Morphological Evolution of Two Dimensional Porous Hexagonal Trimesic acid Framework

Srinu Tothadi [a] [#], Kalipada Koner [b] [#], Kaushik Dey [b], Matthew Addicoat [c] and Rahul Banerjee [b] *.

Abstract: For the first time a hexagonal single crystal structure (Form II) of trimesic acid (TMA) was isolated by dissolving the interpenetrated Form I of TMA in THF. To the best of our knowledge, this is the smallest building block which self-assembles to a 2D hydrogen bonded framework structure. A detailed time dependent FESEM study established a strong correlation between molecular level structure with morphology of TMA. The external morphology of the Form II (hexagonal) illustrates layered hexagonal structure while an inside-out Ostwald ripening is responsible for hexagonal hollow tube formation. These hollow tubes are used for Rhodamine B dye adsorption study, which shows uptake of 82%, much more significant than Form I (interpenetrated) (39%).

Hydrogen bonding is the most studied cohesive force in the field of supramolecular chemistry. [1] It is well exploited in describing the crystallographic packing in small organic molecules as well as in framework materials because of its directionality 1(b,c,d). In the past decade, research on hydrogen bonded organic frameworks (HOFs) has picked up significant momentum due to their diverse applications. [2] The supramolecular self-assembly of organic molecules in HOFs often leads to a three dimensional (3D) structure, because self-assembly of organic molecules by hydrogen bonding is much more stable in 3D than in two dimensions (2D). As a result, only a few 2D HOFs are reported ~~till~~ to date. [3] Apart from HOFs, several other 2D materials like covalent organic frameworks (COFs) [4], coordination polymers [5], metal chalcogenides [6],have attracted the attention of the scientific community due to their potential applications. Among these, COFs having layered structures have arrived at the forefront, but lack of single crystal structures still remains a bottleneck for structural studies of two dimensional COFs 4(e). On the other hand, the accessibility of a single crystal structure allows a great depth of understanding in HOFs. In spite of having such structural advantages, most of the HOFs are composed of large organic moieties because the crystallization of HOFs with~~ a~~ small molecules like trimesic acid (1,3,5-benzenetricarboxylic acid) ~~could ~~is typically~~be~~ very challenging.

Trimesic acid (TMA) is well known in one crystalline form in *C*2/c space group with six molecules in the asymmetric unit which was first reported by Duchamp and Marsh in 1969.[7] In the single crystal structure, molecules are stabilized by intermolecular hydrogen bonding forming the interpenetrated hexagonal framework. From the symmetry point of view, the three carboxylic acid groups of TMA possessing *C*3 symmetry could easily form hexagonal honeycomb motif by self-assembly through acid-acid dimer linkage. At the same time, the presence of six benzene rings in one hexagonal unit always gives a possibility of π-π stacking to form a layer structure which could be a polymorph of TMA. Polymorphism arises from different solid state packing arrangements of the same chemical constituents.[8] It is an important phenomenon in supramolecular chemistry [9], which makes polymorphs having a varibale solid state packing showcasing varibale applications in pharmaceutical [10], agrochemical, and food industries. Researchers have made an extensive effort for the last 50+ years to crystalize TMA as a layered hexagonal framework. However, each time TMA has been crystallised as a TMA-solvate with an interpenetrated network.[11] In another scenario, self-assembly of TMA into two-dimensional chicken wire structure was studied by growing on solid supports like Cu (100), Au (111) and highly oriented pyrolytic graphite (HOPG) under ultra-high vacuum. [12] While preparation of this manuscirpt, recently Cooper and co-workers reported the single crystal structure of the unsolvated hexagonal polymorph of TMA.[13a] Prior to this report, last year we submitted an invention disclosure of the TMA (Form II). [13b] Herein for the first time, we could crystallize the TMA molecule, as a two-dimensional (2D) hydrogen bonded hexagonal layer structure (Form II) which self assembled into a hollowtubular morphology.[13] Equivalence of single crystal structure (packing) and single crystal morphology is a rare phenomenon in the organic crystals, occasionally seen in porous organic cages.[14] Here, in the Form II (hexagonal), the hexagonal channel of the single crystal structure is not only equivalent to the hollow tube morphology of the crystalline material but also mimics natural honeycomb architecture. To the best of our knowledge, this is the smallest building block which self-assembles to a 2D hydrogen bonded framework structure and mimics natural it's honeycomb single crystal structure in to it's external morphology. Block shaped solid crystals of Form I (interpenetrated) of TMA slowly converts to the hexagonal hollow tube in polar aprotic solvent tetrahydrofuran (THF). Subsequently, we have also discussed the mechanism of hollow hexagonal tube formation using microscopic techniques. Hexagonal hollow tube morphology is one of the most desired topologies for accomplishing many potential applications such as dye adsorption. We confirmed the relevance of the layered polymorph by investigating guest molecule uptake capacity. Form II (hexagonal) adsorbs Rhodamine B dye to a greater extent (~82%) as compared to Form I (interpenetrated) (~39%).

