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Antimicrobial proteins are considered to be of interest in food biocontrol, agricultural biotechnology and for the treatment of bacterial infections since they constitute an alternative to classical low molecular weight antibiotics. One group of enzymes generating hydrogen peroxide are the L-amino acid oxidases (LAOs), which oxidize L-amino acids, releasing the corresponding keto-acid and ammonium in addition to hydrogen peroxide. The melanogenic marine bacterium *Marinomonas mediterranea* synthesizes a novel antimicrobial protein (LodA) with lysine-epsilon oxidase activity (EC 1.4.3.20). LodA seems to contain a quinonic cofactor and is very specific for L-lysine, catalyzing the reaction: L-lysine + O_2 + H_2O → 2-aminoadipate 6-semialdehyde + NH_3 +H_2O_2. Homologues to LodA have been detected in several Gram-negative bacteria, where they are involved in biofilm development.

We have obtained crystals of the recombinant LodA protein that belonged to the monoclinic P2 space group. These crystals diffracted up to 2.4 Å in a synchrotron source. The asymmetric unit presented a homodimer. The monomer is made up by 726 amino acids of which only the first 686 are visible in the crystallographic structure, the missing amino acids corresponded to the C-terminal region of the sequence. The structure of the monomer showed the presence of a central core with three different domains (according to its secondary structure), a first domain made up by three beta-sheets, a second made up by alpha-helices, and a third that do not present much ordered secondary structure. Coming out of this central core there are two long pleated beta-sheets (36 and 24 amino acids) that embrace the other monomer giving stability to the crystallographic dimer. The observation of the crystallographic contacts suggests that the biological unit might be a tetramer, this point has to be confirmed by other experiments.

The quinonic cofactor that takes part in the catalytic reaction is made up by a cysteine bound to a modified tryptophan forming a cysteine tryptophylquinone. The active site is located on one side of the central core, and at the same side where the pleated beta-sheets protrude to interact with the other monomer. This geometry will allow the small substrate to diffuse easily into the interior of the active site, but will hamper any bigger substrate containing L-lysine (polypeptide or protein) from entering the active site.

Keywords: LodA, cysteine tryptophylquinone, M. mediterranea

MS.93.5

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Crystal structures of [NiFe] hydrogenase maturase complexes

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[NiFe] hydrogenases catalyze the reversible production of molecular hydrogen in many microorganisms. The active site of [NiFe] hydrogenases carries a NiFe$(CN)_2$CO center. The assembly of the metal center of [NiFe] hydrogenases is a complicated process that requires six specific maturation proteins: Hyp proteins (HypABCDEF). In the maturation process, HypC (metallochaperone), HypD (4Fe-4S protein) and HypE (CN synthesis) are involved in the synthesis and insertion of the Fe$(CN)_2$CO ligand. HypC and HypD form a complex, which receives the CN ligand from HypE through transient interaction between them. The crystal structures of these proteins revealed structural features of each protein and functional roles of conserved motifs [1]. HypD is notable for having a thiol redox cascade similar to the ferredoxin:thioredoxin reductase system. However, it remains unclear how HypC, HypD and HypE form the binary and ternary transient complexes that catalyze the biosynthesis of the Fe$(CN)_2$CO ligand.

In order to gain a better understanding of the maturation process, we have determined the crystal structures of the HypC-HypD (HypCD) and HypC-HypD-HypE (HypCDE) complexes, 2.55Å and 2.25Å resolution, respectively. In the HypCD complex, HypC is bound to the conserved region of HypD through extensive hydrophobic interactions and several hydrogen bonds. HypD undergoes an induced fit conformational change to recognize the β-barrel domain of HypC. In the HypCDE ternary complex, the HypCD complex is loosely bound to each C-terminal side of the HypE dimer using a hydrophobic anchor. The HypC N-terminus and HypE C-terminus, which contain essential cysteine residues, can access the HypD conserved motifs, including a thiol redox cascade. These results provide a structural basis for Fe atom cyanation by the thiol redox cascade in the transient HypCDE complex.

