

Design, Synthesis, Characterisation and Host-Guest Interaction Studies of π -Stacking Self-Assembled Porous Organic Framework

A Thesis submitted to
Indian Institute of Science Education and Research Pune
in partial fulfillment of the requirements for the
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Certificate

This is to certify that this dissertation entitled “Design, synthesis, characterisation and host-guest interaction studies of a π -stacking self-assembled porous organic framework” towards the partial fulfilment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents original research carried out by Amitosh Sharma at IISER Pune under the supervision of Dr. Sujit K. Ghosh, Assistant Professor, Department of Chemistry during the academic year 2011-2012.

Signature of student:

Signature of supervisor:

Date:

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Declaration

I hereby declare that the matter embodied in the report entitled “Design, synthesis, characterisation and host-guest interaction studies of a π -stacking self-assembled porous organic framework” are the results of the investigations carried out by me at the Department of Chemistry, IISER Pune, under the supervision of Dr. Sujit K. Ghosh and the same has not been submitted elsewhere for any other degree.

Acknowledgment

There are many people who I would like to thank for the achievement for this endeavour.

First and foremost, I would like to thank my family for their blessings and for believing in me. All success that I have ever achieved can be directly traced back to them.

With great pleasure, I wish to place on record my profound gratitude and indebtedness to Asst. Prof. Sujit K. Ghosh for giving me the opportunity to work on a fascinating research project and for keeping his door open for discussion at any time. He never settled for anything less than the best. Hence, he could bring out the best in me.

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This thesis is dedicated to my parents, Mr. Hemant Sharma and Mrs. Shashi Sharma, and also Abhijeet Chaudhari.

ABSTRACT

Two naphthaldehyde based fluorescent Schiff bases were designed and synthesised successfully. 2-hydroxy naphthaldehyde and 2-methoxy naphthaldehyde were used for the reactions among which we successfully crystallised the one made with former one. The crystalline structure analysed by single crystal X-ray diffraction study which revealed a chiral non-centrosymmetric space group Trigonal $R3c$ having the polar point group C_{3v} . This is an unusual highly pi-stacked organic discrete framework with six-fold quadrupolar helical arrangement. The single left handedness of the helix was supported by the solid state Circular Dichroism (CD) measurement showing the negative cotton effect and also the Flack parameter of 0.23 is a strong statistical Single Crystal X-Ray Diffraction (SC-XRD) analysis evidence of single handed helical structure. The crystalline form contains the trapped solvent guest molecules i.e. DMF, Acetonitrile and some water molecules making the capsule shaped void with small opening apertures to the surfaces. This is a stable pi-stacked framework up to the 225°C showed no porosity with 8.5 ml of CO₂ uptake at 195 K. It showed a potential fluorescence enhance properties when interacting with electron rich aromatic guests and quenching with electron deficient Nitrobenzene, which make it a promising material for detail exploration of its sensing ability of nitro-explosives.

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Introduction

In the past few years, porous solids either organic based or framework made up of metal and organic linkers i.e. metal-organic frameworks (MOF) specially received extensive importance because of its diverse structural topologies and extensive wide applications. Metal-organic frameworks (MOFs) are a special class of zeolite-like material and are synthesized using ionic or neutral organic ligands and metal ions. MOFs show specific properties such as gas sorption, chemo sensing, heterogeneous catalysis, magnetic, fluorescence, NLO properties and conducting properties. The porous frameworks of MOFs have pores and internal surfaces with high surface area which provides the opportunity for themselves to interact with different guest molecules through hydrophilic, hydrophobic, and electrostatic interactions. The interaction is mainly decided by the type of functional groups present inside the framework. Some other important uses of these multifunctional MOFs are ions detection, gas sensing, separation, and detection of nitro aromatic explosives. The popularity of MOFs is due to the ease of their synthesis based on the self assembly of metal cations with organic linkers having divergent coordinating groups. Another interesting characteristic of this class of materials is their crystallinity which allows for their structural characterization by diffraction methods, thus facilitating their rational design. So it is easily possible to design new frameworks with tailored functionalities with variety of topologies. If the MOF is binding a particular molecule in the porous moiety of the framework, one can prefer a structural motif and then modify the starting ligands to fabricate other properties of this particular MOF by attaching specific functional groups. If post crystallisation changes are not affecting the binding modes of the ligand to the metal, the MOF can be grown further and have the required functionality known as post-synthesis modification. MOFs acts as ideal candidates as heterogeneous catalysts by simultaneously having porosity and catalytic sites. But reactions that can be heterogeneously catalysed by MOFs are limited because of moderate hydrolytic and thermal stabilities of MOFs. Synthesis of chiral porous MOFs that are used for asymmetric catalysis are of great importance because of its high selectivity. These

types of MOFS are synthesized under mild conditions and in aprotic solvents. Chiral MOFs which are used for asymmetric catalytic reactions must possess large nanometer-scale open channels for transport of sterically demanding products and substrates.

For the sensing of small molecules and ions, a few micro-porous luminescent lanthanide MOFs are synthesized. They have free open metal sites and Lewis basic pyridyl sites for recognition of small molecules. So when particular molecule or ion binds to MOF, fluorescence intensity is either quenched or increased. If these types of MOFs are stable in biological environment, they can be of great importance in drug delivery applications. In the past five years of this research field, number of reports has increased tremendously. The scope of research is also ever-expanding and great research has been done. Understanding the underlying geometric principles of synthesis of MOF is very important. Therefore by deconstructing crystal structures of MOFs into their respective topological nets, O'Keeffe and Yaghi¹ has created an approach for subsequent design and description of MOF structures.

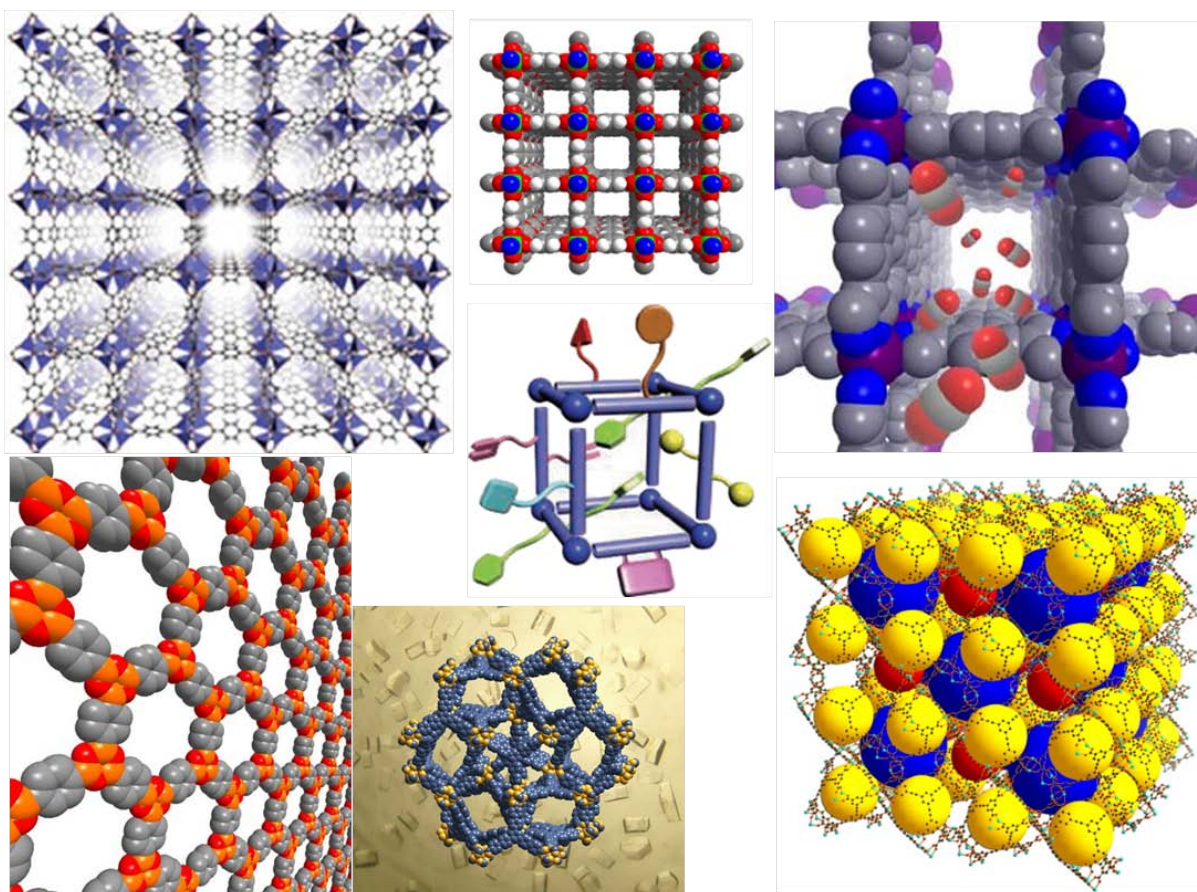


Figure 1:- Some examples of metal organic frameworks^{4,6,15}.

MOFs have been very important for the storage of gas and great results have been achieved. First recent computational studies for the adsorption of methane, acetylene, and hydrogen within MOFs has been summarized by Snurr and co-workers². In recent years, carbon dioxide capture has been very important because of environmental protection and clean energy. So, related work has been done by Long and co-workers³ using MOFs to reduce emissions of carbon dioxide from coal-fired power plants via post combustion capture, pre combustion capture, or oxy-fuel combustion routes. In the article, Kitagawa⁴ and their group synthesized flexible porous coordination polymers having amide group as spacer and bispyridyl as a ligand which gave two-dimensional (2-D) motif with a deformed square grid. These square grid results in three dimensional (3-D) frameworks in which 2-D motifs are connected via complementary hydrogen bond amongst the amide groups. These polymers show very high porosity for the gas adsorption. For hydrogen to be used as energy fuel, storage of hydrogen is a key technology. In the recent review Suh⁵ and

co-workers classified respective MOFs explored for hydrogen storage and discussed problems and prospects of utilizing MOFs for this application. Adsorption of hydrocarbons in MOFs is discussed by Li⁶ and co-workers with emphasis on “commensurate” adsorption, which means the adsorption and packing of guest molecules in the pores of host with perfect matching in orientation and size. Finally great work on selective adsorption and separations of many liquids and gases is done by survey of Li, Sculley, and Zhou⁷. Synthetic-method development is considered as an important role for the advancement in this field. Stock and Biswas⁸ provided different synthetic methods, which includes some basic methods like microwave, electrochemical, mechanochemical, ultrasonic, and high-throughput syntheses. Also Bétard and Fischer⁹ reviewed the intensively growing literature on the preparation, characterization, and potential application of MOF films, which show applications in catalysis, membrane separations, and sensing. Synthesis, principles and examples of MOFs showing second-harmonic generation that is used in nonlinear optics is done by Lin¹⁰ and co-workers. In a recent review by Allendorf, Hupp and co-workers¹¹ explained about the MOF as a functional material for chemical sensing. They highlighted about solvatochromism/vapochromism, interferometry luminescence-based sensing, localized surface plasmon resonance, colloidal crystals, and electromechanical sensors, and impedance spectroscopy. Qian, B. Chen¹² and co-workers presented emphasis on analyzing the origin of MOF luminescence, and explored their potential applications. Zhang and Xiong¹³, in their article, highlighted on ferroelectric MOFs and considered a new class related to this type of material with improvement in synthesis and filling a gap between pure organic and inorganic ferroelectrics. Finally, Horcajada, Serre, and co-workers¹⁴ explored advantages for adsorption purpose and release of drugs. Here, the biostability nature of MOF can be enhanced having proper choice of the metal, organic linker and structure.

In contrast, or the same line of these application approach the other class is of porous organic framework (POFs) consists of extended organic structures synthesized mostly by self assembled methodology. These types of compounds are porous and crystalline and are entirely made up of light elements like hydrogen, carbon, nitrogen, boron, and oxygen. Such systems consist of crystalline covalent

organic frameworks (COFs) constructed by strong covalent bonds, amorphous porous organic coordinated polymers (PCPs), and supramolecular organic assemblies held together through weak non covalent interactions like π - π stacking interactions and hydrogen bonds. These types of solids have rigid structure with high thermal stabilities (temperatures up to 500-600°C) and low densities as compared to MOFs. They exhibit very high permanent porosity having specific surface areas which are surpassing those of known zeolites and porous silicates. Porous organic frameworks are much lighter than MOFs making them special for storage, separations, and sequestration of tiny molecules. Because of the reduced density of these type of materials compared to MOFs, they have demanding utility as gas storage. Initially porous organic frameworks were thought important only for gas storage and molecules sensing purpose. But they have diverse use in present world. Till date adsorption and storage of carbon dioxide and hydrogen gas have been of great importance. Wei Zhang and his co-workers¹⁵, in their paper, synthesized some organic framework and studied the properties that decide carbon dioxide selectivity.