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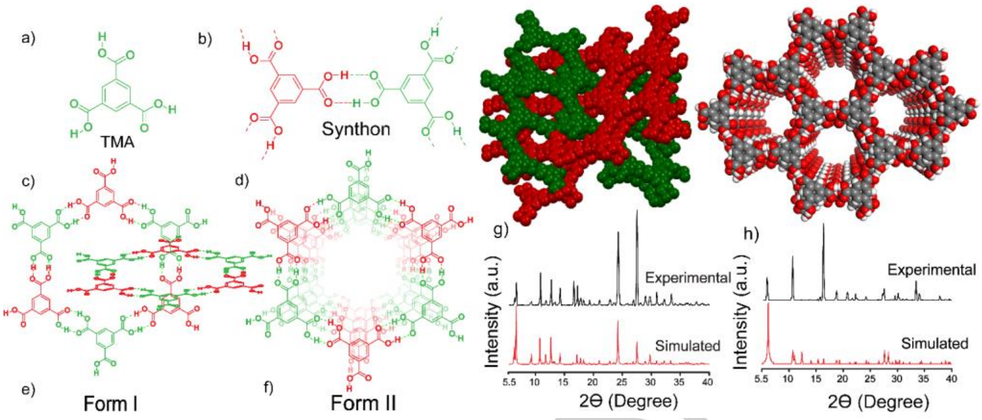

Figure 1. a) & b) Schematic representation of Trimesic acid and synthon of the frameworks. c) & d) Hydrogen bonded frameworks of Form I (interpenetrated) and Form II (hexagonal) respectively. e) & f) Single crystal structures of Form I (interpenetrated) and Form II (hexagonal) respectively. g) & h) Simulated and Experimental PXRD of Form I (interpenetrated) and Form II (hexagonal) respectively.

Our initial goal was to synthesize multicomponent crystals (cocrystals) with the hexagonal framework, which could be used for host-guest chemistry. We selected the well known molecule TMA as our building block. The three-dimensional polymorph (Form I) of the TMA is interpenetrated, i.e., the 14 Å holes of hexagons are catenated (Figure S2). The hydrogen bonding between the carboxylic acid, which is the knot of the whole framework is not in one plane; it grows in the XY plane as well as in the YZ plane. This type of bonding inhibits the possibility of multiple layer π-π stacking along a particular direction. Solvents have direct effects on crystal packing and morphology. Keeping this in prespective, we have done extensive screening of TMA with different solvents (MeOH, CH_3CN, CH_3NO_2, DCM, and $CHCl_3$) (detailed solvent screening is given at ESI). But, most cases, either TMA crystallize as solvates or resulted in the crystal of interpenetrated hexagonal framework (Form I). However, good quality single crystals of Form II (hexagonal) were isolated from a saturated solution of TMA in ~~Tetrahydrogen~~ Tetrahydrofuran (THF) within 3-5 days at room temperature (27 °C). Based on single crystal data, it is evident that molecules are crystallized in trigonal space group $P3_121$ with only one molecule in the asymmetric unit. In the crystal structure, molecules are connected via acid-acid supramolecular homo dimer synthon 14 (c), and it further extends in 2D to form hexagonal sheets without interpenetration (Figure 1). These sheets are further connected *via* π-π stacking to form a 3D network along *c*-axis (Figure S1). As molecules are crystallized in the trigonal crystal system with 3_1 screw axis, those molecules are not superimposable along *c*-axis. Six molecules of trimesic acid form a hexagon and it creates voids in 2D and hexagonal channels along the *c*-axis of the unit cell.. The hexagonal pore diameter is 14.5 Å, which could accommodate small molecules. Moreover, two consecutive layers are separated by 3.3 Å, comparable to the consecutive sheets of other 2D material like graphite and COFs (Figure S3) 14 (d,e). Equivalent experimental and simulated PXRD patterns of Form II (hexagonal) suggests the phase purity of the bulk crystalline material (Figure 1). Form I (interpenetrated) display an intense peak at 6.7 (2θ) which correspond to the 200 planes. The other minor peaks at lower 2θ values at 6.3°and 9.3°correspond to 110 and 202 planes (Figure S4). However, Form II (hexagonal) shows only one sharp peak at 6.3°; which corresponds to 100 planes indicating π-π stacking only in one direction. TGA of Form I (interpenetrated) shows 60 % weight loss around 300-315 °C. Since there is no solvent in the crystalline lattice, this could be attributed to the decomposition of some of the carboxylic acids. Further 20 % weight loss at 369 °C, is due to melting and decomposition of the TMA Form II. TGA of Form II (hexagonal) manifests 10 % weight loss from 110 -150 °C, afterwards it follows the same path as Form I (interpenetrated) (Figure S6). DSC of Form I (interpenetrated) shows the first endotherm at 309 °C and the second endotherm at 369 °C. But, the From II (Hexagonal) manifests one exotherm and three endotherms (Figure S6). The first broad exotherm at 150 °C is an indication of THF solvent loss and the second endotherm at 160 °C suggest the phase change from Form II (hexagonal) to Form I (interpenetrated). Later, it follows the same path as Form I (interpenetrated), *i.e.* melting endotherms at 309 and at 380 °C. Hence, Form II (hexagonal) could be the kinetic form, and it converts to more stable Form I (interpenetrated) when~~ile~~ heated~~ing~~ above 160 °C. Supporting this interpretation, the binding energy of the two forms was calculated using Densty Functional Tight Binding (DFTB). Per TMA monomer, the binding energies were -159.8 and -135.2 kJmol^{-1} for Form I and Form II respectively. ~~–~~Another important aspect of these two forms, is their morphology and their interconvertible nature ~~of these two forms are discussed~~ (Figure 2).

