ESRF	**Experiment title: X-ray reflectivity, GIXD and GISAXS study of unique nanostructures – magnesium porphine supermolecules at the air-water interface**	**Experiment number**: **SC 4819**
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Report: Porphyrins are functional elements of important biomolecules, whose assemblies play a central role in fundamental processes such as electron transfer, oxygen transport, enzymatic catalysis and light-harvesting. It was shown that the properties of the nanostructures, in particular the energy transfer rate between adjacent molecules, are strongly affected by the structure of the ensemble.

Recently we have discovered new unique porphyrin systems – supermolecules of magnesium porphine, structural basis of chlorophyll [1]. They were formed using Langmuir-Schaefer (LS) technique and exhibit strong noncovalent intermolecular interactions and functional properties extrinsic to the constituent molecules.

In this study floating layers and LS films of MgPor were examined by X-ray reflectivity measurements, GIXD and GISAXS. The layers were studied at surface pressures ranging from 0.1 to 45 mN/m and under four different initial surface coverage (ISC face/edge 17/6, 37/12, 64/21, 114/38). The main results were obtained by studiing of LS film formed at big values of surafce pressure and ISC [2,3]. X-ray reflectivity and Grazing incidence XRD of the film are presented in Figures 1b-d. Determined from XRR data (Fig.1b) intermolecular distances in the film are: a=10.1 Å (two orders: Qz= 0.620 1/Å and Qz= 1.243 1/Å) that corresponds to slightly tilted molecules and b=2.7 Å (Qz= 2.30 1/Å). The distances determined from GIXD (Fig.1c,d) data are: a` =8.9 Å (two orders: Qz= 0.723 1/Å and Qz= 1.475 1/Å), b`=2.7 Å (Qz= 2.304 1/Å). On the basis on these data we have concluded, that supermolecules of MgPor are stacks of individual MgPor molecules with very short distance between the molecules. Some of supermolecules are positioned by their long axis along the surface (a=10.1 Å, packing I). They are well ordered (two reflection orders on the XRR). The other ones are positioned perpendicular to the surface (b=2.7 Å, packing II).

But it is known, that a distance between the molecules in usual molecular system with van der Waals interactions should be not less than 3.3-3.2 Å ("L_2" dimension of the monomer is equal to 3.4 ± 0.2 Å, Fig. 1a). The actual distance between the molecules in supermolecule (2.7 Å) is substantially shorter than van der Waals one, and we might claim that some specific force draws and keeps the molecules together. Thus we can conclude that neighbor molecules in formed MgPor supramolecular assemblies exhibit unusually strong, not van der Waals interactions, they are "pressed" into each other. In fact, still no solvent was found that could separate molecules in such assemblies. **Hence supermolecules of magnesium porphine contain a 2.73-Å intermolecular bonds that beyond theoretical limit for noncovalent bonds.**

Full width at half maximum (FWHM) value calculated for the first peak (10.1 Å) is equel to 0.038 1/Å, and FWHM =0.022 1/Å - for the third one (2.7 Å). The correlation length of the first packing was estimated through Δq_{FWHM} of diffraction peaks using Scherrer equation, to be $r \approx 2\pi/\Delta qFWHM$ = 165 Å for the first supermolecular packing, and r ≈290 Å for the second one. So, around 16 supermolecules are well ordered in first packing and around 105 molecules in the second one. The last value is very important. **For the first time the quantity of the individual molecules in the supermolecule (105) and the length of the supermolecules (29 nm) were determined**. GISAXS of the film exhibits wide weak galo in corresponding region what may be due to size variation of the units.

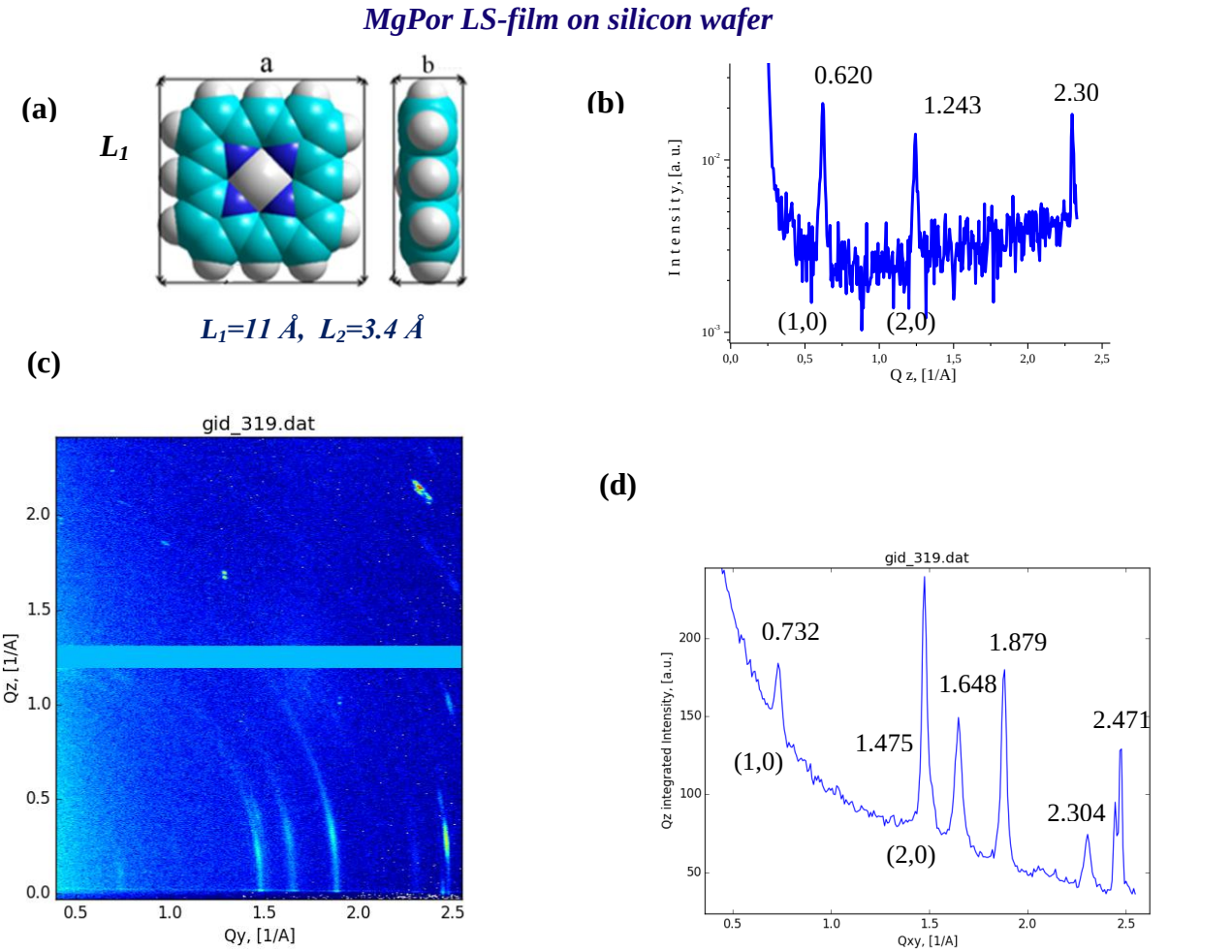

Figure 1. Molecular dimensions of MgPor (a), X-ray reflectivity (b) and Grazing incidence XRD (c,d) from MgPor Langmuir-Schaefer film.

References (All complete references and abstracts were add to the ESRF library)

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