

SYNTHON ROBUSTNESS AND VOID FLEXIBILITY IN ORGANIC HOST-GUEST CRYSTALS

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The design of new microporous solids and their self assembly using hydrogen bonding and intermolecular interactions is a current theme in crystal engineering. Once a new host framework is obtained, the natural question is: Can one alter the cavity size and shape in a systematic way and yet retain the same overall packing? To address this issue, we have used a combination of strong and weak hydrogen bonding (O-H...O, C-H...O) and halogen...halogen interactions to synthesize host-guest systems with wheel-axle, layered-clay and hexagonal-nanotube architectures. A common theme in our host design principle is the use of two sets of interactions that have different strength and directional preferences. Ideally these interactions should be orthogonal, that is geometrically and chemically insulated from each other. In such a crystal design strategy, the strong, recurring hydrogen bond synthon gives structural robustness in a family of inclusion adducts while the weak, soft interactions impart flexibility to tune the cavity shape and channel dimension.

The above approach is implemented as follows: (1) supramolecular synthon with the desired topology is extracted from the Cambridge database, (2) molecules with the appropriate symmetry and functional group are synthesized and then crystallized, (3) clathrate structures are characterized by X-ray diffraction and their packing analyzed. Thus, structure-property relationship in organic clathrates may be understood as the control of target host architecture by recurring, robust synthons and adaptivity for the inclusion of different guest molecules through weak hydrophobic interactions.

References

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Keywords: HOST GUEST CLATHRATE NANOSTRUCTURE

AGGREGATION-CONTROLLED PROTON TAUTOMERIZATION

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Compounds that undergo proton tautomerization can be thermochromic, because the tautomerization involves a proton transfer that accompanies a reorganization of the relevant p-conjugated system. Salicylideneanilines belong to a class of such compounds. In salicylideneanilines OH form is usually much more stable than NH form and the population change of the two tautomers with variation of the temperature has been regarded as an origin of the thermochromism. We observed a crystal structure change associated with the tautomerization from the X-ray crystallographic analysis of a salicylideneaniline and found that NH form of the compound is considerably stabilized by intermolecular hydrogen bonding and electrostatic intermolecular interactions. The results indicate that the association of molecules is essential for the stabilization of NH form. We discovered that a great stabilization of NH form generally takes place even in a fluid solution when the molecules form an aggregate. Many salicylideneanilines in hydrocarbon solvents exhibited a remarkable change in the electronic absorption spectra with lowering of the temperature. At 297 K only OH form is present. As the temperature is lowered, the absorption bands of OH form decrease in intensity and new bands of NH form appear. At 77 K, OH form disappears and only NH form is present. This phenomenon depends on the concentration of the solution. The results indicate the formation of aggregates at low temperature and the stabilization of NH form in the aggregate. Thus, the proton tautomerization is controlled by the aggregation of molecules.

Keywords: THERMOCHROMISM PROTON TAUTOMERIZATION AGGREGATION

MOLECULAR POLYMETAL-OXO CLUSTER AGGREGATES AS BUILDING BLOCKS FOR SUPRAMOLECULAR ARRAYS

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Hydrolysis reactions are a feature of the chemistry of many metal ions and usually lead to the formation of oxo- and hydroxo-bridged aggregates and then hydroxide, hydroxyoxide or oxide minerals. This chemistry can be controlled by supplying templating ligands which direct the size and shape of the intermediate aggregated species in a manner similar to that employed in Nature in biomineralisation processes. This makes it possible to favor the formation of molecular polymetal-oxo clusters, which have different properties from the related extended mineral phases as a result of the strong boundary effects, which operate in such systems. Furthermore, it is possible to functionalize the encapsulating ligands to enhance different types of supramolecular interactions amongst the molecules. In this way it is possible to create, for example, arrays of linked magnetic particles or mesoporous networks of alumina based particles, which have been shown to display a zeotypic behavior. Structure determination using single crystal X-ray diffraction has been used in conjunction with a variety of physical property studies in order to characterize these systems.

Keywords: MOLECULAR AGGREGATES, SUPRAMOLECULAR INTERACTIONS, COORDINATION COMPOUNDS

A NOVEL Fe(II) FRAMEWORK STRUCTURE: CORRELATIONS TO ITS THERMAL AND LIGHT INDUCED SPIN TRANSITIONS

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New opportunities for the development of novel electronic devices may arise from the control of the spin crossover phenomenon. Widely studied in iron(II) molecular complexes, it can be produced by a change of temperature, pressure or by light irradiation. The latter is a most promising feature of the spin transition, with potential applicability in optical storage devices. However, up to now, the LIESST effect (Light Induced Excited Spin State Trapping) has been only observed at very low temperatures. It is then crucial, for useful applications, to determine and study the molecular factors that will predispose a material to undertake a photoconversion at ambient temperatures. In this context, cooperativity appears to be very important and considerable effort is currently being devoted to understanding how the spin transition is propagated through a crystal. Strong cooperativity would be expected to be most likely, and indeed has been observed, in polymeric and 3D extended systems. We present here an iron(II) complex, in which we have tried to enhance cooperativity through interactions via [Ag(CN)₂]⁻ anions. The resulted compound was found to be Fe₂ (pyrimidine) [Ag₂(CN)₃]⁻ [Ag(CN)₂]⁻ and it presents a two-step (at 185 K and 150 K) spin transition showing also the LIESST effect at temperatures below 70 K. X-ray diffraction data has been collected at 290 K, 220 K, 170 K, 90 K, 30 K and at 30 K after irradiating the crystal with a 638 nm He-Ne laser. Fascinating structure-property correlations have been obtained from a molecular structure that shows an unprecedented packing arrangement for a spin crossover compound.

Keywords: LOW TEMPERATURE CRYSTALLOGRAPHY, SPIN CROSSOVER, LIESST EFFECT