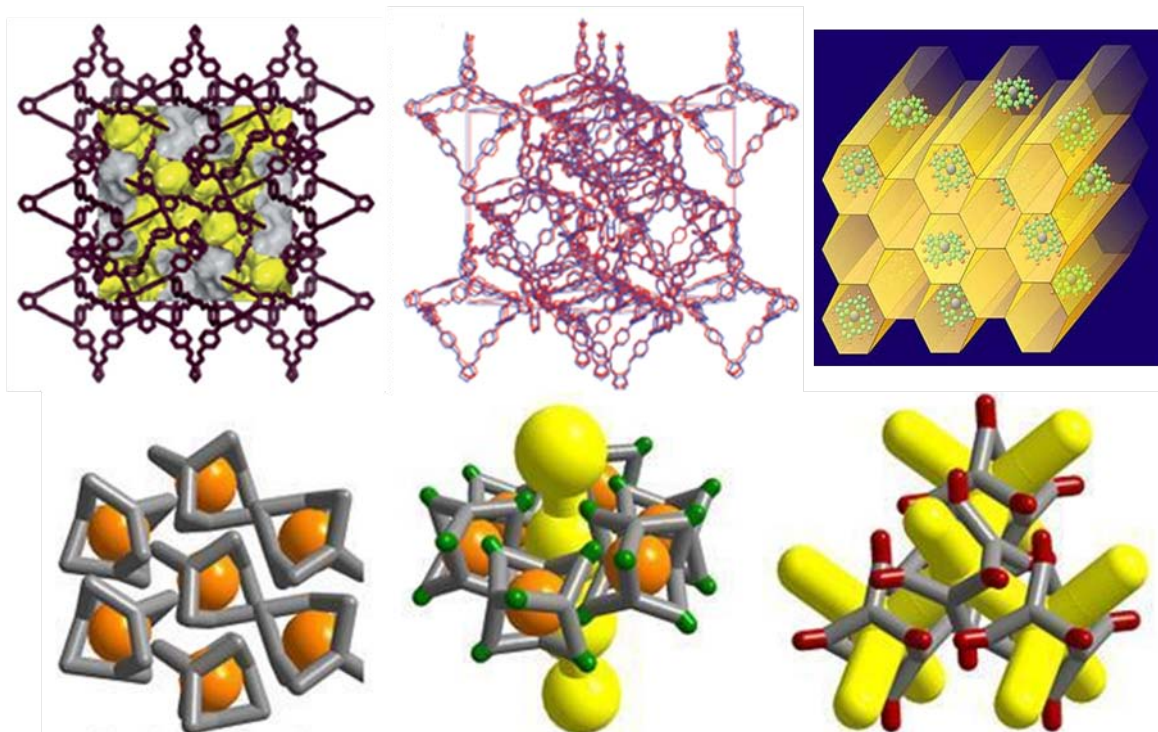


Figure 2:- Few examples of porous organic frameworks^{15,16,17}.

Through Gas adsorption studies they concludes that the high selectivity is not only because of amino group density (mol/g), but also due to the intrinsic pore size of the cage (distance between the bottom and top panels), which can be tuned by choosing building blocks of appropriate size . Not only the absorption of carbon dioxide or hydrogen gas, but also adsorption of many other ions has have been achieved. Andrew I. Cooper¹⁶ and his co-workers have demonstrated in their article how one can synthesis organic frameworks which can adsorb even large size molecules. They doped porous single crystals via vapour sublimation to produce diamond like arrangements of guests such as I_5^- and OsO_4 , which leads to noticeable conductivity enhancement in the case of I_5^- . In an article by Linda S. Shimizu¹⁷, they have synthesized self assembled porous organic framework which provides a robust confined reaction environment or the highly selective [2+2] cycloaddition of an unsaturated Ketones within itself, which forms their respective exo head-to-tail dimers in high conversion.

Sometimes the crystal we get are not stable and even we have porosity doesn't account for use. So a lot of work has been done to gain high stability. Similar work has been done in a paper by John J. Lavigne¹⁸ and his group. They studied about the stability and properties of two-dimensional boronate ester-linked organic frameworks when exposed to aqueous environment. They observed increased stability for frameworks with alkylation in the pores as compared to non-alkylated one. One of the greatest works presented in this field is the use of porous organic frameworks for the gate like systems which have taken chemistry to the frontiers of the nano-science. In the article by Joan Cano¹⁹, they have synthesized mesoporous materials having suitable polyamines on the pore outlets. They observed open/close mechanism which arises because of the hydrogen-bonding interaction between amines at neutral pH (open gate) and Coulombic repulsions at acidic pH (closed gate). This work can be of great use for the purpose in biological as well as circuit purposes. Getting porous frameworks using biological molecules has been of great importance. These frameworks can be use for drug delivery work because of high stability in biological environment. They produced micro porous protein crystals

which can attain chemical and mechanical stability and are capable of separating small molecules by size, chirality and chemical structure.

For the chemo sensing purpose like anion/cation sensing, biomolecular sensing etc., material must possess some special features in it. In past few years the field of anion coordination chemistry has expanded largely with new synthesized molecules having capability of recognizing anions with environmental and biomedical importance. The first synthetic anion receptor was reported in 1968 by Park and Simmons in a journal (seminal communication). Because of the diverse use of anions receptor systems, it has gained much importance. Some of the basic fields where anion receptors are being used are environmental remediation, sensor development and the selective extraction and separation of chemical species. Anions are considered as essential components of biological systems. Chloride ion proves to be an important electrolyte in maintaining potentials across cell membranes.

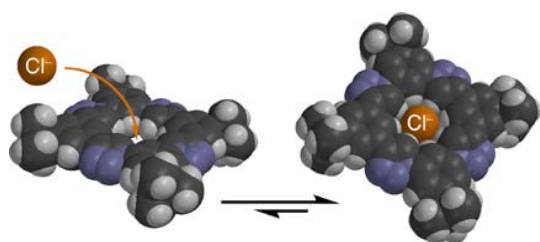


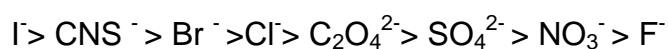
Figure 3:- Selective recognition of Cl^- ion in an organic discrete moiety.

Selective binding of the receptor to chloride ion can help in maintaining potential across membranes. Also sulphate ion plays an important role in biological systems and disease, hydrometallurgy and as a pollutant. Similarly, there are many other anions which have their own role of importance in

general science. Therefore, various synthetic receptors have been made that employ hydrogen bonds offered by special binding sites as in azamacrocycles²⁰, amides²¹, thioamide²¹, urea²², and pyrroles²³ to bind selective anions with various size and shape in different medium. For this chemo sensing ability the luminescent probes are of much interest.

One of the important uses of porous organic framework is the detection of many compounds using fluorescence properties. Fluorescence is a phenomenon of radiative emission from S_1 to S_0 state. A fluorophore can be used to detect many different compounds using fluorescence quenching concept. Fluorescence quenching by molecules of the same type is called self-quenching and quenching by some another added substance is called impurity-quenching. In bimolecular reactions, including quenching, inhibition of emission is seen because bimolecular

collisions frequency either in gas or solvents can compete with fluorescence emission. Solvent quenching is mainly by solvent-solute interactions, but also depends on other physical parameters. Impurity quenching caused by adding another substance with fluorophore generally occurs either by Charge Transfer mechanism or Energy Transfer mechanism. In the case of former mechanism fluorophore and added substance interact having some charge transfer process and a complex is formed (Exciplexes). Here the fluorescent spectrum is changing but absorption spectrum remains as it is. For instance emission from DNA is due to excimer formation between associated bases. Many fluorophores are quenched by ions in the given order:



This relation is because of the increasing ionization potential which indicates that quenching by these ions depends on the ease by which they can have charge transfer. Fluorescence has proved to be an important tool for the sensing purposes and has been used for the detection of many ions and compounds. In our research we synthesised helical structured fluorescence probe that can be used for detection purpose. Methods of detection include metal detectors basically ineffective toward plastics, and trained canines having high expenses due to training and care. Other methods such as X-ray dispersion, nuclear quadruple resonance, and mass spectrometry, require large, expensive instrumentation having difficulties in the producing portable devices. Transduction methods including absorption, conductivity and fluorescence are being used because of their high sensitivity but selectivity for aromatic and aliphatic nitro compounds is still a challenge for sensor studies. Special deal against the anti terrorism and environmental aspects requires a promising fluorescent probe which can easily and selectively detect the nitro-explosive compounds. Because most of the explosives contains trinitrotoluene and dinitrotoulene as the basic component, also some chemical taggants required in plastic explosives have 2,3-dimethyl-2,3- dinitrobutane (DMNB). So the detection of nitro-aromatic/aliphatic compounds is of considerable importance. These compounds mainly rely on electron-rich aromatic rings that can have π -stacking with the electron-poor nitro-aromatics for effective binding. Therefore when these frameworks bind to guest these frameworks sensors are quenched by electron transfer with the

bound nitro-aromatics and causes fluorescence change. So keeping in mind that fluorescence quenching based sensing is a much easy and highly sensitive technique. Mukherjee²⁴ and co-workers synthesized highly luminescent small sized fine particles of a Zn(II) metal organic framework (MOF) of special pi-electron rich tricarboxylate which work as a selective sensory material for the detection of nitro-aromatic explosives through fluorescence quenching mechanism. So they concluded that electron donor conjugated MOFs have excellent capability for the detection of nitro-aromatic explosives. One of the important achievement using organic frameworks for sensing has been demonstrated by Tetsuo nagano and others. Based on the provided facts that the azo functional group has shown excellent properties as the hypoxia-sensor moiety they demonstrated the synthesis of hypoxia-sensitive near-infrared fluorescent probe in which an increase is seen in fluorescence when an azo bond is cleaved. These probes were used as fluorescence imaging of hypoxic cells and also in the liver and kidney of live mice as a real-time monitoring of ischemia.

Another important feature of our study is the supramolecular helical assemblies. Many important organic frameworks with helical structures having its unique



Figure 4:- Some common helical structures of DNA.

properties have been reported²⁵. Helical structures via self-organization are of great interest in supramolecular chemistry because helical structures are reminiscent image of DNA molecules and are considered to be an essence of life.

Helical and homochiral structures seem to be everywhere in nature and are important to various biological functions. Natural existing bio-products such as DNA, RNA and proteins have achieved a definite helical sense (e.g., right handed R-helix)

related with the homochirality of their components (e.g., L-amino acids and D-sugars). Biopolymers have commonly observed phenomenon showing

conformational polymorphism of helical structures and is of significant interest indicating polymorph framework can lead to various physicochemical functions and properties but the influential physical principles providing conformational polymorphism still remain poorly understood. Chemists have put many efforts to relate helicity into synthetic systems. Especially the study of supramolecular helical frameworks that have the significant potential of undergoing conformational reversible changes influenced by external stimuli having structural comparability with those of natural biopolymers are of great importance in having new insight view of the parameters that affects the foldability of a backbone. Also they help in preprogramming the molecules to give specific frameworks and required functionality. With a very few exceptions, however, the artificial polymers fold into one or two helical conformations, and no more conformational polymorphism has been observed for helical organic polymers. Currently centre of attraction are coordination polymers that rely on monomer units which are held together by coordinative bonds because of their significant applications in catalysis, sensor, enantioseparation and photonics. Very few helical structures having multiple strands have been reported including quadruple-stranded helical architectures containing two pyridine units with HgCl_2 reported by Mir Wais Hosseini²⁵ and co-workers.

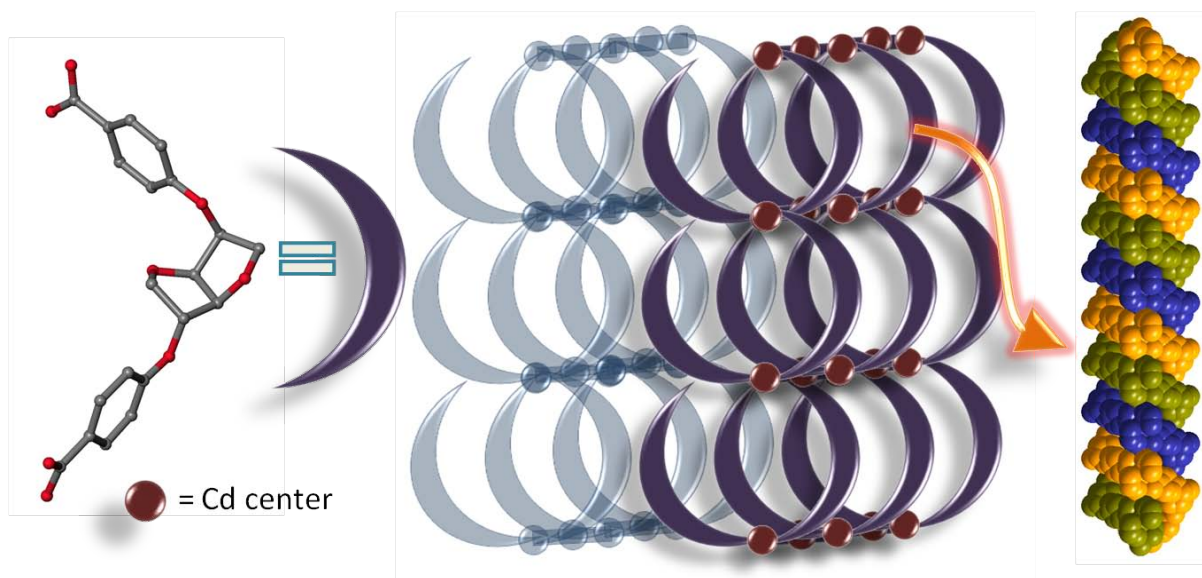
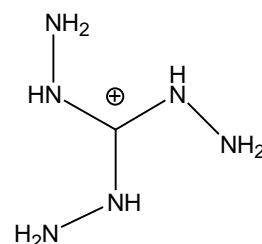
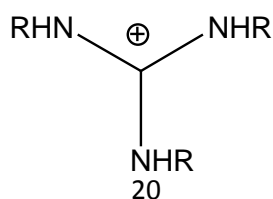
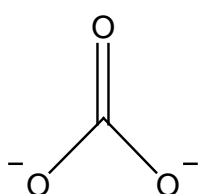


Figure 5: Schematic diagram of triple helix of Cd(II) based MOF

Recently, adding to the same library of chiral frameworks our group has reported a triple helical 2D metal organic framework based on Cd as metal centres and the D-isosorbide based dicarboxylate as an organic linker²⁶.

Henceforth a designing of such supramolecular assemblies for their special applications is of great importance. Mostly, two different ways are considered for subdividing the rapidly growing field of supramolecular chemistry. One is classified as the products that can be formed namely polymers or discrete cages. The other way depends on the molecular building units specifically on the properties of the participating ligands. Up to now, the use of asymmetric or C_2 symmetric ligands are predominant and despite their high potential, very few C_3 symmetric ligands²⁷ or ligands having higher symmetry have been used for supramolecular coordination chemistry. In normal, the C_3 -symmetric ligands can be considered as special category namely triangular building blocks. The smallest possible C_3 symmetric ligand is the carbonate dianion (Scheme 1, a). The guanidinium cation, which is considered isoelectronic with carbonic acid (Scheme 1, b; R = H), is capable of forming be metal complexes and can be modified chemically with ease. A possible synthetic way of producing more stable products is to introduce the stabilizing chelate effect to use as in the case of the triaminoguanidinium cation (Scheme 1, c).. And also if these structures also contain a donor atom, a tris (chelating) ligand with three-fold symmetry will be formed. These types of ligands can be used to bind three metal centres. Mainly the preferred co-ordination geometry of the metal centres determines the number and position of other introduced ligands. With the help of this strategy, different types of complexes, from monomeric species to cage-like compounds with the outer shape of a doughnut, a tetrahedron and an octahedron, can be prepared. With this goal in mind, we present here the synthesis and characterization of tris (2-hydroxynaphthalidene) triaminoguanidinium chloride and tris (2-methoxynaphthalidene) triaminoguanidinium chloride and its applicable studies using their highly π -stacked ordering in crystalline form and luminescent character.

