

Arrangement of Molecules for Photoreactions in Layered Peptide Crystals

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"Solid-state" or "solvent-free" organic synthesis is a promising alternative to the traditional "wet" synthetic techniques [1-2]. The solid state / solvent free methods generally comply with the principles of Green Chemistry [3] and therefore can help make the chemical industry more sustainable and therefore better for the future. However the main problem to be solved in the solid state organic synthesis is the creation of suitable mutual arrangements of reactant molecules for a desired reaction to occur. The problem was emphasized and studied by Schmidt and coworkers who introduced so-called topochemical principles for the case of [2+2] photodimerization and used the term "crystal engineering" to foresee the design of crystals making a target solid state reaction possible [4].

Short hydrophobic peptides may form microporous frameworks with persistent H-bonded layers and interlayer cavity space [5-9]. These crystal frameworks may be suitable for accommodation and appropriate arrangement of reactant molecules. Our studies have focused on creating and utilizing the peptide crystalline materials for the solid state reactions. Both the peptide molecules themselves [10] and reactant molecules accommodated in the cocrystals [11] can react in the solid state showing a promise that the peptide frameworks may become useful in the design of new solid state synthetic methods.

A range of potential reactant molecules have been screened for the formation of cocrystals with several hydrophobic dipeptides. Crotonic acid and dimethylacrylic acid were identified as the most interesting as they displayed photoreactivity in both their pure crystalline state and in cocrystals. Remarkably, the reaction pathways, product yields, and the kinetics of the reactions were different in the cocrystals. In addition, the course of the reactions depended on the irradiation wavelength used and the size of the crystals in the sample. Overall, our results show that the solid state photoreactions in peptide crystals can be controlled, although further studies are needed to understand how various conditions of the experimental setup affect the photoreaction outcome.

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