Varieties of self-assemblies are formed by interactions of discrete molecules or sub-assemblies within an assembly through van der Waals interactions, and various other weak non-covalent interactions such as hydrogen bond, π-π, cation-π, anion-π, C-H···π interactions. Directional properties and hierarchical strengths of weak interactions make avenues to generate different assemblies with novel properties. Inspired by nature emerging concepts of supramolecular building blocks with biological species such as DNA and proteins have been studied. Orderly arranged molecular assemblies guided by directional properties of hydrogen bond helps in function of several natural processes. Intense interest is generated on supramolecular aspects of inorganic complexes to use in bottom-up synthesis procedure to construct assemblies with new material properties. Molecular level understanding of self-assemblies of simple metal complexes requires identifications of sub-assemblies within an assembly to think of new constructions. This is basically important in inorganic chemistry due to presence of relatively strong dative bonds and strong ionic interactions in comparisons to other weak interactions in supramolecular chemistry. These can be utilized to generate supramolecular assembly with ionic compounds as host molecules. A recent literature suggests that conjugate acid base pairs acts as host and have interesting host-guest chemistry. On the other hand, bottom up constructions of coordination polymers, self-assemblies and metal-organic frameworks contribute significantly in design of robust structures in predicted ways. Various factors such as the conformation, stacking, packing solvation, coordination numbers and oxidation state of central metal atoms plays key role in architectures of self-assemblies. With such a background the present thesis comprising of five chapters deals with self-assembling of anionic and cationic complexes and coordination polymer to understand guest recognition and modulation of optical properties.