Scheme 1:

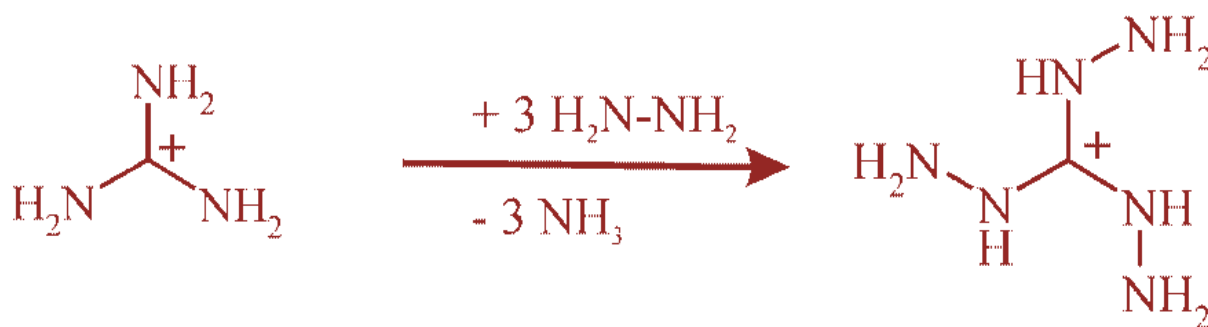


Synthesis and Characterization

Synthesis of triaminoguanidinium chloride:

To the slurry of guanidine hydrochloride (5g, 0.0523mol) in 1,4-dioxane (30ml) was added hydrazine monohydrate(12.0ml,0.3148mol) with stirring. The mixture was heated at 70⁰ C under reflux for 2 hours. After the cooling of mixture to the ambient temperature, the product was filtered. After that the product was washed with 1,4-dioxane, and dried under reduced pressure to give pure Triaminoguanidinium hydrochloride. The product was having white shining amorphous form. Experimental yield was 96 %.

Reaction Scheme 2:



NMR ^{13}C :

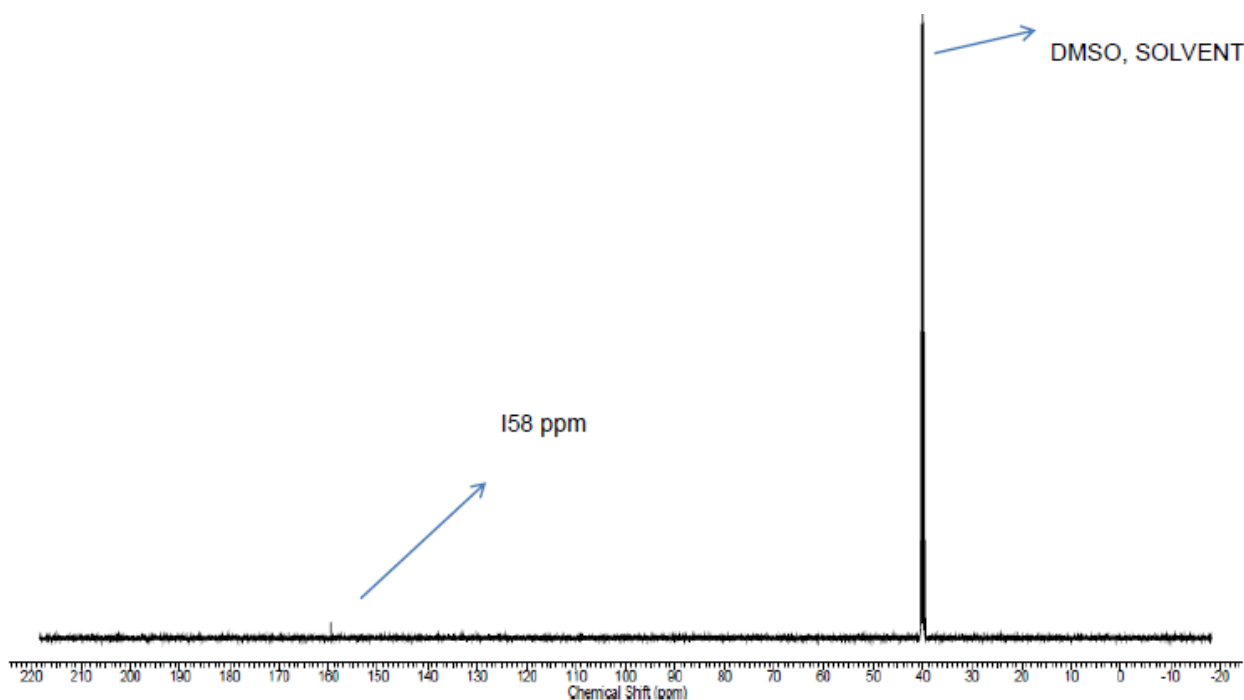


Figure 6: C^{13} NMR of triaminoguanidinium chloride

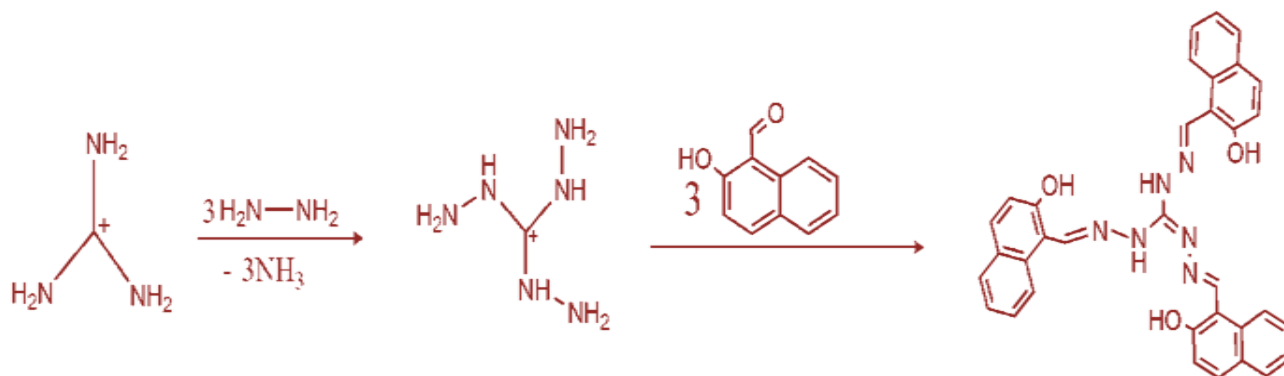
Analysis of the above figure tells us that single peak at 158 ppm confirms the existence of carbon having sp_2 hybridisation.

Synthesis of tris (2-hydroxynaphthalidene) triaminoguanidinium chloride:

Triaminoguanidinium chloride (2g, 0.019mol) was dissolved in a hot mixture of ethanol (30mL) and water (15mL). After adjusting the pH to the value of 3 with $\text{HCl}(\text{aq})$, the solution of 2-hydroxynaphthaldehyde (10.4g, 0.060mol) in methanol (10mL) was added slowly. The solubility of 2-hydroxynaphthaldehyde in methanol was a problem, therefore addition of 2-hydroxynaphthaldehyde was done at high temperature and its solution in methanol was directly added from high temperature. The resulting solution was heated under reflux at 90°C for 6 hours having nitrogen atmosphere. The suspension formed, was then allowed to cool to room temperature.

The reaction mixture then kept for overnight stirring and the crude product was then washed with aqueous methanol solution, collected, and kept under reduced pressure condition to give pure product. Experimental yield was 95%.

Reaction Scheme 3:



PROTON (^1H) NMR:

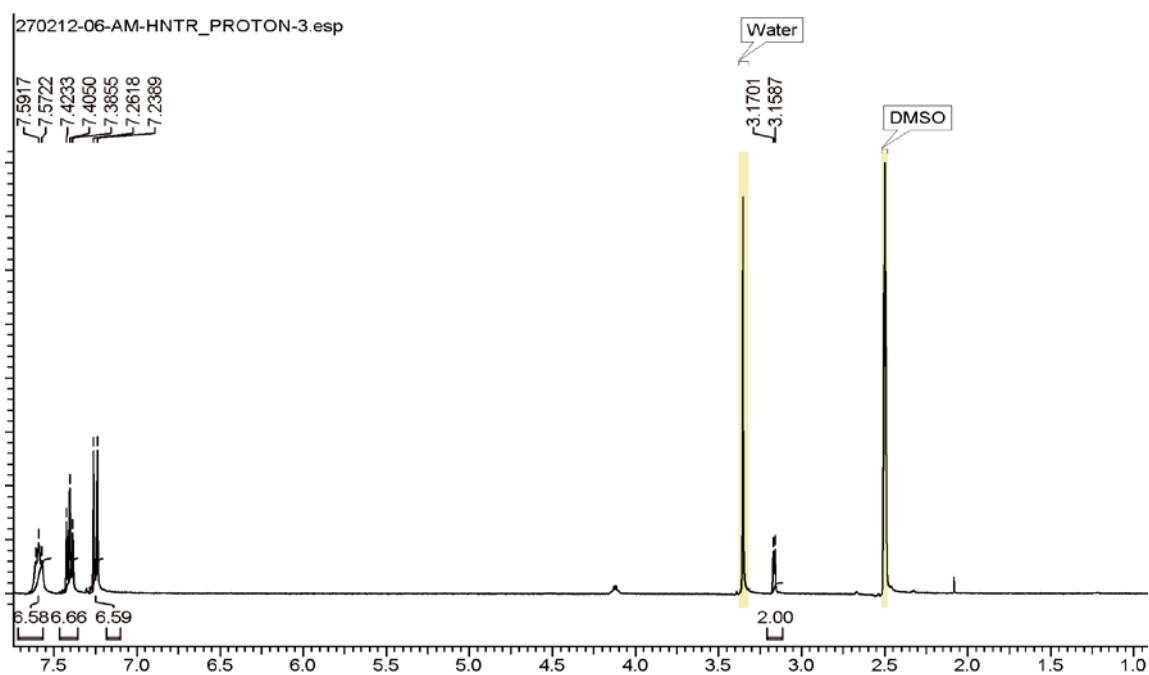


Figure 7: Proton NMR of tris (2-hydroxynaphthalidene) triaminoguanidinium chloride

MASS:

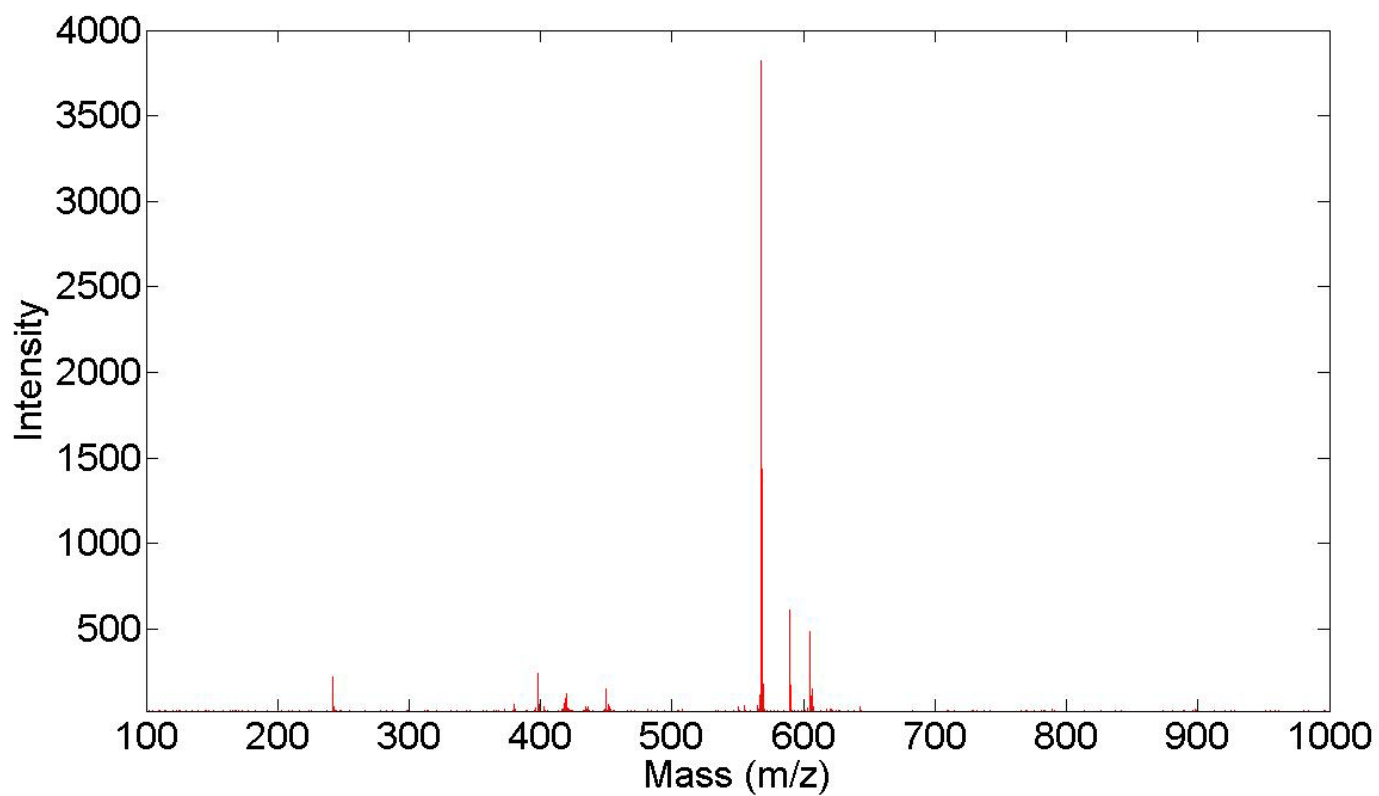
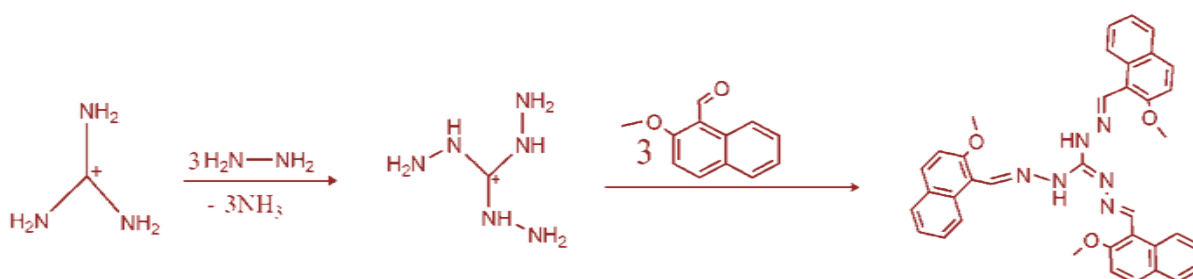