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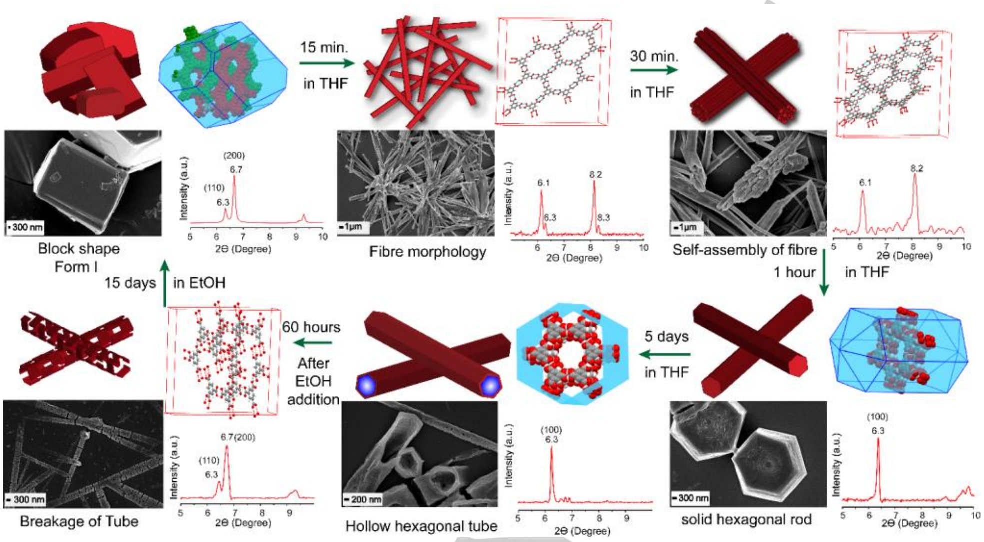

Figure 2. a) Time dependent cyclic conversion of morphology from block shape to hollow hexagonal morphology. The blue simulated morphology of both Form I (interpenetrated) and Form II (hexagonal) are derived from crystal structure. The morphology in red box es are the hypothetical structures corresponding to the respective morphology. The prominent change in PXRD in the range between 2Θ value 5° to 10° is shown with FESEM image.

