

Abstract

This thesis deals with developing crystal engineering strategies to create functional materials and also to promote chemical reactions between molecules which are otherwise unreactive. In particular, the hydrogen (O-H...N) or coordination bonding (Ag-N) template approach was explored for promoting the [2+2] photoreactions of mono- and di-olefins containing pyridine groups as well other interfering functional groups like carbonyl, carboxylic acid, and amides. The crystal packing and photo-reactivity of the olefins has been analyzed prior to the template directed approach. The unreactive olefins were made reactive through template process and olefins which are reactive without template were made to form different products by using templates. The templates promoted the different types of alignments of olefins those results in the synthesis of various regio- and stereo-selective molecules upon photo irradiation. All the compounds synthesized in the thesis have been characterized using spectroscopic techniques and also by powder and single crystal X-ray crystallography. In general, Ag...Ag interactions have exhibited templating effect for several olefins unlike hydrogen bonding resorcinol molecules which are specifically worked for only one type of system studied in the thesis. The mechanism of double [2+2] reaction, in case of bis-olefins, has been established unambiguously by monitoring the irradiation reaction through ^1H NMR and UV-vis spectroscopy. Besides conventional crystallization of template with substrates, the mechanochemical grinding process has also been explored. Certain tetra-pyridyl photodimers have been successfully employed for the construction of metal-organic frameworks. Further, the thesis work also deals with syntheses of hydrogen bonded host frameworks between trimesic acid and a bis-pyridyl molecule that has the pentadienone spacer. Acid-pyridine and acid-carbonyl synthons together have been found to form consistent brick wall type networks with the inclusion of various aromatic guest molecules or guest ensembles.

Keywords: Supramolecular Synthon, Template Effect, Mechanochemistry, Solid State Photodimerization, Reaction Mechanism, Anion Effect, Brick-Wall Host, Coordination Polymers.