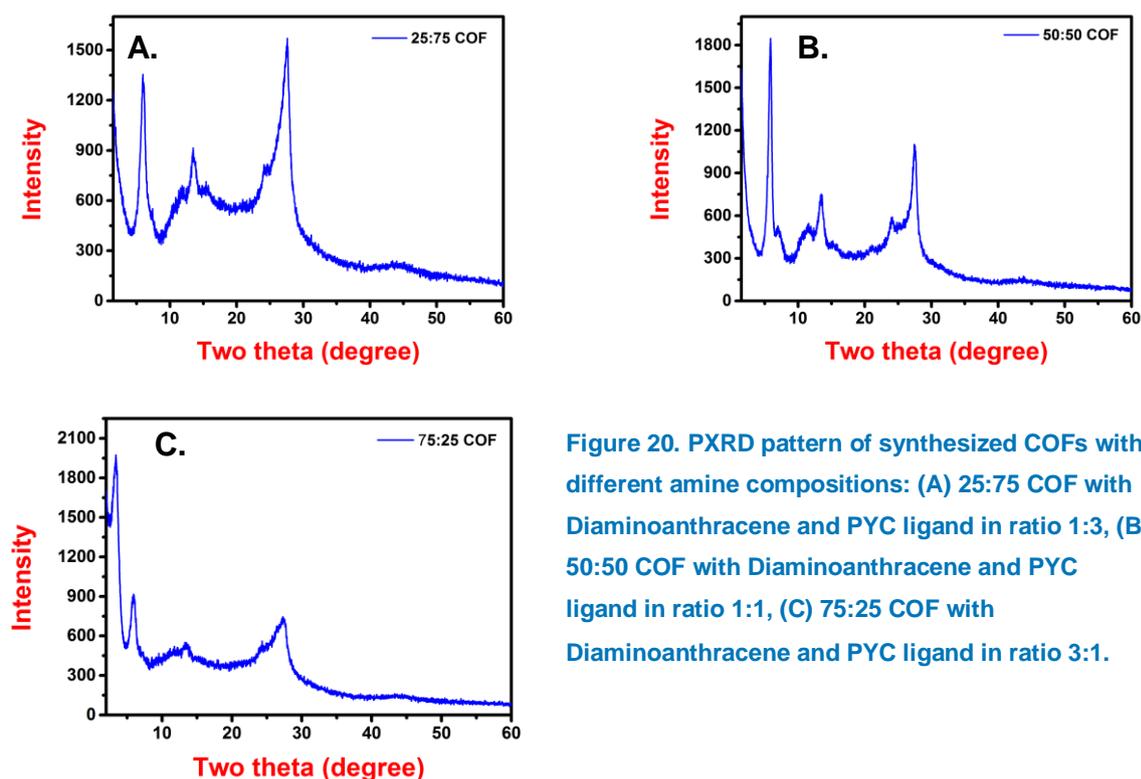


Figure 20. PXRD pattern of synthesized COFs with different amine compositions: (A) 25:75 COF with Diaminoanthracene and PYC ligand in ratio 1:3, (B) 50:50 COF with Diaminoanthracene and PYC ligand in ratio 1:1, (C) 75:25 COF with Diaminoanthracene and PYC ligand in ratio 3:1.

Three COFs were synthesized using 2,4,6-Triformylphloroglucinol as aldehyde and 2,6-Diaminoanthracene and 5,5',5''-(1,3,5-triazine-2,4,6-triyl)tris(pyridin-2-amine) (Pyridine group rich ligand - PYC ligand) as amines in 1:3, 1:1, and 3:1 equivalence ratio. The powder X-ray diffraction (PXRD) pattern of all the COFs hints at amalgamation of two COFs (Figure 20) i.e. two different COFs made from same aldehyde but different amines. Opposite to what was anticipated the solid-state PL spectrum (Figure 21) of the first two COFs (25:75 and 50:50 COF) show no emission

in the blue region giving us emission only in the red region of the visible spectrum. Also, the COF having the highest composition of diamondanthracene (75:25 COF) shows abysmally weak fluorescence. Although, it was anticipated that due to the use of two different amines, the aggregated self-quenching of emission would not happen as the stacking interactions will be weak, but we observe the weak fluorescence of the COFs, which can be attributed to particle aggregation-induced self-quenching.