Form I (interpenetrated) ~~showcase~~ shows a block shape morphology while Form II (hexagonal) adopts a hollow hexagonal tubular morphology with 1μm diameter (Figure S10). Form I (interpenetrated) could easily convert into Form II (hexagonal) in the presence of THF, which further reverts to Form I (interpenetrated) in the presence of polar solvent like EtOH. However, this conversion proceeds through intermediate morphologies. We tried to establish a connection between the crystal structure of each form and the morphology based on the microscopy . The crystal structure of Form I (interpenetrated) does not show any ordered growth in any particular direction. ~~However from t~~The morphology simulation of Form I~~, it~~ shows irregular blocks which match well with the experimental FESEM images. Inspired by this finding, we have also simulated the morphology of Form II (Hexagonal). The resulting solid hexagonal morphology is well accordance with the experimental morphology of Form II (hexagonal) after 1 hour in THF. But the final morphology of ~~the~~ Form II (hexagonal) is a hollow hexagonal tube. To shed more light on the mechanism of the hollow hexagonal tube formation, we have executed the time-dependent electron microscopy study. FESEM images of solution drop-casted after 15 min of addition of TMA in THF revealed fibrillar morphology having 5-10 μm length and 0.3-0.5 μm width. The interpentrated hydrogen bonding network of Form I disintegrates in presence of THF and ag~~i~~ain the solvent (THF) could be resposible for formation of planar hexagonal layer of TMA which can be corelated with fibre morphology. As the time progress, these fibers are self-assembled and after 30 min, resulting bundles of fibers having the same length (5-10 μm) but higher in width of 1-2 μm. This kind of self-assembly is frequently encountered in peptides where β sheet structures are self-assembled into well-ordered nano-fibres due electrostatic interaction 14 (f). Herein, the interaction may be hydrogen bonding and π-π stacking. After one hour, they converted into hexagonal rods. This can be rationalised by extensive π-π stacking in the c direction. However, within five hours, hexagonal rods convert into hollow hexagonal tube with length of 25-30 μm and width of around 1 μm. Based on the above result, we speculate that this transformation can be described as the Ostwald ripening[15] which is further confirmed by the FESEM images, taken at different time intermissions (Figure 2). In absence of THF, this kinetic form starts to degrade and slowly converts to thermodyanic form which is Form I (interpenetrated). This structural conversion is well supported by PXRD. To investigate the cyclic morphology transformation, we choosed a polar protic solvent, EtOH. We put the Form II (hexagonal) crystal in EtOH and studied~~y the~~ both FESEM and PXRD. These hexagonal tube crystals revert back to blocks in the presence of EtOH. After 60 hours in EtOH, hollow tubes break down into uniform hexagon slices, and after 15 days, these completely revert to pristine morphology. This morphology change is in good accordance with the crystal structure changes, which is confirmed by time dependent PXRD studies (Figure 3a).

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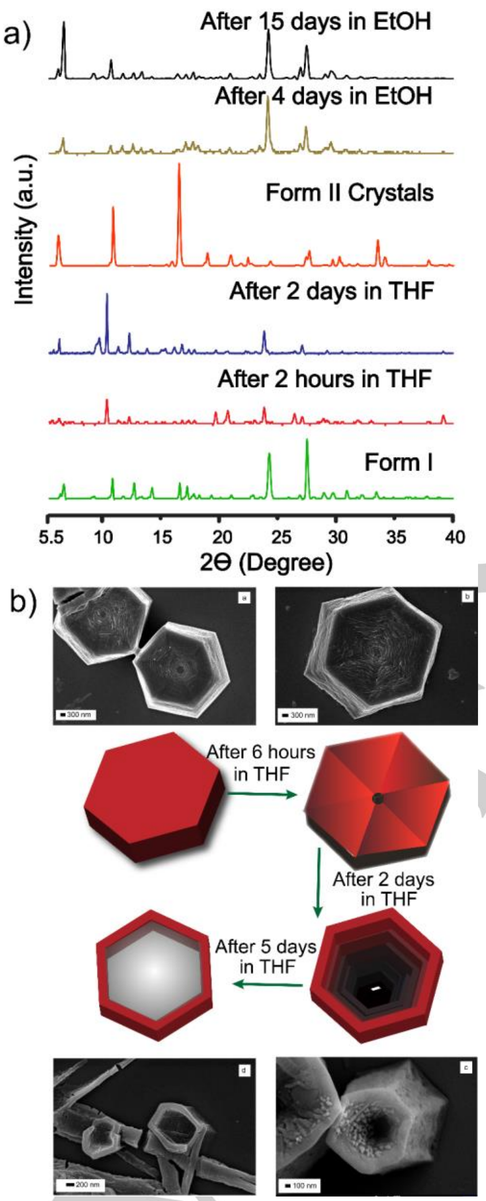

Figure 3. a) Time dependent PXRD from Form I (interpenetrated) to Form II (hexagonal) b) Mechanism of hollow tube formation: Ostwald ripening.