Figure 8:- Mass spectrum of tris (2-hydroxynaphthalidene) triaminoguanidinium chloride

Synthesis of tris (2-methoxynaphthalidene) triaminoguanidinium chloride:

Triaminoguanidinium chloride (2g, 0.019mol) was dissolved in a hot mixture of ethanol (30mL) and water (15mL). After adjusting the pH to the value of 3 with HCl(aq), the solution of 2-methoxynaphthaldehyde (12g, 0.060mol) in methanol (10mL) was added slowly. The solubility of 2-methoxynaphthaldehyde in methanol was a problem, therefore addition of 2-hydroxynaphthaldehyde was done at high temperature and its methanolic solution was added slowly at high temperature. The resulting solution was heated under reflux at 90°C for 6 hours under nitrogen atmosphere. The suspension formed, was then allowed to cool to room temperature. The reaction mixture then kept for overnight stirring and the crude product was then washed with aqueous methanol solution, collected, and kept under reduced pressure condition to give pure product. Experimental yield was 45%.

Reaction Scheme 4:



Proton ¹H NMR:

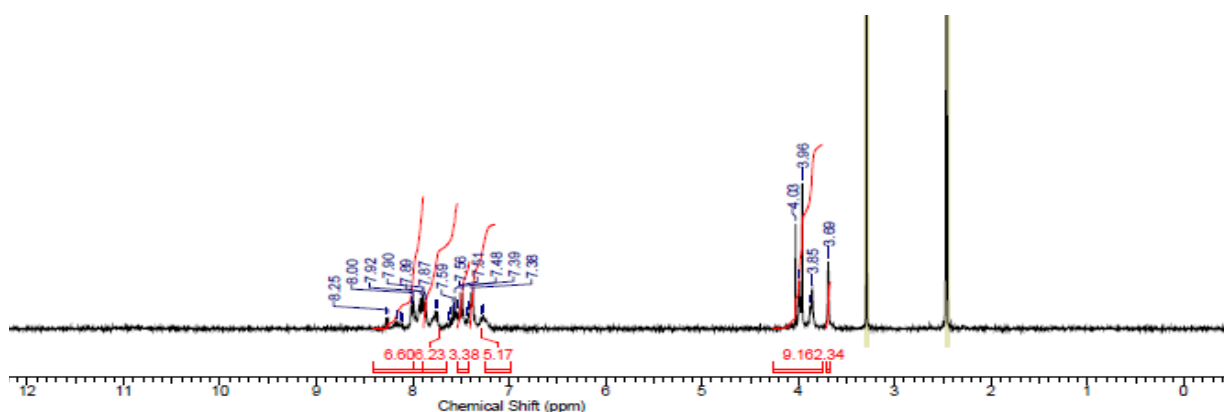


Figure 9: ¹H NMR spectrum of tris (2-methoxynaphthalidene) triaminoguanidinium chloride

Mass:

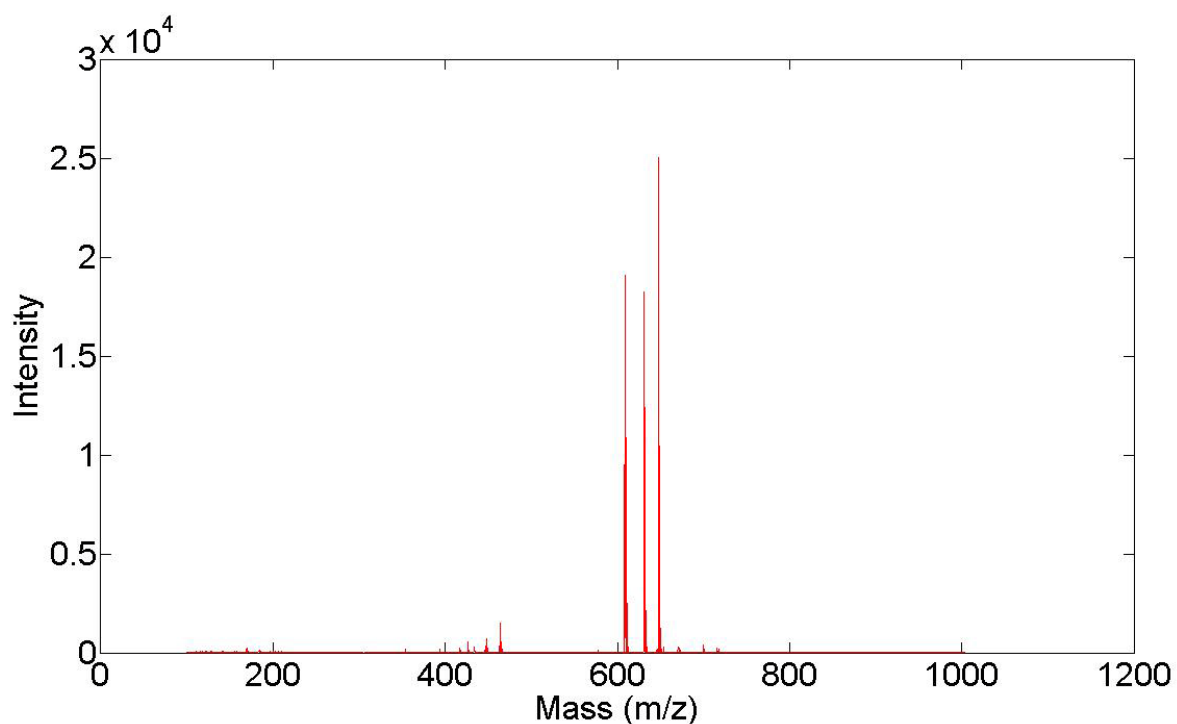


Figure 10:- Mass spectrum of tris (2-methoxynaphthalidene) triaminoguanidinium chloride

A crystalline form of compound 1(1') was obtained by taking the 0.1 mM (0.0565 gm) of the as synthesised pure form (1) taken in the DMF/Acetonitrile in 2:10 (v:v) ratio. Clean and uniform sized pure crystals with high quality were obtained in 10 minute after keeping the reaction mixture at room temperature for crystallisation.

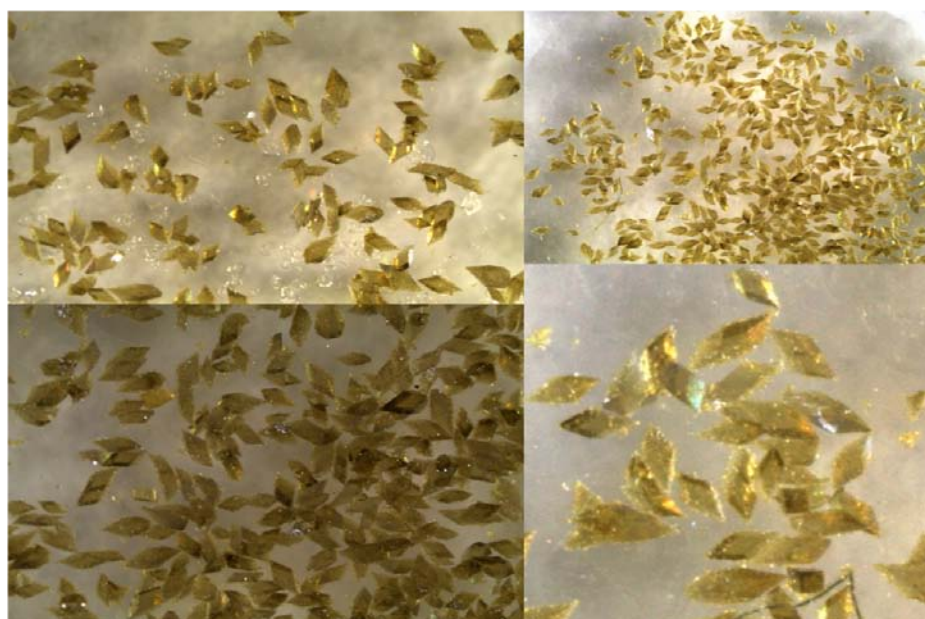


Figure 11: Some pictures of as-synthesized crystal 1'

Physical measurements:

All the reagents and solvents were commercially available and used without further purification.

Single-crystal X-ray data of compound **1** was collected at 200 K on a Bruker KAPPA APEX II CCD Duo diffractometer (operated at 1500 W power: 50 kV, 30 mA) using graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$).

Powder X-ray diffraction (PXRD) patterns were measured on a Bruker D8 Advanced X-ray diffractometer at room temperature (RT) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$).

Thermo gravimetric analyses was Recorded on Perkin-Elmer STA 6000 TGA analyser under N₂ atmosphere with heating rate of 10° C/min.

Low pressure gas sorption measurements were performed using BelSorpmax (Bel Japan). All of the gases used were of 99.999% purity. As-synthesized compound was heated at 150 °C under vacuum for 16 hrs to get guest free compound **1'**. Prior to adsorption measurement the guest free sample **1'** was pretreated at 150 °C under vacuum for 5 hrs using BelPrepvacII and purged with N₂ on cooling.

Results and Discussion:

The designed fluorescent organic ligand crystallised in a chiral Trigonal R3c space group which is a polar C3V point group analysed by single crystal X-ray diffraction studies. The tripodal ligand L comprises three directional fluorescent naphthalene based moiety synthesised by coupling of OH naphthaldehyde and the Triaminoguanidine.

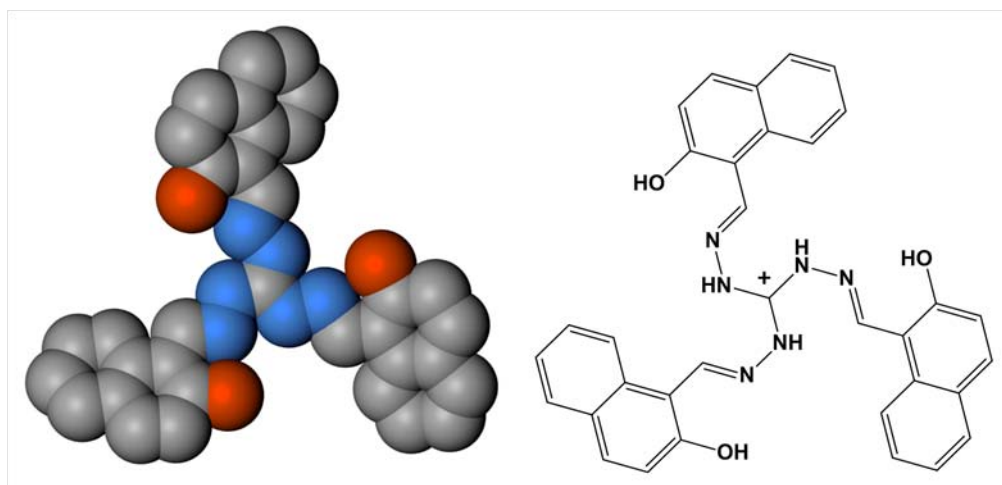


Figure 12:- structure of (2-hydroxynaphthalidene) triaminoguanidinium chloride.

Complexes consisting of aromatic ligands as the basic structural unit can be assembled into different supramolecular architectures via π - π interactions and hydrogen bonding interactions of the aromatic rings. The resulting network formed on crystallisation revealed an uncommon pi-stacked helical arrangement in 1'. All the three sides of tripodal ligand are completely surrounded by other similar ligands to make a complete network of pi-electron rich pure organic based crystalline backbone having pi-stacking.

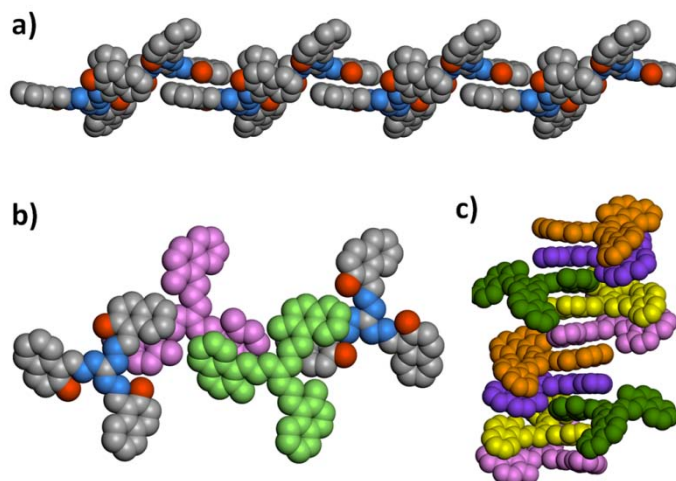


Figure 13: These figures show π - π interactions between different molecules of same kind.