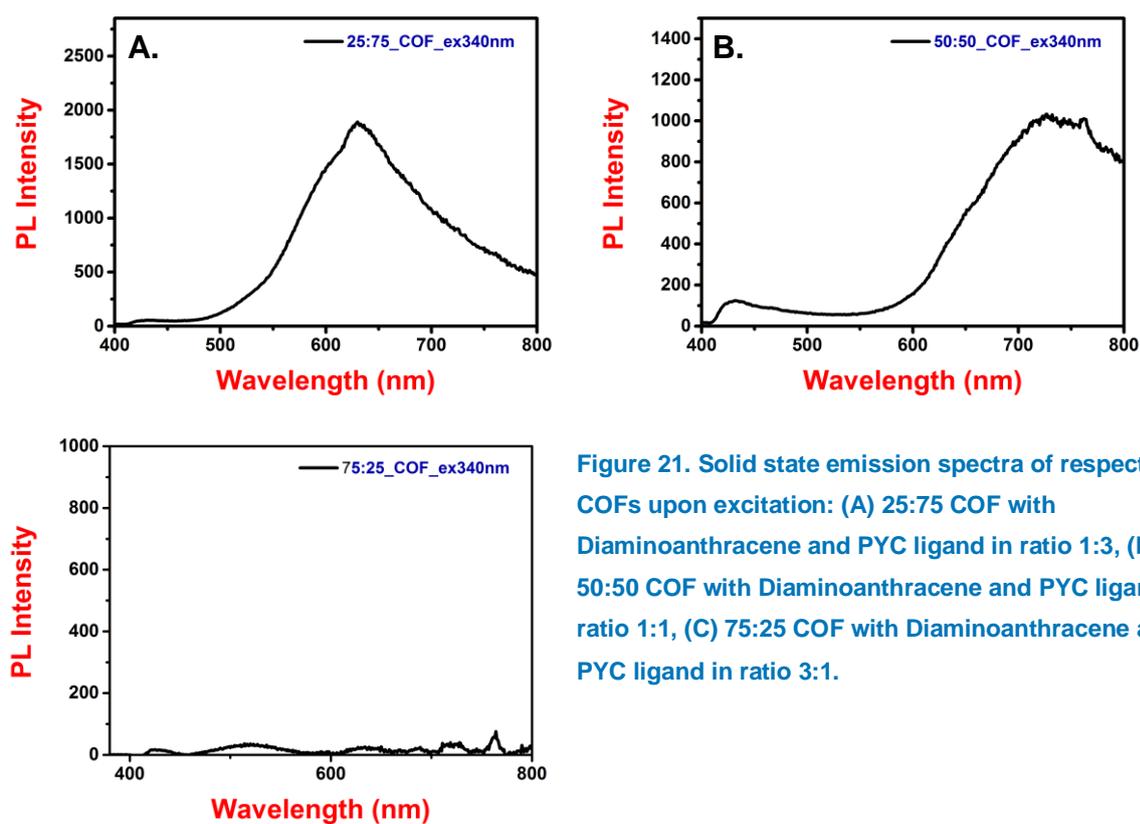


Figure 21. Solid state emission spectra of respective COFs upon excitation: (A) 25:75 COF with Diaminoanthracene and PYC ligand in ratio 1:3, (B) 50:50 COF with Diaminoanthracene and PYC ligand in ratio 1:1, (C) 75:25 COF with Diaminoanthracene and PYC ligand in ratio 3:1.

## **DISCUSSION**

Combining the results from the model compounds we find that with increasing the number of electron-rich groups in the aldehyde and amines the emission spectra shift towards the blue region, while the resorcinol/phenol/phloroglucinol type of units provide access to the yellow-red-orange part of the visible spectra. However, when this understanding is transported to the design of the COFs with tri formyl phloroglucinol as aldehyde and two different amines anticipating white light emission, the outcome is not so interesting. The COFs synthesized using this strategy show low solid-state fluorescence and non-white light emission in dispersion. From Figure 26, it can be observed that there are faint or weak peaks in the blue region and relatively intense peaks in the green-red region, however the blue region does not seem to have sufficient overlap with the latter. This could be the problem that needs to be addressed to introduce the missing WLE. Thus the white light emission from a single COF still needs manoeuvring and creative processing.

## **CONCLUSION**

The work shows how the fluorescence of the model compounds can be tuned to some extent by changing the type of aldehyde and amine. Also, the compounds synthesized show solution processability. The COFs so synthesized in anticipation of white light emission turned out to be not so effective solid-state fluorescent compounds. This is probably as a result of aggregation-induced self-quenching. Hence, synthesizing COFs with components capable of emission across visible spectra and without any problem of quenching still pose a challenge.

