

Molecular Recognition

MS11.01.01 COMPLEXES OF FULLERENES WITH HOST MOLECULES. Jerry L. Atwood, Department of Chemistry, University of Missouri, 6091 S. College Ave., Columbia, MO 65211

Because of the shape and symmetry of C₆₀, crystallographic structure determinations often involve problems, such as disorder. Host-guest complexes of C₆₀ and calixarenes and cyclotrimerarylenes (CTV) have provided ways of ordering the fullerene. In this discussion I will address the strategy for the complexation of C₆₀, C₇₀, and higher fullerenes. Specifically, attention will be paid to the matching of symmetry of the fullerene with the host molecule.

MS11.01.02 REACTIVITY AND STRUCTURE OF CHIRAL CRYSTAL. Fumio Toda, Department of Applied Chemistry, Faculty of Engineering, Ehime University, Matsuyama, Ehime 790, Japan

We have been studied the relationship between reactivity and structure of inclusion chiral crystal prepared from chiral host and achiral guest. In this microsposium, we present some interesting difference of selectivity of photoreaction in the chiral crystal prepared by recrystallization of chiral host and achiral guest compounds from solvent and that prepared by mixing of powdered both components in the solid state. In most cases, photoreaction of the host-guest inclusion crystal prepared by recrystallization of chiral host and achiral guest from solvent and that prepared by mixing powdered both components gave the optically active product of the same chirality. X-ray analysis of the inclusion crystal prepared by the recrystallization showed that achiral guest molecules are arranged in a chiral form in the inclusion crystal. In a special case, however, photoradiation of the host-guest inclusion crystal prepared by recrystallization of an achiral guest and chiral host compound from solvent gave (+)-chiral photo-reaction product. On the other hand, the same reaction of the inclusion crystal prepared by mixing the both in the solid state gave (-)-chiral photoreaction product.

The very interesting difference of inclusion behavior by chiral host and racemic host was found. Chiral and racemic 7-bromo-1,4,8-triphenyl-2,3-benzo[3.3.0]octa-2,4,7-trien-6-one include 4-picoline and 2-picoline, respectively.

MS11.01.03 CRAFTING POROUS CRYSTALLINE NETWORKS IN MOLECULAR BASED SOLIDS. Israel Goldberg, School of Chemistry, Tel Aviv University, 69978 Ramat-Aviv, Israel

The versatility of porphyrin-based metallomacrocycles as crystalline hosts appears to be unequaled due to the large size, high symmetry, rigidity and thermal stability of the molecular framework. It is feasible to tailor their shape and functionality features by organic synthesis, and thus affect the microstructure of the resulting assembly. In this study we demonstrate that a suitable functionalization of the metallomacrocyclic framework with polarized aryl groups can be used to develop simple chemical models of self-assembly via weak intermolecular forces, and to control the spontaneous built-up of the porphyrin lattice by molecular recognition properties of the respective sensor groups. The strength and multiplicity of the noncovalent interactions are expected to act in concert to reinforce directional preferences and dominate the crystal field. In the resulting crystalline materials the molecular building blocks are incorporated into pseudo-rigid polymeric arrangements with a porous architecture.

Our preparative efforts focused on the design of several new classes of hollow crystalline networks in which the metallomacrocyclic units are linked into multidimensional poly-

meric architectures via metal-ligand coordination, hydrogen-bonding, dipolar association, halogen-halogen interaction, π - π stacking and C-H- π -contacts. The size and shape characteristics of the pore structure in these networks are determined by the nature of the particular supramolecular synthon involved in steering the intermolecular self-assembly. Most of the porphyrin-based solids have a strong tendency to incorporate molecular guest components of complementary shape into the lattice, and thus provide novel types of potential solid state receptors for isolation, separation, transport, exchange and controlled release of molecular entities. The structural and inclusion features of the various motifs will be discussed in some detail.

MS11.01.04 MODELLING MICELLAR AGGREGATION OF BILE SALTS. Sofia Candeloro De Sanctis, Facolta' di Medicina, Dipartimento di Chimica, Universita' di Roma "La Sapienza"

The bile salts anions are amphiphilic steroid-like molecules with a rigid backbone of four fused rings from which three methyl and a variable number of hydroxyl groups are protruding. The molecules have flexible side chains of variable length and chemical constitution. In the physiological medium they interact through micellar aggregation, with important molecules like cholesterol, bilirubin, phospholipids, fatty acids. In most of the crystals we have studied so far they aggregate into very stable helical structures.

The helices are stabilized by an extended network of hydrogen bonds, as well as ion-ion and ion-dipole interactions. Molecules with different side chains and counterions can give rise to very similar packing motifs with similar hydrogen bonding schemes, indicating the important role of the hydrogen bonds for such structures.

The outer surfaces of the helices in the crystals have large non polar regions. However, for some of the bile salts we have evidences indicating the stability of the helical structures in the aqueous solutions, suggesting their presence possibly in the physiological medium as well. We are, therefore, using the helical arrangements found in the crystals as models for the micellar aggregation of bile salts and for their possible selective interactions with the molecules of the biological medium.

MS11.01.05 MOLECULAR RECOGNITION OF DIHOMOOCALIX[4]ARENE IN THE CRYSTAL STRUCTURES OF (1:1) COMPLEXES WITH XYLENE ISOMERS. Ken-ichi Tomita*, Kenji Suzuki#, Isao Nakanishi+, Anthony E. Armah*, Zouhair Asfari@, Jacques Vicens@, *Faculty of Pharmaceutical Sciences, Osaka University, Suita, Osaka 565, #Dainihon Pharmaceutical Co., Enokicho, Suita, Osaka 564, +Fujisawa Pharmaceutical Co., Kashima, Yodogawa-ku, Osaka 532, Japan, @Laboratoire de Chimie Minerale et Analytique, E.H.I.C.S., Strasbourg, France

Dihomooxalix[4]arenes(1) are macrocycles made from four phenolic units meta-linked by three methylene and one methylene oxy-methylene bridges at positions ortho to the hydroxy groups, and the hydrogen atom at the position para to the hydroxy group of phenolic residues was replaced with bulky aliphatic groups (p-isopropyl or p-tert-butyl). Recently, we have reported our results on the isomer separation of the xylenes by extractive crystallization with calix[4]arenes including dihomooxalix[4]arene(2), and p-isopropyl dihomooxalix[4]arene extracted oxylene with 84 % selectivity while para-xylene with only 16 % selectivity. This fact may indicate the difference and strength of molecular recognition of xylene isomers by dihomooxalix[4]arene. Therefore, we solved the crystal structures of (1:1) complexes of dihomooxalix[4]arenes with xylene isomers(3) and we tried to simulate the specific molecular recognition mechanism exhibited