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Acta Cryst. (2011) A67, C377**Ternary inclusion compounds based on the gossypol-chloroform host matrix - stabilizing effect of the aromatic guest component**

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Gossypol (Gp), the natural product of a polyphenolic nature, is known to form a large variety of inclusion compounds with solvent molecules as the guest components. From aprotic solvents Gp inclusion compounds are formed that are based on the host matrix constructed from columnar Gp assemblies, that in the highest symmetrical case belong to the $P12/c1$ rod group [1]. This group of compounds is represented by unstable Gp/CHCl₃ (1/1) inclusion compound that crystallizes in the C2/c space group with $Z'=1$. It has been proposed that desolvation of this compound proceeds stepwise *via* crystalline forms with the 4:3, 4:2 and 4:1 host:guest ratio [2]. Indeed, inclusion compounds having these stoichiometries and constructed from similar host columnar aggregates were prepared when Gp was recrystallized from toluene, benzene and p-xylene, respectively. Moreover, the intermediate form of Gp/CHCl₃ inclusion compound with the 4:2 host:guest ratio was also obtained.

To our surprise, when Gp was recrystallized from a mixture of solvents: CHCl₃/benzene, CHCl₃/toluene, CHCl₃/p-xylene, stable ternary inclusion compounds were formed with the aromatic molecules (Ar) occupying every second centrosymmetric void in the basic Gp/CHCl₃ (1/1) matrix. These inclusion compounds have Gp/CHCl₃/Ar ratio of 4/4/1 and crystallize in the P-1 or P2₁/c space groups with $Z'=4$. Similar ternary compounds were also obtained with naphthalene or pentafluoroaniline as the third component. In turn, when Gp crystallization was performed from mixtures of CHCl₃ with o- or m-xylenes another group of ternary inclusion compounds was obtained with Gp/CHCl₃/Ar ratio of 4/2/1 (P2₁/c, $Z'=2$). Structure of these compounds is to a large extent isostructural with the binary inclusion compound Gp/toluene (4/3), but with two symmetry independent guest sites occupied in ternary compounds by different guest components.

In addition to structural studies, stability data for the ternary Gp compounds will be presented.

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Keywords: inclusion compound, packing motif, intermolecular interactions

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Acta Cryst. (2011) A67, C377**Exploring the assembly possibilities of calix[4]dihydroquinone**

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The strong interest towards the synthesis of new building blocks in the field of the Crystal Engineering is related to the aim of this discipline that is "the rational design of functional molecular solids" [1].

Calix[4]arenes are a class of organic compounds investigated to meet this aim. 4,4'-Bipyridine is a rigid linker frequently used in the assembly of supramolecular architectures [2]. In fact it is able to act as hydrogen bond acceptor and to give rise to stacking $\pi - \pi$ or to other van der Waals-like interactions. Despite of these features, only few

examples of co-crystals between calix[4]arenes and 4,4'-bipyridine have been reported [3].

At the Dept. of Chemistry and Biology of the University of Salerno we prepared and characterized a new crystalline solid based on *p*-Bu'-calix[4]dihydroquinone **1**. The molecule, thanks to the presence of two vicinal hydroquinone moieties and to the large *t*-butyl substituents, is able to form a zeolite-like network [4].

Recently we have shown that **1** exhibits a certain variety of assembly possibilities, which can be triggered by appropriate solvent choice. [5] In particular, by using as crystallization solvents chloroform and water, it is possible to obtain a triclinic system. The unit cell contains two equivalent calixarene molecules, two water molecules and two chloroform molecules. The water molecules bridge the calixarene molecules through hydrogen bonds. The chloroform molecule is located inside the cavity of the calixarene molecule (Figure 1)

Considering the packing features we decided to replace the water molecules with the 4,4'-bipyridine molecules and to verify if the general arrangement was preserved. Triclinic single crystals have been obtained. The unit cell contains two equivalent calixarene molecules, one 4,4'-bipyridine molecule and two ethyl acetate molecules. Thanks to the similar molecular interactions the packing of the new structure is very similar to the one containing water. Nevertheless the 4,4'-bipyridine molecules show additional stacking $\pi - \pi$ interactions with the calixarene's aromatic rings (Figure 2).

These first results on the rational study of the possible intermolecular interactions could define a design strategy that could lead to predictable packing modes and be useful to obtain peculiar properties.