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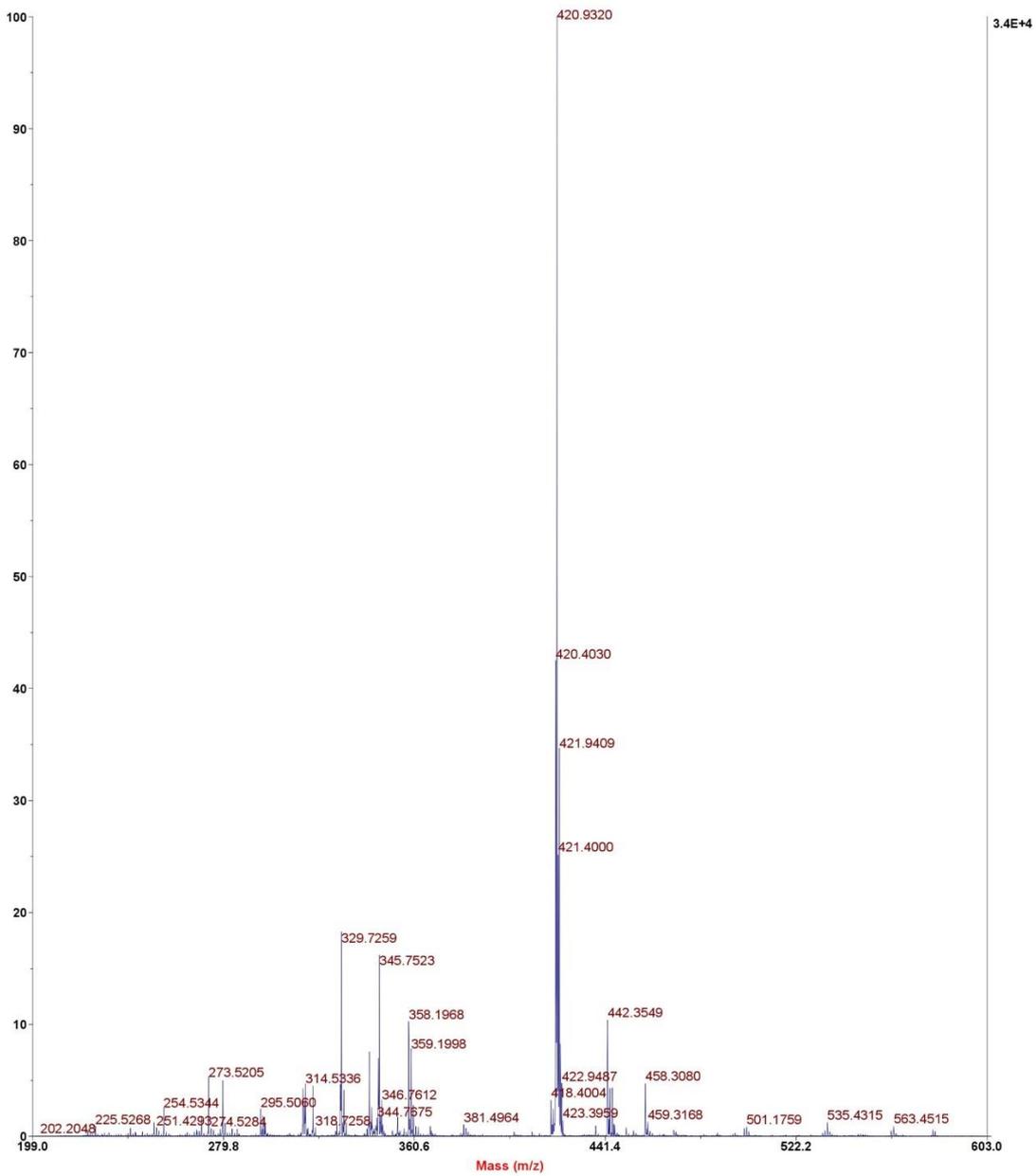
# APPENDIX

## A. MASS SPECTRA OF MODEL COMPOUNDS

### Spectrum Report

Final - Shots 400 - IISER-96-1-2019; Label D2

A.



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Figure A1. MALDI spectra of 1OHMC showing peaks at  $M = 404.93$  for the compound and  $329.72$  with loss of phenyl carbocation.

