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## 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].

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### Facet-specific binding of amino-acid analogues on quartz

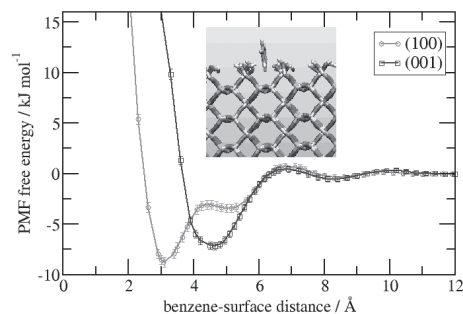
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Silica-binding peptides have a wide range of potential applications such as controlled fabrication of silica nanostructures. Quartz-binding peptides have been identified [1, 2], but their modes of binding remain less well understood [3]. As part of 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.



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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<sub>6</sub> 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<sup>-1</sup>.

In transition metal complexes planar chelate rings with delocalized  $\pi$ -bonds can form stacking [2]. interactions. Our results showed stacking interactions between chelate and C<sub>6</sub>-aromatic rings in crystal