[1] S. Watanabe, R. Matsumi, T. Arai, H. Atomi, T. Imanaka, K. Miki *Mol. Cell* **2007**, *27*, 29-40.

Keywords: metallocenter assembly, transient protein-protein interaction, thiol redox

MS.94.1

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Metastability in supersaturated solution and transition towards chirality in the Crystallization of $NaClO_3$

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The crystallization of $NaClO_3$ in supersaturated boiling solutions leads to a strong bias of enantiomorphic crystals of the same chiral sign, which in the range of the experimental errors cannot be distinguished from that of a homochiral crystal mixture [1]. The crystallization reactor is a closed system but with a temperature gradient between the walls of the reactor and the air/liquid interface that entails an intense recycling of the sub-critical nuclei formed during the induction period of the primary nucleation in the bulk. During this period, the evolution of the population of sub-critical nuclei takes place without any other noticeable crystal growth process. The fast evolution of a myriad of supercritical nuclei and the immediate separation of the crystals formed excludes secondary nucleation and Ostwald ripening as the cause of the transition towards chirality in these experimental conditions. Therefore, the evolution towards homochirality should be attributed to the primary nucleation process. The bifurcation towards a stationary homochiral state is a consequence of the instability of the system due to the chiral recognition of enantiomorphic solid phases as thermodynamically distinguishable entities and the absence of degrees of freedom when P and T are fixed in the 2-component system (compound and solvent). Analysis of the chiral composition of the crystal mixture obtained from samples of boiling solutions of $NaClO_3$ indicates that symmetry breaking towards homochiral compositions may begin in the metastable stage preceding crystallization, i.e. at the level of subcritical clusters. The general thermodynamic conditions for such a spontaneous mirror symmetry breaking are discussed.

[1] a) J. Crusats, S. Veintemillas-Verdaguer, *Chem. Eur. J.* **2006**, *12*, 7776-7781. b) Z. El-Hachemi, J. Crusats, J.M. Ribo, S. Veintemillas-Verdaguer, *Cryst. Growth Design* **2009**, *9*, 4802-48205. c) Z.- El-Hachemi, J. Crusats,

J.M. Ribo, J.M. McBride, S. Veintemillas-Verdaguer, *Angew. Chem. Int. Ed.* **2011**, *50*, 2359-2363.

Keywords: chirality, cluster, critical

MS.94.2

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Sergeants and soldiers in two dimensions: Amplification of chirality in molecular monolayers at surfaces

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A promising approach to study chiral molecular recognition is studying two-dimensional (2D) crystallization phenomena on well-defined surfaces via scanning tunneling microscopy (STM). We present studies on different two-dimensional chiral systems and discuss their tendency to undergo enantiomeric separation. A special surface enantiomorphism is observed via STM after adsorption of the enantiomers of a helical aromatic hydrocarbon on Cu(111). Instead of crystallization into homochiral 2D domains on the surface [1], racemic enantiomorphs are observed. In this situation, a small excess of one enantiomer is sufficient to create domains possessing single handedness throughout the entire surface layer [2]. The induction of homochirality by chiral doping has also been observed for succinic acid and achiral (*R,S*)-tartaric acid [3,4]. Our findings are explained by cooperative interactions between many chiral units, similar to the mechanism of chiral amplification observed in helical polymers and coined as "Sergeant and Soldiers" principle. Another recently observed phenomenon is single enantiomorphism due to chiral conflict. Depending on the handedness of a chiral adduct to a racemic situation suppresses one enantiomorph during crystal growth, but supports the other by forming a quasiracemic solid solution [5].

[1] R. Fasel, M. Parschau, K.-H. Ernst, Angew. *Chem. Int. Ed.* **2003**, *42*, 5178-5181. [2] R. Fasel, M. Parschau, K.-H. Ernst, *Nature* **2006**, *439*, 449-452. [3] M. Parschau, S. Romer, K.-H. Ernst, *J. Am. Chem. Soc.* **2004**, *126*, 15398-15399. [4] M. Parschau, T. Kampen, K.-H. Ernst, *Chem. Phys. Lett.* **2005**, *407*, 433-437. [5] C. Roth, D. Passerone, K.-H. Ernst, *Chem. Comm.* 2010**,** *46*, 8645-8647.

