Structure–Property Studies of Self-Assembling [n.n]Paracyclophanes

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Supramolecular polymers formed by self-assembly of discotic aromatics through a combination of hydrogen bonding and π–π interactions have been extensively studied, but until now, all structure–property studies have focused on manipulating the molecular recognition unit at the monomer level. By covalently linking two otherwise independent self-assembling arenes, novel stereochemical, conformational, and dipolar properties emerge. These [n.n]paracyclophanes are a unique class of arenes in which molecular information can be programmed at the dimer level. Here we present examples of [2.2] and [3.3]paracyclophanes (**[2.2]pCpTA**, **[3.3]pCpTA**) which self-assemble through a combination of double-helical transannular and intermolecular amide hydrogen bonding to create homochiral assemblies in solution and in the solid state. Increasing the interatomic distances between benzene decks by increasing the length of the covalent linker leads to structural and conformational changes that weaken intermolecular assembly for **[3.3]pCpTA** compared to its **[2.2]pCpTA** counterpart.