Spectrum Report

Final - Shots 400 - IISER-96-1-2019; Label D2

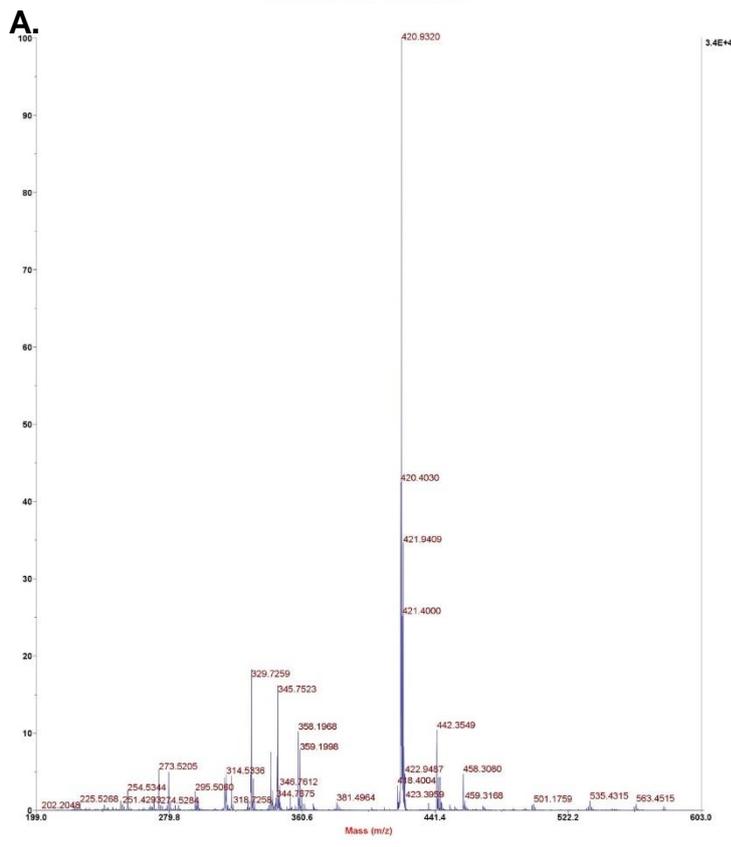


Figure A2. (A) MALDI spectra of 2OHMC showing peaks at  $M = 420.93.93$  for compound. (B) HRMS spectra of 2OHMC showing peaks at  $M = 420.1713$  for the compound and  $345.1243$  with loss of phenyl carbocation.