After dissolving Form I (interpenetrated) in THF, we measured the PXRD at different time intervals by drop casting the solution. After 2 hours, there is a minor peak at 6.3° and which emerges more intense after two days, and it corresponds 100 plane of Form II (hexagonal). Moreover, the absence of two peaks at 6.7° and 9.3° indicates that the interlocked structure completely converts to the sheet like structure (Form II). The PXRD of Form II (hexagonal) shows a peak at 6.7° and very small peak at 9.3° after 4 days in EtOH which implies that in EtOH, Form II (hexagonal) is slowly converted into Form I (interpenetrated). These peaks (6.7° and 9.3°) are more prominent after 15 days hence Form II (hexagonal) completely converges to Form I (interpenetrated). Although, we anticipated that Form II (hexagonal) should show porosity due to the presence of pore channels in the crystal structure, but in the crystal packing is unstable which made it difficult to measure the surface area.

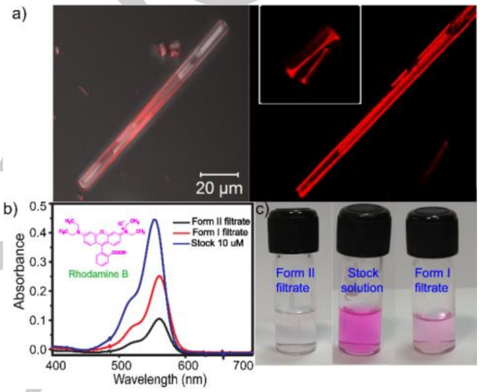

Figure 4. a) Optical image and CLSM images of Form II (hexagonal) after RhB dye adsorption indicating the presence of dye in both surface and in hollow channel. b) UV-vis absorption spectra of the filtrates. c) Digital images after dye adsorption.

Keeping that in perspective, we have tried to measure the porosity in the presence of some guest molecule adsorption. For this purpose, we have checked the Rhodamine B (RhB) dye adsorption for these forms. Interestingly. Form II (hexagonal) shows guest molecule uptake more than that of Form I (interpenetrated), which indicates that the pores of the hollow hexagon, as well as the surface, are accessible, which is not the case for Form I (interpenetrated). The unusual shape of single crystals provokes us to look for some conceivable application. As part of that the Rhodamine B (RhB) adsorption on the crystals is measured by UV-Visible spectroscopy. Typically, 0.479 mg RhB is dissolved in 100 ml of deionized water to make 10 μM stock solution. 2ml of stock, the solution is poured in a vial containing 50 mg of both Form II (hexagonal) and Form I (interpenetrated) crystals separately. Both the solutions are then kept for 12 hours, after which the crystals are separated by filtration and the absorbance of the filtrates is measured. The absorbances at wavelength 560nm were used to estimate the RhB concentration. Form II (hexagonal) adsorbs 82% while Form I (interpenetrated) adsorbs only 39% (Figure 4). The confocal laser scanning microscopy (CLSM) images showed the hollow tube, which is well in accordance with the FESEM and TEM images.

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Meanwhile, the intensive pink fluorescence_behavior of RhB indicates that it is adsorbed in the hollow channel as well as in the surface of Form II (hexagonal). After the dye adsorption, the structure of Form II (hexagonal) remains same which is confirmed by PXRD studies (Figure S12).

50-year-old trimesic acid molecules always converges to its native interpenetrated structure or with coformers or with solvates. In such a scenario the isolation of hexagonal framework crystal structure is challenging. However, we successfully isolated the smallest honeycomb crystal structure without interpenetration of the hexagonal framework or any solid support. It forms a layered hexagonal framework which are stacked along *c*-axis that results in hexagonal channels along the *c*-axis. Afterwards, we investigated the morphology evolution of hexagonal rod crystals from block shape crystals. It follows the Ostwald ripening mechanism. The more exciting part is that the crystal packing takes after the crystal morphology and also it mimics nature's honeycomb. Morphology evolution of Form I (interpenetrated) to Form II (hexagonal) is depicted via FESEM. The crystalline material Form II (hexagonal) reverts back to Form I (interpenetrated) in the presence of polar solvent EtOH. Finally, the utility and application perspective, Rhodamine B (RhB), a common pollutant in the textile industry, adsorption on the crystals Form II (hexagonal) and Form I (interpenetrated) is measured. More interestingly, Form II (hexagonal) shows 2 times more adsorption than Form I (interpenetrated). As TMA Form II (hexagonal) follows all basic aspects of patent for instance novelty (new single crystal structure), non-obviousness (it only obtained in THF) and utility (more adsorption of Rhodamine B) hence it was patented.

Keywords: Hydrogen bonded framework • Trimesic acid • Morphology Evaluation• Hollow hexagonal Rod • Dye adsorption

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