ESRF	**Self-assembly of thin films of mono-peptide wedge-shaped molecules with L-alanine**	**Experiment number**: **MA-821**
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Report:

The influence of molecular structure on supramolecular organization is a key question in modern science.[1] A very interesting challenge is to understand the origin of supramolecular assemblies, i.e. formation of supramolecular non-covalent objects with 2D or 3D positional ordering of structural units. Wedge-shaped amphiphilic molecules provide powerful building blocks for the construction of supramolecular objects of cylindrical or spherical shapes In the columnar structures one can discriminate several hierachic levels. Particularly, the molecules organize disc-like clusters[1,2] which, in turn, stacks into columns usually stabilized by π–π interactions[1], H-bonding[3], ionic interactions[4] as well as Van der Waals interactions. Such self-assemblies attract interest as *transporting systems* (for charges or ions[4]) in future future nano-devices.

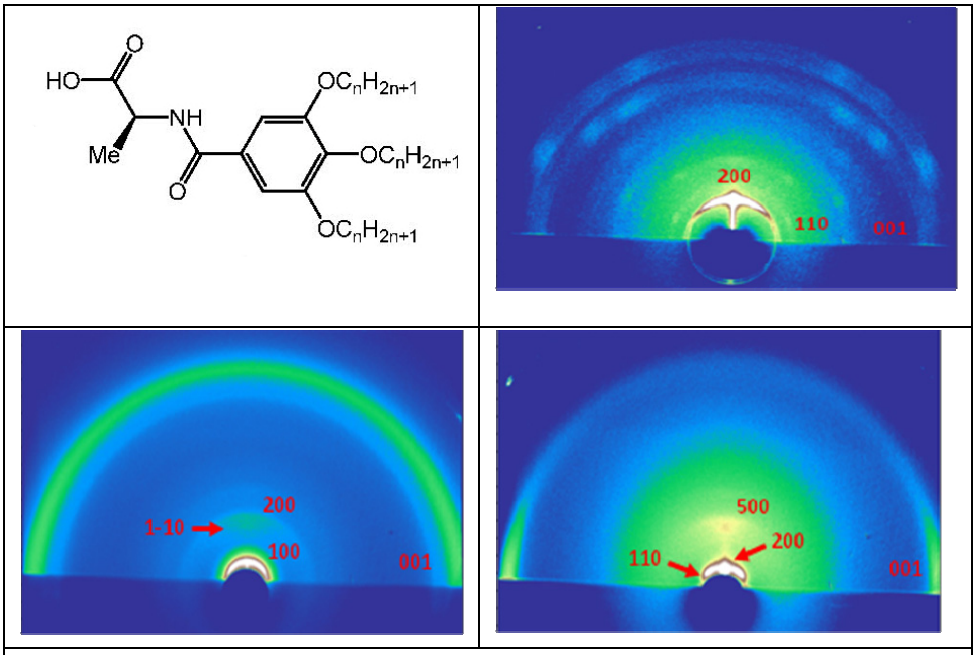

Fig.1: Structure of the studied molecules (**top left**), GIWAXS patterns of thin films of C6-Ala-COOH (**top right**), C12-Ala-COOH (**bottom left**) and C16-Ala-COOH (**bottom right**).

In our work a series of N-3,4,5-trisalkyloxy-L-alanine (Cn-Ala-COOH, n=6,12 and 16) with different length of alkyl side chains is studied to adress the role of ratio between polar core and non-polar periphery in formation of complex supramolecular structures (Fig.1, top left). All samples were prepared by spin-coating of 10mg/ml solution in chloroform on cleaned silicon wafers. Grazing incidence wide-angle X-ray diffraction (GIWAXS) measurements were performed with wavelength of 1.13 Å and incidence angle of 0.2°. The signal was recorded with MAR CCD camera and corrected for geometrical distorsion.

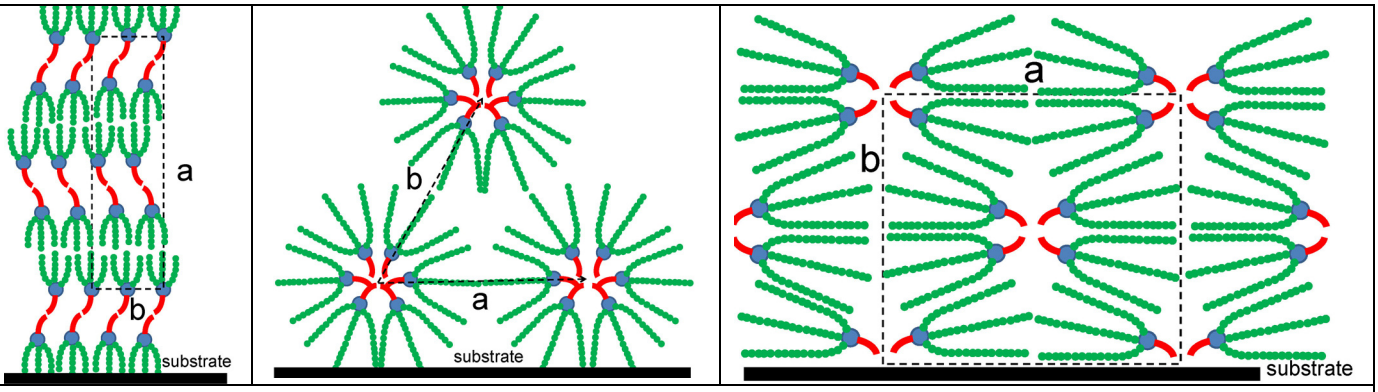

Fig.2: Models of the crystal structures for C6-Ala-COOH (**left**), C12-Ala-COOH (**middle**) and C16-Ala-COOH (**right**).

The 2D GIWAXS pattern of C6-Ala-COOH reveals multiple well-oriented reflexes corresponding to orthorhombic lattice with a=39.12Å; b=16.44Å; c=9.68Å (Fig. 1 top right). The unit cell contains 8 molecules which are organized in 4 dimers connected by hydrogen bonds (Fig.2, left). The second layer is propably shifted by half-period in the a-direction. Thy hexyl side chains are oriented normal to the substrate (along the a-direction). The increase of the side-chain length to dodecyl changes drastically the molecular ordering. The pattern of C12-Ala-COOH shows hexagonal columnar phase with columns parallel to the substrate (Fig.1, bottom left). Each unit cell contains a cluster of 6 molecules organized in discs of 43 Å in diameter stabilized by H-bonds (Fig.2, middle). The c-axis is parallel to the columnar direction and the c-parameter of 4.2 Å indicates planar conformation of the disc in the cluster. Futher increase of the side chain length leads to modification of the columnar structure. The pattern of C16-Ala-COOH indicates formation of columnar rectangular phase (Fig.1, bottom right). The columns are parallel to the substrate and the unit cell contains two clusters of 4 molecules in each (Fig.2, right). The a-parameter is slightly smaller than the double molecular length (54 Å) so we can conclude that the molecules are inclined in respect to the ab-plane by 22° (so-called “hering-bone” structure). Since the a-parameter is parallel to the substrate, the side chains are parallel to the film surface, which is in contrast to the C6-Ala-COOH and C12-Ala-COOH molecules.

In conclusion, in this work we performed structural analysis of wedge-shaped molecules with different length of side groups. It has been demonstrated that with increase of the non-polar periphery the structure evolves from layer-like to columnar hexagonal and futher to columnar rectangular phase. The relative volume of the alkyl part also affects the number of molecules in a cluster. The obtained results allow to better understand the self-assembly mechanisms in such bio-mimetic systems.

References:

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