Polymorphism is considered as a fundamental problem in crystal engineering. Although there have been many studies carried out over the years to understand this phenomenon, the understanding of why a particular molecule adopts a certain polymorph in respective conditions is still unclear in most of the cases and the occurrence of polymorphism is often difficult to predict. It was shown in the recent past that tuning the solvent composition might provide some help to this end as solvents often affect the formation of primary synthons that are carried forward to the crystal structures. Apart from the traditional solvents which are used for crystallization studies over the years, ionic liquids have emerged as potential solvents for crystallization especially through the research done in last few decades.[1] Ionic liquids offer advantages over the conventional solvents especially in terms of its green nature and their tunability with respect to the constituent ionic components. It has been shown recently that cooling crystallization can be an effective way to facilitate crystallization from ionic liquids.[2] With this background, we have studied the role of ionic liquids (by tuning its anionic components) on the crystallization behavior of tetrolic acid. Tetrolic acid is a dimorphic compound and crystallizes in α and β forms. While metastable α form sustains through a carboxyl dimer, the stable β form is formed by catemers. Earlier studies have shown that there is a link between the solution aggregates and the crystal structures for this system.[3] Here, we have chosen two ionic liquids by keeping the cationic component as constant (Ethyl methyl imidazolium, Emim+) while varying the anionic components with very high (acetate, OAc-) and very low (bis(trifluoromethanesulfonyl)imide, NTf2-) basicity. While it was observed that the crystallization outcomes in these cases are different, unlike traditional solvents (e.g. chloroform) it lacks a straightforward solution-structure link. Why does the crystallization outcome differ? What could possibly be the crystallization mechanism? These are some of the questions addressed with an ensemble of analytical techniques.


**Keywords:** Polymorphism, ionic liquids, crystallization