CRYSTAL ENGINEERING: REACTIVITY TO PHARMACEUTICS

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The ability to reliably form covalent bonds in organic crystalline solids promises to provide access to product molecules that may be completely unavailable to chemists in solution. Covalent bond formations in crystals can also generate polymers with unique bulk physical properties. Crystal packing, however, is a nemesis of the crystal engineer since covalent bond formations generally require reactive sites to be deliberately assembled and oriented in close proximity. In this presentation, we describe a method to direct the formation of covalent bonds in crystals using principles of supramolecular chemistry. Our reaction is well-documented in the field of crystal engineering; namely, the [2+2] photodimerization. The method relies on the use of small molecules, coordination complexes, and metal-organic frameworks as templates to assemble olefins via supramolecular synthons into geometries for inter- and intramolecular cycloadditions. The method enables the synthesis of complex molecules such as [2.2]cyclophanes and [*n*]-ladderanes with emerging properties (e.g. ligands in coordination chemistry). Related work in the field of pharmaceutics will also be described. Implications to organic synthesis, materials science, and molecular manufacturing will be discussed.