Table 1: Crystal data and structure refinement for 1'

Empirical formula	$C_{120} H_{70} Cl_{24} N_{20} O_{10}$
Formula weight	2802.76
Temperature	296(2) K
Wavelength	0.71073 \AA
Crystal system, space group	Trigonal, R3
Unit cell dimensions	$a = 18.519(7) \text{\AA}$ $b = 18.519(7) \text{\AA}$ $c = 99.57(4) \text{\AA}$
Volume	$29574(19) \text{\AA}^3$
Z, Calculated density	121.888 Mg/m^3
Absorption coefficient	0.747 mm^{-1}
F(000)	17016
Crystal size	0.10 x 0.06 x 0.04 mm
Theta range for data collection	3.02° to 27.00°
Limiting indices	$-23 \leq h \leq 23, -23 \leq k \leq 21, -126 \leq l \leq 93$
Reflections collected / unique	54286 / 12326 [R(int) = 0.0835]
Completeness to theta = 27.00	99.7 %
Max. and min. transmission	0.9707 and 0.9290

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12326 / 2 / 665
Goodness-of-fit on F^2	0.774
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0723, wR2 = 0.2015
R indices (all data)	R1 = 0.1067, wR2 = 0.2306
Absolute structure parameter	0.23(8)
Extinction coefficient	0.00000(3)
Largest diff. peak and hole	0.616 and -0.554 e. \AA^{-3}

The arrangement of one above another L is in double propeller fashion showed in figure 14. These two propellers are running opposite to each other. These three fold symmetric propellers are of same composition with three blades.

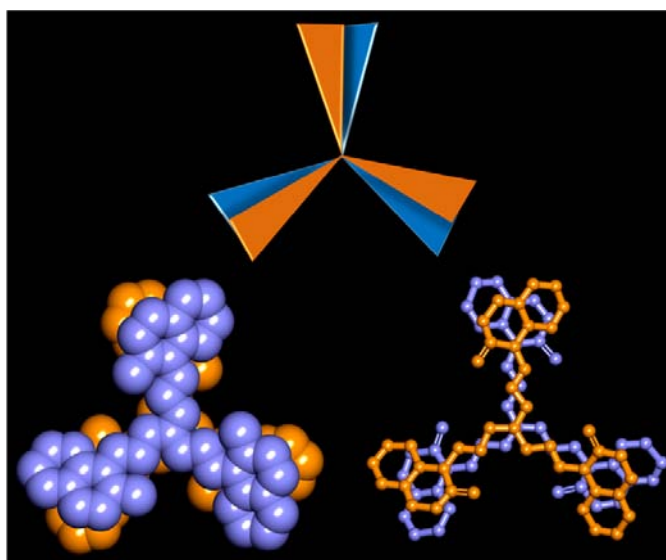


Figure 14:- Figure showing double propeller arrangement

The pi-stacked arrangement was favoured due to highly pi-electron rich naphthalene terminal arms of the C_3 symmetric tripodal ligand. This moiety can easily make very strong pi interaction with the next one to make a strong 3D discrete organic framework hold by pi-stacking and hydrogen bonding.

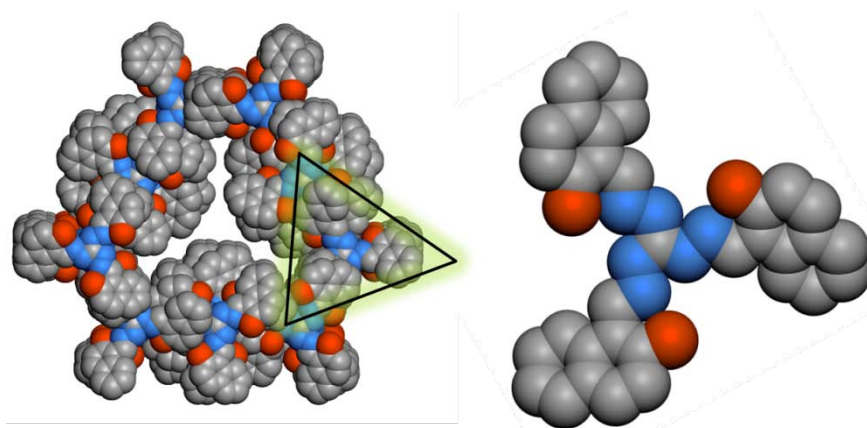


Figure 15: Compound having void cavity.

In further, part of structure elucidation by SCXRD studies tells that there is hollow capsule void present occupying some guest DMF and other solvent molecules inside the pi-stacked framework which is repeated along a axis. This void is of dimensions $3.0 \times 2.5 \text{ \AA}$ showed in figure 16. From along a axis it is clear that the framework formed with pi-stacked arrangement of L gives so many empty spaces inside the framework.

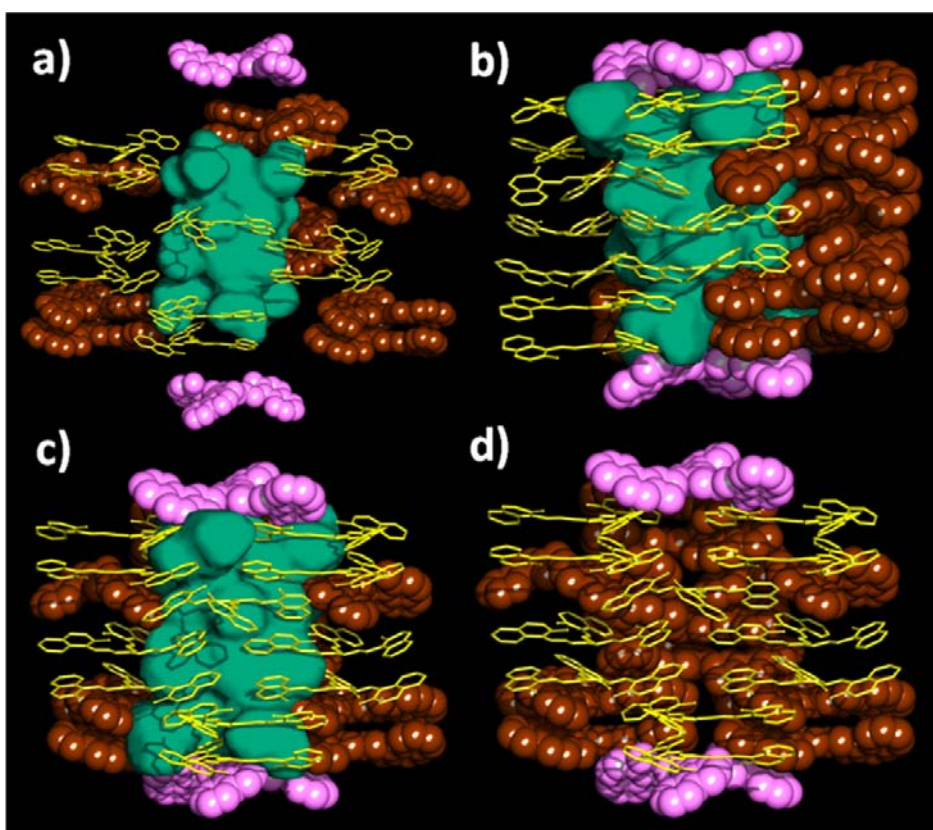


Figure 16: Structure of 1' showing void capsules

There is very strong hydrogen bonding observed for the NH protons of central guanidine moiety and the guest DMF molecules. However, in this case, hydrogen bond leads to the formation of double layers, which consist of a layer of DMF molecules. The bond length and angles observed in the structure seems to be in the expected ranges. All the atoms of carbon and nitrogen show sp_2 hybridisation having the distance between the central carbon atom and the closest three nitrogen atoms are 1.346, 1.347 and 1.38 Å, which is considered to be the constant value. The distance of closest two pi-stack rings of two different L observed was in the range of 3.45-3.89 Å.

For the construction of helical architectures, the rigid naphthaldehyde ring proves to be an interesting backbone, consisting of both pi-pi and hydrogen bonding interactions. The naphthalene rings of our ligand are alternately trapped to form the helical channels and to give hydrophobic moiety. Helicity and chirality are believed to be associated with living processes even their origins are unclear. Most of the biological substance like DNA and polypeptides seems to consist of helical structure. The basic motifs of helical structures includes 1D helical chains with righthanded (Δ or P), left-handed (λ or M) and meso-helices as well as 2D sheets and 3D frameworks having 1D helical features. These type of structures can be achieved using racemic, achiral and enantiopure compounds. When enantiopure chiral compounds are used as basic building block, the chiral helical compounds with right or left handed feature are formed. Whereas achiral or racemic compounds are used for producing meso compounds having same amount of right and left handed helices. Therefore it is still a problem to a chemist to control over the design and construction of helices.

So in our work we synthesised helices crystal mainly having π - π interactions. One moiety is running exactly reverse to the other two ligands present above and below to the one we compares. This cationic fluorescent moiety having very strong end to face pi-stacking makes six-fold helical arrangement running together along a axis showed in figure 19. It is a quadrupolar helical arrangement of six-fold symmetry where the distance between one pitch of the same helix is 47.091 Å.

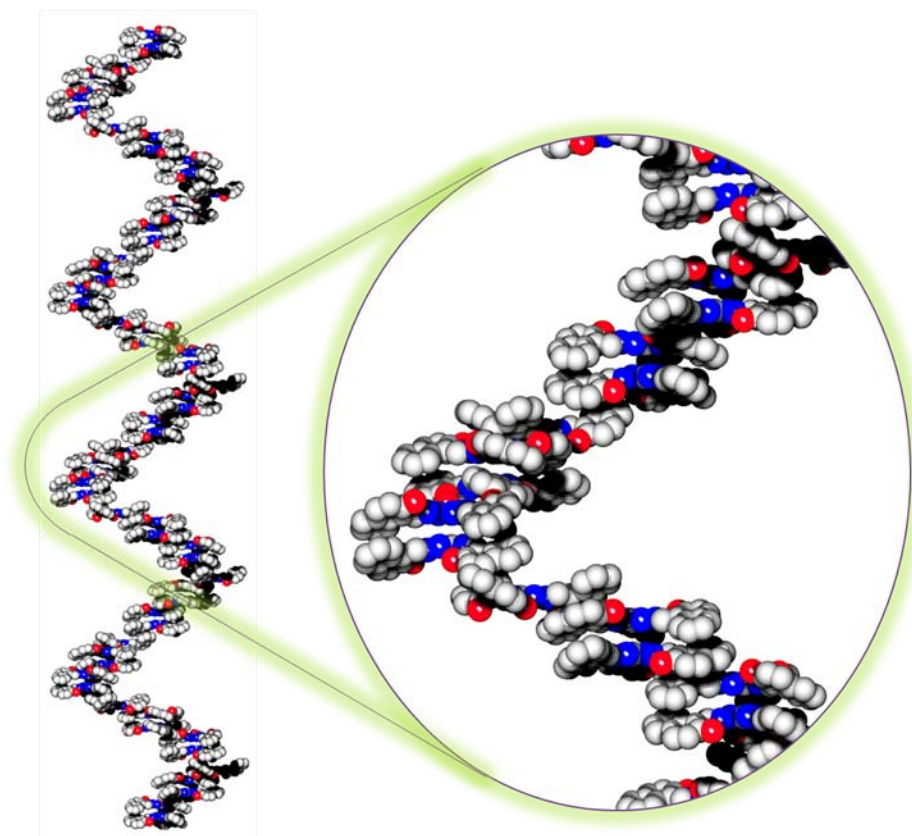


Figure 17:- Helical arrangement of 1'

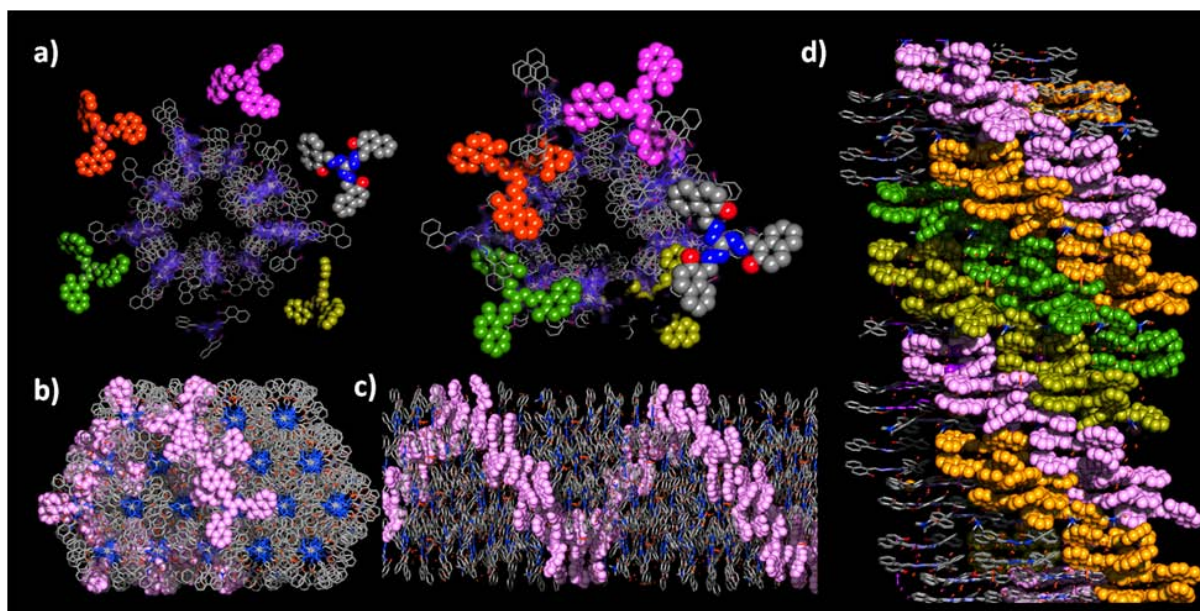


Figure 18: Frameworks showing edge to face π - π interactions and the six fold quadrupolar helical formation on crystallisation from achiral organic ligand.

The different types of arrangements for interaction of aromatic rings are: stacked arrangement which includes face-to-face, perfect alignment, slipped, and parallel displaced and edge or point-to-face, T-shaped conformation. T shaped arrangement is mainly because of C-H ... π interactions. The facial arrangements are important mainly for the case of the ligands having pyridyl sites. The π - π interactions seen our structure are mostly edge-to-face interactions. Geometries made of π - π interactions are controlled by electrostatic interactions but the major energy contribution mainly comes from other factors. Edge-to-face interaction seems to have more compact structure as compared to face-to-face interactions. Therefore, it is considered that interaction will be enhanced in edge-to-face interactions and structure will be more stable.

