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Structure and polymerization of vapour deposited adenine on a nanostructured perovskite surface - implications for prebiotic molecular organization

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The origin of biological homochirality is a key question for research on the origin of life and there is increasing interest in the self organization of adsorbed molecular layers to form chiral domains and other structures. These can form during deposition from the vapour. Here we report structures observed from deposition under high vacuum of the nucleic acid base, adenine, on the surface of the perovskite mineral SrTiO<sub>3</sub> which condenses with CaTiO<sub>3</sub> to form a solid in the earliest stages of planetary formation as observed in inclusions in the meteorite, Murchison. The free adenine molecule is planar with a single mirror plane that gives rise to the point group  $C_s$ . However adsorption onto a surface breaks this symmetry and adenine behaves as a protochiral molecule and adsorbed adenine is thus chiral.

Reactions on the surfaces of interstellar dust grains are probably a major source of complex organic material in space. This material includes simple molecules such as  $CH_4$ ,  $NH_3$  and HCN as well as diamonds, aldehydes, ketones, acids, aromatic hydrocarbons and possibly fullerenes and bucky tubes. In particular, the unambiguous identification of glycine in hot molecular cores associated with early phases of star formation may be of central importance to studies of the origin of life.

The perovskite material  $SrTiO_3$  can form a rich variety of surface nanostructures and provides an exciting oxide substrate for investigating heterogeneous catalysis and organization of molecules such as adenine.  $SrTiO_3$  also exhibits interesting photocatalytic properties which may offer further possibilities in exploring the ways in which biomolecules behave in a photo-active environment. Recent laboratory data show that adenine is stable in simulated space conditions at 12K under UV irradiation. In the present experiments, a Knudsen cell was used to present a molecular beam of adenine to a carefully cleaned  $SrTiO_3$  surface. We report here the results of a high resolution STM study, under UHV conditions, of the organization of adenine molecules and layers on these  $SrTiO_3$  surface nanostructures.

We observe that adenine adsorbs on nanostructured  $SrTiO_3$  (100) surfaces to form random islets at low coverage. However in monolayers, it forms organized arrays on underlying perovskite nanostructures. The adenine layer has a periodicity related to the underlying structure with a width mirroring  $6 \times 2$  surface patterns and with a 2.4nm repeat distance. In addition, ordering occurs along these nanostructures with a 1.6nm periodicity that contrasts with the 0.8nm repeat of the underlying  $6 \times 2$  pattern.

We believe that adenine may adsorb on nanostructured  $SrTiO_3$  as self-organized chains of  $(ad)_2$  dimers with chains linked by H-bonding and corrugated along the length of  $SrTiO_3$  nanostructures. Detailed examination of the image contrast suggests that there may be further self-organisation with opposing chains of elements being related by a perpendicular mirror plane and thus facing each other. Investigation of the detail of these structures may prove feasible in the near future and we hope to be able to report with more data by the time of the presentation. If true, this self-organization carries the tantalizing prospect of observing chiral self-organization in situ on these nanostructured oxide surfaces.