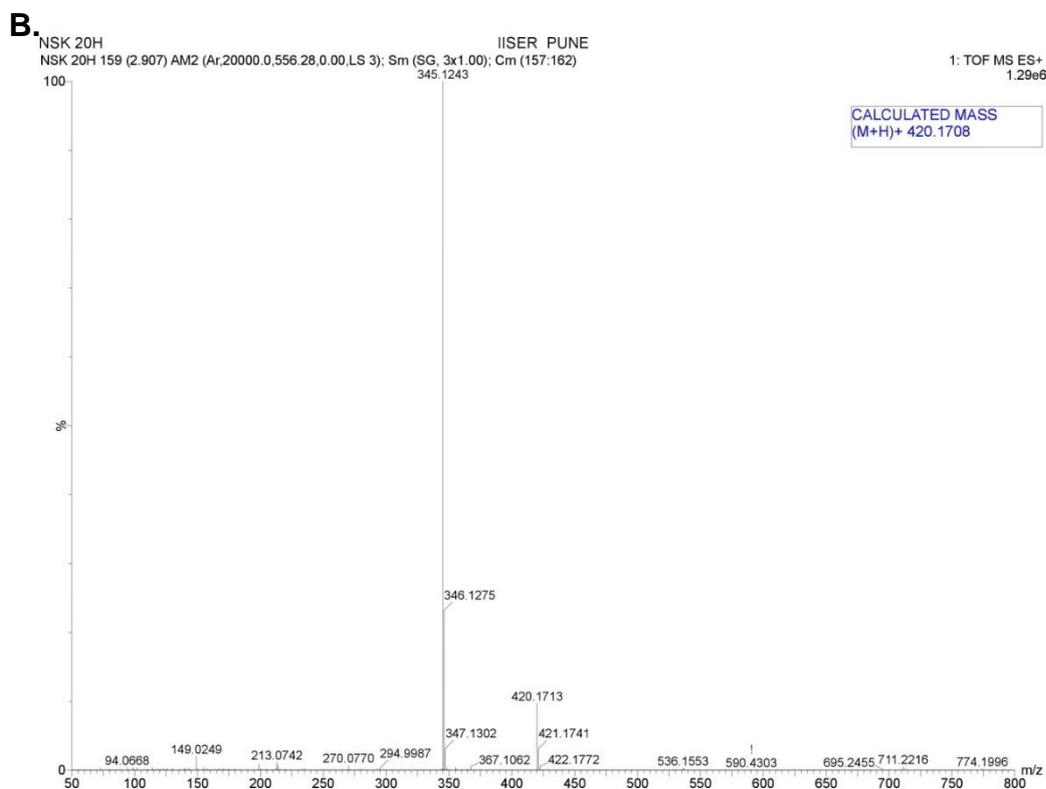
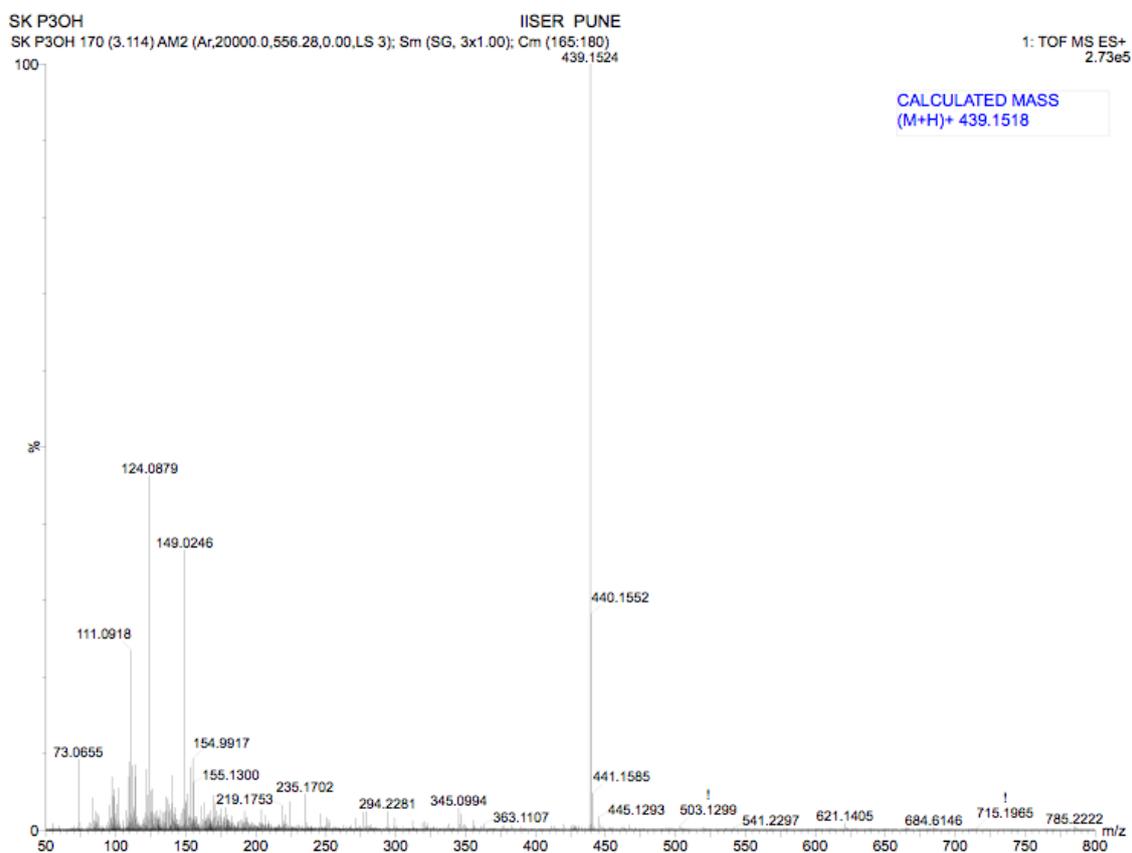




Figure A4. HRMS spectra of 3OHA model compound showing peak for compound at M = 439.1524.



## B. Synthesis and characterization of aldehydes

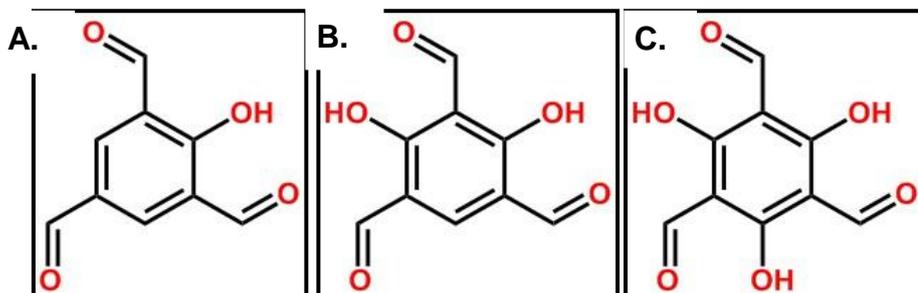


Figure A5. Aldehydes; (A) 2, 4, 6-Triformylphenol, (B) 2, 4, 6-Triformylresorcinol, (C) 2, 4, 6-Triformylphloroglucinol.