Thermo gravimetric Analysis:

For the stability of the all three compounds 1 (as-synthesized amorphous powder), 1' (as-synthesized crystalline powder), and 1'' (crystalline heated powder at 150°C), we performed the TG analysis over a range of 30°C to 900°C. From the data analysis it has been found that the all three samples 1, 1' and 1'' showed the well stable with respect to temperature. 1 showed the stability up to 245°C, 1' showed some guest solvent loss of about upto 70°C and further around 140°C upto 170°C, 1'' showed excellent stability up to 225°C temperature as showed in figure.

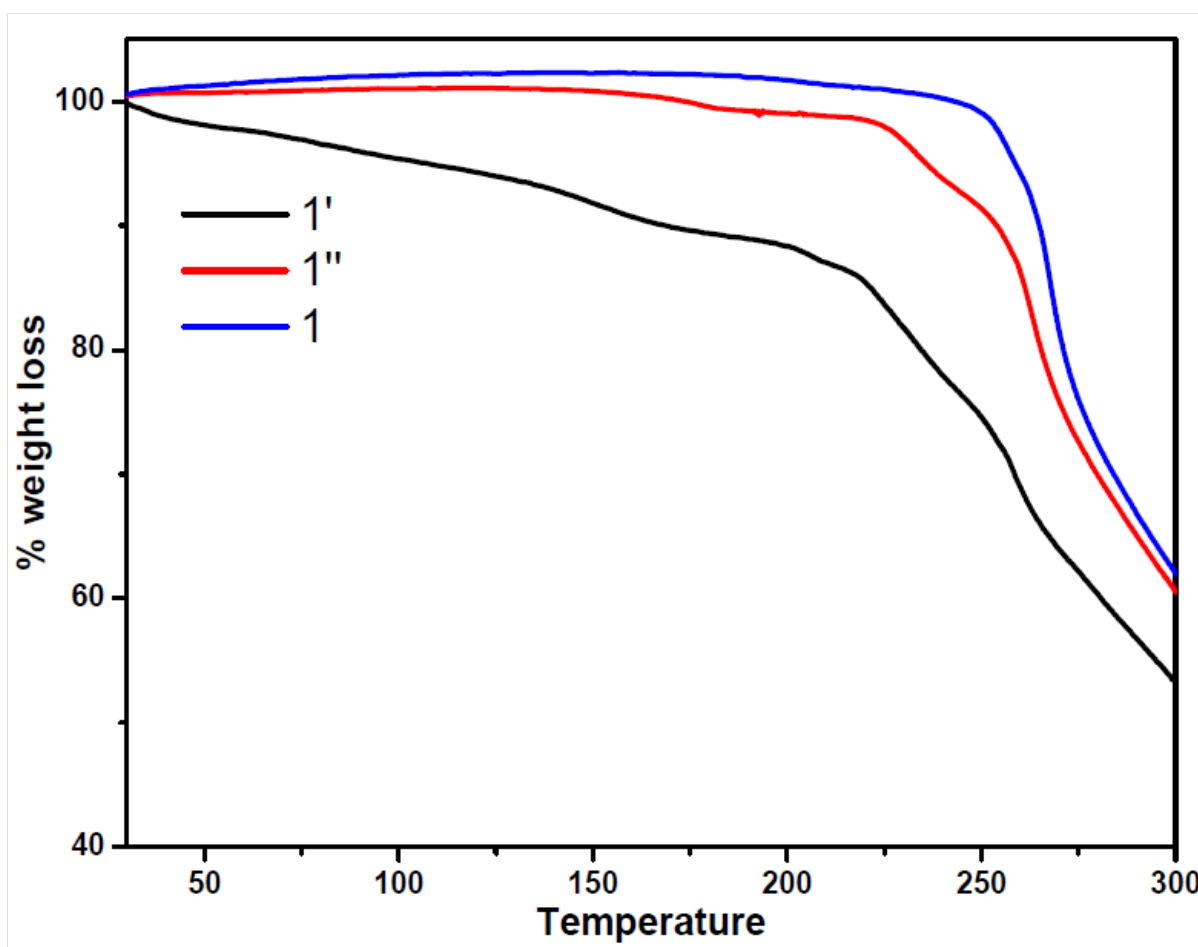


Figure 19: Thermo gravimetric analysis data showing weight loss. 1= powder form of 1, 1'= as-synthesized crystal, 1''= as-synthesized heated at 150°C.

Powder X-Ray Diffraction (PXRD):

To confirm the crystallinity and stability of as synthesised crystalline form, the PXRD pattern obtained at R.T. and variable temperature ranges up to 550°C. The variable temperature PXRD studies revealed the phase transformation as we heat the sample. Till 75°C the structure remains same, as temperature increases further structural changes can be easily observed. Noticeably the peak intensity increased as we heat the sample after phase change started. Around 75°C PXRD peak intensity is going down suggesting the randomisation of structure from ordered pi-stacked array with the solvent evaporation trapped inside the capsule void. And again peak positions are shifted towards right around 125°C, indicating squeezing of the structure with the slow removal of solvent guest molecules from the temperature range of 75°C to 125°C.

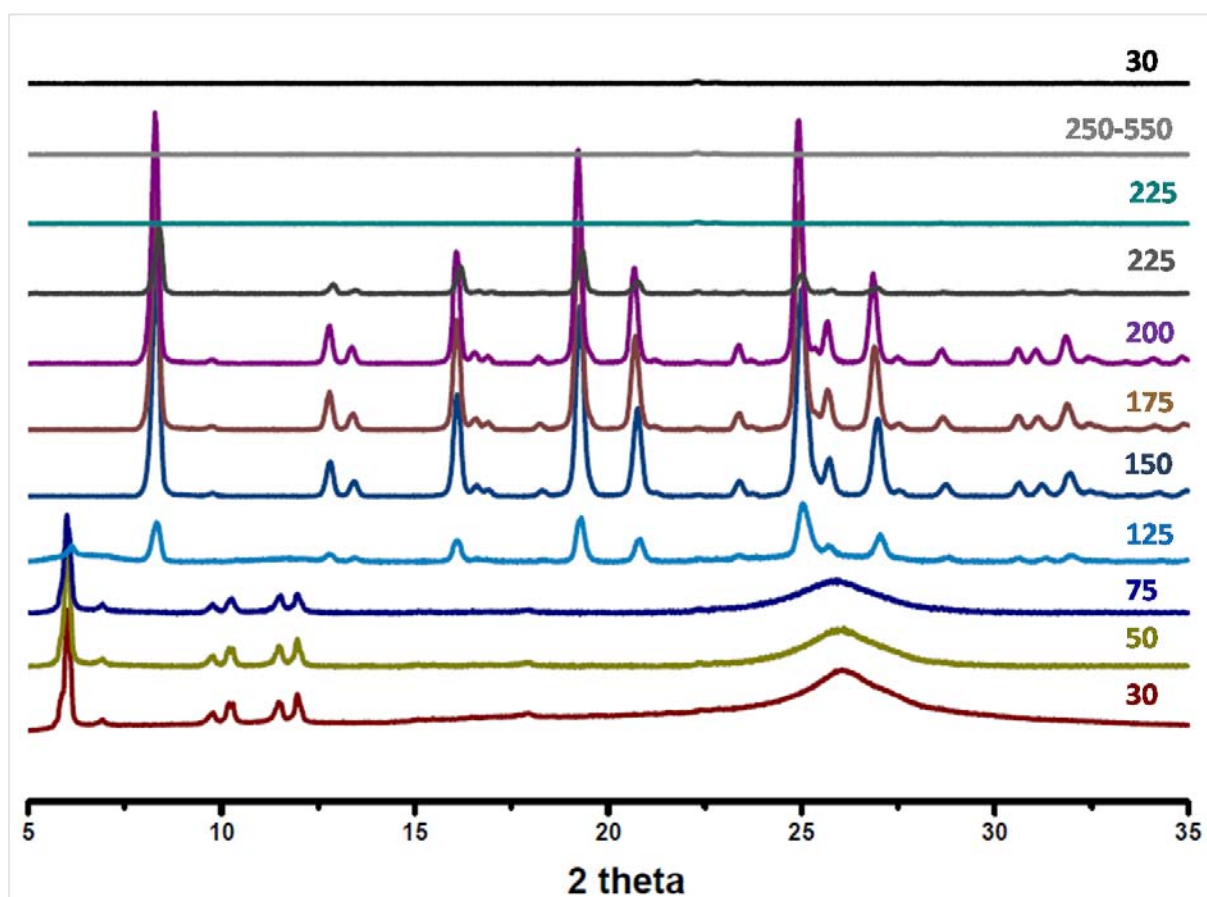


Figure 20: PXRD pattern at variable temperature

As we go along 125°C to 225°C temperature peak intensity started increasing indicating that structure is getting more ordered with high crystallinity and rigidity and more packed than the previous packing when solvent trapped inside. This type of structural behaviour is rarely observed in supramolecular assemblies. There are some reports where the compound got transformed from crystalline to amorphous then again to crystalline.

Sorption studies done over the compound 1'' to check its potential in gas storage and separation as from the SC-XRD analysis revealed the capsule open voids of the opening apertures of the size 3.0 X 2.5 Å°. Sorption was checked for amorphous as synthesized powder i.e. 1 and as synthesized heated crystalline form of 1' after removal of guest solvent molecules (1''). Highly ordered pi-stacked framework is showed high stability up to 225°C temperature as confirmed by TGA and variable temperature PXRD patterns. As the moiety contains nitrogen and oxygen rich centres having lone pair of electrons which are good factors for the more interaction with the CO₂ gas adsorptive molecules we first studied the CO₂ sorption at 195K for both the crystalline and amorphous forms.

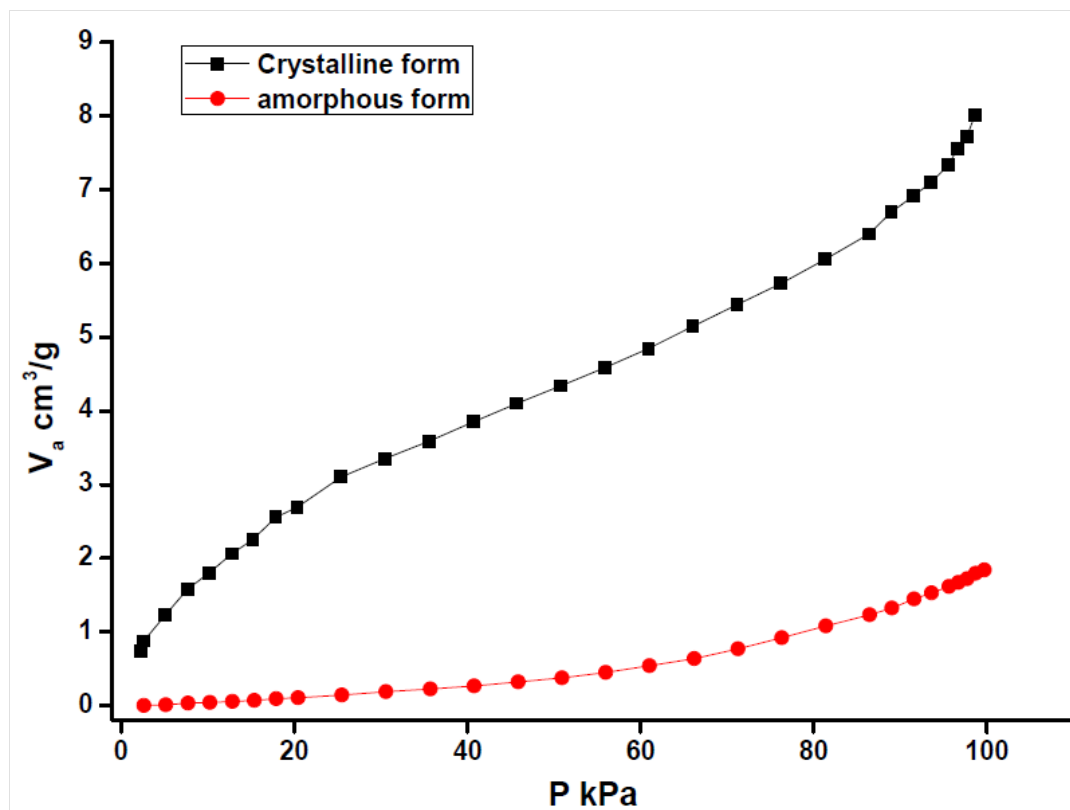


Figure 21:- CO₂ sorption of crystalline form and amorphous form.

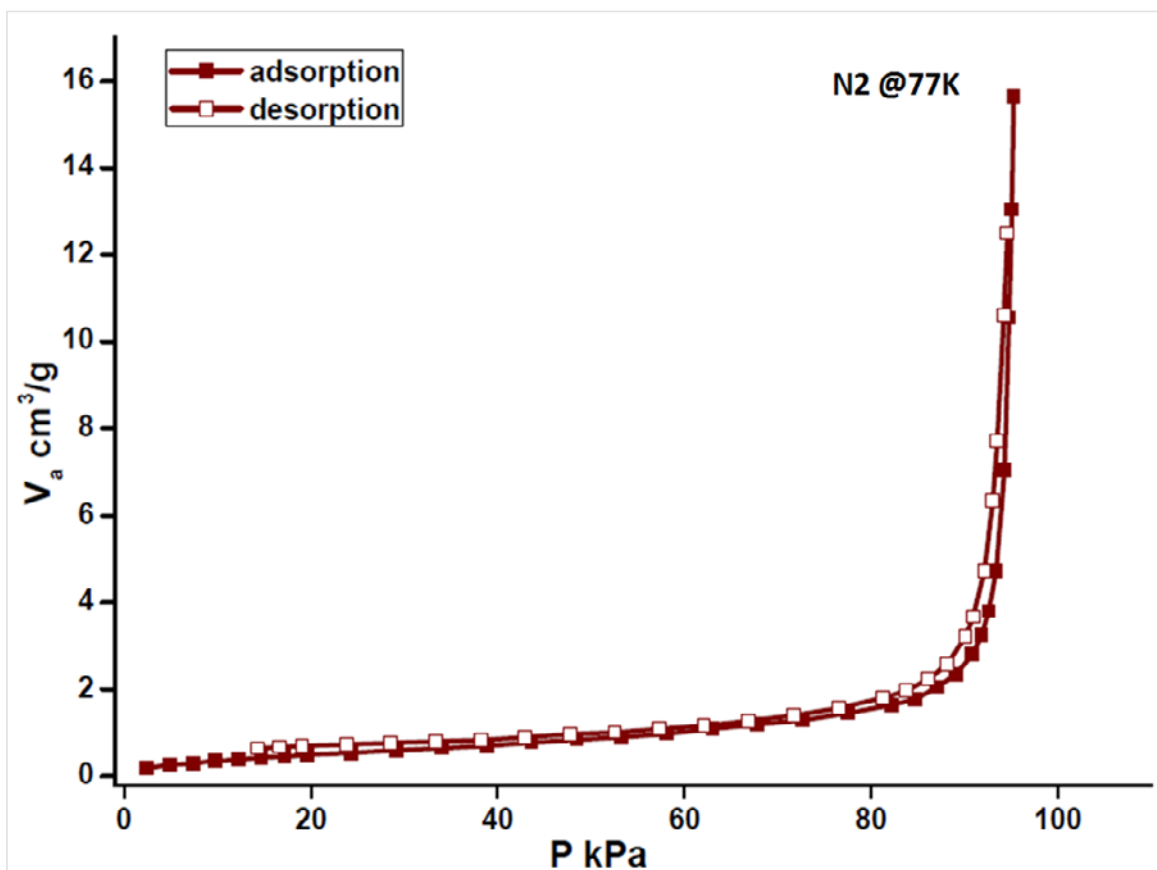


Figure 22:- N₂ sorption of as-synthesized 1'.

