

## **Abstract**

The thesis entitled ‘Crystal Engineering of Azolate-based Frameworks: Synthesis and Structural Chemistry’ is focused on understanding the nucleation of crystals grown from solution. Today’s analytical techniques are not capable enough to study this phenomenon. Our objective is to understand the underlying mechanism of the formation of MOFs and utilize it to engineer new MOFs with desired properties. Yaghi’s work on MOFs is unprecedented in the design and synthesis of new porous solids. His SBU approach and topological considerations or reticular chemistry has provided greater insights towards engineering new targeted MOFs, though it is still difficult to predict the outcome of any crystallization reaction. Note, the SBU approach lacks molecular insights towards understanding nucleation of a crystal.

Crystallization is a supramolecular reaction. Supramolecular interactions involve all non-covalent interactions though H-bonding and coordination interactions dominate in most of the cases. Monitoring crystallization on a real time scale, especially at supersaturation involving relatively small number of molecules, calls for advanced imaging and spectroscopic techniques supported by logical theoretical models. Nucleation of a crystal is still a poorly understood phenomenon. Present day techniques used to study and understand the nucleation of a crystal are not efficient enough to access the size of critical nucleus ( $< 1\text{nm}$ ) and its periodic structure which falls in the range of a few thousands of molecules. It is difficult to know how a system chooses a specific pathway in the supersaturated solution from aggregating molecules to form a crystal nucleus. In this context, retrosynthetic analysis is a useful methodology to hypothesize a liquid like structure for this state. Retrosynthetic approach provides a link between aggregation in the solution and the solid-state structure observable by diffraction techniques. Here, we have adopted the retrosynthetic analysis to rationalise the crystal structures of related solids in a particular system available in the

structural database. The approach provides better picture of nucleation phenomenon of crystals growing from a solvent. (Chapter I)

Retrosynthetic analysis of the crystal structures revealed how the structural landscape of the different systems could be readily interpreted in terms of supramolecular aggregation between soluble molecular species present in the solution to facilitate the favorable interaction forming multidimensional coordination networks. First, we analyzed zinc–benzene dicarboxylate (BDC) system and showed how 1:1 Zn:BDC complex supramolecularly aggregates among themselves or with other ion pairs present in the solution under different reaction condition to finally result in a particular assembly (Chapter II). We extended this analysis to zinc imidazole dicarboxylate system and provided an experiment as a proof of concept to synthesize new solids (Chapter III). We succeeded in crystallizing one-dimensional zig-zag chains though our focus was to engineer new three-dimensional MOFs for gas storage applications. We opted for triazole instead of imidazole as the former showed a better tendency to form higher dimensional structures. This approach proved to be useful as we have successfully synthesized thirteen new three-dimensional cadmium triazolate polycarboxylates (Chapter IV). In Chapter V, a database analysis of another system, i.e., cobalt triazolate di/tricarboxylates led to the isolation of three new solids. we have also reported some preliminary studies on magnetism and hydrogen adsorption of **IITD-27**. In Chapter VI, we have summarized the significant results obtained in this study and the conclusions drawn from the overall investigation. The chapter also provides future scope of the work.