**a. Synthesis of 2, 4, 6-Triformylphenol:** To 6.9 g of phenol 70 mL trifluoroacetic acid (TFA) was added, then 20 g hexamine was added, and the resulting solution was refluxed at 120<sup>0</sup> C for 20 hours. After 20 hours the solution was heated at 150<sup>0</sup> C for 3 hours and cooled back to 120<sup>0</sup> C. To hydrolyze the compound 100 ml 3 N HCl was added, and the solution was heated at 102<sup>0</sup> C for 30 minutes followed by cooling, filtration and drying. The compound was recrystallized in dimethylformamide (DMF) and characterization was done using <sup>1</sup>H NMR and Fourier transform infra-red (FT-IR) (Figure A6) studies [10].

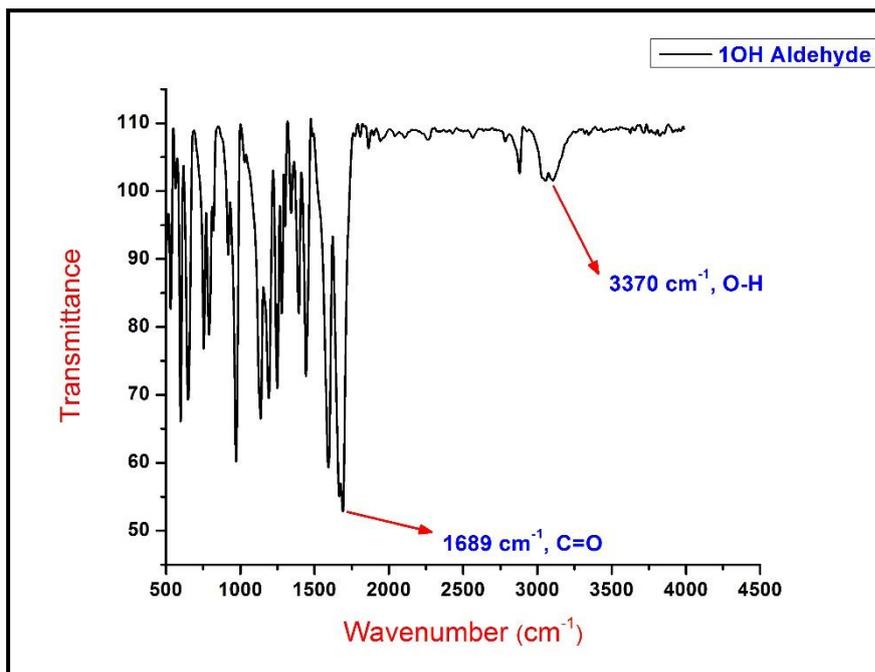


Figure A6. FT-IR spectra of the triformylphenol showing peaks due to carbonyl (C=O) stretching frequency (1689 cm<sup>-1</sup>) and enolic OH (3370 cm<sup>-1</sup>).

**b. Synthesis of 2, 4, 6-Triformylresorcinol:** To 7.16 g of resorcinol 70 mL TFA was added, then 20 g hexamine was added, and the resulting solution was refluxed at 120<sup>0</sup> C for 24 hours under N<sub>2</sub> atmosphere. After 24 hours the solution was heated at 15<sup>0</sup> C for 3 hours and cooled back to 120<sup>0</sup> C. To hydrolyze the compound 110ml 3N HCl was added, and the solution was heated at 105<sup>0</sup> C for 30 minutes followed by cooling, filtration and drying. The compound was recrystallized in DMF and characterization was done using <sup>1</sup>H NMR (Figure A7) and FT-IR (Figure A8) studies [11].