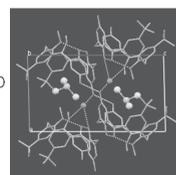
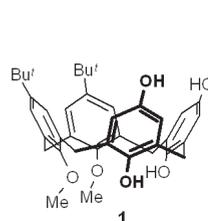


Figure 1

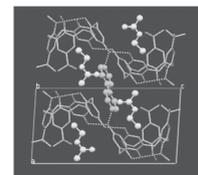


Figure 2

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Keywords: crystal engineering, hydrogen bonds, calixarene

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Acta Cryst. (2011) A67, C377-C378**Ultra high porosity, multi-variant MOFs and conducting porous materials**

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In the present abstract we summarize part of the work that we are currently carrying out within the reticular chemistry field. In particular, some of the objectives in which we have focused our efforts are preparing materials with ultra high porosity, functionalizing the open spaces of MOFs in a controlled manner, and providing crystalline porous materials with new properties:

Poster Sessions

Ultra-high porosity in MOFs: One of the most important properties of metal-organic frameworks (MOFs) is their high porosity and high specific surface area, which has led to many applications concerned with gas storage, separations, and catalysis. An important consideration in maximizing the uptake of gases within porous MOF crystals is to increase the number of adsorptive sites within a given material. We have succeeded in preparing materials with ultra high porosity (10400 m²/g Langmuir) by combining octahedral SBUs with tritopic linkers, following the isoreticular expansion principle (MOF-180, -200). In addition, the combination of tritopic and ditopic linkers also led us to highly porous materials with new topologies (MOF-210, -205).

Multiple Functional Groups of Varying Ratios in Metal-Organic Frameworks (MTV-MOFs): We show that MOFs can incorporate a large number of different functionalities on linking groups in a way that mixes the linker, rather than forming separate domains. Our strategy to making MTV-MOFs is to assemble their structures from links with different functional groups whose orientation, number, relative position, and ratio along the backbone can be controlled by virtue of the unchanged length of the link and its unaltered connectivity. In this way, each of the pores within the MOF would have an array of functionalities pointing into its center.

Porous Materials with charge mobility and electrical conductivity:

We have prepared two covalent organic frameworks (COFs) with structures based on covalently linked porphyrin units to afford sheets in which the porphyrin units are stacked laterally to give an efficient conducting interface. The two porphyrin COFs (COF-66 and COF-366) have been found to be hole conducting with mobilities as high as 8.1 and 3.0 cm²V⁻¹s⁻¹. Such multifunctional conducting COFs combine thermal stability, electrical conductivity, high charge mobility, and pore accessibility and, as the first members of the COF family to exhibit such properties, represent an important step towards plastic electronics and optoelectronics.

By combining 1,2,3-triazole and divalent metal atoms, a new family of seven metal-triazolates, METs, has been prepared. The crystal structure of the compounds has been determined *ab initio* by applying the charge flipping method to powder X-ray diffraction data obtained from a laboratory X-ray source. The new compounds exhibit a dia network type, built up from tetrahedral secondary building units. All the materials are porous, having surface area in the range 480 - 1100 m²/g. The Fe(II)-MET material has proven to have electrical conductivity. Measurements carried out in a pressed pellet of Fe-MET reveals a conductivity value of 10⁻³ S cm⁻¹.

Keywords: porous, powder, MOFs

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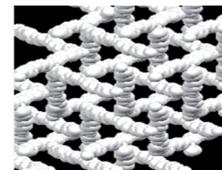
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A series of rarely observed all helical 3-D coordination polymers derived from various chiral amino acids :effect of amino acid side chain & their unique ability of separating cations & anions

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Design and synthesis of functional MOF is an active area of material research for their various potential applications viz. molecular storage, catalysis, magnetism, non-linear optical material, selective anion separation etc. Crystal engineering is a major support in developing different novel functional MOFs.[1] When these tailor-made MOFs engineered by crystal engineering approach are chiral then these become even more important for their immense possibility to be used as a promising functional material. Moreover chiral helical coordination polymers are also interesting for their fascinating supramolecular architectures. Four rarely observed all

helical 3-D coordination polymers (all belong to enantiomorphic P3₂1 space group) derived from chiral amino acid based viz. Phenyl alanine, alanine, leucine bis pyridyl bis amide ligands with Cu⁺² are studied by single crystal X-ray diffraction. The study is undertaken in order to demonstrate the effect of amino acid side chain on overall supramolecular architecture. This is a part of our ongoing research efforts which include a detail and systematic study of amino acid side chain on overall supramolecular architecture within a coordination network[2]. The unique ability of those MOF to separate cations and anions are also worthwhile to be mentioned here.



General views of MOFs along c-direction

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Photonic materials: how protonation influence structure and properties

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Salt formation is the most common and effective method to increase solubility and dissolution rates of drugs. For compounds containing amino groups their protonation in presence of acids leads to formation of salts with better solubility than for neutral compounds. On the other hand, if consider compounds for potential application as photonic materials in photodynamic therapy, it should be taken into account that protonation might significantly influence molecular polarizability, and hence photonic properties of such materials. Series of neutral, mono- and triprotonated (dialkylammonio)-benzylidenepiperidones was structurally characterized and geometrical characteristics were compared with results of quantum-chemical computations. Spectroscopic evaluation of one and two-photon absorption properties, and hyperpolarizabilities values are compared with geometrical characteristics obtained for neutral and protonated materials.

Keywords: organic salts, NLO properties, benzylidenepiperidones

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Two Co(III) dioximates with unprecedented V-shape ligands in apical positions

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