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When the Unexpected Shapes Supramolecularity

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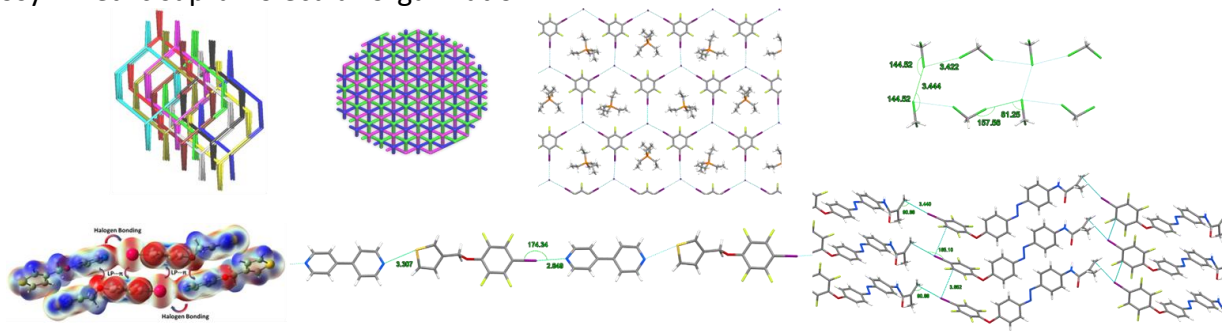
Tetragonal building blocks can self-assemble with complementary partners to form structural motifs featuring large cavities. These voids are often occupied by guest molecules, leading to interpenetrated networks with unpredictable entanglements.[1][2] Spherical anions such as halides are capable of multidentate binding, with coordination numbers ranging from one to nine. In the presence of diiodoperfluorinated chains, they give rise to Borromean rings, remarkable supramolecular structures with high topological complexity.[3][4] Alternatively, with trigonal partners and specific cations, these systems can form (6,3) networks.[5][6] In the study of halogenated and hydroxyl hydrazones derived from pharmaceutical compounds, an unexpected linear arrangement of clathrated dichloromethane molecules is observed.[7] In modified thiophenes, N···I halogen bonding and lone pair···π interactions act cooperatively to direct supramolecular organization, as confirmed by X-ray and theoretical analyses.[8] In related systems, the self-assembly of a halogen bond donor thiophene with a series of bipyridyl derivatives leads to the unexpected formation of N···S chalcogen bonds.[9][10] Finally, the crystal structure of a halogen-bonded azobenzene bearing a methacrylate group reveals a surprising I···CH_2=C contact and a non-centrosymmetric supramolecular organization.[11][12]



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