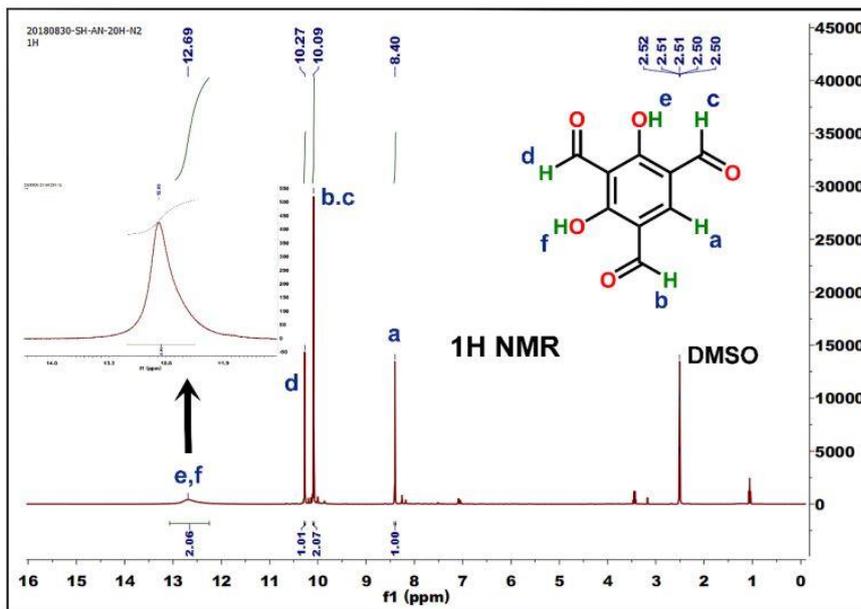


Figure A7. <sup>1</sup>H-NMR of 2, 4, 6-Triformylresorcinol was recorded in deuterated Dimethylsulfoxide (DMSO-d<sub>6</sub>) at room temperature. Chemical shifts of <sup>1</sup>H-NMR at δ = 2.45ppm is from DMSO-d<sub>6</sub>. Atoms of the triformylresorcinol corresponding to the specific peaks are marked in the insets.

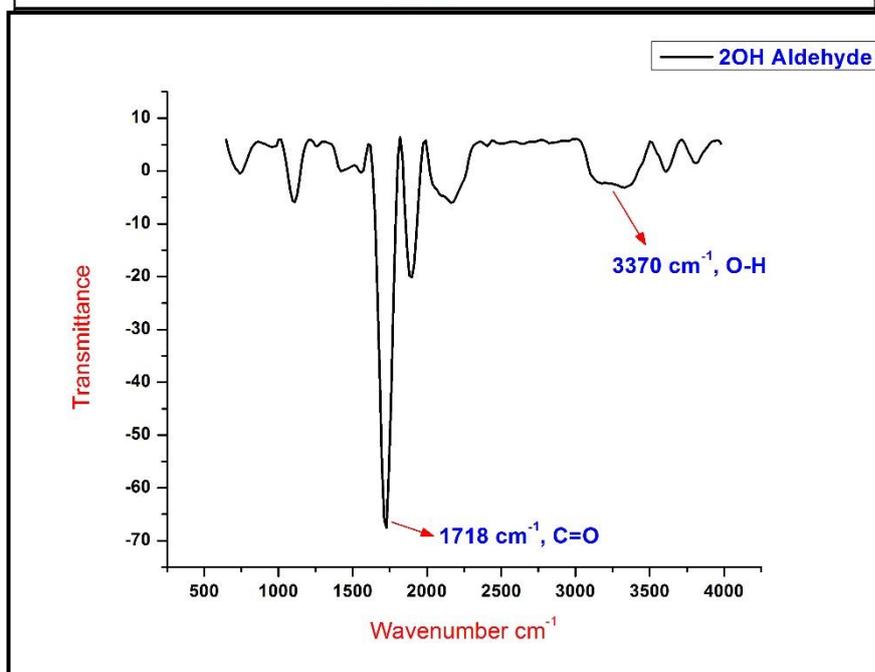


Figure A8. FT-IR spectra of the triformylresorcinol showing peaks due to carbonyl (C=O) stretching frequency (1718 cm<sup>-1</sup>) and enolic OH (3370 cm<sup>-1</sup>).

**c. Synthesis of 2, 4, 6-Triformylphloroglucinol:** To hexamine (15.098 g) and dried phloroglucinol (6.014 g) 90 mL trifluoroacetic acid was added under N<sub>2</sub> atmosphere. The resulting solution was heated at 100° C for 2.5 h. To hydrolyze the compound 150 mL 3N HCl was added with heating at 100° C for 1 h. After cooling at room temperature, the compound was filtered through celite. The resulting filtrate was extracted using 350 mL dichloromethane and dried over magnesium sulfate and then filtered. The solvent was evaporated by rotary evaporation, giving off-white compound. The compound was recrystallized in DMF and characterization was done using <sup>1</sup>H NMR (Figure A9) and FT-IR (Figure A10) studies [11].