The compound could not show fair uptake of gas amount for the both forms. Crystalline form showed more uptake than the amorphous. Crystalline heated sample took 8 cm³/g while amorphous sample took 1.8 cm³/g. According to Cooper and co-workers some organic porous solid in amorphous form are more potential to store and separate CO₂ than the crystalline form of the same organic compound. The reason they explained for this kind of behaviour is that the amorphous form can have more porous surfaces available due to the random distribution of molecules for the diffusion of gas molecules inside them compared to the crystalline form which are more ordered arrays with uniform porous surfaces. These uniform surfaces are having less interaction than the same in amorphous form. Same observation did not observed in the compound we synthesized may be due to the exactly opposite reason, that is more interaction possible with the crystalline form than amorphous one. The low uptake is attributed to the surface interaction of the N₂ sorption for the crystalline form that is 1'' at 77K showed 15 cm³/g of uptake with a typical type – BET curve suggesting the monolayer adsorption supported by no hysteresis on desorption of N₂.

Luminescence:

For as synthesized and the crystalline form the excitation maximum observed at 394 nm. We found the intense luminescence with 514 nm emission maximum. For the heated form of 1' at 150 °C 28.33% enhancement of fluorescence was observed. This is the unusual observation of fluorescence enhancement after the heating of a fluorophore. This is attributed to the more ordered and compact arrangement of the pi-stacked framework after removal of solvent molecule by heating at 150°C. A broad hump observed at 472 nm for the as synthesized crystalline form that is 1'. This is possibly due to the flexible behaviour of the framework bearing the solvent trapped guests molecules exhibiting two step emission relaxations.

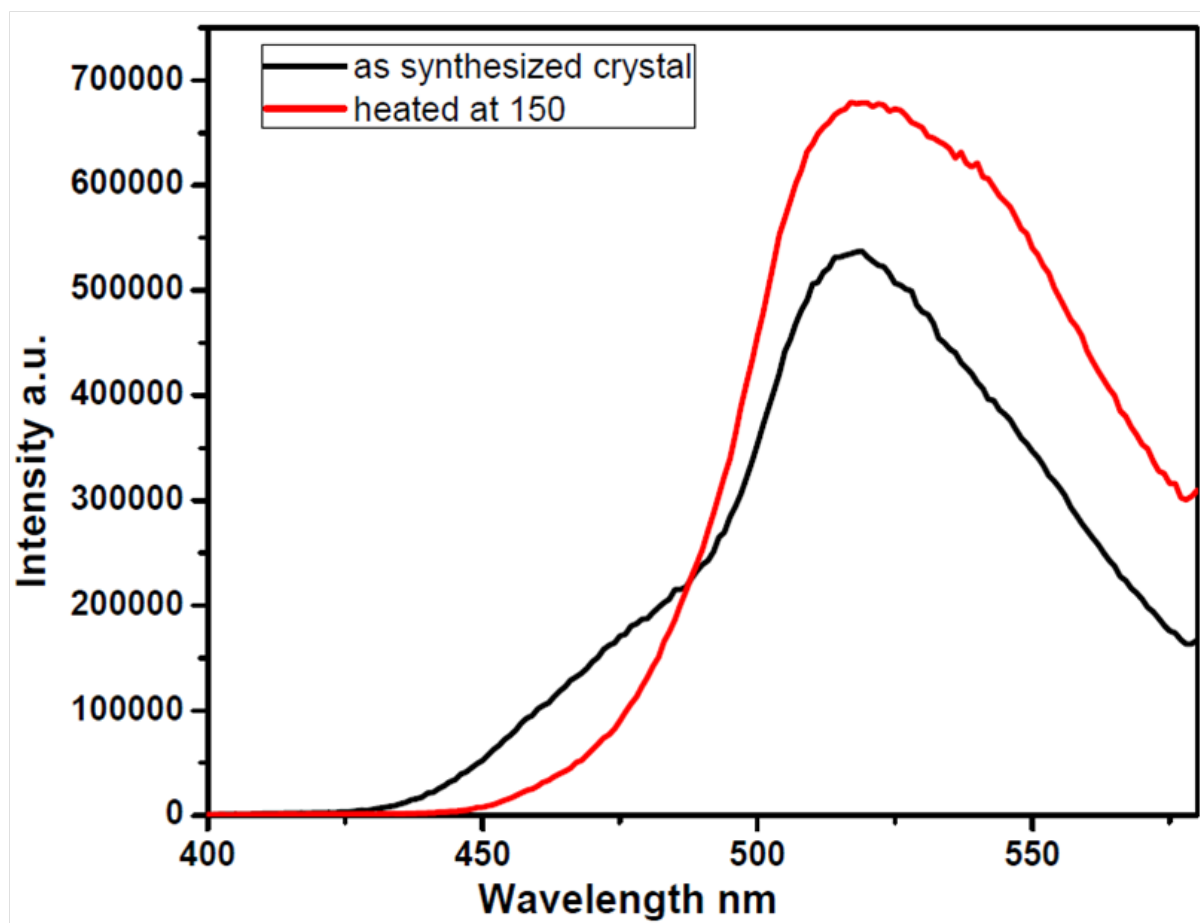


Figure 23:- Fluorescence spectrum of as-synthesized 1' and as-synthesized heated at 150°C

CD spectra:

To check the one handed helix formed while crystallisation of pi-stacked array we performed the solid state CD measurement over the as synthesized crystalline powder. A negative cotton effect was observed for the crystalline --- indicating the single handed helix is formed without racemisation on crystallising the compound. Amorphous as synthesised powder also checked for comparison which showed zero cotton effect with no helical arrangement in it as a result.

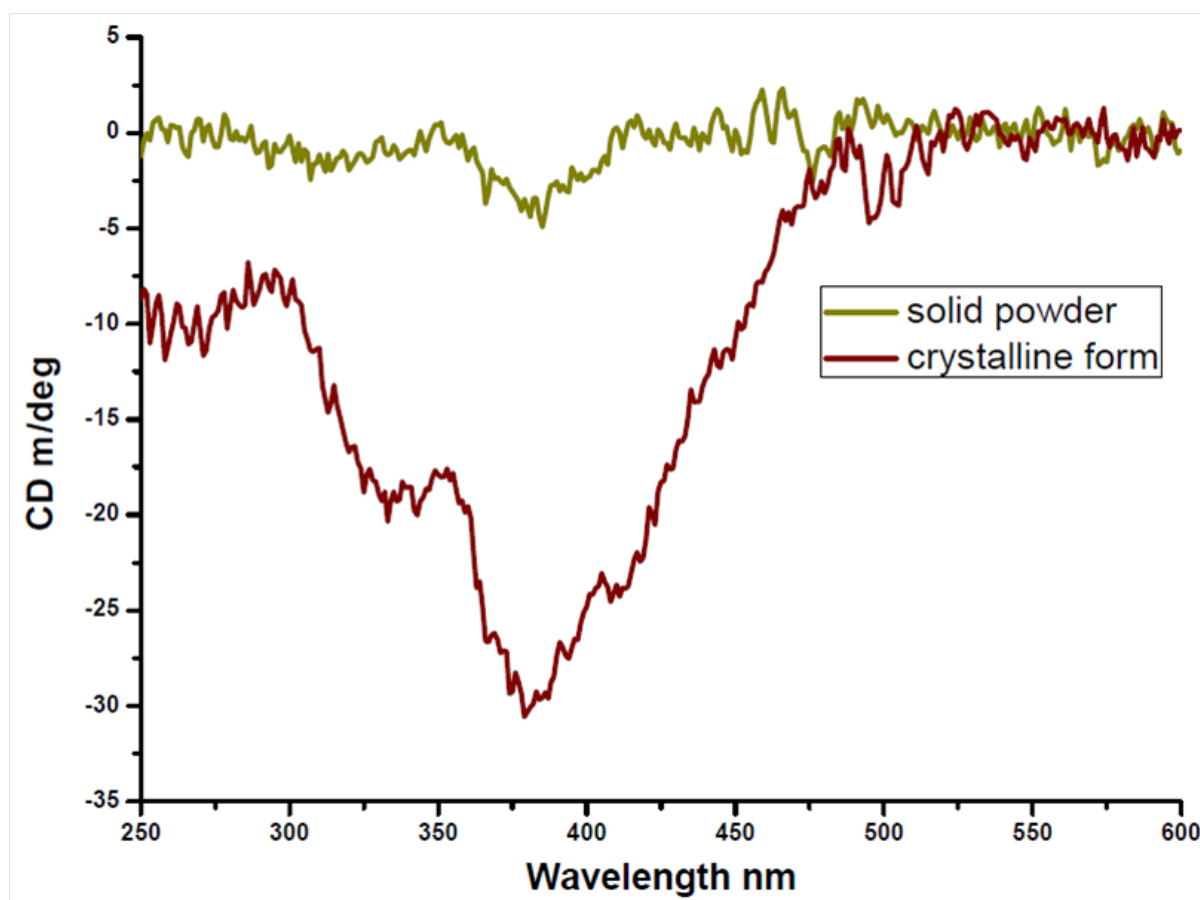


Figure 24:- Solid state CD spectra Of ligand 1 and as-synthesized 1'.

Aromatic Guest Inclusion study:

We studied the different aromatic system interaction with our pi-stacked framework. For doing this, we exposed the crystalline in as synthesised form that is 1' to the vapours of different aromatic guests from electron rich to the electron deficient system.

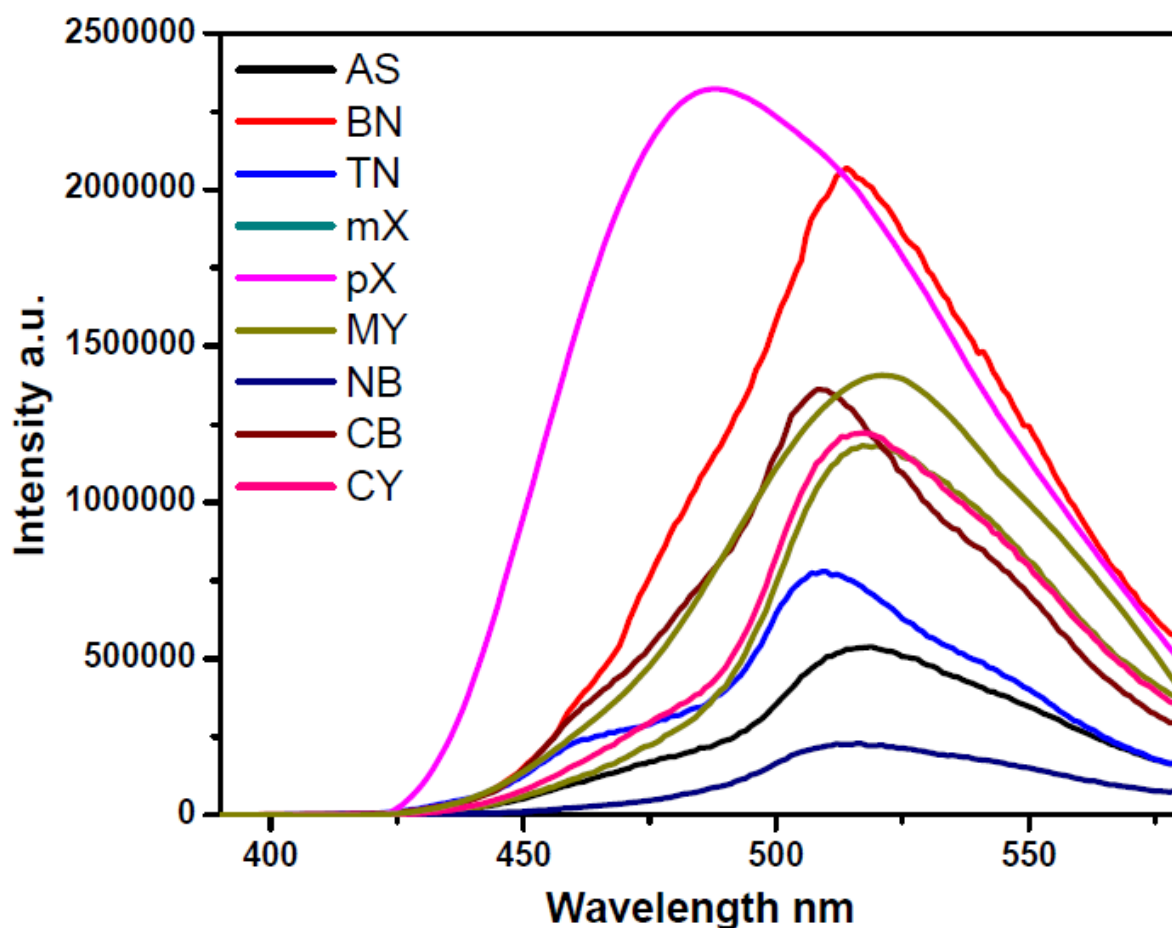


Figure 25:- Fluorescence spectra on addition of different aromatic guests. AS = as - synthesised, BN = Benzene, TN = Toulene, mX = meta Xylene, pX = pera Xylene, MY = Mesitylene, NB = Nitrobenzene, CB = Chlorobenzene, CY = Cyclohexane

Then we moved to examine the effect of this vapour exposure of aromatic guets on the luminescence property of host pi-stacked framework. We studied the luminescence on exciting the 1' at 394 nm which exhibited the strong luminescence with maximum emission at 510 nm. The complete series of compounds under study gave very good agreement of fluorescence enhancement of parent 1' for the electron

rich system while drastic quenching was observed in case of the electron deficient aromatic nitrobenzene guest. Amongst all the enhancer p-Xylene has highest effect and toluene has least effect. The enhancement (%) of guest was calculated using the formula.

$$\text{enhancement}(\%) = \frac{I - I_0}{I_0} * 100\%$$

$$\text{quenching}(\%) = \frac{(I_0 - I)}{I_0} * 100\%$$

where I_0 is the maximum fluorescence intensity of 1' before exposure to the guests.