Keywords: 2D crystals, chirality

MS.94.3

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Facet-specific binding of amino-acid analogues on quartz

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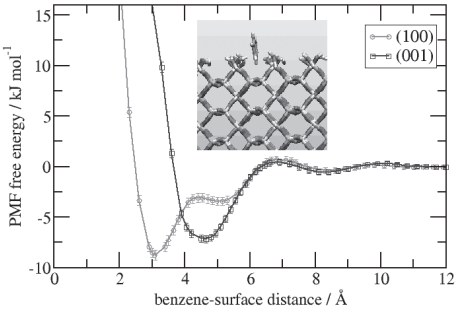
Silica-binding peptides have a wide range of potential applications such as controlled fabrication of silica nanostructures. Quartz-binding peptides have been identified [1, 2], but their modes of binding remain less well understood [3]. As part of a programme to address the fundamentals of this problem, the free energy of adsorption of amino acid analogues on the (100), (001) and (011) hydroxylated alpha-quartz surfaces under aqueous conditions are calculated using the potential of mean constraint force method and atomistic molecular dynamics simulations. The analogues considered are methane (alanine), methanol (serine), ammonium (lysine), benzene (phenylalanine) and ethanoate (aspartic/glutamic acid). To probe the effect arising from the presence of the linkers in the side-chains in the case of ammonium (lysine) adsorption, we also report results of simulations on butyl ammonium.

The most favourable free energies of adsorption are observed for the non-polar adsorbates methane and benzene, and also for the negatively-charged ethanoate ion, whilst the positively-charged ammonium ion showed negligible binding. The polar adsorbate methanol showed intermediate adsorption strength. Shielding of hydrophobic regions of polar and charged adsorbates by the surface are thought to contribute significantly to their surface binding, with the adsorption of methane and butyl ammonium being more favourable than that of water and ammonium respectively.

Several of these analogues show facet-specificity in their binding to these quartz surfaces. Although this energetic effect is not large for the analogues, this facet-specific adsorption may operate collectively for facet-specific peptide/biomolecule adsorption on quartz. These findings, used alongside peptide conformation data, provide a basis from which we can start to design quartz-binding peptides with controllable properties such as facet-specific binding.



[1] N. Kroger, R. Deutzmann, M. Sumper, *Science* **1999**, *286*, 1129-1132 [2] E. E. Oren, C. Tamerler, D. Sahin, M. Hnilova, U.O.S. Seker, M. Sarikaya, R. Samudrala, *Bioinformatics* **2007**, ***23,*** 2816-2822 [3] E.E. Oren, R. Notman, I. W. Kim, J.S. Evans, T.R. Walsh, R. Samudrala, C. Tamerler, M. Sarikaya, *Langmuir* **2010**, *26*, 11003-11009.

Keywords: selectivity, adsorption, molecular simulation

MS.94.4

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Noncovalent interactions of aromatic molecules

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A characterization of noncovalent interaction of aromatic molecules is very important for crystal engineering. Aromatic molecules can form several types of noncovalent interactions, however, the best known interactions of aromatic molecules are stacking interactions with parallel alignment of the molecules. Most of the studies consider organic aromatic molecules, however, other planar molecules and fragments can also be involved in stacking interactions. We showed that a water molecule can form a parallel alignment interaction with C_6 aromatic rings [1]. Analyzes of crystal structures from the Cambridge Structural Database (CSD) showed that a water molecule or one of its O-H bonds can be found parallel to the aromatic ring plane at distances typical for stacking interactions. The interaction energies obtained by *ab initio* calculations performed on model systems are as large as 2.45 kcal mol^{-1}.

In transition metal complexes planar chelate rings with delocalized π-bonds can form stacking [2]. interactions. Our results showed stacking interactions between chelate and C_6-aromatic rings in crystal