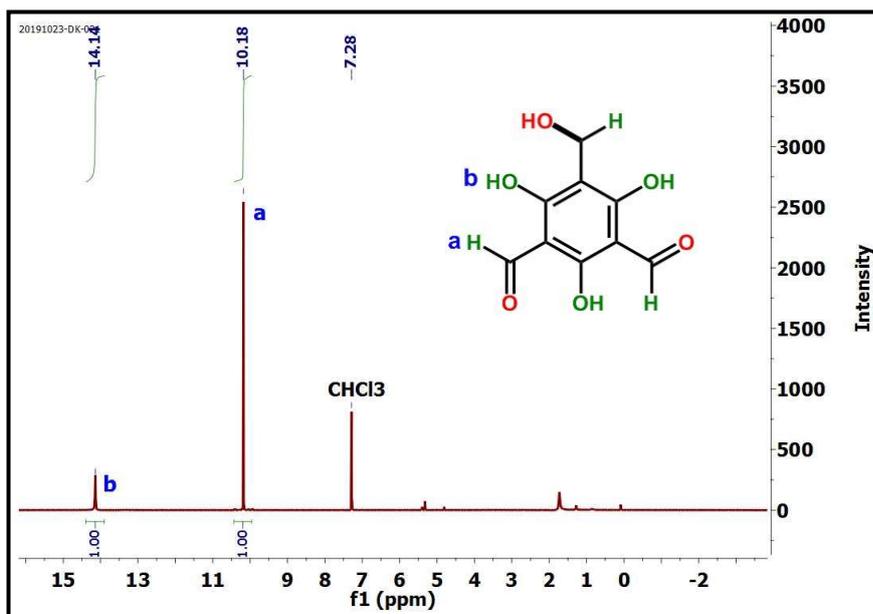


Figure A9.  $^1\text{H-NMR}$  of 2, 4, 6-Triformylphloroglucinol was recorded in Chloroform-D ( $\text{CDCl}_3$ ) at room temperature. Chemical shifts of  $^1\text{H-NMR}$  at  $\delta = 7.3\text{ppm}$  is from  $\text{CHCl}_3$ . Atoms of the triformylphloroglucinol corresponding to the specific peaks are marked in the insets.

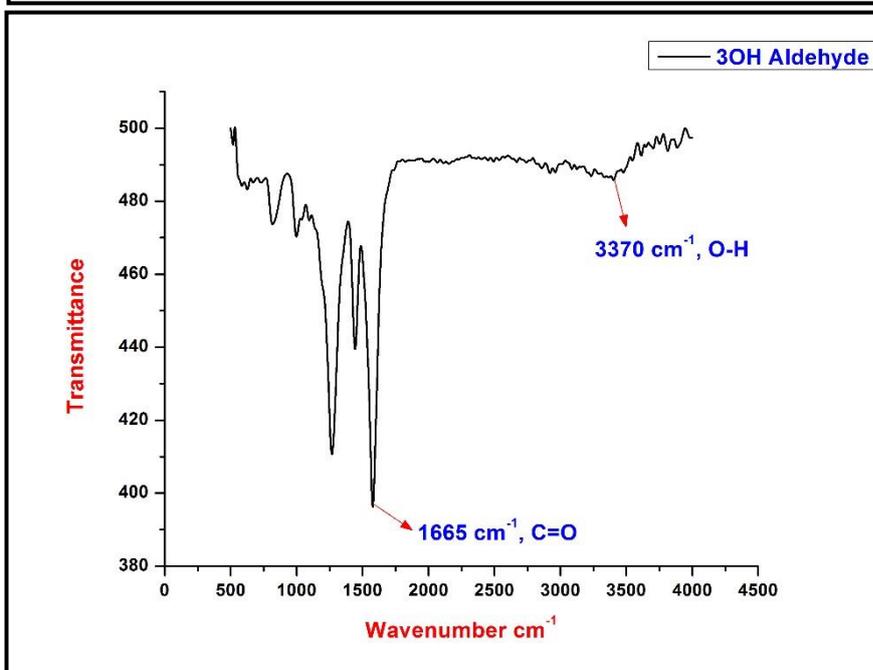


Figure A10. FT-IR spectra of the triformylphloroglucinol showing peaks due to carbonyl ( $\text{C=O}$ ) stretching frequency ( $1665\text{ cm}^{-1}$ ) and enolic OH ( $3370\text{ cm}^{-1}$ ).