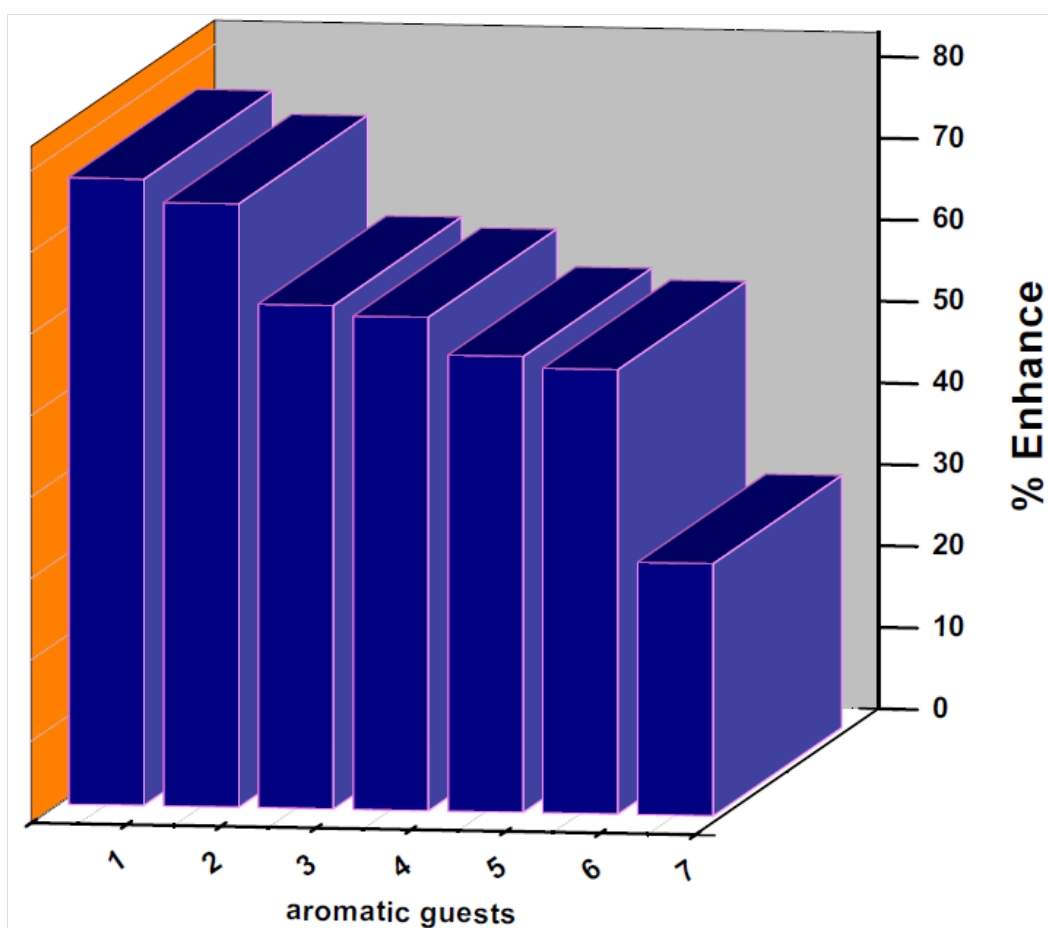


Figure 26:- Graph showing % enhancement for different guests with 1'. 1= P-Xylene, 2= Benzene, 3= Mesityline, 4= Chlorobenzene, 5= Cyclohexane, 6= M-Xylene, 7= Toulene.

The fact that nitrobenzene show strong quenching effect is because of high vapour pressure and the electron-withdrawing group attached with guest molecule. Also the strong pi-interaction is possible by overlapping of LUMO of nitrobenzene over the HOMO of the electron rich host molecule. An opposite effect was observed for the electron-rich guests. Unlike nitrobenzene these electron-rich guests appeared to enhance the fluorescence of 1'. The highest increase in fluorescence intensity is shown by p-Xylene with an enhancement of 77%. The remaining effect is like benzene (74.03%) > mesitylene (61.77%) > Chlorobenzene (60.50%) > Cyclohexane (55.93%) > m-Xylene (54.51%) > toluene (30.92%). The result seems to be consistent with their vapour pressure and electron-donating nature. The attenuation and enhancement of fluorescence observed in our results can be demonstrated by donor-acceptor mechanism of electron transfer. If we consider the case of electron-donating guests, the electrons are transferred from high-lying LUMO (having energy higher than conduction band) to conduction band of 1', causing fluorescence enhancement.

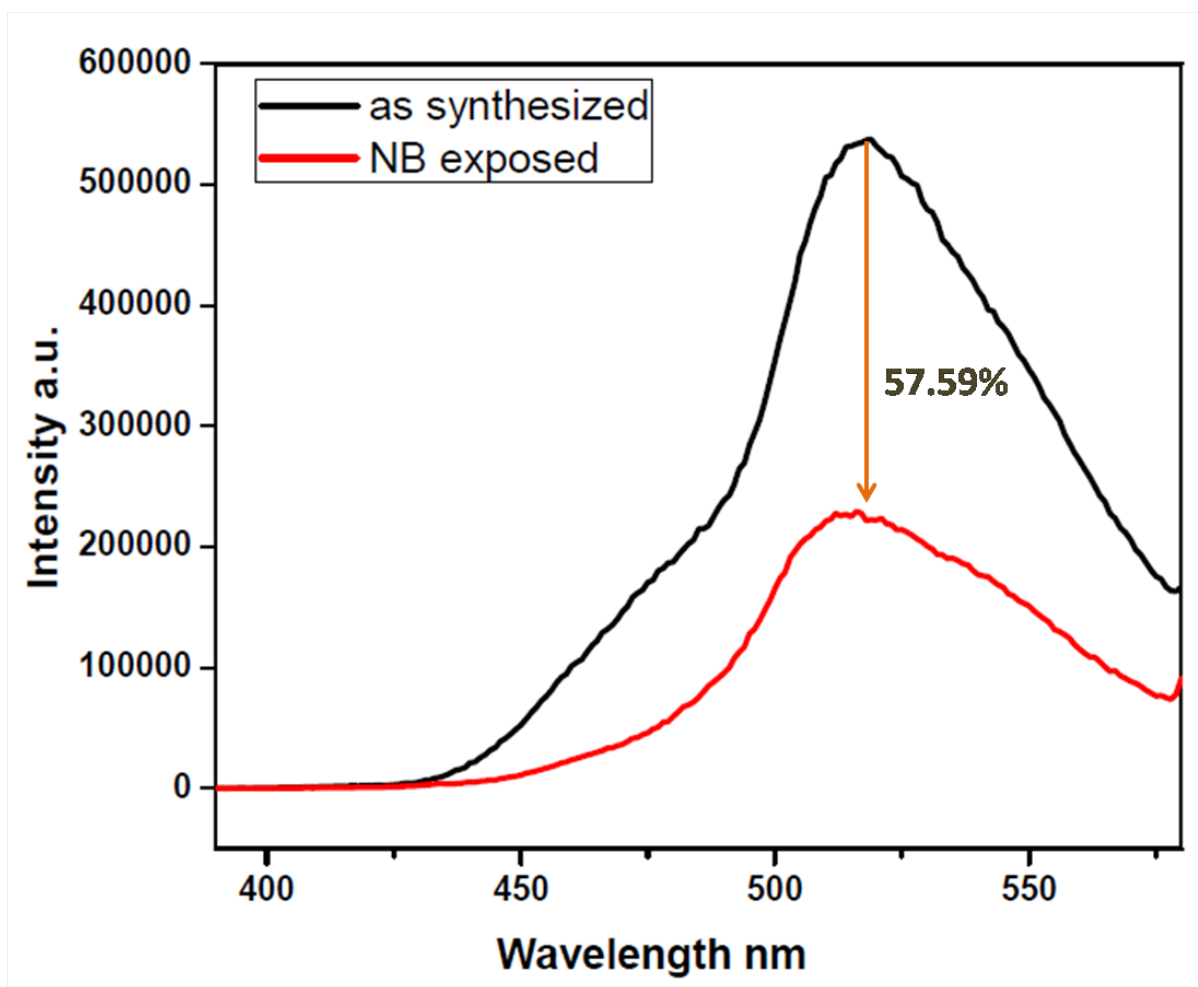


Figure 27:- Fluorescence spectrum of 1' and nitrobenzene with 1'.

In case of nitrobenzene 57.59% quenching is observed. In nitrobenzene, the LUMO is a low lying pi-type orbital, which in case is normalised by NO₂ group of nitrobenzene via conjugation and also its energy is less, therefore lie below conduction band of 1'. Upon excitation, transferring of electrons takes place from conduction band of 1' to LUMO of the guest molecule, which leads to quenching effect. Mostly, conjugated polymers are seen to have this type of mechanism. The overlap between LUMO of nitrobenzene and conduction band of 1' is very high, causing high quenching. A drastic visual changes was not observed as a colour change of 1' on exposure to the vapours of aromatic compounds but an intense luminescent changes were observed under the U.V. light for the solid compound for the 1',

1'>Nitrobenzene exposed and 1'>p-Xylene exposed showed in figure—with the highest luminescence with p-xylene and quenching with nitrobenzene.

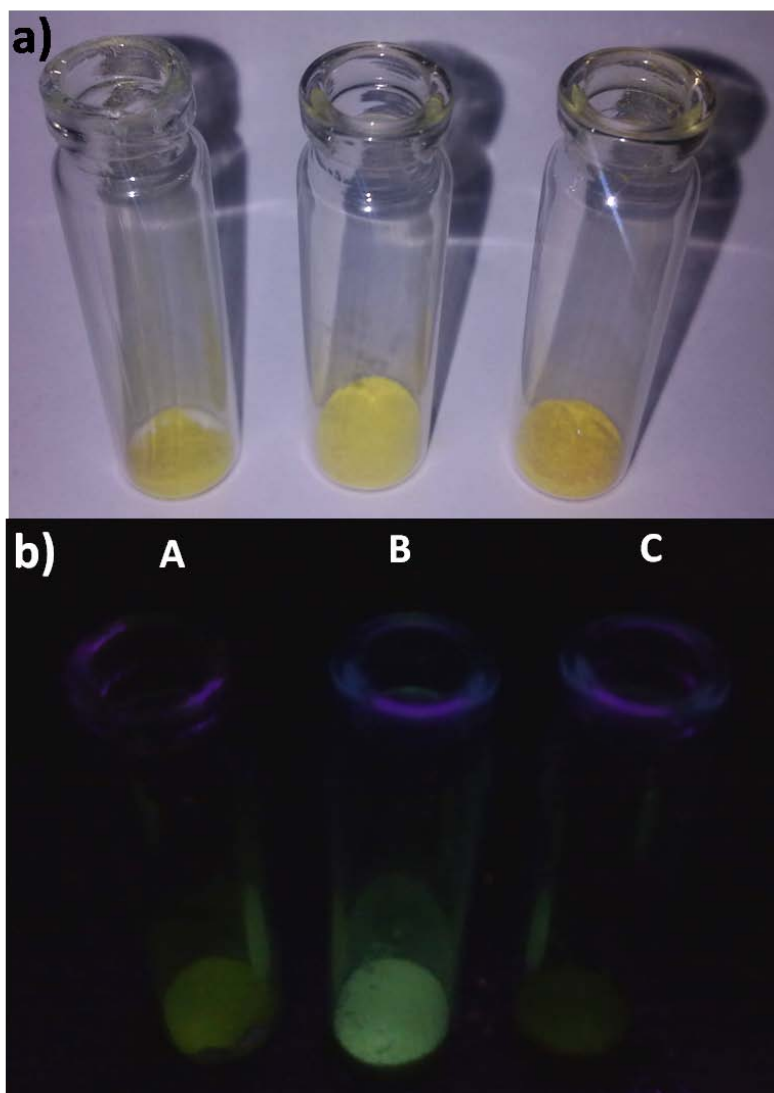


Figure 28:- a) Photos of different compounds in visible light; b) Photos of different compounds in UV light. A= 1', B= 1' after inclusion of P-Xylene, c= 1' after inclusion of Nitrobenzene.

Conclusion:

In summary we have successfully designed, synthesized, characterized and studied the tripodal fluorescent pi-stacked organic moiety bearing capsule void pores with small opening apertures. The synthesized framework contains cationic central triaminoguanidine core and to this, three directional luminescent terminal of hydroxynaphthaldehyde are lying. This tripodal organic solid is making highly stable discrete pi-stacking framework upto 240°C. The CO₂ uptake studies revealed that the amount it absorbed is negligible indicating the framework squeezing after heating thje compound. The potential aromatic guest interaction revealed the drastic changes in fluorescence intensity by electron rich aromatic system and fluorescence quenching by electron deficient nitrobenzene. This makes it a potential material for the exploring nitro-explosive detection property in detail for the further approach and aromatic guest inclusion study with changes in their physical properties.

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