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Synthesis and solid state self-assembly of an isatin-thiazoline hybrid driven by three self-complementary dimeric motifs

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ABSTRACT

An interesting isatin-thiazoline hybrid molecule having C=N-N=N bonds has been synthesized and its solid state self-assembly behavior was studied by X-ray diffraction technique. A layered structure based on hexameric supracycles, which are formed through three different self-complementary dimeric motifs, was obtained. The supramolecular forces involved in the stabilization of this structure are NH-O, CH-O, CH-N, CH-π, π-π, CH-Cl and unconventional N-O interactions.

Molecules are assemblies of atoms formed by the selective formation of kinetically stable covalent bonds between smaller molecules (typical bond enthalpies are 100-400 kJ/mol). Apart from these stronger covalent bond interactions, molecules can also interact through weaker and kinetically labile non-covalent interactions such as hydrogen bonding, π-π, CH-π, cation-π, anion-π, van der Waals, etc.[1] These interactions are the most important in biology and are responsible for the transduction of signals, folding of large proteins into a 3D-structure and the selective transport of ions.[2] Such interactions are also important in Nature and the abiotic world, where they determine the physical properties of common materials such as wood and plastic.[3] The process in which molecules use these interactions to adopt a defined arrangement without any external guidance is called molecular self-assembly.[4]

Molecular self-assembly with a precision analogous to that found in Nature demands a complete understanding and control of non-covalent interactions.[5] It has become a vital 'bottom-up'' approach to create fascinating materials from simple components/molecules and to understand the complexity of systems created by Nature through self-assembly, ranging from cell membranes to organisms. This is the main driving force for crystal engineers to construct novel molecular assemblies of distinct shapes. The symmetry, shape and functionality of the individual components are the key requirements for constructing complex self-assembled structural materials of different shapes for applications in many fields, including microelectronics,[6] medicine and biotechnology,[7] catalysis,[8] sensors,[9] and solar-fuel cells.[10]

Molecular complementarity is highly desired for the tight and highly specific binding of molecules. Biomacromolecules such as proteins and DNA represent the best examples. Inspired by Nature, supramolecular chemists have also used complementary or self-complementary non-covalent interactions between individual building blocks to develop well-defined, discrete aggregates.[11] Multiple parallel or near parallel hydrogen bonds are commonly used motifs for this purpose. Important examples include self-assembling container molecules and supramolecular tubes.[12] Apart from the tremendous progress, complementary motifs involving relatively weak interactions other than hydrogen bonds have not been explored so far. Herein, we report on the multi-layered structure of an isatin-thiazoline hybrid molecule (**5**), having diverse supramolecular interactions. It has three self-complementary motifs, one involving very strong hydrogen bond supported by some unconventional nitrogen-oxygen (N-O) interactions; the second includes CH-π and CH-Cl interactions, whereas the third involves π-π and CH-Cl interactions, arranging

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